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Zastosowanie pochodnych kwasów fenolowych do stabilizacji bioolejów roślinnych

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Application of phenolic acid derivatives for stabilization of vegetable bio-oils

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Rodzina jest w życiu oparciem, czymś co chroni, co daje siłę.

- Sophia Loren

Niniejszą rozprawę doktorską dedykuję najbliższym,
w szczególności **Moim Rodzicom**,
w podziękowaniu za trud wychowania,
za miłość i uśmiech każdego dnia,
za pogodne dni pełne radości i szczęścia,
za Waszą pomoc i wsparcie w każdej chwili mojego życia.

Przede wszystkim, z całego serca dziękuję Wam za dzisiejszy dzień,
za wiarę we mnie, będącą większa niż własna
oraz za ogromny wysiłek jaki włożyliście w to,
abym mogła być tu, gdzie teraz jestem
i być główną częścią tego, co właśnie się dzieje.

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Serdeczne podziękowania
za trud, wsparcie merytoryczne i poświęcony czas
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Z wyrazami szacunku,
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Streszczenie

Oleje farmaceutyczne (biooleje) to oleje roślinne otrzymywane zachowawczymi metodami ekstrakcji i rafinacji (np. tłoczenie na zimno, ekstrakcja CO_2 w stanie nadkrytycznym, rafinacja fizyczna), pozyskiwane z surowców roślinnych charakteryzujących się unikalnym składem składników bioaktywnych i/lub kwasów tłuszczowych. Kwasy tłuszczowe, w szczególności nienasycone, odgrywają ważną rolę w zapewnieniu prawidłowego funkcjonowania organizmu człowieka, jednakże ich stosunkowo wysoki udział w olejach roślinnych stanowi bezpośrednią przyczynę niskiej trwałości tych produktów.

Ostatnio szczególną uwagę zwrócono na związki fenolowe jako dodatki przeciwutleniające, przy czym aktualna literatura sugeruje, że nie tylko kwasy fenolowe, ale także ich pochodne mogą być skutecznymi przeciwutleniaczami stosowanymi w przemyśle spożywczym, w tym również w przemyśle olejarskim. Niektórzy badacze sugerują, że związki fenolowe jako przeciwutleniacze polarne mogą lepiej chronić matryce hydrofobowe niż typowe przeciwutleniacze niepolarne, takie jak np. tokoferole (teoria „paradoksu polarnego").

Zaplanowane w niniejszej rozprawie doktorskiej badania opierają się na najnowszej wiedzy nt. zawartości i aktywności przeciwutleniającej związków fenolowych w olejach, którą opisano w pracy przeglądowej. W części eksperymentalnej zbadano zawartość związków fenolowych naturalnie występujących w dostępnych na polskim rynku bioolejach roślinnych (z różnych surowców oraz z jednego surowca różniące się zawartością wody) oraz skuteczność dodatku dwóch pochodnych kwasów fenolowych (4-winylogwajakolu i 4-winylosyringolu) w hamowaniu utleniania lipidów oraz ograniczaniu degradacji składników bioaktywnych w bioolejach podczas ich przechowywania.

Badania prowadzone w ramach rozprawy doktorskiej potwierdziły, że związki fenolowe, w tym pochodne kwasów fenolowych, wpływają na stabilność oksydacyjną bioolejów roślinnych i mogą być stosowane jako dodatki istotnie zwiększające ich trwałość, ale również mogą działać ochronnie na zawarte w nich składniki bioaktywne. W badaniach wykazano, że skuteczność stabilizującego działania pochodnych kwasów fenolowych zależy od ich rodzaju i stężenia, a także od rodzaju biooleju.

Słowa kluczowe: biooleje roślinne; związki fenolowe; 4-winylosyringol; 4-winylogwajakol; stabilność oksydacyjna; składniki bioaktywne

Abstract

Pharmaceutical oils (bio-oils) are vegetable oils obtained by conservative extraction and refining methods (e.g., cold pressing, supercritical CO_2 extraction, physical refining), extracted from vegetable raw materials characterized by a unique composition of bioactive compounds and/or fatty acids. Fatty acids, especially unsaturated ones, play an important role in ensuring the proper functioning of the human body, but their relatively high proportion in vegetable oils is a direct cause of the low shelf life of these products.

Recently, special attention has been paid to phenolic compounds as antioxidant additives, with current literature suggesting that not only phenolic acids, but also their derivatives can be effective antioxidants used in the food industry, including the oil industry. Some researchers suggest that phenolic compounds as polar antioxidants can better protect hydrophobic matrices than typical non-polar antioxidants, such as tocopherols (the "polar paradox" theory).

The research planned in this dissertation is based on the latest knowledge of the content and antioxidant activity of phenolic compounds in oils, as described in the review paper. The experimental part investigated the content of naturally occurring phenolic compounds in vegetable bio-oils available on the Polish market (from different raw materials and from a single raw material differing in water content) and the effectiveness of the addition of two phenolic acid derivatives (4-vinylguaiacol and 4-vinylsyringol) in inhibiting lipid oxidation and reducing the degradation of bioactive compounds in bio-oils during storage.

Research carried out within the framework of the dissertation confirmed that phenolic compounds, including phenolic acid derivatives, affect the oxidative stability of vegetable bio-oils and can be used as additives to significantly increase their shelf life, but also have a protective effect on the bioactive compounds they contain. Studies have shown that the effectiveness of the stabilizing effect of phenolic acid derivatives depends on their type and concentration, and also on the type of bio-oil.

Keywords: vegetable bio-oils; phenolic compounds; 4-vinylsyringol; 4-vinylguaiacol; oxidative stability; bioactive compounds

Informacja o finansowaniu badań

Badania prowadzone w ramach niniejszej rozprawy doktorskiej zostały sfinansowane ze środków przeznaczonych na działalność związaną z prowadzeniem badań naukowych oraz zadań z nimi związanych, służących rozwojowi młodych naukowców oraz uczestników studiów doktoranckich, a także ze środków Narodowego Centrum Nauki w Krakowie:

1) Finansowanie z projektu wewnętrznego Wydziału Nauki o Żywności UWM w Olsztynie, nr 17.620.025-300, środki finansowe przeznaczone na działalność związaną z prowadzeniem badań naukowych oraz zadań z nimi związanych, służących rozwojowi młodych naukowców oraz uczestników studiów doktoranckich:
   Tytuł projektu: *Wpływ dodatku pochodnych kwasów fenolowych (4-vinylsyringol i 4-vinylguaiacol) na stabilność oksydacyjną i jakość wybranych olejów roślinnych*;
   Okres trwania: 1.01.2017 - 31.12.2017;
   Wartość projektu: 15 400 zł.
2) Finansowanie z projektu zewnętrznego przez Narodowe Centrum Nauki w Krakowie w ramach konkursu PRELUDIUM 16, nr 2018/31/N/NZ9/01273, środki finansowe przeznaczone na wsparcie badań prowadzonych przez osoby rozpoczynające karierę naukową, nieposiadające stopnia naukowego doktora:
   Tytuł projektu: *Badania modelowe dotyczące zastosowania pochodnych kwasów hydroksycynamonowych do stabilizacji olejów farmaceutycznych (biooleje) o różnej zawartości wody*;
   Okres trwania: 1.08.2019 - 31.07.2021;
   Wartość projektu: 139 500 zł.

Wykaz publikacji stanowiących przedmiot rozprawy doktorskiej

Przedmiotem rozprawy doktorskiej są 4 publikacje stanowiące powiązany tematycznie cykl przeglądu literatury oraz badań laboratoryjnych na temat zastosowania pochodnych kwasów fenolowych do stabilizacji bioolejów roślinnych.

P1. Mikołajczak N., Tańska M., Ogrodowska D., 2021, Phenolic compounds in plant oils: A review of composition, analytical methods, and effect on oxidative stability, *Trends in Food Science & Technology*, 113, 110–138, https://doi.org/10.1016/j.tifs.2021.04.046

IF = 12,563; MEiN$_{2021}$ = 200 pkt.

Wkład w powstanie publikacji polegał na współudziale w opracowaniu koncepcji manuskryptu, zebraniu literatury, uczestniczeniu w przygotowaniu wstępnej i ostatecznej wersji manuskryptu. Mój udział procentowy szacuję na 75%.

P2. Mikołajczak N., Tańska M., 2022, Effect of initial quality and bioactive compounds content in cold-pressed flaxseed oils on oxidative stability and oxidation products formation during one-month storage with light exposure, *NFS Journal*, 26, 10–21, https://doi.org/10.1016/j.nfs.2022.02.001

IF = 3,111; MEiN$_{2022}$ = 140 pkt.

Wkład w powstanie publikacji polegał na współudziale w opracowaniu koncepcji badań, zebraniu literatury, zaplanowaniu doświadczenia, doborze metod analitycznych, przeprowadzeniu doświadczeń, opracowaniu i interpretacji wyników, uczestniczeniu w przygotowaniu wstępnej i ostatecznej wersji manuskryptu.
Mój udział procentowy szacuję na 80%.

P3. Mikołajczak N., Tańska M., Ogrodowska D., Czaplicki S., 2022, Efficacy of canolol and guaiacol in the protection of cold-pressed oils being a dietary source linoleic acid against oxidative deterioration, *Food Chemistry*, 393, 133390, https://doi.org/10.1016/j.foodchem.2022.133390

IF = 7,514; MEiN$_{2022}$ = 200 pkt.

Wkład w powstanie publikacji polegał na współudziale w opracowaniu koncepcji badań, zebraniu literatury, zaplanowaniu doświadczenia, doborze metod analitycznych,

przeprowadzeniu doświadczeń, opracowaniu i interpretacji wyników, uczestniczeniu w przygotowaniu wstępnej i ostatecznej wersji manuskryptu.
Mój udział procentowy szacuję na 65%.

P4. Mikołajczak N., Tańska M., Konopka I., 2019, Impact of the addition of 4-vinyl derivatives of ferulic and sinapic acids on retention of fatty acids and terpenoids in cold-pressed rapeseed and flaxseed oils during the induction period of oxidation, *Food Chemistry*, 278, 119–126, https://doi.org/10.1016/j.foodchem.2018.11.001

IF = 6,306; MNiSW$_{2019}$ = 200 pkt.

Wkład w powstanie publikacji polegał na współudziale w opracowaniu koncepcji badań, zebraniu literatury, zaplanowaniu doświadczenia, doborze metod analitycznych, przeprowadzeniu doświadczeń, opracowaniu i interpretacji wyników, uczestniczeniu w przygotowaniu wstępnej i ostatecznej wersji manuskryptu.
Mój udział procentowy szacuję na 70%.

Suma punktów MNiSW/MEiN: 740

Sumaryczny IF: 29,494

1. Wstęp – uzasadnienie podjęcia badań

1.1. Znaczenie bioolejów w diecie człowieka

Oleje roślinne odgrywają istotną rolę w żywieniu człowieka nie tylko ze względu na wysoką wartość energetyczną, ale przede wszystkim dlatego, że są źródłem wielu składników biologicznie aktywnych, takich jak nienasycone kwasy tłuszczowe, fitosterole, tokoferole, karotenoidy, skwalen i związki fenolowe (Rhazi i in., 2022; Dąbrowski i Konopka, 2016). Do szczególnie cennych olejów roślinnych należą tzw. biooleje, zwane inaczej olejami farmaceutycznymi, o unikalnej kompozycji nienasyconych kwasów tłuszczowych i/lub bogate w określone związki bioaktywne (El Asbahani i in., 2015; Czaplicki i in., 2011). Przykładowo, oleje z nasion chia i lnu są źródłem kwasów omega-3 (Saini i in., 2021), oleje z nasion amarantusa i dyni są źródłem skwalenu (Czaplicki i in., 2016a), a oleje z owoców rokitnika kwasu palmitoleinowego i karotenoidów (Czaplicki i in., 2017). Biooleje można pozyskiwać zarówno z nasion roślin niszowych (m.in. wiesiołka, ogórecznika, konopi), jak i z typowych surowców olejarskich (m.in. lnu, rzepaku) (Rój i in., 2011), przy użyciu zachowawczych metod wydobywania i oczyszczania oleju, tj. tłoczenie na zimno, ekstrakcja CO_2 w stanie nadkrytycznym, rafinacja fizyczna (Dąbrowski i Konopka, 2016). Należy jednak zaznaczyć, że na zawartość i skład kwasów tłuszczowych oraz składników bioaktywnych, a tym samym wartość biologiczną olejów, ma wpływ zarówno jakość surowca (m.in. gatunek, odmiana, warunki klimatyczne i agrotechniczne w czasie uprawy), jak i sposób ich pozyskiwania i przechowywania (Tańska i in., 2020). Skład chemiczny bioolejów roślinnych determinuje również ich potencjał zdrowotny oraz zastosowanie (Chandra i in., 2020), przy czym ich spożycie szczególnie zalecane jest przy chorobach układu krążenia, nowotworach i otyłości (Obiedzińska i Waszkiewicz-Nowak, 2012; Chandra i in., 2020).

Kwasy tłuszczowe są podstawowym składnikiem strukturalnym bioolejów roślinnych, a obecność w diecie unikalnych form tych kwasów (np. kwasów omega-3) ma wpływ na stan fizjologiczny organizmu (Nagy i Tiuca, 2017). Przykładowo, nienasycone kwasy tłuszczowe stanowią materiał wyjściowy w syntezie hormonów tkankowych oraz są budulcem błon komórkowych, przyczyniają się do obniżenia poziomu cholesterolu i agregacji płytek krwi, wpływają na układ odpornościowy, a także hamują rozwój chorób układu krążenia, nowotworów i cukrzycy (Kaur i in., 2014). Mimo iż, obecność nienasyconych kwasów tłuszczowych w diecie człowieka jest szczególnie pożądana z punktu zdrowotnego, to istotnym czynnikiem ograniczającym ich spożycie jest podatność na utlenianie (Symoniuk i in., 2017). Szybkość i zasięg reakcji utleniania zwiększają się wraz ze stopniem nienasycenia kwasów

tłuszczowych (wraz z tzw. „indeksem utlenienia") i są determinowane różnymi czynnikami fizykochemicznymi, np. obecnością tlenu, wody, przeciwutleniaczy, enzymów, światła, temperatury (Mancebo-Campos i in., 2022; Ahmed i in., 2016). Lipidy w żywności podlegają różnym procesom utleniania, tj. autooksydacja, utlenianie fotosensybilizowane i utlenianie enzymatyczne (Ahmed i in., 2016). Efektem tych procesów jest w pierwszym etapie akumulacja związków pierwotnych (np. wodoronadtlenków), które następnie przekształcane są w produkty wtórne, m.in. aldehydy, ketony, polimery (Ayala i in., 2014), o udowodnionym negatywnym wpływie zarówno na cechy fizyczne, jak i sensoryczne produktów spożywczych (Huang i Ahn, 2019; Tao, 2015). Ponadto, dochodzi nie tylko do obniżenia zawartości nienasyconych kwasów tłuszczowych, ale także do powstania wiązań między produktami utleniania a innymi składnikami żywności (np. witaminami), co w konsekwencji przekłada się na obniżenie wartości zdrowotnej produktów spożywczych (Tao, 2015). Udowodniono, że wtórne produkty utlenienia mają również niekorzystny wpływ na organizm konsumenta, powodując wiele uszkodzeń wewnątrzkomórkowych i zmian zwyrodnieniowych poprzez gromadzenie się tych związków w tkankach. W konsekwencji mogą przyczyniać się do rozwoju przewlekłych chorób niezakaźnych, takich jak m.in. choroby układu krążenia, choroby układu pokarmowego, insulinooporność czy nowotwory (Schaich, 2020). Badania przeprowadzone przez Edera (1999) potwierdziły, że spożywanie utlenionych tłuszczów powoduje uszkodzenia w obrębie serca, wątroby i dróg żółciowych. Z kolei Wąsowicz i in. (2004) zwrócili uwagę na ich niekorzystny wpływ na błonę śluzową jelit i żołądka. Ponadto, utlenione tłuszcze przyspieszają wszystkie stadia rozwojowe miażdżycy, powodując uszkodzenie śródbłonka i nagromadzenie warstwy tłuszczowej w tętnicach, co w konsekwencji może prowadzić do wystąpienia zakrzepicy (Rafieian-Kopaei i in., 2014). Literatura jednoznacznie wskazuje również, że wykazują one właściwości toksyczne i mutagenne (Schaich, 2020).

Szczególnie podatne na procesy utleniania są biooleje, co znacząco skraca ich okres przydatności do spożycia (Cai i in., 2021). Generalnie, dla większości bioolejów roślinnych szacowany okres przydatności do spożycia wynosi od 6 do 12 miesięcy (Bojanowska i Lamorska, 2016; Tańska i in., 2016), jednakże w niektórych bioolejach może być on znacznie krótszy i wynosić jedynie 30 dni po otwarciu opakowania, np. olej tłoczony na zimno z nasion chia (informacja na podstawie przeglądu deklaracji na etykietach produktów dostępnych na polskim rynku). Przykładowo, okres przydatności do spożycia oleju lnianego tłoczonego na zimno waha się od 5 tygodni do 3 miesięcy (Tańska i in., 2016), z kolei oleju rzepakowego tłoczonego na zimno najczęściej wynosi 6 miesięcy (Zychnowska i in., 2013).

1.2. Ograniczanie procesów utleniania w olejach roślinnych

Szybkość niekorzystnych procesów utleniania można opóźnić poprzez m.in. dodatek substancji o charakterze przeciwutleniającym (antyoksydanty) (Balasubramaniam i in., 2019). Ze względu na mechanizm działania przeciwutleniaczy można wyróżnić: pierwotne – będące akceptorami wolnych rodników (działające jako donory wodoru, np. tokoferole) oraz wtórne – działające poprzez różne mechanizmy, takie jak reduktory czy chelatory metali (np. kwas cytrynowy) lub pochłaniacze tlenu i środki redukujące (takie jak kwas askorbinowy) (Reische i in., 2002). Powszechnymi i bezpiecznymi przeciwutleniaczami stosowanymi w żywności są tokoferole, karotenoidy i kwas askorbinowy (Zehiroglu i Ozturk, 2019), natomiast w olejach mogą być stosowane jedynie te związki, które rozpuszczalne są w środowisku niepolarnym (Zhong i Shahidi, 2011). W związku z tym, najszerzej stosowane są tokoferole, dodawane zarówno w postaci naturalnych ekstraktów, jak i czystych związków (Barouh i in., 2022). Często również wykorzystywany jest dodatek substancji pochodzenia syntetycznego, głównie butylohydroksyanizolu (BHA), butylohydroksytoluenu (BHT), galusanu propylu (PG) lub tert-butylohydrochinonu (TBHQ) (Lourenço i in., 2019), które wykazują wysoką skuteczność przeciwutleniającą w olejach roślinnych (Taghvaei i Jafari, 2013). Dodatek syntetycznych przeciwutleniaczy (zwłaszcza do bioolejów) jest dyskusyjny z wielu względów, w szczególności bezpieczeństwa zdrowotnego. Dlatego poszukuje się naturalnych przeciwutleniaczy, które zwiększą nie tylko stabilność oksydacyjną, ale także wartość odżywczą produktów spożywczych (Wang i in., 2021).

Ostatnio szczególną uwagę zwrócono na związki fenolowe jako przeciwutleniacze olejów roślinnych (Tańska i in., 2016; Roszkowska i in., 2015; Siger i in., 2015), stanowiące wtórne metabolity roślin (Zhang i in., 2022). Wyróżnia się różne grupy związków fenolowych, jednakże najczęściej występującymi są kwasy fenolowe (Minatel i in., 2017). Liczne badania wykazały, że właściwości przeciwutleniające kwasów fenolowych są istotnie związane z ich budową chemiczną (Kumar i Goel, 2019). Generalnie, w związkach z jedną grupą hydroksylową aktywność przeciwutleniająca wzrasta wraz z dodatkową obecnością jednej lub dwóch grup metoksylowych w pierścieniu, podobnie jak podstawienie w pozycji orto- grupy z donorem elektronowym, grupy alkilowej lub grupy metoksylowej (Kurek-Górecka i in., 2013). Przykładowo, różne poziomy aktywności przeciwutleniającej kwasu kawowego, ferulowego i p-kumarowego wynikają głównie z liczby grup hydroksylowych w cząsteczce, przy zaznaczeniu, że jest ona również wyższa w obecności form zestryfikowanych (Kumar i Goel, 2019). Natomiast, kwas sinapowy z dwiema grupami metoksylowymi jest bardziej

aktywny niż kwas ferulowy (jedna grupa metoksylowa) i jest bardziej aktywny niż kwas kumarowy (jedna grupa hydroksylowa) (Mikucka i in., 2022). Dużą aktywność przeciwutleniającą wykazuje również kwas chlorogenowy głównie ze względu na obecność grup hydroksylowych w pierścieniu aromatycznym, które posiadają niższe wartości energii dysocjacji wiązania (BDE) i większą stabilność wolnych rodników (Jiang i in., 2021; Saqib i in., 2015). Udowodniono także, że kwasy orto- i para-hydroksybenzoesowe nie wykazują właściwości przeciwutleniających wobec wolnych rodników w fazie wodnej, jednakże mogą być skutecznymi zmiataczami rodników hydroksylowych w innych matrycach (Godlewska-Żyłkiewicz i in., 2020).

1.3. Mechanizmy przeciwutleniające związków fenolowych w olejach roślinnych

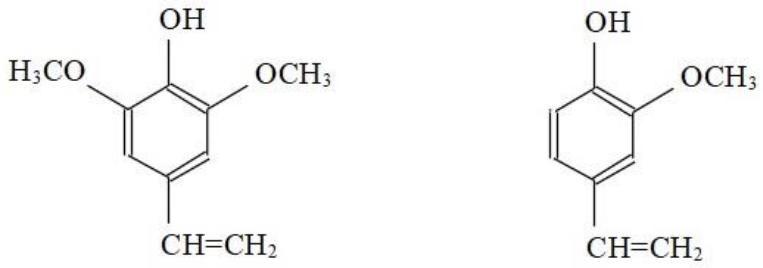
Literatura podaje, że kluczowe mechanizmy przeciwutleniające związków fenolowych zachodzą poprzez przeniesienie atomu wodoru (HAT) lub przeniesienie pojedynczego elektronu (SET) (Koroleva i in., 2014), przy czym wskazuje się, że w olejach dominuje mechanizm HAT (Zhu i in., 2013). Ponadto, wartość energii dysocjacji wiązania (BDE) dla grupy O-H przeciwutleniacza fenolowego prognozuje jego aktywność przeciwutleniającą i stabilność utworzonego rodnika antyoksydacyjnego (niższe BDE skutkuje bardziej aktywnym antyoksydantem i bardziej stabilnym rodnikiem antyoksydacyjnym) (Chen i in., 2020). Na siłę wiązania O-H przeciwutleniacza fenolowego ma wpływ nie tylko podstawienie wodoru w pierścieniu benzenowym, ale również każdy podstawnik destabilizujący lub stabilizujący stan podstawowy przeciwutleniacza fenolowego (Choe i Min, 2009). Jednakże, oprócz zmienności BDE, potencjał przeciwutleniacza do stabilizacji oleju przed utlenianiem może być również uwarunkowany jego polarnością (Zhong i Shahidi, 2011). Zgodnie z tzw. teorią „paradoksu polarnego", przeciwutleniacze polarne (takie jak związki fenolowe) lepiej chronią matryce hydrofobowe niż typowe przeciwutleniacze niepolarne (takie jak tokoferole). Najnowsza interpretacja tego zjawiska sugeruje, że prawdziwym miejscem utleniania w oleju jest granica faz olej-woda, ponieważ praktycznie każdy olej zawiera niewielkie ilości wody (Laguerre i in., 2015). Dane literaturowe wskazują, że oleje roślinne mogą zawierać do 3% wody (olej palmowy), przy czym najczęściej oznaczana zawartość mieści się w zakresie od 0,1 do 0,5% (Roszkowska i in., 2015; Odoom i in., 2014; Zhao i in., 2014; Ngado-Ebongue i in., 2013; Al-Alawi i in., 2006). Należy również zaznaczyć, że woda powstaje również w procesie utleniania lipidów w wyniku redukcji wodoronadtlenków (Jung i in., 2016; Budilarto i Kamal-Eldin, 2015).

Znaczenie wody w procesie utleniania olejów roślinnych można również tłumaczyć w oparciu o proces tworzenia koloidów asocjacyjnych, w którym woda stanowi główny czynnik (Bąkowska i in., 2021). Koloidy asocjacyjne w środowisku niepolarnym i w obecności niewielkiej ilości wody formowane są poprzez związki powierzchniowo czynne, które są składnikami naturalnych olejów roślinnych (fosfolipidy, sterole, wolne kwasy tłuszczowe, związki fenolowe, itp.) lub mogą powstawać podczas procesu utleniania (Chaiyasit i in., 2007). Te struktury koloidalne są rozproszone w oleju jako sferyczne odwrócone micele (przy zawartości wody poniżej 0,3%) lub jako struktury lamelarne w wyższych stężeniach (Laguerre i in., 2015). Literatura podaje, że koloidy asocjacyjne mogą wpływać na efektywność działania przeciwutleniaczy, ze względu na ich położenie w heterogenicznej matrycy olejowej (Kittipongpittaya i in., 2014). Związki fenolowe jako składniki hydrofilowe, zdolne są do gromadzenia się na granicy faz olej-woda i mogą ingerować w strukturę miceli, co w konsekwencji zmienia ich aktywność przeciwutleniającą (Rokosik i in., 2020a; Laguerre i in., 2011). Ponadto, gromadzenie polarnych przeciwutleniaczy na granicy faz olej-woda, a tym samym tworzenie struktury mikroemulsji, pozwala zabezpieczyć micele przed dostaniem się do ich wnętrza związków o charakterze prooksydacyjnym (Budilarto i Kamal-Eldin, 2015). Badacze sugerują, że stężenie przeciwutleniacza również może odgrywać znaczącą rolę w mechanizmie działania „paradoksu polarnego". Przeciwutleniacze polarne mogą być bardziej efektywne w środowisku niepolarnym głównie w wysokich stężeniach (powyżej ich krytycznego stężenia, które określa granicę wyznaczania ich aktywności przeciwutleniającej) ze względu na dominację zjawisk zachodzących na granicy faz olej-woda. Z kolei przeciwutleniacze niepolarne mogą wykazywać wyższą aktywność przeciwutleniającą w środowisku niepolarnym (nawet w niskich stężeniach) ze względu na dominację procesów wynikających z ich rozpuszczalności (Zhong i Shahidi, 2011; Barouh i in., 2022). Wydaje się więc, że skutecznymi przeciwutleniaczami bioolejów roślinnych mogą być przeciwutleniacze niepolarne w stężeniu poniżej ich stężenia krytycznego, a także przeciwutleniacze polarne w stężeniu powyżej ich stężenia krytycznego.

1.4. Rola pochodnych kwasów fenolowych w hamowaniu utleniania olejów roślinnych

Dane literaturowe sugerują, że nie tylko kwasy fenolowe – natywne składniki surowców, ale również ich pochodne mogą być silnymi przeciwutleniaczami produktów spożywczych (Chen i in., 2015; Terpinc i in., 2011). Do tej grupy związków zalicza się 4-winylosyringol (rysunek 1a) i 4-winylogwajakol (rysunek 1b), dwie pochodne fenolowe

powstające w wyniku dekarboksylacji kwasów fenolowych, odpowiednio kwasu sinapowego (Nićiforović i Abramovič, 2013) oraz kwasu ferulowego (Shin i in., 2018). Badania przeprowadzone przez Koski i in. (2003) oraz Kuwahara i in. (2004) wykazały wysoką zdolność 4-winylosyringolu do zmiatania wolnych rodników, podobnie jak badania Shin i in. (2018) z udziałem 4-winylogwajakolu.



Rysunek 1. Cząsteczka 4-winylosyringolu (po lewej) i 4-winylogwajakolu (po prawej) (opracowanie własne za pomocą https://www.molinspiration.com/cgi-bin/properties).

Surowce olejarskie zawierają różne ilości związków fenolowych, jednakże nie ma dokładnych informacji na temat występowania w nich tych dwóch pochodnych kwasów fenolowych. Wiadomo, że synteza tych związków związana jest z zastosowaniem odpowiednich parametrów technologicznych podczas obróbki surowców i ich przetwarzania. Przykładowo, 4-winylogwajakol może być syntezowany w wyniku obróbki wysokotemperaturowej (Wakamatsu i in., 2005), obróbki enzymatycznej lub obróbki mikrobiologicznej z udziałem takich szczepów bakteryjnych jak *Lactobacillus brevis* (Curiel i in., 2010), *Lactobacillus farciminis* (Hadiza i in., 2012) oraz *Bacillus coagulans* BK07 (Karmakar i in., 2000), z kolei parametrami niezbędnymi do syntezy 4-winylosyringolu jest wysoka temperatura (Wroniak i in., 2016) oraz ciśnienie (Koski i in., 2003). Istotną rolę w syntezie 4-winylosyringolu odgrywają również dodatkowe procesy obróbki wstępnej nasion takie jak mikrofalowanie (Rękas i in., 2015) czy prażenie (Siger i in., 2015; Wagner i Jahreis, 2007). Ostatnie badania wskazują również na próby syntezy 4-winylofenoli poprzez mikrobiologiczną lub chemiczną dekarboksylację kwasów cynamonowych, m.in. kwasu ferulowego, kawowego, sinapinowego i p-kumarowego, z różnych surowców roślinnych (Khattab i in., 2014; Siger i in., 2013; Azadmard-Damirchi i in., 2011).

Zastosowanie winylowych pochodnych kwasów fenolowych jako przeciwutleniaczy może być bardziej zasadne niż ich związków macierzystych ze względu na wyższą

rozpuszczalność w matrycach olejowych (Pudel i in., 2014). Dodatkowo, wskazuje się, że obecność grupy metoksylowej i hydroksylowej w strukturze tych związków poprawia ich właściwości przeciwutleniające (Terpinc i in., 2011; Karamać i in., 2005). Terpinc i in. (2011) potwierdzili, że pochodne fenolowe (w tym 4-winylosyringol i 4-winylogwajakol) mogą być skutecznymi przeciwutleniaczami w wodnym układzie emulsyjnym, zawierającym kwas linolowy i β-karoten. Z kolei badania prowadzone przez Tańską i in. (2018) zasugerowały, że pochodne kwasów fenolowych mogą ograniczać utlenianie w tłoczonych na zimno olejach lnianym i rzepakowym oraz oliwie extra virgin. W badaniach tych wykazano, że 4-winylgwajakol skuteczniej hamował utlenianie lipidów niż 4-winylosyringol, przy czym lepsze właściwości przeciwutleniające 4-winylgwajakolu mogły wynikać z jego niższej topologicznej powierzchni polarnej (TPSA) cząsteczki (29,46 vs. 38,70). Niemniej jednak, w cytowanej pracy badano jedynie pojedyncze oleje handlowe, o istotnie różnym składzie kwasów tłuszczowych oraz różnej zawartości małocząsteczkowych składników o właściwościach pro- lub przeciwutleniających, które niewątpliwie mogły mieć wpływ na mechanizm przeciwutleniającego działania tych pochodnych kwasów fenolowych. Wskazuje się, że substancje te mogą wykazywać działanie antagonistyczne lub synergistyczne w stosunku do przeciwutleniaczy fenolowych (Rokosik i in., 2020b; Zhong i Shahidi, 2011). Jak już wcześniej wspomniano, również zawartość wody w olejach może determinować zarówno przebieg procesu utleniania lipidów, jak i skuteczność zawartych w nich przeciwutleniaczy. W dostępnej literaturze brak jest jednak dokładnych informacji dotyczących wpływu związków fenolowych i ich pochodnych na proces utleniania olejów roślinnych o różnej zawartości wody. Badania takie prowadzono dotychczasowo jedynie z użyciem emulsji, głównie typu olej w wodzie. Przykładowo, Di Mattia i in. (2010) stwierdzili, że w emulsji zawierającej 20% oliwy, kwas galusowy i kwercetyna opóźniały tworzenie się wodoronadtlenków i zmniejszały ich akumulację. Z kolei Jung-Ah i in. (2018) wykazali, że kwas ferulowy i 4-winylogwajakol w emulsji zawierającej 10% oleju sojowego miały pozytywny wpływ na jego stabilność oksydacyjną.

Zrozumienie mechanizmów przeciwutleniających związków fenolowych, w tym pochodnych kwasów fenolowych, zachodzących w olejach stało się dużym wyzwaniem dla badaczy. Jest to szczególnie trudne z uwagi na złożoność matrycy olejów nierafinowanych, determinowaną dodatkowo przez wiele czynników. Znalezienie związku pomiędzy składem bioolejów a efektywnością działania przeciwutleniającego winylowych pochodnych kwasów fenolowych, 4-winylosyringolu i 4-winylogwajakolu, może przyczynić się do opracowania nowatorskich metod przedłużania trwałości bioolejów roślinnych.

2. Hipotezy badawcze, cel główny i cele szczegółowe rozprawy doktorskiej

2.1. Hipotezy badawcze

Na podstawie przeprowadzonego przeglądu literatury postawiono następujące hipotezy badawcze:

1) Biooleje roślinne zawierają zróżnicowane zawartości związków fenolowych, od których istotnie zależy ich stabilność oksydacyjna;
2) Pochodne kwasów fenolowych dodane do bioolejów roślinnych poprawiają ich stabilność oksydacyjną;
3) Początkowy skład i początkowa jakość bioolejów roślinnych wpływają na skuteczność hamowania procesów utleniania przez pochodne kwasów fenolowych;
4) Pochodne kwasów fenolowych skutecznie ograniczają degradację składników bioaktywnych będącą następstwem procesów utleniania w bioolejach roślinnych.

2.2. Cel główny

Za główny cel badawczy niniejszej rozprawy doktorskiej przyjęto ocenę możliwości zastosowania pochodnych kwasów fenolowych (tj. 4-winylogwajakolu i 4-winylosyringolu) jako przeciwutleniaczy bioolejów roślinnych.

2.3. Cele szczegółowe

W ramach rozprawy doktorskiej realizowano następujące cele szczegółowe:

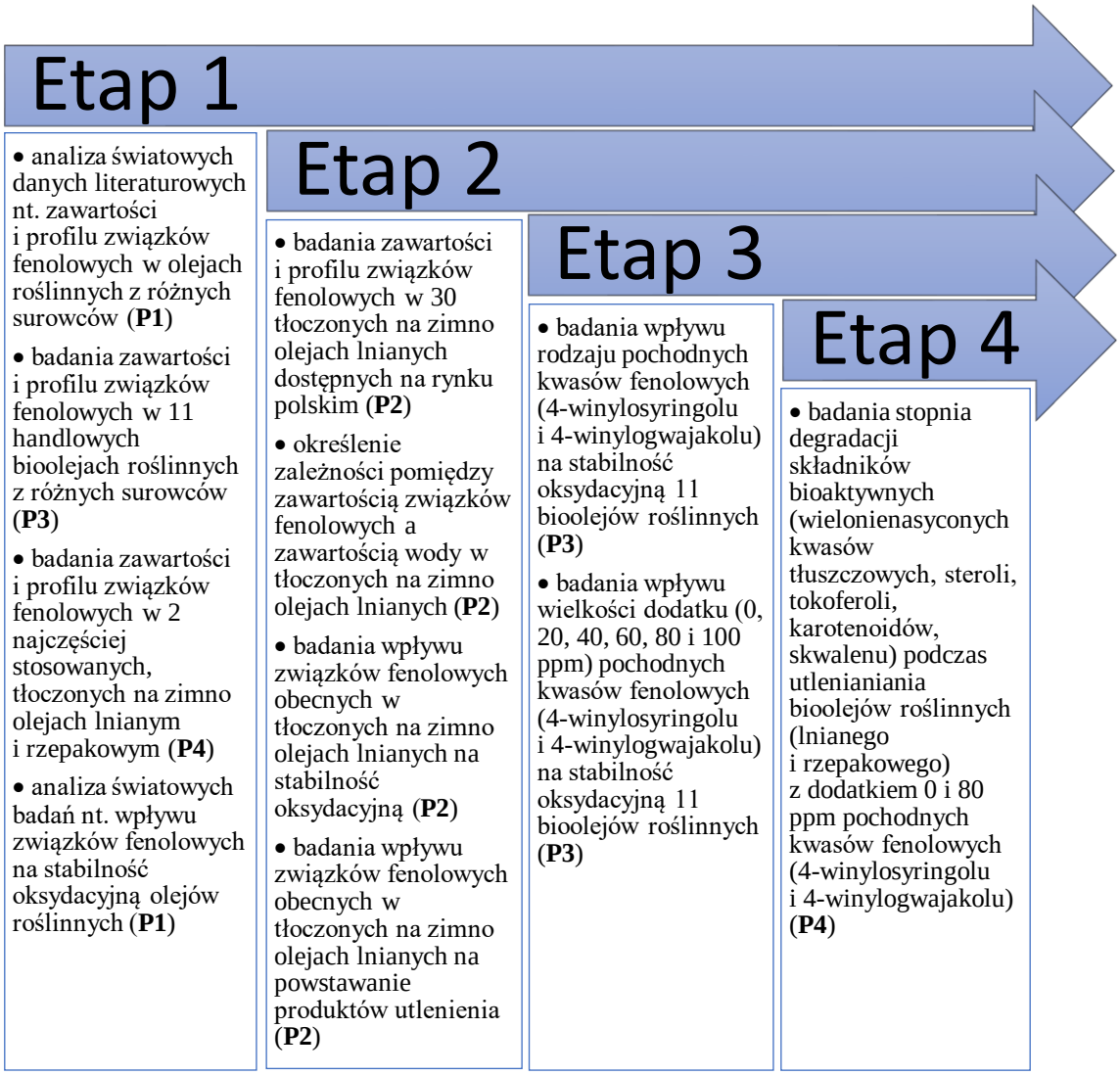
- Określenie zmienności zawartości związków fenolowych w bioolejach z różnych gatunków roślin oraz ich wpływu na stabilność oksydacyjną;
- Określenie zmienności zawartości związków fenolowych w bioolejach lnianych o różnej zawartości wody oraz ich wpływu na stabilność oksydacyjną i powstawanie produktów utlenienia;
- Określenie wpływu wielkości i rodzaju dodatku pochodnych kwasów fenolowych na stabilność oksydacyjną bioolejów roślinnych;
- Określenie wpływu dodatku pochodnych kwasów fenolowych na hamowanie degradacji natywnych składników bioaktywnych bioolejów roślinnych podczas procesów utleniania.

3. Organizacja i metodyka badań

3.1. Organizacja badań

Badania zaplanowane w niniejszej rozprawie doktorskiej podzielono na cztery zadania badawcze (schemat 1):

- **etap 1** – ocena zmienności zawartości związków fenolowych i profilu fenolowego w bioolejach roślinnych otrzymanych z różnych surowców oraz ocena wpływu dodatku związków fenolowych na stabilność oksydacyjną bioolejów (przegląd dostępnych światowych badań naukowych dotyczących składu i poprawy stabilności oksydacyjnej bioolejów oraz badania własne składu handlowych bioolejów);
- **etap 2** – zbadanie zawartości związków fenolowych w bioolejach roślinnych różniących się zawartością wody oraz ich wpływu na stabilność oksydacyjną i powstawanie produktów utlenienia w bioolejach (badania z użyciem handlowych olejów lnianych tłoczonych na zimno, w teście przechowalniczym w naturalnych warunkach);
- **etap 3** – zbadanie wpływu rodzaju i wielkości dodatków pochodnych kwasów fenolowych na stabilność oksydacyjną bioolejów roślinnych (badania z użyciem 4-winylogwajakolu i 4-winylosyringolu, handlowych olejów tłoczonych na zimno: kukurydzianego, wiesiołkowego, konopnego, makowego, dyniowego, krokoszowego, sezamowego, sojowego, słonecznikowego, z czarnuszki i z ostropestu, w teście Rancimat w 110°C);
- **etap 4** – zbadanie wpływu dodatku pochodnych kwasów fenolowych na degradację składników bioaktywnych w bioolejach roślinnych podczas utleniania (badania z użyciem 4-winylogwajakolu i 4-winylosyringolu, handlowych olejów tłoczonych na zimno rzepakowego i lnianego, w teście termostatowym w 110°C z wykorzystaniem komory do badań cieplnych).



Schemat 1. Etapy badań rozprawy doktorskiej z uwzględnieniem obejmowanych publikacji.

3.2. Materiał badań

Materiał badań laboratoryjnych stanowiły oleje tłoczone na zimno nierafinowane (bioolejе):

- otrzymane z surowca tego samego gatunku, tj. oleje lniane, które zakupiono w sklepach stacjonarnych i internetowych, wyprodukowane przez różnych producentów, w tym 29 z Polski (JAW Łącz Przetwórstwo Roślin Oleistych-Nasiennictwo Sp. z o.o./Oleje Świecie, Świecie nad Osą; Miramar, Wałbrzych; OlVita, Pszenno; Olejowy Raj, Wasilków; MWM/Oleje Ziębice, Ziębice; Oleofarm, Wrocław; Dr Gaja, Warszawa; Dary Natury, Koryciny; Bio-Line, Bydgoszcz, dystrybutor F.H.U. 4MAGIC, Andrychów; Semco, Śmiłowo; Zakłady Tłuszczowe „Kruszwica”, Kruszwica;

VitaCorn, Poznań; FONDERHILL/Eurolen, Iława; Złoto Polskie - Family Business s.c., Kalisz (Ekologiczny, Olandia i Złotolen); Sto Procent z Natury, Radziemice; Look Food, Warszawa; Instytut Włókien Naturalnych i Roślin Zielarskich/Bioflax, Poznań; Polska Olejarnia, Mielec; Gospodarstwo Rolne Piotr Marciniak/Olej Lubuski, Lubusko; Sosta, Rydułtowy; Niwiki, Zwoleń; Skolej SC, Pakość; Olejarnia Kropla Omega, Starachowice; BIOOIL s.c., Zielona Góra; Olejarnia Kołodziejewo, Kołodziejewo; Barwy Zdrowia, Tarnogród; Zakład Wytłaczania Oleju, Grodzisk Wielkopolski) oraz 1 z Niemiec (Bio Planète/Ölmühle Moog GmbH, Lommatzsch, dystrybutor Bio Planet, Leszno, Polska) (**P2**),

- otrzymane z surowców różnych gatunków, tj. oleje: dyniowy (Semco, Śmiłowo, Polska), konopny (Semco, Śmiłowo, Polska), krokoszowy (Niwiki, Zwoleń, Polska), kukurydziany (OlVita, Pszenno, Polska), makowy (Niwiki, Zwoleń, Polska), rzepakowy (Oleofarm, Wrocław, Polska), sezamowy (Niwiki, Zwoleń, Polska), słonecznikowy (Niwiki, Zwoleń, Polska), sojowy (OlVita, Pszenno, Polska), wiesiołkowy (Semco, Śmiłowo, Polska), z czarnuszki (Semco, Śmiłowo, Polska) oraz z ostropestu (Semco, Śmiłowo, Polska) (**P3**);
- najczęściej stosowane ze względu na łatwą dostępność i przystępną cenę, tj. oleje lniany (JAW Łącz Przetwórstwo Roślin Oleistych-Nasiennictwo Sp. z o.o./Oleje Świecie, Świecie nad Osą) i rzepakowy (Oleofarm, Wrocław, Polska).

Zgodnie z informacjami producentów zamieszczonymi na etykiecie opakowania, wszystkie oleje cechowały się aktualną datą przydatności do spożycia. Materiał badań analizowano bezpośrednio po otwarciu opakowania i przechowywano między analizami w zamrażarce (w temperaturze -20°C) nie dłużej niż 4 tygodnie.

W badaniach zastosowano dwie pochodne kwasów fenolowych jako wzorce analityczne o deklarowanej czystości >95%; 4-winylogwajakol (2-metoksy-4-winylofenol) zakupiony od firmy Sigma-Aldrich (St. Louis, Missouri, Stany Zjednoczone, dostawca Poznań, Polska) oraz 4-winylosyringol (4-etenylo-2,6-dimetoksyfenol) zakupiony od firmy EnamineStore (Ryga, Łotwa).

3.3. Metody badawcze

3.3.1. Oznaczenie parametrów jakościowych bioolejów

Wskaźniki jakości, takie jak liczba kwasowa (mg KOH/g), liczba nadtlenowa (mEq O_2/kg) i liczba anizydynowa (-) oraz zawartość kwasów sprzężonych, dienów (%) i trienów

(%), oznaczono na podstawie metod standardowych zgodnie z metodyką opisaną przez Japan Oil Chemists' Society (JOCS) do analizy tłuszczów, olejów i materiałów pokrewnych (Standard Methods, 2013).

Zawartość wody (ppm) oznaczono przy wykorzystaniu zestawu do miareczkowania Karla Fischera (Coulometer 917, Metrohm, Herisau, Szwajcaria) wyposażonego w elektrodę generacyjną z diafragmą zgodnie z metodyką standardową (EN-ISO 8534:2017) z pewnymi modyfikacjami. Próbkę oleju wstrzyknięto do celi pomiarowej za pomocą strzykawki (z igłą o średnicy 0,8 mm). W analizie kulometrycznej wykorzystano jednoskładnikowy odczynnik HYDRANAL Coulomat AG (Honeywell, Charlotte, Karolina Północna, Stany Zjednoczone), jako katolit zastosowano HYDRANAL Coulomat CG (Honeywell, Charlotte, Karolina Północna, Stany Zjednoczone). Parametry urządzenia były następujące: wartość startu dryftu 20 µg/min, względna wartość stopu dryftu 5 µg/min, prąd polaryzacji 10 µA, czas ekstrakcji próbki 90 s, prędkość miareczkowania 8/10 (gdzie 10 stanowi maksymalną prędkość miareczkowania urządzenia).

Barwę zmierzono za pomocą cyfrowej analizy obrazu (DIA) zgodnie z metodyką opisaną przez Tańską i in. (2005). Próbkę oleju (15 ml w zlewce o pojemności 25 ml, wysokość warstwy 2 cm) naniesiono na białą płytkę, a obraz uzyskano dzięki niskoszumowej kamerze CCD o wysokiej rozdzielczości (Nikon DXM-1200, Nikon Inc., Melville, Nowy Jork, Stany Zjednoczone). Jako źródło światła zastosowano zestaw typu RB 5004 HF-High (Frequency Daylight Copy Light) wyposażony w 2 lampy z 2 świetlówkami o temperaturze barwowej około 5400 K (odpowiada naturalnemu światłu dziennemu) (Kaiser Fototechnik GmbH & Co.KG, Buchen, Niemcy). Obraz analizowano przy użyciu oprogramowania LUCIA G v. 4.80 (Laboratory Imaging, Praga, Czechy), a wyniki wyrażono jako parametry składowe modelu barwy CIEL*a*b*, w którym L* – oznacza jasność barwy, a* – oznacza zieloność/czerwoność (ujemne/dodatnie wartości) barwy, b* – oznacza niebieskość/żółtość (ujemne/dodatnie wartości) barwy.

3.3.2. Oznaczenie składu kwasów tłuszczowych w bioolejach

Metylację kwasów tłuszczowych przeprowadzono zgodnie z metodyką podaną przez Zadernowskiego i Sosulskiego (1978). Estry metylowe kwasów tłuszczowych analizowano z wykorzystaniem techniki chromatografii gazowej w systemie GC–MS QP2010 PLUS (Shimadzu, Kyoto, Japonia). Rozdział kwasów tłuszczowych przeprowadzono na kolumnie kapilarnej BPX70 (25 m × 0,22 mm × 0,25 µm, SGE Analytical Science, Victoria, Australia)

przy udziale helu jako gazu nośnego o natężeniu przepływu 0,9 ml/min. Parametry temperaturowe rozdziału kwasów tłuszczowych były następujące: temperatura nastrzyku 240°C, temperatura źródła jonów 240°C, temperatura kolumny w zakresie od 150°C do 250°C. Energię elektronów ustawiono na 70 eV, natomiast tryb całkowitego prądu jonowego (TIC) mieścił się w zakresie 50–500 m/z. Kwasy tłuszczowe zidentyfikowano na podstawie czasów retencji oraz widm masowych pików, a ich zawartość określono masowo (g/100 g) w odniesieniu do wzorca wewnętrznego (kwas margarynowy) lub procentowo (%).

W oparciu o skład kwasów tłuszczowych oszacowano sumę kwasów tłuszczowych nasyconych (SFA), jednonienasyconych (MUFA) i wielonienasyconych (PUFA), stosunek kwasów tłuszczowych omega 3 (n-3) do omega 6 (n-6) oraz wskaźniki utleniania takie jak liczba Cox'a, SFA-do-USFA (nienasycone kwasy tłuszczowe, suma MUFA i PUFA), PUFA-do-SFA, MUFA-do-PUFA, C16:0-do-C18:2, C18:2-do-C18:0 i C18:3-do-C18:2. Wartość liczby Cox'a obliczono według wzoru podanego przez Cao i in. (2015), gdzie Cox = (% C18:1 × 1 + % C18:2 × 10,3 + % C18:3 × 21,6)/100. Dodatkowo, oszacowano wskaźnik peroksydacji (PI) na podstawie składu kwasów tłuszczowych według wzoru podanego przez Yun i Surh (2012), gdzie PI = (% monoenowego kwasu tłuszczowego × 0,025) + (% dienowego kwasu tłuszczowego × 1) + (% trienowego kwasu tłuszczowego × 2) + (% tetraenowego kwasu tłuszczowego × 4) + (% pentaenowego kwasu tłuszczowego × 6) + (% heksaenowego kwasu tłuszczowego × 8).

3.3.3. Oznaczenie zawartości związków anty- i prooksydacyjnych w olejach

Zawartość skwalenu i steroli oznaczono zgodnie z metodyką podaną przez Roszkowską i in. (2015). Próbki olejowe po procesie derywatyzacji rozcieńczono w *n*-heptanie i poddano analizie na chromatografie gazowym GC-MS QP2010 PLUS 176 (Shimadzu, Kyoto, Japan) sprzężonym ze spektrometrem mas i wyposażonym w kolumnę kapilarną ZB-5MSi (30 m × 0,25 mm × 0,25 µm, Phenomenex, Torrance, Kalifornia, Stany Zjednoczone) przy udziale helu jako gazu nośnego o natężeniu przepływu 0,9 ml/min. Parametry temperaturowe rozdziału związków były następujące: temperatura nastrzyku 230°C, temperatura kolumny początkowo 70°C przez 2 min, wzrost do 230°C z szybkością 15°C/min, do 310°C z szybkością 3°C/min i wstrzymanie 10 min, temperatura interfejsu 240°C, temperatura źródła jonów 220°C. Energię elektronów ustawiono na 70 eV, natomiast tryb TIC mieścił się w zakresie 100–600 m/z. Skwalen i poszczególne sterole zidentyfikowano na podstawie widm masowych w porównaniu z bibliotekami widm masowych (biblioteka NIST08, Shimadzu, Kyoto, Japonia) oraz czasów

retencji pików, a ich zawartość w oleju określono masowo (mg/100 g) w odniesieniu do wzorca wewnętrznego (5-α-cholestan).

Zawartość tokoferoli oznaczono w oparciu o metodykę opisaną w pracy Dąbrowskiego i in. (2017). Próbki olejów rozcieńczone w *n*-heksanie poddano analizie za pomocą chromatografu cieczowego HPLC Agilent Technologies 1200 (Santa Clara, Kalifornia, Stany Zjednoczone) wyposażonego w detektor fluorescencyjny tej samej firmy i kolumnę LiChrospher Si 60 (0,25 m × 4 mm × 5 μm, Merck, Darmstadt, Niemcy). Jako fazę ruchomą zastosowano 0,7% roztwór izopropanolu w *n*-heksanie o natężeniu przepływu 1 ml/min, natomiast długości fali wzbudzenia i emisji detektora fluorescencyjnego ustawiono odpowiednio na 296 nm i 330 nm. Zawartość tokoferoli w oleju wyznaczono z krzywych kalibracyjnych przygotowanych dla wzorców tokoferoli (α-tokoferol, γ-tokoferol, δ-tokoferol) i podano w mg/100 g.

Zawartość karotenoidów oznaczono zgodnie z metodyką podaną przez Czaplickiego i in. (2016b). Otrzymane roztwory analizowano techniką chromatografii cieczowej RP-HPLC przy użyciu aparatu Agilent Technologies 1200 RP-HPLC (Santa Clara, Kalifornia, Stany Zjednoczone), wyposażonego w detektor z matrycą diodową (DAD) oraz kolumnę chromatograficzną YMC-C30 (0,15 m × 4,6 mm × 5 μm, YMC-Europe GmbH, Dinslaken, Niemcy). Temperatura kolumny wynosiła 30°C, a do elucji związków zastosowano gradient metanolu (A) i eteru metylowo-tert-butylowego (B) zaprogramowany w następujący sposób: od 0 do 5 min 95% A, do 25 min spadek do 72% A z dalszym spadkiem do 33 min do 5% A, następnie wzrost do 95% A oraz stabilizacja do 60 min. Absorbancję roztworu mierzono przy 450 nm. Karotenoidy zidentyfikowano na podstawie czasów retencji i widm absorpcji pików, a ich zawartość w oleju określono masowo (mg/100 g) w odniesieniu do wzorca wewnętrznego (β-apo-8'-karotenalu).

Całkowitą zawartość barwników chlorofilowych oznaczono spektrofotometrycznie zgodnie z metodyką opisaną przez Roszkowską i in. (2015) przy użyciu wielofunkcyjnego czytnika mikropłytek FLUOstar OMEGA (BMG Labtech GmbH, Ortenberg, Niemcy). Absorbancję czystych olejów zmierzono przy 630, 670 i 710 nm względem powietrza, a całkowitą zawartość chlorofili w oleju wyrażono w mg/100 g.

Całkowitą zawartość związków fenolowych w formie wolnej oznaczono spektrofotometrycznie w reakcji barwnej z odczynnikiem Folina-Ciocialteu'a według metodyki opisanej przez Tańską i in. (2018). Absorbancję roztworów zmierzono za pomocą wielofunkcyjnego czytnika mikropłytek FLUOstar OMEGA (BMG Labtech GmbH,

Ortenberg, Niemcy), a całkowitą zawartość związków fenolowych w oleju obliczono na podstawie krzywej kalibracyjnej sporządzonej dla D-katechiny i wyrażono w mg/100 g.

Skład kwasów fenolowych oznaczono zgodnie z metodyką podaną przez Tańską i in. (2018) z wykorzystaniem szklanej komory próżniowej (Witko, Łódź, Polska) oraz kolumnienek SPE Supelco wypełnionych diolem (500 mg) (Sigma-Aldrich, Poznań, Polska). Otrzymane roztwory analizowano techniką chromatografii cieczowej RP-HPLC przy użyciu aparatu Agilent Technologies 1200 RP-HPLC (Santa Clara, Kalifornia, Stany Zjednoczone) wyposażonego w detektor fotodiodowy i kolumnę chromatograficzną Eclipse XDB-C18 (0,15 m × 4,6 mm × 5 μm, Agilent Technologies, Santa Clara, Kalifornia, Stany Zjednoczone). Temperatura kolumny wynosiła 30°C, natomiast faza ruchoma składała się z wody dejonizowanej:acetonitrylu:kwasu mrówkowego (88:10:2, v/v/v) o natężeniu przepływu 0,8 ml/min. Detekcję kwasów fenolowych prowadzono przy długościach fal 260 i 320 nm. Kwasy fenolowe zidentyfikowano na podstawie czasów retencji i widm absorpcji pików, a ich zawartość w oleju wyznaczono z krzywych kalibracyjnych przygotowanych dla wzorców kwasów fenolowych (wanilinowego, kawowego, ferulowego, p-kumarowego, sinapowego, itp.) i podano w mg/100g.

3.3.4. Oznaczenie stabilności oksydacyjnej olejów

3.3.4.1. Test Rancimat

Stabilność oksydacyjną olejów (próbki 2,5 ± 0,001 g) wyznaczono za pomocą aparatu Rancimat 743 (Metrohm, Herisau, Szwajcaria) w 110°C przy natężeniu przepływu powietrza 20 l/h zgodnie z metodyką opisaną przez Tańską i in. (2018). Pomiar stabilności oksydacyjnej oparto na detekcji konduktometrycznej lotnych produktów utlenienia, a czas, który upłynął do pojawienia się lotnych produktów utlenienia oznaczono jako czas indukcji (h). Analizie poddano oleje bez dodatków oraz z dodatkiem pochodnych kwasów fenolowych w postaci roztworów etanolowych w stężeniu 20, 40, 60, 80 i 100 ppm, po czym rozpuszczalnik odparowano w strumieniu azotu.

3.3.4.2. Test przechowalniczy w warunkach naturalnych

Oleje (200 ml zamknięte w podobnych butelkach o pojemności 250 ml, bez usuwania powietrza) przechowywano przez okres 30-stu dni (w maju) w oświetlonym miejscu tj. na półce wystawionej na działanie naturalnego (światło dzienne) i sztucznego źródła światła (oświetlenie sufitowe LED o mocy 50 W) przez 15 h dziennie; symulacja przechowywania

w warunkach sklepowych w temperaturze otoczenia (21 ± 2°C) i wilgotności względnej 35 ± 3,0% mierzonej elektronicznym termometrem z higrometrem typu LB-710 (LAB-EL, Reguły, Polska).

3.3.4.3. Test przechowalniczy w warunkach wymuszonych

Oleje (100 g umieszczone w otwartych zlewkach o pojemności 400 ml, średnicy 8 cm i wysokości 11 cm), bez oraz z dodatkiem pochodnych kwasów fenolowych (jako roztworów etanolowych) w ilości 80 mg/100 g, przechowywano w komorze do badań cieplnych typu KBC-100W (WAMED, Warszawa, Polska) w temperaturze 110 ± 1°C przez okres odpowiedni dla czasu indukcji danego rodzaju oleju wyznaczonego w teście Rancimat (tj. 8,80 h, 9,08 h i 10,83 h odpowiednio dla oleju rzepakowego i olejów z 4-winylosyringolem i 4-winylogwajakolem, oraz 1,96 h, 2,00 h i 3,00 h dla oleju lnianego i olejów z 4-winylosyringolem i 4-winylogwajakolem). Po zakończeniu testu przechowalniczego, zlewki z olejami natychmiast schłodzono i przechowywano w lodówce (w temperaturze 8°C) nie dłużej niż 5 dni. Aby uniknąć utleniania, zlewki po schłodzeniu przedmuchano azotem i szczelnie zamknięto parafilmem.

3.3.5. Analiza statystyczna

Wszystkie oznaczenia wykonano w 3 równoległych pomiarach (z wyjątkiem analizy barwy, która wymagała dziesięciu pomiarów) dla każdej próbki oleju. Wyniki przeprowadzonych badań analizowano za pomocą najnowszych wersji programu Statistica PL (StatSoft, Kraków, Polska) przy wykorzystaniu jednoczynnikowej analizy wariancji (ANOVA) z testem Tukey'a na poziomie istotności $p \leq 0,05$ oraz z testem Duncan'a na poziomie istotności $p \leq 0,05$, dwuczynnikowej analizy wariancji (ANOVA) z testem Tukey'a na poziomie istotności $p \leq 0,05$, analizy głównych składowych (PCA) na poziomie istotności $p \leq 0,05$, a także analizy korelacji Pearson'a na poziomie istotności $p \leq 0,05$. Analizę korelacji Pearson'a przeprowadzono dodatkowo za pomocą programu RStudio wersja 4.0.2 (RStudio Inc., Boston, Massachusetts, Stany Zjednoczone) przy użyciu pakietu Corrplot, w celu graficznego przedstawienia zależności pomiędzy analizowanymi cechami.

5. Rezultaty badań przedstawione w monotematycznym cyklu publikacji

5.1. Zawartość związków fenolowych w bioolejach z różnych gatunków roślin oraz ich wpływ na stabilność oksydacyjną

Publikacja **P1** stanowi przegląd i zbiór danych literaturowych na temat zawartości i rodzaju związków fenolowych obecnych w olejach roślinnych, a także metod ich oznaczania. Ponadto, w publikacji **P1** omówiono również dostępne w literaturze wyniki badań dotyczących wpływu związków fenolowych na stabilność oksydacyjną olejów roślinnych.

Przegląd literaturowy w publikacji **P1** wykazał, że zarówno całkowita zawartość związków fenolowych, jak i profil fenolowy, są wysoce zróżnicowane i zależą przede wszystkim od surowca oraz metody produkcji oleju. Badacze zwrócili uwagę, że tłoczenie na zimno i tłoczenie na gorąco z surowca poddanego uprzednio ogrzewaniu mikrofalowemu pozwala na uzyskanie oleju o wyższej zawartości związków fenolowych. Generalnie, głównym źródłem związków fenolowych są oleje otrzymane z takich surowców roślinnych jak otręby ryżowe oraz owoce oliwki, ale znaczne ich ilości można również znaleźć w olejach z nasion rzepaku i lnu oraz pestek winogron i dyni. W olejach otrzymanych z innych surowców roślinnych, tj. nasion żmijowca, orzechów laskowych i zarodków kukurydzy, zawartość związków fenolowych jest na ogół niska. Z kolei dane literaturowe dotyczące olejów tłoczonych na zimno z owoców awokado, nasion chia czy nasion słonecznika są niejednoznaczne, co wskazuje na potrzebę prowadzenia dalszych badań w tym zakresie. W profilu fenolowym olejów roślinnych najczęściej występują kwasy fenolowe i flawonoidy, natomiast lignany, sekoirydoidy oraz inne pochodne fenolowe są obecne znacznie rzadziej i w mniejszych ilościach.

W **tabeli 1** zestawiono dane literaturowe nt. zawartości i profilu fenolowego typowych bioolejów roślinnych uzyskane w światowych badaniach. Przedstawione wyniki potwierdzają wysoki stopień zróżnicowania zawartości wolnych związków fenolowych w bioolejach roślinnych (zawartość w granicach 0,39-760 mg/100 g). Wysoką zawartość związków fenolowych zaobserwowano w oleju z czarnuszki (>640 mg/100 g), ale oleje takie jak konopny, dyniowy i rzepakowy również mogą zawierać ich znaczne ilości (>165 mg/100 g). Olej żmijowcowy i olej makowy cechują się niską zawartością związków fenolowych (<19 mg/100 g), z kolei oleje ogórecznikowy, wiesiołkowy, krokoszowy i oliwkowy mogą zawierać około 50 mg/100 g tych związków. W oleju lnianym stwierdzono obecność takich kwasów fenolowych jak kwas protokatechowy, kwas wanilinowy, kwas p-kumarowy, kwas ferulowy i kwas sinapowy, jednakże ich zawartości były generalnie niskie (<6 μg/100 g). Podobnie jak

w oleju makowym, w którym zidentyfikowano kwasy wanilinowy, p-kumarowy, ferulowy i sinapowy w ilościach <3 μg/100 g. Generalnie, dużą różnorodność kwasów fenolowych i stosunkowo wysoką zawartość poszczególnych ich frakcji stwierdzono tylko w oleju dyniowym i oleju oliwkowym. Zgodnie z **tabelą 1**, w profilu fenolowym tych olejów występują głównie kwasy wanilinowy, kawowy, p-kumarowy i ferulowy, a ich zawartości mogą osiągać odpowiednio 2750, 3830, 2660 i 5170 μg/100 g w oleju dyniowym oraz 440, 3000, 254 i 620 μg/100 g w oleju oliwkowym. Z kolei w oleju rzepakowym potwierdzono jedynie wysoką zawartość kwasu ferulowego (do 160 μg/100 g) i kwasu sinapowego (do 680 μg/100 g). Dane przedstawione w **tabeli 1** wskazują również, że typowe biooleje roślinne są generalnie ubogie we flawonoidy lub nie były pod tym względem dostatecznie zbadane. Jedynie w oleju oliwkowym oznaczono wysoką zawartość apigeniny (do 930 μg/100 g) i luteoliny (do 3800 μg/100 g). Xuan i in. (2018) potwierdzili obecność flawonoidów również w innych olejach, jednak ich ilość była ponad 40-krotnie mniejsza niż związków fenolowych. Cytowani autorzy zidentyfikowali w oleju rzepakowym eskuletynę i izokwercytynę, w oleju lnianym – eskuletynę, kempferol i ramnetynę, a w oleju z chia – mirycetynę i luteolinę.

Tabela 1. Zawartość i profil związków fenolowych w bioolejach roślinnych badanych na świecie (opracowanie własne na podstawie danych z publikacji **P1**).

Rodzaj biooleju	**Związki fenolowe w formie wolnej (mg/100 g)**	**Kwasy fenolowe (μg/100 g)**						**Flawonoidy (μg/100 g)**	
		kwas protokatechowy	kwas wanilinowy	kwas kawowy	kwas p-kumarowy	kwas ferulowy	kwas sinapowy	apigenina	luteolina
olej amarantusowy	33,50	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
olej ogórecznikowy	58,10	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
olej z czarnuszki	648,00-760,00	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
olej z chia	2,00-94,00	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
olej żmijowcowy	3,56	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
olej wiesiołkowy	67,90	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
olej lniany	0,39-29,40	0,00-1,47	0,00-1,00	0,00	0,00-1,90	0,00-5,80	0,00-0,60	b.d.	b.d.
olej konopny	2,45-267,50	0,00	2,00	0,00	2,00	1,00	3,00	b.d.	b.d.
olej makowy	1,33-19,00	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
olej dyniowy	0,46-224,00	0,00-2070,00	0,00-2750,00	0,00-3830,00	0,00-2660,00	0,00-5170,00	0,00	0,00-0,20	0,00
olej rzepakowy	0,57-165,45	0,00	0,00-1,00	0,00-3,33	0,00-34,00	3,00-160,00	12,31-680,00	b.d.	b.d.
olej krokoszowy	2,62-52,53	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
olej oliwkowy	9,76-57,32	0,00	0,00-440,00	0,00-3000,00	0,00-254,00	0,00-620,00	0,00	0,00-920,00	0,00-3800,00

b.d.–brak danych.

W publikacjach **P3** i **P4** zbadano zawartość wolnych związków fenolowych i kwasów fenolowych w handlowych bioolejach roślinnych (oleje konopny, makowy, krokoszowy, wiesiołkowy, z ostropestu, sojowy, słonecznikowy, kukurydziany, sezamowy, z czarnuszki, dyniowy, lniany, rzepakowy). Wśród bioolejów roślinnych dostępnych na rynku polskim również zaobserwowano wyraźne różnice w zawartości wolnych związków fenolowych w zależności od gatunku surowca, z którego został wyprodukowany (**tabela 2**). Analiza wyników wykazała, że badane biooleje roślinne cechowały się generalnie niską zawartością wolnych związków fenolowych, przy czym w olejach makowym, sojowym i słonecznikowym ich zawartość była śladowa (<0,07 mg/100 g) (**tabela 2**). Najwyższą zawartość tych związków oznaczono w oleju z czarnuszki (20,42 mg/100 g), natomiast w pozostałych bioolejach ich zawartość mieściła się w granicach 1,03-5,35 mg/100 g. W badanych bioolejach roślinnych dominujące okazały się takie kwasy fenolowe jak kwas p-kumarowy (0,23-44,38 μg/100 g), kwas ferulowy (2,31-94,89 μg/100 g) i kwas sinapowy (2,98-226,69 μg/100 g). Generalnie, wysoką zawartość kwasu p-OH-hydroksybenzoesowego stwierdzono w oleju lnianym (1,17 μg/100 g), kwasu wanilinowego w oleju z ostropestu (3,35 μg/100 g), kwasu protokatechowego w oleju lnianym (1,48 μg/100 g), kwasu p-kumarowego w oleju kukurydzianym (44,38 μg/100 g), kwasu ferulowego i kwasu sinapowego w oleju z czarnuszki (odpowiednio 94,89 i 226,69 μg/100 g). Ponadto, w oleju kukurydzianym i oleju z czarnuszki stwierdzono wysoką całkowitą zawartość wolnych kwasów fenolowych (odpowiednio 150,18 i 321,59 μg/100 g).

Tabela 2. Zawartość i profil związków fenolowych w różnych bioolejach roślinnych dostępnych na rynku (opracowanie własne na podstawie danych z publikacji **P3** i **P4**).

Rodzaj biooleju	**Związki fenolowe w formie wolnej (mg/100 g)**	**Kwasy fenolowe (μg/100 g)**						
		kwas p-OH-hydroksybenzoesowy	kwas wanilinowy	kwas protokatechowy	kwas p-kumarowy	kwas ferulowy	kwas sinapowy	całkowita zawartość
olej konopny	2,70	0,00	0,00	0,00	1,58	2,31	4,86	10,49
olej makowy	ilość śladowa	0,00	0,00	0,00	0,00	4,40	11,96	16,38
olej krokoszowy	3,26	0,00	0,00	0,00	1,42	3,33	8,84	13,59
olej wiesiołkowy	2,26	0,00	0,00	0,00	0,00	5,71	2,98	8,69
olej z ostropestu	5,35	0,00	3,35	0,00	1,69	11,32	7,95	24,31
olej sojowy	0,07	0,00	0,00	0,00	1,72	8,76	33,32	43,80
olej słonecznikowy	ilość śladowa	0,00	0,00	0,00	1,45	4,22	8,76	26,72
olej kukurydziany	1,53	0,00	0,00	0,00	44,38	30,01	75,79	150,18
olej sezamowy	1,88	0,00	0,00	0,00	4,97	31,58	8,35	44,90
olej z czarnuszki	20,42	0,00	0,00	0,00	0,00	94,89	226,69	321,59
olej dyniowy	2,68	0,00	0,00	0,00	0,29	3,10	0,00	6,31
olej lniany	1,56	1,17	0,00	1,48	0,23	0,00	0,00	4,38
olej rzepakowy	1,03	0,00	0,00	0,00	3,33	5,42	12,30	21,10

Przegląd literaturowy w publikacji **P1** dodatkowo wskazał, że różnica w oznaczanej zawartości związków fenolowych może wynikać również z wybranej metody analitycznej. Zauważono, że najbardziej popularne są dwie metody oznaczania związków fenolowych w olejach roślinnych, a mianowicie metoda spektrofotometryczna i metoda chromatograficzna. Parametry obu metod są jednak często modyfikowane przez badaczy by dostosować je do warunków prowadzonych przez nich badań, co w konsekwencji może również przekładać się na ostateczny wynik oznaczenia. Ponadto, kilku badaczy w swoich pracach zasugerowało potrzebę oznaczania całkowitej zawartości związków fenolowych (zarówno w formie wolnej, jak i związanej) w olejach roślinnych. Jednakże zwrócono również uwagę, że zastosowanie metod ilościowych opartych na selektywnej fragmentacji MS/MS względem form sprzężonych może powodować wątpliwości co do prawidłowości takich pomiarów i wyciągniętych na ich podstawie wniosków (Bellumori i in., 2019; Celano i in., 2018). Z drugiej jednak strony, włączenie hydrolizy chemicznej w procedurę oznaczania całkowitej zawartości związków fenolowych może być przydatne głównie przy oszacowaniu składu sekoirydoidów w olejach roślinnych (Mulinacci i in., 2006).

Wielu badaczy wskazuje, że związki fenolowe mają duży wpływ na stabilność oksydacyjną olejów roślinnych, i w konsekwencji podejmuje się próby zastosowania tych związków jako przeciwutleniaczy, szczególnie w olejach o niskiej ich zawartości (zgodnie z danymi w publikacji **P1**). Przegląd literatury wskazał dwa podstawowe mechanizmy działania przeciwutleniającego związków fenolowych w olejach roślinnych, tj. przeniesienie pojedynczego elektronu (SET) i przeniesienie atomu wodoru (HAT), który określa się jako dominujący (Koroleva i in., 2014; Zhu i in., 2013). Aktywność przeciwutleniającą związków fenolowych przewiduje się również na podstawie ich budowy chemicznej, a także wartości energii dysocjacji wiązania (BDE) dla grupy O-H przeciwutleniacza fenolowego (Choe i Min, 2009). Jednakże, badania ostatnich lat sugerują, że działanie przeciwutleniające związków fenolowych w olejach roślinnych może wynikać również z polarności przeciwutleniacza. Wielu badaczy opiera swoje wnioski na teorii „paradoksu polarnego", zgodnie z którym przeciwutleniacze polarne (takie jak związki fenolowe) są lepszymi przeciwutleniaczami matryc hydrofobowych niż typowe niepolarne odpowiedniki (takie jak tokole) (Budilarto i Kamal-Eldin, 2015).

W publikacji **P1** zebrano dane literaturowe dotyczące wpływu związków fenolowych, tj. kwasów fenolowych, flawonoidów oraz pochodnych kwasów fenolowych, aldehydów fenolowych i alkoholi fenolowych, na stabilność oksydacyjną olejów roślinnych. Dane literaturowe uzupełniono również o polarność związków fenolowych, wyrażoną jako

topologiczna powierzchnia polarna (TPSA). Analiza zebranych danych wykazała jednak niejednoznaczny wpływ tego czynnika na stabilność oksydacyjną olejów roślinnych, co sugeruje konieczność rozpatrywania działania przeciwutleniającego związków fenolowych w wielu aspektach. W **tabeli 3** zestawiono wyniki badań stabilności oksydacyjnej bioolejów roślinnych z dodatkiem związków fenolowych (tj. kwasów fenolowych i ich pochodnych, flawonoidów). Dotychczasowo, w badaniach wykorzystano 5 rodzajów kwasów fenolowych (ferulowy, kawowy, cynamonowy, sinapowy, syringowy), które dodawano w postaci czystych związków (w stężeniu 0,5 mM) lub w formie roztworów alkoholowych (w stężeniu 100, 250, 500 μM) do dwóch typowych bioolejów roślinnych (olej lniany i olej rzepakowy). Zauważono, że jedynie kwasy ferulowy i kawowy cechowały się korzystnym wpływem na stabilność oksydacyjną olejów (zwiększenie czasu indukcji o 12-94%) podczas obróbki wysokotemperaturowej (≥120°C). Z kolei pozostałe kwasy fenolowe wykazały prooksydacyjne efekty działania w oleju rzepakowym, a spadek jego stabilności oksydacyjnej sięgał nawet 44% (po zastosowaniu kwasu cynamonowego). Dostępne badania wykazały również, że flawonoidy były dość licznie stosowane jako przeciwutleniacze (czyste związki w stężeniu 200 ppm) oleju rzepakowego (test przechowalniczy w 60°C), i skutecznie chroniły matrycę olejową przed procesem utleniania (zmiana stabilności oksydacyjnej od +9,38% do prawie +370%). Generalnie, kwercetyna, mirycetyna, morina, rutyna, naringina i [-]epikatechina wykazały bardziej korzystne efekty działania na stabilność oksydacyjną oleju rzepakowego (zwiększenie o co najmniej 71%) niż pozostałe flawonoidy. Spośród pochodnych kwasów fenolowych dotychczasowo stosowane były jedynie takie związki jak 4-winylosyringol, 4-winylogwajakol (w postaci roztworów w stężeniu 20, 40, 80 mg/100 g) i wanilina (czysty związek w stężeniu 0,5 mM) jako przeciwutleniacze bioolejów roślinnych ogrzewanych w wysokiej temperaturze (testy w 110 i 140°C). Z przeprowadzonych badań wynika, że 4-winylogwajakol i wanilina cechowały się lepszym efektem przeciwutleniającym (zmiana stabilności w granicach 13-50%) niż 4-winylosyringol.

Należy jednak zaznaczyć, że badania stabilności oksydacyjnej bioolejów roślinnych z dodatkiem przeciwutleniaczy fenolowych są nadal nieliczne. Zebrane dane literaturowe generalnie sugerują, że kwasy fenolowe mogą wykazywać działanie prooksydacyjne w olejach roślinnych, w przeciwieństwie do flawonoidów i pochodnych kwasów fenolowych, które wywierają korzystny wpływ na ich stabilność oksydacyjną. Z drugiej jednak strony, wartości TPSA flawonoidów są stosunkowo wysokie (>90), co wskazuje na trudności ich rozpuszczania w olejach roślinnych, zwłaszcza o niskiej zawartości wody.

Tabela 3. Wpływ dodatku związków fenolowych na stabilność oksydacyjną bioolejów roślinnych (opracowanie własne na podstawie danych z publikacji **P1**).

Związek fenolowy	**Forma/dodana ilość**	**Rodzaj stabilizowanego oleju**	**Temperatura testu przechowalniczego**	**Zmiana stabilności oksydacyjnej**
Kwasy fenolowe				
ferulowy (TPSA=66,76)	czysty związek/stężenie 0,5 mM	lniany	140°C	+85%
ferulowy (TPSA=66,76)	roztwór w etanolu/stężenie 100, 250, 500 μM	rzepakowy	120°C	od +12% do +24%
kawowy (TPSA=77,75)	czysty związek/stężenie 0,5 mM	lniany	140°C	+94%
cynamonowy (TPSA=37,30)	roztwór w etanolu/stężenie 100, 250, 500 μM	rzepakowy	120°C	od -32% do -44%
sinapowy (TPSA=76,00)	roztwór w etanolu/stężenie 100, 250, 500 μM	rzepakowy	120°C	od -24% do -36%
syringowy (TPSA=76,00)	roztwór w etanolu/stężenie 100, 250, 500 μM	rzepakowy	120°C	od -8% do -32%
Flawonoidy				
apigenina (TPSA=90,89)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+9,38%
chryzyna (TPSA=70,67)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+9,38%
kemferol (TPSA=111,12)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+9,38%
naringenina (TPSA=86,99)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+9,38%
kwercetyna (TPSA=131,35)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+81,25%
mirycetyna (TPSA=151,58)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+368,75%
morina (TPSA=131,35)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+71,88%
rutyna (TPSA=269,43)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+87,5%
naringina (TPSA=225,06)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+71,88%
taksyfolina (TPSA=127,44)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+25%
[-]epikatechina (TPSA=110,37)	czysty związek/stężenie 200 ppm	rzepakowy	60°C	+118,75%
Pochodne kwasów fenolowych				
4-winylogwajakol (TPSA=29,46)	roztwór w acetonie/stężenie 20, 40, 80 mg/100 g	lniany, rzepakowy	110°C	od +13 do +50%
4-winylosyringol (TPSA=38,70)	roztwór w acetonie/stężenie 20, 40, 80 mg/100 g	lniany, rzepakowy	110°C	+2 do +5%
wanilina (TPSA=46,53)	czysty związek/stężenie 0,5 mM	lniany	140°C	+50%

TPSA–Topologiczna Powierzchnia Polarna Cząsteczki (oszacowana przy użyciu http://www.molinspiration.com 1.06.2022).

Analizując dane literaturowe zauważono, że większość dostępnych badań naukowych opierała się na wykorzystaniu testu przechowalniczego w wymuszonych warunkach, tj. testu przyspieszonego utleniania, w temperaturach powyżej 100°C. Zasadnym byłoby rozszerzenie badań naukowych o analizę skuteczności działania związków fenolowych jako przeciwutleniaczy olejów roślinnych z wykorzystaniem testów przechowalniczych w naturalnych warunkach (symulacja użytkowania domowego), ponieważ kinetyka utleniania lipidów i działanie przeciwutleniające związków fenolowych może różnić się względem warunków przechowalniczych. Ponadto stwierdzono, że należy również rozważyć prowadzenie badań naukowych pozwalających na określenie interakcji związków fenolowych z innymi związkami anty- i prooksydacyjnymi obecnymi w olejach roślinnych (ze względu na wysoki stopień złożoności matryc olejowych), by zaprojektować skuteczne przeciwutleniacze do przyszłych zastosowań.

Reasumując, analiza dostępnej literatury oraz badania własne wykazały wysoki stopień zróżnicowania zawartości wolnych związków fenolowych i profilu fenolowego w bioolejach roślinnych. Można zatem uznać, że jednym z głównych czynników determinujących zawartość i skład profilu fenolowego olejów roślinnych jest surowiec. Należy jednak zaznaczyć, że obserwuje się również dużą zmienność w zawartości i profilu fenolowym w obrębie olejów otrzymanych z jednego gatunku surowca (zgodnie z publikacją **P1**). Dane literaturowe sugerują wpływ wielu czynników na zawartość i profil fenolowy olejów roślinnych, jednakże brak jest konkretnych badań naukowych określających i wyjaśniających, które z tych czynników mogą mieć największe znaczenie w przypadku migracji związków fenolowych z surowca do oleju. Wyniki badań własnych wskazują również, że stabilność oksydacyjna bioolejów roślinnych może wynikać z obecności w nich związków fenolowych. Zauważa się rosnące zainteresowanie wśród naukowców badaniami nad wpływem związków fenolowych i ich dodatku na stabilność oksydacyjną bioolejów roślinnych. Generalnie, ze względu na polarny charakter związków fenolowych wydaje się, że ilość wody w oleju roślinnym może wpływać na ich właściwości przeciwutleniające i warunkować ich rozpuszczalność w olejach roślinnych. Jednakże, trudności związane z przewidywaniem zawartości wody oraz zdolności związków fenolowych do rozpuszczania w olejach roślinnych mogą wskazywać na uzasadnione dodawanie związków o niższej wartości TPSA.

5.2. Zawartość związków fenolowych w bioolejach lnianych o różnej zawartości wody oraz ich wpływ na stabilność oksydacyjną i powstawanie produktów utlenienia

Wielu badaczy wskazuje, że zawartość i profil związków fenolowych w olejach roślinnych zależy od takich czynników jak: odmiana, miejsce pochodzenia, technika uprawy, stopień dojrzałości surowca, a także otrzymywania, pakowania i przechowywania oleju (Delgado-Adámez i in., 2014; Ghafoor i in., 2020). W publikacji **P2** dokonano analizy zawartości wolnych związków fenolowych i kwasów fenolowych w 30 dostępnych handlowo olejach lnianych tłoczonych na zimno o wysokiej zawartości kwasu α-linolenowego. Wyniki (**tabela 4**) wskazują, że oleje lniane tłoczone na zimno cechują się niską, ale zróżnicowaną zawartością wolnych związków fenolowych (ogółem 0,04-2,79 mg/100 g, kwasów fenolowych 7,49-160,38 μg/100 g). Dominujące w badanych olejach były takie kwasy fenolowe jak ferulowy (0-38 μg/100 g) i sinapowy (1-91 μg/100 g). Zróżnicowany skład i zawartość związków fenolowych w olejach lnianych tłoczonych na zimno może wynikać zarówno z różnej jakości nasion lnu wykorzystanych w procesie tłoczenia oleju, jak i samego procesu jego produkcji (warunków tłoczenia, rodzaju prasy, sposobu oczyszczania). Oba czynniki mogą determinować zawartość wody w oleju, a tym samym zwiększać lub zmniejszać rozpuszczalność związków fenolowych w oleju. Wskazywać na to mogą obliczone współczynniki korelacji liniowej Pearsona, r w zakresie 0,30-0,39 dla zależności zawartości wody z zawartością związków fenolowych oraz głównych kwasów fenolowych, potwierdzające istnienie przeciętnej korelacji.

Kolejnym celem publikacji **P2** było zbadanie wpływu stanu wyjściowego olejów lnianych tłoczonych na zimno na stabilność oksydacyjną i powstawanie produktów utlenienia podczas przechowywania w naturalnych warunkach: 30 dni w temperaturze otoczenia z ekspozycją na światło (symulacja przechowywania w warunkach sklepowych). W badaniach wykazano, że dostępne w handlu oleje lniane tłoczone na zimno były generalnie dobrej jakości, o zbliżonych parametrach barwy i porównywalnym składzie kwasów tłuszczowych, ale najbardziej zróżnicowane pod względem zawartości karotenoidów, chlorofili i związków fenolowych. Przechowywanie olejów z ekspozycją na światło spowodowało pogorszenie ich jakości, przede wszystkim zaobserwowano znaczne zwiększenie (co najmniej 24,8-krotne) liczby nadtlenkowej olejów. Ponadto, pozostałe parametry jakościowe również uległy pogorszeniu, w tym barwa olejów.

Tabela 4. Zawartość i profil związków fenolowych w tłoczonych na zimno olejach lnianych dostępnych na rynku polskim (opracowanie własne na podstawie danych z publikacji **P2**).

Numer oleju lnianego	**Zawartość wody (mg/100 g)**	**Zawartość związków fenolowych (mg/100 g)**	**Kwasy fenolowe (µg/100 g)**					
			kwas p-OH-hydroksybenzoesowy	kwas kawowy	kwas p-kumarowy	kwas ferulowy	kwas sinapowy	całkowita zawartość
1	57,22	0,95	0,00	0,00	7,29	6,07	50,30	63,67
2	75,18	ilość śladowa	0,00	0,00	1,30	1,96	5,88	9,14
3	33,81	0,16	0,00	0,00	6,64	7,22	13,16	26,04
4	71,39	ilość śladowa	0,00	0,00	1,22	2,27	5,16	8,65
5	89,21	ilość śladowa	0,00	0,00	1,99	4,14	28,42	34,55
6	71,77	0,22	0,00	0,00	1,86	1,48	17,99	21,33
7	88,15	ilość śladowa	5,75	0,00	1,21	4,82	11,25	23,03
8	84,12	ilość śladowa	7,07	0,00	1,50	4,34	36,71	49,62
9	92,55	2,79	0,00	14,67	17,28	37,84	90,59	160,38
10	68,30	0,18	0,00	5,10	2,28	11,61	1,31	20,30
11	67,21	ilość śladowa	0,00	0,00	2,05	2,14	36,60	40,79
12	71,99	ilość śladowa	0,00	0,00	4,12	2,51	18,04	24,66
13	94,74	0,05	0,00	25,34	1,50	10,16	49,80	86,81
14	78,90	ilość śladowa	0,00	0,00	3,00	5,57	15,06	23,63
15	100,43	0,73	0,00	0,00	1,51	1,42	9,66	12,59
16	78,49	0,33	0,00	6,99	4,53	20,45	20,54	52,50
17	94,84	ilość śladowa	0,00	0,00	3,27	4,89	16,49	24,66
18	65,33	ilość śladowa	0,00	0,00	3,52	5,42	35,94	44,88
19	124,57	1,04	0,00	8,73	3,46	12,11	38,07	62,38
20	66,00	0,78	0,00	0,00	5,75	4,43	16,16	26,34
21	97,41	ilość śladowa	0,00	0,00	0,37	2,19	19,01	21,57
22	67,14	ilość śladowa	0,00	2,82	0,24	2,74	2,38	8,18
23	84,84	0,13	0,00	0,00	0,00	6,42	10,39	16,81
24	81,63	ilość śladowa	0,00	0,00	3,61	5,36	48,82	57,79
25	82,09	0,04	0,00	0,00	1,34	0,00	8,00	9,34
26	75,01	ilość śladowa	0,00	0,00	1,52	2,76	6,28	10,56
27	134,17	0,93	1,54	0,00	0,00	25,62	54,09	81,25
28	65,75	ilość śladowa	0,00	0,00	0,00	3,11	4,38	7,49
29	80,68	ilość śladowa	0,00	0,00	0,03	6,03	26,61	32,66
30	89,41	ilość śladowa	0,00	0,00	1,12	9,24	28,74	39,18
współczynnik korelacji z zawartością wody (*r*)		0,30	0,16	0,25	-0,16	0,39	0,35	0,36

Badania przedstawione w publikacji **P2** wykazały, że stabilność oksydacyjna olejów lnianych tłoczonych na zimno była silnie dodatnio skorelowana z zawartością wolnych związków fenolowych (r=0,62) (**tabela 5**). Ponadto, ze stabilnością oksydacyjną olejów dodatnio skorelowana była również zawartość kwasu kawowego (r=0,19). Wolne związki fenolowe, w tym głównie zawartość kwasów ferulowego i sinapowego, mogły również wpływać na przebieg procesu utleniania i hydrolizy, i w konsekwencji, decydować o jakości końcowej olejów lnianych, w szczególności o wartości liczby kwasowej i wartości parametru L* określającego jasność barwy (r w zakresie 0,26-0,52).

Tabela 5. Współczynniki korelacji (r) między zawartością związków fenolowych a stabilnością oksydacyjną, zmianami jakości oraz barwy badanych olejach lnianych tłoczonych na zimno (opracowanie własne na podstawie danych z publikacji **P2**).

Rodzaj składnika	Stabilność oksydacyjna	ΔLK	ΔLN	ΔLA	ΔD	ΔL*	Δa*	Δb*	ΔE
kwas p-OH-hydroksybenzoesowy	0,02	-0,03	-0,04	0,17	-0,01	-0,25	-0,03	-0,06	-0,13
kwas kawowy	0,19	-0,08	-0,19	-0,17	0,12	0,02	0,02	0,05	-0,19
kwas p-kumarowy	0,04	-0,13	-0,08	0,08	0,16	0,23	0,14	-0,07	-0,17
kwas ferulowy	0,04	0,47**	0,12	-0,05	0,20	0,52**	0,22	-0,18	-0,04
kwas sinapowy	-0,28	0,26	0,01	0,11	0,18	0,35	0,10	-0,05	0,04
KF	-0,13	0,25	-0,01	0,04	0,20	0,36**	0,13	-0,08	-0,04
ZFW	0,62**	0,26	0,08	-0,26	0,02	0,33	0,09	-0,11	-0,12

Δ–różnica wartości wskaźników jakości i parametrów barwy między olejami świeżymi i utlenionymi.; KF–kwasy fenolowe; ZFW–związki fenolowe w formie wolnej; LK–liczba kwasowa; LN–liczba nadtlenkowa; LA–liczba anizydynowa; D–kwasy sprzężone (dieny); L*, a*, b*–poszczególne parametry modelu barwy CIEL*a*b*; E–całkowita różnica barwy. ** oznacza wartość istotną statystycznie (p≤0,05).

Wyniki badań opisanych w publikacji **P2** wskazują, że powstawanie produktów utlenienia w olejach lnianych tłoczonych na zimno przechowywanych w naturalnych warunkach z ekspozycją na światło wynika głównie z początkowej jakości oleju. Stwierdzono, że początkowe wartości liczby kwasowej, zawartości dienów i trienów, a także wody determinowały przebieg procesu hydrolizy i tworzenie się wolnych kwasów tłuszczowych w olejach lnianych podczas ich przechowywania (korelacja dodatnia, r>0,56). Z kolei początkowe wartości liczby kwasowej, nadtlenkowej i anizydynowej, a także zawartość trienów wpływały na przebieg procesu utleniania i tworzenie się zarówno pierwotnych jak i wtórnych produktów utlenienia (korelacja dodatnia, r>0,27). W prowadzonych badaniach zauważono również, że wartości początkowe wskaźników jakości olejów lnianych, zawartości kwasów tłuszczowych oraz innych związków bioaktywnych miały wpływ również na zmianę

barwy olejów podczas przechowywania. Zawartość MUFA, liczba kwasowa oraz zawartości dienów i trienów były dodatnio skorelowane z wartością parametru L* po przechowywaniu (r>0,44). Z kolei, między wartością początkową liczby anizydynowej i wartością parametru a* oraz zawartością wody i wartością parametru b* odnotowano ujemną korelację (odpowiednio r=-0,22 i r=-0,26). Występowanie ujemnej korelacji odnotowano również w analizie wartości r dla całkowitej zmiany barwy (ΔE) olejów lnianych po przechowywaniu, w tym głównie między zawartością kampesterolu, γ-tokoferolu, plastochromanolu-8 i całkowitą zawartością tokoferoli (r w zakresie -0,37 do -0,47).

W publikacji **P2** potwierdzono, że dla stabilności oksydacyjnej olejów lnianych tłoczonych na zimno przechowywanych przez okres 30 dni w warunkach naturalnych z ekspozycją na światło kluczowe były zawartości nienasyconych kwasów tłuszczowych oraz związków fenolowych. Dowiedziono, że wysoka zawartość kwasu oleinowego (C18:1) może zapewnić dobrą odporność olejów roślinnych na procesy oksydacyjne, podobnie jak wysoka zawartość związków fenolowych. Także skwalen mógł przyczynić się do spowolnienia procesu utleniania olejów lnianych tłoczonych na zimno ze względu na jego zdolność do wygaszania tlenu singletowego lub działanie synergistyczne z α-tokoferolem (Shimizu i in., 2019; Finotti i in., 2002). W badaniach zauważono ponadto, że końcowa wysoka wartość liczby anizydynowej po przechowywaniu mogła wynikać z wysokiej zawartości wody (>100 mg/100 g) w oleju lnianym ze względu intensyfikację procesu hydrolizy oraz tworzenie się znacznej ilości wolnych kwasów tłuszczowych, które mogą działać jako katalizatory i znacznie przyspieszać tworzenie się produktów utlenienia (Orhevba i in., 2013; Endo, 2018). Również wysoka zawartość tokoferoli (>250 mg/100 g) mogła przyczynić się do skrócenia czasu indukcji oleju lnianego ze względu na ich właściwości prooksydacyjne w wyższych stężeniach (Dolde i Wang, 2011). W konsekwencji, następuje nie tylko pogorszenie stabilności oksydacyjnej, ale również jakości olejów roślinnych. Jednakże zaobserwowano, że wyższa zawartość tokoferoli ograniczyła zmiany barwy olejów lnianych podczas utleniania. Dane literaturowe sugerują, że tokoferole wykazują zdolność do wychwytywania wolnych rodników i w konsekwencji spowalniają reakcje łańcuchowe utleniania barwników obecnych w żywności (Delgado i in., 2020). Warto podkreślić, że producenci decydują się na stosowanie różnych przeciwutleniaczy olejów roślinnych, niekiedy bez wyszczególniania ich dodatku na etykiecie opakowania. Wysoką zawartość octanu etylu (>60 mg/100 g) wykryto w 4 olejach lnianych tłoczonych na zimno. Realizując badania w ramach publikacji **P2** stwierdzono również, że stabilność oksydacyjna olejów lnianych tłoczonych na zimno określona w teście Rancimat oraz zmiany wskaźników jakości podczas testu przechowalniczego nie są spójne. Sugeruje to,

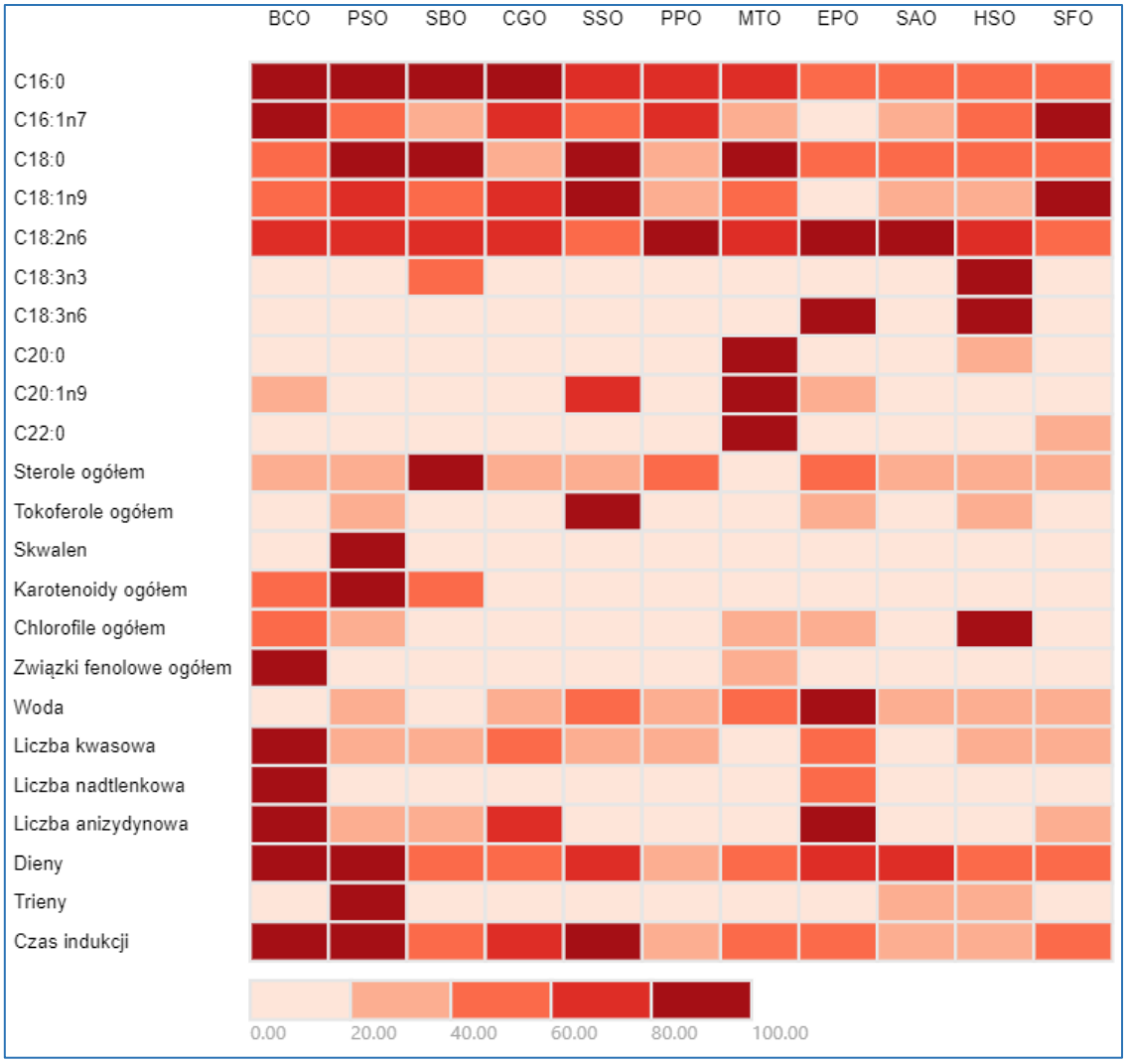
że test Rancimat może być słabym wskaźnikiem szybkości utleniania (trwałości) olejów podczas przechowywania w warunkach naturalnych i z ekspozycją na światło. Informacje te mogą być szczególnie pomocne w doborze i kontroli jakości tłuszczów i olejów roślinnych wykorzystywanych w produkcji żywności.

Podsumowując, wyniki badań przedstawione w publikacji **P2** jednoznacznie wskazują, że początkowa jakość i zawartość związków bioaktywnych w olejach lnianych tłoczonych na zimno ma wpływ na stabilność oksydacyjną (czas indukcji) i powstawanie produktów utleniania podczas przechowywania. Generalnie, czas indukcji w wyższych temperaturach był bardziej zależny od składu kwasów tłuszczowych (głównie procentowej zawartości kwasu linolenowego i oleinowego) oraz zawartości wolnych związków fenolowych, z kolei jakość początkowa olejów (zawartość wody, liczba kwasowa, liczba nadtlenkowa, liczba anizydynowa, zawartość kwasów sprzężonych) intensyfikowała lub spowalniała procesy tworzenia się pierwotnych i wtórnych produktów utleniania.

5.3. Wpływ dodatku pochodnych kwasów fenolowych na stabilność oksydacyjną bioolejów roślinnych

W badaniach przedstawionych w publikacji **P3**, w celu zwiększenia stabilności oksydacyjnej różnych bioolejów roślinnych, dodawano dwie pochodne kwasów fenolowych (4-winylogwajakol i 4-winylosyringol) w różnych ilościach (20, 40, 60, 80 i 100 ppm). Materiał badań stanowiło 11 olejów roślinnych tłoczonych na zimno (tj. kukurydziany, wiesiołkowy, konopny, makowy, dyniowy, krokoszowy, sezamowy, sojowy, słonecznikowy, z czarnuszki, z ostropestu), które cechowały się wysoką zawartością wielonienasyconych kwasów tłuszczowych, w tym zwłaszcza kwasu linolowego (od 41 do 77% sumy wszystkich kwasów tłuszczowych). Wyniki badań wykazały, że materiał do badań był generalnie dobrej jakości, a skład kwasów tłuszczowych i związków bioaktywnych był typowy dla danego oleju. Najbogatsze w kwas linolowy były oleje wiesiołkowy, krokoszowy i makowy (>70% sumy kwasów tłuszczowych), natomiast oleje dyniowy, słonecznikowy i sezamowy charakteryzowały się najniższą procentową zawartością tego kwasu (<48%). Dodatkowo, oszacowane na podstawie składu kwasów tłuszczowych wartości wskaźnika peroksydacji pozwoliły na wyodrębnienie 3 grup olejów, tj. wysoko (oleje konopny, wiesiołkowy, krokoszowy, makowy), średnio (oleje sojowy, z ostropestu, kukurydziany, z czarnuszki) i nisko (oleje dyniowy, słonecznikowy, sezamowy) podane na utlenienie. Analiza oparta na głównych składowych potwierdziła, że zawartości związków wykazujących działanie pro-

i antyoksydacyjne w olejach tłoczonych na zimno były dość podobne, szczególnie w olejach krokoszowym, makowym, z ostropestu, kukurydzianym, słonecznikowym i sezamowym (**rysunek 2**).



BCO–z czarnuszki, PSO–dyniowy, SBO–sojowy, CGO–kukurydziany, SSO–sezamowy, PPO–makowy, MTO–z ostropestu, EPO–wiesiołkowy, SAO–krokoszowy, HSO–konopny, SFO–słonecznikowy.

Rysunek 2. Mapa zróżnicowania składu i jakości bioolejów roślinnych, gdzie 0% – minimalna a 100% – maksymalna wartość badanego wyróżnika (opracowanie własne na podstawie danych z publikacji **P3**).

Analiza korelacji w publikacji **P3** wykazała (obliczone współczynniki korelacji przedstawiono w **tabeli 6**), że stabilność oksydacyjna olejów tłoczonych na zimno była dodatnio skorelowana z procentową zawartością kwasu palmitynowego (r=0,77), zawartością kwasu ferulowego (r=0,64) i innych karotenoidów (r=0,63), oraz ujemnie skorelowana

z procentową zawartością wielonienasyconych kwasów tłuszczowych (r=-0,66). Na stabilność oksydacyjną olejów tłoczonych na zimno wpływać mogły również procentowa zawartość kwasów tłuszczowych jednonienasyconych (głównie kwasu C18:1), oraz zawartość fenoli ogółem, kwasów fenolowych ogółem i karotenoidów ogółem (r w zakresie 0,4-0,6).

Tabela 6. Współczynniki korelacji (r) między składem a stabilnością oksydacyjną (określoną jako czas indukcji) olejów tłoczonych na zimno (opracowanie własne na podstawie danych z publikacji **P3**).

Rodzaj składnika	**Stabilność oksydacyjna**	**Rodzaj składnika**	**Stabilność oksydacyjna**
Procentowa zawartość kwasów tłuszczowych		*Zawartość steroli*	
kwas palmitynowy	0,77*	kampesterol	-0,31
kwas palmitoleinowy	0,50	stigmasterol	-0,07
kwas stearynowy	0,36	β-sitosterol	-0,26
kwas oleinowy	0,59	cykloartenol	0,44
kwas linolowy	-0,52	inne sterole	-0,12
kwas γ-linolenowy	-0,47	całkowita zawartość	-0,04
kwas α-linolenowy	-0,36	*Zawartość skwalenu*	
kwas arachidowy	-0,31	całkowita zawartość	0,50
kwas eikozenowy	0,07	*Zawartość karotenoidów*	
kwas behenowy	-0,33	luteina	-0,13
SFA	0,55	zeaksantyna	0,49
MUFA	0,59	β-karoten	0,47
PUFA	-0,66*	α-karoten	0,42
		inne karotenoidy	0,63*
		całkowita zawartość	0,59
		Zawartość chlorofilów	
		całkowita zawartość	-0,21
		Zawartość tokoferoli	
		α -tokoferol	0,36
		γ-tokoferol	-0,14
		δ-tokoferol	-0,47
		całkowita zawartość	0,33
		Zawartość związków fenolowych	
		kwas p-kumarowy	0,11
		kwas ferulowy	0,64*
		kwas sinapowy	0,51
		kwas kawowy	-0,20
		kwas wanilinowy	0,23
		KF całkowita zawartość	0,55
		ZFW całkowita zawartość	0,48

SFA–kwasy tłuszczowe nasycone; MUFA–kwasy tłuszczowe jednonienasycone; PUFA–kwasy tłuszczowe wielonienasycone; KF–kwasy fenolowe; ZFW–związki fenolowe w formie wolnej; * oznacza wartość istotną statystycznie ($p \leq 0,05$).

Wyniki eksperymentu prowadzonego w ramach publikacji **P3** wykazały, że dodatki pochodnych kwasów fenolowych generalnie poprawiły stabilność oksydacyjną (badania w teście Rancimat w temperaturze 110°C) olejów tłoczonych na zimno bogatych w kwas linolowy, ale ich skuteczność była różna. Dodatkowo, zaobserwowano liniowe zależności

między czasem indukcji a ilością pochodnych kwasów fenolowych, przy czym zakres liniowości był zależny zarówno od rodzaju oleju, jak i dodatku. Wskazuje to, że oba dodatki fenolowe mogą być stosowane jako przeciwutleniacze w olejach roślinnych, przy czym 4-winylosyringol wykazał silniejsze działanie antyoksydacyjne (ponad 4-krotnie) w porównaniu do 4-winylogwajakolu (**tabela 7**). Dodatek 4-winylosyringolu w ilości 100 ppm spowodował znaczną poprawę stabilności oksydacyjnej większości badanych olejów tłoczonych na zimno (37-69%), w szczególności olejów konopnego i makowego. Z kolei, dodatek 4-winylogwajakolu cechował się znacznie mniejszą skutecznością i spowodował zauważalne wydłużenie czasu indukcji jedynie w oleju konopnym i sezamowym (<13%). W pozostałych olejach tłoczonych na zimno, 4-winylogwajakol był w stanie zapewnić jedynie nieznaczną ochronę przed procesem utleniania (maksymalna skuteczność mieściła się w zakresie 2-7%). Procentowe zmiany w czasie indukcji badanych bioolejów roślinnych wskazują, że oleje o niższej początkowej stabilności oksydacyjnej (tj. oleje tłoczone na zimno konopny i makowy) generalnie są lepiej chronione poprzez dodatek pochodnych kwasów fenolowych niż pozostałe oleje roślinne.

Tabela 7. Czasy indukcji (CI) w 110°C badanych bioolejów roślinnych oraz procentowe zmiany CI po wprowadzeniu dodatku pochodnych kwasów fenolowych (opracowanie własne na podstawie danych z publikacji **P3**).

Rodzaj biooleju	**CI (h)**	**Maksymalna efektywność dodatku 4-winylosyringolu**			**Maksymalna efektywność dodatku 4-winylogwajakolu**		
		stężenie (ppm)	CI (h)	% zmiana*	stężenie (ppm)	CI (h)	% zmiana*
olej konopny	2,80	100	4,71	+68,21	100	3,12	+11,43
olej makowy	4,21	100	7,13	+69,36	80	4,49	+6,66
olej krokoszowy	4,40	100	5,41	+22,96	60	4,35	-1,14
olej wiesiołkowy	4,79	100	5,69	+18,79	60	5,00	+4,38
olej z ostropestu	4,85	100	7,13	+47,01	40	5,18	+6,80
olej sojowy	5,61	100	8,61	+53,48	100	5,92	+5,53
olej słonecznikowy	6,00	100	8,24	+37,33	20	6,36	+6,00
olej kukurydziany	7,69	100	11,11	+44,73	60	7,71	+2,21
olej sezamowy	10,65	100	16,82	+57,93	80	11,68	+12,30
olej z czarnuszki	11,65	100	12,79	+9,79	60	11,60	-0,43
olej dyniowy	11,59	100	16,32	+40,81	80	11,58	-0,09

* procentowa zmiana obliczona względem czasu indukcji oleju wyjściowego.

Niską skuteczność antyoksydacyjną obu pochodnych kwasów fenolowych zaobserwowano w olejach tłoczonych na zimno o niższej jakości wyjściowej, tj. olejach wiesiołkowym i z czarnuszki (**rysunek 2**). Może to wynikać z obecności w olejach produktów

utlenienia lipidów (wodoronadtlenki, aldehydy, ketony, itp.), które ze względu na amfifilowy charakter mogą tworzyć z niewielką ilością wody koloidy asocjacyjne. Dane literaturowe sugerują, że utworzone koloidy asocjacyjne mogą wpływać na proces utleniania i zmniejszać skuteczność antyoksydacyjną związków fenolowych (Rokosik i in., 2020a).

W przeprowadzonych badaniach zauważono generalnie dodatnią korelację między stężeniem 4-winylosyringolu a czasem indukcji olejów tłoczonych na zimno (stabilność oksydacyjna zwiększała się wraz ze zwiększaniem stężenia tego dodatku). Z kolei, dodatek 4-winylogwajakolu w stężeniu 80 ppm był najskuteczniejszy w olejach dyniowym, sezamowym i makowym, w stężeniu 60 ppm w olejach kukurydzianym, krokoszowym, wiesiołkowym i z czarnuszki, natomiast w stężeniu 40 ppm w oleju ogórecznikowym (wyniki w publikacji **P3**).

Dwuczynnikowa analiza statystyczna przeprowadzona w publikacji **P3** potwierdziła istotny wpływ rodzaju i stężenia pochodnych kwasów fenolowych na stabilność oksydacyjną badanych olejów tłoczonych na zimno (**tabela 8**), przy czym odnotowano silniejszy wpływ rodzaju dodatku (>48% wyjaśnianej wariancji) niż jego stężenia. Rodzaj pochodnej kwasu fenolowego miał największe znaczenie dla stabilności oksydacyjnej olejów sojowego i konopnego (>80% wyjaśnianej wariancji), z kolei stężenie dodatku dla oleju wiesiołkowego (19,34% wyjaśnianej wariancji). Ponadto, skumulowany efekt dwóch badanych czynników był najsilniejszy w przypadku oleju słonecznikowego (40,26% wyjaśnianej wariancji).

Tabela 8. Wpływ rodzaju i stężenia pochodnych kwasów fenolowych na stabilność oksydacyjną badanych bioolejów roślinnych (% wyjaśnianej wariancji) (opracowanie własne na podstawie danych z publikacji **P3**).

Rodzaj biooleju	**Czynniki**			
	rodzaj pochodnej kwasu fenolowego	stężenie pochodnej kwasu fenolowego	rodzaj × stężenie pochodnej kwasu fenolowego	inne
olej wiesiołkowy	60,37	19,34	16,26	4,03*
olej słonecznikowy	48,95	10,38	40,26	0,21*
olej dyniowy	75,45	9,96	14,47	0,12*
olej konopny	81,56	9,14	9,11	0,20*
olej makowy	76,27	8,44	14,96	0,32*
olej kukurydziany	79,35	7,83	12,67	0,15*
olej sezamowy	78,96	7,62	13,11	0,31*
olej z czarnuszki	63,16	7,35	28,23	1,26*
olej sojowy	83,59	6,99	9,21	0,20*
olej krokoszowy	76,37	6,17	15,91	1,55*
olej z ostropestu	68,04	4,59	26,78	0,59*

* oznacza wartość nieistotnie statystyczną, dwuczynnikowa analiza z testem Wilksa ($p \leq 0{,}05$).

Na podstawie przeprowadzonych badań ustalono również, że działanie ochronne 4-winylosyringolu było silniejsze w olejach roślinnych tłoczonych na zimno o lepszej jakości wyjściowej (mniejszy stopień hydrolizy i utlenienia), co sugeruje, że początkowy skład i jakość olejów roślinnych może istotnie wpływać na działanie przeciwutleniające pochodnych kwasów fenolowych. Nasze poprzednie badania (Tańska i in., 2018) wykazały, że dodatek 4-winylogwajakolu był skuteczniejszym przeciwutleniaczem dla tłoczonych na zimno olejów lnianego i rzepakowego niż dodatek 4-winylosyringolu (test Rancimat w temperaturze 110°C ze strumieniem powietrza o natężeniu przepływu 20 l/h, stężenie dodatku w oleju 80 ppm). Różnica może prawdopodobnie wynikać z innego składu chemicznego olejów w porównaniu z olejami analizowanymi w publikacji **P3**. Przypuszcza się, że większa skuteczność 4-winylogwajakolu może być związana z większą zawartością kwasu α-linolenowego, ponieważ czas indukcji był dłuższy w olejach o wyższym udziale tego kwasu tłuszczowego (obliczony *r* dla zależności wynosił 0,72). Potrzebne są jednak dalsze badania z udziałem pochodnych kwasów fenolowych, aby w pełni poznać i zrozumieć mechanizm ich działania oraz utleniania w matrycach olejowych, zwłaszcza w tych różniących się zawartością natywnych przeciwutleniaczy ze względu na możliwość występowania interakcji pochodnych kwasów fenolowych z natywnymi przeciwutleniaczami (np. tokoferolami, karotenoidami), które mogą zachodzić podczas procesu utleniania olejów roślinnych tłoczonych na zimno.

Publikacja **P3** dowodzi, że pochodne kwasów fenolowych mogą być stosowane jako dodatki przeciwutleniające do bioolejów roślinnych ze względu na ich działanie ochronne, przy czym dodatek 4-winylosyringolu może być bardziej skuteczny. Należy jednak zaznaczyć, że wybór odpowiedniego dodatku przeciwutleniającego wynika nie tylko z rodzaju i stężenia tego dodatku, ale również ze składu i jakości wyjściowej biooleju roślinnego, co może determinować właściwości ochronne zastosowanego przeciwutleniacza. W publikacji **P3** udowodniono, że związki fenolowe to istotne przeciwutleniacze olejów roślinnych tłoczonych na zimno. Chociaż tokoferole są powszechnie stosowane jako komercyjne przeciwutleniacze w celu ograniczenia procesu degradacji olejów (Cao i in., 2015), wyniki przedstawione w publikacji **P3** nie potwierdziły ich stabilizującego wpływu na procesy oksydacyjne. Ponadto, obecność kwasów ferulowego i sinapowego wydaje się mieć większe znaczenie dla stabilności oksydacyjnej olejów roślinnych niż zawartość i rodzaj tokoferoli. Zgodnie z powyższym, pochodne kwasów fenolowych mogą być stosowane jako nowe przeciwutleniacze w przemyśle olejarskim, a także mogą być przydatne w opracowywaniu rozwiązań pozwalających na zastąpienie przeciwutleniaczy syntetycznych naturalnymi. Dodatek pochodnych kwasów fenolowych do olejów roślinnych nie tylko zwiększa stabilność oksydacyjną, ale także może minimalizować powstawanie metabolitów wtórnych (tj. wolnych rodników, aldehydów, ketonów, oksysteroli) o udowodnionym niekorzystnym wpływie na zdrowie konsumentów. Ponadto, wydaje się również, że pochodne kwasów fenolowych mogą hamować degradację lipofilowych związków bioaktywnych rozpuszczonych w olejach (np. skwalen, sterole, nienasycone kwasy tłuszczowe), co może przynosić znaczące korzyści odżywcze i zdrowotne.

5.4. Wpływ pochodnych kwasów fenolowych na szybkość degradacji składników bioaktywnych w bioolejach roślinnych podczas procesu ich utleniania

Nadrzędnym celem publikacji **P4** było zbadanie wpływu dwóch pochodnych kwasów fenolowych (4-winylogwajakolu i 4-winylosyringolu) dodanych w stężeniu 80 ppm na stopień degradacji związków fenolowych, nienasyconych kwasów tłuszczowych, steroli, tokoferoli, karotenoidów i skwalenu, obecnych w olejach tłoczonych na zimno, lnianym i rzepakowym. Degradację składników bioaktywnych w olejach analizowano w teście przechowalniczym w warunkach wymuszonych (temperatura 110°C) przez okres odpowiadający czasowi indukcji danego rodzaju oleju wyznaczony w teście Rancimat. Procentowe zmiany składników bioaktywnych w badanych olejach po przechowywaniu przedstawiono w **tabeli 9**.

Związki fenolowe

Dodatek pochodnych kwasów fenolowych zwiększył początkową zawartość związków fenolowych w badanych olejach tłoczonych na zimno do poziomu ok. 81 mg/100 g, który można uznać za średni w porównaniu do poziomów zawartości związków fenolowych oszacowanych w różnych olejach roślinnych (zgodnie z publikacją **P1**). Zarówno natywne, jak i dodane do olejów tłoczonych na zimno związki fenolowe, uległy prawie całkowitej degradacji w teście przechowalniczym. Zauważono, że ok. 81% 4-winylosyringolu i ok. 95% 4-winylogwajakolu uległo rozkładowi w procesie utleniania, co sugeruje, że związki te stanowiły podstawowe przeciwutleniacze badanych olejów tłoczonych na zimno.

Kwasy tłuszczowe

Skład kwasów tłuszczowych w olejach tłoczonych na zimno analizowanych w publikacji **P4** był typowy dla danego rodzaju oleju, a zawartość kwasu α-linolenowego wynosiła ok. 12% w oleju rzepakowym i ok. 45% w oleju lnianym. Dodatek pochodnych kwasów fenolowych do oleju rzepakowego tłoczonego na zimno pozwolił ograniczyć niekorzystne zmiany w zawartości i składzie kwasów tłuszczowych. W oleju kontrolnym (bez dodatków), spadek zawartości kwasu α-linolenowego sięgał prawie 14%, natomiast w olejach wzbogaconych pochodnymi kwasów fenolowych wynosił jedynie 2,9-3,5% w zależności od użytej pochodnej. Generalnie zauważono, zawartość poszczególnych kwasów tłuszczowych w olejach rzepakowych tłoczonych na zimno z dodatkiem pochodnych kwasów fenolowych była zbliżona względem oleju wyjściowego. Znacznie większy wpływ procesów oksydacyjnych zaobserwowano w oleju lnianym tłoczonym na zimno, również po zastosowaniu dodatku pochodnych kwasów fenolowych. W oleju kontrolnym, udział kwasu α-linolenowego zmniejszył się o ponad 22%, natomiast kwasu γ-linolenowego o ponad 45%. Zauważono, że dodatek 4-winylosyringolu do oleju lnianego tłoczonego na zimno sprzyjał degradacji wszystkich kwasów tłuszczowych, z kolei dodatek 4-winylogwajakolu generalnie pozwolił ograniczyć straty kwasów tłuszczowych (głównie kwasu α-linolenowego).

Sterole

W olejach kontrolnych zauważono znaczne zmniejszenie zawartości steroli w wyniku procesu utleniania, przy czym największe straty odnotowano dla brassikasterolu w oleju rzepakowym i β-sitosterolu w oleju lnianym (>50%). Zastosowanie dodatku pochodnych kwasów fenolowych pozwoliło utrzymać na wyjściowym poziomie zawartości aż 95% natywnych steroli obecnych w oleju rzepakowym tłoczonym na zimno, przy czym dodatek 4-winylosyringolu okazał się mniej skuteczny. W oleju lnianym tłoczonym na zimno dodatek

pochodnych kwasów fenolowych zapewnił zatrzymanie aż 86-87% natywnych steroli, zależnie od użytej pochodnej.

Tokoferole

Degradacja tokoferoli w obu olejach kontrolnych była względnie niska, w oleju rzepakowym straty tych związków wynosiły 8%, natomiast w oleju lnianym 4%. Po zastosowaniu dodatku 4-winylosyringolu do oleju rzepakowego zaobserwowano znaczne zmniejszenie zawartości α-tokoferolu, plastochromanolu-8 i γ-tokoferolu, odpowiednio o 75%, 67% i 47%. Podobny wpływ odnotowano również po zastosowaniu 4-winylogwajakolu, jednakże zakres obserwowanych zmian był zdecydowanie niższy. Wskazuje to, że dodatek pochodnych kwasów fenolowych, zwłaszcza 4-winylosyringolu, sprzyjał degradacji tokoferoli w olejach tłoczonych na zimno. Wydaje się, że taki efekt może wynikać z większej polarności 4-winylosyringolu (TPSA = 38,70) niż 4-winylogwajakolu (TPSA = 29,46) i świadczyć o znacznej degradacji α-tokoferolu ze względu na konieczność ochrony bardziej polarnego przeciwutleniacza. Literatura sugeruje również, że stabilność tokoferoli (w tym α-tokoferolu) może wynikać z kilku czynników, m.in. stężenia w oleju roślinnym. Szacuje się, że przy stężeniu α-tokoferolu powyżej 100 mg/kg związek ten jest mniej stabilny niż inne tokoferole (Lampi i in., 1999).

Tabela 9. Procentowe zmiany (%) wybranych składników bioaktywnych w olejach tłoczonych na zimno lnianym i rzepakowym po przechowywaniu (opracowanie własne na podstawie danych z publikacji **P4**).

Rodzaj biooleju /składnika bioaktywnego	**Olej lniany**			**Olej rzepakowy**		
	kontrolny	z dodatkiem 4-winylosyringolu	z dodatkiem 4-winylogwajakolu	kontrolny	z dodatkiem 4-winylosyringolu	z dodatkiem 4-winylogwajakolu
Kwasy tłuszczowe						
kwas linolowy	-20,23%	-33,31%	-7,21%	-3,85%	+1,23%	+2,21%
kwas γ-linolenowy	-45,00%	-60,00%	-15,00%	ns.	ns.	ns.
kwas α-linolenowy	-22,32%	-32,52%	-8,25%	-13,77%	-2,95%	-3,54%
MUFA	-12,43%	-24,99%	-2,99%	-0,58%	-2,85%	+3,91%
PUFA	-21,80%	-32,85%	-7,98%	-7,26%	-0,17%	+0,27%
Sterole						
kampesterol	-32,56%	-4,00%	-6,40%	-44,64%	-21,84%	-7,28%
β-sitosterol	-52,47%	-16,62%	-18,18%	-41,45%	-9,69%	-2,56%
brassikasterol	ns.	ns.	ns.	-50,51%	-22,79%	-6,96%
całkowita zawartość	-45,86%	-13,05%	-14,46%	-43,65%	-15,64%	-4,93%
Tokoferole						
α-tokoferol	ns.	ns.	ns.	-17,29%	-74,51%	-39,10%
γ-tokoferol	-2,83%	-8,78%	-0,28%	-0,75%	-46,99%	-13,57%
δ-tokoferol	-40,00%	-30,00%	-45,00%	-15,45%	-6,01%	-23,18%
plastochromanol-8	-5,04%	0,00%	-1,68%	-50,00%	-66,67%	-47,06%
całkowita zawartość	-3,59%	-6,75%	-0,84%	-9,47%	-56,69%	-24,79%
Karotenoidy						
luteina	-87,93%	-6,03%	-15,52%	-78,83%	-6,44%	-22,39%
zeaksantyna	-45,46%	-27,27%	-27,27%	-16,67%	-33,33%	-66,67%
β-karoten	-63,28%	-27,16%	-33,73%	-11,04%	-16,55%	-29,65%
całkowita zawartość	-64,92%	-18,91%	-26,68%	-53,99%	-9,70%	-24,53%
Skwalen						
całkowita zawartość	-78,66%	-3,35%	-1,26%	-81,19%	-11,93%	-8,72%
Związki fenolowe						
kwas sinapowy	ns.	ns.	ns.	-13,82%	-7,32%	-26,83%
kwas p-kumarowy	-38,44%	-36,04%	-8,41%	-100,00%	-100,00%	-100,00%
kwas ferulowy	ns.	ns.	ns.	-6,83%	-32,66%	-27,12%
KF całkowita zawartość	-69,64%	-43,84%	-76,48%	-16,11%	-18,48%	-24,17%
ZFW całkowita zawartość	-92,95%	+860,90%	+201,92%	-98,06%	+1399,03%	+233,01%

ns.–niestwierdzony; MUFA–kwasy tłuszczowe jednonienasycone; PUFA–kwasy tłuszczowe wielonienasycone; KF–kwasy fenolowe; ZFW–związki fenolowe w formie wolnej.

Karotenoidy

Większość natywnych karotenoidów w analizowanych w olejach tłoczonych na zimno uległa degradacji podczas utleniania, zwłaszcza luteina, której zawartość zmniejszyła się o 79% w oleju rzepakowym i o 88% w oleju lnianym. Dodatek pochodnych kwasów fenolowych do olejów tłoczonych na zimno skutecznie chronił karotenoidy podczas utleniania (w tym luteinę i β-karoten), przy czym bardziej skuteczny okazał się dodatek 4-winylosyringolu. Generalnie, pochodne kwasów fenolowych pozwoliły zatrzymać co najmniej 75% karotenoidów w oleju rzepakowym i 73% w oleju lnianym (z największą retencją luteiny w obu olejach).

Skwalen

Podczas utleniania badanych olejów tłoczonych na zimno odnotowano znaczny spadek zawartości skwalenu. Po okresie przechowywania zachowane było jedynie 19% wartości wyjściowej tego związku w oleju rzepakowym i ok. 22% w oleju lnianym. Zastosowanie dodatku pochodnych kwasów fenolowych do olejów pozwoliło zmniejszyć straty skwalenu podczas testu przechowalniczego, retencja tego związku wahała się od 88 do 92% w oleju rzepakowym i od 97 do 99% w oleju lnianym. W obu olejach tłoczonych na zimno dodatek 4-winylogwajakolu okazał się bardziej skuteczny.

Badania prowadzone w ramach publikacji **P4** dowiodły, że związki bioaktywne w popularnych olejach tłoczonych na zimno (rzepakowym i lnianym) ulegają znacznej degradacji podczas utleniania. W analizowanych próbkach olejów po przechowywaniu oznaczono jedynie 54-56% steroli, 35-46% karotenoidów, 19-22% skwalenu i 78-84% kwasu α-linolenowego. Dodatek pochodnych kwasów fenolowych pozwolił zatrzymać większość natywnych składników olejów tłoczonych na zimno, w tym głównie steroli oraz karotenoidów (co najmniej 2-krotnie mniejsza degradacja) i skwalenu (co najmniej 4-krotnie mniejsza degradacja). Ponadto, dodatek 4-winylogwajakolu ograniczył również starty kwasu α-linolenowego w obu olejach (ok. 4-krotnie mniejsze w oleju rzepakowym i ok. 3-krotnie mniejsze w oleju lnianym). Jedynym negatywnym skutkiem obu dodatków okazała się degradacja α-tokoferolu w oleju rzepakowym, przy czym wpływ 4-winylogwajakolu był ponad 2-krotnie niższy niż 4-winylosyringolu. Jednakże, aby w pełni wyjaśnić mechanizm relacji pochodne kwasów fenolowych-tokoferole ważne jest prowadzenie dalszych badań naukowych. Aktualna literatura na ten temat jest nadal nieliczna, i brakuje badań nad interakcjami pochodnych kwasów fenolowych z innymi składnikami olejów roślinnych w procesach utleniania i hydrolizy.

6. Wnioski i podsumowanie badań

Badania przeprowadzone w ramach niniejszej rozprawy doktorskiej potwierdziły postawione hipotezy badawcze, że natywne polifenole obecne w oleju oraz dodane winylowe pochodne kwasu ferulowego i sinapowego zwiększają stabilność oksydacyjną bioolejów roślinnych. W szczególności wykazano, że:

1. Całkowita zawartość związków fenolowych oraz profil fenolowy bioolejów roślinnych są wysoce zróżnicowane i są uwarunkowane zwłaszcza gatunkiem surowca olejarskiego i metodą wydobycia oleju.
2. Zawartość związków fenolowych w bioolejach roślinnych otrzymanych z tego samego rodzaju surowca jest zależna m.in. od ilości wody przenikającej do oleju podczas procesu wydobycia i rafinacji.
3. W profilu fenolowym bioolejów roślinnych najczęściej występują kwasy fenolowe i flawonoidy, natomiast lignany, sekoirydoidy oraz inne pochodne fenolowe są obecne rzadziej i/lub w mniejszych ilościach.
4. Zawartość natywnych związków fenolowych wpływa na stabilność oksydacyjną oraz trwałość barwy bioolejów roślinnych podczas przechowywania.
5. Winylowe pochodne kwasów fenolowych mogą być stosowane jako dodatki zwiększające stabilność oksydacyjną bioolejów roślinnych.
6. Skuteczniejszym przeciwutleniaczem w olejach bogatych w kwas linolowy jest 4-winylosyringol, natomiast w olejach bogatych w kwas α-linolenowy 4-winylogwajakol.
7. Pochodne kwasów fenolowych pozwalają zachować większość natywnych składników bioaktywnych w olejach roślinnych, ale mogą intensyfikować degradację α-tokoferolu.

Wyniki badań zaprezentowane w monotematycznym cyklu publikacji pt. „Zastosowanie pochodnych kwasów fenolowych do stabilizacji bioolejów roślinnych" mają charakter poznawczy i wdrożeniowy, a także wnoszą nowe informacje dotyczące związków fenolowych jako przeciwutleniaczy olejów roślinnych. Należy jednak zaznaczyć, iż mimo potwierdzenia głównych hipotez badawczych konieczne jest prowadzenie dalszych badań naukowych, gdyż skuteczność działania natywnych i dodanych związków fenolowych zależy nie tylko od ich rodzaju i stężenia, ale także od charakterystyki jakościowej stabilizowanego oksydacyjnie oleju. Wydaje się zatem zasadne rozszerzenie prowadzonych badań naukowych w szczególności o analizę skuteczności działania różnych pochodnych kwasów fenolowych jako przeciwutleniaczy olejów roślinnych z wykorzystaniem testów przechowalniczych

w naturalnych warunkach oraz analizę interakcji pochodnych kwasów fenolowych z innymi związkami anty- i prooksydacyjnymi obecnymi w olejach roślinnych.

7. Literatura

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8. Załączniki

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Phenolic compounds in plant oils: A review of composition, analytical methods, and effect on oxidative stability

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ABSTRACT

Background: Phenolic compounds from different plant sources, like fruits, vegetables, cereals, and herbs, have been excessively studied and widely used in different industrial areas, including food, medicine, and pharmaceuticals. Recently, special attention has been paid to the phenolic compounds of plant oils that have recently been found to vastly affect the oxidative stability of these products.

Scope and approach: This paper reviews the contents and types of phenolic compounds in their initial forms in plant oils and methods of their determination. Also, their impact on the oxidative stability of oils is discussed.

Key findings and conclusions: The total free content of phenolic compounds and the phenol profile in plant oils are very diverse and depend on the oil source and production method. Generally, the main oily source of these compounds is rice bran and olive fruits. Their high amounts can also be found in rapeseed, flaxseed, grapeseed, and pumpkin oils. The main groups of phenolic compounds in oils are phenolic acids and flavonoids. Additionally, lignans, secoiridoids, and phenolic derivatives are identified in some oils. The two main methods for the determination of phenolic compounds in oils include the spectrophotometric and chromatographic ones. The general principles of these assays are often modified by various authors to adapt them to research conditions. Available literature data confirmed the strong antioxidative activity of some phenolic compounds found in oils. However, further studies are needed to better understand the mechanism of their protective action on oils, especially under natural storage.

1. Introduction

Edible plant oils, especially the cold-pressed types, represent a rich source of biologically-active compounds. In the past, the characterisation of oils carried out by researchers concerned mainly lipophilic compounds (sterols, tocopherols, and carotenoids) and was not explicitly focused on phenolic compounds. The exception was olive oil as the content of phenolic compounds is one of its quality parameters (Servili & Montedoro, 2002; Servilli et al., 2014) and affects its sensory properties (Cerretani, Bendini, Rodriguez-Estrada, Vittadini, & Chiavaro, 2009; Pedan, Popp, Rohn, Nyfeler, & Bongartz, 2019).

Phenolic compounds found in food products significantly affect their stability, sensory and nutritional characteristics, and may prevent their spoilage through quenching radical reactions responsible for lipid oxidation (Ghafoor et al., 2020; Koski, Pekkarinen, Hopia, Wähälä, & Heinonen, 2003; Tuberoso, Kowalczyk, Sarritzu, & Cabras, 2007). It has also been proven that dietary inclusion of phenolic compounds provides many benefits due to their anti-inflammatory and anti-carcinogenic effects, especially in breast cancer therapy (Pandey & Rizvi, 2009). Furthermore, phenolic compounds prevent hyperlipidaemia, obesity, inflammatory conditions, oedema, and allergic reactions (Pandey & Rizvi, 2009; Shahidi & Yeo, 2018).

Phenolic compounds represent a very diverse group of substances. The structure of their carbon chain allows dividing them into different groups, of which phenolic acids (derivatives of benzoic and cinnamic acids), flavonoids (in particular flavonols), and lignans are the major ones found in oils (Alu'datt et al., 2017; Neo, Ariffin, Tan, & Tan, 2010).

Recently, special attention has been paid to phenolic compounds as oil antioxidants. They were assayed as primary antioxidants of olive oils by many researchers (e.g. Gutiérrez, Arnaud, & Garrido, 2001; Lanza & Ninfali, 2020; Velasco & Dobarganes, 2002). Various authors have demonstrated a positive linear relationship between olive oil stability and both the total content of phenolic compounds (Blekas, Vassilakis, Harizanis, Tsimidou, & Boskou, 2002; Mansouri et al., 2016; Nieves Franco et al., 2014) and the contents of individual groups, such as phenolic alcohol derivatives (Cerretani, Bendini, Rotondi, Lercker, &

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Toschi, 2005), secoiridoids (Baccouri et al., 2008), and aglyconic derivatives (Bendini, Cerretani, Vecchi, Carrasco-Pancorbo, & Lercker, 2006; Mansouri et al., 2016). However, studies on the protective action of these compounds in other oils are scarce. Gruzdiene and Anelauskaite (2011) and Roszkowska, Tańska, Czaplicki, and Konopka (2015) corroborated a positive correlation between their content and induction time in rapeseed oils. In turn, Redondo-Cuevas, Castellano, Torrens, and Raikos (2018) found that the total phenolic compounds were the main factors that correlated positively with the oxidative stability of 22 commercial oils and fats studied. Also, Dąbrowski, Konopka, Czaplicki, and Tańska (2017) explained the higher oxidative stability of acetone-extracted chia oil with a higher amount of phenolics compared to the pressed and hexane-extracted oils. Due to the low content of native phenolic compounds in most oils, many attempts have been undertaken to prevent the oxidative deterioration of lipids by using natural plant extracts, especially these obtained by alcoholic or water extraction (Blasi & Cossignani, 2020). Nevertheless, it should be noted that such extracts are mixtures of different compounds featuring anti- and pro-oxidative activities and that the oil oxidative stability is the outcome of their interactions. Therefore, the feasibility of stabilizing plant oils through the addition of individual phenolic compounds is increasingly tested to better explain their role in lipid oxidation retardation.

The objective of this article was to prepare a set of numerical data showing the contents of phenolic compounds (including phenolic acids, flavonoids, lignans, secoiridoids, and other phenolics) in plant oils produced with different methods (including pressing and extraction methods), to review the available literature on the methods of their determination in oils, and finally to compare the effects of phenolic compounds on the oxidative stability of these products proved by various researchers.

2. Phenolic compound composition in oils

2.1. Content of total free phenolic compounds

Table 1 summarises the numerical data showing the content of total free phenolic compounds in plant oils. All data were collected from studies where no hydrolytic (acid/alkali) or enzyme treatment before phenolic compounds extraction was applied. It should be mentioned that the content of phenolic compounds depends on many factors, i.e. condition of the raw material and its variety, degree of its maturity, cultivation (e.g. weather conditions, agrotechnical operations) and methods of extraction and purification of oil (Delgado-Adámez, Baltasar, Yuste, & Martín-Vertedor, 2014; García, Ruiz-Méndez, Romero, & Brenes, 2006; Ghafoor, Özcan, Al Juhaimi, Babiker, & Fadimu, 2018; Van Hoed, 2010). The literature also indicates that the parameters of the isolation procedure, such as type and volume of solvent, solid-to-solvent ratio, temperature, pressure and time of extraction, have an impact on the final test result (and thus on the total content in oil) (Khoddami, Wilkes, & Roberts, 2013; Siger, Nogala-Kalucka, & Lampart-Szczapa, 2008).

The highest total content of free phenolic compounds was found in oils obtained from rice brans. In the oil extracted with hexane, it may reach 928 mg GA/100 g, while in the oil extracted with SC-CO_2 it may even exceed 1020 mg GA/100 g (Mingyai, Kettawan, Srikaeo, & Singanusong, 2017). The oil from olive fruit is a valuable source of total free phenolic compounds, although their contents vary significantly across various studies. Their content in virgin oil can reach up to 218 mg/100 g (Del Monaco et al., 2015), but most often ranges from 10 to 40 mg/100 g, regardless of the extraction method. Smeriglio et al. (2016) also determined a high total content of free phenolic compounds in cold-pressed oil from hemp seeds (almost 270 mg GAE/100 g), while 10-fold lower results were obtained by Mińkowski, Zawada, Ptasznik, and Kalinowski (2013) and Siger et al. (2008). Many authors have also reported oil from grape seeds to be rich in phenolic compounds, ensuring their content as high as 105–115 mg GAE/100 g (Bail, Stuebiger, Krist, Unterweger, & Buchbauer, 2008). However, the total content of free phenolic compounds in this oil is strongly dependent on its production method, e.g., it reaches 1.15 mg/100 g in virgin oil (Matthäus, 2008), up to 45 mg GAE/100 g in oil extracted with hexane (Konuskan, Kamiloglu, & Demirkeser, 2019), and 70 mg GAE/100 g in refined oil (Bail et al., 2008). The extraction method also affects the total free phenolic content in the oil from pistachio nuts, which was found to reach 180 mg/100 g in the cold-pressed oil and to increase by almost 20% upon SC-CO_2 extraction (Gharsallaoui et al., 2016). Similarly, in oil pressed from rapeseeds, the total content of free phenolic compounds is 156 mg GAE/100 g (Kostadinović Veličkovska & Mitrev, 2013), but the use of microwaves before oil extraction increased their content by up to 6% (Rękas, Wroniak, Siger, & Ścibisz, 2017). However, most researchers have indicated that the total free phenolic compounds content in oil from rapeseeds ranges from 0.08 to 28 mg/100 g, but does not exceed 0.11 mg/100 g in the refined oil (Rokosik, Dwiecki, & Siger, 2019; Tańska, Mikołajczak, & Konopka, 2018; Zheng, Yang, Zhou, Liu, & Huang, 2014). In other commonly used oils, including cold-pressed oils from flax, pumpkin, sesame, or sunflower seeds, the total content of free phenolic compounds in 100 g ranges from 1 mg CAE (from sunflower seeds) to even 224 mg GAE (from pumpkin seeds) (Aktaş, Gerçekaslan, & Uzlaşır, 2018; De Leonardis, Macciola, & Di Rocco, 2003).

The lowest levels of total free phenolic compounds, not exceed 6 mg/100 g, are found in oils extracted from camellia seeds (cold-pressed, refined), chia seeds (pressed, extracted), corn germs (cold-pressed, refined), hazelnuts (pressed, extracted), marula seeds (extracted), peanuts (cold-pressed, extracted), poppy seeds (pressed), and walnuts (pressed) (Table 1). However, according to some studies, the content of total free phenolic compounds can reach up to 17 mg D-catechin/100 g in cold-pressed oil from chia seeds (Dąbrowski et al., 2017), up to 40–50 mg/100 g in virgin and refined oil from peanuts and in oil extracted from poppy seeds using a chloroform-methanol mixture (Ishtiaque, Khan, Siddiqui, Siddiqi, & Naz, 2013; Muneeshwari et al., 2017), and over 55 mg/100 g in cold-pressed oil from walnuts (Czaplicki, Ogrodowska, Derewiaka, Tańska, & Zadernowski, 2011).

Data presented in Table 1 show a high variation in the total content of free phenolic compounds in oils obtained with the same method from various raw materials (avocado fruits, seeds of camelina, chia, flax, grape, hemp, and safflower, nuts of pistachio and cashew, rice bran). For example, the total content of these compounds in cold-pressed oil from avocado fruits ranges from about 1 mg CAE to 77 mg GAE/100 g (Haiyan, Bedgood Jr., Bishop, Prenzler, & Robards, 2007; Krumreich, Borges, Mendonça, Jansen-Alvesa, & Zambiazi, 2018), in cold-pressed oil from camelina seeds from about 3 mg GAE to 40 mg/100 g (Czaplicki et al., 2011; Ergönül & Özbek, 2018), and in cold-pressed oil from hemp seeds from 2 mg CAE to 267 mg GAE/100 g (Siger et al., 2008; Smeriglio et al., 2016). It was stated that the differences between cited studies are highly attributed to the isolation of phenolic compounds. The higher values were obtained in case of extraction with 80% methanol while the lower amounts of these compounds were extracted with pure or 60% methanol (Table 1). Hovewer, despite the use of typical isolation procedures (extraction with 60% or 80% methanol), there were noted particularly high values in cold-pressed oils studied by some researchers, i.e. Aktaş et al. (2018), Kostadinović Veličkovska and Mitrev (2013), and Mingyai et al. (2017). This confirms that the quality of the raw material and the cultivation technology are also important factors affecting the content of free phenolic compounds.

Recently, researchers have indicated the need to determine not only content of free/non-conjugated phenolic compounds, but also the content of all phenolic compounds in plant oils, including conjugated forms (Bellumori et al., 2019). This is mainly explained in the aspect of quantitative methods based on selective MS/MS fragmentation with relative to conjugate forms, which in turn leads to questionable conclusions about the reliability of such measurements (Celano et al., 2018). Several authors have attempted to use of chemical hydrolytic procedures to determination of total phenolic compounds content in

Table 1
Content of total free phenolic compounds in plant oils.

Oil source	Oil type	Isolation of phenolic compounds	Determination method	Content of free phenolic compounds (in 100 g)	Reference
Amaranth seeds	Cold-pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	33.5 mg D-catechin	Czaplicki et al. (2011)
Avocado fruits	Cold-pressed	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	4.26–5.69 mg GA	Flores, Del Carmen Perez-Camino, and Troca (2014)
		Extraction with shaking and methanol	Spectrophotometric	1.16 mg CAE	Haiyan, Bedgood, Bishop, Prenzler, and Robards (2007)
		Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	46.06–77.35 mg GAE	Krumreich et al. (2018)
	Extracted with petroleum ether	Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	10.87–39.53 mg GAE	Krumreich et al. (2018)
	Extracted with hexane	Extraction with vortexing and methanol	Spectrophotometric	128.17 mg GAE	Tan, Chong, Hamzah, and Ghazali (2018)
	Extracted with SC-CO_2	Extraction with vortexing and methanol	Spectrophotometric	111.27 mg GAE	Tan et al. (2018)
	Ultrasound-assisted aqueous extraction	Extraction with vortexing and methanol	Spectrophotometric	130.17 mg GAE	Tan et al. (2018)
	Refined	Extraction with shaking and methanol	Spectrophotometric	1.28 mg CAE	Haiyan et al. (2007)
Borage seeds	Cold-pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	58.1 mg D-catechin	Czaplicki et al. (2011)
Black cumin seeds	Cold-pressed	Extraction with shaking and methanol	Spectrophotometric	648–760 mg GAE	Haron, Grace-Lynn, and Shahar (2014)
	Supercritical fluid extraction	Extraction with shaking and methanol	Spectrophotometric	96–179 mg GAE	Haron et al. (2014)
Camelina seeds	Cold-pressed	Extraction with vortexing and methanol-water solution (60:40 v/v)	Spectrophotometric	2.59–11.27 mg GAE	Ergönül and Özbek (2018)
		Extraction with shaking and methanol	Spectrophotometric	3.95 mg FAE	Mińkowski et al. (2013)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	40 mg D-catechin	Czaplicki et al. (2011)
	Dried, milled, mix with water seeds and cold-pressed	Extraction with shaking on separatory funnel and methanol-water solution (80:20 v/v)	Spectrophotometric	12.6 mg CGA	Abramovic, Butinar, and Nikolic (2007)
Camellia seeds	Cold-pressed	Extraction with vortexing and methanol-water solution (60:40 v/v)	Chromatographic	4.33–7.28 mg	Wang, Zeng, del Mar Contrerasc, and Wang (2017)
		Extraction with shaking and methanol	Spectrophotometric	1.19 mg CAE	Haiyan et al. (2007)
	Refined	Extraction with shaking and methanol	Spectrophotometric	0.41 mg CAE	Haiyan et al. (2007)
		Extraction with methanol	Spectrophotometric	3.81 mg SAE	Cong, Zhang, Liu, and Huang (2019)
Cashew nuts	Cold pressed	Extraction with shaking and methanol	Spectrophotometric	73.02 mg GAE	Dang and Nguyen (2019)
		Extraction with ultrasonic water-bath and methanol	Spectrophotometric	1.13 mg GAE	Al Juhaimi, Özcan, Ghafoor, Babiker, and Hussain (2018)
	Enzyme assisted aqueous extracted	Extraction with shaking and methanol	Spectrophotometric	25.62 mg GAE	Dang and Nguyen (2019)
	Extracted with hexane	Extraction with shaking and methanol	Spectrophotometric	58.67 mg GAE	Dang and Nguyen (2019)
	Extracted with petroleum ether	Extraction with ultrasonic water-bath and methanol	Spectrophotometric	1.03 mg GAE	Al Juhaimi et al. (2018)
Chia seeds	Cold-pressed	Extraction with ultrasonic water-bath and methanol	Spectrophotometric	2.0 mg GAE	Oliveira-Alves et al. (2017)
		Extraction with ethanol	Chromatographic	94 mg GAE	da Silva Marineli et al. (2014)
	Extracted with acetone	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	17.24 mg D-catechin	Dąbrowski et al. (2017)
	Extracted with hexane	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	0.14–2.53 mg D-catechin	Dąbrowski, Konopka, and Czaplicki (2018)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	1.64 mg D-catechin	Dąbrowski et al. (2017)
	Extracted with SC-CO_2	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	0.06–0.71 mg D-catechin	Dąbrowski et al. (2017)
	Hot-pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	0.65 mg D-catechin	Dąbrowski et al. (2017)
Coconuts	Cold-pressed	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	48.60–57.89 mg GAE	Arlee, Suanphairoch, and Pakdeechanuan (2013)
	Extracted by boiling coconut milk	Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	61.8 mg GAE	Seneviratne and Dissanayake (2008)

(*continued on next page*)

Table 1 (*continued*)

Oil source	Oil type	Isolation of phenolic compounds	Determination method	Content of free phenolic compounds (in 100 g)	Reference
	Pressed	Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	9.1 mg GAE	Seneviratne and Dissanayake (2008)
	Refined	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	22.04 mg GAE	Pazzoti, Souza, Veronezi, Luzia, and Jorge (2018)
		Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	6–14 mg GAE	Nevin and Rajamohan (2004)
		Extraction with methanol	Spectrophotometric	8.1 mg GAE	Muneeshwari et al. (2017)
	Refined, bleached and deodorized	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	13.5 mg GAE	Marina et al. (2008)
	Virgin	Extraction with methanol	Spectrophotometric	19.8 mg GAE	Muneeshwari et al. (2017)
		Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	19 mg GAE	Marina et al. (2008)
		Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	7.78–29.18 mg GAE	Nevin and Rajamohan (2004)
	Virgin and fermented	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	25 mg GAE	Marina et al. (2008)
	Virgin, integrated wet process	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	16.02 mg GAE	Ahmad, Hasham, Aman Nor, and Sarmidi (2015)
	n.s.	n.s.	Spectrophotometric	1.50 mg GAE	Perera, Hewavitharana, and Navaratne (2020)
Corn germs	Cold-pressed	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	1.62–5.36 mg GA	Güneşer et al. (2017)
		Extraction with methanol on SPE column filled with diol	Spectrophotometric	1.26 mg CAE	Siger et al. (2008)
		Extraction with SPE column filled with diol	Spectrophotometric	5.36 mg GAE	Güneşer et al. (2017)
	Refined winterized	Extraction with SPE column filled with diol	Spectrophotometric	1.62 mg GAE	Güneşer et al. (2017)
Echium seeds	Cold-pressed	Extraction with shaking and methanol	Spectrophotometric	3.56 mg FAE	Mińkowski et al. (2013)
	Extracted with 2-propanol at room temperature	Extraction with vortexing and methanol-ultrapure distilled water solution (60:40 v/v)	Spectrophotometric	5.35 mg GAE	Rincón-Cervera et al. (2020)
	Extracted with ethanol at room temperature	Extraction with vortexing and methanol-ultrapure distilled water solution (60:40 v/v)	Spectrophotometric	7.1 mg GAE	Rincón-Cervera et al. (2020)
	Extracted with ethyl acetate at room temperature	Extraction with vortexing and methanol-ultrapure distilled water solution (60:40 v/v)	Spectrophotometric	8.05 mg GAE	Rincón-Cervera et al. (2020)
	Extracted with hexane at room temperature	Extraction with vortexing and methanol-ultrapure distilled water solution (60:40 v/v)	Spectrophotometric	1.35 mg GAE	Rincón-Cervera et al. (2020)
	Randall extracted with 2-propanol	Extraction with vortexing and methanol-ultrapure distilled water solution (60:40 v/v)	Spectrophotometric	17.2 mg GAE	Rincón-Cervera et al. (2020)
	Randall extracted with ethanol	Extraction with vortexing and methanol-ultrapure distilled water solution (60:40 v/v)	Spectrophotometric	20.9 mg GAE	Rincón-Cervera et al. (2020)
	Randall extracted with hexane	Extraction with vortexing and methanol-ultrapure distilled water solution (60:40 v/v)	Spectrophotometric	1.3 mg GAE	Rincón-Cervera et al. (2020)
Evening primrose seeds	Cold-pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	67.9 mg D-catechin	Czaplicki et al. (2011)
Flaxseeds	Cold-pressed	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	28.5 mg GAE	Kostadinović Veličkovska and Mitrev (2013)
		Extraction with methanol on SPE column filled with diol	Spectrophotometric	1.14 mg CAE	Siger et al. (2008)
		Extraction with shaking and methanol	Spectrophotometric	1.17 mg FAE	Mińkowski et al. (2013)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	0.39–2.19 mg D-catechin	Tańska, Roszkowska, Skrajda, and Dąbrowski (2016)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	1.56 mg D-catechin	Tańska et al. (2018)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	21.41 mg GAE	Pazzoti et al. (2018)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	29.4 mg D-catechin	Czaplicki et al. (2011)
	Enzyme assisted cold-pressed	Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	8.61–10.50 mg GAE	Anwar et al. (2013)
	Extracted with chloroform-methanol mixture (2:1)		Spectrophotometric	0.38–1.07 mg CAE	Herchi et al. (2011)

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Table 1 (*continued*)

Oil source	Oil type	Isolation of phenolic compounds	Determination method	Content of free phenolic compounds (in 100 g)	Reference
		Extraction with shaking on separatory funnel and methanol-water solution (80:20 v/v)			
	Extracted with hexane	Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	5.20 mg GAE	Anwar et al. (2013)
	Virgin	n.s.	Spectrophotometric	0.95 mg	Matthäus (2008)
	Refined	Extraction with methanol	Spectrophotometric	5.42 mg SAE	Cong et al. (2019)
Grape seeds	Cold-pressed	Extraction with methanol on SPE column filled with diol	Spectrophotometric	0.51 mg CAE	Siger et al. (2008)
		Extraction with magnetic agitation, ultrasonic water-bath and methanol-water solution (80:20 v/v)	Spectrophotometric	4.8–15.3 mg GAE	Rombaut et al. (2014)
		Extraction with vortexing and methanol-water solution (90:10 v/v)	Spectrophotometric	59.0–115.5 mg GAE	Bail et al. (2008)
		Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	10.26–18.24 mg GAE	Konuskan et al. (2019)
		Extraction with vortexing and methanol-water solution (90:10 v/v)	Spectrophotometric	13.92–27.87 mg GAE	Shinagawa, De Santana, Araujo, Purgatto, and Mancini-Filho (2018)
		Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	10.26–18.24 mg GAE	Konuskan et al. (2019)
	Extracted with hexane	Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	12.88–45.30 mg GAE	Konuskan et al. (2019)
	Extracted with hexane and stimulated by ultrasound	Extraction with ultrasonic water-bath and methanol-water solution (90:10 v/v)	Spectrophotometric	1.70–6.31 mg GA	Malićanin et al. (2014)
	Extracted with hexane	Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	12.88–45.30 mg GAE	Konuskan et al. (2019)
	Heated and cold-pressed	Extraction with vortexing and methanol-water solution (90:10 v/v)	Spectrophotometric	63.5–105.5 mg GAE	Bail et al. (2008)
	Refined	Extraction with vortexing and methanol-water solution (90:10 v/v)	Spectrophotometric	70 mg GAE	Bail et al. (2008)
	Virgin	n.s.	Spectrophotometric	1.15 mg	Matthäus (2008)
Hazelnuts	Cold-pressed	Extraction with ultrasonic water-bath and methanol	Spectrophotometric	1.29 mg GAE	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	Extraction with ultrasonic water-bath and methanol	Spectrophotometric	0.95 mg GAE	Al Juhaimi et al. (2018)
	Pressed	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	1.61 mg CA	Gordon, Covell, and Kirsch (2001)
Hemp seeds	Cold-pressed	Extraction with shaking and methanol	Spectrophotometric	4.11 mg FAE	Mińkowski et al. (2013)
		Extraction with methanol on SPE column filled with diol	Spectrophotometric	2.45 mg CAE	Siger et al. (2008)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	267.5 mg GAE	Smeriglio et al. (2016)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	48 mg GAE	Parry et al. (2005)
Marula seeds	Extracted with hexane	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	3.25 mg GAE	Mariod, Matthäus, Eichner, and Hussein (2015)
Olive fruits	Cold-pressed	Extraction with vortexing, ultrasonic water-bath and methanol-water solution (60:40 v/v)	Spectrophotometric	9.76–57.32 mg GAE	Fanali et al. (2018)
		Extraction with vortexing and methanol	Spectrophotometric	34.3–35.0 mg OE	Cioffi et al. (2010)
	Crushing the olives and extracted with water	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	13.28–31.89 mg GAE	Soufi et al. (2018)
	Extracted with water	n.s.	Spectrophotometric	21.64–26.31 mg GAE	Sicari (2017)
	Refined	Extraction with vortexing and methanol	Chromatographic	6.20 mg	Owen et al. (2000)
	Virgin	Extraction with vortexing and methanol-1% aqueous HCl solution (70:30 v/v)	Spectrophotometric	29–218 mg GAE	Del Monaco et al. (2015)
			Spectrophotometric	13.37–25.69 mg GAE	Baiano, Terracone, Viggiani, and Del Nobile (2009)

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Table 1 (*continued*)

Oil source	Oil type	Isolation of phenolic compounds	Determination method	Content of free phenolic compounds (in 100 g)	Reference
		Extraction with vortexing and methanol-water solution (70:30 v/v)			
		Extraction with methanol	Chromatographic	25.08–92.98 mg GAE	Kotsiou and Tasioula–Margari (2016)
		Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	13.8–27.8 mg GAE	Negro et al. (2019)
		Extraction with vortexing and methanol-water solution (80:20 v/v)	Chromatographic	13.3–42.1 mg GAE	Tuberoso et al. (2007)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	2.3–64.1 mg	Kalogeropoulos and Tsimidou (2014)
		Extraction with vortexing and methanol-water solution (70:30 v/v)	Spectrophotometric	25.5 mg GAE	Baiano et al. (2009)
		Extraction with methanol-water solution (80:20 v/v)	Chromatographic	5.85–61.80 mg	Bellumori et al. (2019)
		Extraction with vortexing and methanol	Spectrophotometric	34.3–35.0 mg OE	Cioffi et al. (2010)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	11.57–42.10 mg	Laincer, Laribi, Tamendjari, Arrar, Rovellini, and Venturini (2014)
		Extraction with vortexing and methanol	Chromatographic	23.20 mg	Owen et al. (2000)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	21.79 mg D-catechin	Tańska et al. (2018)
		Extraction with methanol	Spectrophotometric	124.61 mg SAE	Cong et al. (2019)
Palm fruits	Crude	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	3.12–7.02 mg GAE	Abdullah, Ismail, Ghazali, and Idris (2018)
		Extraction with methanol	Spectrophotometric	6.1–9.1 mg GAE	Szydłowska-Czerniak, Trokowski, Karlovits, and Szłyk (2013)
	Cold-pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	19.04–26.38 mg GAE	Rodríguez et al. (2016)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	40.30 mg GAE	Muneeshwari et al. (2017)
	Refined	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	1.82–2.69 mg GAE	Abdullah et al. (2018)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	18.76 mg GAE	Muneeshwari et al. (2017)
		Extraction with methanol	Spectrophotometric	4.1–4.5 mg GAE	Szydłowska-Czerniak et al. (2013)
Palm kernels	Crude	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	1.68–2.72 mg GAE	Abdullah et al. (2018)
	Refined	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	0.32–0.38 mg GAE	Abdullah et al. (2018)
Peanuts	Cold-pressed	Extraction with ultrasonic water-bath and methanol	Spectrophotometric	0.98 mg GAE	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	Extraction with ultrasonic water-bath and methanol	Spectrophotometric	0.57 mg GAE	Al Juhaimi et al. (2018)
	Refined	Extraction with methanol	Spectrophotometric	40.16 mg GAE	Muneeshwari et al. (2017)
	Virgin	Extraction with methanol	Spectrophotometric	50.13 mg GAE	Muneeshwari et al. (2017)
	Refined	Extraction with methanol	Spectrophotometric	21.35 mg SAE	Cong et al. (2019)
Pistachio nuts	Cold-pressed	Extraction with shaking and methanol	Spectrophotometric	3.87 mg GAE	Ling, Yang, Li, and Wang (2016)
		Extraction with ultrasonic water-bath and methanol	Spectrophotometric	2.36 mg GAE	Al Juhaimi et al. (2018)
		n.s.	Spectrophotometric	180 mg GA	Gharsallaoui et al. (2016)
	Extracted with petroleum ether	Extraction with ultrasonic water-bath and methanol	Spectrophotometric	1.34 mg GAE	Al Juhaimi et al. (2018)
	Extracted with hexane	n.s.	Spectrophotometric	50 mg GA	Gharsallaoui et al. (2016)
	Extracted with SC-CO_2	n.s.	Spectrophotometric	210 mg GA	Gharsallaoui et al. (2016)
	Pressed	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	2.20–2.33 mg CA	Sena-Moreno, Pardo, Pardo-Giménez, Gómez, and Alvarez-Ortí (2016)
	Roasted and cold-pressed	Extraction with shaking and methanol	Spectrophotometric	4.70–4.95 mg GAE	Ling et al. (2016)
Poppy seeds	Cold-pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	19 mg D-catechin	Czaplicki et al. (2011)
		Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	1.33–2.63 mg GA	Dündar Emir, Aydeniz, & Yilmaz (2015)
	Enzyme assisted cold-pressed	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	1.01–7.59 mg GA	Dündar Emir et al. (2015)
	Extracted with chloroform-methanol mixture (1:2)	Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	48.50 mg GAE	Ishtiaque et al. (2013)
	Roasted and cold-pressed	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	2.42–3.47 mg GA	Dündar Emir et al. (2015)

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Table 1 (*continued*)

Oil source	Oil type	Isolation of phenolic compounds	Determination method	Content of free phenolic compounds (in 100 g)	Reference
Pumpkin seeds	Cold-pressed	Extraction with shaking and methanol-water solution (60:40 v/v)	Spectrophotometric	0.76–0.78 mg GAE	Can-Cauich, Sauri-Duch, Moo-Huchin, Betancur-Ancona, and Cuevas-Glory (2019)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	19.20 mg D-catechin	Czaplicki et al. (2011)
		Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	68.40 mg GAE	Kostadinović Veličkovska and Mitrev (2013)
		Extraction with methanol on SPE column filled with diol	Spectrophotometric	2.46 mg CAE	Siger et al. (2008)
		Extraction with shaking in water bath and methanol-water solution (80:20 v/v)	Spectrophotometric	3.96–5.82 mg GAE	Akin et al. (2018)
		Extraction with SPE column filled with diol	Spectrophotometric Chromatographic	2.47–5.09 mg GAE	Andjelkovic et al. (2010)
		Extraction with shaking and methanol	Spectrophotometric	1.59 mg CAE	Haiyan et al. (2007)
		Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	218–224 mg GAE	Aktaş et al. (2018)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	37–60 mg GA	Kulaitienė, Černiauskienė, Jarienė, Danilčenko, and Levickienė (2018)
		Extraction with methanol	Spectrophotometric	0.46 mg GA	Vujasinovic, Djilas, Dimic, Basic, and Radocaj (2012)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	3.98 mg GAE	Rezig et al. (2018)
	Extracted with chloroform-methanol mixture (3:1)	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	5.44 mg GAE	Rezig et al. (2018)
	Extracted with hexane	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	2.33 mg GAE	Rezig et al. (2018)
		Extraction with shaking and methanol-water solution (60:40 v/v)	Spectrophotometric	0.44–0.62 mg GAE	Can-Cauich, Sauri-Duch, Moo-Huchin, Betancur-Ancona, and Cuevas- Glory (2019)
	Extracted with pentane	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	2.33 mg GAE	Rezig et al. (2018)
	Refined	Extraction with shaking and methanol	Spectrophotometric	0.39 mg CAE	Haiyan et al. (2007)
	Roasted and cold-pressed	Extraction with SPE column filled with diol	Spectrophotometric	6.77–29.94 mg CAE	Van Hoed et al. (2017)
		Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	215–236 mg GAE	Aktaş et al. (2018)
		Extraction with methanol	Spectrophotometric	1.35–1.96 mg GA	Vujasinovic et al. (2012)
Rapeseeds	Cold-pressed	Extraction with methanol on SPE column filled with diol	Spectrophotometric	1.31 mg CAE	Siger et al. (2008)
		Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	155.9 mg GAE	Kostadinović Veličkovska and Mitrev (2013)
		Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	10.17–27.75 mg SAE	Zheng et al. (2014)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	1.03 mg D-catechin	Tańska et al. (2018)
	Hot-pressed	Extraction with vortexing and methanol	Chromatographic	0.08 mg SAE	Rokosik et al. (2019)
	Microwaved and cold-pressed	Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	0.57–165.45 mg SA	Rękas et al. (2017)
		Extraction with vortexing and methanol-water solution (80:20 v/v)	Spectrophotometric	80.63 mg SAE	Zheng et al. (2014)
	Refined	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	0.11 mg D-catechin	Tańska et al. (2018)
		Extraction with shaking and methanol	Spectrophotometric	12 mg SA	Szydłowska-Czerniak and Rabiej (2020)
		Extraction with methanol	Spectrophotometric	14.84 mg SAE	Cong et al. (2019)
Rice bran	Cold-pressed	Extraction with methanol on SPE column filled with diol	Spectrophotometric	1.44 mg CAE	Siger et al. (2008)
		Extraction with shaking and methanol-water solution (80:20 v/v)	Spectrophotometric	684–926 mg GA	Mingyai et al. (2017)
	Extracted with hexane	Extraction with shaking and methanol-water solution (80:20 v/v)	Spectrophotometric	733–928 mg GA	Mingyai et al. (2017)
	Extracted with SC-CO_2		Spectrophotometric	663-1022 mg GA	Mingyai et al. (2017)

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Table 1 (*continued*)

Oil source	Oil type	Isolation of phenolic compounds	Determination method	Content of free phenolic compounds (in 100 g)	Reference
		Extraction with shaking and methanol-water solution (80:20 v/v)			
	Refined	Extraction with methanol	Spectrophotometric	5.67 mg SAE	Cong et al. (2019)
Safflower seeds	Cold-pressed	Extraction with vortexing and methanol-water solution (60:40 v/v)	Spectrophotometric	27.22–52.53 mg GAE	Ergönül and Özbek (2018)
		Extraction with shaking on separatory funnel and methanol-water solution (80:10 v/v)	Spectrophotometric	2.62 mg GAE	Aydeniz, Güneşer, and Yılmaz (2014)
	Extracted	Extraction with vortexing and methanol-water solution (60:40 v/v)	Spectrophotometric	19.9–22.8 mg GAE	Taha and Matthäus (2018)
	Extracted with cyclohexane	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	14.09–41.28 mg GAE	Zemour et al. (2019)
	Extracted with hexane	Extraction with shaking and methanol-water solution (80:20 v/v)	Spectrophotometric	7.95–4.37 mg CA	Ben Moumen et al. (2014)
	Microwaved and cold-pressed	Extraction with shaking on separatory funnel and methanol-water solution (80:10 v/v)	Spectrophotometric	4.08 mg GAE	Aydeniz et al. (2014)
	Roasted and cold-pressed	Extraction with shaking on separatory funnel and methanol-water solution (80:10 v/v)	Spectrophotometric	2.86 mg GAE	Aydeniz et al. (2014)
	Roasted and extracted	Extraction with vortexing and methanol-water solution (60:40 v/v)	Spectrophotometric	20.2–71.1 mg GAE	Taha and Matthäus (2018)
	Virgin	n.s.	Spectrophotometric	3.60 mg	Matthäus (2008)
	Refined	Extraction with methanol	Spectrophotometric	2.93 mg SAE	Cong et al. (2019)
Sesame seeds	Cold-pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	28.30 mg D-catechin	Czaplicki et al. (2011)
		Extraction with shaking and methanol	Spectrophotometric	2.27 mg CAE	Haiyan et al. (2007)
	Pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	0.04 mg GAE	Borjian Borojeni, Goli, and Gharachourloo (2016)
	Refined	Extraction with methanol	Spectrophotometric	25.82 mg GAE	Muneeshwari et al. (2017)
	Roasted and pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	0.73 mg GAE	Borjian Borojeni et al. (2016)
	Virgin	Extraction with methanol	Spectrophotometric	39.21 mg GAE	Muneeshwari et al. (2017)
	Refined	Extraction with methanol	Spectrophotometric	133.75 mg SAE	Cong et al. (2019)
Soybeans	Crude	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	64.37 mg GA	EL-Razek Mohdaly, El-Hameed Seliem, EL-Moneam Maher, EL-Hassan, and Tawab Mahmoud (2017)
	Cold-pressed	Extraction with methanol on SPE column filled with diol	Spectrophotometric	1.48 mg CAE	Siger et al. (2008)
	Refined	Extraction with shaking and methanol	Spectrophotometric	0.42 mg CAE	Haiyan et al. (2007)
		Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	32.94 mg GA	EL-Razek Mohdaly et al. (2017)
		Extraction with methanol	Spectrophotometric	3.69 mg SAE	Cong et al. (2019)
Sunflower seeds	Cold-pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	1.00 mg CA	De Leonardis et al. (2003)
		Extraction with methanol on SPE column filled with diol	Spectrophotometric	1.20 mg CAE	Siger et al. (2008)
		Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	192 mg GAE	Kostadinović Veličkovska and Mitrev (2013)
	Refined	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	18.2–54.8 mg GAE	Kostadinović Veličkovska and Mitrev (2013)
		Extraction with methanol	Spectrophotometric	4.47 mg SAE	Cong et al. (2019)
		Extraction with methanol	Spectrophotometric	14.33 mg GAE	Muneeshwari et al. (2017)
	Virgin	Extraction with methanol	Spectrophotometric	26.13 mg GAE	Muneeshwari et al. (2017)
Tiger nuts	Aqueous enzymatic extracted	Extraction with vortexing and methanol-water solution (60:40 v/v)	Spectrophotometric	14.50 mg GAE	Ezeh, Niranjan, and Gordon (2016)
	Enzyme aided pressed	Extraction with vortexing and methanol-water solution (60:40 v/v)	Spectrophotometric	13.20 mg GAE	Ezeh et al. (2016)
	Pressed	Extraction with vortexing and methanol-water solution (60:40 v/v)	Spectrophotometric	17.90 mg GAE	Ezeh et al. (2016)
Walnuts	Cold-pressed	Extraction with methanol-water solution (80:20 v/v)	Spectrophotometric	55.40 mg D-catechin	Czaplicki et al. (2011)
		Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	1.97–8.00 mg GAE	Slatnar, Mikulic-Petkovsek, Stampar, Veberic, and Solar (2015)

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Table 1 (*continued*)

Oil source	Oil type	Isolation of phenolic compounds	Determination method	Content of free phenolic compounds (in 100 g)	Reference
		Extraction with SPE column filled with diol	Spectrophotometric	2.83 mg GAE	Gao, Cao, Liu, Jin, and Wang (2019)
		Extraction with ultrasonic water-bath and methanol	Spectrophotometric	0.84 mg GAE	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	Extraction with ultrasonic water-bath and methanol	Spectrophotometric	0.88 mg GAE	Al Juhaimi et al. (2018)
	Pressed	Extraction with methanol-water solution (60:40 v/v)	Spectrophotometric	1.70–2.90 mg CA	Sena-Moreno et al. (2016)
	Pressed at different rotational speeds (30–90 rpm) and different nozzle diameters (6–10 mm)	Extraction with sonification and methanol-water solution (50:50 v/v)	Spectrophotometric	0-11,672 mg GAE	Kiss, Mašán, and Híc (2020)
	Roasted and cold-pressed	Extraction with SPE column filled with diol	Spectrophotometric	3.01–4.48 mg GAE	Gao et al. (2019)

CAE – caffeic acid equivalent; CA – caffeic acid; CGA – chlorogenic acid; FAE – ferulic acid equivalent; GAE – gallic acid equivalent; GA – gallic acid; OE – oleuropein equivalent; SAE – sinapic acid equivalent; SA – sinapic acid; n.s. – not specified.

plant oils, and studies have shown that the use of hydrolytic procedures appears useful in providing a more realistic estimate of the composition of mainly secoiridoids in plant oils (Mulinacci et al., 2006). Bellumori et al. (2019) stated that the use of acidic hydrolysis has proved to be a fast and satisfactory analytical method for quantifying the content of hydroxytyrosol and tyrosol (free and/or linked to secoiridoidic molecules) in olive oil, and allowed to obtain even more than 80% higher content of hydroxytyrosol and tyrosol in relation to the non-hydrolyzed samples. Similar observations were noted by Brenes, García, García, and Garrido (2001) and Marx et al. (2020). It should also be mentioned that hydrolysis process transforms complex lipophilic compounds (e.g. secoiridoid aglycones) into simpler hydrophilic substances (e.g. hydroxytyrosol and tyrosol), which are important for the antioxidant activity of phenolic compounds in micellar systems as well as are also more easily absorbed by human body (Brenes et al., 2001).

2.2. Content of phenolic acids

Table 2 presents the contents of individual phenolic acids in plant oils. A good source of protocatechuic acid are oils obtained from camellia (cold-pressed), grape (cold-pressed, extracted with petroleum ether), and pumpkin seeds (cold-pressed, roasted and cold-pressed), wherein its content can reach up to 385; 8120; and 2070 μg/100 g, respectively (Wang et al., 2017; Al Juhaimi & Özcan, 2017; Akin, Arslan, & Karuk, 2018). Protocatechuic acid is also found in virgin olive oil (up to 19 μg/100 g) (Tańska et al., 2018) and in refined, bleached, and deodorized oil from coconuts at similar levels (Marina, Cheman, Nazimah, & Amin, 2008). In oils (both pressed and extracted) obtained from such raw materials as cashew nuts, flaxseeds, hazelnuts, peanuts, pistachio nuts, and walnuts, its content is low, usually not exceeding 0.5 μg/100 g, except for the oil cold-pressed from flaxseeds (approx. 1.5 μg/100 g) (Al Juhaimi et al., 2018; Tańska et al., 2018). According to other researchers, protocatechuic acid is not found in oils obtained from corn germs, hemp seeds, rapeseeds, rice bran, nor soybeans (Siger et al., 2008; Tuberoso et al., 2007).

A review of the literature data has shown that the largest amounts of *p*-hydroxybenzoic acid are found in cold-pressed oil from camellia seeds, reaching up to 310 μg/100 g (Wang, Zeng, delMar Contrerasc, & Wang, 2017). Virgin olive oil contains this acid but in a substantially fewer amount (up to 20 μg/100 g) (Pedan et al., 2019). *p*-Hydroxybenzoic acid is also present in oils pressed from corn germs, flaxseeds, soybeans, and sunflower seeds (in an amount not exceeding 3 μg/100 g) (Table 2). Its content in oil from rapeseeds varies from 1 to 5 μg/100 g depending on the extraction method, with the highest amounts obtained by the microwave assisted cold-pressed method (McDowell, Elliott, & Koidis, 2017).

The main vanillic acid sources include cold-pressed oils from camellia seeds (up to 1764 μg/100 g) and pumpkin seeds (up to 2750 μg/100 g) (Akin et al., 2018; Wang et al., 2017). Pedan et al. (2019) also determined its high content in virgin olive oil, while Al Juhaimi and Özcan (2017) in oil from grape seeds (cold-pressed, extracted with petroleum ether). Some authors have determined significant amounts of vanillic acid in oil from coconuts, ranging from 103 to 208 μg/100 g (Srivastava, Semwal, & Majumdar, 2016). Traces of this acid were also found in oils made of cashew nuts, flaxseeds, hazelnuts, peanuts, pistachio nuts, soybeans, and walnuts (Al Juhaimi et al., 2018; Anwar, Zreen, Sultana, & Jamil, 2013). Siger et al. (2008) estimated vanillic acid content in cold-pressed oil from sunflower seeds at almost 7 μg/100 g, and in cold-pressed oil from hemp seeds at 2 μg/100 g, but did not detect in oils pressed from rice bran and corn germs.

Other acids from the hydroxybenzoic acid group have been described in the works of many authors. For example, the content of gallic acid in the oil pressed from corn germs was at 1680 μg/100 g and that of syringic acid was at 691 μg/100 g (Güneşer, Yılmaz, & Oka, 2017). A high content of gallic acid was also found in virgin olive oil, i.e., from 1140 to 4380 μg/100 g. The content of syringic acid in this oil reaches up to 1920 μg/100 g (Cioffi et al., 2010). Gallic acid was also determined in the oil from coconuts (hot- and cold-extracted) at almost 3000 μg/100 g (Srivastava et al., 2016) and in nut oils (cold-pressed, extracted with petroleum ether) at a level not exceeding 1 μg/100 g (Al Juhaimi et al., 2018).

Caffeic acid, which is a derivative of cinnamic acid, is found mainly in oils obtained from coconuts, olive fruits, and pumpkin seeds. Its content in these oils ranges from 159 to even 3830 μg/100 g (Akin et al., 2018; Srivastava et al., 2016). Its lower content was determined in cold-pressed oil from camellia seeds (over 62 μg/100 g) (Wang et al., 2017), and in cold-pressed oil from sunflower seeds (only about 5 μg/100 g) (Siger et al., 2008). Nut oils were characterised by a low content of caffeic acid, reaching over 1 μg/100 g in the oil from pistachio nuts obtained by extraction with petroleum ether (Al Juhaimi et al., 2018). The presented data show that caffeic acid is absent in oils obtained from such raw materials as corn germs, grape and hemp seeds, and rice bran (Anwar et al., 2013; Siger et al., 2008).

A review of the literature data has shown that oil from pumpkin seeds is a valuable source of *p*-coumaric acid. Akin et al. (2018) stated that its content could reach up to 2660 μg/100 g in cold-pressed oil. In addition, significant amounts of *p*-coumaric acid are found in oils from camellia seeds (cold-pressed, up to 203 μg/100 g), coconuts (extracted by boiling coconut milk, 200 μg/100 g; and refined, bleached and deodorized, 160 μg/100 g), grape seeds (cold-pressed, 180 μg/100 g), and olive fruits (virgin, 254 μg/100 g) (Marina et al., 2008; Pedan et al., 2019; Seneviratne & Dissanayake, 2008; Siger et al., 2008; Wang et al.,

Table 2
Content of main phenolic acids in plant oils.

Oil source	Oil type	Content of phenolic acids (μg/100 g)							Reference
		Protocatechuic	*p*-Hydroxybenzoic	Vanillic	Caffeic	*p*-Coumaric	Ferulic	Sinapic	
Camellia seeds	Cold-pressed	182.68–385.34	163.16–309.95	699.34-1764.44	39.29–62.29	109.47–203.04	35.16–99.62	86.48–300.65	Wang et al. (2017)
Cashew nuts	Cold-pressed	0.28	nd.	0.16	0.09	0.19	0.16	0.23	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	0.30	nd.	0.28	0.17	0.28	0.21	0.34	Al Juhaimi et al. (2018)
Coconuts	Cold extracted virgin	nd.	nd.	103	0.00	0.00	236	189	Srivastava et al. (2016)
	Extracted by boiling coconut milk	nd.	nd.	nd.	300	200	330	nd.	Seneviratne and Dissanayake (2008)
	Hot extracted virgin	nd.	nd.	180	159	53	1283	335	Srivastava et al. (2016)
	Pressed	nd.	nd.	nd.	13	34	31	nd.	Seneviratne and Dissanayake (2008)
	Refined, bleached and deodorized	16	nd.	0.00	0.00	168	139	nd.	Marina et al. (2008)
	Virgin	0.00	nd.	0.00–208	0.12	55–57	504–509	nd.	Marina et al. (2008)
Corn germs	Cold-pressed	nd.	nd.	nd.	nd.	nd.	194	691	Güneşer et al. (2017)
		0.00	1.70	0.00	0.00	1.90	5.80	0.60	Siger et al. (2008)
Flaxseeds	Cold-pressed	0.00	3.10	1.00	0.00	0.00	1.00	0.00	Siger et al. (2008)
		1.47	1.17	0.00	0.00	0.23	0.00	0.00	Tańska et al. (2018)
		nd.	nd.	0.00	nd.	0.00	<0.50	0.00	Tuberoso et al. (2007)
	Enzyme-assisted and cold-pressed	nd.	2.34–3.20	0.75–1.00	0.00	nd.	0.57–0.95	nd.	Anwar et al. (2013)
	Extracted with hexane	nd.	1.21	0.67	0.00	nd.	0.45	nd.	Anwar et al. (2013)
	Extracted with chloroform-methanol mixture (2:1)	nd.	nd.	1.00–42	nd.	nd.	1.00–215	nd.	Herchi et al. (2011)
Grape seeds	Cold-pressed	nd.	nd.	0.00	nd.	0.00	0.00	0.00	Tuberoso et al. (2007)
		0.00	0.00	0.80	0.00	180	0.00	0.20	Siger et al. (2008)
		2713 -6841	nd.	97–371	nd.	nd.	228–584	nd.	Al Juhaimi and Özcan (2017)
	Extracted with petroleum ether	2911–8119	nd.	97–447	nd.	nd.	348–683	nd.	Al Juhaimi and Özcan (2017)
Hazelnuts	Cold-pressed	0.47	nd.	0.03	0.67	0.17	0.38	0.42	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	0.59	nd.	0.28	0.78	0.28	0.45	0.51	Al Juhaimi et al. (2018)
Hemp seeds	Cold pressed	0.00	6.00	2.00	0.00	2.00	1.00	3.00	Siger et al. (2008)
Olive fruits	Virgin	nd.	nd.	40	nd.	30	0.00	0.00	Tuberoso et al. (2007)
		nd.	nd.	0.00	2070–3000	nd.	460–620	nd.	Cioffi et al. (2010)
		0.00	0.00	10–88	0.00	6–29	˂0.09	0.00	Kotsiou and Tasioula–Margari (2016)
		nd.	2.00–20	20–440	nd.	4.00–254	0.00–48	nd.	Pedan et al. (2019)
		nd.	nd.	0.00–63	nd.	27–72	nd.	nd.	Soufi et al. (2018)
		18.72	0.00	50.05	10.25	5.03	0.00	0.00	Tańska et al. (2018)
Peanuts	Cold-pressed	nd.	nd.	0.00	nd.	0.00	0.00	0.00	Tuberoso et al. (2007)
		0.32	nd.	0.05	0.21	0.15	0.09	0.11	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	0.47	nd.	0.13	0.37	0.21	0.18	0.19	Al Juhaimi et al. (2018)
Pistachio nuts	Cold-pressed	0.67	nd.	0.34	1.13	0.34	0.13	0.83	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	0.74	nd.	0.42	1.28	0.40	0.22	0.89	Al Juhaimi et al. (2018)

(*continued on next page*)

Table 2 (*continued*)

Oil source	Oil type	Content of phenolic acids (μg/100 g)							Reference
		Protocatechuic	*p*-Hydroxybenzoic	Vanillic	Caffeic	*p*-Coumaric	Ferulic	Sinapic	
Pumpkin seeds	Cold-pressed	nd.	nd.	0.00	nd.	0.00	0.00	0.00	Tuberoso et al. (2007)
		3.10	0.00	11.40	0.00	3.80	3.80	0.00	Siger et al. (2008)
		1560–2070	nd.	2440–2750	3410–3830	2480–2660	4720–5170	nd.	Akin et al. (2018)
	Roasted and cold pressed	0.00–620	nd.	10–220	nd.	10–60	10–180	nd.	Van Hoed et al. (2017)
Rapeseeds	Cold-pressed	0.00	0.00	0.00	3.33	0.00	5.42	12.31	Tańska et al. (2018)
		nd.	nd.	<0.50	nd.	<0.50	160.00	680.00	Tuberoso et al. (2007)
		0.00	1.60	0.00	0.30	13.10	5.60	236	Siger et al. (2008)
		nd.	nd.	nd.	nd.	17–34	15–26	199–311	Rękas et al. (2017)
		nd.	1.00	1.00	0.00	0.00	3.00	107	McDowell et al. (2017)
	Hot-pressed	nd.	4.00	1.00	0.00	1.00	7.00	282	McDowell et al. (2017)
	Microwave assisted cold-pressed	nd.	5.00	2.00	0.00	0.00	8.00	305	McDowell et al. (2017)
		nd.	nd.	nd.	nd.	16–31	13–25	199–307	Rękas et al. (2017)
	Refined	0.00	0.00	0.00	0.00	0.00	0.00	0.00	Tańska et al. (2018)
Rice bran	Cold-pressed	0.00	0.00	0.00	0.00	0.00	0.40	0.00	Siger et al. (2008)
Soybeans	Cold-pressed	nd.	nd.	0.00	nd.	0.00	0.00	0.00	Tuberoso et al. (2007)
		0.00	0.80	1.10	0.80	1.50	1.20	0.90	Siger et al. (2008)
Sunflower seeds	Cold-pressed	0.00	1.50	6.90	4.90	1.80	1.30	1.40	Siger et al. (2008)
		nd.	nd.	<0.50	nd.	0.00	0.00	<0.50	Tuberoso et al. (2007)
Walnuts	Cold-pressed	0.42	nd.	0.18	0.18	0.22	0.23	0.41	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	0.58	nd.	0.29	0.27	0.27	0.34	0.41	Al Juhaimi et al. (2018)

nd. – no data.

2017). Various production methods allow obtaining high *p*-coumaric acid contents also in rapeseed oil, ranging from 13 to 34 μg/100 g in the cold-pressed oil and from 16 to 31 μg/100 g in microwave assisted cold-pressed oil (Rękas et al., 2017). Other oils have low contents of *p*-coumaric acid, up to 2 μg/100 g in cold-pressed oil from corn germs (Siger et al., 2008). In turn, some researchers have shown that cold-pressed oil from rice bran does not contain *p*-coumaric acid (Siger et al., 2008), similarly to cold-extracted virgin oil and refined oil from rapeseeds (Srivastava et al., 2016; Tańska et al., 2018).

Table 2 shows that ferulic acid is the most common phenolic acid in plant oils. Its content ranges from 0.09 to 5170 μg/100 g, depending on the production method and raw material used. The highest ferulic acid content is found in oils obtained from raw materials such as pumpkin seeds from Turkey (4720–5170 μg/100 g), coconuts (up to 1283 μg/100 g), grape seeds (up to 683 μg/100 g), and olive fruits (up to 620 μg/100 g) (Akin et al., 2018; Al Juhaimi & Özcan, 2017; Cioffi et al., 2010; Srivastava et al., 2016). However, variations within oil types can also be observed. For example, Tuberoso et al. (2007) found that ferulic acid content in cold-pressed oil from rapeseeds was at 160 μg/100 g, while Rękas et al. (2017) determined its significantly lower amount in the range of 15–26 μg/100 g. The smallest amounts of ferulic acid (up to μg/100 g) can be found in oils from nuts, e.g., cashew nuts, hazelnuts, peanuts, pistachio nuts and walnuts (Al Juhaimi et al., 2018).

Oils obtained from rapeseeds by cold or hot pressing contain mainly sinapic acid, with its content ranging from 12 to 680 μg/100 g (Tańska et al., 2018; Tuberoso et al., 2007). However, it is completely removed from the oil during refining (Tańska et al., 2018). A high content of this phenolic acid, reaching almost 692 μg/100 g, is found in the oil pressed from corn germs (Güneşer et al., 2017). Cold-pressed oil from camellia seeds is characterised by an almost 2-fold lower content of sinapic acid than oil pressed from corn germs (Wang et al., 2017). Its high content was also determined in oil cold-pressed from coconuts (189 μg/100 g), but its almost 2-fold higher content was found in the coconut oil obtained by hot extraction (Srivastava et al., 2016). In other oils (from nuts and hemp seeds), the sinapic acid content is low, below 3 μg/100 g (Al Juhaimi et al., 2018; Siger et al., 2008). Collected data show that this acid is absent in oils from flaxseeds, pumpkin seeds, and olive fruits (Kotsiou & Tasioula–Margari, 2016; Siger et al., 2008; Tańska et al., 2018).

2.3. Content of flavonoids

The contents of total flavonoids in various plant oils are listed in Table 3. Usually, their contents are expressed per the content of major flavonoids, i.e., apigenin (API), luteolin (LUT), or quercetin equivalent (QCE). A review of the literature data shows that oils obtained from cashew nuts, coconuts, flaxseeds, and camellia seeds are good sources of these compounds; however, their contents are strongly dependent on the oil production method. The total content of flavonoids in oil from cashew nuts can reach up to 17 mg QCE in 100 g in case of cold-pressing, but is 1.8-fold lower in enzyme assisted aqueous extracted oil, and 10-fold lower in oil extracted with petroleum ether (Al Juhaimi et al., 2018; Dang & Nguyen, 2019). In turn, oil extracted by boiling coconut milk contains about 14 mg of total flavonoids in 100 g, which is over 5-fold more than in the oil obtained by pressing (Seneviratne & Dissanayake, 2008). The literature data indicates that the total flavonoid content in oil from flaxseeds can reach over 4 mg LUT/100 g (Kostadinović Veličkovska, Brühl, Mitrev, Mirhosseini, & Matthäus, 2015). The content of flavonoids in virgin olive oil does not exceed 5 mg/100 g and is even lower, reaching trace levels (below 0.50 mg LUT/100 g) in the oil extracted with water (Laincer et al., 2014; Sicari, 2017). The total flavonoid content in cold-pressed oils from rape, sesame, sunflower, and hemp seeds is low and does not exceed 3 mg/100 g (Kostadinović Veličkovska et al., 2015).

The content of individual flavonoids in plant oils also varies (Table 3). A review of the literature data has shown that oil from grape

Table 3
Total flavonoid content and content of main flavonoids in plant oils.

Oil source	Oil type	Total content (in 100 g)	Content of main flavonoids (μg/100 g)								Reference
			Catechin	Epicatechin	Apigenin	Luteolin	Kaempferol	Quercetin	Myricetin	Naringenin	
Camellia seeds	Cold-pressed	nd.	186.76	32.21	tr-0.39	1.00–3.13	1.53–5.34	1.49–3.27	0.46–0.66	384.74–1076.74	Wang et al. (2017)
Cashew nuts	Cold-pressed	17.39 mg QCE	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Dang and Nguyen (2019)
		0.97 mg CE	0.56	nd.	nd.	0.21	0.11	0.03	nd.	0.54	Al Juhaimi et al. (2018)
	Enzyme assisted aqueous extracted	9.49 mg QCE	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Dang and Nguyen (2019)
	Extracted with petroleum ether	1.66 mg CE	0.64	nd.	nd.	0.36	0.19	0.15	nd.	0.63	Al Juhaimi et al. (2018)
	Extracted with hexane	10.72 mg QCE	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Dang and Nguyen (2019)
Coconuts	Cold extracted virgin	nd.	1235	0.00	nd.	nd.	nd.	0.00	nd.	nd.	Srivastava et al. (2016)
	Extracted by boiling coconut milk	13.70 mg	290	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Seneviratne and Dissanayake (2008)
	Hot extracted virgin	nd.	1815	262	nd.	nd.	nd.	162	nd.	nd.	Srivastava et al. (2016)
	Pressed	2.46 mg	87	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Seneviratne and Dissanayake (2008)
Corn germs	Cold-pressed	nd.	0.00	nd.	nd.	nd.	0.00	nd.	nd.	nd.	Güneşer et al. (2017)
Flaxseeds	Cold-pressed	4.51 mg LUT	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Kostadinović Veličkovska et al. (2015)
		nd.	nd.	nd.	0.00	0.00	nd.	nd.	nd.	nd.	Tuberoso et al. (2007)
Grape seeds	Cold-pressed	nd.	nd.	nd.	0.00	0.00	nd.	nd.	nd.	nd.	Tuberoso et al. (2007)
		nd.	42,780–84,714	nd.	nd.	nd.	nd.	51–144	nd.	nd.	Al Juhaimi and Özcan (2017)
	Extracted with petroleum ether	nd.	53,711–83,688	nd.	nd.	nd.	nd.	63–183	nd.	nd.	Al Juhaimi and Özcan (2017)
Hazelnuts	Cold-pressed	1.21 mg CE	0.89	nd.	0.97	nd.	0.21	0.03	nd.	1.13	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	1.87 mg CE	1.09	nd.	1.15	nd.	0.37	0.13	nd.	1.22	Al Juhaimi et al. (2018)
Hemp seeds	Cold-pressed	1.46 mg LUT	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Kostadinović Veličkovska et al. (2015)
Olive fruits	Extracted with water	0.14–0.47 mg (LUT + API)	nd.	nd.	19.7–90	11.30–15.40	nd.	nd.	nd.	nd.	Sicari (2017)
	Virgin	nd.	0.00	0.00	24–57	11–169	0.00	0.00	0.00	0.00	Kotsiou and Tasioula–Margari (2016)
		nd.	nd.	nd.	10–820	50–940	nd.	nd.	nd.	nd.	Pedan et al. (2019)
		nd.	nd.	nd.	20–920	220-1670	nd.	nd.	nd.	nd.	Negro et al. (2019)
		nd.	nd.	nd.	20–650	20-1610	nd.	nd.	nd.	nd.	-Tuberoso et al. (2007)
		1.00–4.40 mg	nd.	nd.	300–140	1200–3800	nd.	nd.	nd.	nd.	Laincer et al. (2014)
		nd.	nd.	nd.	2.00–92	4.00–657	nd.	nd.	nd.	nd.	Talhaoui et al. (2016)
		0.65–1.36 mg QCE	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Soufi et al. (2018)
		nd.	nd.	nd.	140	400	nd.	nd.	nd.	nd.	Tuberoso et al. (2007)
Peanuts	Cold-pressed	nd.	nd.	nd.	0.00	0.00	nd.	nd.	nd.	nd.	Tuberoso et al. (2007)
		0.09 mg CE	1.37	nd.	nd.	0.68	0.12	0.12	nd.	0.98	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	0.61 mg CE	1.47	nd.	nd.	0.81	0.21	0.19	nd.	1.09	Al Juhaimi et al. (2018)
Pistachio nuts	Cold-pressed	1.17 mg CE	3.76	nd.	nd.	1.14	0.45	0.29	nd.	2.75	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	2.82 mg CE	3.82	nd.	nd.	1.24	0.51	0.43	nd.	2.87	Al Juhaimi et al. (2018)
Pumpkin seeds	Cold-pressed	nd.	nd.	nd.	nd.	0.00	0.00	nd.	nd.	nd.	Tuberoso et al. (2007)
	Roasted and cold-pressed	nd.	nd.	nd.	nd.	20.00	nd.	nd.	nd.	nd.	Van Hoed et al. (2017)
Rapeseeds	Cold-pressed	1.13 mg LUT	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Kostadinović Veličkovska et al. (2015)
		nd.	nd.	nd.	0.00	0.00	nd.	nd.	nd.	nd.	Tuberoso et al. (2007)
Soybeans	Cold-pressed	nd.	nd.	nd.	0.00	0.00	nd.	nd.	nd.	nd.	Tuberoso et al. (2007)
Sunflower seeds	Cold-pressed	nd.	nd.	nd.	0.00	0.00	nd.	nd.	nd.	nd.	Tuberoso et al. (2007)
		1.21 mg LUT	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Kostadinović Veličkovska et al. (2015)
Sesame seeds	Cold-pressed	1.91–2.82 mg LUT	nd.	nd.	nd.	nd.	nd.	nd.	nd.	nd.	Kostadinović Veličkovska et al. (2015)
Walnuts	Cold-pressed	3.89 mg CE	1.67	nd.	nd.	0.55	0.21	0.27	nd.	3.86	Al Juhaimi et al. (2018)
	Extracted with petroleum ether	4.89 mg CE	1.78	nd.	nd.	0.75	0.28	0.38	nd.	3.94	Al Juhaimi et al. (2018)

tr – trace amounts; nd. – no data; API – apigenin; CE – catechol equivalent; LUT – luteolin; QCE – quercetin equivalent.

seeds is a good catechin source, wherein its content can reach up to 84,714 μg/100 g in cold-pressed oil, and 83,688 μg/100 g in oil extracted with petroleum ether (Al Juhaimi & Özcan, 2017). Oil from coconuts (cold/hot extracted, virgin) and cold-pressed oil from camellia seeds also have a high catechin content, which is, however, almost 50-fold lower than in oil from grape seeds (Srivastava et al., 2016). In other oils, i.e., these made of cashew nuts, hazelnuts, peanuts, the catechin content is low and does not exceed 1.5 μg/100 g. Only oils from pistachio nuts contain up to 4 μg catechin/100 g (Al Juhaimi et al., 2018). Epicatechin is found only in cold-pressed oil from camellia seeds at about 32 μg/100 g, but the high-temperature treatment used during the production of oil from coconuts allows obtaining a final product rich in this flavan-3-ol (up to 262 μg/100 g) (Wang et al., 2017). In turn, the research of Wang et al. (2017) detected epigallocatechin, epigallocatechin gallate, and taxifolin in cold-pressed oil from camellia seeds.

A valuable and main source of flavones is olive oil. It contains significant amounts of apigenin, from 2 to 920 μg/100 g, depending on the production method, with virgin oil having a higher content of this compound (Negro et al., 2019; Talhaoui et al., 2016). In the oil pressed from roasted pumpkin seeds, apigenin was found at 20 μg/100 g (Van Hoed et al., 2017). It was also detected in oil extracted with petroleum ether from hazelnuts and cold-pressed from camellia seeds, but in an amount not exceeding 1.2 μg/100 g (Al Juhaimi et al., 2018). Apigenin is absent in the composition of oils from such raw materials like flax, grape, rape, and sunflower seeds, also peanuts and soybeans (Tuberoso et al., 2007). Similarly to apigenin, luteolin is mainly found in olive oil. Literature data indicate that its content in virgin oil can range from 4 to even 3800 μg/100 g (Laincer et al., 2014; Talhaoui et al., 2016), whereas in oil extracted with water can be almost 400-fold lower (Sicari, 2017). Luteolin is also found in oils from pistachio nuts, peanuts, walnuts, cashew nuts and camellia seeds, in amounts up to 3 μg/100 g (Al Juhaimi et al., 2018; Wang et al., 2017), whereas is absent in cold-pressed oils from such conventional raw materials as flax, grape, rape, and sunflower seeds (Tuberoso et al., 2007). Pedan et al. (2019) detected other flavones in virgin olive oil, i.e., luteolin-7-*O*-glucoside and apigenin-7-*O*-glucoside, in a total amount of 33 μg/100 g. In turn, Talhaoui et al. (2016) found that this oil also contained such flavones as, e.g., diosmetin (up to 26 μg/100 g), apigenin rutinoside (up to 70 μg/100 g), and luteolin glucoside isomer (up to 1263 μg/100 g).

Flavonols are also found in plant oils. Kaempferol is mainly present in cold-pressed oil from camellia seeds, up to 5 μg/100 g (Wang et al., 2017). It is also found in nut oils (cashew and pistachio nuts, walnuts, hazelnuts, peanuts) with content up to 0.5 μg/100 g (Al Juhaimi et al., 2018; Al Juhaimi & Özcan, 2017). According to Güneşer et al. (2017), kaempferol is absent in cold-pressed oil from corn germs, and – as claimed by Kotsiou and Tasioula–Margari (2016) – also in virgin oil from coconuts. The main source of quercetin is the oil from grape seeds. Pressing allows producing oil with a quercetin content of up to 144 μg/100 g, while extraction spikes its content by almost 30% (Al Juhaimi & Özcan, 2017). Also, oil from coconuts is rich in quercetin when produced via hot pressing (162 μg/100 g) (Srivastava et al., 2016). Myricetin is only present in cold-pressed oil from camellia seeds, with contents below 1 μg/100 g (Wang et al., 2017). Rutin is present at 1417 μg/100 g in cold-pressed oil from corn germs (Güneşer et al., 2017); at up to 23 μg/100 g in nut oils (Al Juhaimi et al., 2018); at up to 1801 μg/100 g in virgin olive oil; and at up to 258 μg/100 g in hot-pressed oil from coconuts (Srivastava et al., 2016).

Naringenin (from the group of flavanone) is mainly found in cold-pressed oil from camellia seeds, wherein its content ranges from 385 to 1077 μg/100 g (Wang et al., 2017). It is also present in oils from walnuts (up to 4 μg/100 g) and pistachio nuts (up to 3 μg/100 g). Oils from other nuts contain an almost 3-fold lower amount of this compound (Al Juhaimi et al., 2018). In turn, naringenin is not determined in virgin olive oil (Kotsiou & Tasioula–Margari, 2016). Additionally, hesperidin is present in cold-pressed oil from corn germs, with its content reaching 2381 μg/100 g (Güneşer et al., 2017).

2.4. Content of other phenolic compounds

2.4.1. Lignans

The available literature data analysis shows lignans can be found in 3 popular oils obtained from flaxseeds, olive fruits, and sesame seeds (Table 4). According to Herchi et al. (2011), the content of lignans in oil extracted from flaxseeds with a chloroform-methanol mixture (2:1) was at 11 μg/100 g. These authors demonstrate the major lignan fractions in this type of oil to be diphyllin, secoisolariciresinol, and matairesinol, which may individually account for 30–40% of total lignans. In turn, pinoresinol occurs in oil from flaxseeds only in trace amounts (up to 0.5 μg/100 g).

Olive oil is also a good source of lignans, but cold-pressed oil contains almost 6-fold more lignans than refined oil, i.e., 4153 vs. 729 μg/100 g, respectively (Owen et al., 2000). It has been shown that the content of total phenolic compounds in olive oil decreases after the refining process, also the content of the main lignan fractions, i.e. pinoresinol and acetoxypinoresinol, is consistently lower than in pressed oils (García et al., 2006). Cecchi et al. (2017) pointed out that the most noticeable changes in the content of lignans (incl. pinoresinol and acetoxypinoresinol) occur at the bleaching step due to the chemical modification of compounds, as well as the formation of new isobaric forms of pinoresinol and acetoxypinoresinol. Arslan, Karabekir, and Schreiner (2013) estimated that the content of pinoresinol in cold-pressed oil can reach even 11,930 μg/100 g, while Lopes de Souza, Marcadenti, and Portal (2017) specified the content as only 2405 μg/100 g in refined oil. The content of acetoxypinoresinol in olive oil highly varies in different studies. According to several authors, it exceeds 1000 μg/100 g, but Arslan et al. (2013) showed it to be much higher (over 12,300 μg/100 g). In the review article prepared by López-Biedma, Sánchez-Quesada, Delgado-Rodríguez, and Gaforio (2016), data was collected for the contents of pinoresinol and acetoxypinoresinol in oils obtained from various olive fruits varieties. According to this work, pinoresinol content ranges from 62 to 5510 μg/100 g, while that of acetoxypinoresinol from 17 to 8200 μg/100 g. In turn, Arslan et al. (2013) showed that the oil pressed from olive fruits contained also hydroxypinoresinol in the amount of 2790 μg/100 g, whereas Ben Moumen et al. (2014) detected pinoresinol also in oil from safflower seeds.

Many researchers have attempted to characterise lignans in oil from sesame seeds. Literature data have shown that their content in sesame seed oil can be as high as 1,601,000 μg/100 g (Moazzami, Haese, & Kamal-Eldin, 2007). Similarly to olive fruits, the method of seed treatment and oil extraction may affect the lignan content of sesame seed oil. According to research performed by Shi et al. (2018), the content of sesamin and sesamolin in oils pressed from sesame seeds is up to 751,000 and 390,000 μg/100 g, respectively. In turn, Moazzami et al. (2007) reported their slightly lower contents (605,000 μg/100 g for sesamin and 264,000 μg/100 g for sesamolin). Moazzami et al. (2007) analysed the lignan composition in oil extracted from sesame seeds. They noted that by roasting the seeds, it was possible to obtain the oil with a high content of sesamin (up to 1,248,000 μg/100 g) and that sesamin prevailed in the refined oil, accounting for over 70% of total lignans. They also detected other lignans in refined oil, including episesamin, sesaminol, 6-*epi*-sesaminol, and 2-*epi*-sesaminol.

Rodríguez-García, Sánchez-Quesada, Toledo, Delgado-Rodríguez, and Gaforio (2019) reported lariciresinol, matairesinol, and secoisolariciresinol presence in oil from peanuts, but in trace amounts. In turn, research carried out by Bhatnagar, Prasanth Kumar, Hemavathy, and Gopala Krishna (2009) showed no lignans in oils obtained from soybeans, palm kernels, rice bran, sunflower seeds, safflower seeds, mustard seeds, and coconuts.

2.4.2. Secoiridoids

A literature review has shown that secoiridoids are mainly identified

Table 4
Content of other phenolic compounds and phenolic derivatives in plant oils.

Oil source	Oil type	Phenolic group	Phenolic compounds	Content (μg/100 g)	Reference
Flaxseeds	Extracted with chloroform-methanol mixture (2:1)	Lignans	All	9.3–11.0	Herchi et al. (2011)
			Secoisolariciresinol	3.0–3.2	Herchi et al. (2011)
			Pinoresinol	0.4–0.5	Herchi et al. (2011)
			Matairesinol	3.0–3.1	Herchi et al. (2011)
			Diphyllin	2.8–4.2	Herchi et al. (2011)
Olive fruits	Cold-pressed	Lignans	All	4153	Owen et al. (2000)
			Pinoresinol	419-2371	Lopes de Souza et al. (2017)
				4530–10,930	Arslan et al. (2013)
				1506–4430	Dabbou et al. (2011)
				50-3410	Cicerale et al. (2008)
				tr-5253	Giuffrè et al. (2010)
				1162–6769	Soufi et al. (2018)
			Acetoxypinoresinol	443–663	Lopes de Souza et al. (2017)
				5430–12,350	Arslan et al. (2013)
				97–964	Dabbou et al. (2011)
				20-3620	Cicerale et al. (2008)
				82-2447	Giuffrè et al. (2010)
				642-4204	Soufi et al. (2018)
		Secoiridoids	All	2772	Owen et al. (2000)
			Oleuropein	0–165	Lopes de Souza et al. (2017)
				200	Coni et al. (2000)
			Elenolic acid	1680–4520	Arslan et al. (2013)
				6068–7378	Kesen et al. (2013)
			Verbascoside	22–34	Arslan et al. (2013)
		Aglyconic derivatives	Oleuropein aglycone	tr-87	Sicari et al. (2010)
				3663–12,057	Lopes de Souza et al. (2017)
			Ligstroside aglycone (*p*-HPA-EA)	1744–8201	Lopes de Souza et al. (2017)
			Monoaldehydic form of oleuropein aglycone (3,4-DHPEA-EA)	7220–9500	Lopes de Souza et al. (2017)
				7330–19,715	Dabbou et al. (2011)
				180-35,170	Cicerale et al. (2008)
			Monoaldehydic form of ligstroside aglycone (*p*-HPEA-EA)	2290–4420	Arslan et al. (2013)
				3804–6905	Lopes de Souza et al. (2017)
				420–650	Arslan et al. (2013)
			Dialdehydic form decarboxymethyl oleuropein aglycon (3,4-DHPEA-EDA)	9474–27,962	Dabbou et al. (2011)
				470-52,220	Cicerale et al. (2008)
				9140–20,300	Arslan et al. (2013)
				1802–4792	Sicari et al. (2010)
				124-5260	Giuffrè et al. (2010)
				7783–25,160	Lopes de Souza et al. (2017)
			Dialdehydic form decarboxymethyl ligustroside aglycon (*p*-HPEA-EDA)	7147–14,277	Lopes de Souza et al. (2017)
				4906–12,901	Dabbou et al. (2011)
				2990–5210	Arslan et al. (2013)
				840-29,810	Cicerale et al. (2008)
				101-1394	Giuffrè et al. (2010)
				809–881	Sicari et al. (2010)
			Dialdehydic form oleuropein aglycon	14-2031	Giuffrè et al. (2010)
				1525–2031	Sicari et al. (2010)
			Dialdehydic form ligstroside aglycon	46–539	Giuffrè et al. (2010)
		Phenolic alcohol derivatives	All	4187	Owen et al. (2000)
			Tyrosol	5000	García et al. (2006)
				2745	Owen et al. (2000)
				534-1132	Lopes de Souza et al. (2017)
				583–968	Arslan et al. (2013)
				1025–1482	Kesen et al. (2013)
				312-2825	Soufi et al. (2018)
			Hydroxytyrosol	1442	Owen et al. (2000)
				353–772	Lopes de Souza et al. (2017)
				127–214	Arslan et al. (2013)
				50-1440	Cicerale et al. (2008)
				518–553	Kesen et al. (2013)
				50–793	Giuffrè et al. (2010)
				22–591	Soufi et al. (2018)
	Refined	Lignans	All	729	Owen et al. (2000)

(*continued on next page*)

Table 4 (*continued*)

Oil source	Oil type	Phenolic group	Phenolic compounds	Content (μg/100 g)	Reference
				tr-1067	Giuffrè et al. (2010)
			Pinoresinol	2405	Lopes de Souza et al. (2017)
			Acetoxypinoresinol	752	Lopes de Souza et al. (2017)
		Secoiridoids	All	930	Owen et al. (2000)
		Aglyconic derivatives	Oleuropein aglycone	12,540	Lopes de Souza et al. (2017)
			Ligstroside aglycone(*p*-HPA-EA)	5993	Lopes de Souza et al. (2017)
			Monoaldehydic form of oleuropein aglycone (3,4-DHPEA-EA)	1090	Lopes de Souza et al. (2017)
			Monoaldehydic form of ligstroside aglycone (*p*-HPEA-EA)	1520	Lopes de Souza et al. (2017)
			Dialdehydic form decarboxymethyl oleuropein aglycone (3,4-DHPEA-EDA)	5737	Lopes de Souza et al. (2017)
			Dialdehydic form decarboxymethyl ligustroside aglycone (*p*-HPEA-EDA)	3895	Lopes de Souza et al. (2017)
		Phenolic alcohol derivatives	All	472	Lopes de Souza et al. (2017)
			Tyrosol	298	Owen et al. (2000)
				411	Lopes de Souza et al. (2017)
			Hydroxytyrosol	174	Owen et al. (2000)
				677	Lopes de Souza et al. (2017)
				170	Cicerale et al. (2008)
Pumpkin seeds	Cold-pressed	Phenolic alcohol derivatives	Tyrosol	158-1769	Andjelkovic et al. (2010)
				60,000–730,000	Van Hoed et al. (2017)
		Phenolic acid derivatives	Vanilin	0-2610	Andjelkovic et al. (2010)
Rapeseeds	Cold-pressed	Phenolic acid derivatives	4-vinylsyringol (canolol)	17,712–17,950	Siger et al. (2017)
	Hot-pressed	Phenolic acid derivatives	4-vinylsyringol (canolol)	20,793–28,500	Siger et al. (2017)
	Cold-pressed	Phenolic acid derivatives	4-vinylsyringol (canolol)	tr-4250	Harbaum-Piayda et al. (2010)
			4-vinylsyringol dimer (phenylindan)	0-1040	Harbaum-Piayda et al. (2010)
	Refined	Phenolic acid derivatives	4-vinylsyringol dimer (phenylindan)	tr-6300	Harbaum-Piayda et al. (2010)
Sesame seeds	Cold-pressed	Lignans	All	444,000–869,000	Moazzami et al. (2007)
				666,000–988,000	Shi et al. (2018)
			Sesamin	261,000–605,000	Moazzami et al. (2007)
				378,000–594,000	Shi et al. (2018)
			Sesamolin	183,000–264,000	Moazzami et al. (2007)
				287,000–390,000	Shi et al. (2018)
			Sesamol	0-4000	Shi et al. (2018)
	Hot-pressed	Lignans	All	338,000–1,153,000	Shi et al. (2018)
			Sesamol	7000–31,000	Shi et al. (2018)
			Sesamin	207,000–751,000	Shi et al. (2018)
			Sesamolin	105,000–372,000	Shi et al. (2018)
	Extracted from roasted seeds	Lignans	All	453,000–1,601,000	Moazzami et al. (2007)
			Sesamin	355,000–1,248,000	Moazzami et al. (2007)
			Sesamolin	98,000–353,000	Moazzami et al. (2007)
	Extracted with hexane from roasted seeds	Lignans	All	200	Hadeel, Khalida, and Walsh (2020)
			Sesamol	8	Hadeel et al. (2020)
			Sesamin	119	Hadeel et al. (2020)
			Sesamolin	71	Hadeel et al. (2020)
	Extracted with hexane from unroasted seeds	Lignans	All	180	Hadeel et al. (2020)
			Sesamin	110	Hadeel et al. (2020)
			Sesamolin	71	Hadeel et al. (2020)
	Refined	Lignans	All	183,000–509,000	Moazzami et al. (2007)
				541,000–927,000	Shi et al. (2018)
			Sesamin	118,000–401,000	Moazzami et al. (2007)
				394,000–636,000	Shi et al. (2018)
			Episesamin	12,000–206,000	Moazzami et al. (2007)
			Sesaminol	3000–15,000	Moazzami et al. (2007)
			6-Epi-sesaminol	1000–11,000	Moazzami et al. (2007)
			2-Epi-sesaminol	1000–9000	Moazzami et al. (2007)
			Sesamol	0-12,000	Shi et al. (2018)
			Sesamolin	29,000–280,000	Shi et al. (2018)

tr – trace amounts.

in olive oil (Table 4). In cold-pressed oil, their content was estimated at 2772 μg/100 g, while it was 3-fold lower in the refined oil (Owen et al., 2000). Literature reports that olive oil contains such secoiridoids as oleuropein, elenolic acid, and verbascoside. The prevailing among them is elenolic acid, with its content reaching even 7380 μg/100 g (Kesen, Kelebek, & Selli, 2013). The content of oleuropein in olive oil is up to 200 μg/100 g (Coni et al., 2000), and that of verbascoside is almost 6-fold lower (Arslan et al., 2013).

2.4.3. Aglyconic derivatives

Olive oil contains aglyconic derivatives, such as oleuropein aglycone, ligstroside aglycone (*p*-HPA-EA), monoaldehydic form of oleuropein aglycone (3,4-DHPEA-EA), monoaldehydic form of ligstroside aglycone (*p*-HPEA-EA), dialdehydic form of decarboxymethyl oleuropein aglycone (3,4-DHPEA-EDA), and dialdehydic form of decarboxymethyl ligustroside aglycone (*p*-HPEA-EDA) (Table 4). The content of these derivatives in olive oil is highly diverse. For example, the content of oleuropein aglycone ranges from trace amounts (cold-pressed) to 12,540 μg/100 g (refined) (Owen et al., 2000; Sicari, Giuffrè, Louadj, & Poiana, 2010), while that of ligstroside aglycone ranges from 1744 to 8201 μg/100 g (Lopes de Souza et al., 2017).

The content of monoaldehydic form of oleuropein aglycone in cold-pressed oils from olive fruits can exceed 35,170 μg/100 g, and that of the monoaldehydic form of ligstroside aglycone is on average 6-fold lower (Cicerale, Conlan, Sinclair, & Keast, 2008). In refined oils, the content of both compounds is similar and exceeds 1000 μg/100 g (Lopes de Souza et al., 2017). The content of the dialdehydic form of decarboxymethyl oleuropein aglycone is up to 27,962 μg/100 g in olive oils (Dabbou et al., 2011). Several researchers have reported that the maximum content of dialdehydic form of decarboxymethyl oleuropein aglycone in olive oil is on average 5000 μg/100 g, and is close to the amount found in refined oil. In turn, the content of the dialdehydic form of decarboxymethyl ligustroside aglycone in cold-pressed and refined oils is lower (up to 14, 280 μg/100 g) (Lopes de Souza et al., 2017).

Giuffrè, Piscopo, Sicari, and Poiana (2010) detected two other aglyconic derivatives in cold-pressed olive oil, i.e., dialdehydic form of oleuropein aglycone and dialdehydic form of ligstroside aglycone. According to these authors, the content of dialdehydic forms of oleuropein aglycone is higher (almost 2-fold) than of the dialdehydic forms of ligstroside aglycone. Cicerale et al. (2008) reported in their review article that olive oil also contained other compounds from the group of aglyconic derivatives, i.e., dialdehydic form of decarboxymethyl elenolic acid linked to *p*-HPEA/p-HPEA-EDA (deacetoxy-ligstroside aglycone) and dialdehydic form of decarboxymethyl elenolic acid linked to 3, 4-DHPEA/3,4-DHPEA-EDA, with their contents ranging from 470 to 52,220 μg/100 g. Also, Negro et al. (2019) demonstrated the presence of other aglyconic derivatives in olive oil. They identified such compounds as decarboxymethyl 10-hydroxy oleuropein aglycone, 10-hydroxy oleuropein aglycone, methyl oleuropein aglycone, and hydroxymethyl decarboxymethyl ligstroside aglycone. Moreover, Soufi, Romero, Hadid, Hamoumraoui, and Louaileche (2018) identified elenolic acid linked to hydroxytyrosol and elenolic acid linked to tyrosol in olive oil of different varieties. According to these authors, their contents were up to 3765 and 4854 μg/100 g, respectively. Cicerale, Lucas, and Keast (2012) showed that the dialdehydic form of deacetoxy-ligstroside aglycone (oleocanthal) was also present in olive oil. They suggested that its content varied, depending on oil origin, ranging from 2260 μg/100 g in the oils produced in the US to 19,180 μg/100 g in these produced in Italy. They also pointed out the cultivar as a factor determining the content of dialdehydic form of deacetoxy-ligstroside aglycone in olive oil.

2.4.4. Phenolic alcohol derivatives

Contents of phenolic alcohol derivatives in olive oils vary and depend on the oil production method, reaching 4187 μg/100 g in cold-pressed oil and 472 μg/100 g in refined oil (Table 4). Their main representatives in oils include tyrosol and hydroxytyrosol. The analysis of literature data has shown a higher content of tyrosol in olive oil compared to hydroxytyrosol. García et al. (2006) estimated tyrosol content at 5000 μg/100 g, while Owen et al. (2000) and Soufi et al. (2018) showed it to be 2-fold lower. In turn, a low its content was reported in refined oil, reaching maximally 420 μg/100 g. The content of hydroxytyrosol in cold-pressed olive oil ranges from 22 to even 1440 μg/100 g, while in refined oil from 170 to 677 μg/100 g (Cicerale et al., 2008; Lopes de Souza et al., 2017; Soufi et al., 2018).

According to literature data, olive oil also contains a derivative of hydroxytyrosol, namely hydroxytyrosol-acetate, with its content highly varying across various studies, e.g., from 166 μg/100 g in a work of Carrasco-Pancorbo et al. (2007) to 1112–3216 μg/100 g in a work of Sicari et al. (2010). García et al. (2006) found also other alcohol derivatives in olive oils, i.e., Hy-AC (4-(acetoxyethyl)-1,2-dihydroxybenzene, in the amount of 1450 μg/100 g.

Research carried out by Andjelkovic, Van Camp, Trawka, and Verhé (2010) showed tyrosol also in oil from pumpkin seeds, with its content reaching up to 1769 μg/100 g. Van Hoed et al. (2017) also found tyrosol in pumpkin seed oil but in an over 2-fold lower amount. In addition, Ben Moumen et al. (2014) identified tyrosol in oils from several varieties of safflower seeds.

2.4.5. Phenolic acid derivatives

Several derivatives of phenolic acids were found in rapeseed oil (Table 4). Siger, Józefiak, and Górnaś (2017) analysed the content of 4-vinylsyringol (canolol) – a sinapic acid derivative – in cold- and hot-pressed oils and showed its increase along with an increasing temperature of the pressing process (20,793–28,500 μg/100 g). Harbaum-Piayda et al. (2010) identified also a derivative of 4-vinylsyringol, i.e., 4-vinylsyringol dimer (phenylindan), in oils from rapeseeds. The content of this dimer was up to 1040 μg/100 g in cold-pressed oil and up to 6300 μg/100 g in refined oil.

The pumpkin seed oil also contains a ferulic acid derivative – vanillin, and its content reaches 2610 μg/100 g (Andjelkovic et al., 2010). Research conducted by García et al. (2006) demonstrated that this derivative was also found in olive oil, at 4700 μg/100 g. It also identified a *p*-coumaric acid derivative, 4-ethylphenol, in an amount exceeding 30,000 μg/100 g.

3. Methods for the determination of phenolic compounds in oils

Phenolic compounds can exist in a bound or free form, and the method of their determination in foodstuffs mainly depends on their group that needs to be analysed. Oils contain only a small part of phenolic compounds found in seeds used to produce them (Van Hoed, 2010). Literature data is mainly limited to the determination of free (non-conjugated) phenolic compounds in oils. Two methods most commonly used for determining this group of phenolic compounds in plant oils, namely the spectrophotometric method and the chromatographic method.

3.1. Sample preparation

In analytics, it is important to choose the right method of isolating the phenolic fraction from plant material due to the differences in particle size, polarity and stability of phenolic compounds (Hrncirik & Fritsche, 2004). Two basic procedures for extracting phenolic compounds from plant oils are described in the literature, i.e. the liquid-liquid separation (LLE) and the solid-phase extraction (SPE) with using various solvents (Tasioula-Margari & Tsabolatidou, 2015).

Generally, LLE aims to separate components of liquid samples where the isolation of the analyte (phenolic compounds) is sequential and systematically carried out using a solvent (Ross, Beta, & Arntfield, 2009). Inés Isla, Salas, Danert, Zampini, and Ordoñez (2014) showed that temperature and solvent content were more important than pH when extracting phenolic compounds from the research material. In

addition, Liyana-Pathirana and Shahidi (2005) reported that extraction time, sample-to-solvent ratio, and solvent type could also significantly affect extraction efficiency. The polarity of phenolic compounds is varied, and therefore a wide range of solvents, can be used for their extraction (Durling et al., 2007). In particular, water-ethanol mixtures are of interest for the extraction of natural antioxidants, since water and ethanol can be used as food solvents, and their mixtures have proved to be more effective for phenolic compound extraction than pure solvents (Liyana-Pathirana & Shahidi, 2005). The authors most often use methanol and methanol-water solution (60–90:10–40 v/v) to extract phenolic compounds from oily material. However, da Silva Marineli et al. (2014) used ethanol to extract them from chia seed oil, while Rombaut et al. (2014) used an ethanol-water solution at 50 °C (50:50, v/v) to extract them from grape seed oil. The oil-to-solvent ratio is also often modified, e.g., 5:1 in the research conducted by Mińkowski et al. (2013), p. 1:100 in the research conducted by Güzel, Herken, and Erel (2009), or 1:1 in the research conducted by Zemour et al. (2019). The literature states that LLE is a time-consuming technique and can lead to possible degradation of phenolic compounds, it is also dangerous due to the use of organic solvents, which are undesirable for health reasons (Mahugo, Sosa, Torres, & Santana, 2009). However, LLE is still used as the standard step for the determination of phenolic compounds because it is cheap and easy (Garcia-Salas, Morales-Soto, Segura-Carretero, & Fernández-Gutiérrez, 2010).

SPE technique is an alternative to LLE due to reduction the amount of organic solvent, time of the analysis, and can be automated (Liberatore, Procida, D'Alessandro, & Cichelli, 2001). SPE is based on various migration processes in which analytes (phenolic compounds) are adsorbed in a solid sorbent and then eluted with an eluting solvent (e.g. methanol, acetone, acetonitrile) which depends on the type of sorbent and the polarity of phenolic compounds (Tasioula-Margari & Tsabolatidou, 2015). In SPE is used commercially available prepackaged disposable polymer or glass columns (cartridges) or disks, which retain phenolic compounds from the oily material (accompanying compounds and contaminations are removed) (Panagiotopoulou & Tsimidou, 2002). Columns with diol, C8 and C18 inserts are often used for the isolation of phenolic compounds from plant oils, but the recovery in the diol phase is more than 90% for all major phenolic compounds (Tasioula-Margari & Tsabolatidou, 2015). Siger et al. (2008), as well as Tańska et al. (2018) used SPE column filled with a diol (500 mg, 50 μm, pore diameter 70 Å) in extraction of phenolic compounds from plant oils. In the cited works, the extraction process consisted of four stages: column conditioning (5 ml of methanol and 5 ml of n-hexane), sample placing (2.5 g of oil in 5 ml of n-hexane and 5 ml of n-hexane), column washing (5 ml n-hexane/ethyl acetate 90:10, v/v), and leaching the phenolic fractions with methanol and collecting in a volumetric flask. A similar procedure was used by Zheng, Yang, Huang, Zhou, and Cao (2013), but the volumes of the used solvents were changed (e.g. the column was washed with 8 ml of the same solvent mixture), and also phenolic compounds were eluted with a mixture of methanol and formic acid (99:1, v/v).

Researchers are increasingly describing modern techniques for the extraction of phenolic compounds from plant materials, use i.a. supercritical fluid extraction (SFE) or ultrasound assisted extraction (UAE). The main purpose of using the improved techniques is to reduce the amount of used solvent and to reduction the time of extraction process (Garcia-Salas et al., 2010).

3.2. Spectrophotometric methods

As indicated by data collected in Table 5, the total content of phenolic compounds in plant oils is measured with the colorimetric method. Phenolic compounds in plant extracts react with specific redox reagents (Folin-Ciocalteu reagent) to form a blue complex that can be quantified by visible light spectrophotometry (Schofield, Mbugua, & Pell, 2001). The literature data indicates that the spectrophotometric method for determining total phenolic compounds is more often used than other methods (e.g., chromatography) because it is easier and cheaper, requires fewer equipment resources, and allows for the quantitative determination of phenolic compounds in various extracts (Pelozo, Cardoso, & Mello, 2008; Tsao & Yang, 2003). This method is based on the reaction of the Folin-Ciocalteu reagent (consisting of phosphotungstic acid and phosphomolybdic acid) with phenolic compounds present in the sample, as a result of which a chromophore composed of the phosphotungstic phosphomolybdenum complex is formed (Escarpa & Gonzalez, 2001; Gülçin, Sat, Beydemir, Elmastas, & Küfrevioğlu, 2004). The reaction takes place in an alkaline medium, and the intensity of the blue colour developed depends on the amount of phenolic compounds in the tested solution. However, this colour is not stable and evolves over time after two phases: I – fast phase (0–30 min) leading to a blue colour and II – slow phase after 30 min, with the colour turning to dark blue (Bancuta et al., 2016). The Folin-Ciocialteu reagent quickly degrades in alkaline solutions, which necessitates using its excess quantities to make the reaction complete. The use of this excess can cause precipitation and high turbidity, due to which the spectrophotometric analysis is impossible (Gülçin et al., 2004). Nonetheless, it should be highlighted that this test is not specific, because the Folin-Ciocialteu reagent will oxidise any reducing substances, and – in some cases – the content of phenolic compounds in the sample would be overestimated (Van Hoed, 2010).

The spectrophotometric method for total phenolics content determination is often modified and adapted by each author accordingly to the desired applications and available resources. The list of the most commonly adopted steps, extraction solvents, reagent dose, and analytical conditions of total phenolic compound determination in plant oils is summarised in Table 5. The general principle of this analysis is to prepare an extract of phenolic compounds from the material and to add the Folin-Ciocalteu reagent, sodium carbonate (7–35% or 0.1 N), and distilled water. The solution prepared in this way is allowed to react for 15–120 min. The collected literature has shown that the most common wavelengths at which the absorbance of the solution is measured are 720, 725, 745, 750, 760, and 765 nm. Mathematical and statistical research conducted by Bancuta et al. (2016) showed that the best wavelength for determining total phenolic compounds in extracts using linear regression was 725 nm ($R^2 = 0.9993$), but the other wavelengths (i.e., 750, 760 and 765 nm) could be used as well because the $R^2 > 0.995$ condition was met ($R^2 = 0.9988$). According to these authors, the measurements of extracts showed no differences related to the wavelength using Pearson's correlation, but the analysis of a gallic acid solution at different wavelengths showed that the best wavelengths were 725 and 750 nm. The total content of phenolic compounds in plant oils is expressed in mg of the equivalent of, e.g., caffeic acid, ferulic acid or gallic acid, or is converted into D-catechin content (mg) in the mass unit (1 g, 100 g, or 1 kg of oil).

The main polyphenols of olive fruit oil, such as oleoeuropein, have a diphenol structure and are important product markers to determine its actual condition because diphenols are easily oxidised during prolonged or improper storage (Del Carlo et al., 2012). During the determination of the diphenol content, brownish-red (characteristic of pyrocatechol) and yellowish-red (characteristic of pyrogallol) products are formed on the interface of the sodium-molybdate-diphenol phase in the first stage of the reaction. The second stage of the reaction involves the diffusion of phenols through the above-mentioned product layers to react at the product-sodium-molybdate interface. Consequently, after shaking the extracts with a sodium molybdate solution, an orange colour develops when diphenols are present (Height & Pargamian, 1960). The content of diphenols in plant oils is assessed by measuring the absorbance of the tested solutions (water-methanol extracts) after reaction with a 5% solution of sodium molybdate at 370 nm (Table 5). As in total diphenol content, the final result is expressed as phenolic acid equivalents in the mass unit of the product. With regard to the Folin-Ciocalteu method, the diphenol test is more time-saving (absorbance can be read as early as 15 min after the end of the reaction) and is selective for catechol-like

Table 5
Spectrophotometric methods used for determining phenolic compounds in oils.

Type of phenolic compounds	Oily material	Extraction solvent, its ratio to mass	Reagents used in the assay	Reaction time (min)	Wavelength (nm)	Final result	Reference
Total free phenolic compounds	Flaxseed oil Camelina oil Hemp oil Echium oil	Methanol, 5:1	Folin-Ciocalteu reagent, saturated sodium carbonate solution, distilled water	60	725	mg FAE per 100 g of oil	Mińkowski et al. (2013)
	Soybean oil Rapeseed oil Corn germ oil Hemp oil Flaxseed oil Pumpkin oil Olive oil	Methanol, 2:1	Folin-Ciocalteu reagent, saturated sodium carbonate solution, distilled water	60	725	mg CAE per 100 g of oil	Siger et al. (2008)
	Rapeseed oil Hemp seed oil Flaxseed oil	Methanol-water solution (60:40 v/v), 2:1	Folin-Ciocalteu reagent, 35% solution of sodium carbonate, distilled water	60	725	mg of GAE per 100 g of oil	Teh and Birch (2013)
	Olive oil	Methanol-water solution (60:40 v/v), n.s.	Folin-Ciocalteu reagent	120	725	mg of CA per 1 kg of oil	Gómez-Alonso, Fregapane, Salvador, and Gordon (2003)
	Olive oil Palm oil	Methanol, 6:1	Folin-Ciocalteu reagent, sodium carbonate solution	–	725	mg of CA per 1 kg of oil	Salta, Mylona, Chiou, Boskou, and Andrikopoulos (2007)
	Pistachio oil	Methanol, n.s.	Folin-Ciocalteu reagent, 7% solution of sodium carbonate	40	760	mg of GAE per 1 g of oil	Bouyahya et al. (2018)
	Sunflower oil	Methanol-water solution (80:20 v/v), 1:1	Folin-Ciocalteu reagent, sodium carbonate solution, distilled water	40	725	mg of GAE per 1 kg of oil	Zemour et al. (2019)
	Chia oil	Methanol-water solution (80:20 v/v), 1:2.5	0.25 N Folin-Ciocalteu reagent, 0.1 N sodium carbonate solution, distilled water	120	725	mg of GAE per 1 g of oil	Oliveira-Alves et al. (2017)
	Chia oil	Ethanol, 1:10	0.25 N Folin-Ciocalteu reagent, 0.1 N sodium carbonate solution, distilled water	120	725	mg of GAE per 1 g of oil	da Silva Marineli et al. (2014)
	Corn germ oil Hazelnut oil Soybean oil Olive oil	Methanol, 1:100	Folin-Ciocalteu reagent, 7.5% solution of sodium carbonate	120	750	mM of GAE per l g of oil	Güzel et al. (2009)
	Grape seed oil	Ethanol-water solution at 50 °C (50:50 v/v), 1:5	Folin-Ciocalteu reagent, 7.5% solution of sodium carbonate	15	750	mg of GAE per 1 kg of oil	Rombaut et al. (2014)
	Grape seed oil	Methanol-water solution (90:10 v/v), 1:3	Folin-Ciocalteu reagent, 7.5% solution of sodium carbonate	60	765	mg of GAE per 1 g of oil	Bail et al. (2008)
	Grape seed oil	Methanol-water solution (80:20 v/v), 1:3	Folin-Ciocalteu reagent, 10% solution of sodium carbonate, distilled water	30	765	mg of GAE per 1 kg of oil	Konuskan et al. (2019)
	Pumpkin oil Amaranth oil Sesame oil Flaxseed oil Camelina oil Evening primrose seed oil Borage seed oil Poppy seed oil Walnut oil	Methanol-water solution (80:20 v/v), n.s.	Folin-Ciocalteu reagent, 14% solution of sodium carbonate, distilled water	30	720	mg of D-catechin per 100 g of oil	Czaplicki et al. (2011)
	Coconut oil	Methanol-water solution (80:20 v/v), 5:1	Folin–Denis reagent, 35% solution of sodium carbonate, distilled water	45	745	mg of GAE per 1 kg of oil	Seneviratne and Dissanayake (2008)
Diphenols	Olive oil	Methanol-water solution (60:40 v/v), n.s.	5% solution of sodium molybdate in a water-ethanol mixture (1:1 v/v)	15	370	mg of CA per 1 kg of oil	Gómez-Alonso et al. (2003); Laincer et al. (2014)
Flavonoids	Pistachio oil	Methanol, n.s.	2% solution of aluminium chloride	40	430	mg of QCE per 1 g of oil	Bouyahya et al. (2018)
	Cashew oil Hazelnut oil Peanut oil Pistachio oil Walnut oil	Methanol, 1:3	5% solution of sodium nitrite, 10% solution of aluminium chloride, 0.1 M sodium hydroxide, distilled water	5	510	mg per 100 g of oil	Al Juhaimi et al. (2018)

n.s. – not specified; CAE – caffeic acid equivalent; CA – caffeic acid; FAE – ferulic acid equivalent; GAE – gallic acid equivalent; QCE – quercetin equivalent.

molecules. The ability to complex molybdate to diphenols was used for their selective electrochemical detection. According to Del Carlo et al. (2012), using a mediator (in the form of a Mo-MW-CNT-NH2 modified electrode) allowed detecting diphenols in the ppm range. These authors reported that the electrochemical method seemed to be suitable for monitoring contents of diphenols in oil samples. In addition, the method was found easy to use, fast (does not require incubation time), potentially automated, highly sensitive and selective.

The spectrophotometric test based on an aluminium complex is one of the most commonly used procedures for determining total flavonoid content (Table 5). Firstly, an aluminium chloride solution is added to the sample, and then the complexation reaction is carried out in the presence of a sodium nitrite solution in an alkaline medium. After Al(III) addition, a yellow complex is formed as a result of the reaction with carbonyl and hydroxyl groups of flavones and flavonols, which immediately turns into red after sodium hydroxide solution addition (Popova et al., 2004; Pękal & Pyrzynska, 2014). The total flavonoid content in plant oils is determined by measuring the absorbance of the prepared solutions; methanol or water-methanol extracts (60:40) after reaction with a solution of aluminium chloride (2–10%) and/or without a sodium nitrite solution (5%) at 430 nm or 510 nm. Depending on the researcher, the reaction time ranges from 5 to even 40 min. The final result is expressed as the mg of quercetin equivalent in the mass unit of the product. The spectrophotometric test based on an aluminium complex formation is one of the most commonly used procedures for determining the total content of flavonoids in foodstuff. Several factors have been identified as critical during complex formation, such as reaction time, reagent concentration (especially of an aluminium chloride solution), flavonoid content/plant material, and the chemical structure of phenolic compounds (Petry, Gonzalez Ortega, & Silva, 2001). Pękal and Pyrzynska (2014) evaluated two widely used procedures (with and without a sodium nitrite solution) to analyse several compounds from different classes of the flavonoid family and natural samples. They noted that both methods did not respond evenly, indicating they were inappropriate to assess the total flavonoid content of unknown samples. With a sodium nitrite solution present in an alkaline medium, the procedure appears to be specific for rutin, luteolin, and catechins. In turn, the procedure carried out in neutral media (without the sodium nitrite solution) can only be used to determine the content of flavonols and luteolin (from the flavone family). The authors also emphasised that some phenolic acids might show significant absorbance at 510 nm. Ji et al. (2017) reported that the coloured complex formed in the reaction was stable and the absorbance value did not change within 60 min. This finding indicates that this spectrophotometric method is reliable in determining the total flavonoid content and suitable for their quantitative analysis.

3.3. Chromatographic methods

Evaluation of the content of individual phenolic compounds in plant oils is carried out by liquid chromatography (LC) and high-performance liquid chromatography (HPLC) directly coupled to various detectors, e.g, ultraviolet (UV) detectors (including UV–visible detector (UV–Vis), diode/photodiode array detector (DAD/PDA)), mass spectrometry detector (MS) and fluorescence detector (FLU); as well as using gas chromatography with mass spectrometry (GC-MS). Parameters and conditions employed by different authors to determine the contribution of individual phenolic compounds in plant oils using the chromatographic method are presented in Table 6.

The HPLC technique is the most commonly used technique for separating and characterising phenolic compounds. It is a versatile and adaptable instrument with various advantages, such as high selectivity, sensitivity, resolution, precision, and sample behaviour (Balas & Popa, 2007; Naczk & Shahidi, 2006). The method's principle lies in the separation of compounds from complex mixtures on the basis of their solubility and/or interaction between a less polar stationary phase and a more polar mobile phase (Coskun, 2016). Due to the use of various detectors, the HPLC technique allows increasing the possibility of identifying and determining phenolic compounds in the sample, e.g., HPLC-DAD provides extensive information on phenolic compound structures (Rajaei, Barzegar, Mobarez, Sahari, & Esfahani, 2010). Spectral data for phenolic compounds in oils are most often collected in the range from 190 to 400 nm (Memon, Memon, Luthria, Pitafi, & Bhanger, 2012). Due to the presence of internal conjugated double and aromatic bonds, each phenol shows a higher or lower absorption value in the UV or UV/VIS region. Phenolic acids with the carbon skeleton of benzoic acid have their maxima ranging from 200 to 290 nm, while derivatives of cinnamic acids (due to additional conjugation) show a wide absorbance band from 270 to 360 nm (Stalikas, 2007). All flavonoid aglycones contain at least one aromatic ring and this results in effective UV absorption, the first maximum is in the range of 240–285 nm (related to A-ring) and the second maximum is in the range of 300–550 nm (related to conjugation of C-ring) (Tošović & Marković, 2015).

However, to obtain information about a specific phenolic compound, it is necessary to compare its retention time with the standard (Fulcrand et al., 2008). The lack of standards for some classes of polyphenols, mainly for flavonoid glycosides and proanthocyanidins, is a major hurdle when using the HPLC technique (Ignat, Volf, & Popa, 2011). Therefore, some compounds in the chromatogram may not be identified and quantified, resulting in underestimation (Van Hoed, 2010). Chromatographic conditions for the separation of various phenolic compounds include almost exclusively the use of a C18 column with a length of 50–250 mm, inner diameter from 2.1 mm to 4.6 mm, a particle size of the stationary phase from 1.8 μm to 5 μm, and a system of various solvents, including among others water with the addition of formic acid, acetic acid or orthophosphoric acid, methanol, and acetonitrile. The use of different wavelengths is required during chromatographic analysis to target individual phenolic compounds. The collected literature data have shown that the wavelength range is 200–600 nm, with 280, 320, 340, and 360 nm most frequently chosen by the authors.

The literature indicates that many factors, such as sample purification, column and detector types, solvents used as the mobile phase and their purity, as well as pH affect the analysis of phenolic compounds using HPLC (Kumar & Goel, 2019). However, this method is characterised by the high versatility and accuracy (Francisco & Resurreccion, 2009), and also proved to be the most suitable due to the structural similarity and diversity of phenolic compounds, enabling analysis with sufficient precision, selectivity, and within a reasonable time. Of all detectors coupled with HPLC to enable the determination of phenolic compounds, MS is the most expensive and unusual, while UV and DAD are the most useful and common (Zhang et al., 2013). The DAD detector can simultaneously scan the whole UV/VIS spectrum of the analytes and provide information about special spectral properties for compound identification (Huang & Liu, 2005). Generally, HPLC-DAD is deemed a simple, cost-effective, reliable, and sufficiently sensitive analytical platform for analysing food constituents (Rejczak & Tuzimski, 2017).

LC-MS combines the separation power of HPLC with the selectivity of MS detection and is an excellent technique for reliable identification of the compounds. This technique is currently the best analytical approach to study phenolic compounds of various biological resources and the most effective tool in analysing their structure (Khoddami et al., 2013). However, its main disadvantage is the high cost of the device (Rejczak & Tuzimski, 2017). Seneviratne and Dissanayake (2008) used this technique and a C18 column with an inverted phase, 125 mm long, with an inner diameter of 4 mm, a stationary phase particle size from 5 μm, and a system of various solvents, such as methanol, formic acid, and deionised water.

The GC is a technique used to separate, identify, and quantify such phenolic compounds as phenolic acids, flavonoids, and condensed tannins (Khoddami et al., 2013). It employs the evaporation temperature specific for each compound to separate it from the solution by passing

Table 6
Capillary electrophoresis and chromatographic methods used for determining phenolic compounds in oils.

Chromatographic method	Detection method	Oily material	Extraction solvent, its ratio to oil mass	Column characteristics (LxODxID/ LxID)	Reagents used in the assay	Reference
CE	UV	Olive oil	Methanol-water mixture (60:40 v/v), 1:1	Uncoated fused-silica capillaries from Beckman (Fullerton, CA, USA), dimensions 470 × 0.38 mmx50 μm	Buffer i.e. sodium tetraborate solution (45 mM, pH 9.6), grade water	Bonoli et al. (2003)
			Methanol-water mixture (60:40 v/v), 1:3	Bare fused-silica capillaries from Beckman (Fullerton, CA, USA), dimensions 570 × 0.38 mmx75 μm	Buffer i.e. sodium borate solution (25 mM, pH 9.6), water	Carrasco Pancorbo et al. (2004)
			Methanol-water mixture (60:40 v/v), 1:3	Fused-silica capillaries from Beckman (Fullerton, CA, USA), dimensions 570 × 0.38 mmx75 μm	Buffer i.e. sodium borate solution (50 mM, pH 9.6), water	Carrasco Pancorbo et al. (2005)
	DAD	Olive oil	Ethanol-water mixture (80:20 v/v), 5:1	Fused-silica capillaries from PolymicroTechnologies (Phoenix, AZ, USA), dimensions 520 mmx50 μm	Buffer i.e. sodium tetraborate decahydrate (45 mM, pH 9.6), water	Vulcano et al. (2015)
GC	MS	Olive oil	Methanol-water mixture (60:40 v/v), n.s.	BPX5, dimensions 30 m × 0.3 mm, 0.25 μm film thickness	Helium (gas)	Tasioula-Margari and Okogeri (2001)
			Methanol, 5:1	OV-101, dimensions 30 m × 0.25 mm, 0.25 μm film thickness	Helium (gas)	Owen et al. (2000)
HPLC	UV/ UV–Vis	Olive oil	Methanol, 3:1 Methanol-water mixture (1:1 v/v), 3: 1 Acetonitrile, 3:1 Dimethylformamide, 3:1	RP-C18 Luna, dimensions 250 × 4.60 mm, size of particles 5 μm	Water-acetic acid solution (97.5:2.5 v/v), methanol-acetonitrile solution (1:1 v/v)	Tasioula-Margari and Tsabolatidou (2015)
			Methanol-water mixture (60:40 v/v), 10:1	Apex octadecyl 104 C18, dimensions 250 × 4.0 mm, size of particles 5 μm	Water-acetic acid solution (98:2 v/v), methanol, acetonitrile, isopropanol	Tasioula-Margari and Okogeri (2001)
			Methanol-water mixture (60:40 v/v), n.s.	Spherisorb S3 ODS2, dimensions 250 × 4.6 mm, size of particles 5 μm	Water-acetic acid solution (95:5 v/v), methanol, acetonitrile	Gómez-Alonso et al. (2003)
			Methanol-water mixture (80:20 v/v), 1:2.5	RP-C18 Spherisorb ODS-2, dimensions 250 × 4.6 mm, size of particles 5 μm	Water-orthophosphoric acid solution (99.8:0.02 v/v), methanol, acetonitrile	Laincer et al. (2014)
			Methanol, 5:1	RP-C18 Latex, dimensions 250 × 4.0 mm, size of particles 5 μm	Water-acetic acid solution (99.8:0.2 v/v), methanol	Owen et al. (2000)
		Safflower oil	Methanol-water mixture (80:20 v/v), 1:1	Zorbax SB-C18, dimensions 250 × 4.6 mm, size of particles 5 μm	Water-formic acid solution (95:5 v/v), methanol	Ben Moumen et al. (2014)
		Hazelnut oil Olive oil	Methanol-water mixture (60:40 v/v), 2:1	Kromasil 100-5C18 connected with 100 RP-C18, dimensions 250 × 4.0 mm, size of particles 5 μm	Acetonitrile, water, methanol, hydrochloric acid	Gordon et al. (2001)
		Soybean oil Rapeseed oil Corn germ oil Hemp seed oil Flaxseed oil Pumpkin oil Olive oil	Methanol, 2:1	NovaPakC18, dimensions 150 × 3.9 mm, size of particles 5 μm	Methanol, water-acetic acid solution (97.5:2.5 v/v)	Siger et al. (2008)
	DAD/PDA	Rapeseed oil	Methanol, 1:5	RP-XBridgeTM C18, dimensions 100 × 4.6 mm, size of particles 3.5 μm	Water-acetonitrile solution (50:50 v/v), water adjusted to pH 2.7 with orthophosphoric acid	Rokosik et al. (2019)
		Olive oil	Methanol-water mixture (80:20 v/v), 1:1	Zorbax C18 50, dimensions 50 × 2.1 mm, size of particles 1.8 μm	Water-formic acid solution (99.9:0.1 v/v), acetonitrile	Negro et al. (2019)
		Rapeseed oil	Methanol-water mixture (n.s.), 1:2	Synergi 4 μ Fusion-RP 80, dimensions 150 × 4.0 mm, size of particles 4 μm	Water-methanol solution (90:10 v/v) with *o*-phosphoric acid (1.25%), methanol with *o*-phosphoric acid (1%)	Khattab, Rempel, Suh, and Thiyam (2012)
		Flaxseed oil Rapeseed oil Olive oil	Methanol-water mixture (80:20 v/v), n.s.	Eclipse XDB-C18, dimensions 150 × 4.6 mm, size of particles 5 μm	Acetonitrile-formic acid solution (99.85:0.15 v/v), water-formic acid solution (99.85:0.15 v/v),	Tańska et al. (2018)
		Corn germ oil	Methanol, 1.5:1	Zorbax Eclipse Plus C18, dimensions 250 × 4.6 mm, size of particles 5 μm	Acetonitrile, water-sulphuric acid solution (99.8:0.02 v/v)	Güneşer et al. (2017)
		Cashew nut oil Hazelnut	Methanol, 1:3	Inertsil ODS-3, dimensions 250 × 4.6 mm, size of particles 5 μm	Acetonitrile, water-acetic acid solution (99.5:0.05 v/v)	Al Juhaimi et al. (2018)

(*continued on next page*)

Table 6 (*continued*)

Chromatographic method	Detection method	Oily material	Extraction solvent, its ratio to oil mass	Column characteristics (LxODxID/ LxID)	Reagents used in the assay	Reference
		oil Peanut oil Pistachio oil Walnut oil				
	DAD-ESI-MS/MS	Pumpkin oil	Methanol-water mixture (80:20 v/v), 1:2	Pre-column Zorbax, Eclipse XDB-C8, dimensions 125 × 2.1 mm, size of particles 5 μm Zorbax Eclipse XDB-C18, dimensions 150 × 2.1 mm, size of particles 3.5 μm	Water-acetonitrile solution with formic acid (3:88.5:8.5 v/v/v and 50:41.5:8.5 v/v/v), water-methanol solution with formic acid (90:1.5:8.5 v/v/v)	Rezig et al. (2018)
	DAD-FLU	Hemp seed oil	Methanol-water mixture (80:20 v/v), 2:1	Prodigy ODS3, dimensions 250 × 4.6 mm, size of particles 5 μm	Water-acetic acid solution (97:3 v/v), methanol	Smeriglio et al. (2016)
	DAD-MS	Pumpkin oil	Methanol, 1:2	C18 Luna, dimensions 250 × 4.6 mm, size of particles 5 μm	Water-acetic acid solution (99.8:0.2 v/v), methanol, acetonitrile	Van Hoed et al. (2017)
	FLU	Coconut oil	Methanol-water solution (80:20 v/v), 5:1	Zorbax SB-C18, dimensions 250 × 4.6 mm size of particles 5 μm	Deionised water-sulphuric acid solution, methanol	Seneviratne and Dissanayake (2008)
	MS	Olive oil	Methanol, 3:1 Methanol-water mixture (1:1 v/v), 3:1 Acetonitrile, 3:1 Dimethylformamide, 3:1	Agilent 1100 Series Thermostatted Column Compartment	Water- acetonitrile solution (97.5:2.5 v/v), methanol-acetonitrile solution (1:1 v/v)	Tasioula-Margari and Tsabolatidou (2015)
LC	MS	Coconut oil	Methanol-water solution (80:20 v/v), 5:1	LiCroCART RP-18, dimensions 125 × 4.0 mm, size of particles 5 μm	Methanol, formic acid, deionised water	Seneviratne and Dissanayake (2008)
	DAD-MS	Olive oil	Methanol, 3:1 Methanol-water mixture (1:1 v/v), 3: 1 Acetonitrile, 3:1 Dimethylformamide, 3:1	RP-C18 Luna, dimensions 250 × 4.60 mm, size of particles 5 μm	Water-acetic acid solution (97.5:2.5 v/v), methanol-acetonitrile solution (1:1 v/v)	Tasioula-Margari and Tsabolatidou (2015)
TLC		Camellia seed oil	Diethyl ether, 60:1	Glass plates coated with silica gel	Petroleum-diethyl ether- acetic acid solution (70:30:2 v/v/v)	Wang et al. (2018)
		Soybean oil Corn oil Sunflower seed oil	Ethanol, 1:5	Glass plates coated with silica gel	Benzene-ethyl acetate-methanol-acetic acid solution (25:5:5:1 v/v/v/v)	Alnokkari et al. (2014)

L – length; OD – outer diameter; ID – inner diameter; CE – capillary electrophoresis; GC – gas chromatography; HPLC – high performance liquid chromatography; LC – liquid chromatography; TLC – thin layer chromatography; UV – ultraviolet detector; UV/Vis – ultraviolet–visible spectrophotometry; DAD – diode array detector; PDA – photodiode array detector; MS – mass spectrometry; ESI – electrospray ionization; FLU – fluorescent detector; n.s. – not specified.

the sample through a heated column where it is divided between an inert gas under pressure and a thin layer of non-volatile liquid covered with an inert substrate inside the column (Balas & Popa, 2007). The GC technique provides greater sensitivity and selectivity when combined with mass spectrometry (Ignat et al., 2011). For example, problems encountered during the evaluation of flavonoid glycosides using conventional GC were solved when high-temperature mass spectrometry was used (Pereira, Valentão, Pereira, & Andrade, 2009). Other studies have shown that the GC-MS analysis of phenol and flavonoid standards was more efficient than the HPLC analysis. It provides rapid evaluation with better resolution and baseline separation of all standards with minimal co-elution (Khoddami et al., 2013). The columns most commonly used in the GC technique to analyse phenolic compounds include 30 m long capillary columns, with an outer diameter of 0.25–0.30 mm, and an inner diameter of 0.25 μm. Helium is usually used as the carrier gas.

The main disadvantage of the GC analysis is the need to perform derivatization due to low volatility of phenolic compounds. The derivatization reaction is usually simple, free of undesirable by-products, and produces extremely volatile products without interfering with the analysis (Robbins, 2003). However, the preparation of samples for analysis requires several additional steps, such as purification, e.g., removal of lipids from the extract, modification needed to release phenols from ester and glycosidic bonds or convert them into more volatile derivatives (Liu, Cai, & Shao, 2008).

Thin layer chromatography (TLC) is a mixture separation technique in which the principle is based on the use of a sheet of glass, plastic or aluminium foil covered with a thin layer of adsorbent (stationary phase) and a solvent or mixture applied to the plate (mobile phase) (Bele & Khale, 2011). The literature states that TLC is a frequently used analytical tool due to the high separation speed and the possibility of its application in a large number of compounds (Alnokkari, Ataie, Rajab, & Alassaf, 2014). Wang, Liu, and Sun (2018) used TLC to identify phenolic compounds in camellia seeds oil. In the work of these authors, a glass chromatographic column with silica gel were used – adjusted to a water content of 5%, and elution of polar compounds was carried out with diethyl ether. For the chromatographic analysis, glass plates covered with silica gel (layer – 0.25 mm) and a mixture of petroleum ether, diethyl ether and acetic acid were used as solvent. In turn, Alnokkari et al. (2014) used TLC to analyse propyl gallate in some vegetable oils. The sample was applied to a silica gel plate and developed with benzene, ethyl acetate, methanol and acetic acid.

3.4. Other methods

Capillary electrophoresis (CE) is an electrically assisted separation technique that is used to determine both ionic and neutral compounds of various molecular weights (from 18 Da to ~17 MDa). This technique has many advantages, i.e. allows for quick analysis of compounds and is characterized by a high ability to separate chemically similar

compounds, and the use of small wavelengths method provides high sensitivity (Bakar, Makahleh, & Saad, 2012). CE combined with UV-DAD and DAD has been the subject of research by several authors to detect the phenolic profile of olive oil. The analyzes used fused-silica capillaries (length from 470 to 570 mm, inner diameter from 50 to 75 μm) and a system of solvents constituting a buffer (sodium tetraborate solution/sodium borate solution with pH 9.6) and water (Bonoli, Montanucci, Gallina Toschi, & Lercker, 2003; Carrasco Pancorbo, Cruces-Blanco, Segura Carretero, & Fernández Gutiérrez, 2004; Carrasco Pancorbo, Segura Carretero, & Fernández Gutiérrez, 2005; Vulcano, Halabalaki, Skaltsounis, & Ganzera, 2015).

4. Phenolic compounds as antioxidants in oils

The key antioxidative mechanisms of phenolic compounds proceed by hydrogen atom transfer (HAT) or by single electron transfer (SET) (Koroleva et al., 2014; Leopoldini, Marino, Russo, & Toscano, 2004). The HAT mechanism predominates in bulk oils (Zhu, Long, Zhou, Prenzler, & Zhong, 2013). The value of bond dissociation energy (BDE) for O–H group of the phenolic antioxidant predicts its antioxidative activity and the stability of the antioxidant radical formed (a lower BDE results in a more active antioxidant and a more stable antioxidant radical). The O–H bond strength of phenolic antioxidants is affected by hydrogen substitution in a benzene ring. Any substituent destabilizing the ground-state of phenolic antioxidant and/or stabilizing antioxidant radical reduces the O–H bond strength (Choe & Min, 2009). However, besides BDE variation, the potential to stabilize bulk oil against oxidation is affected by the antioxidant's polarity. Many researchers have explained the lipid-protective effect of phenolic compounds based on the "polar paradox" theory (Budilarto & Kamal-Eldin, 2015), according to which polar antioxidants (like phenolic compounds) are better protectors of hydrophobic matrices than typical non-polar counterparts (like tocols). However, the "polar paradox" has been shown to experience some limitations, and its validity was found to depend on antioxidant's molecular size, configuration, and concentration (Budilarto & Kamal-Eldin, 2015; Shahidi & Zhong, 2011). More and more studies are being done to determine the inhibiting effect of phenolic compounds on lipid oxidation. Table 7 summarises the literature data on the effect of phenolic compounds, i.e., phenolic acids, flavonoids, phenolic acid derivatives, phenolic aldehydes, and alcohols, on the oxidative stability of plant oils. Most studies focused on the type and concentration of phenolic compounds added to rapeseed, flaxseed, sunflower, peanut, corn, and olive oils. The collected results show the ambiguous effects of these factors on oil oxidative stability. Furthermore, the polarity of phenolic compounds (expressed as Topological Polar Surface Area (TPSA)) fails to explain the observed relationships. Thus, the antioxidative action of phenolic compounds should be considered in multiple aspects.

Researchers most often use phenolic acids as antioxidants for plant oils. Hasiewicz-Derkacz et al. (2015) analysed the effect of two hydroxycinnamic acids (ferulic and caffeic acid at the concentration of 0.5 mM) on the oxidative stability of cold-pressed flaxseed oil from transgenic seeds. The test used by the authors was TBARS reaction at 140 °C for 30 min in the air atmosphere. The authors noted that ferulic and caffeic acids could be used as oil antioxidants (oxidation stability was 85–94% higher compared to the control sample). Also, according to Tundis et al. (2017), ferulic acid may be an effective oil antioxidant (the oxidation stability increased by 12–24% compared to the control sample), especially for cold-pressed rapeseed oil. These authors used its ethanol solution at various concentrations (from 100 to 500 μM) and the Rancimat test at 120 °C. However, it was also found that the use of other phenolic acids, such as cinnamic, sinapic, and syringic, significantly intensified the oxidative process in oil, even by 36–44%. Nergiz (1991) studied various phenolic acids as antioxidants of refined olive oil using a diethyl ether solution of compounds with different concentrations (from 0.025% to 0.1%), and the active oxygen method (AOM-test) at 97.8 °C. They noted that *p*-hydroxybenzoic acid did not affect the oxidative stability of refined olive oil, and that *p*-coumaric acid and vanillic acid (at a higher concentration, i.e., 0.1%) exhibited pro-oxidative properties. Other phenolic acid additives showed a different effect on the oxidative stability of the oil, but the most beneficial one was noted for 3, 4-dihydroxyphenyl acetic acid (almost 150% increase of the stability value compared to the control sample). According to Chen and Ho (1997), methanolic solutions of such phenolic acids as caffeic, rosmarinic, and chlorogenic (at a concentration of 2 mM) used in the Rancimat test performed at 110 °C could be corn oil antioxidants (oxidative stability increased from 133% to 196% compared to the control sample). These authors' studies also showed that the addition of ferulic acid proved to be the least effective because it increased the oxidative stability of corn oil by only 7%.

Shahidi and Wanasundara (1995) analysed the effect of flavonoids (added as pure compounds at a concentration of 200 ppm) on the oxidative stability of canola oil during the Schaal oven test at 60 °C for 30 days. The most favourable effects were seen after the addition of myricetin (almost 400% higher oxidative stability compared to the control sample) and epicatechin (almost 120% higher oxidative stability compared to the control sample). Equally strong antioxidant properties were shown by such compounds as quercetin, morin, rutin, and naringin (oxidative stability was higher by approx. 80% compared to the control sample). Chu and Hsu (1999) also analysed flavonoids as oil antioxidants. They conducted studies using catechin at various concentrations (from 500 to 3000 ppm) and cold-pressed peanut oil in the accelerated oxidative stability test. They demonstrated that catechin addition increased the stability of cold-pressed peanut oil by almost 360%.

Several authors have shown that the addition of phenolic acid derivatives could also be a barrier to the oxidation of plant oils. For example, Tańska et al. (2018) assessed the possibility of using 4-vinylguaiacol (ferulic acid derivative) and 4-vinylsyringol (sinapic acid derivative) as antioxidants in such commercial plant oils as cold-pressed flaxseed and rapeseed oils, extra virgin olive oil, and refined rapeseed oil. The research was carried out using the Rancimat test at 110 °C and an acetone solution of these compounds at concentrations of 20, 40, and 80 mg/100 g. The addition of 4-vinylguiacol proved to be more effective (oxidative stability increased by 13–50% compared to the control sample) than 4-vinylsyringol. In turn, Silva, Borges, and Ferreira (2001) noticed that the oxidative stability of refined sunflower oil at 110 °C increased significantly after propyl caffeate and propyl hydrocaffeate addition (by 17 and 35%, respectively) at a concentration of 160 ppm. These authors also pointed out that the addition of other phenolic acid derivatives, such as propyl ferulate and propyl isoferulate, did not ensure antioxidative protection in the oil matrix. The possibility of using octyl derivatives (i.e., octyl sinapate, octyl ferulate, and octyl caffeate) was analysed by Szydłowska-Czerniak, Rabiej, Kyselka, Dragoun, and Vladimí (2018). The scope of their analysis included adding the purified compounds to refined rapeseed oil at concentrations from 0.005 to 0.9% and performing the Rancimat test at 120 °C. According to these authors, the oxidative stability of refined rapeseed oil increased by 18–59%, 3–20%, and 23–220%, respectively. Chen and Ho (1997) also analysed the effect of phenolic acid derivatives on the oxidative stability. They noted that a methanolic solution of caffeic acid phenethyl ester (at a concentration of 2 mM) extended the oxidative stability at 110 °C by more than 140% compared to the control sample, while the methanolic solution of ferulic acid phenethyl ester (at the same concentration) showed no influence. In turn, Hasiewicz-Derkacz et al. (2015) analysed the effect of 0.5 mM vanillin addition on the oxidative stability of cold-pressed flaxseed oil from transgenic seeds. These authors used TBARS reaction at 140 °C for 30 min in the air atmosphere. The results clearly indicated the antioxidant properties of vanillin, as the stability of the research material increased by half after its addition.

Two scientific publications were found about phenolic alcohols and their antioxidant properties in the oil matrix. Mateos, Domiänguez, Espartero, and Cert (2003) analysed the effect of a methanolic solution

Table 7
Effect of phenolic compounds on plant oil oxidative stability.

Oily material	Test type	Phenolic compound type	Addition of phenolic compounds	Antioxidative/ prooxidative effect	Oxidative stability change (%)	Reference
Phenolic acids						
Cold-pressed flaxseed oil from transgenic seeds	TBARS reaction at 140 °C for 30 min in air atmosphere	Ferulic acid (TPSA = 66.76)	Pure compounds at 0.5 mM concentration	Antioxidative effect	85%	Hasiewicz-Derkacz et al. (2015)
		Caffeic acid (TPSA = 77.75)	Pure compounds at 0.5 mM concentration	Antioxidative effect	94%	
Cold-pressed rapeseed oil	Rancimat test at 120 °C	Ferulic acid (TPSA = 66.76)	Ethanol solution at 100, 250, 500 μM concentration	Antioxidative effect	12–24%	Tundis et al. (2017)
		Cinnamic acid (TPSA = 37.30)	Ethanol solution at 100, 250, 500 μM concentration	Prooxidative effect	32–44%	
		Sinapic acid (TPSA = 76.00)	Ethanol solution at 100, 250, 500 μM concentration	Prooxidative effect	24–36%	
		Syringic acid (TPSA = 76.00)	Ethanol solution at 100, 250, 500 μM concentration	Prooxidative effect	8–32%	
Refined olive oil	The active oxygen method (AOM-test) at 97.8 °C	*p*-hydroxybenzoic acid (TPSA = 57.53)	Diethyleter solution at 0.025, 0.05, 0.1% concentration	No effect	0.00%	Nergiz (1991)
		Protocatechuic acid (TPSA = 77.75)	Diethyleter solution at 0.025, 0.05, 0.1% concentration	Antioxidative effect	36.11–86.11%	
		o-coumaric acid (TPSA = 57.53)	Diethyleter solution at 0.025, 0.05, 0.1% concentration	Antioxidative effect	5.56%	
		Caffeic acid (TPSA = 77.75)	Diethyleter solution at 0.025, 0.05, 0.1% concentration	Antioxidative effect	8.33–55.56%	
		Ferulic acid (TPSA = 66.76)	Diethyleter solution at 0.025, 0.05, 0.1% concentration	Antioxidative effect	2.78–16.67%	
		4-hydroxyphenyl acetic acid (TPSA = 57.53)	Diethyleter solution at 0.025, 0.05, 0.1% concentration	Antioxidative effect	5.56–11.11%	
		3,4-dihydroxyphenyl acetic acid (TPSA = 77.75)	Diethyleter solution at 0.025, 0.05, 0.1% concentration	Antioxidative effect	69.44–144.44%	
		Vanillic acid (TPSA = 66.76)	Diethyleter solution at 0.025, 0.05, 0.1% concentration	Prooxidative effect (0.1%)	19.44%	
		p-coumaric acid (TPSA = 57.53)	Diethyleter solution at 0.025, 0.05, 0.1% concentration	Prooxidative effect	5.56%	
Corn oil	Rancimat test at 110 °C	Caffeic acid (TPSA = 77.75)	Methanol solution at 2 mM concentration	Antioxidative effect	151.72%	Chen and Ho (1997)
		Ferulic acid (TPSA = 66.76)	Methanol solution at 2 mM concentration	Antioxidative effect	6.40%	
		Rosmarinic acid (TPSA = 144.52)	Methanol solution at 2 mM concentration	Antioxidative effect	196.55%	
		Chlorogenic acid (TPSA = 164.74)	Methanol solution at 2 mM concentration	Antioxidative effect	133.50%	
Flavonoids						
Canola oil	Schaal oven test at 60 °C for 30 days	Apigenin (TPSA = 90.89)	Pure compounds at 200 ppm concentration	Antioxidative effect	9.38%	Shahidi and Wanasundara (1995)
		Chrysin (TPSA = 70.67)	Pure compounds at 200 ppm concentration	Antioxidative effect	9.38%	
		Kaempferol (TPSA = 111.12)	Pure compounds at 200 ppm concentration	Antioxidative effect	9.38%	
		Naringenin (TPSA = 86.99)	Pure compounds at 200 ppm concentration	Antioxidative effect	9.38%	
		Quercetin (TPSA = 131.35)	Pure compounds at 200 ppm concentration	Antioxidative effect	81.25%	
		Myricetin (TPSA = 151.58)	Pure compounds at 200 ppm concentration	Antioxidative effect	368.75%	
		Morin (TPSA = 131.35)	Pure compounds at 200 ppm concentration	Antioxidative effect	71.88%	
		Rutin (TPSA = 269.43)	Pure compounds at 200 ppm concentration	Antioxidative effect	87.5%	
		Naringin (TPSA = 225.06)	Pure compounds at 200 ppm concentration	Antioxidative effect	71.88%	
					25%	

(*continued on next page*)

Table 7 (*continued*)

Oily material	Test type	Phenolic compound type	Addition of phenolic compounds	Antioxidative/ prooxidative effect	Oxidative stability change (%)	Reference
		Taxifolin (TPSA = 127.44)	Pure compounds at 200 ppm concentration	Antioxidative effect		
		[-]epicatechin (TPSA = 110.37)	Pure compounds at 200 ppm concentration	Antioxidative effect	118.75%	
Cold-pressed peanut oil	Accelerated oxidative stability measurement method (OSI, Method Cd 12b-92)	Catechin (TPSA = 110.37)	Pure compounds at 500, 1000, 1500, 2000, 2500, 3000 ppm concentration	Antioxidative effect	51.99–355.97%	Chu and Hsu (1999)
Phenolic acid derivatives						
Cold-pressed flaxseed oil Cold-pressed rapeseed oil Extra virgin olive oil Refined rapeseed oil	Rancimat test at 110 °C	4-vinylguaiacol (TPSA = 29.46)	Acetone solution at 20, 40, 80 mg/100 g concentration	Antioxidative effect	13–50%	Tańska et al. (2018)
		4-vinysyringol (TPSA = 38.70)	Acetone solution at 20, 40, 80 mg/100 g concentration	Antioxidative effect	2–5%	
Refined sunflower oil	Rancimat test at 110 °C	Propyl caffeate (TPSA = 66.76)	Pure compounds at 160 ppm concentration	Antioxidative effect	17.54%	Silva et al. (2001)
		Propyl hydrocaffeate (TPSA = nd.)	Pure compounds at 160 ppm concentration	Antioxidative effect	35.09%	
		Propyl ferulate (TPSA = 55.77)	Pure compounds at 160 ppm concentration	No effect	0.00%	
		Propyl isoferulate (TPSA = 55.77)	Pure compounds at 160 ppm concentration	No effect	1.75%	
Refined rapeseed oil	Rancimat test at 120 °C	Octyl sinapate (TPSA = 65.00)	The purified compounds at 0.005, 0.01, 0.05, 0.1, 0.5, 0.9% concentration	Antioxidative effect	17.95–58.97%	Szydłowska-Czerniak et al. (2018)
		Octyl ferulate (TPSA = 55.77)	The purified compounds at 0.005, 0.01, 0.05, 0.1, 0.5, 0.9% concentration	Antioxidative effect	2.56–20.51%	
		Octyl caffeate (TPSA = 66.76)	The purified compounds at 0.005, 0.01, 0.05, 0.1, 0.5, 0.9% concentration	Antioxidative effect	23.08–220.51%	
Corn oil	Rancimat test at 110 °C	Caffeic acid phenethyl ester (TPSA = 66.76)	Methanol solution at 2 mM concentration	Antioxidative effect	140.89%	Chen and Ho (1997)
		Ferulic acid phenethyl ester (TPSA = 55.77)	Methanol solution at 2 mM concentration	No effect	0.99%	
Cold-pressed flaxseed oil from transgenic seeds	TBARS reaction at 140 °C for 30 min in air atmosphere	Vanillin (TPSA = 46.53)	Pure compounds at 0.5 mM concentration	Antioxidative effect	50%	Hasiewicz-Derkacz et al. (2015)
Phenolic alcohol derivatives						
Purified olive oil	Rancimat test at 100 °C	Hydroxytyrosol (TPSA = 60.68)	Methanol solution at 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0, 1.1 mmol/kg concentration	Antioxidative effect	1435.07–4828.91%	Mateos et al. (2003)
Secoiridoids						
Refined olive oil	Rancimat test at 120 °C	Oleuropein (TPSA = 201.68)	Methanol olive leaves extract at 400 ppm concentration	Antioxidative effect	88.37%	Bouaziz et al. (2008)
	Storage test at 50 °C for 6 months	Oleuropein (TPSA = 201.68)	Methanol olive leaves extract at 400 ppm concentration	Antioxidative effect	129.44%	
Refined olive husk oil	Rancimat test at 120 °C	Oleuropein (TPSA = 201.68)	Methanol olive leaves extract at 400 ppm concentration	Antioxidative effect	102.75%	Bouaziz et al. (2008)
	Storage test at 50 °C for 6 months	Oleuropein (TPSA = 201.68)	Methanol olive leaves extract at 400 ppm concentration	Antioxidative effect	189.94%	

TPSA – Topological Polar Surface Area (TPSA was calculated with the use of http://www.molinspiration.com); nd. – no data.

of hydroxytyrosol (at concentrations from 0.1 to 1.1 mmol/kg) on the oxidative stability of purified olive oil at 100 °C. They noted a significant increase in the oil stability by almost 5000% compared to the control sample. Whereas, Bouaziz, Fki, Jemai, Ayadi, and Sayadi (2008) added oleuropein to 2 refined oils (olive oil, olive husk oil) as methanolic olive leaf extract at 400 ppm in two tests, i.e., the Rancimat test at 120 °C and storage test at 50 °C for 6 months. They showed that oleuropein had strong antioxidative properties, with a stronger effect noted during the storage test (oxidative stability was higher by almost 130% (refined olive oil) and 190% (refined olive husk oil) compared to the control sample). In the Rancimat test, oil stability was also increased, but by almost 100% compared to the control sample (in both oils).

The antioxidant activity of phenolic compounds depends on various mechanisms, i.e. phenolic compounds show reducing properties (give off electron or hydrogen), binding free radicals (stabilize or delocalize an unpaired electron), chelating metal ions of enzymes catalyzing the oxidation reactions, disrupting radical chain reactions and stabilizing free radicals formed in reactions oxidation by hydrogenation or complexation processes (Procházková, Bousová, & Wilhelmová, 2011; Tsao & Yang, 2003). A common feature of phenolic compounds is the

presence of hydroxyl groups linked to the benzene ring in the molecule (Chirinos et al., 2009). In compounds with one hydroxyl group, the antioxidant activity increases with the additional presence of one or two methoxyl groups in the ring. Substitution in the position of an ortho-group with an electron, alkyl or methoxyl donor, increases the stability and antioxidant properties of phenolic acids (Brand-Williams, Cuvelier, & Berset, 1995). Different levels of antioxidant activity of caffeic acid, ferulic acid and *p*-coumaric acid are related to their chemical structure – it depends on the number of hydroxyl groups in the molecule and is higher when they are esterified. Sinapic acid with two methoxyl groups is more active than ferulic acid (one methoxyl group), and it is more active than coumaric acid (one hydroxyl group). High antioxidant activity is also shown by chlorogenic acid (Godlewska-Żyłkiewicz et al., 2020; Velika & Kron, 2012). Ortho- and *para*-monohydroxybenzoic acids do not have antioxidant properties against free radicals generated in the aqueous phase, whereas monohydroxybenzoic acids are effective scavengers of hydroxyl radicals (Velika & Kron, 2012). Bubols et al. (2013) stated that the antioxidant activity of flavonoids is also connected with structures and substituents of heterocyclic rings. Heijnen, Haenen, van Acker, van der Vijgh, and Bast (2001) suggest that hydroxyl groups are dominant in the applicability of flavonoids as antioxidants, is also confirmed by the studies of Moalin et al. (2011). According to the research of these authors, quercetin and its derivatives are more potent antioxidants than other flavonoids, and their higher antioxidant activity is due to the total number and linearity of the hydroxyl groups in B-ring. The presence of the 3-hydroxyl group in the ring heterocyclic group also increases the antioxidant activity, while the additional hydroxyl or methoxyl groups at the 3, 5 and 7 positions of A and C rings appear to be less important. Accordingly, the flavonols and flavones containing a catechol group in the B-ring are very active, but the flavonols are stronger due to the presence of the 3-hydroxyl group (Sekher Pannala, Chan, O'Brien, & Rice-Evans, 2001). Flavanonols and flavanones are weak antioxidants due to the lack of conjugation provided by the 2,3-double bond with the 4-oxo group (Kumar & Pandey, 2013). Similar observations are made in relation to other groups of phenolic compounds, e.g. anthocyanins and isoflavones (Pietta, 2000).

5. Conclusions and future research needs

This review shows that numerous publications on the content and analysis of phenolic compounds in oils have appeared in the last two decades. Their results proved that these compounds are present in most plant oils, and that their especially higher amounts are determined in those obtained by cold-pressing or hot-pressing from microwaved seeds. The main sources of phenolic compounds are rice bran and olive oils, but some authors also found their high contents in the oils from rape, flax, grape, and pumpkin seeds. In oils produced from other raw materials (e.g., camellia seeds, echium seeds, marula seeds, hazelnuts, corn germs), the content of phenolic compounds generally does not exceed 10 mg/100 g of the product. The content of individual phenolic compounds, such as phenolic acids, flavonoids, lignans, and phenolic derivatives, in oils is highly variable. Many authors have shown that individual phenol profiles and the total content of free phenolic compounds in oil depend on cultivars, place of origin, growing techniques, agronomic factors, the degree of maturity, processing, packaging, and storing. The highly diversified total content of free phenolic compounds in cold-pressed oils from some raw materials (e.g., avocado fruits, chia seeds, sunflower seeds) is questionable, which indicates that subsequent studies are needed in this field.

There are two main methods used to determine phenolic compounds in oils, i.e., the colorimetric method based on the spectrophotometric measurement of total phenolic content and chromatography used to identify individual phenolic compounds. Authors modify both these methods to best adapt them to their research conditions. Because of the presence of different phenolic compounds and their various concentrations in oil matrices, the sample preparation procedure is a critical step in their analysis. Many researchers proposed alcohol and water mixtures for the extraction of phenolic compounds. Nonetheless, there are still no standardised conditions (i.e., solvent composition and solvent-to-oil mass ratio, extraction temperature, time, and replication number) available for their extraction.

Recent literature data clearly indicate that phenolic compounds are the important antioxidants present in oils. Due to their low level in oil, many tests are carried out to increase oxidative stability by adding phenolic compounds. Although several studies confirmed the high efficiency of some phenolic compounds in oil stabilization, the mechanism of their action is still not fully understood. It is also worth considering studies on the efficiency of phenolic compounds as lipid oxidation inhibitors using storage test under normal conditions (e.g., tests simulating domestic usage). No data is provided from such tests. Most authors carried out studies using an accelerated storage test at temperatures exciding 100 °C. However, lipid oxidation kinetics and antioxidant action in the test carried out at a high temperature may differ from these obtained in the test performed at room temperature. Interactions of phenolic compounds with other oil compounds should also be reconsidered to design more effective antioxidants for future applications.

Declaration of competing interest

The authors declare that there is no conflict of interest.

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FLA

Effect of initial quality and bioactive compounds content in cold-pressed flaxseed oils on oxidative stability and oxidation products formation during one-month storage with light exposure

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ABSTRACT

Flaxseed oils contain significant amounts of unsaturated fatty acids and, consequently, are susceptible to oxidative process. Additionally, inadequate conditions of storage result in the intensification of unfavorable processes. This problem is becoming more and more serious due to the high intensity of illumination of shop display cases and storage rooms, as well as the exposure to sunlight. Although literature data suggests that light may be an even more important oxidizing agent than oxygen, experiments are mainly focused on the oxidation progress in oils from varied raw materials or the changes in oil characteristics under different storage conditions. The aim of the study was to investigate the effect of the initial state of 30 commercial cold-pressed flaxseed oils on oxidative stability and oxidation product formation during storage under simulated store conditions (one-month at ambient temperature with light exposure). The oil quality was analyzed qualitatively (characteristic quality values, content of conjugated fatty acids, induction period, color parameters) and quantitatively (content of water and bioactive compounds, fatty acid composition). Oxidation progress in the oils was monitored by the characteristic quality values, content of conjugated fatty acids and color parameters.

It was shown that commercially available cold-pressed flaxseed oils were generally good quality with similar color parameters and fatty acid composition, but mostly varied in terms of carotenoids, chlorophylls and phenolic compounds. Storage with light exposure caused the deterioration of the oil quality, and at least a 1.0-fold increase in acid and anisidine values and at least a 24.8-fold increase in peroxide value were determined. Also, the color of all oils changed after storage, and the calculated total color differences (ΔE) were in the range of 0.2–8.7. The results highlighted that the formation of oxidation products in flaxseed oil during storage in light resulted mainly from its initial quality indices. In turn, the induction period tested by Rancimat was dependent on the fatty acid percentages and total phenolic compound content. In conclusion, the Rancimat test is a poor indicator of the oxidative stability of oils under storage at ambient temperature with light exposure.

1. Introduction

The demand for flaxseed is increasing day by day among consumers due to its nutritional value and health benefits. Flaxseed contains significant amounts of compounds with bioactive and functional properties, such as easily digestible proteins, soluble fiber, lignans, and fat, which is a unique mixture of fatty acids [1]. There are four known forms of flaxseed intended for human consumption, but the most popular is flaxseed oil [2].

Fat content in flaxseed ranges from 35% to 45% [3], and additionally is rich in essential n-3 fatty acids, mainly ALA (α-linolenic acid) [1,3]. The literature shows that the share of ALA in flaxseed oil from high-linolenic varieties can be from 50% [4] to even 70% [5]. It should also be noted that flaxseed oil is the most effective means of delivering ALA to the human body and may provide an alternative source for populations with little access to marine food [6,7]. After entering the tissues, ALA is the basis of elongation and enzymatic transformations leading to the synthesis of fatty acids with longer chains, such as EPA (eicosapentaenoic acid), DPA (docosapentaenoic acid), and in some tissues DHA (docosahexaenoic acid) [8]. There are many significant scientific studies showing the beneficial effects of ALA; it has been proven that ALA affects the concentration of lipoproteins in the blood

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plasma, lowers the level of LDL (low-density lipoproteins) and improves cellular lipid metabolism [1], has antiarrhythmic and cardioprotective properties [8], and exhibits antiallergic, antioxidant and anti-inflammatory effects [9]. Generally, ALA and other n-3 fatty acids are useful in the prevention and treatment of chronic non-communicable diseases such as type 2 diabetes, coronary heart disease, stroke, kidney disease, rheumatoid arthritis, Alzheimer's disease, and some types of cancer [1]. An appropriate ratio of n-6 and n-3 fatty acids (from 0.3 to 4.3:1 for low linolenic form) is also found in flaxseed oil [10], which ensures proper blood pressure, functioning of the brain and hormone production [11].

Flaxseed oil is sensitive to light, heat and oxygen exposure, mainly due to its high ALA content [12]. It is estimated that the stability of cold-pressed flaxseed oil is from 5 weeks to 3 months if stored in the refrigerator [13]. Inadequate storage parameters can change oil quality characteristics, which ultimately differ from those indicated on the label [14]. This problem is becoming more serious because of the high level of intensity of illumination of shop display cases and storage rooms [15] and/or oil exposure to sunlight [16]. Velasco and Dobarganes [17] suggest that light is even more important than triplet oxygen (ground-state of the oxygen molecule) during oxidation, because it contributes to photo-oxidation of other oil components (e.g. chlorophylls) and then turns oxygen into singlet form (with a much greater oxidation rate compared to atmospheric triplet oxygen). This phenomenon leads to a loss of valuable nutrients, changes in the color of the oil, as well as the formation of compounds with an unpleasant taste and aroma [14]. In addition, oxidized plant oils can pose a health risk due to the formation of toxic and reactive oxidation products [12].

PV (peroxide value/number, formation of primary oxidation products), AnV (anisidine value/number, formation of secondary oxidation products) and AV (acid value/number, free fatty acids due to rancidity) are key parameters in quality control of oils [18]. Researchers often use these parameters to characterize the oxidation process of oils, as well as to determine changes in the quality and degree of degradation of their compounds. For example, de Almeida et al. [19] analyzed changes in palm oil (refined, crude) in the twelve-month storage (in sunny place, in dark place, in cool place) by measuring the values of PV, AnV and AV, Grajzer et al. [20] studied the oxidation process of 33 cold-pressed seed oils (i.e. walnut, pumpkin, camellia, milk thistle) during three-month storage (in dark and exposed to cold fluorescent light place) using AV, PV and AnV, while at work of Cobzaru et al. [21] evaluated the oxidation progress of virgin olive oil during forty eight-month storage of natural condition by determining PV and AV as indicators of oxidation and degree of hydrolysis processes. However, in the literature there are a small number of studies showing a direct role of the initial state of oil (including the content of bioactive compounds) on oxidative stability and formation of oxidation products during storage. This seems to be especially important in the case of oils with a short shelf life, including the currently nutritionally fashionable cold-pressed flaxseed oil. Recently, it has become very popular to determine the stability of oils using accelerated oxidation tests, especially the Rancimat test [22]. Furthermore, some researchers proposed quantitative indices defined by fatty acid composition for the prediction of oil susceptibility to oxidation [23].

Therefore, the study attempted to investigate the mentioned above significance of the initial quality and bioactive compounds of commercially available cold-pressed flaxseed oils on their oxidative stability and the formation of oxidation products during one-month storage with light exposure. Additionally, the relationships between the theoretical (indices calculated based on fatty acid composition) and experimental (induction period, formation of primary and secondary oxidation products) oxidizability of flaxseed oils were evaluated.

2. Materials and methods

2.1. Reagents and chemicals

Analytical-grade reagents such as p-anisidine, Folin-Ciocalteau reagent (Sigma-Aldrich, Saint Louis, Missouri, United States), sodium carbonate and sodium hydroxide (POCH, Gliwice, Poland) were used. Analytical standards such as D-catechin, 5α-cholestane, β-apo-8′-carotenal and phenolic acids were purchased from Sigma-Aldrich and tocopherols from Calbiochem (Nottingham, United Kingdom). Chromatography-grade solvents, i.e. acetone, *n*-hexane, isopropanol, pyridine, N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) were purchased from Sigma-Aldrich. HYDRANAL-Coulomat reagents for Karl Fischer titration were purchased from Honeywell (Charlotte, North Carolina, United States). Deionized water was obtained from the HLP 5 deionizer (Hydrolab, Gdańsk, Poland).

2.2. Research materials

The research materials were 30 commercial cold-pressed flaxseed oils from various manufacturers available on the market in Poland. The oils were produced mainly in Poland (except no. 4 made in Germany) and, according to the manufacturer, had a suitable shelf life (Supplementary material 1). The oils were analyzed immediately after opening the packaging and after storage in an illuminated place i.e. on the shelf exposed to natural (daylight) and artificial light sources (LED ceiling lighting with power 50 W) for 15 h a day, simulation of storage in store conditions at ambient temperature (21 ± 2 °C) and relative humidity of 35 ± 3.0% measured with electronic thermometer-hygrometer type LB-710 (LAB-EL, Reguły, Poland) for one-month (storage for 30 days in May, 200 mL of oils were enclosed in similar bottles of 250 mL without removing air). The oils were kept between analyses in a freezer (at −20 °C).

2.3. Determination of fatty acid composition in flaxseed oils

Methyl-esters of fatty acids contained in oil samples were prepared according to Zadernowski and Sosulski [24], by adding a methylating mixture (methanol:chloroform:sulfuric acid, 100:100:1, *v/v/v*) at 70 °C for 2 h. After neutralizing the sulfuric acid with zinc, the solvent was evaporated, and the residue was dissolved in *n*-hexane. The methyl-esters were analyzed according to the work of Czaplicki et al. [25] using a GC–MS QP2010 PLUS gas chromatograph (Shimadzu, Japan) with an SGE BPX-70 capillary column (25 m × 0.22 mm × 0.25 μm, SGE Analytical Science, Australia) with helium as a carrier gas applied at a flow rate of 0.9 mL/min. The temperatures of GC–MS were set as follows: interface 240 °C, the ion source 240 °C, column temperature was programmed in the range from 150 °C to 250 °C. The electron energy was set at 70 eV. The total ion current (TIC) mode was used in 50–500 *m/z* range. Fatty acids were identified based on mass spectra and expressed as a percentage of all fatty acids. The sum of saturated (SFA), monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids, and the ratio between n-3 and n-6 fatty acids were calculated.

Additionally, the oxidation indices were evaluated based on fatty acid composition, such as Cox value and SFA-to-USFA (unsaturated fatty acids, sum of MUFA and PUFA), PUFA-to-SFA, MUFA-to-PUFA, C16:0-to-C18:2, C18:2-to-C18:0 and C18:3-to-C18:2 ratios. The Cox value was calculated according to the formula given by Cao et al. [26], where Cox = (% C18:1 × 1 + % C18:2 × 10.3 + % C18:3 × 21.6)/100.

2.4. Determination of bioactive compounds content in flaxseed oils

The content of sterols and squalene was determined using the GC–MS QP2010 PLUS chromatograph (Shimadzu, Japan) coupled with a mass spectrometer and equipped with a ZB-5MSi capillary column (30 m ×

0.25 mm, 0.25 μm, Phenomenex, USA). The sample preparation and chromatographic conditions were described in the work of Roszkowska et al. [27]. Sterols and squalene were identified using retention times and mass spectra of peaks, and their contents were calculated with reference to the internal standard and expressed as mg/100 g of oil.

The content of tocol was determined using the HPLC Agilent Technologies 1200 chromatograph (Santa Clara, USA) equipped with a fluorescence detector from the same company and a LiChrospher Si 60 column (250 mm × 4 mm × 5 μm, Merck, Germany). The sample preparation and chromatographic conditions were the same as in the work of Czaplicki et al. [25]. The content of tocols was determined from calibration curves prepared for tocol standards and expressed as mg/100 g of oil.

The content of carotenoids was determined using the HPLC Agilent Technologies 1200 chromatograph equipped with a diode array detector (DAD) from the same company and a YMC-C30 column (150 mm × 4.6 mm × 3 μm, Dinslaken, Germany). The sample preparation and chromatographic conditions were described in the work of Czaplicki et al. [25]. The content of carotenoids was calculated with reference to the internal standard and expressed as mg/100 g of oil.

The total chlorophyll content was determined spectrophotometrically using a microplate reader FLUOstar OMEGA (BMG Labtech GmbH, Ortenberg, Germany), according to the method described by Roszkowska et al. [27]. The absorbance was measured at 630, 670 and 710 nm for pure oil against air, and the content of total chlorophyll was expressed as mg/100 g of oil.

The total phenolic compound content was determined spectrophotometrically with a Folin-Ciocalteau reagent according to the method described by Siger et al. [28]. The extraction of phenolic compounds was carried out using 80% methanol (*v/v*). The absorbance was measured using a microplate reader FLUOstar OMEGA. The phenolic compound content was calculated based on the D-catechin calibration curve and expressed as mg/100 g of oil.

The phenolic acids were determined by the RP-HPLC technique using an Agilent Technologies (Santa Clara, USA) 1200 series system fitted out with a photodiode detector and an Agilent Technologies Eclipse XDB-C18 column (150 mm × 4.6 mm × 5 μm). The extraction was conducted according to the method described by Siger et al. [28] using a vacuum manifold (J.T. Baker purchased from Witko, Łódź, Poland) with a SPE Supelco (Sigma-Aldrich) column filled with diol (500 mg). The conditions of phenolic acid separation were described by Mikołajczak et al. [29]. The content of phenolic acids was determined from calibration curves prepared for phenolic acid standards and expressed as μg/100 g of oil.

2.5. Determination of quality indices of oils

The quality indices of the cold-pressed flaxseed oils, such as acid (AV), peroxide (PV) and anisidine values (AnV), and the content of conjugated dienes (CD) and trienes (TC) were determined based on the JOCS Standard Methods for Analysis of Fats, Oils and Related Materials [30].

2.6. Determination of water content in oils

The water content (WC) in the cold-pressed flaxseed oils was determined based on Karl Fischer titration using a 917 Coulometer with generator electrode with diaphragm (Metrohm, Herisau, Switzerland). The sample was injected into the Karl Fischer cell using a syringe (with a needle Ø of 0.8 mm). In the study, a single-component ingredient was used for the coulometric analysis, i.e. HYDRANAL Coulomat AG, and the catholyte was HYDRANAL Coulomat CG. The parameter settings were as follows: drift start value of 20 μg/min, relative drift stop value of 5 μg/min, polarization current of 10 μA, point setting at 50 mV and normal rate of current generation, sample extraction time of 90 s, titration speed of 8. The water content in the oils was expressed in ppm.

2.7. Determination of color parameters for oils

The color parameters were measured using digital image analysis (DIA) according to the method described by Tańska et al. [31]. The oil sample (20 mL in a beaker, height of the layer was 2 cm) was put on the white plate and the image was acquired by a high-resolution and low-noise CCD (charge-coupled device) Nikon DXM-1200 color camera (Nikon Inc., Melville, USA). The light source was the RB 5004 HF-High Frequency Daylight Copy Light set (color temperature of about 5400 K) (Kaiser Fototechnik GmbH & Co.KG, Buchen, Germany). The image was analyzed using LUCIA G v. 4.80 software (Laboratory Imaging, Prague, Czech Republic). The results were expressed as parameters of the CIE-L*a*b* color space.

2.8. Determination of oxidative stability of oils

An accelerated oxidation test was evaluated on a Rancimat apparatus 743 (Metrohm, Herisau, Switzerland) at 110 °C and with an air flow rate of 20 L/h. Measurement of the oxidative stability of oils was based on the conductometric detection of volatile oxidation products. The time that elapsed until volatile oxidation products appeared was saved as the induction period (IP).

2.9. Statistical analysis

All data presented were collected in triplicate (except for color analysis, which required ten measurements) for each oil sample and analyzed with Statistica 13.3 PL software (StatSoft, Cracow, Poland). The differences between the oils were determined using one-way analysis of variance (ANOVA), followed by a Tukey's test at $p \leq 0.05$ significance level. The intra-sample variability in properties of oils was assayed using principal component analysis (PCA) at the significance level of $p \leq 0.05$. Further, the relationships between the initial quality, content of bioactive compounds and theoretical oxidizability of studied oils and their experimentally determined oxidizability were calculated as correlation coefficients (r) at the significance level of $p \leq 0.05$.

3. Results and discussion

3.1. Fatty acid composition and theoretical oxidizability of cold-pressed flaxseed oils at their initial state

Immediately after opening the packaging, five major fatty acids were identified in flaxseed oils (Table 1), with α-linolenic acid (C18:3) being the most abundant, followed by oleic acid (C18:1) and linoleic acid (C18:2) (the sum of these unsaturated fatty acids represented approximately 90% of total fatty acids). The share of C18:3 acid accounted for an average of 55.63% of total fatty acids, but the oils nos. 5, 27 and 30 had a very high share of C18:3 acid (at least 60% of total fatty acids). The highest degree of polyunsaturation belonged to oil no. 30, which contained the highest percentage of C18:3 acid (62.76% of total fatty acids). The share of C18:2 acid in oils was almost 4-fold lower than C18:3 acid, and the highest value was found in oil no. 23 (21.87% of total fatty acids). An equally high share of C18:2 acid (>16% of total fatty acids) was observed in oils nos. 4, 8, 10, 13, 16, 24 and 26. The highest share (26.08% of total fatty acids) of C18:1 acid was observed in oil no. 25, but oils nos. 1, 3, 6, 9–12, 14 and 18 were also characterized by high shares of this fatty acid (20.56–23.16% of total fatty acids). The share of SFA in total fatty acids of oils was low; it ranged from 7.90 (no. 1) to 11.24% (no. 12). Palmitic (C16:0) and stearic (C18:0) acids dominated in SFA, but the share of C16:0 acid was almost 1.5-fold higher. The share of C16:0 and C18:0 acids ranged from 4.83% (no. 10) to 6.23% (no. 12) and from 2.55 (no. 1) to 4.70% (no. 18) of total fatty acids, respectively. Intra-sample variability of the fatty acid composition showed the lowest variation of C16:0 and C18:3 acids, with values of variation coefficient (CV) equal to 5.26% and 5.66%, respectively, whereas the share of

Table 1
Fatty acids composition (%) of studied cold-pressed flaxseed oils.

Oil number	Fatty acids										Theoretical oxidizability indices						
	C16:0	C18:0	C18:1	C18:2	C18:3	Others	SFA	MUFA	PUFA	n-3/n-6	Cox value	SFA/ USFA	MUFA/ PUFA	PUFA/ SFA	C16:0/ C18:2	C18:2/ C18:0	C18:3/ C18:2
1	5.16^{l}	2.55^{n}	20.66^{e}	14.20^{l}	57.02^{f}	0.42^{abcd}	7.90^{p}	20.89^{e}	71.20^{f}	4.02^{d}	13.98	0.09	0.29	9.02	0.36	0.69	2.76
2	5.71^{fghi}	4.00^{ghijk}	17.30^{j}	15.73^{ij}	56.93^{h}	0.33^{ghijk}	9.92^{hijk}	17.43^{k}	72.66^{h}	3.62^{f}	14.09	0.11	0.24	7.33	0.36	0.91	3.29
3	5.69^{efg}	4.19^{f}	20.56^{e}	15.14^{jk}	54.04^{klm}	0.38^{def}	10.10^{efg}	20.72^{e}	69.18^{klm}	3.57^{fghi}	13.44	0.11	0.30	6.85	0.38	0.74	2.63
4	5.96^{b}	3.64^{lm}	18.54^{h}	16.49^{cde}	55.07^{hi}	0.29^{klm}	9.75^{hij}	18.68^{h}	71.57^{a}	3.34^{lm}	13.78	0.11	0.26	7.34	0.36	0.89	2.97
5	5.19^{l}	4.00^{ghi}	17.04^{j}	11.72^{p}	61.77^{a}	0.29^{klm}	9.38^{lm}	17.13^{k}	73.48^{hi}	5.27^{a}	14.72	0.10	0.23	7.83	0.44	0.69	3.62
6	5.90^{bc}	3.99^{ghi}	20.68^{e}	15.03^{jk}	54.09^{jk}	0.31^{jklm}	10.08^{efg}	20.80^{e}	69.12^{jk}	3.60^{f}	13.44	0.11	0.30	6.86	0.39	0.73	2.62
7	5.66^{ghij}	4.13^{gh}	19.68^{fg}	15.28^{k}	54.91^{lm}	0.34^{fghij}	9.98^{hijk}	19.83^{g}	70.20^{lm}	3.59^{fg}	13.63	0.11	0.28	7.04	0.37	0.78	2.79
8	5.43^{fghij}	3.69^{kl}	15.78^{kl}	16.30^{bc}	58.52^{c}	0.28^{lm}	9.30^{jkl}	15.89^{lm}	74.81^{c}	3.59^{fg}	14.48	0.10	0.21	8.04	0.33	1.03	3.71
9	5.64^{ghij}	4.03^{ghij}	21.02^{e}	15.40^{jk}	53.47^{opq}	0.43^{abc}	9.91^{hijk}	21.22^{e}	68.87^{opq}	3.47^{hijk}	13.35	0.11	0.31	6.95	0.37	0.73	2.54
10	4.83^{n}	3.89^{hijk}	22.92^{b}	16.31^{de}	51.68^{q}	0.37^{efg}	8.93^{no}	23.06^{b}	68.01^{q}	3.17^{n}	13.07	0.10	0.34	7.61	0.30	0.71	2.26
11	5.86^{bc}	4.67^{a}	21.27^{d}	15.21^{jk}	52.55^{nop}	0.44^{ab}	10.78^{b}	21.46^{d}	67.76^{nop}	3.46^{ijk}	13.13	0.12	0.32	6.28	0.39	0.71	2.47
12	6.23^{a}	4.72^{ab}	23.16^{b}	11.83^{p}	53.62^{n}	0.44^{ab}	11.24^{a}	23.31^{b}	65.45^{n}	4.53^{b}	13.03	0.13	0.36	5.82	0.53	0.51	2.31
13	5.33^{k}	3.64^{lm}	17.09^{j}	16.20^{ef}	57.46^{e}	0.27^{m}	9.13^{mn}	17.21^{jk}	73.67^{e}	3.55^{fghij}	14.25	0.10	0.23	8.07	0.33	0.95	3.36
14	5.58^{efgh}	4.45^{cb}	21.97^{c}	15.23^{ij}	52.44^{no}	0.34^{ijkl}	10.22^{cde}	22.12^{c}	67.67^{no}	3.44^{ghijk}	13.12	0.11	0.33	6.62	0.37	0.69	2.39
15	5.36^{jk}	3.85^{ijk}	16.27^{k}	15.89^{fg}	58.32^{d}	0.31^{hijkl}	9.40^{jkl}	16.39^{l}	74.21^{d}	3.67^{fg}	14.40	0.10	0.22	7.89	0.34	0.98	3.58
16	5.54^{efg}	4.19^{ef}	16.77^{j}	16.38^{bc}	56.73^{e}	0.39^{efgh}	9.97^{def}	16.91^{jk}	73.11^{e}	3.46^{fghij}	14.11	0.11	0.23	7.33	0.34	0.98	3.38
17	5.64^{efg}	4.51^{bcd}	17.75^{i}	15.49^{i}	56.23^{g}	0.38^{cde}	10.39^{cd}	17.89^{i}	71.73^{g}	3.63^{ijk}	13.92	0.12	0.25	6.90	0.36	0.87	3.17
18	5.86^{bcd}	4.70^{a}	21.38^{d}	15.20^{jk}	52.41^{pq}	0.45^{def}	10.82^{b}	21.55^{d}	67.62^{pq}	3.45^{f}	13.10	0.12	0.32	6.25	0.39	0.71	2.45
19	5.42^{hijk}	4.54^{abc}	16.74^{j}	13.06^{n}	59.84^{b}	0.40^{a}	10.23^{cde}	16.87^{k}	72.90^{b}	4.58^{jkl}	14.44	0.11	0.23	7.13	0.41	0.78	3.57
20	5.69^{efg}	4.68^{ab}	19.31^{g}	15.27^{jk}	54.66^{kl}	0.39^{bcde}	10.63^{bc}	19.43^{g}	69.94^{kl}	3.58^{b}	13.57	0.12	0.28	6.58	0.37	0.79	2.83
21	5.45^{ijk}	4.57^{abc}	17.35^{j}	14.22^{l}	58.01^{e}	0.40^{cde}	10.26^{def}	17.51^{j}	72.23^{e}	4.08^{fgh}	14.17	0.11	0.24	7.04	0.38	0.82	3.34
22	5.28^{l}	4.50^{de}	18.89^{h}	14.71^{l}	56.22^{i}	0.39^{bcde}	10.03^{ghi}	19.04^{h}	70.93^{i}	3.82^{d}	13.85	0.11	0.27	7.07	0.36	0.78	2.98
23	5.16^{mn}	3.65^{m}	17.68^{j}	21.87^{a}	51.30^{r}	0.33^{cde}	9.00^{o}	17.83^{jk}	73.17^{r}	2.35^{e}	13.51	0.10	0.24	8.13	0.24	1.24	2.90
24	5.71^{cde}	3.61^{lm}	17.74^{i}	16.83^{b}	55.81^{q}	0.29^{ghijk}	9.49^{ijkl}	17.86^{i}	72.63^{g}	3.31^{o}	13.97	0.10	0.25	7.65	0.34	0.95	3.15
25	5.35^{ijk}	4.19^{ef}	26.08^{a}	15.31^{hi}	48.68^{r}	0.39^{klm}	9.75^{fgh}	26.27^{a}	63.98^{r}	3.18^{m}	12.35	0.11	0.41	6.56	0.35	0.59	1.87
26	5.61^{fghij}	4.68^{ab}	19.08^{gh}	16.05^{gh}	54.19^{m}	0.39^{cde}	10.54^{cd}	19.22^{gh}	70.24^{m}	3.38^{n}	13.55	0.12	0.27	6.66	0.35	0.84	2.84
27	5.55^{ijk}	3.90^{jk}	16.13^{l}	14.01^{m}	60.05^{d}	0.36^{cde}	9.67^{kl}	16.27^{m}	74.06^{d}	4.28^{klm}	14.57	0.11	0.22	7.66	0.40	0.87	3.72
28	5.49^{ghij}	4.45^{cd}	19.50^{f}	15.79^{gh}	54.41^{ij}	0.37^{efghi}	10.15^{def}	19.66^{f}	70.18^{ij}	3.45^{c}	13.57	0.11	0.28	6.91	0.35	0.81	2.79
29	5.84^{def}	4.16^{g}	18.30^{i}	15.55^{jk}	55.79^{ijk}	0.36^{efg}	10.23^{fgh}	18.43^{i}	71.33^{jk}	3.59^{jkl}	13.84	0.11	0.26	6.97	0.38	0.85	3.05
30	5.21^{lm}	3.91^{kl}	15.16^{m}	12.65^{o}	62.76^{b}	0.31^{efghi}	9.31^{n}	15.28^{n}	75.42^{b}	4.96^{fg}	15.01	0.10	0.20	8.10	0.41	0.83	4.14
$\bar{x}$	5.54	4.12	19.06	15.28	55.63	0.36	9.88	19.21	70.91	3.69	13.78	0.11	0.27	7.22	0.37	0.82	2.98
CV	5.26	11.40	13.25	11.77	5.66	14.29	6.79	13.24	3.92	15.57	4.28	7.50	17.88	9.50	12.90	17.48	17.44
min	4.83	2.55	15.16	11.72	48.68	0.27	7.90	15.28	63.98	2.35	12.35	0.09	0.20	5.82	0.24	0.51	1.87
max	6.23	4.72	26.08	21.87	62.76	0.45	11.24	26.27	75.42	5.27	15.01	0.13	0.41	9.02	0.53	1.24	4.14

C16:0 – palmitic acid; C18:0 – stearic acid; C18:1 – oleic acid; C18:2 – linoleic acid; C18:3 – linolenic acid; SFA – sum of saturated fatty acids; MUFA – sum of monounsaturated fatty acids; PUFA – sum of polyunsaturated fatty acids; USFA – unsaturated fatty acids (MUFA+PUFA); Cox value (calculated based on % of C18); $\bar{x}$ – mean value; CV – variation coefficient (%); min – minimal value; max – maximal value; a,b,c, … – mean values in the same column followed by different letters are significantly different ($p \leq 0.05$).

C18:1 was the most variable (CV = 13.25%). The ratio of n-3 and n-6 fatty acids in oils was characterized by higher variability (CV = 15.57%) and ranged from 2.35 (no. 23) to 5.27 (no. 5). The PCA analysis was performed to visualize the variability of the studied flaxseed oils in the fatty acid profile (Fig. 1A). The first principal component (PC1) and second principal component (PC2) in the PCA score plot explained 68.40% of the total variance (42.12% and 26.28% for PC1 and PC2, respectively). The fatty acid composition appeared to be quite different in most oils. It was observed that oils nos. 10, 12, 23 and 25, differed significantly from the others, mainly due to the higher content of C18:1, C18:2 and/or C18:3 acids. Other researchers noticed similar results in terms of the composition of fatty acids in flaxseed oils [10,29,32,33], which also confirms the authenticity of the analyzed oils [34]. The authors state that possible differences may result from i.a. environmental conditions, growing techniques or the variety of flaxseeds used.

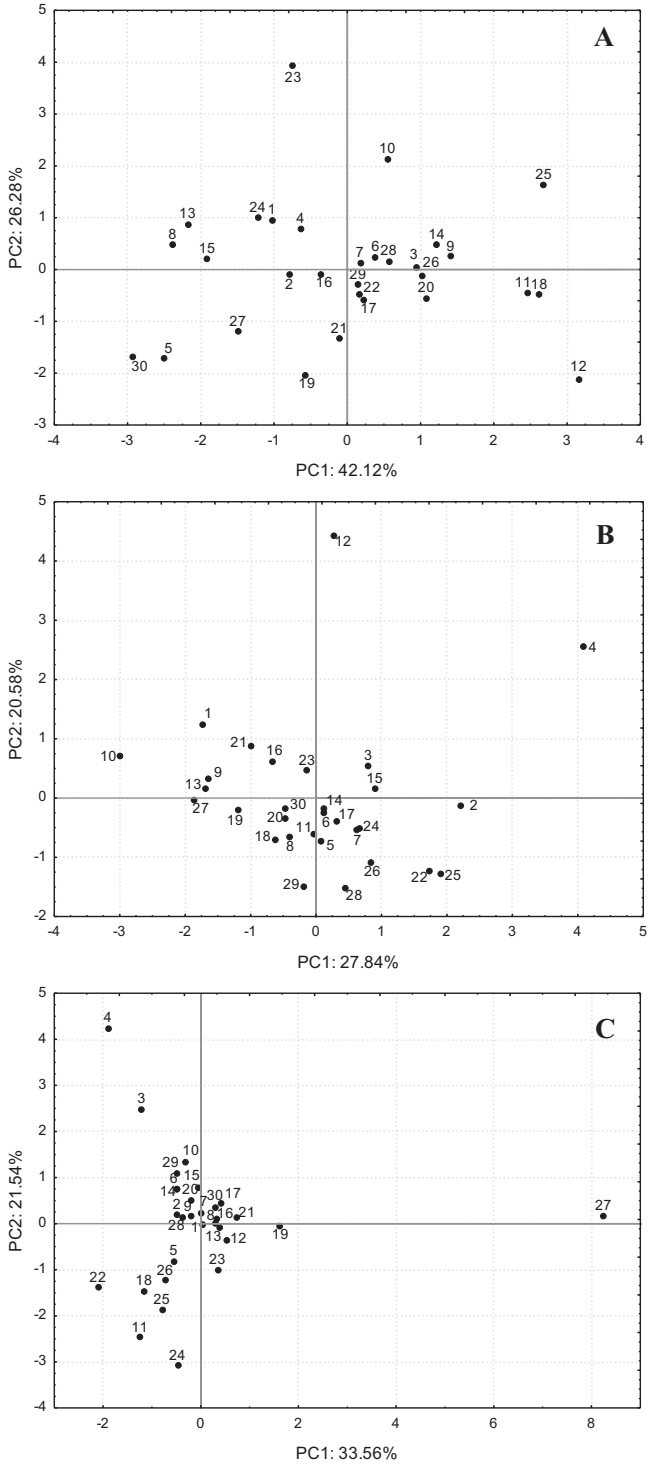


Fig. 1. Projection of cold-pressed flaxseed oils (1−30) in the space defined by the first two principal components (PC1 and PC2) based on the initial fatty acids composition (A), bioactive compounds content (B), and quality indices and water content (C).

Theoretical calculations of oxidizability were applied to predict the susceptibility of the flaxseed oils to oxidation (Table 1). Generally, the Cox values calculated for oils were similar (CV < 5%), and the highest value was observed in oil no. 30 (15.01), while the lowest was in oil no. 25 (12.35). Similarly, the SFA-to-USFA ratio was low variable, but values of the oxidizability index ranged between 0.09 and 0.13. The ratio of PUFA-to-SFA in oils averaged 7.22. A high value of the MUFA-to-SFA ratio was noticed in oil no. 1 (9.02), but similarly high was in oils nos. 8, 13, 23 and 30. The C18:3-to-C18:2 ratio was almost 2-fold lower than the ratio of MUFA-to-SFA. The values of the ratio did not exceed 5, and the highest value was observed in oil no. 30 (4.14), while the lowest values were in oils nos. 10 (2.26) and 25 (1.87). In turn, the values of MUFA-to-PUFA and C16:0-to-C18:2 ratios were within a narrow range, from 0.20 to 0.53. However, the lowest values characterized completely different oil samples, no. 30 for MUFA-to-PUFA ratio and no. 23 for C16:0-to-C18:2. Slightly higher values (0.51–1.24) characterized the C18:2-to-C18:0 ratio, and the highest value of the index reached oil no. 23. When the correlations between these oxidizability indices were examined, the Cox value was shown to be substantially linked with the MUFA-to-PUFA ($r = -0.93$) and the C18:2-to-C18:0 ratios ($r = 0.98$). The mentioned indices proved the highest susceptibility of oil no. 30 to oxidation and the lowest of oil no. 25. Also, the SFA-to-USFA and PUFA-to-SFA ratios as well as the MUFA-to-PUFA and C18:3-to-C18:2 ratios were strongly corelated ($r = -0.94$ and -0.95, respectively). However, according to the SFA-to-USFA and PUFA-to-SFA ratios, oil no. 1 and oil no. 12 turned out to be extremely different in terms of resistance to oxidation.

3.2. Bioactive compound content of cold-pressed flaxseed oils at their initial state

The predominant bioactive compounds in initial flaxseed oils were sterols and tocols (Table 2). The total sterols (TS) in oils accounted for 580 mg/100 g on average, and the highest values (>610 mg/100 g) were found in oils nos. 1, 10, 12, 13, 16, 21 and 23. However, the TS content in oil no. 25 was the lowest, and 100 g of the oil contained only 480 mg of these compounds. The highest share among all TS had two fractions, β-sitosterol (β-SIT) and cycloartenol (CYCA), 34% and 30%, respectively. The greatest amount of β-SIT was noted in oils nos. 12 and 21 (>240 mg/100 g), while CYCA in oil no. 23 (207.71 mg/100 g). The individual content of the other sterols (i.e. STIG, 25-H-24-MC, CAM) reached an average of 30–80 mg/100 g, and only oils nos. 1 and 12 showed higher contents of CAM. The content of tocols in oils ranged from 84.68 (no. 18) to 264.61 mg/100 g (no. 4), but most often it was ca. 100 mg/100 g. The main fractions of tocols were γ-T and Pl-8, and the content of γ-T was almost 3-fold higher than that of Pl-8 (on average 73.98 mg/100 g vs. 27.60 mg/100 g). Only oil no. 5 showed a low content of Pl-8 (the lowest of all oils, approx. 17 mg/100 g). The presence of α-T was found only in oils nos. 1, 4, 9, 16, 19, 26 and 29 (from 2.80 to 94.83 mg/100 g). The content of δ-T was low and oscillated mainly around 0.7–1.5 mg/100 g. It was also found that oils nos. 4, 6 and 9 contained the addition of α-tocopheryl acetate (65.25, 5.40 and 2.64 mg/100 g, respectively). The sterols and tocols (with the exception of α-T and δ-T) were found to be more stable than other bioactive compounds in commercial flaxseed oils (CV < 20%).

The analyzed oils also contained squalene, the content of which was highly varied (CV > 35%) and ranged from 2.43 (no. 10) to 7.68 mg/100 g (no. 4) (Table 2). A high content of squalene was also found in oil

Table 2
Content of squalene, sterols and tocols in studied cold-pressed flaxseed oils.

Oil number	Squalene (mg/100 g)	Sterols (mg/100 g)						Tocols (mg/100 g)				
		CAM	STIG	β-SIT	25-H-24-MC	CYCA	TS*	α-T	γ-T	δ-T	Pl-8	TT*
1	3.21^{hijkl}	115.36^{a}	34.10^{hijk}	221.42^{c}	54.80^{cd}	183.22^{bc}	663.39^{b}	6.00^{c}	74.67^{gh}	1.36^{cd}	36.94^{a}	118.98^{c}
2	7.42^{a}	81.69^{hijk}	35.66^{efgh}	184.84^{klm}	45.89^{ijkl}	159.34^{ijk}	560.82^{lmnop}	0.00^{f}	74.69^{gh}	0.75^{i}	29.69^{f}	105.13^{i}
3	5.37^{bc}	83.11^{hi}	37.38^{cd}	192.68^{ij}	44.25^{lm}	166.98^{gh}	583.35^{hi}	0.00^{f}	71.22^{kl}	0.88^{ghi}	36.61^{a}	108.70^{h}
4	7.68^{a}	77.88^{lmn}	34.84^{ghi}	180.29^{mn}	51.72^{ef}	159.83^{ijk}	560.35^{mnop}	94.83^{a}	71.52^{kl}	0.78^{i}	32.23^{cd}	264.61^{a}
5	3.71^{fg}	74.17^{op}	25.72^{s}	173.81^{o}	56.85^{c}	181.91^{bc}	558.47^{mnopq}	0.00^{f}	75.58^{fg}	1.01^{efgh}	16.88^{s}	93.46^{o}
6	3.37^{ghij}	80.05^{ijkl}	37.24^{cde}	188.22^{jk}	50.74^{efg}	161.40^{ij}	576.70^{ij}	9.89^{b}	71.70^{k}	0.75^{i}	28.22^{hi}	116.06^{d}
7	4.25^{ef}	81.30^{ijk}	31.70^{mn}	186.10^{kl}	44.03^{lm}	154.40^{l}	551.92^{q}	0.00^{f}	69.85^{mn}	0.76^{i}	28.44^{h}	99.05^{kl}
8	2.95^{ijklm}	82.67^{hij}	33.91^{ijkl}	179.75^{n}	45.47^{klm}	163.62^{hi}	553.27^{pq}	0.00^{f}	69.45^{mn}	0.00^{j}	28.04^{hi}	97.49^{mn}
9	2.83^{jklmn}	95.10^{d}	37.43^{cd}	208.60^{e}	44.50^{lm}	157.87^{jkl}	598.33^{f}	5.77^{c}	67.47^{o}	0.89^{fghi}	33.57^{b}	110.24^{g}
10	2.43^{n}	99.71^{c}	36.06^{defg}	220.82^{c}	52.31^{de}	175.65^{e}	627.05^{d}	0.00^{f}	79.84^{d}	2.02^{b}	31.93^{d}	113.78^{e}
11	4.14^{ef}	75.54^{no}	39.83^{b}	198.72^{gh}	32.89^{p}	172.05^{ef}	570.12^{ijk}	0.00^{f}	60.51^{q}	0.92^{fghi}	23.25^{mn}	84.68^{q}
12	4.84^{c}	102.88^{b}	44.60^{a}	242.18^{b}	50.04^{efgh}	159.43^{ijk}	661.39^{b}	0.00^{f}	92.20^{a}	1.41^{c}	32.78^{bc}	126.39^{b}
13	2.90^{jklmn}	86.92^{f}	34.99^{ghi}	214.40^{d}	56.20^{c}	181.43^{bc}	630.54^{d}	0.00^{f}	76.74^{f}	0.90^{fghi}	22.51^{no}	100.15^{jk}
14	3.86^{efg}	77.16^{mn}	32.87^{jklm}	196.21^{hi}	49.26^{fgh}	166.02^{gh}	586.69^{h}	0.00^{f}	68.04^{o}	1.02^{efg}	27.57^{ij}	96.63^{n}
15	5.63^{b}	84.14^{gh}	35.39^{fghi}	185.87^{kl}	48.13^{hij}	167.47^{gh}	569.02^{jkl}	0.00^{f}	73.31^{ij}	0.84^{hi}	26.78^{jk}	100.92^{j}
16	3.91^{efg}	91.91^{e}	34.84^{ghi}	203.05^{fg}	48.35^{ghi}	181.44^{bc}	616.57^{e}	2.86^{e}	73.85^{hi}	0.90^{fghi}	27.16^{j}	104.77^{i}
17	3.48^{ghi}	86.01^{fg}	34.43^{ghij}	194.34^{hi}	40.56^{n}	158.13^{jkl}	563.90^{klmno}	0.00^{f}	74.44^{ghi}	9.86^{a}	30.97^{e}	115.27^{de}
18	2.86^{jklmn}	72.01^{opq}	37.07^{def}	194.26^{hi}	29.90^{q}	184.97^{b}	565.17^{klmn}	0.00^{f}	60.69^{q}	0.75^{i}	23.48^{m}	84.92^{q}
19	2.86^{jklmn}	71.47^{pq}	28.55^{pqr}	169.83^{op}	55.87^{c}	180.30^{cd}	556.44^{opq}	2.80^{e}	74.46^{ghi}	0.88^{fghi}	20.95^{qr}	99.09^{kl}
20	2.78^{klmn}	80.59^{ijk}	32.32^{lm}	183.26^{lmn}	45.75^{jklm}	169.28^{fg}	565.95^{klm}	0.00^{f}	80.10^{d}	1.06^{ef}	29.49^{f}	110.66^{fg}
21	2.55^{mn}	99.09^{c}	38.90^{bc}	251.44^{a}	67.47^{a}	160.35^{ijk}	679.29^{a}	0.00^{f}	84.68^{c}	1.19^{de}	32.12^{cd}	117.98^{c}
22	5.44^{b}	68.15^{r}	27.55^{qr}	165.86^{p}	36.16^{o}	160.17^{ijk}	495.92^{t}	0.00^{f}	62.70^{p}	0.00^{j}	24.71^{l}	87.41^{p}
23	4.37^{de}	87.44^{f}	26.84^{rs}	207.48^{ef}	60.99^{b}	207.71^{a}	650.08^{c}	0.00^{f}	78.40^{e}	1.17^{e}	20.50^{r}	100.07^{jkl}
24	5.33^{bc}	67.87^{r}	29.55^{op}	173.06^{o}	48.24^{ghij}	172.14^{ef}	536.43^{r}	0.00^{f}	69.29^{n}	0.00^{j}	29.32^{fg}	98.62^{lm}
25	5.18^{bc}	64.94^{s}	25.61^{s}	159.90^{q}	28.86^{q}	156.83^{kl}	480.66^{u}	0.00^{f}	74.65^{gh}	0.78^{i}	28.66^{gh}	104.09^{i}
26	3.27^{hijk}	71.32^{q}	30.45^{no}	169.91^{op}	38.14^{no}	158.66^{jkl}	512.77^{s}	2.95^{de}	71.66^{kl}	0.83^{hi}	28.66^{gh}	104.10^{i}
27	2.71^{lmn}	79.02^{klm}	31.83^{mn}	198.37^{gh}	61.84^{b}	176.28^{de}	596.25^{fg}	3.29^{d}	72.39^{ijk}	1.05^{efg}	22.08^{op}	98.80^{klm}
28	3.03^{ijklm}	77.49^{lmn}	32.60^{klm}	182.13^{lmn}	43.26^{m}	169.21^{fg}	557.43^{nopq}	0.00^{f}	84.71^{c}	0.90^{fghi}	26.16^{k}	111.77^{f}
29	2.57^{mn}	79.63^{klm}	33.79^{ijkl}	188.21^{jk}	47.72^{hijk}	160.89^{ijk}	565.40^{klmn}	0.00^{f}	89.98^{b}	0.82^{i}	26.88^{jk}	117.68^{c}
30	3.25^{hijkl}	75.50^{no}	28.73^{pq}	184.61^{klm}	65.44^{a}	183.49^{bc}	588.08^{gh}	0.00^{f}	70.50^{lm}	0.84^{hi}	21.38^{pq}	92.72^{o}
$\bar{x}$	3.94	82.34	33.49	193.32	48.19	169.68	579.39	4.28	73.98	1.18	27.60	109.47
CV	35.05	13.78	13.06	10.95	19.79	7.07	8.07	403.48	9.99	143.15	17.41	28.40
min	2.43	64.94	25.61	159.90	28.86	154.40	480.66	0.00	60.51	0.00	16.88	84.68
max	7.68	115.36	44.60	251.44	67.47	207.71	679.29	94.83	92.20	9.86	36.94	264.61

CAM – campesterol; STIG – stigmasterol; β-SIT – β-sitosterol; 25-H-24-MC – 25-hydroxy-24-metoxycholesterol; CYCA – cycloartenol; TS – total sterols (contains unidentified other sterols-like compounds <65 mg/100 g); α-T – α-tocopherol; γ-T – γ-tocopherol; δ-T – δ-tocopherol; Pl-8 – plastochromanol-8; TT* – total tocopherol (contains identified α-tocopheryl acetate); $\bar{x}$ – mean value; CV – variation coefficient (%); min – minimal value; max – maximal value; a,b,c, … – mean values in the same column followed by different letters are significantly different ($p \leq 0.05$).

no. 2, but the content most often oscillated at the level of 2.5–3 mg/100 g.

The total contents of carotenoids (TC), chlorophylls (TCh) and phenolic compounds (TPC) were low and highly variable (Table 3). TC in oils did not exceed 1 mg/100 g, except for oil no. 12, which showed a higher value of TC (4.36 mg/100 g). The major fraction of carotenoids in all oils was zeaxanthin (ZEA) (over 40% of TC). The content of ZEA was up to 0.4 mg/100 g, with the exception of oil no. 12 (0.61 mg/100 g). The contents of lutein (LUT) and β-carotene (β-C) were similar in oils and ranged from 0.1 to 0.2 mg/100 g (except oil no. 12, 0.69 and 2.07 mg/100 g, respectively). Generally, the content of TCh in oils was below 0.10 mg/100 g, but a higher content was observed in oils nos. 13, 28 and 29 (Table 3). It was noted that oil no. 9 was characterized by a high content of TPC (2.79 mg/100 g), but almost 3-fold lower values were found in oils nos. 1, 19 and 27. In other oils, TPC did not exceed 0.3 mg/100 g and even trace amounts (<0.02 mg/100 g) were detected in some oils. The content of total phenolic acids (TPA) in oils ranged from 7.49 (no. 28) to 160.38 μg/100 g (no. 9). High TPA was noted in oils nos. 13 and 27, as well as oils nos. 1 and 19 (>60 μg/100 g). The main phenolic acid in oils was sinapic acid (SA), but its content was significantly varied (CV = 82.87%). The SA content was found to be above 30 μg/100 g in oils nos. 1, 9, 11, 13, 18, 19, 24 and 27, while oils nos. 10 and 22 had the lowest content (1.31 and 2.38 μg/100 g, respectively). The content of ferulic acid (FA) reached up to 37.84 μg/100 g (no. 9), but high contents were also observed in oils nos. 16 and 27. In other oils, its content was below 10 μg/100 g (often 2–5 μg/100 g) or absent (no. 25). The content of other phenolic acids was highly varied (CV > 120%). The content of p-OH-benzoic acid (p-OH-BA) was found only in oils nos. 7 and 8 (5.75 and 7.07 μg/100 g, respectively) and caffeic acid (CA) in oils nos. 9, 10, 13, 16, 19, 22 and 27 (from 1.54 to 25.34 μg/100 g). The content of p-coumaric acid (p-CA) was 2.78 μg/100 g on average, but in oil no. 9 it was estimated at 17.28 μg/100 g. In oils nos. 23, 27 and 28 p-CA was not identified.

Generally, the PCA analysis showed that most commercial flaxseed oils did not differ significantly based on the content of bioactive compounds (Fig. 1B). Although two oils, nos. 4 and 12, were clearly distinguished from others because of their high content of tocols (α-T, TT) or sterols (STIG, β-SIT), carotenoids and tocols (γ-T), respectively.

The obtained results of the content of bioactive compounds in flaxseed oils are in agreement with those previously reported by other researchers, e.g. Mikołajczak et al. [29], Lewinska et al. [32], Siger et al. [33].

3.3. *Quality indices and color of cold-pressed flaxseed oils at their initial state*

The initial quality of flaxseed oils is presented in Table 4. It was found that oil no. 27 had the highest content of free fatty acids, AV was almost 8 mg KOH/g. A high value of AV was also noted in oils nos. 23 and 19 (ca. 2 mg KOH/g), but most of the analyzed oils were characterized by AV ranging from 0.60 to 1.50 mg KOH/g, and additionally they did not contain primary oxidation products. In other oils, PV was low and did not exceed 1 mEq O_2/kg, only the higher values were found in oils nos. 4 and 10, 0.83 and 0.69 mEq O_2/kg, respectively. A high AnV

Table 3
Content of carotenoids, chlorophylls and phenolic compounds in studied cold-pressed flaxseed oils.

Oil number	Carotenoids (mg/100 g)					TCh (mg/100 g)	TPC (mg/100 g)	Phenolic acids (μg/100 g)					
	LUT	ZEA	β-C	α-C	TC*			p-OH-BA	CA	p-CA	FA	SA	TPA
1	0.12^{efgh}	0.32^{ghij}	0.12^{ghij}	0.03^{bcd}	0.61^{hijkl}	0.01^{k}	0.95^{c}	0.00^{d}	0.00^{g}	7.29^{b}	6.07^{gh}	50.30^{bc}	63.67^{c}
2	0.12^{defgh}	0.27^{klmn}	0.05^{lm}	0.01^{d}	0.47^{pq}	0.07^{e}	tr	0.00^{d}	0.00^{g}	1.30^{ij}	1.96^{lm}	5.88^{lmn}	9.14^{lm}
3	0.14^{cde}	0.47^{b}	0.23^{b}	0.03^{bcd}	0.93^{b}	0.01^{k}	0.16^{fg}	0.00^{d}	0.00^{g}	6.64^{b}	7.22^{g}	13.16^{hij}	26.04^{k}
4	0.12^{defgh}	0.26^{lmn}	0.14^{efghi}	0.03^{bcd}	0.59^{klmn}	0.00^{l}	tr	0.00^{d}	0.00^{g}	1.22^{j}	2.27^{lm}	5.16^{mno}	8.65^{lm}
5	0.11^{fgh}	0.26^{lmn}	0.05^{m}	0.01^{d}	0.43^{q}	0.03^{i}	tr	0.00^{d}	0.00^{g}	1.99^{hi}	4.14^{ijk}	28.42^{e}	34.55^{hi}
6	0.11^{fgh}	0.23^{n}	0.12^{ghij}	0.03^{bcd}	0.49^{nopq}	0.04^{h}	0.22^{f}	0.00^{d}	0.00^{g}	1.86^{hij}	1.48^{m}	17.99^{fg}	21.33^{k}
7	0.11^{fgh}	0.29^{jklm}	0.07^{jklm}	0.02^{bcd}	0.50^{mnopq}	0.01^{k}	tr	5.75^{b}	0.00^{g}	1.21^{j}	4.82^{hi}	11.25^{ij}	23.03^{k}
8	0.12^{efgh}	0.29^{jklm}	0.10^{hijk}	0.02^{bcd}	0.57^{lmno}	0.02^{j}	tr	7.07^{a}	0.00^{g}	1.50^{ij}	4.34^{ij}	36.71^{d}	49.62^{ef}
9	0.11^{gh}	0.23^{n}	0.10^{ijkl}	0.03^{bcd}	0.49^{nopq}	0.01^{k}	2.79^{a}	0.00^{d}	14.67^{b}	17.28^{a}	37.84^{a}	90.59^{a}	160.38^{a}
10	0.12^{defgh}	0.29^{jklm}	0.12^{ghij}	0.03^{bcd}	0.59^{klm}	0.02^{j}	0.18^{fg}	0.00^{d}	5.10^{e}	2.28^{gh}	11.61^{de}	1.31^{o}	20.30^{k}
11	0.10^{h}	0.39^{cd}	0.12^{ghij}	0.03^{bcd}	0.70^{fghij}	0.08^{d}	tr	0.00^{d}	0.00^{g}	2.05^{hi}	2.14^{lm}	36.60^{d}	40.79^{gh}
12	0.69^{a}	0.61^{a}	2.07^{a}	0.52^{a}	4.36^{a}	0.01^{k}	tr	0.00^{d}	0.00^{g}	4.12^{de}	2.51^{lm}	18.04^{fg}	24.66^{k}
13	0.13^{cdef}	0.36^{defg}	0.21^{bc}	0.04^{bc}	0.79^{cde}	0.12^{c}	0.05^{hi}	0.00^{d}	25.34^{a}	1.50^{ij}	10.16^{ef}	49.80^{bc}	86.81^{b}
14	0.12^{defgh}	0.38^{cde}	0.14^{efghi}	0.03^{bcd}	0.76^{cdefg}	0.05^{g}	tr	0.00^{d}	0.00^{g}	3.00^{fg}	5.57^{ghi}	15.06^{ghi}	23.63^{k}
15	0.13^{cdefg}	0.38^{cde}	0.20^{bcd}	0.03^{bcd}	0.80^{cde}	0.03^{i}	0.73^{d}	0.00^{d}	0.00^{g}	1.51^{ij}	1.42^{mn}	9.66^{jkl}	12.59^{lm}
16	0.13^{cdefg}	0.41^{c}	0.17^{cdefg}	0.04^{bc}	0.83^{cd}	0.02^{j}	0.33^{e}	0.00^{d}	6.99^{d}	4.53^{d}	20.45^{c}	20.54^{f}	52.50^{de}
17	0.11^{efgh}	0.25^{mn}	0.08^{jklm}	0.02^{bcd}	0.48^{opq}	0.03^{i}	tr	0.00^{d}	0.00^{g}	3.27^{f}	4.89^{hi}	16.49^{fgh}	24.66^{k}
18	0.11^{gh}	0.34^{efghi}	0.10^{ijklm}	0.02^{bcd}	0.60^{jkl}	0.02^{j}	tr	0.00^{d}	0.00^{g}	3.52^{ef}	5.42^{ghi}	35.94^{d}	44.88^{fg}
19	0.14^{cd}	0.33^{fghij}	0.18^{bcdef}	0.04^{bc}	0.78^{cdef}	0.01^{k}	1.04^{b}	0.00^{d}	8.73^{c}	3.46^{ef}	12.11^{d}	38.07^{d}	62.38^{c}
20	0.13^{cdefg}	0.35^{defgh}	0.15^{defgh}	0.03^{bcd}	0.72^{efgh}	0.06^{f}	0.78^{d}	0.00^{d}	0.00^{g}	5.75^{c}	4.43ij	16.16^{fgh}	26.34^{jk}
21	0.13^{cdefg}	0.30^{jkl}	0.13^{fghi}	0.03^{bcd}	0.67^{ghijk}	0.06^{f}	tr	0.00^{d}	0.00^{g}	0.37^{k}	2.19^{lm}	19.01^{fg}	21.57^{k}
22	0.11^{fgh}	0.30^{ijkl}	0.06^{jklm}	0.01^{bcd}	0.52^{lmnop}	0.02^{j}	tr	0.00^{d}	2.82^{f}	0.24^{k}	2.74^{klm}	2.38^{no}	8.18^{lm}
23	0.12^{defgh}	0.29^{jklm}	0.14^{efghi}	0.04^{bc}	0.62^{ijkl}	0.08^{d}	0.13^{gh}	0.00^{d}	0.00^{g}	0.00^{k}	6.42^{g}	10.39^{ijk}	16.81^{l}
24	0.12^{defgh}	0.37^{cdef}	0.06^{klm}	0.01^{cd}	0.61^{jkl}	0.05^{g}	tr	0.00^{d}	0.00^{g}	3.61^{ef}	5.36^{ghi}	48.82^{c}	57.79^{cd}
25	0.12^{efgh}	0.31^{hijk}	0.10^{ijkl}	0.02^{bcd}	0.56^{klmn}	0.05^{g}	0.04^{i}	0.00^{d}	0.00^{g}	1.34^{ij}	0.00^{n}	8.00^{jklm}	9.34^{lm}
26	0.12^{cdefgh}	0.32^{ghij}	0.10^{ijkl}	0.02^{bcd}	0.65^{hijkl}	0.03^{i}	tr	0.00^{d}	0.00^{g}	1.52^{hij}	2.76^{klm}	6.28^{klmn}	10.56^{lm}
27	0.11^{fgh}	0.26^{lmn}	0.07^{jklm}	0.02^{bcd}	0.44^{q}	0.01^{k}	0.93^{c}	1.54^{c}	0.00^{g}	0.00^{k}	25.62^{b}	54.09^{b}	81.25^{b}
28	0.15^{c}	0.37^{def}	0.14^{efghi}	0.03^{bcd}	0.77^{defg}	0.31^{b}	tr	0.00^{d}	0.00^{g}	0.00^{k}	3.11^{jkl}	4.38^{mno}	7.49^{m}
29	0.21^{b}	0.35^{defgh}	0.19^{bcde}	0.04^{b}	0.86^{bc}	0.36^{a}	tr	0.00^{d}	0.00^{g}	0.03^{k}	6.03^{gh}	26.61^{e}	32.66^{ij}
30	0.22^{b}	0.31^{hijk}	0.12^{ghij}	0.03^{c}	0.72^{efghi}	0.02^{j}	tr	0.00^{d}	0.00^{g}	1.12^{j}	9.24^{f}	28.74^{e}	39.18^{gh}
$\bar{x}$	0.15	0.33	0.19	0.04	0.76	0.05	0.68	0.43	2.17	2.76	7.05	24.18	36.59
CV	72.33	23.87	190.31	206.20	90.60	148.51	113.52	382.71	253.08	121.62	114.45	82.87	87.25
min	0.10	0.23	0.05	0.01	0.43	0.00	0.04	0.00	0.00	0.00	0.00	1.31	7.49
max	0.69	0.61	2.07	0.52	4.36	0.36	2.79	7.07	25.34	17.28	37.84	90.59	160.38

LUT – lutein; ZEA – zeaxanthin; β-C – β-carotene; α-C – α-carotene; TC* – total carotenoids (contains unidentified other carotenoids <0.47 mg/100 g); TCh – total chlorophylls; TPC – total phenolic compounds; tr – trace amounts (<0.02 mg/100 g); p-OH-BA – p-OH-benzoic acid; CA – caffeic acid; p-CA – p-coumaric acid; FA – ferulic acid; SA – sinapic acid; TPA – total phenolic acid; $\bar{x}$ – mean value; CV – variation coefficient (%); min – minimal value; max – maximal value; a,b,c, … – mean values in the same column followed by different letters are significantly different ($p \leq 0.05$).

(1.29) was observed in oil no. 4, which indicates the highest degree of oil oxidation. In oils nos. 3 and 22, AnV was slightly above 0.4, while in other oils, no secondary oxidation products were found, or their content was low (AnV < 0.1). The content of conjugated dienes (CD) in oils was low and similar to each other, ranging from 0.16 to 0.24%. Only in oil no. 27, CD was observed at 0.28%. The content of conjugated trienes (CT) was not found in oils, but the exception constituted oil no. 27 (0.01%). The water content (WC) was the highest in oils nos. 27 and 19 (>1200 ppm), and the lowest in oil no. 3 (<400 ppm). A similarly low amount of WC (almost 600 ppm) was observed in oil no. 1. However, the majority of oils studied had WC values in the range of 800–900 ppm. In turn, PV and AnV were found to be the most variable quality indices (CV > 160%), which indicates a significant diversity of oils in terms of oxidation degree. It is probably a result of raw material quality, manufacturer practices, and/or time from production to opening the packaging. For example, the varied oxidation degree of fresh flaxseed oils was reported by Zhang et al. [3], Tańska et al. [10], and Choo et al. [13].

The results of the initial state parameters of the analyzed flaxseed oils indicate that the oily research materials are generally of good quality and have a low degree of hydrolysis and oxidation processes. Parameter values do not exceed the levels specified by the Codex Standard [35] for edible fats and oils. Questionable is only oil no. 27 due to the high content of products of the hydrolysis process (AV). The high AV is probably associated with the higher WC in flaxseeds, which affected the quality of the cold-pressed oil [36]. The literature states that the moisture content of seeds depends both on the length and parameters of storage (mainly on temperature and relative humidity) [37], and is also subject to changes due to the diffusion and adsorption of water from the air as well as the absorption of water released during seed respiration [38]. The WC in the studied flaxseed oils complies with the requirements of Codex Alimentarius [35], according to which matter volatile at 105 °C in oils should be below 0.2%.

The L* parameter (brightness parameter) in oils ranged from 80.34% (no. 12) to 86.85% (no. 4) (Table 4). Generally, the average value of the L* parameter was 84.58%, and this parameter was very stable (CV = 1.52%). The a* parameter (color intensity from green to red) was characterized by negative values (values characteristic of green color), and oscillated from −18.70 (no. 14) to −14.02 (no. 12). Equally low values of the a* parameter were observed in oils nos. 6, 17, 20, 28, 29 and 30 (below −18) as opposed to oils nos. 11, 22 and 24 (high values of the a* parameter, ca. –15). In turn, the b* parameter (color from blue to yellow) was more varied and ranged from 59.84 (no. 24) to 85.94 (no. 6). High and positive values of this parameter indicate the presence of the yellow color. However, oils nos. 1, 5, 11, 18, 23, 24 and 26 were characterized by a lower yellowness compared to the other oils (b* parameter from 63.15 to 80.99). The color measurements performed by using digital image analysis confirmed only a small variation between the studied flaxseed oils (CV of all color parameters up to 7.97%), that is also visible in the photographs (Supplementary material 2). Attention was mainly focused on oil no. 12, which had a low level of brightness and a higher share of green color.

The PCA analysis based on the initial quality and color characteristics of oils (Fig. 1C) indicated 3 oils as different, i.e. nos. 3, 4 and 27, mainly due to low WC (no. 3), high AnV (no. 4) or high AV and WC (no.

Table 4
Quality indices and color parameters of cold-pressed flaxseed oils before and after one-month storage with light exposure.

Oil number	Initial characteristics of oils										Characteristics of oxidized oils							
	WC (ppm)	IP (h)	AV1 (mg KOH/g)	PV1 (mEq O_2/kg)	AnV1 (−)	CD1 (%)	CT1 (%)	L*1 (%)	a*1 (−)	b*1 (−)	AV2 (mg KOH/g)	PV2 (mEq O_2/kg)	AnV2 (−)	CD2 (%)	CT2 (%)	L*2 (%)	a*2 (−)	b*2 (−)
1	572.25^{u}	2.44^{e}	0.88^{ijk}	0.00^{k}	0.08^{de}	0.24^{b}	0.00^{b}	83.56^{u}	-17.04^{i}	80.99^{q}	1.59^{fghij}	18.28^{jk}	0.59^{k}	0.41^{ab}	0.00^{b}	84.03^{ji}	-17.74^{lmnop}	82.47^{bcdef}
2	751.80^{n}	2.15^{hij}	0.71^{lmn}	0.00^{k}	0.02^{gh}	0.18^{h}	0.00^{b}	84.06^{rq}	-17.63^{n}	83.64^{h}	1.24^{ijk}	9.71^{n}	0.03^{op}	0.34^{cde}	0.00^{b}	83.82_{j}	-17.82^{mnopq}	83.43^{ab}
3	338.10^{w}	2.02^{kl}	0.85^{ijkl}	0.57^{c}	0.46^{b}	0.22^{d}	0.00^{b}	83.63^{t}	-17.78^{p}	83.27^{k}	1.40^{hijk}	20.48^{i}	1.84^{c}	0.33^{cdef}	0.00^{b}	84.78^{gh}	-17.91^{opq}	83.12^{bc}
4	713.90^{p}	1.58^{op}	0.37^{o}	0.83^{a}	1.29^{a}	0.18^{h}	0.00^{b}	83.68^{s}	-17.55^{lm}	83.33^{j}	0.80^{l}	20.62^{i}	3.31^{a}	0.33^{cdef}	0.00^{b}	83.25^{k}	-17.70^{klmno}	82.95^{cd}
5	892.10^{g}	1.69^{n}	1.75^{d}	0.00^{k}	0.03^{gh}	0.17^{i}	0.00^{b}	86.85^{a}	-17.77^{p}	78.00^{r}	2.56^{c}	18.37^{jk}	1.63^{e}	0.37^{bc}	0.00^{b}	87.14^{a}	-16.93^{f}	71.47^{l}
6	717.65^{op}	2.32^{f}	1.14^{gh}	0.15^{gh}	0.00^{h}	0.18^{h}	0.00^{b}	84.82^{lk}	-18.23^{t}	85.94^{a}	1.85^{efg}	18.22^{j}	0.00^{p}	0.29^{defg}	0.00^{b}	84.60^{gh}	-18.41st	85.74^{a}
7	881.45^{h}	2.71^{c}	0.99^{hi}	0.00^{k}	0.09^{de}	0.19^{g}	0.00^{b}	84.06^{rq}	-17.63^{n}	83.64^{h}	1.66^{fgh}	13.45^{m}	0.12^{no}	0.35^{bcd}	0.00^{b}	84.43^{ghi}	-17.59^{ijklm}	80.66^{defghi}
8	841.20^{j}	1.93^{m}	1.66^{d}	0.00^{k}	0.00^{h}	0.20^{f}	0.00^{b}	84.81^{l}	-17.80^{p}	84.27^{e}	2.56^{c}	27.62^{g}	2.04^{b}	0.28^{efgh}	0.00^{b}	83.78^{jk}	-18.05^{qr}	83.38^{bc}
9	925.50^{f}	4.64^{a}	1.42^{e}	0.00^{k}	0.28^{c}	0.16^{j}	0.00^{b}	83.08^{v}	-16.28^{e}	82.57^{m}	2.26^{cde}	27.23^{g}	0.29^{m}	0.28^{efgh}	0.00^{b}	84.23^{hij}	-15.67^{c}	79.43^{hij}
10	683.00^{q}	2.08^{jk}	0.74^{klm}	0.69^{b}	0.00^{h}	0.23^{c}	0.00^{b}	84.31^{o}	-17.09^{j}	81.48^{u}	1.64^{fghi}	20.80^{i}	1.41^{f}	0.45^{a}	0.00^{b}	85.56^{d}	-16.69^{e}	79.70^{ghij}
11	672.10^{r}	1.99^{klm}	1.20^{fg}	0.00^{k}	0.00^{h}	0.18^{h}	0.00^{b}	85.11^{i}	-15.27^{c}	63.15^{y}	1.97^{def}	23.44^{h}	1.73^{d}	0.30^{defg}	0.00^{b}	86.63^{ab}	-16.58^{e}	69.35^{l}
12	719.85^{o}	2.82^{b}	0.67^{lmn}	0.00^{k}	0.00^{h}	0.22^{d}	0.00^{b}	$80.34^{\times}$	-14.02^{a}	84.97^{b}	1.23^{ijk}	27.92^{g}	0.00^{p}	0.33^{cdef}	0.00^{b}	80.58^{l}	-13.85^{a}	82.33^{bcdef}
13	947.40^{e}	2.42^{e}	1.11^{gh}	0.00^{k}	0.00^{h}	0.20^{f}	0.00^{b}	84.07^{q}	-17.52^{l}	82.53^{n}	1.10^{kl}	15.48^{l}	0.00^{p}	0.30^{defg}	0.00^{b}	83.68^{jk}	-17.55^{ijkl}	83.33^{bc}
14	788.95^{m}	2.23^{gh}	0.69^{lmn}	0.13^{ghi}	0.00^{h}	0.18^{h}	0.00^{b}	84.64^{n}	-18.70^{w}	84.07^{g}	1.11^{kl}	9.47^{n}	0.00^{p}	0.26^{gh}	0.00^{b}	85.32^{gh}	-17.66^{ijklmn}	79.38^{defghi}
15	1004.30^{c}	1.96^{lm}	0.67^{lmn}	0.39^{e}	0.00^{h}	0.20^{f}	0.00^{b}	85.41^{g}	-17.70^{o}	84.78^{c}	1.33^{hijk}	29.44^{f}	0.50^{kl}	0.33^{cdef}	0.00^{b}	85.36^{def}	-17.92^{nopq}	84.73^{bcd}
16	784.85^{m}	2.88^{b}	1.46^{e}	0.06^{j}	0.00^{h}	0.22^{d}	0.00^{b}	84.85^{k}	-17.57^{m}	84.32^{e}	2.43^{c}	27.14^{g}	0.00^{p}	0.28^{efgh}	0.00^{b}	85.66^{d}	-17.29^{hijk}	82.84^{ab}
17	948.35^{e}	2.39^{ef}	1.37^{ef}	0.21^{f}	0.00^{h}	0.22^{d}	0.00^{b}	85.84^{d}	-18.36^{u}	84.01^{g}	2.36^{cd}	37.08^{ab}	0.17^{n}	0.22^{h}	0.00^{b}	85.42^{cd}	-17.46^{gh}	80.53^{bcde}
18	653.30^{t}	2.20^{hi}	1.18^{g}	0.18^{fg}	0.00^{h}	0.19^{g}	0.00^{b}	85.55^{f}	-16.19^{d}	$67.40^{\times}$	1.90^{efg}	32.92^{e}	1.37^{fg}	0.34^{cde}	0.00^{b}	86.64^{de}	-14.63^{hij}	59.99^{efghi}
19	1245.70^{b}	2.14^{hij}	1.96^{c}	0.00^{k}	0.04^{fg}	0.21^{e}	0.00^{b}	84.03^{r}	-17.52^{l}	84.98^{b}	3.54^{b}	1.96^{o}	0.08^{nop}	0.33^{cdef}	0.00^{b}	84.81^{ab}	-17.56^{b}	82.14^{n}
20	659.95^{s}	1.96^{lm}	0.97^{hij}	0.06^{j}	0.00^{h}	0.21^{e}	0.00^{b}	84.68^{m}	-18.47^{v}	84.12^{f}	1.67^{fgh}	36.46^{bc}	1.05^{i}	0.24^{gh}	0.00^{b}	84.49^{fg}	-18.43^{ijkl}	81.96^{bcdef}
21	974.10^{d}	2.03^{kl}	1.37^{ef}	0.00^{k}	0.00^{h}	0.21^{e}	0.00^{b}	84.18^{p}	-17.88^{q}	84.58^{d}	2.22^{efg}	36.18^{c}	1.22^{h}	0.28^{efgh}	0.00^{b}	84.40^{ghi}	-17.97^{t}	81.06^{bcdefg}
22	671.35^{r}	2.31^{fg}	0.65^{mn}	0.00^{k}	0.44^{b}	0.16^{j}	0.00^{b}	85.88^{c}	-15.24^{c}	69.59^{u}	1.11^{kl}	32.51^{e}	1.83^{c}	0.44^{a}	0.00^{b}	84.49^{ghi}	-18.18^{pqr}	77.61^{cdefgh}
23	848.40^{i}	2.54^{d}	2.16^{b}	0.11^{hij}	0.06^{ef}	0.22^{d}	0.00^{b}	85.12^{i}	-16.68^{g}	72.72^{t}	3.58^{b}	33.24^{e}	1.28^{gh}	0.28^{efgh}	0.00^{b}	85.39^{ghi}	-17.44^{rs}	76.59^{jk}
24	816.25^{k}	1.95^{lm}	0.80^{jklm}	0.00^{k}	0.02^{gh}	0.24^{b}	0.00^{b}	85.89^{c}	-15.01^{b}	59.84^{z}	1.50^{ghjik}	18.33^{jk}	0.02^{p}	0.30^{defg}	0.00^{b}	86.13^{de}	-15.99^{hi}	64.29^{k}
25	820.90^{k}	2.63^{c}	0.68^{lmn}	0.00^{k}	0.00^{h}	0.20^{f}	0.00^{b}	85.69^{e}	-16.46^{f}	67.54^{v}	1.12^{kl}	0.68^{p}	0.00^{p}	0.33^{cdef}	0.00^{b}	87.05^{bc}	-16.12^{d}	66.07^{m}
26	750.10^{n}	2.13^{ij}	0.67^{lmn}	0.00^{k}	0.00^{h}	0.21^{e}	0.00^{b}	86.22^{b}	-16.82^{h}	75.32^{s}	1.21^{jkl}	16.26^{l}	0.87^{j}	0.34^{cde}	0.00^{b}	86.23^{a}	-17.54^{d}	78.40^{m}
27	1341.70^{a}	1.54^{p}	7.32^{a}	0.12^{hi}	0.00^{h}	0.28^{a}	0.01^{a}	82.08^{w}	-17.45^{k}	81.98^{o}	13.07^{a}	37.45^{a}	0.31^{m}	0.44^{a}	0.01^{a}	84.95^{b}	-17.15^{ijkl}	78.74^{ijk}
28	657.50st	1.97^{lm}	0.64^{n}	0.00^{k}	0.09^{de}	0.22^{d}	0.00^{b}	84.91^{j}	-18.16^{s}	81.06^{p}	2.45^{c}	17.87^{k}	0.45^{l}	0.30^{defg}	0.00^{b}	85.38^{efg}	-17.56^{fg}	77.52^{hijk}
29	806.75^{l}	2.01^{klm}	1.39^{e}	0.47^{d}	0.00^{h}	0.18^{h}	0.00^{b}	85.34^{h}	-18.03^{r}	83.59^{i}	1.60^{fghij}	27.55^{g}	1.58^{e}	0.27^{fgh}	0.00^{b}	85.38^{de}	-17.68^{ijkl}	80.48^{jk}
30	894.10^{g}	1.66^{no}	0.77^{klm}	0.09^{ij}	0.00^{h}	0.22^{d}	0.00^{b}	84.82^{kl}	-18.47^{v}	82.91^{l}	1.67^{fgh}	35.23^{d}	0.16^{n}	0.35^{bcd}	0.00^{b}	85.17^{de}	-17.75^{jklmno}	79.27^{fghi}
$\bar{x}$	810.76	2.24	1.28	0.14	0.10	0.20	0.00	84.58	−17.21	79.69	2.19	24.85	0.80	0.32	0.00	84.96	−17.23	78.63
CV	23.45	25.31	95.90	166.23	266.86	12.29	31.10	1.52	6.61	9.01	98.79	33.45	106.79	17.45	31.10	1.52	6.12	7.97
min	338.10	1.54	0.37	0.00	0.00	0.16	0.00	80.34	−18.70	59.84	0.80	9.46	0.00	0.22	0.00	80.58	−18.43	59.99
max	1341.70	4.64	7.32	0.83	1.29	0.28	0.01	86.85	−14.02	85.94	13.07	37.45	3.31	0.45	0.01	87.14	−13.85	85.74

WC – water content; IP – induction period; AV – acid value; PV – peroxide value; AnV – anisidine value; CD – conjugated dienes content; CT – conjugated trienes content; L*, a*, b* – color parameters; $\bar{x}$ – mean value; CV – variation coefficient (%); min – minimal value; max – maximal value; 1 or 2 – fresh or oxidized oil; a,b,c, … – mean values in the same column followed by different letters are significantly different ($p \leq 0.05$).

27). In choosing the first two PCs, 55.10% of the total variability was explained (PC1 = 33.56%, PC2 = 21.54%). It was found that AV, CT and WC are positively correlated with PC1, whereas PV and AV and b* color parameter are strongly positively correlated with PC2.

3.4. Oxidation stability and formation of oxidation products during storage of cold-pressed flaxseed oils

The oxidative stability of the studied flaxseed oils was determined immediately after opening the package using the Rancimat test, in which the induction period (IP) was computed. The IP of oils ranged from 1.54 h (no. 27) to 4.64 h (no. 9) (Table 4). An equally long IP was observed for oils nos. 12 and 16 (almost 3 h), while oils nos. 4, 5 and 30 were characterized by a short IP (<1.7 h). However, the IP of the oils most often oscillated around 2–2.5 h.

Generally, the storage of oils with light exposure (one month) resulted in an increase in the values of individual parameters and thus a deterioration of the quality of the products (Table 4, Supplementary material 3). The AV of oxidized oils increased at least 1.5-fold, and the most noticeable changes were observed in the values for oils nos. 4, 10,

Table 5
Calculated linear correlation coefficients between the initial state parameters and induction period and differences in oxidation products and color parameters after storage of cold-pressed flaxseed oils.

Initial state parameters	IP	ΔAV	ΔPV	ΔAnV	ΔCD	ΔCT	ΔL*	Δa*	Δb*	ΔE
Fatty acids composition										
C16:0	0.09	−0.09	0.05	−0.07	−0.32	0.00	−0.03	0.09	−0.07	−0.06
C18:0	0.02	−0.04	0.11	0.02	−0.17	0.00	0.06	0.13	−0.19	0.40*
C18:1	0.37*	−0.28	−0.36	−0.07	0.16	0.00	0.31	0.10	−0.02	0.07
C18:2	0.12	−0.08	0.06	0.16	−0.31	0.00	−0.13	−0.22	0.42*	−0.18
C18:3	−0.38*	0.28	0.23	−0.03	0.10	0.00	−0.18	0.02	−0.19	−0.01
TFA	0.40*	0.06	0.14	−0.02	0.04	0.00	0.41*	0.01	−0.05	0.33
SFA	0.07	−0.07	0.11	−0.01	−0.26	0.00	0.04	0.13	−0.17	0.27
MUFA	0.37*	−0.28	−0.36	−0.07	0.16	0.00	0.31	0.09	−0.01	0.07
PUFA	−0.35	0.27	0.30	0.07	−0.09	0.00	−0.29	−0.12	0.05	−0.13
n-3/n-6	−0.24	0.19	0.07	−0.10	0.27	0.00	0.04	0.18	−0.39*	0.18
Theoretical oxidizability indices										
Cox value	−0.39*	0.29	0.27	0.01	0.02	0.00	−0.24	−0.04	−0.09	−0.07
SFA/USFA	0.07	−0.07	0.11	−0.01	−0.26	0.00	0.04	0.13	−0.17	0.27
PUFA/SFA	−0.19	0.15	0.05	0.04	0.16	0.00	−0.14	−0.15	0.16	−0.25
PUFA/MUFA	0.36	−0.26	−0.34	−0.08	0.14	0.00	0.32	0.11	−0.03	0.09
C16:0/C18:2	−0.03	0.06	0.02	−0.15	0.13	0.00	0.14	0.23	−0.39*	0.18
C18:2/C18:0	−0.16	0.15	0.29	0.13	−0.34	0.00	−0.30	−0.21	0.30	−0.20
C18:3/C18:2	−0.40*	0.31	0.31	0.01	−0.07	0.00	−0.23	−0.02	−0.09	−0.07
Bioactive compounds										
Squalene	−0.11	−0.26	−0.26	0.01	0.21	0.00	−0.25	−0.35	0.38*	−0.20
CAM	0.36*	−0.04	0.25	−0.07	−0.08	0.00	0.04	0.09	−0.10	−0.37*
STIG	0.22	−0.14	0.23	0.02	−0.17	0.00	0.08	0.14	−0.10	−0.27
ß-SIT	0.27	0.03	0.36	−0.05	−0.16	0.00	0.19	0.16	−0.15	−0.13
25-H-24-MC	−0.22	0.32	0.21	−0.09	−0.08	0.00	0.03	0.11	−0.19	−0.23
CYCA	−0.17	0.24	0.17	0.09	−0.03	0.00	0.24	0.07	0.03	0.20
TS	0.17	0.11	0.33	−0.06	−0.20	0.00	0.18	0.18	−0.17	−0.22
α-T	−0.17	−0.07	−0.07	0.30	0.11	0.00	−0.16	−0.04	0.04	−0.26
γ-T	−0.05	0.00	0.05	−0.09	−0.29	0.00	−0.09	0.22	−0.28	−0.38*
Δ-T	0.07	0.04	0.26	−0.15	−0.38*	0.00	−0.07	0.29	−0.21	−0.01
Pl-8	0.32	−0.29	−0.04	−0.06	−0.13	0.00	−0.07	−0.04	0.06	−0.47*
TT	−0.13	−0.12	−0.04	0.25	−0.01	0.00	−0.20	0.03	−0.03	−0.40*
LUT	0.13	−0.09	0.12	−0.18	−0.07	0.00	−0.05	0.09	−0.14	−0.08
ZEA	0.00	−0.20	−0.02	−0.10	−0.20	0.00	0.09	−0.02	0.06	−0.04
β-C	0.19	−0.10	0.09	−0.18	−0.07	0.00	−0.03	0.06	−0.09	−0.10
α-C	0.21	−0.07	0.10	−0.19	−0.07	0.00	−0.02	0.06	−0.09	−0.08
TC	0.16	−0.12	0.08	−0.17	−0.10	0.00	−0.02	0.05	−0.08	−0.09
TCh	−0.14	−0.07	−0.03	0.09	−0.26	0.00	−0.09	0.10	−0.06	0.02
TPC	0.62*	0.26	0.08	−0.26	0.02	0.00	0.33	0.09	−0.11	−0.12
p-OH-BA	0.02	−0.03	−0.04	0.17	−0.01	0.00	−0.25	−0.03	−0.06	−0.13
CA	0.19	−0.08	−0.19	−0.17	0.12	0.00	0.02	0.02	0.05	−0.19
p-CA	0.04	−0.13	−0.08	0.08	0.16	0.00	0.23	0.14	−0.07	−0.17
FA	0.04	0.47*	0.12	−0.05	0.20	0.00	0.52*	0.22	−0.18	−0.04
SA	−0.28	0.26	0.01	0.11	0.18	0.00	0.35	0.10	−0.05	0.04
TPA	−0.13	0.25	−0.01	0.04	0.20	0.00	0.36*	0.13	−0.08	−0.04
Quality indices										
AV1	−0.15	0.92*	0.31	−0.04	0.02	0.00	0.55*	0.11	−0.17	0.16
PV1	−0.29	−0.09	0.08	0.44*	0.12	0.00	0.05	0.16	−0.09	−0.30
AnV1	−0.06	−0.13	−0.02	0.39*	0.26	0.00	−0.20	−0.22	0.18	−0.11
CD1	−0.29	0.62*	0.21	−0.23	−0.24	0.00	0.44*	0.09	−0.03	−0.18
CT1	−0.23	0.93*	0.27	−0.10	0.14	0.00	0.57*	0.07	−0.12	0.10
WC	−0.01	0.56*	0.07	−0.33	−0.08	0.00	0.21	0.18	−0.26	0.03
Color parameters										
L*1	−0.26	−0.32	−0.07	0.26	−0.02	0.00	−0.31	−0.11	0.16	0.33
a*1	0.30	−0.08	0.02	0.03	0.29	0.00	0.10	−0.46*	0.48*	0.39*
b*1	0.06	0.07	0.06	−0.19	−0.17	0.00	−0.16	0.38*	−0.49*	−0.60*

* Means that correlation coefficients are significant at $p \leq 0.05$; abbreviations are explained in Tables 1–4; Δ – differences of quality indices and color parameters between fresh and oxidized oils.

28 and 30. Most often, the AV ranged from 1 to 2.5 mg KOH/g. The highest AV was observed for oil no. 27 (13.07 mg KOH/g), but also nos. 19 and 23 had relatively high AV. The lowest AV (only 0.8 mg KOH/g) was noted in oil no. 4. There were no changes in AV in oil no. 13. In all oils, a significant increase in the degree of oxidation was observed, which is indicated by the values of the PV parameter. Oils nos. 17, 18, 20–23, 27 and 30 had a high PV (>30 mEq O_2/kg), but also a large number of oils had a PV higher than 20 mEq O_2/kg. The lowest PV was observed for oils nos. 19 (1.96 mEq O_2/kg) and 25 (0.68 mEq O_2/kg). The values of the AnV parameter were also several fold higher in oxidized oils, and the highest value was found in oil no. 4 (>3). An equally high AnV was noted in oils nos. 3, 5, 8, 11 and 22, while in oils nos. 12–14, 16 and 25 no secondary products of the oxidation process were detected. It was found that the content of CD in the oxidized oils ranged from 0.22% (no. 17) to 0.45% (no. 10). A high CD content was also noted in oils nos. 22 and 27, but the most frequently values of this parameter oscillated around 0.30–0.35%. There were no changes in the content of CT compared to the initial oils.

According to research by Tańska et al. [10], the IP of initial flaxseed oils is highly diversified and may range from 2 h to even 5 h. The literature suggests that the lower IP is a consequence of changes in the oil and/or raw materials used for its production (e.g. changes in unsaturated fatty acids, presence of primary/secondary oxidation products, increase in the moisture content of raw material as a result of improper storage) [12].

3.5. Effect of initial state of cold-pressed flaxseed oils on the rate of their oxidation

Table 5 shows linear correlation coefficients between the initial state parameters and induction period and detected differences in oxidation products and color parameters after storage of cold-pressed flaxseed oils.

The correlation coefficients indicate that the PUFA share (mainly C18:3 acid) of oils affects the IP, which have a mutually negative correlation ($r = -0.35$ and $r = -0.38$, respectively). A different relationship occurs with the share of MUFA (mainly C18:1 acid) and IP, where a positive correlation was noted ($r = 0.37$). In addition, the Cox value and C18:3-to-C18:2 ratio also seem to have negative effects on IP ($r = -0.39$ and $r = -0.40$, respectively). Among the bioactive compounds of oils, the content of CAM ($r = 0.36$) and TPC ($r = 0.62$) were the most favorable for IP due to a positive correlation. A negative correlation was observed between individual parameters of the initial state of oils and IP (r ranged from −0.29 to −0.06).

The share of MUFA (mainly C18:1 acid) was negatively correlated with the content of ΔPV ($r = -0.36$), while the share of SFA (mainly C16:0 acid) with the content of ΔCD ($r = -0.26$ and $r = -0.32$, respectively). It also seems that the PUFA-to-MUFA ratio was important for the hydrolysis and oxidation processes and influenced ΔAV and ΔPV (negative correlation, r = −0.26 and −0.34, respectively). On the other hand, there was a positive correlation between theoretical oxidizability indices such as Cox value, C18:2-to-C18:0 and C18:3-to-C18:2 ratios, and ΔAV and ΔPV ($r > 0.15$). Such bioactive compounds as phenolic compounds (mainly FA) and tocols (mainly α-T) may have contributed to the quality of stored oils, as confirmed by positive correlations, in particular with ΔAV (FA, $r = 0.47$), ΔPV (ß-SIT, r = 0.36, TS, $r = 0.30$), ΔAnV (α-T, r = 0.30). Also, the content of δ-T and ΔCD were correlated, but there was a negative correlation of $r = -0.38$. Correlation coefficients show that the initial state of oils was important for the changes in the quality of oxidized oils. It can be assumed that AV1, CD1, CT1 and WC influenced ΔAV (positive correlation, $r > 0.56$), AV1 and CT1 significantly conditioned ΔPV (positive correlation, $r > 0.27$), while PV1 and AnV1 were strongly correlated with ΔAnV (r > 0.27).

It also seems that the initial state parameters determine the changes in color parameters after storage of flaxseed oils. The content of TFA was positively correlated with ΔL* ($r = 0.41$), similar to the share of MUFA (including C18:1 acid) ($r = 0.31$). A positive correlation was also observed between C18:2 and Δb*, as well as C18:0 and ΔE ($r > 0.40$). On the other hand, for the color parameters, in particular PUFA share (including C18:2 acid) (for ΔL* and Δa*), as well as the n-3-to-n-6 ratio (for Δb*) had negative effects. There was a more frequent negative correlation between the estimated theoretical oxidizability indices and changes in individual color parameters, e.g. C18:2-to-C18:3 ratio and ΔL* ($r = -0.30$), Cox value and ΔL* ($r = -0.24$), C16:0-to-C18:2 and Δb* ($r = -0.39$), as well as PUFA-to-SFA and ΔE ($r = -0.25$). The content of bioactive compounds may also affect the color of flaxseed oils after storage. The positive correlation was between TPC ($r = 0.33$), FA ($r = 0.52$), SA ($r = 0.35$), TPA ($r = 0.36$) and ΔL*, Δ-T and Δa* ($r = 0.29$), and squalene content and Δb* ($r = 0.38$). The occurrence of a negative correlation can be seen mainly in the analysis of the r values for ΔE, i.e. between CAM, γ-T, Pl-8, and TT (r from −0.37 to −0.47). Quality indices such as AV1, CD1, CT1 were positively correlated with ΔL* ($r > 0.44$), while a negative correlation can be observed between AnV1 and Δa* ($r = -0.22$), WC and Δb* ($r = -0.26$), and PV1 and ΔE (r = −0.30). It was also confirmed that the color parameters of oxidized oil are related to the color of initial oil, where a*1 and b*1 parameters may be of the greatest importance. It was noted that a*1 was positively correlated with Δb* and ΔE ($r > 0.39$), and thus negatively correlated with Δa* ($r = -0.46$), while b*1 was positively correlated with Δa* (r = 0.38) and also negatively correlated with Δb* and ΔE ($r > -0.60$).

Research results indicated that the content of unsaturated fatty acids (mainly C18:1 and C18:3 acids) and phenolic compounds are crucial in the oxidative stability of cold-pressed flaxseed oils during one-month storage with light exposure. The high content of C18:1 acid determines the good resistance of the oil to the oxidation process, which was confirmed by oil no. 25. In this oil, both the high content of C18:1 acid (25.63 g/100 g) and the high value of IP (2.63 h) were found, and after storage small amounts of primary and secondary oxidation products were formed. It has been proven by now that the ease of formation of radicals of fatty acids increases with the unsaturation of the oil and it is estimated that the C18:1 acid is 10–40 times less susceptible to oxidation than the C18:2 acid [39]. In oil no. 9 were found high values of TPC (2.79 mg/100 g) and IP (4.64 h), and it was also noted that AnV did not change during storage of this oil. Literature reports that phenolic compounds can act as reducing agents, hydrogen donors, singlet oxygen quenchers and metal chelators, which translates into their activity as antioxidants [40,41]. The above observations confirm the obtained values of correlation coefficients. Additionally, PCA analysis based on the content of bioactive compounds suggests that oil no. 12 was different to the others, which may indicate a relationship the oxidative stability of oil with high content of carotenoids and tocols (mainly γ-T). Although the IP in oil no. 12 was high (2.82 h), the correlation analysis did not show this assumption. This shows that storage conditions (temperature and light) affect the rate of lipid oxidation and oxidation product formation.

It was estimated that the initial state parameters of cold-pressed flaxseed oils influence the formation of oxidation products during one-month storage with light exposure. High AV2 in oil no. 27 (13.07 mg KOH/g) may be due to the high WC (>1000 ppm) because water intensifies the hydrolysis process and leads to the formation of a significant amount of free fatty acids [42]. The influence of WC on AV in plant oils was also noticed by Orhevba et al. [43] as well as Ngando-Ebongue et al. [18]. According to the authors, WC above the critical limit is additionally intensified by autocatalytic hydrolysis, in which free fatty acids initially present in the oil act as catalysts and consequently strongly enhance the formation of other free fatty acids. In oil no. 4 was found high AnV1 (1.29), which could contribute to the formation of oxidation products in the oil during storage (AnV2 was 3.31). It should be noted that both oils nos. 27 and 4 achieved a low IP (1.54 and 1.58 h, respectively). The literature also suggests that in high concentrations, tocols can have a pro-oxidative effect [44] and, consequently, deteriorate both the oxidative stability and the quality of oils. The high content of TT determined in oil no. 4 (mainly α-T (94.83 mg/100 g) and added

α-tocopheryl acetate (65.25 mg/100 g)), probably influenced the oxidation process intensification, which resulted in the high value of AnV2. It is worth mentioning that α-tocopheryl acetate is widely used for food fortification purposes since it is characterized by higher oxidative stability than α-tocopherol. However, its ability to protect lipids against photo- and autoxidation has not been proven [45]. Oils nos. 5, 11, 22 and 18 were characterized by the highest values of ΔE (ranged from 6.52 to 8.56) and additionally had a low content of TT (ranged from 84.68 to 93.46 mg/100 g). Delgado et al. [46] indicate that tocols play an important role in the color and flavor stability of foods due to their ability to accept high-energy electrons (free radicals) and complete oxidation chain reactions. Therefore, the high content of TT in oils allows the preservation of the proper sensory quality of food and, consequently, limits changes in color and taste.

Although squalene is also recognized as an antioxidant in the oil matrix, there was no distinct relationship between its content and oxidation progress in this study. Squalene is a triterpene hydrocarbon [47] and due to its characteristic chemical structure (it contains double bonds), it is susceptible to the oxidation process, which generally weakens its antioxidant effect [48]. On the other hand, research conducted by Dessi et al. [49] has shown that squalene can act as an effective singlet oxygen quencher and may also exhibit a synergistic effect with α-T [50]. Accordingly, squalene may, at least in part, contribute to the prevention of oxidation in oils. However, the literature reports that this phenomenon depends mainly on the factors causing the oxidation process, and thus on the mechanism of its course [46].

4. Conclusion

The results of our research indicate that the initial quality and content of bioactive compounds in cold-pressed flaxseed oils have different effects on the induction period and formation of oxidation products during storage at ambient temperature with light exposure. Generally, the induction period at elevated temperatures is more dependent on fatty acid composition (mainly percentages of linolenic and oleic acids) and the content of total phenolic compounds, while the initial quality indices have a greater impact on the increase of primary and secondary oxidation products at room temperature. Furthermore, it was noted that commercially available cold-pressed flaxseed oils are generally of good quality but differ in the content of bioactive compounds. A greater variability was noted for the content of oil-soluble minor compounds such as carotenoids, chlorophylls and phenolic compounds. Although cold-pressed flaxseed oils are characterized by similar color, some oils may have a more intense color. It was also noticed that the oxidative stability of cold-pressed flaxseed oils determined in accelerated oxidation tests (e.g. Rancimat test) and by changes in quality indices during storage under typical domestic or store conditions are not consistent. Also, the prediction of flaxseed oil susceptibility to oxidation during this storage based on theoretical oxidizability indices calculated from fatty acid percentages is complicated. This information can particularly help in the selection and quality control of fats and oils used in further food production.

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CRediT authorship contribution statement

Natalia Mikołajczak: Conceptualization, Resources, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Małgorzata Tańska:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Visualization, Validation, Supervision, Project administration.

Declaration of Competing Interest

The authors have declared no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nfs.2022.02.001.

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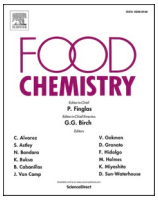
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Efficacy of canolol and guaiacol in the protection of cold-pressed oils being a dietary source linoleic acid against oxidative deterioration

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ABSTRACT

Oils high in linoleic acid are the main sources of polyunsaturated fatty acids in the human diet. The study attempted to increase the oxidative stability of 11 cold-pressed oils with various linoleic acid percentages by adding phenolic acid derivatives (canolol, guaiacol) at concentrations of 20–100 ppm. The oils were characterized by acid, peroxide and anisidine values, diene, triene, and water contents, fatty acid composition, and bioactive compounds. Their oxidative stability was evaluated before and after the addition of phenolic acid derivatives in the Rancimat test. The results indicate that both additives can be deployed as antioxidants in linoleic acid-rich oils, but canolol elicits a stronger protective effect (over fourfold). 100 ppm of canolol caused a significant increase in the oxidative stability of most oils (31–79%). The guaiacol effectiveness was greater (13–19% increase) at higher concentrations in hemp and poppy oils, but its lower amounts were more relevant for other oils.

1. Introduction

Even though oilseeds account for only 20% of the global grain production, they have spurred a growing interest among producers over the last 25 years. The global production of the top 10 oilseeds (i.e., rapeseed, sesame, peanuts, soybeans, copra, palm, sunflower, cotton, linseed, and castor seeds) increased from around 190 Million Metric Ton (MMT) in 1985/1986 to over 570 MMT in 2019/2020 (Mittaine & Mielke, 2012; USDA, 2020). Oilseeds are used primarily to produce food and animal feed, and as a raw material for the extraction of vegetable oil (Sarwar, Sarwar, Sarwar, Qadri, & Moghal, 2013). The USDA report showed an increase in vegetable oil consumption; as evidenced by 204 MMT of these products manufactured in the years 2019/2020 (USDA, 2020). In addition, it has been noted that consumers are increasingly inclined to purchase cold-pressed oils, due to the lack of their drastic heat treatment and to their nutritional value which surpasses that of the refined oils (Chandra, Kumar, Dwivedi, & Shinde, 2020). Most of them are good sources of polyunsaturated fatty acids (PUFAs), including mainly linoleic acid (C18:2n6), which may account for even>50% of the PUFAs (Whelan & Fritsche, 2013). It is worth noting that, compared to past decades, C18:2n6 intake has increased by more than threefold (Taha, 2020), accounting for approximately 8–10% of the total calorie intake in the Western diet (DiNicolantonio & O'Keefe, 2018). The highest concentrations of C18:2n6 (50–80% of the total fatty acids) are found in oils obtained from safflower, grape, sunflower, wheat germ, hemp, soybean, and pumpkin seeds (Orsavova, Misurcova, Ambrozova, Vicha, & Mlcek, 2015; Szabo et al., 2022). The share of PUFAs in oils is a particularly important factor determining their oxidative stability, because the more unsaturated the fat is, the faster the oxidation reaction proceeds (Yun & Surh, 2012).

Researchers undertake multiple actions aimed at ensuring high stability of cold-pressed oils with a high PUFAs content. The most common way in this case is to add antioxidants. Tocopherols are widely believed to be the main antioxidants in oil matrices (Cao et al., 2015); however, according to the polar paradox theory, polar antioxidants (i.e., phenolic compounds) may be more effective in this respect (Budilarto & Kamal-Eldin, 2015). Currently, the most popular forms of adding phenolic compounds to vegetable oils are the extracts obtained from vegetable raw materials (Moslavac, Šubarić, Šarić, Čepo, & Jozinović, 2019). The effects of individual and typical phenolic fractions on the stability of vegetable oils have been studied over the years, including e.g. phenolic acids such as ferulic, caffeic, syringic, and sinapic acids (Hasiewicz-Derkacz et al., 2015; Tundis et al., 2017); flavonoids such as quercetin, morin, rutin, and naringin (Shahidi & Wanasundara, 1995; Chu & Hsu, 1999); phenolic aldehydes such as vanillin (Hasiewicz-Derkacz et al., 2015); as well as phenolic alcohols such as hydroxytyrosol and

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oleuropein (Bouaziz, Fki, Jemai, Ayadi, & Sayadi, 2008). Literature data also suggests that derivatives of phenolic acids (e.g. canolol and guaiacol), may provide a barrier against the oxidation of vegetable oils (Tańska, Mikołajczak, & Konopka, 2018; Silva, Borges, & Ferreira, 2001; Szydłowska-Czerniak, Rabiej, Kyselka, Dragoun, & Vladimí, 2018). Terpinc et al. (2011) reported that the antioxidant activity of these phenolic acid derivatives in bulk oils was even higher than that of their parental moieties, which is due to their higher solubility in oil matrices (Pudel et al., 2014). Furthermore, it was emphasized that their antioxidant activity mechanisms vary in aqueous and lipid matrices. For example, canolol is predicted to react about 3.6-times faster in lipid media than in aqueous solution (Galano, Francisco-Márquez, & Alvarez-Idaboy, 2011). Generally, there are two antioxidant mechanisms of phenolic compounds, i.e., hydrogen atom transfer (HAT) or single electron transfer (SET) (Koroleva et al., 2014), but the HAT mechanism prevails in bulk oil (Zhu, Long, Zhou, Prenzler, & Zhong, 2013). The real site of the oxidation process in bulk oil is the oil–water interface (Laguerre et al., 2015), since practically each oil contains small amounts of water. In addition, water is also formed during the course of lipid oxidation due to hydroperoxide reduction (Budilarto & Kamal-Eldin, 2015). Moreover, the oxidation of lipids resulting in the formation of various free radicals (initiated by hydrogen excitation or by the addition of an oxygen radical, which results in damages to the structure of polyunsaturated fatty acids) that can be scavenged by phenolic radicals formed (Kumar & Goel, 2019).

Although there have been some experimental works focused on the antioxidant properties of phenolic acid derivatives in food matrices, studies addressing their influence on the oxidative stability of cold-pressed oils are still scarce. Generally, emulsion systems and refined oils are preferred in these studies, with usually one concentration of the antioxidant or one type of oil matrix is tested (e.g., Silva et al., 2001; Szydłowska-Czerniak et al., 2018; Bouaziz et al., 2008). In our previous work, vinyl derivatives of phenolic acids, i.e., canolol (derivative of sinapic acid) and guaiacol (derivative of ferulic acid) were used as effective antioxidants of typical commercial oils, such as cold-pressed flaxseed oil, cold-pressed and refined rapeseed oils, and extra virgin olive oil. Flaxseed oil was proved to be generally better protected by the phenolic additives than other oils (Tańska et al., 2018), which may indicate more effective protection of oils richer in PUFAs. This hypothesis was verified in the present study, the aim of which was to evaluate the applicability of canolol and guaiacol as antioxidants of commonly used cold-pressed oils rich in C18:2n6, such as black cumin, evening primrose, hemp, milk thistle, pumpkin, poppy seed, safflower, sesame, sunflower, corn, and soybean oils. In the study, different concentrations of these phenolic antioxidants were added to oils, and the oxidative stability of the obtained mixtures was evaluated in an accelerated oxidation test. In addition, the influence of the initial chemical composition (fatty acid percentages, bioactive compounds content) and quality parameters of oils on the antioxidant efficiency of phenolic acid derivatives was established. The research results could provide the opportunity to gain new knowledge on the antioxidant activity of phenolic acid derivatives in PUFA-rich oil matrices, and thus on the possibility of deploying them as antioxidants in various food and pharmaceutical applications.

2. Materials and methods

2.1. Research materials and phenolic acid derivatives

The research materials were 11 commercially available cold-pressed oils such as black cumin (Semco, Śmiłowo, Poland), corn (OlVita, Pszenno, Poland), evening primrose (Semco, Śmiłowo, Poland), hemp (Semco, Śmiłowo, Poland), milk thistle (Semco, Śmiłowo, Poland), poppy seed (Niwiki, Zwoleń, Poland), pumpkin (Semco, Śmiłowo, Poland), safflower (Niwiki, Zwoleń, Poland), sesame (Niwiki, Zwoleń, Poland), soybean (OlVita, Pszenno, Poland), and sunflower (Niwiki, Zwoleń, Poland). Oils were analyzed immediately after opening the packaging and kept between analyses in a freezer (at −20 °C) but not longer than 4 weeks.

The phenolic acid derivatives used in the research were analytical standards with a declared purity of > 95%. Canolol (4-ethenyl-2,6-dimethoxyphenol) was purchased from EnamineStore (Riga, Latvia) and guaiacol (2-methoxy-4-vinylphenol) from Sigma-Aldrich (Poznań, Poland). Derivatives were added to the oils as ethanol solutions at a concentration of 20, 40, 60, 80, and 100 ppm, and the solvent was evaporated under a stream of nitrogen.

2.2. Solvents and reagents

Analytical grade solvents and reagents such as anhydrous sodium sulfate, chloroform, diethyl ether, ethanol (99.9% purity), ethyl acetate, Folin-Ciocialteu reagent, formic acid, methanol, sodium carbonate, potassium hydroxide, sulfuric acid, and zinc were purchased from Chempur (Piekary Śląskie, Poland), while single-component catholyte HYDRANAL Coulomat CG from Honeywell (Warsaw, Poland). Chromatographic solvents and reagents, such as pyridine (anhydrous, 99.8% purity), N,O-bis(trimethylsilyl)trifluoroacetamide with 1% trimethylchlorosilane, *n*-hexane (≥95% purity, HPLC grade), isopropanol (99.5% purity, HPLC grade), methyl *tert*-butyl ether (>99.8% purity, HPLC grade), methanol (>99.9% purity, HPLC grade), vanillic acid (≥97% purity), caffeic acid (≥98% purity), ferulic acid (≥99% purity), p-coumaric acid (≥98% purity), sinapic acid (≥98% purity) were purchased from Sigma-Aldrich (Poznań, Poland). Standards, such as 5-α-cholestane (≥97% purity), β-apo-8′-carotenal (≥96% purity), α-tocopherol (≥96% purity), γ-tocopherol (≥96% purity), and δ-tocopherol (≥96% purity) were purchased from Sigma-Aldrich (Poznań, Poland). Helium for GC (99.999% purity) was purchased from Eurogaz-Bombi (Olsztyn, Poland). Deionized water was obtained from the HLP 5 deionizer (Hydrolab, Gdańsk, Poland).

2.3. Fatty acid composition and peroxidability index of oils

The procedure of fatty acid determination was similar to that in the work of Roszkowska, Tańska, Czaplicki, and Konopka (2015). The oil sample was methylated in a methylating mixture (methanol:chloroform: sulfuric acid, 100:100:1, v/v/v) at 70 °C for 2 h. After neutralizing the sulfuric acid through the addition of zinc, the solvent was evaporated under a stream of nitrogen. The residue was dissolved in *n*-hexane and analyzed using a GC–MS QP2010 PLUS chromatograph (Shimadzu, Kyoto, Japan) with an SGE BPX-70 capillary column (25 m × 0.22 mm × 0.25 μm, SGE Analytical Science, Ringwood, Australia) and helium as a carrier gas applied with a flow rate at 1.3 mL/min. The temperatures of GC–MS were set as follows: interface 240 °C, the ion source 240 °C, column temperature was programmed in the range from 150 °C to 250 °C. The electron energy was set at 70 eV. The total ion current (TIC) mode was used in 50–500 *m/z* range. Fatty acids were identified based on mass spectra and their contents were given as percentage shares (%). Additionally, the peroxidability index (PI) was calculated based on the average share of fatty acid (FA) composition, according to the formula given by Yun & Surh (2012): PI = (% monoenoic FA × 0.025) + (% dienoic FA × 1) + (% trienoic FA × 2) + (% tetraenoic FA × 4) + (% pentaenoic FA × 6) + (% hexaenoic FA × 8).

2.4. Quality parameters of oils

The quality parameters such as acid, peroxide and anisidine values, and content of conjugated dienes and trienes were determined based on JOCS Standard Methods for Analysis of Fats, Oils and Related Materials (2013).

The water content was determined based on Karl Fischer titration using a 917 Coulometer with a generator electrode and diaphragm (Metrohm, Herisau, Switzerland) according to the standard method (EN-

ISO 8534:2017) with some modifications. The sample was injected into the Karl Fischer cell with a single component catholyte using a syringe (with a needle Ø of 0.8 mm). The parameter settings were as follows: drift start – 20 μg/min, relative drift stop – 5 μg/min, polarization current – 10 μA, point setting – 50 mV, and normal rate of current generation, sample extraction time – 90 s, titration speed – 8.

2.5. Content of compounds with anti- and prooxidant activities in oils

The contents of squalene and sterols were determined according to Roszkowska et al. (2015). Compounds were extracted from the oils as follows: a solution of 5-α-cholestane as an internal standard, 2 M solution of potassium hydroxide in ethanol and ethanol was added to the sample. The mixture was heated at 70 °C for 30 min. The non-saponifying fraction was extracted 3-times with diethyl ether, and the collected extracts were rinsed with deionized water. Then the solvent was evaporated on a Büchi R-210 rotary evaporator (BÜCHI Labortechnik AG, Flawil, Switzerland) at 225 mbar and 45 °C. Derivatization was carried out as follows: pyridine and N,O-bis(trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane was added to the dry extract, and the mixture was heated at 60 °C for 1 h. Next, the solution was diluted in heptane and analyzed using the GC–MS QP2010 PLUS chromatograph (Shimadzu, Kyoto, Japan) coupled with a mass spectrometer and equipped with a ZB-5MSi capillary column (30 m × 0.25 mm, 0.25 μm, Phenomenex, Torrance, CA, USA). Helium was applied as a carrier gas with a flow rate of 0.9 mL/min. The temperatures were as follows: injector – 230 °C; column – 70 °C for 2 min, a subsequent increase to 230 °C at the rate of 15 °C/min, to 310 °C at the rate of 3 °C/min, and then a 10-min hold; GC–MS interface – 240 °C; ion source – 220 °C. Electron energy was set at 70 eV. The total ion current (TIC) mode was used for quantification (100–600 *m/z* range). Compounds were identified based on their mass spectra compared with mass spectral libraries (NIST08 library, Shimadzu, Kyoto, Japan). Squalene and sterols were identified based on retention times and mass spectra, and their contents were calculated with reference to the internal standard and given as mg/100 g. The repeatability for 5-α-cholestane determination (expressed as a coefficient of variation) was 2.5%. The limit of quantification was 0.05 μg/g of oil.

The content of tocopherols was determined based on the methodology described by Dąbrowski, Konopka, Czaplicki, and Tańska (2017). The oil sample was diluted in *n*-hexane and purified by centrifugation on an Eppendorf Centrifuge 5417R type (Eppendorf AG, Hamburg, Germany) for 10 min (25,000 g). The resultant solution was analyzed using HPLC Agilent Technologies 1200 chromatograph (Santa Clara, CA, USA) equipped with a fluorescence detector from the same company and a LiChrospher Si 60 column (250 mm × 4 mm × 5 μm, Merck, Darmstadt, Germany). A 0.7% solution of isopropanol in *n*-hexane was used as the mobile phase at a flow rate of 1 mL/min. The fluorescence detector was set at excitation and emission wavelengths of 296 nm and 330 nm, respectively. The content of tocopherols was determined from calibration curves prepared for tocopherol standards (α-tocopherol, γ-tocopherol, δ-tocopherol) and given as mg/100 g. The repeatability for α-, γ-, and δ-tocopherol determinations (expressed as coefficient of variation) was 2.5%. The limits of quantification were respectively 0.45, 0.4, and 0.2 μg/g of sample, while the linearity of the calibration curve was confirmed in the range of 0.02–16 mg/L.

The content of carotenoids was prepared and analyzed according to the methodology given by Czaplicki, Tańska, and Konopka (2016). The oil sample was diluted in *n*-hexane with β-apo-8′-carotenal as an internal standard and saponified by the addition of a 40% potassium hydroxide solution in methanol. The solution was shaken in a Multi Rotator RS-60 (Biosan, Riga, Latvia) in the dark at room temperature for 16 h. After saponification, 10% anhydrous sodium sulfate was added to the sample and extraction of carotenoids was carried out 4-times with *n*-hexane. The collected extracts were evaporated on a Büchi R-210 rotary evaporator at 225 mbar and 45 °C, and dry residue was dissolved in methanol:dichloromethane mixture (45:55, v/v). The resultant solution was analyzed by the RP-HPLC technique using an Agilent Technologies 1200 RP-HPLC apparatus (Santa Clara, CA, USA), equipped with a diode array detector (DAD), a YMC-C30 chromatography column (150 mm × 4.6 mm × 5 μm) and a YMC-C30 precolumn (10 mm × 4.6 mm × 3 μm) (YMC-Europe GmbH, Dinslaken, Germany). The column temperature was set at 30 °C and a methanol (A) and methyl *tert*-butyl ether (B) gradient was used for elution. The gradient was programmed as follows: 0–5 min 95% of A, until 25 min decreases to 72% of A and continues to decrease until 33 min to 5% of A. Then it increases to 95% of A and is stable until 60 min. Absorbance was measured at 450 nm. Carotenoids were identified based on retention times and absorption spectra of the internal standard, and their contents were calculated with reference to the internal standard (β-apo-8′-carotenal) and given as mg/100 g. The repeatability for β-apo-8′-carotenal determination (expressed as coefficient of variation) was 2.5%. The limit of quantification was 0.05 μg/g of sample, while the linearity of the calibration curve was confirmed in the range of 1–150 mg/L.

The content of total chlorophylls was determined spectrophotometrically in accordance with the method described by Roszkowska et al. (2015) using a microplate reader FLUOstar OMEGA (BMG Labtech GmbH, Ortenberg, Germany). The absorbance for pure oil was measured at 630, 670, and 710 nm against air, and the content of total chlorophyll was expressed as mg/100 g.

The content of total free phenolic compounds was determined spectrophotometrically by color reaction with Folin-Ciocialteu reagent according to the method of Tańska et al. (2018). Phenolic compounds from the oil sample (1 g) were extracted 3-times with 80% methanol (5 mL). The collected extracts were evaporated under vacuum using a Büchi R-210 rotary evaporator. To the dry residue was added a solution of Folin-Ciocialteu reagent in water (1:2, v/v), a 14% sodium carbonate solution, and deionised water. The mixture was incubated in a dark place at room temperature for 1 h. The absorbance of the solutions was measured using a microplate reader FLUOstar OMEGA, and the content of total free phenolic compounds was calculated based on the calibration curve prepared for D-catechin and given as mg/100 g.

The extraction of phenolic acids was determined according to the methodology provided by Tańska et al. (2018) using a vacuum equalizer (Witko, Łódź, Poland) and SPE Supelco columns filled with diol (500 mg) (Sigma-Aldrich, Poznań, Poland). The oil sample was diluted in *n*-hexane and phenolic acid extraction was performed as follows: column conditioning (5 mL methanol and 5 mL *n*-hexane), placing samples (sample and 5 mL *n*-hexane); washing column (5 mL *n*-hexane/ethyl acetate 90:10, v/v) and elution of phenolic acids with methanol. The phenolic acids were analyzed by the RP-HPLC technique using an Agilent Technologies 1200 RP-HPLC apparatus (Santa Clara, CA, USA), equipped with a photodiode detector and an Eclipse XDB-C18 chromatography column (150 mm × 4.6 mm × 5 μm, Agilent Technologies, Santa Clara, CA, USA). The column temperature was 30 °C and the mobile phase consisted of deionized water:acetonitrile:formic acid (88:10:2, v/v/v). The isocratic flow rate was equal to 0.8 mL/min. Detection was performed at wavelengths of 260 and 320 nm. Phenolic acids were identified based on the retention times and absorption spectra of the individual phenolic acids. The content of phenolic acid was determined from calibration curves prepared for phenolic acid standards (i.e., vanillic acid, caffeic acid, ferulic acid, *p*-coumaric acid, sinapic acid) and given as mg/100 g. The repeatability for phenolic acid determination (expressed as coefficient of variation) was at least 2.1%. The limit of quantification was at least 0.05 μg/g of sample, while the linearity of calibration curves was confirmed in the range of 1–150 mg/L.

2.6. Oxidation stability of oils

An accelerated oxidation test was evaluated on a Rancimat apparatus 743 (Metrohm, Herisau, Switzerland) at 110 °C and with an air flow rate

of 20 L/h (Tańska et al., 2018). The conductometric detection of volatile oxidation products was used to measure oils (with and without the addition of phenolic acid derivatives), and the result was saved as induction time (IT) and given in hours.

2.7. Statistical analysis

All data were performed in triplicate and analyzed using Statistica 13.1 PL software (StatSoft, Cracow, Poland). The differences between the oils were determined using one-way analysis of variance (ANOVA), followed by a Tukey test at a $p \leq 0.05$ significance level. A principal component analysis (PCA) was also performed to determine the degree of similarity of the studied oils in terms of fatty acid composition, content of anti- and prooxidants, quality and oxidative stability. Two-way ANOVA was used to assess the effect of the phenolic acid derivative type and concentration on the oxidative stability of studied oils. Additionally, the correlation plots were drawn to investigate the relationship between oxidative stability and chemical composition of the studied oils. Pearson correlation analyses were performed with RStudio version 4.0.2 for Windows (RStudio Inc., Boston, MA, USA; https://www.rstudio.com) using the Corrplot package.

3. Results and discussion

3.1. Characterization of cold-pressed linoleic acid-rich oils

3.1.1. Fatty acid composition and peroxidability index (PI)

The studied cold-pressed oils were rich in PUFAs (Table 1), with C18:2n6 found to be the major fatty acid, accounting for 41.06% to 77.55% of the total fatty acids. The richest in C18:2n6 (>70% of the total fatty acids) were evening primrose (EPO), safflower (SAO) and poppy seed oils (PPO). In turn, pumpkin (PSO), sunflower (SFO), and sesame (SSO) oils were characterized by the lowest percentages of this fatty acid (<48.15%). The percentage content of α-linolenic acid (C18:3n3) in oils highly varied. Its highest value (16.82%) was determined in hemp oil (HSO), followed by soybean oil (SBO) (8.55%). In the case of the other oils tested, the percentages of C18:3n3 were low and did not exceed 3.5%. In HSO and EPO, γ-linolenic acid (C18:3n6) was detected but its contents were only 4.10% and 3.43%, respectively. Oleic acid (C18:1n9) was the major MUFA, with its content ranging from 8.89% (EPO) to 45.83% (SFO). A high concentration (>30% of total fatty acids) of C18:1n9 was also found in SSO, PSO, and corn germ (CGO) oils. Saturated fatty acids (SFAs) accounted for<20% of the total fatty acids in all oils. Palmitic acid (C16:0) and stearic acid (C18:0) predominated among SFAs. The C16:0 percentage contents ranged from 5.88% (SFO) to 12.22% (black cumin oil, BCO), while these of C18:0 were definitely lower than those of C16:0 (max. 6.18% in PSO). The HSO and milk thistle oil (MTO) were also found to contain arachidic acid (C20:0); which accounted for 3.10% and 1.04% of the total fatty acids, respectively. The concentrations of other detected fatty acids (i.e., palmitoleic (C16:1n7), eicosenoic (C20:1n9), and behenic (C22:0) acids) were low and their sum did not exceed 1% of the total fatty acids. As shown by the PCA (Figure SM1a, supplementary material), it was possible to identify the presence of two groups of oils sharing a similar fatty acid composition, the first composed of EPO and HSO, and the second composed of BCO, CGO, PSO, SFO, and SSO. In turn, MTO was clearly distinguished from the other oils in terms of the fatty acid composition.

The studied oils featured a broad range of PUFAs-to-SFAs ratios (based on the average shares), from 2.58 to 7.89, but significantly higher ratios (higher than 6.5) were found in SAO, EPO, HSO, and PPO. The PI value calculated based on fatty acid percentages ranged from 42.17 (SSO) to 98.09 (HSO). High PI values were also obtained for EPO (84.59), SAO (77.86), and PPO (75.51). In oils produced from sunflower

Table 1
Fatty acid composition (%) and peroxidability index (PI) of studied cold-pressed oils rich in linoleic acid.

Acids/PI	HSO	EPO	SAO	PPO	SBO	BCO	MTO	CGO	PSO	SFO	SSO
C16:0	6.38 ± 0.00^{h}	6.89 ± 0.04^{g}	6.42 ± 0.03^{h}	8.89 ± 0.09^{e}	10.84 ± 0.07^{b}	12.22 ± 0.39^{a}	7.73 ± 0.16^{f}	10.15 ± 0.13^{c}	12.15 ± 0.08^{a}	5.88 ± 0.08^{i}	9.27 ± 0.19^{d}
C16:1n7	0.07 ± 0.01^{f}	0.03 ± 0.00^{i}	0.06 ± 0.00^{g}	0.11 ± 0.02^{d}	0.05 ± 0.01^{h}	0.18 ± 0.01^{a}	0.05 ± 0.01^{h}	0.12 ± 0.01^{c}	0.09 ± 0.01^{e}	0.15 ± 0.01^{b}	0.09 ± 0.00^{e}
C18:0	2.89 ± 0.01^{e}	2.76 ± 0.06^{f}	3.10 ± 0.11^{d}	2.03 ± 0.02^{g}	4.95 ± 0.06^{c}	2.89 ± 0.06^{e}	5.75 ± 0.20^{b}	1.83 ± 0.02^{h}	6.18 ± 0.05^{a}	3.02 ± 0.06^{de}	5.11 ± 0.01^{c}
C18:1n9	12.37 ± 0.07^{h}	8.89 ± 0.07^{i}	12.15 ± 0.32^{h}	14.19 ± 0.23^{g}	23.84 ± 0.34^{f}	24.28 ± 0.25^{f}	26.52 ± 0.20^{e}	33.83 ± 0.07^{c}	32.89 ± 0.16^{d}	45.83 ± 0.13^{a}	43.55 ± 0.18^{b}
C18:2n6	55.94 ± 0.39^{e}	76.96 ± 0.16^{b}	77.55 ± 0.16^{a}	74.06 ± 0.31^{c}	50.87 ± 0.14^{h}	56.73 ± 0.17^{d}	53.72 ± 0.03^{f}	52.22 ± 0.22^{g}	48.15 ± 0.05^{i}	44.08 ± 0.04^{j}	41.06 ± 0.02^{k}
C18:3n6	4.10 ± 0.12^{a}	3.43 ± 0.00^{b}	0.00 ± 0.00^{c}	0.00 ± 0.00^{c}	0.00 ± 0.00^{c}	0.00 ± 0.00^{c}	0.00 ± 0.00^{c}	0.00 ± 0.00^{c}	0.00 ± 0.00^{c}	0.00 ± 0.00^{c}	0.00 ± 0.00^{c}
C18:3n3	16.82 ± 0.31^{a}	0.27 ± 0.01^{g}	0.00 ± 0.00^{j}	0.55 ± 0.01^{e}	8.55 ± 0.26^{b}	3.28 ± 0.21^{c}	0.36 ± 0.04^{f}	1.27 ± 0.06^{d}	0.10 ± 0.02^{h}	0.04 ± 0.02^{i}	0.00 ± 0.00^{j}
C20:0	1.04 ± 0.02^{b}	0.36 ± 0.02^{d}	0.33 ± 0.02^{e}	0.09 ± 0.01^{i}	0.38 ± 0.01^{c}	0.15 ± 0.01^{h}	3.10 ± 0.15^{a}	0.33 ± 0.03^{e}	0.30 ± 0.02^{f}	0.18 ± 0.01^{g}	0.33 ± 0.06^{e}
C20:1n9	0.08 ± 0.00^{i}	0.20 ± 0.00^{d}	0.09 ± 0.02^{h}	0.06 ± 0.01^{j}	0.14 ± 0.01^{f}	0.23 ± 0.01^{c}	0.80 ± 0.06^{a}	0.15 ± 0.01^{e}	0.04 ± 0.00^{k}	0.11 ± 0.00^{g}	0.49 ± 0.03^{b}
C22:0	0.39 ± 0.01^{b}	0.21 ± 0.01^{d}	0.18 ± 0.01^{e}	0.02 ± 0.00^{i}	0.36 ± 0.02^{c}	0.04 ± 0.00^{h}	0.00 ± 0.00^{j}	0.09 ± 0.00^{g}	0.10 ± 0.00^{f}	0.72 ± 0.02^{a}	0.10 ± 0.01^{f}
SFA	10.70 ± 0.04^{g}	10.22 ± 0.12^{g}	10.14 ± 0.05^{g}	11.03 ± 0.10^{f}	16.55 ± 0.03^{b}	15.30 ± 0.34^{c}	18.54 ± 0.58^{a}	12.40 ± 0.12^{e}	18.73 ± 0.11^{a}	9.80 ± 0.15^{h}	14.81 ± 0.26^{d}
MUFA	12.52 ± 0.06^{i}	9.12 ± 0.08^{j}	12.31 ± 0.30^{i}	14.36 ± 0.26^{h}	24.03 ± 0.34^{g}	24.69 ± 0.26^{f}	27.38 ± 0.26^{e}	34.10 ± 0.06^{c}	33.02 ± 0.17^{d}	46.08 ± 0.11^{a}	44.13 ± 0.16^{b}
PUFA	76.86 ± 0.82^{b}	80.66 ± 0.03^{a}	77.55 ± 0.19^{b}	74.61 ± 0.31^{c}	59.43 ± 0.39^{e}	60.01 ± 0.37^{d}	54.08 ± 0.01^{f}	53.49 ± 0.28^{g}	48.25 ± 0.03^{h}	44.12 ± 0.02^{i}	41.06 ± 0.02^{j}
PUFA/SFA	7.18	7.89	7.65	6.76	3.59	3.92	2.92	4.31	2.58	4.50	2.77
PI	98.09^{a}	84.59^{b}	77.86^{c}	75.51^{d}	68.58^{e}	63.91^{f}	55.12^{g}	55.62^{g}	49.18^{h}	45.30^{i}	42.17^{j}

C16:0 – palmitic acid; C16:1n7 – palmitoleic acid; C18:0 – stearic acid; C18:1n9 – oleic acid; C18:2n6 – linoleic acid; C18:3n6 – γ-linolenic acid; C18:3n3 – α-linolenic acid; C20:0 – arachidic acid; C20:1n9 – eicosenoic acid; C22:0 – behenic acid; SFA – saturated fatty acids; MUFA – monounsaturated fatty acids; PUFA – polyunsaturated fatty acids; HSO – hemp seed oil; EPO – evening primrose seed oil; SAO – safflower seed oil; PPO – poppy seed oil; SBO – soybean oil; BCO – black cumin seed oil; MTO – milk thistle seed oil; CGO – corn germ oil; PSO – pumpkin seed oil; SFO – sunflower seed oil; SSO – sesame seed oil; a–k – mean values in the same line denoted by different letters are significantly different ($p \leq 0.05$).

(SFO) and sesame seeds (SSO), the PI was>2-fold lower compared to HSO. Thus, the fatty acid composition of oils appears to be a dominating factor of the oils' oxidative stability over their various native anti- and prooxidants. Based on the PI values, the studied oils may be divided into three groups: highly (HSO, EPO, SAO, and PPO), moderately (SBO, BCO, MTO, and CGO) and poorly (PSO, SFO, and SSO) susceptible to oxidation.

The fatty acid composition was typical of the studied cold-pressed oils, and similar percentage contents of individual fatty acids were determined by Kostadinović Veličkovska et al. (2018), Symoniuk, Ratusz, Ostrowska-Ligęza, and Krygier (2017), Bialek, Bialek, Jelinska, Tokarz, and Bialek (2017), Dąbrowski, Konopka, and Czaplicki (2020). These authors suggested that the composition of fatty acids in vegetable oils might be influenced by several factors, e.g., variety, growing conditions, weather conditions, method of oil extraction, and also the method of fatty acid determination. The PI estimated from fatty acid composition was also comparable to literature values (Bialek et al., 2017; Yun & Surh, 2012), while differences, if any, were due to the percentages of individual fatty acids in the vegetable oils.

3.1.2. Quality parameters and oxidative stability

All the studied oils were characterized by an acid value ranging from 0.22 (MTO) to 2.47 mg KOH/g (BCO), with the most common values being 0.65–0.69 mg KOH/g (Table 2). EPO and CGO also had higher acid values, reaching 1.37 and 1.06 mg KOH/g, respectively. BCO was characterized by the highest peroxide value, which was over 2 mEq O_2/kg. An equally high peroxide value was determined for EPO (1.14 mEq O_2/kg). The peroxide value in other oils was low and did not exceed 0.5 mEq O_2/kg. BCO and EPO, with anisidine values of 1.94 and 1.83, respectively, showed the highest amounts of secondary oxidation products. Also, CGO had an equally high anisidine value (1.41). In the case of the other oils, the value of this parameter ranged from 0.14 (PSO) to 0.64 (SBO), but trace amounts of secondary oxidation products were recorded in MTO and SAO (anisidine value < 0.04). The content of dienes was low and most often ranged from 0.10% (PPO) to 0.17% (MTO, CGO), and exceeded 0.3% only in BCO and PSO. Trienes were not detected in the studied oils. The highest water content was determined in EPO (0.19%). In the other oils, it was below 0.1%, with BCO and SBO featuring the lowest values, being almost 6.5-fold lower than in EPO.

The qualitative analysis of the cold-pressed oils showed that they were generally of good quality. Their acid and peroxide values did not exceed those indicated in the standards specified for cold-pressed oils, i.e., 4.0 mg KOH/g and 15.0 mEq O_2/kg in accordance with FAO/WHO Codex Alimentarius Commission (1999) for edible fats and oils. Elevated values of quality parameters, i.e., acid, peroxide and anisidine values in EPO and BCO, can indicate the initiated lipid oxidation process in these products. These parameters distinguished EPO and BCO from other oils, as confirmed on the PCA score plot (Figure SM1b, supplementary material). Also, the water content of the analyzed oils, except for EPO, meet the value (0.1%) stipulated for fresh vegetable oils (Yun & Surh, 2012). The present study has shown that the water content of oils results from the moisture content of the raw material used in the pressing process, while the higher moisture content of the raw material promotes its greater transition into oil. It is assumed that the water content of the product affects the rate of lipid hydrolysis and oxidation (Yun & Surh, 2012), which may partly explain the high values of quality parameters characterizing these processes in EPO. Additionally, some differences were observed in the color of the studied oils. Notably, two oils were different in this respect (Figure SM1b, supplementary material), i.e., HSO and PSO, which were characterized by a dark green color, and their total color was 2985 and 3308, respectively.

3.1.3. Content of anti- and pro-oxidative compounds

Table 3 shows the content of bioactive compounds in the studied cold-pressed oils. The squalene content ranged from 3.54 (SAO) to 173 mg/100 g (PSO), but its high content was also found in SBO (31.86 mg/100 g) and SFO (14.17 mg/100 g). The sterols were predominated by the β-sitosterol fraction, whose content in SBO was as much as 965 mg/100 g. Its high contents were also found in EPO and PPO, but their values were almost 2-fold lower than in SBO. The contents of such fractions as 25-hydroxy-24-methylcholesterol and campesterol were strongly differentiated. The lowest contents of 25-hydroxy-24-methylcholesterol were determined in SFO and CGO (<10 mg/100 g), and that of campesterol in PSO (<3 mg/100 g). However, the highest contents of these fractions were found in EPO and PSO (25-hydroxy-24-methylcholesterol) as well as SBO, PPO, and HSO (campesterol). The content of stigmasterol in oils reached up to 65 mg/100 g, while the cycloartenol content was up to 84 mg/100 g. The exception was BCO, where cycloartenol was found to prevail with its content approximating that of β-sitosterol. The total sterol content varied, reaching almost 1,500 mg/100 g in SBO and 2-fold less in both EPO and PPO. The α-tocopherol fraction was identified in almost all oils, and its content was also diversified. In SSO, the content of this fraction was almost 830 mg/100 g, while it was not detected in BCO. Also, EPO (>120 mg/100 g) as well as SFO and SAO (>70 mg/100 g) had a high α-tocopherol content. Furthermore, the highest content of γ-tocopherol was determined in HSO, PSO and EPO, ranging from 94.71 to 180 mg/100 g, whereas the other oils contained up to 44 mg/100 g of this homologue. In turn,

Table 2
Quality parameters and oxidative stability (induction time evaluated in Rancimat apparatus at 110 °C) of studied cold-pressed oils rich in linoleic acid.

	HSO	EPO	SAO	PPO	SBO	BCO	MTO	CGO	PSO	SFO	SSO
Acid value (mg KOH/g)	0.67 ± 0.00^{de}	1.37 ± 0.04^{b}	0.31 ± 0.08^{f}	0.69 ± 0.08^{de}	0.80 ± 0.08^{d}	2.47 ± 0.10^{a}	0.22 ± 0.05^{f}	1.06 ± 0.08^{c}	0.98 ± 0.04^{c}	0.67 ± 0.05^{de}	0.65 ± 0.08^{e}
Peroxide value (mEq O_2/kg)	0.40 ± 0.00^{c}	1.14 ± 0.03^{b}	0.16 ± 0.02^{e}	0.13 ± 0.00^{e}	0.40 ± 0.05^{c}	2.38 ± 0.07^{a}	0.12 ± 0.02^{e}	0.44 ± 0.02^{c}	0.28 ± 0.03^{d}	0.16 ± 0.00^{e}	0.12 ± 0.02^{e}
Anisidine value (-)	0.28 ± 0.03^{g}	1.83 ± 0.04^{b}	0.01 ± 0.00^{j}	0.14 ± 0.01^{h}	0.64 ± 0.02^{d}	1.94 ± 0.02^{a}	0.04 ± 0.01^{i}	1.41 ± 0.02^{c}	0.42 ± 0.03^{f}	0.56 ± 0.00^{e}	0.37 ± 0.02^{f}
Content of dienes (%)	0.15 ± 0.00^{d}	0.21 ± 0.00^{e}	0.22 ± 0.00^{d}	0.10 ± 0.00^{i}	0.16 ± 0.00^{g}	0.34 ± 0.01^{a}	0.17 ± 0.00^{f}	0.17 ± 0.00^{f}	0.33 ± 0.00^{b}	0.16 ± 0.00^{g}	0.23 ± 0.00^{c}
Content of trienes (%)	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}
Total color (-)	2985 ± 4.95^{b}	485 ± 0.71^{e}	176 ± 1.41^{i}	149 ± 1.41^{j}	1142 ± 0.71^{c}	957 ± 0.71^{d}	261 ± 1.41^{g}	466 ± 2.83^{f}	3308 ± 6.36^{a}	149 ± 2.83^{j}	197 ± 1.41^{h}
Water content (%)	0.04 ± 0.00^{e}	0.19 ± 0.01^{a}	0.07 ± 0.00^{c}	0.07 ± 0.00^{c}	0.03 ± 0.00^{f}	0.03 ± 0.00^{f}	0.08 ± 0.00^{b}	0.04 ± 0.00^{e}	0.06 ± 0.00^{d}	0.07 ± 0.00^{c}	0.08 ± 0.00^{b}
Induction time (h)	2.80 ± 0.01^{i}	4.79 ± 0.05^{f}	4.40 ± 0.12^{g}	4.21 ± 0.02^{h}	5.61 ± 0.04^{e}	11.65 ± 0.06^{a}	4.85 ± 0.03^{f}	7.69 ± 0.04^{c}	11.59 ± 0.01^{a}	6.00 ± 0.07^{d}	10.65 ± 0.22^{b}

HSO – hemp seed oil; EPO – evening primrose seed oil; SAO – safflower seed oil; PPO – poppy seed oil; SBO – soybean oil; BCO – black cumin seed oil; MTO – milk thistle seed oil; CGO – corn germ oil; PSO – pumpkin seed oil; SFO – sunflower seed oil; SSO – sesame seed oil; a–j – mean values in the same line denoted by different letters are significantly different ($p \leq 0.05$).

Table 3
Content of anti- and prooxidants in studied cold-pressed oils rich in linoleic acid.

	HSO	EPO	SAO	PPO	SBO	BCO	MTO	CGO	PSO	SFO	SSO
Campesterol	79.33 ± 1.53^{b}	77.45 ± 0.57^{b}	22.85 ± 0.43^{f}	86.71 ± 1.11^{b}	231 ± 7.68^{a}	28.68 ± 0.24^{e}	18.31 ± 0.09^{g}	43.31 ± 0.37^{d}	2.65 ± 0.10^{h}	28.09 ± 0.95^{e}	61.94 ± 1.14^{c}
Stigmasterol	9.82 ± 0.02^{g}	0.00 ± 0.00^{j}	12.89 ± 0.56^{f}	32.93 ± 0.95^{c}	63.56 ± 1.77^{a}	31.86 ± 0.23^{c}	25.31 ± 1.16^{d}	57.21 ± 0.34^{b}	0.84 ± 0.11^{i}	23.87 ± 0.07^{e}	7.21 ± 0.46^{h}
β-sitosterol	267 ± 2.43^{d}	519 ± 2.77^{b}	144 ± 4.74^{i}	467 ± 21.23^{c}	965 ± 13.11^{a}	237 ± 1.94^{f}	107 ± 1.17^{j}	187 ± 0.82^{g}	157 ± 0.38^{h}	248 ± 4.27^{e}	243 ± 2.51^{e}
25-OH-24-methylcholesterol	60.37 ± 1.68^{c}	98.51 ± 0.95^{a}	10.02 ± 0.38^{h}	46.57 ± 0.60^{d}	59.27 ± 0.90^{c}	21.05 ± 0.13^{g}	28.10 ± 0.56^{f}	9.21 ± 0.22^{i}	76.91 ± 0.31^{b}	6.89 ± 0.72^{j}	36.37 ± 2.70^{e}
Cycloartenol	11.01 ± 0.19^{g}	17.40 ± 0.10^{f}	83.64 ± 1.52^{b}	6.54 ± 0.72^{h}	20.22 ± 0.82^{e}	211 ± 2.12^{a}	77.85 ± 0.65^{c}	19.54 ± 0.71^{e}	60.20 ± 0.00^{d}	61.29 ± 1.94^{d}	2.58 ± 0.13^{i}
Others	20.77 ± 0.31^{g}	37.25 ± 1.00^{c}	16.74 ± 0.02^{i}	22.30 ± 1.31^{g}	67.95 ± 4.67^{a}	25.28 ± 0.21^{f}	19.54 ± 0.75^{h}	27.97 ± 2.04^{e}	32.30 ± 0.91^{d}	40.85 ± 0.20^{b}	7.94 ± 1.05^{j}
Total sterols	449 ± 8.13^{f}	755 ± 3.21^{b}	294 ± 4.47^{h}	670 ± 23.41^{c}	1439 ± 28.80^{a}	563 ± 3.08^{d}	284 ± 4.75^{i}	354 ± 1.50^{g}	502 ± 0.83^{e}	423 ± 2.20^{def}	559 ± 7.44^{d}
Squalene	3.96 ± 0.02^{h}	4.54 ± 0.00^{g}	3.54 ± 0.09^{i}	4.51 ± 0.29^{g}	31.86 ± 0.16^{b}	8.10 ± 0.24^{e}	7.20 ± 0.36^{f}	9.55 ± 0.19^{d}	173 ± 1.80^{a}	14.17 ± 0.19^{c}	4.40 ± 0.29^{g}
α-tocopherol	26.52 ± 0.60^{h}	123 ± 0.29^{b}	72.99 ± 0.00^{d}	4.79 ± 0.19^{j}	19.26 ± 0.41^{i}	0.00 ± 0.00^{k}	50.52 ± 0.00^{e}	29.76 ± 0.17^{g}	38.80 ± 0.34^{f}	81.88 ± 0.86^{c}	823 ± 3.08^{a}
γ-tocopherol	179 ± 0.43^{a}	94.71 ± 0.03^{c}	0.00 ± 0.00^{h}	10.72 ± 0.11^{f}	29.23 ± 0.39^{e}	14.75 ± 0.21^{f}	4.22 ± 0.16^{g}	44.03 ± 0.20^{d}	125 ± 0.10^{b}	0.00 ± 0.00^{h}	3.94 ± 0.09^{g}
δ-tocopherol	11.35 ± 0.67^{a}	2.67 ± 0.18^{c}	0.00 ± 0.00^{d}	0.00 ± 0.00^{d}	7.11 ± 0.02^{b}	0.00 ± 0.00^{d}	0.00 ± 0.00^{d}	2.70 ± 0.06^{c}	0.00 ± 0.00^{d}	0.00 ± 0.00^{d}	0.00 ± 0.00^{d}
Total tocopherols	217 ± 0.84^{c}	223 ± 2.29^{b}	72.99 ± 0.00^{g}	15.51 ± 0.00^{i}	55.59 ± 0.78^{h}	14.75 ± 0.00^{j}	54.74 ± 0.16^{h}	76.49 ± 0.30^{f}	166 ± 0.98^{d}	81.88 ± 0.86^{e}	827 ± 3.00^{a}
Lutein	0.56 ± 0.04^{b}	0.23 ± 0.01^{c}	0.00 ± 0.00^{d}	0.00 ± 0.00^{d}	1.09 ± 0.05^{a}	0.00 ± 0.00^{d}	0.00 ± 0.00^{d}	0.00 ± 0.00^{d}	0.51 ± 0.08^{b}	0.00 ± 0.00^{d}	0.00 ± 0.00^{d}
Zeaxanthin	0.00 ± 0.00^{e}	0.00 ± 0.00^{e}	0.31 ± 0.02^{b}	0.26 ± 0.05^{bcd}	0.22 ± 0.02^{bcd}	1.91 ± 0.32^{a}	0.27 ± 0.03^{bc}	0.19 ± 0.04^{d}	0.00 ± 0.00^{e}	0.35 ± 0.09^{b}	0.28 ± 0.01^{b}
β-carotene	0.27 ± 0.01^{c}	0.20 ± 0.01^{cd}	0.05 ± 0.00^{f}	0.06 ± 0.00^{f}	1.15 ± 0.11^{b}	0.21 ± 0.09^{cd}	0.01 ± 0.00^{h}	0.25 ± 0.05^{cd}	4.08 ± 0.35^{a}	0.08 ± 0.05^{e}	0.02 ± 0.00^{g}
α-carotene	0.04 ± 0.01^{d}	0.02 ± 0.00^{e}	0.00 ± 0.00^{g}	0.01 ± 0.00^{e}	0.30 ± 0.03^{b}	0.00 ± 0.00^{g}	0.00 ± 0.00^{g}	0.08 ± 0.02^{c}	0.68 ± 0.04^{a}	0.02 ± 0.01^{d}	0.01 ± 0.00^{f}
Others	0.30 ± 0.05^{b}	0.10 ± 0.03^{d}	0.12 ± 0.02^{d}	0.02 ± 0.01^{f}	0.20 ± 0.01^{c}	0.73 ± 0.11^{a}	0.06 ± 0.02^{e}	0.26 ± 0.04^{b}	0.68 ± 0.03^{a}	0.14 ± 0.01^{d}	0.01 ± 0.00^{f}
Total carotenoids	1.17 ± 0.01^{c}	0.57 ± 0.05^{de}	0.48 ± 0.05^{e}	0.35 ± 0.04^{ef}	2.96 ± 0.21^{b}	2.95 ± 0.30^{b}	0.35 ± 0.04^{ef}	0.78 ± 0.15^{d}	6.25 ± 0.43^{a}	0.60 ± 0.02^{d}	0.31 ± 0.00^{f}
Total chlorophylls	0.17 ± 0.00^{a}	0.05 ± 0.00^{bc}	0.01 ± 0.00^{e}	0.07 ± 0.00^{b}	0.02 ± 0.00^{d}	0.02 ± 0.00^{d}	0.04 ± 0.00^{c}	0.01 ± 0.00^{e}	0.05 ± 0.00^{bc}	0.03 ± 0.00^{cd}	0.02 ± 0.00^{d}
Total phenolics	2.70 ± 0.10^{d}	2.26 ± 0.07^{e}	3.26 ± 0.01^{c}	traces	0.07 ± 0.00^{h}	20.42 ± 0.04^{a}	5.35 ± 0.07^{b}	1.53 ± 0.08^{g}	2.68 ± 0.02^{d}	traces	1.88 ± 0.09^{f}
p-coumaric acid	1.58 ± 0.11^{cd}	0.00 ± 0.00^{f}	1.42 ± 0.02^{d}	0.00 ± 0.00^{f}	1.72 ± 0.26^{c}	0.00 ± 0.00^{f}	1.69 ± 0.59^{c}	44.38 ± 2.65^{a}	0.29 ± 0.00^{e}	1.45 ± 0.21^{cd}	4.97 ± 0.15^{b}
Ferulic acid	2.31 ± 0.05^{h}	5.71 ± 0.23^{e}	3.33 ± 0.46^{g}	4.40 ± 0.15^{f}	8.76 ± 0.24^{d}	94.89 ± 3.92^{a}	11.32 ± 0.46^{c}	30.01 ± 1.04^{b}	3.10 ± 0.10^{g}	4.22 ± 0.08^{e}	31.58 ± 1.88^{b}
Sinapic acid	4.86 ± 0.01^{g}	2.98 ± 0.24^{h}	8.84 ± 0.14^{e}	11.96 ± 0.04^{d}	33.32 ± 0.57^{c}	227 ± 5.79^{a}	7.95 ± 0.59^{f}	75.79 ± 2.64^{b}	0.00 ± 0.00^{i}	8.76 ± 0.81^{ef}	8.35 ± 0.38^{b}
Caffeic acid	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	3.35 ± 0.03^{a}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}
Vanillic acid	1.74 ± 0.03^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	2.92 ± 0.22^{a}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}
Total phenolic acids	10.49 ± 0.10^{g}	8.69 ± 0.00^{h}	13.59 ± 0.62^{b}	16.37 ± 0.11^{f}	43.80 ± 0.55^{c}	322 ± 9.72^{a}	24.31 ± 1.67^{e}	150 ± 6.32^{b}	6.31 ± 0.12^{i}	26.72 ± 0.51^{d}	44.90 ± 2.41^{c}

Results of tocopherols, sterols, carotenoids, total phenolic compounds are expressed in mg/100 g, results of phenolic acids are expressed in μg/100 g; HSO – hemp seed oil; EPO – evening primrose seed oil; SAO – safflower seed oil; PPO – poppy seed oil; SBO – soybean oil; BCO – black cumin seed oil; MTO – milk thistle seed oil; CGO – corn germ oil; PSO – pumpkin seed oil; SFO – sunflower seed oil; SSO – sesame seed oil; a–k – mean values in the same line denoted by different letters are significantly different ($p \leq 0.05$).

δ-tocopherol was found only in HSO, SBO, PSO, and EPO (with its contents ranging from 2.67 to 11.35 mg/100 g). The analysis showed that particularly SSO (over 800 mg/100 g), but also EPO, HSO, and PSO (166–223 mg/100 g) contained significant amounts of total tocopherols. The studied oils were characterized by a low content of carotenoids (0.31–1.17 mg/100 g). Its higher amounts were found only in PSO, SBO, and BCO. The content of individual carotenoids in oils reached up to 0.73 mg/100 g (depending on the oil type), but distinctive were the contents of such fractions as lutein in SBO (1.09 mg/100 g), zeaxanthin in BCO (1.91 mg/100 g), and β-carotene in PSO (4.08 mg/100 g) and SBO (1.15 mg/100 g). The highest contents of phenolic acids were found in CGO and BCO (150 and 322 μg/100 g, respectively), while the lowest were in PSO and EPO (<10 μg/100 g). *p*-Coumaric acid predominated in CGO (accounted for almost 30% of total phenolic acids); ferulic acid in BCO, CGO, and SSO (accounted for 20 to 30% of total phenolic acids); and sinapic acid in BCO, CGO, and SBO (accounted for 50 to 80% of total phenolic acids). Caffeic acid was found only in MTO (3.35 μg/100 g), and vanillic acid in HSO and PSO (1.74 and 2.92 μg/100 g, respectively). In addition, BCO (20.42 mg/100 g) had the highest content of total phenolic compounds, but their high content was also found in MTO (though 4-fold lower than BCO). Traces of total phenolic compounds were determined in SFO and PPO. The PCA confirmed that the contents of compounds exhibiting pro- and antioxidative activities were quite similar in SAO, PPO, MTO, CGO, SFO, and SSO (Figure SM1c, supplementary material).

A review of literature data has shown that the composition of bioactive compounds is typical of the cold-pressed oils studied (e.g., Kostadinović Veličkovska et al., 2018; Bialek et al., 2017; Dąbrowski

et al., 2020). Possible differences in the content of bioactive compounds may have resulted from a complex interaction between genetic, environmental, agronomic, and technological factors. This means that such factors as the type of raw material, country of origin, weather and cultivation conditions, and oil extraction techniques also affect the rate of oil accumulation in oilseeds as well as the final composition and contents of bioactive compounds in the oil.

3.2. Relationships between composition and oxidative stability of cold-pressed linoleic acid-rich oils

Fig. 1 shows the positive and negative correlations between composition of cold-pressed oils and their oxidative stability expressed as an induction time (IT). The estimated values of the correlation coefficients (r) are presented in Table SM1 (supplementary material). The analysis of the relationships showed that IT of the oils was significantly positively correlated (high correlation) with the percentage content of palmitoleic acid (r = 0.77), and the content of ferulic acid (r = 0.64) and other carotenoids (r = 0.63), but negatively with the percentages of polyunsaturated fatty acids (r = −0.66). However, the content of monounsaturated (mainly oleic acid) and saturated fatty acids as well as the content of total phenolics, total phenolic acids, total carotenoids, squalene, α- and β-carotene, zeaxanthin, sinapic acid, and cycloartenol were also important (moderate correlation) for oxidative stability (r in the range of 0.4–0.6). On the other hand, the contents of other compounds of the oils, i.e., most sterols, α- and γ-tocopherol, lutein, chlorophylls, and *p*-coumaric, caffeic and vanillic acids, seem to be of insignificant importance for their oxidative stability, as indicated by r < 0.2 (no relationship, weak correlation). Research conducted by Symoniuk et al. (2017) also showed that the oxidative stability of the oil determined in the Rancimat test depended on many factors. They observed a significant correlation between IT and the content of carotenoid pigments (r = 0.66) in cold-pressed oils. However, according to the research by Tura et al. (2007), the oxidative stability was positively correlated with the content of total polyphenols (r = 0.669) and δ-tocopherol (r = 0.474) in virgin olive oil, but in contrast to our findings, the contents of α-tocopherol (r = 0.554) and total tocopherols (r = 0.553) were also important for the oxidative stability.

3.3. Oxidative stability of cold-pressed linoleic acid-rich oils with the addition of phenolic acid derivatives

Results of the accelerated oxidation experiment using the Rancimat test showed that the canolol and guaiacol additives generally improved the oxidative stability of all cold-pressed oils rich in linoleic acid (Figure SM2, supplementary material), but their effectiveness varied. Additionally, linear relationships were observed between IT and phenolic acid derivative amount, but the range of linearity was dependent on both the oil type and the additive type (Table 4). The addition of canolol proved to be the most effective for HSO and PPO, where the highest IT increase (68.21 and 69.56%, respectively) was established at 100 ppm. An equally significant extension of IT was found in PSO, SFO, SSO, SBO, MTO and CGO. The observed changes were linear in the full range (0–100 ppm) and ranged from 41.95% (SFO) to 56.17% (SBO). Guaiacol as an antioxidant exhibited lower effectiveness and caused a noticeable elongation of IT only in the HSO (up to 18.86%). An increase in IT was also observed in PPO but the percentage change reached up to 13.54% at 80 ppm of this phenolic acid derivative. In the case of the other oils, guaiacol was able to provide only slight protection against the oxidation process (maximal effectiveness was in the range of 2.43–8.06%). Interestingly, low antioxidant efficacy of both phenolic acid derivatives was observed in the oils of lower initial quality, i.e., EPO and PPO. It is probably related to the presence of lipid autoxidation products in these oils that are amphiphilic (hydroperoxides, aldehydes, ketones, and others). These compounds with a small amount of water form association colloids that can affect the oxidation process and

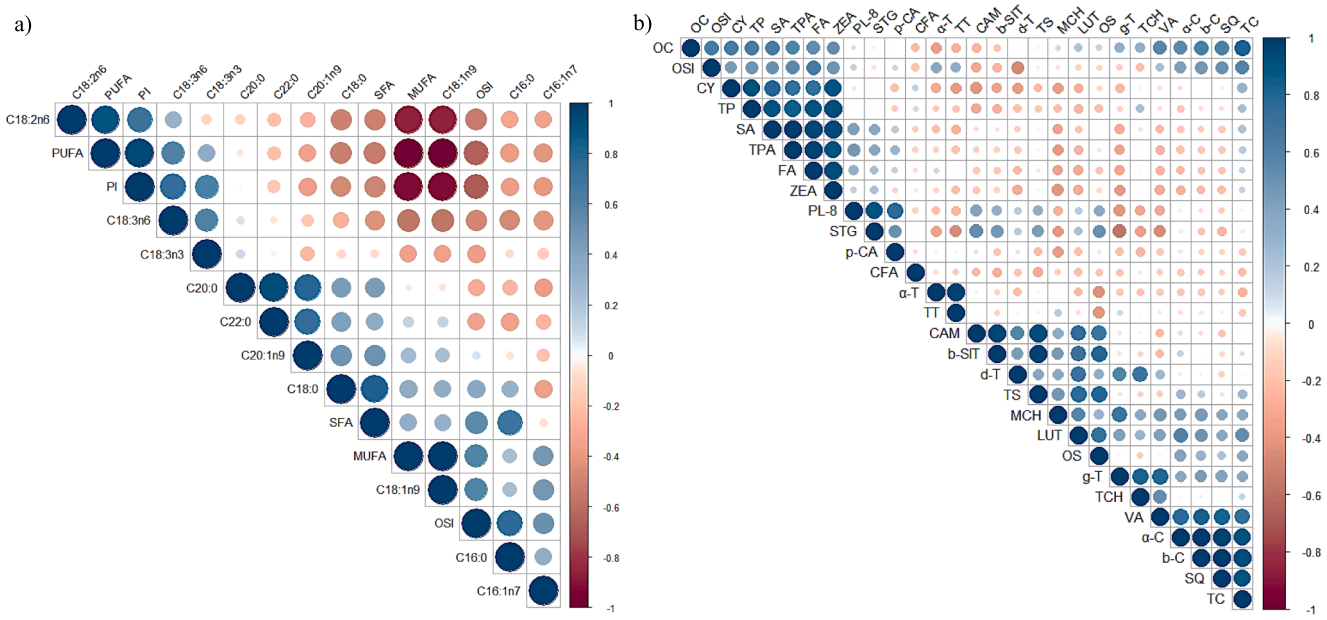


Fig. 1. Correlation matrix between oxidative stability (OSI, expressed as an induction time (IT)) and fatty acid composition (a) and bioactive compounds content (b) of studied cold-pressed oils rich in linoleic acid. Positive and negative correlations are indicated according to the colored scale. The size of the circles is proportional to the Pearson's correlation coefficients (r). Abbreviations: C16:0 – palmitic acid; C16:1n7 – palmitoleic acid; C18:0 – stearic acid; C18:1n9 – oleic acid; C18:2n6 – linoleic acid; C18:3n6 – γ-linolenic acid; C18:3n3 – α-linolenic acid; C20:0 – arachidic acid; C20:1n9 – eicosenoic acid; C22:0 – behenic acid; SFA – saturated fatty acids; MUFA – monounsaturated fatty acids; PUFA – polyunsaturated fatty acids; α-T – α-tocopherol; PL-8 – plastochromanol-8; g-T – γ-tocopherol; d-T – δ-tocopherol; TT – total tocopherols; SQ – squalene; CAM – campesterol; STG – stigmasterol; b-SIT – β-sitosterol; MCH – 25-OH-24-methylcholesterol; CY – cycloartenol; OS – other sterols; TS –total sterols; TP – total phenolics; p-CA – *p*-coumaric acid; FA – ferulic acid; SA – sinapic acid; CFA – caffeic acid; VA – vanillic acid; TPA – total phenolic acids; LUT – lutein; ZEA – zeaxanthin; b-C – β-carotene; α-C – α-carotene; OC – other carotenoids; TC – total carotenoids; TCH – total chlorophylls.

Table 4
Linear relationships between canolol and guaiacol additions (x) and oxidative stability expressed as an induction time (IT) for studied cold-pressed oils rich in linoleic acid.

Cold-pressed oil	Canolol addition				Guaiacol addition			
	Regression equation	R^2	Linear range (ppm)	Max. effectiveness (%)	Regression equation	R^2	Linear range (ppm)	Max. effectiveness (%)
HSO	IT = 0.0186x + 2.8819	0.9819	0–100	79.43	IT = 0.0040x + 2.6614	0.9182	0–100	18.86
EPO	IT = 0.0087x + 4.7771	0.9842	0–100	16.48	IT = 0.0034x + 4.804	0.9512	0–60	3.52
SAO	IT = 0.0093x + 4.3898	0.9641	0–100	30.87	IT = 0.0024x + 4.1945	0.9563	0–60	3.21
PPO	IT = 0.0285x + 4.2698	0.9919	0–100	72.64	IT = 0.0032x + 4.200	0.9089	0–80	13.54
SBO	IT = 0.0298x + 5.8848	0.9621	0–100	56.17	IT = 0.0034x + 5.5664	0.9031	0–100	7.44
BCO	IT = 0.0108x + 11.681	0.8801	0–100	11.90	IT = 0.0148x + 11.64	0.9337	0–60	2.65
MTO	IT = 0.0232x + 4.8055	0.9927	0–100	50.26	IT = 0.0082x + 4.845	0.9973	0–40	7.25
CGO	IT = 0.0329x + 7.7748	0.9854	0–100	48.03	IT = 0.0026x + 7.552	0.9941	0–60	8.06
PSO	IT = 0.0497x + 11.488	0.9941	0–100	44.42	IT = 0.0080x + 10.934	0.9577	0–80	2.43
SFO	IT = 0.0227x + 5.805	0.9680	0–100	41.95	IT = 0.0042x + 5.9498	0.8880	0–100	3.63
SSO	IT = 0.0572x + 11.347	0.9403	0–100	42.60	IT = 0.0097x + 10.973	0.9424	0–80	5.46

HSO – hemp seed oil; EPO – evening primrose seed oil; SAO – safflower seed oil; PPO – poppy seed oil; SBO – soybean oil; BCO – black cumin seed oil; MTO – milk thistle seed oil; CGO – corn germ oil; PSO – pumpkin seed oil; SFO – sunflower seed oil; SSO – sesame seed oil; R^2 – coefficient of determination.

diminish the antioxidant effectiveness of phenolic compounds (Rokosik, Siger, Rudzińska, Siejak, & Dwiecki, 2020). Jo and Lee (2021) confirmed that aldehydes formed from lipid oxidation affected the association of colloidal structures and accelerated the lipid oxidation in heated soybean oil.

A positive correlation was noticed between the canolol concentration and IT of the studied cold-pressed oils, i.e., oxidative stability increased with an increasing concentration of the additive (Table 4). In turn, guaiacol addition at 80 ppm was the most effective in PSO, SSO, and PPO (IT increased up to 11.58 h, 11.68 h, and 4.49 h, respectively), whereas in CGO, BCO, SAO, and EPO – at a concentration of 60 ppm (IT increased up to 7.71 h, 11.60 h, 4.35 h, and 5.00 h, respectively). However, the best additive for MTO turned out to be 40 ppm of guaiacol (IT was 5.18 h). The observed relationships between IT and concentration of phenolic acid derivatives allowed determining the linear function equations for each oil (Table 4). However, the lines plotted for the oils were characterized by varied values of intercept and slope. For canolol addition, the values of slope in the linear function were significantly higher for SSO and PSO (0.0527 and 0.497, respectively), which indicates a more dynamic oxidative stability increase. In turn, guaiacol addition ensured the highest rate of IT increase for BCO (the slope was 0.0148). Two-way ANOVA confirmed the statistically significant effect of the type and concentration of phenolic acid derivative on the oxidative stability of the cold-pressed oils studied (Table 5). Nevertheless, a stronger effect of the additive type (>48% of the explained variance) than its concentration was noted. The phenolic acid derivative type was the most decisive for SBO and HSO (83.59 and 81.56% of the explained variance, respectively). In turn, the strongest effect of additive concentration was found in the case of EPO (19.34% of explained variance), while the cumulative effect of interactions of both factors tested was the strongest in SFO (40.26% of the explained variance).

Our research indicates that phenolic compounds are the major antioxidants of the analyzed oils. Similarly, Farhoosh and Hoseini-Yazadi (2013) found that phenols underlie the high oxidative stability of olive oil, and the analyses conducted by Mikołajczak and Tańska (2022) and Roszkowska et al. (2015) confirmed a strong correlation (r = 0.62, and r = 0.76) between the content of phenolic compounds and resistance to the oxidation processes of rape seed and flaxseed oils. Literature

Table 5
Effect of type and concentration of phenolic acid derivative on oxidative stability of individual cold-pressed oil (% of the explained variance).

Oil	Factors			
	Type of phenolic acid derivative (T)	Concentration of phenolic acid derivative (C)	T × C	Other factors
HSO	81.56	9.14	9.11	0.20^{ns}
EPO	60.37	19.34	16.26	4.03^{ns}
SAO	76.37	6.17	15.91	1.55^{ns}
PPO	76.27	8.44	14.96	0.32^{ns}
SBO	83.59	6.99	9.21	0.20^{ns}
BCO	63.16	7.35	28.23	1.26^{ns}
MTO	68.04	4.59	26.78	0.59^{ns}
CGO	79.35	7.83	12.67	0.15^{ns}
PSO	75.45	9.96	14.47	0.12^{ns}
SFO	48.95	10.38	40.26	0.41^{ns}
SSO	78.96	7.62	13.11	0.31^{ns}

HSO – hemp seed oil; EPO – evening primrose seed oil; SAO – safflower seed oil; PPO – poppy seed oil; SBO – soybean oil; BCO – black cumin seed oil; MTO – milk thistle seed oil; CGO – corn germ oil; PSO – pumpkin seed oil; SFO – sunflower seed oil; SSO – sesame seed oil; ns – not statistically significant, two-way analysis with Wilks test ($p \leq 0.05$).

data suggests that the antioxidant activity of phenolic compounds in oils depends on many factors, i.a. their concentration as well as chemical structure (Mikołajczak, Sobiechowska, & Tańska, 2020; Terpinc et al., 2011). Our previous study has shown that guaiacol was a better antioxidant for cold-pressed flax and rape seed oils than canolol during the Rancimat test at 110 °C with a stream of purified air at a flow rate of 20 L/h and the concentration of 0.08% (Tańska et al., 2018). This was probably due to a different chemical composition of these oils compared to those analyzed in this study. The higher efficiency of guaiacol seems to be related to the higher percentage of α-linolenic acid. It was observed that IT was longer in oils with a higher share of this fatty acid (the calculated correlation coefficient for the relationship was 0.72). Zhou et al. (2019) noticed that refined rape seed oil with a high content of canolol (>50 mg/100 g) showed good resistance to oxidation during frying (temperature near its smoke point), and it was confirmed by a

significant positive correlation between the canolol content and IT ($r = 0.874$). Better oxidative stability of oil from roasted rape seeds (with a high content of canolol) was also shown by Koski, Pekkarinen, Hopia, Wähälä, and Heinonen (2003); and Wijesundera, Ceccato, Fagan, and Shen (2008). This is consistent with the findings reported by Matthäus, Pudel, Chen, Achary, and Thiyam-Holländer (2016) who showed that the canolol-rich extracts were potent to retard the degradation rate of high oleic canola oil (in the concentration range of 0.02–0.075%) during frying at 185 °C. Furthermore, the research by Wang et al. (2014) indicated that soybean oil containing 500 ppm of canolol showed obviously higher oxidative stability during the accelerated oxidation process (exposed to air in an oven at 60 °C) than the same oil with 500 ppm of α-tocopherol. They noticed that changes in fatty acid composition, and primary and secondary oxidation products were almost undetectable in the soybean oil with canolol even after 19 days of oxidation. Additionally, the synergistic antioxidant effect of tocopherol with canolol was not observed in their study. In turn, Shin, Jeong, Jia, Hong, and Lee (2019) determined lower values of quality parameters of the O/W emulsion (with stripped soybean oil) after guaiacol addition (at a concentration of 0.02%) and storage in a dark place at 37 °C for 50 days.

More and more researchers attempt to determine the effects of various phenolic derivatives on the oxidative stability of edible vegetable oils. For example, research by Wang et al. (2014) focused on the possibility of using alkyl caffeates (e.g., methyl caffeate, ethyl caffeate, propyl caffeate, octyl caffeate) as antioxidants in rapeseed oil, peanut oil, and silkworm pupae oil during the Rancimat test at 121.6 °C with a stream of air at a flow rate of 20 L/h (concentrations not specified). In turn, Silva et al. (2001) added propyl caffeate and propyl hydrocaffeate in a concentration of 0.016% to refined sunflower oil during the Rancimat test at 110 °C with a stream of purified air at a flow rate of 20 L/h. The addition of caffeic acid derivatives (caffeic acid phenethyl ester and 4-vinylcatechol in the concentrations of 0.01–0.02%) to strip soybean oil during storage at 60 °C in a dark place was studied by Jia, Wang, Qi, Hong, and Lee (2015). Also, Chen and Ho (1997) investigated the effect of caffeic acid phenethyl ester, but at a concentration was 2%, on the oxidative stability of corn oil analyzed in the Rancimat test at 110 °C with a stream of air at a flow rate of 20 L/h. In turn, Szydłowska, Czerniak, and Rabiej (2018) used octyl sinapate in a concentration of 0.9% to stabilize refined rapeseed oil in accelerated conditions at 40 °C with light exposure during 4-week storage. Although these studies have confirmed that derivatives of phenolic compounds may constitute novel antioxidants for lipophilic food matrices, comparing their efficacy in inhibiting oxidation processes is quite difficult due to different oxidation test conditions, amounts of phenolic acid derivatives, and oils used.

4. Conclusion

The results obtained in this research indicate the feasibility of using phenolic acid derivatives (sinapic and ferulic acids) as antioxidants in cold-pressed oils with a high content of linoleic acid. However, their efficacy in protecting the oils against oxidative deterioration was found to depend more on the type/composition of oil and the type of the additive than its concentration. The addition of canolol was proved to be more effective for the studied oils because the extension of the induction time was at least 4-fold greater than upon guaiacol addition (at the same concentration). The best effect of canolol was noticed at its highest concentration (100 ppm), especially on hemp and poppy seed oils (the induction time increased by 73–79%). It was found that the canolol protective effect was stronger in the oils with a better initial quality (a lower degree of hydrolysis and oxidation). On the other hand, it was observed that guaiacol could be a good antioxidant for hemp and poppy seed oils (an average increase of the induction time by 16.2%) at a concentration of 100 and 80 ppm, respectively. However, this additive was generally more effective at lower concentrations, from 40 to 80 ppm, depending on the oil type. Furthermore, guaiacol was confirmed to be more effective in the case of oils with a higher α-linolenic percentage and a lower linoleic percentage at the same time.

As demonstrated in the study, the initial oil composition and quality significantly affect the protective effect of the phenolic acid derivatives against oxidation process. The analyzed cold-pressed oils rich in linoleic acid were generally of good quality, but some variations were found in their content of bioactive compounds and quality. The most distinguished in chemical characteristics were black cumin, evening primrose, hemp, and pumpkin seed oils. The oxidative stability of these oils was negatively correlated with the peroxidability index (theoretical susceptibility to oxidation), but the contents of squalene, carotenoids (α- and β-carotenes and zeaxanthin) and phenolics (ferulic and sinapic acids) also affected this parameter. Although tocopherols are commonly deployed as commercial antioxidants to reduce oil deterioration, our study did not confirm their stabilizing effect on the purchased oils. In addition, the presence of ferulic and sinapic acids seems to be more important for the oil's oxidative stability than the content and type of tocopherols.

The results of our research confirm that phenolic acid derivatives can serve as novel antioxidants used in the edible oil industry and be useful in the development of solutions replacing synthetic antioxidants with natural ones to prevent oxidative lipid degradation in response to thermal exposure. It also appears to not only increase the stability of the oils, but also minimize the formation of secondary metabolites (i.e., free radicals, low molecular weight aldehydes and ketones, oxysterols) with adverse effects on consumers. Moreover, the phenolic acid derivatives are likely to inhibit the degradation of lipophilic bioactive compounds dissolved in oils (e.g., squalene, sterols, unsaturated fatty acids), which may elicit significant nutritional and health benefits.

As highlighted in the present study, canolol can be an effective antioxidant in linoleic acid-rich oils, while guaiacol would probably show greater efficacy in minimizing the oxidation of oils with a high content of α-linolenic acid. Nonetheless, the initial quality of the oils can affect the antioxidant efficiency of these additives. However, further studies with phenolic acid derivatives are needed to understand their oxidation mechanism in oil matrices, especially those varying in the content of native antioxidants. It is speculated that interactions of phenolic acid derivatives with native antioxidants (e.g., tocopherols, carotenoids) are also likely to occur during the oxidation process of cold-pressed oils.

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CRediT authorship contribution statement

Natalia Mikołajczak: Conceptualization, Resources, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Małgorzata Tańska:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization, Validation, Supervision, Project administration. **Dorota Ogrodowska:** Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision. **Sylwester Czaplicki:** Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2022.133390.

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Impact of the addition of 4-vinyl-derivatives of ferulic and sinapic acids on retention of fatty acids and terpenoids in cold-pressed rapeseed and flaxseed oils during the induction period of oxidation

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ABSTRACT

In the western diet there is an oversupply of n-6 fatty acids. This adverse trend can be balanced by the consumption of rapeseed and flaxseed oils rich in α-linolenic acid (n-3). However, the high share of this fatty acid contributes to low oxidative stability of oil. Oxidation decreases n-3 fatty acid and other bioactive compounds contents, which adversely affects oil nutritional value. In this study, the impact of ferulic and sinapic acids vinyl derivatives on the fatty acids and oil terpenoids (sterols, tocols, carotenoids, squalene) retention at the end of induction period during accelerated oxidation of rapeseed and flaxseed cold-pressed oils was investigated. It was found that the use of 4-vinylsyringol (4-VS) or 4-vinylquaiacol (4-VQ) increased the retention of intact sterols and carotenoids (at least 2-fold) and squalene (at least 4-fold). The 4-VQ addition also inhibited the α-linolenic acid loss. Unfortunately, both phenolic derivatives favoured α-tocopherol decay in rapeseed oil.

1. Introduction

In recent years, an increase in the production and use of cold-pressed plant oils has been observed. Depending on the plant material used, they are characterized by specific colour, taste, fatty acid composition and profile of lipid-soluble compounds (Choe & Min, 2006; Prescha, Grajzer, Dedyk, & Grajeta, 2014). Oils rich in n-3 linolenic acid are especially valuable, since replacing with them other oils containing mainly n-6 fatty acids can improve the balance between n-6 and n-3 fatty acids in the human diet (Shukla & Bhattacharya, 2004). Despite many oils being abundant in n-3 linolenic acid, the most popular are still rapeseed (canola) and flaxseed oils. Unfortunately, along with the increase of share of this fatty acid there is an increase in oil susceptibility to oxidative deterioration, which causes significant degradation of unsaturated fatty acids and other bioactive compounds (Gutiérrez, Villafranca, & Castellano, 2002). The creation of low molecular weight off-flavour compounds makes oil less acceptable to consumers and industry (Choe & Min, 2006) and can have adverse, even toxic, effects on human health (Rudzińska, Korczak, & Wąsowicz, 2005).

Unrefined cold-pressed oils are naturally protected by native antioxidants (Fig. 1). Among them, phenolic compounds have recently attracted broad scientific interest. Many studies have shown that the oxidative stability of plant oils is highly related to their abundance in phenolic compounds (Dąbrowski, Konopka, Czaplicki, & Tańska, 2017; Gruzdiene & Anelauskaite, 2011; Roszkowska, Tańska, Czaplicki, & Konopka, 2015). However, the content of phenolic compounds in each type of oil is differentiated by the method of production. For example, rapeseed oil can contain from mere traces of phenolic compounds (Roszkowska et al., 2015) to above 8000 mg/kg (Gruzdiene & Anelauskaite, 2011). Generally, the lowest amounts are found in cold-pressed oils, which contain up to 32 mg/kg of these compounds (Roszkowska et al., 2015; Siger, Nogala-Kalucka, & Lampart-Szczapa, 2008). The main phenolic compounds in rapeseed oil are sinapic acid and its derivatives (Niu, Jiang, Wan, Yang, & Hu, 2013), such as dominant 4-vinylsyringol (canolol) which can account for 85% of total phenolics in crude rapeseed oil (Kraljić et al., 2015). Similar variation in phenolic compounds is noted for flaxseed oil. The cold-pressed flaxseed oils contain from ca. 4–48 mg/kg (Khattab & Zeitoun, 2013; Siger et al., 2008; Tańska, Mikołajczak, & Konopka, 2018) to as high as 895–3242 mg of phenolic compounds per kg (Choo, Birch, & Dufour, 2007). According to various authors, the major phenolics of this oil are: p-hydroxybenzoic, vanillic and ferulic acids (Siger et al., 2008); vanillic acid (Tuberoso, Kowalczyk, Sarritzu, & Cabras, 2007) or vanillin (derivative of ferulic acid) (Hasiewicz-Derkacz et al., 2015). Some oils can also contain selected lignans, such as secoisolariciresinol diglycoside (Herchi, Sakouhi, Khaled, & Curtis, 2011; Khattab & Zeitoun, 2013). The minor phenolic components in this oil are non-hydrolysable proanthocyanidins and hydrolysable tannins, p-coumaric acid, caffeic

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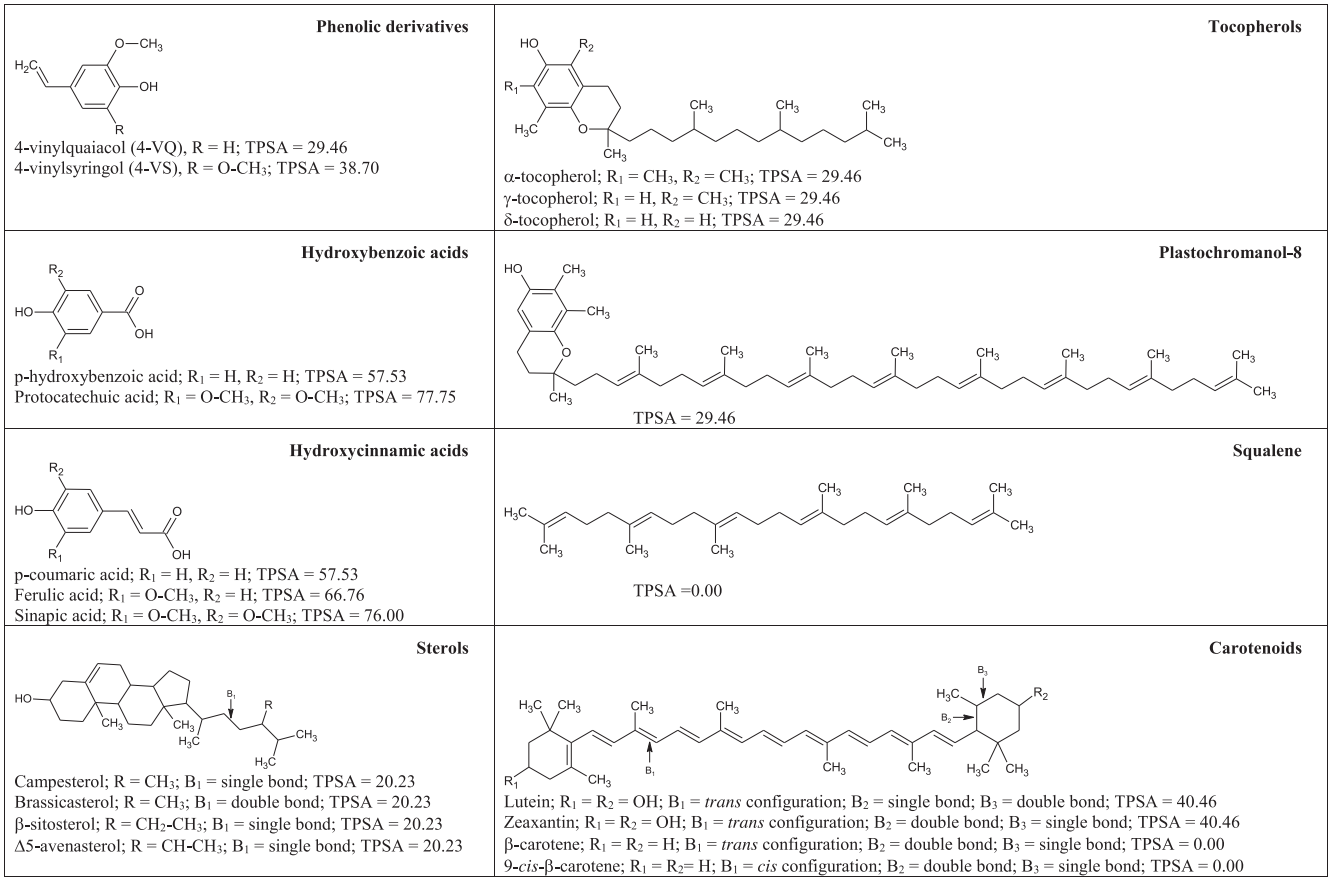


Fig. 1. A comparative scheme of the molecular structures and topological polar surface area (TPSA) values of phenolic additives and bioactive compounds found in used oils. TPSA was calculated with the use of http://www.molinspiration.com.

acid, coniferyl- and syringaldehyde and small amounts of flavonoids (Hasiewicz-Derkacz et al., 2015). In general, phenolic compounds are preferentially co-extracted to oil after thermal, pressure or microbial seed pre-treatment (Galano, Francisco-Márquez, & Alvarez-Idaboy, 2011). For example, microwave treatment can increase the canolol yield from 50 to 800 mg/kg of pressed rapeseed oil (Zheng, Yang, Zhou, Liu, & Huang, 2014). In contrast, refining can decrease the total content of phenolic compounds by 90% (Kraljić et al., 2015).

Since the phenolic compounds concentration in cold-pressed oils is relatively low, it seems reasonable to enrich them with natural phenolic compounds. In the authors' recent study, it was found that the addition of 4-vinylguaiacol (4-VQ) or 4-vinylsyringol (4-VS) increases the induction period (IP) of flaxseed, olive and rapeseed oils, with the highest increase (53%) for the addition of 80 mg 4-VQ per 100 g of flaxseed oil (Tańska, et al., 2018). We assumed that such prolongation of shelf-life of this oil is commercially reasonable, while the higher addition may affect the oils' sensory properties, since phenolic acids give astringency and bitterness to food. An important reason for the use of vinyl derivatives is their higher solubility in oil matrices than their parental moieties (Pudel et al., 2014). For example, the topological polar surface area of ferulic acid is 66.76, while for its vinyl derivative it is only 29.46 (own calculations with the use of http://www.molinspiration.com).

The key antioxidative mechanisms of phenolic compounds proceed by hydrogen atom transfer (HAT) or by single electron transfer (SET) (Koroleva et al., 2014). For bulk oil, the HAT mechanism predominates (Zhu, Long, Zhou, Prenzler, & Zhong, 2013). The value of bond dissociation energy (BDE) for the O—H group of the phenolic antioxidant predicts its antioxidative activity and the stability of the formed antioxidant radical (a lower BDE results in a more active antioxidant and a more stable antioxidant radical). The O—H bond strength of phenolic antioxidants is affected by the substitution of hydrogen in a benzene ring. Any substituent destabilizing the ground-state of phenolic antioxidant and/or stabilizing antioxidant radical reduces the O—H bond strength (Choe & Min, 2009). Higher antioxidative activity of 4-VQ than 4-VS suggests a lower BDE of O—H bond in this first molecule. However, besides variation of BDE, the potential to stabilize bulk oil against oxidation is conditioned by the polarity of the antioxidant. According to the "polar paradox" theory, polar antioxidants (like phenolic compounds) are better protectors of hydrophobic matrices than typical non-polar counterparts (like tocols). According to a recently proposed hypothesis, the real site of oxidation in bulk oil is the oil-water interface (Budilarto & Kamal-Eldin, 2015; Laguerre et al., 2015). The formation of colloid associations with traces of water is facilitated by surface-active compounds, which are components of natural plant oils (phospholipids, sterols, free fatty acids, phenolic compounds, etc.) or can be created during oxidation (Chaiyasit, Elias, McClements, & Decker, 2007). Lipid oxidation in such bulk oil starts by pseudo-first order slow build-up of hydroperoxides until these reach their critical micelle concentration (CMC) and start aggregation to form reversed micelles (Brimberg & Kamal-Eldin, 2003). The main effects of anti- and pro-oxidants depend on their modulation of the CMC of lipid hydroperoxides (Budilarto & Kamal-Eldin, 2015). In summary, oxidized oil is a mixture of reversed nano-/micro- micelles and other colloidal structures suspended in a matrix of triacylglycerols (TAGs) and compounds of low polarity (squalene, carotenoids, sterols, etc.) (Budilarto & Kamal-Eldin, 2015). At a water content less than 0.3 wt% they are dispersed in bulk oil as spherical reverse micelles or as lamellar structures (more details in Laguerre et al., 2015).

Although vinyl-derivatives of phenolic acids are less polar than parental counterparts, they still have higher affinity to an oil-water interface than typical lipophilic antioxidants. In this study, the impact of vinyl derivatives of ferulic and sinapic acids on the retention of fatty

acids (mainly α-linolenic) and natural terpenoids (sterols, tocols, carotenoids, squalene) in cold-pressed rapeseed and flaxseed oils at the end of induction period during oxidation was investigated. The study was a continuation of our earlier work (Tańska et al., 2018), in which we found that 4-vinyl-derivatives of ferulic and sinapic acids efficiently increased induction period of cold-pressed flaxseed and rapeseed oils.

2. Materials and methods

2.1. Research materials

The research materials were two types of commercial cold-pressed plant oils (rapeseed and flaxseed oils) from the local market in Poland. Both oils were produced in Poland and according to the manufacturer were of a suitable shelf life. The oils were analysed after opening the packaging and kept between analyses in a freezer (at −20 °C).

2.2. Reagents and chemicals

Phenolic acids derivatives, 4-vinylsyringol (4-ethenyl-2,6-dimethoxyphenol, 4-VS) and 4-vinylguaiacol (2-methoxy-4-vinylphenol, 4-VG), were used as commercially available analytical standards with a declared purity > 95%. The 4-VS was purchased from Sigma-Aldrich (St. Louis, MO, United States, supplier Poznań, Poland) and the 4-VG from EnamineStore (Riga, Latvia).

Analytical standards: D-catechin (declared purity > 98%), 5α-cholestane (declared purity > 97%), β-apo-8′-carotenal (declared purity > 96%), phenolic acids (declared purity > 98%) and margaric acid (declared purity > 98%) were purchased from Sigma-Aldrich and tocopherols (declared purity > 95%) from Calbiochem (Nottingham, United Kingdom). Chromatography-grade solvents: acetone, hexane, isopropanol, pyridine, N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) were purchased from Sigma-Aldrich. Analytical-grade reagents: Folin–Ciocalteau reagent (Sigma-Aldrich), sodium carbonate and sodium hydroxide (POCH, Gliwice, Poland) were used. Deionized water was obtained from HLP 5 deionizer (Hydrolab, Gdańsk, Poland).

2.3. Accelerated oxidation test

The phenolic acid derivatives were dissolved in acetone and added to each oil sample to obtain a final concentration of 80 mg of 4-VS or 4-VG per 100 g of oil. Fresh oils and oxidized oils, both without and with 80 mg/100 g addition of phenolic acids derivatives, were analysed. The oxidized oils were obtained by using an accelerated oxidation test with a thermal research chamber KBC-100 W type (WAMED, Warsaw, Poland). Briefly, six oil samples (100 g of each oil, without and with addition of phenolic acids derivatives) were placed in a separate 400 mL open beakers (8 cm diameter and 11 cm height) and held in an oven at 110 ± 1 °C for the “induction time” determined in the Rancimat test (8.80 h, 9.08 h and 10.83 h for control rapeseed oil and oils with 4-VS and 4-VQ, respectively and 1.96 h, 2.00 h and 3.00 h for control flaxseed oil and oils with 4-VS and 4-VQ, respectively). Once removed from the oven, beakers with oil samples were immediately cooled and stored at approx. 8 °C before further analyses (up to five days). To avoid oxidation, the beakers after cooling were purged with nitrogen and tightly covered with parafilm. Samples for analyses were collected successively (each group of compounds at the same time, as follows: tocopherols, carotenoids, fatty acids, phenolic compounds, sterols and squalene). After each use of a beaker, it was purged with nitrogen and again tightly covered.

2.4. Analysis of phenolic compounds

The total content of phenolic compounds was determined spectrophotometrically with Folin-Ciocalteu reagent using UNICAM UV/Vis UV2 spectrophotometer (ATI Unicam, Cambridge, United Kingdom) according to method proposed by Siger et al. (2008). The phenolic compounds were extracted with 80% methanol (v/v), and the final results were calculated on the basis of the calibration curve on the content of D-catechins.

The phenolic acids were analysed by RP-HPLC technique using an Agilent Technologies 1200 RP-HPLC apparatus (Santa Clara, CA, USA), equipped with a photodiode detector and Eclipse XDB-C18 chromatography column (150 mm × 4.6 mm × 5 µm, Agilent Technologies, Santa Clara, CA, USA). The extraction of phenolic acids was performed according to the method given by Siger et al. (2008) using a vacuum equalizer (Witko, Łódź, Poland) and SPE Supelco columns filled with diol (500 mg) (Sigma-Aldrich, Poznań, Poland). Chromatographic separation and identification of individual compounds was based on the methodology described by Konopka, Tańska, Faron, and Czaplicki (2014). The column temperature was 30 °C and the mobile phase consisted of water:acetonitrile:formic acid (88:10:2, v/v/v). The isocratic flow rate was equal to 0.8 mL/min. Detection was performed at the wavelength of 260 and 320 nm. Phenolic acids were identified by comparing with retention times and absorption spectra of the reference phenolic acids. The content of phenolic acids was determined from calibration curves prepared for phenolic acid standards.

2.5. Analysis of fatty acid composition

Fatty acid composition was determined according to the method described by Czaplicki, Tańska, and Konopka (2016). To the oil samples margaric acid solution as an internal standard and chloroform:methanol:sulfuric acid mixture (100:100:1, v/v/v) were added. The methylation of fatty acids was carried out by heating the mixture at 70 °C for 2 h. After cooling, the powdered zinc was added to the mixtures. The obtained methyl esters were dried in a stream of nitrogen, redissolved in hexane and centrifuged. The analysis was carried out with the use of gas chromatography technique using a GC–MS QP2010 PLUS system (Shimadzu, Japan). Fatty acids separation was performed on a BPX70 capillary column (25 m × 0.22 mm × 0.25 µm, SGE Analytical Science, Victoria, Australia). The temperatures of GC–MS were set as follows: interface 240 °C, the ion source 240 °C, column temperature was programmed in the range from 150 °C to 250 °C. Helium was used as the carrier gas at a flow rate of 0.9 mL/min. The electron energy was set at 70 eV. Fatty acids were identified using retention times and mass spectra of peaks. Their content was determined based on the concentration of the internal standard.

2.6. Analysis of squalene and sterols

The squalene and sterol fractions were analysed by gas chromatography using a GC–MS QP2010 PLUS (Shimadzu, Kyoto, Japan), equipped with a ZB-5MSi capillary column (30 m × 0.25 mm × 0.25, Phenomenex, Torrance, CA, USA). Samples were prepared and analysed according to the methodology provided by Roszkowska et al. (2015). The oil samples were dissolved in ethanol, and 5α-cholestane solution was added as an internal standard. The mixtures were saponified by adding 10 M KOH solution in ethanol at a temperature of 70 °C for 30 min. The unsaponifiables were extracted with diethyl-ether and evaporated in a vacuum evaporator at 45 °C. The dry extracts were redissolved in hexane, centrifuged and evaporated under a nitrogen stream. To the residues pyridine and N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) were added, and the mixtures were heated at 60 °C for 60 min. After derivatization heptane was added, and the mixtures were analysed. The helium as a carrier gas with a 0.9 mL/min flow rate was used. The temperatures were as follows: injector −230 °C, column −70 °C increased to 230 °C at 15 °C/min, and to 310 °C at 3 °C/min, and maintained for 10 min, GC–MS interface −240 °C, ion source −220 °C. Electron energy was set as 70 eV. The total ion current (TIC) mode was

used for quantification (100–600 *m/z* range). Sterols were identified using retention times and mass spectra of peaks, and their content and content of squalene were determined based on the concentration of internal standard.

2.7. Analysis of tocols

The tocol analysis was performed by RP-HPLC technique using an Agilent Technologies 1200 RP-HPLC apparatus (Santa Clara, CA, USA), equipped with a fluorescent detector of the same company and a LiChrospher Si 60 chromatography column (250 mm × 4 mm × 5 μm, Merck, Darmstadt, Germany). Samples were prepared and analysed according to the methodology provided by Czaplicki et al. (2016). The oil samples were diluted in hexane and subsequently centrifuged. The mobile phase was 0.7% isopropanol in a hexane solution and flow rate was at 1 mL/min. The fluorescence detector was set at excitation and emission wavelengths of 296 nm and 330 nm, respectively. The content of tocols was determined from calibration curves prepared for tocol standards.

2.8. Analysis of carotenoids

The carotenoids were determined by RP-HPLC technique using an Agilent Technologies 1200 RP-HPLC apparatus (Santa Clara, CA, USA), equipped with a diode array detector (DAD), a YMC-C30 chromatography column (150 mm × 4.6 mm × 5 μm) and a YMC-C30 precolumn (10 mm × 4.6 mm × 3 μm) (YMC-Europe GmbH, Dinslaken, Germany). Samples were prepared and analysed according to the methodology provided by Czaplicki et al. (2016). The oil samples were diluted in hexane with β-apo-8′-carotenal as an internal standard and saponified with 40% KOH solution in methanol. The solutions were vigorously shaken in Multi Rotator RS-60 (Biosan, Riga, Latvia) in the dark at room temperature for 16 h saponification. After saponification 10% Na_2SO_4 was added to each sample and extraction of carotenoids were performed fourfold with hexane. Collected extracts were evaporated to dryness and then dissolved in methanol:dichloromethane mixture (45:55, v/v). The column temperature was 30 °C and a methanol (A) vs. methyl tert-butyl ether (MTBE) (B) gradient was used for elution. The gradient was programmed as follows: 0–5 min 95% of A, until 25 min decreases to 72% of A and keep decreasing until 33 min to 5% of A. Then it increases to 95% of A and is stable until 60 min. Absorbance was measured at 450 nm. Carotenoids were identified by comparing with retention times and absorption spectra of the reference carotenoids and their content was determined based on the concentration of the internal standard.

2.9. Statistical analysis

All analyses of the research material were performed in triplicate. The obtained results were analysed using Statistica 12.5 PL software (StatSoft, Kraków, Poland). One-way analysis of variance (ANOVA) with post-hoc mean separation was performed by Duncan's multiple range test at $p \leq 0.05$ significance level.

3. Results and discussion

3.1. Phenolic compounds in native and enriched rapeseed and flaxseed oils and their retention upon oxidation

The initial content of total phenolic compounds equalled 1.03 mg/100 g in rapeseed oil and 1.56 mg/100 g in flaxseed oil (Table 1). These values were relatively low, since in typical cold-pressed rapeseed oil their content is up to 32 mg/100 g (Roszkowska et al., 2015), while in flaxseed oil they can reach 137–324 mg/100 g (Choo et al., 2007), although some flaxseed oils contain only 0.4 mg/100 g (Tańska, Roszkowska, Skrajda, & Dąbrowski, 2016). The highest content of phenolic compounds in flaxseed oils can be found following extraction from not fully ripened seeds (Herchi et al., 2011) or from seeds of new genotypes (Hasiewicz-Derkacz et al., 2015). Among the determined compounds, phenolic acids existed only in trace amounts, reaching 21.10 μg/100 g in rapeseed oil and 4.38 μg/100 g in flaxseed oil. The following have been identified: protocatechuic, p-OH-benzoic and p-coumaric acids in flaxseed oil and sinapic, ferulic and p-coumaric acids in rapeseed oil, with the maximal amount of sinapic acid in rapeseed oil equalling 12.30 μg/100 g of oil. The addition of vinyl derivatives of phenolic acids increased the concentration of phenolic compounds to ca. 81 mg/100 g, which is the medium level found in various plant oils.

Native and added phenolic compounds were nearly completely destroyed during oil oxidation and only 2% and 7% of them survived in rapeseed and flaxseed oils, respectively. In oils enriched with vinyl derivatives, the total content of phenolic compounds decreased to 14.99–15.44 mg/100 g for 4-VS and to 3.43–4.71 mg/100 g for 4-VQ. This indicates ca. 81% and ca. 95% decomposition of 4-VS and 4-VQ, respectively. The observed decay of phenolic compounds suggests their consumption as primary antioxidants. In further paragraphs, the impact of added phenolic compounds on the retention of fatty acids and other minor lipophilic compounds will be determined.

3.2. Alfa-linolenic and other fatty acid retention during oil oxidation

In cold-pressed plant oils, TAGs constitute 94–98% of oil mass (McGinley, 1991), while the fatty acids share varies from 87% to 91% of TAGs mass (D'Souza, 1979). The rest of the oil matrix is composed of sterols, tocols, carotenoids, chlorophylls, phospholipids, phenolic compounds, squalene, water and volatile matter (Choo et al., 2007; Roszkowska et al., 2015).

In the study, fresh cold-pressed rapeseed and flaxseed oils contained 87.20 and 87.19 g/100 g of fatty acids, respectively. Shares of α-linolenic acid were 11.7% in rapeseed oil and 45.2% in flaxseed oil (Table 2) and overlapped with previously determined results. It is worth noting that the fatty acid composition of rapeseed oil is relatively constant (Roszkowska et al., 2015), while commercial flax oils highly differ in composition, with a variation of α-linolenic acid share from 36.7% to 60.7% (Tańska et al., 2016).

The impact of oxidation was different for each kind of oil (Fig. 2). In rapeseed oil, relatively small changes in fatty acid content and composition were determined. In control oil (unprotected), the decrease of α-linolenic acid was 13.7%, while in oils enriched with vinyl derivatives of phenolic acids, the decrease of this fatty acid reached only 2.9–3.5% in relation to the used derivative. Among the remaining fatty acids, the main changes were noted for two fatty acids present in trace amounts: palmitoleic and arachidic acids. A substantially higher impact of oxidation was observed for flaxseed oil. In oxidized control oil, the decrease of α-linolenic acid was 22.3%, accompanied by 45.1% decay of γ-linolenic acid and 27.1% of palmitoleic acid. Unfortunately, for flaxseed oil, 4-VS favoured the breakdown of all fatty acids. In contrast, after the use of 4-VQ, the decay of α-linolenic acid was restricted to 8.3% only.

3.3. Sterol retention during oil oxidation

The initial sterol content was 700 mg/100 g in rapeseed oil and 283 mg/100 g in flaxseed oil (Table 3). Used rapeseed oil was abundant in these compounds, since cold-pressed oils usually contain an approx. 2-fold lower level of them (Roszkowska et al., 2015). In contrast, used flaxseed oil was relatively poor in sterols, considering the level of 689 mg/100 g found by Schwartz, Ollilainen, Piironen, and Lampi (2008) and range 331–441 mg/100 g of oil determined by Matthaus and Ozcan (2017) and Shim, Gui, Wang, and Reaney (2015). In fresh oils, the main sterol, regardless of the oil type, was β-sitosterol, constituting 50.1% in rapeseed oil and 67.9% in flaxseed oil. Less abundant were campesterol (37.3% in rapeseed oil and 22.0% in flaxseed oil),

Table 1
Content of total phenolic compounds (mg/100 g) and phenolic acids (μg/100 g) in fresh and oxidized rapeseed and flaxseed oils.

Phenolic compounds	Rapeseed oil				Flaxseed oil			
	Fresh*	Oxidized	4-VS	4-VQ	Fresh*	Oxidized	4-VS	4-VQ
Sinapic	12.30^{a}	10.60^{b}	11.40^{a}	9.00^{c}	0.00^{a}	0.00^{a}	0.00^{a}	0.00^{a}
p-coumaric	3.33^{a}	2.05^{b}	2.13^{b}	3.05^{a}	0.23^{a}	0.00^{b}	0.00^{b}	0.00^{b}
Protocatechuic	0.00^{a}	0.00^{a}	0.00^{a}	0.00^{a}	1.48^{a}	0.76^{b}	1.45^{a}	0.00^{c}
p-OH-benzoic	0.00^{a}	0.00^{a}	0.00^{a}	0.00^{a}	1.17^{a}	0.57^{b}	1.01^{c}	1.03^{c}
Ferulic	5.42^{a}	5.05^{b}	3.65^{c}	3.95^{c}	0.00^{a}	0.00^{a}	0.00^{a}	0.00^{a}
Total phenolic acids	21.10^{a}	17.70^{b}	17.20^{b}	16.00^{c}	4.38^{a}	1.33^{b}	2.46^{c}	1.03^{d}
Total phenolic compounds	1.03^{a}	0.02^{b}	15.44^{c}	3.43^{d}	1.56^{a}	0.11^{b}	14.99^{c}	4.71^{d}

a, b, c, … Mean values in the same line separately for each oil type followed by different letters are significantly different ($p \leq 0.05$).
* Results of fresh oils are taken from the study of Tańska et al. (2018).

brassicasterol (11.3%, only in rapeseed oil), and Δ5-avenasterol (1.3% in rapeseed oil and 10.1% in flaxseed oil). The determined composition of sterols overlapped with shares presented elsewhere (Matthaus & Ozcan, 2017; Roszkowska et al., 2015; Schwartz, et al., 2008).

In oxidized oils, a substantial reduction of native sterols was observed. In both oils, ca. 45% of sterols were destroyed, with the highest decay of brassicasterol in rapeseed oil (51%) and β-sitosterol in flaxseed oil (52%). Among the determined sterols, the highest oxidative resistance was found for Δ5-avenasterol (60% and 70% was retained in rapeseed and flaxseed oils after oxidation, respectively). The formation of oxysterols proceeds through a free radical chain reaction and is accelerated at a temperature typical of frying (Dutta, Przybylski, Eskin, & Appelqvist, 2007). For sterols, hydrogen donors can be hydroxyl O—H and C—H bonds, but the C—H bonds with lower BDE values correspond to the dominant site of oxidation attack (Skorna, Lengyel, Rimarcik, & Klein, 2014). It seems that molecules with a C14 atom in the α-position to a C=C double bond are probably the major donor of hydrogen (Skorna et al., 2014). According to the cited study, sterol nuclei are more susceptible to the oxidation than side chains, which contradicts the current view on the antioxidant potential of ethylidene group found, for example, in Δ5-avenasterol. Used vinyl derivatives of phenolic acids improved sterol retention in oils. For rapeseed oil, the addition of 4-VQ resulted in 95% retention of native sterols, with variation from 91% to 97% in relation to homologue type. 4-VS was less efficient, with the lowest impact on the retention of brassicasterol (77%) and campesterol (78%). In summary, the impact of phenolic acids derivatives was less spectacular for flaxseed oil, with retention of 86–87% of total sterols, regardless of the type of vinyl-derivative.

3.4. Tocol retention during oil oxidation

The output content of tocols was 71.8 mg/100 g in rapeseed oil and 47.4 mg/100 g in flaxseed oil (Table 3). Among these compounds, γ-tocopherol prevailed, reaching 55.4% in rapeseed oil and 74.5% in flaxseed oil. Besides this, rapeseed oil contained α-tocopherol (37.0% of total) and small shares of δ-tocopherol and plastochromanol-8. In contrast, the latter compound constituted 25.1% of flaxseed tocols and was accompanied by a trace share of δ-tocopherol. The determined contents overlapped with the results cited for rapeseed oil (Roszkowska et al., 2015; Schwartz et al., 2008) and flaxseed oil (Khattab & Zeitoun, 2013; Matthaus & Ozcan, 2017; Shim et al., 2015). However, some flax genotypes can contain an extremely high tocol content, like Railinus with ca. 437 mg/100 g of oil (Matthaus & Ozcan, 2017). For flaxseed oil, tocol composition can also be highly varied. For example, Khattab & Zeitoun (2013) identified only α-, γ + β and δ-homologues, while Matthaus & Ozcan (2017) found a high share of plastochromanol-8 (up to 33% of the total fraction) in some genotypes.

Surprisingly, the decay of tocols in both oxidized control oils was relatively low. For rapeseed oil, only a 9% decrease in total tocols was found, which was the highest for plastochromanol-8 (50%), while γ-tocopherol survived almost entirely (99%). In flaxseed oil, tocols were only 4% destroyed. Among them, the highest decrease (40%) was noted for δ-tocopherol, but in quantitative terms it was a decline from 0.20 to 0.12 mg/100 g. Unfortunately, the addition of vinyl derivatives of phenolic acids favoured tocol degradation, especially in rapeseed oil. This was mainly visible for 4-VS, for which the decline of α-tocopherol, plastochromanol-8, and γ-tocopherol was 75%, 67% and 47%, respectively. The overall impact of 4-VQ was similar, but the extent of adverse effects was substantially lower. Interestingly, this effect was not stated for flaxseed oil. In this oil, almost all intact forms of tocopherols were

Table 2
Content of fatty acids (g/100 g) in fresh and oxidized rapeseed and flaxseed oils.

	Rapeseed oil				Flaxseed oil			
	Fresh*	Oxidized	4-VS	4-VQ	Fresh*	Oxidized	4-VS	4-VQ
Palmitic	5.94^{ac}	6.23^{b}	5.85^{c}	5.98^{a}	6.06^{a}	5.99^{a}	4.95^{b}	5.99^{a}
Palmitoleic	0.28^{a}	0.25^{a}	0.25^{a}	0.25^{a}	0.06^{a}	0.05^{a}	0.03^{b}	0.05^{a}
Stearic	2.60^{a}	2.73^{b}	2.52^{c}	2.56^{ac}	3.48^{a}	3.54^{a}	2.82^{b}	3.49^{a}
Oleic	45.98^{a}	46.31^{b}	47.39^{c}	47.89^{c}	21.69^{a}	19.00^{b}	16.30^{c}	21.04^{ad}
Linoleic	19.47^{a}	18.72^{b}	19.71^{ac}	19.90^{c}	15.82^{a}	12.62^{b}	10.55^{c}	14.68^{d}
γ-Linolenic	0.00^{a}	0.00^{a}	0.00^{a}	0.00^{a}	0.20^{a}	0.11^{b}	0.08^{c}	0.17^{a}
α-Linolenic	10.17^{a}	8.77^{b}	9.87^{c}	9.81^{c}	39.39^{a}	30.60^{b}	26.58^{c}	36.14^{d}
Arachidic	0.95^{a}	0.95^{a}	0.88^{b}	0.88^{b}	0.18^{a}	0.17^{a}	0.14^{b}	0.19^{a}
Eicosenoic	1.83^{a}	1.80^{a}	1.82^{a}	1.83^{a}	0.30^{a}	0.26^{b}	0.21^{c}	0.30^{a}
SFA	9.48^{a}	9.91^{b}	9.25^{c}	9.42^{a}	9.73^{a}	9.70^{a}	7.92^{b}	9.67^{a}
MUFA	48.09^{a}	48.37^{a}	49.46^{b}	49.97^{b}	22.05^{a}	19.31^{b}	16.54^{c}	21.39^{d}
PUFA	29.63^{ac}	27.48^{b}	29.58^{a}	29.71^{c}	55.41^{a}	43.33^{b}	37.21^{c}	50.99^{d}

a, b, c, … Mean values in the same line separately for each oil type followed by different letters are significantly different ($p \leq 0.05$).
* Results of fresh oils are taken from the study of Tańska et al. (2018).

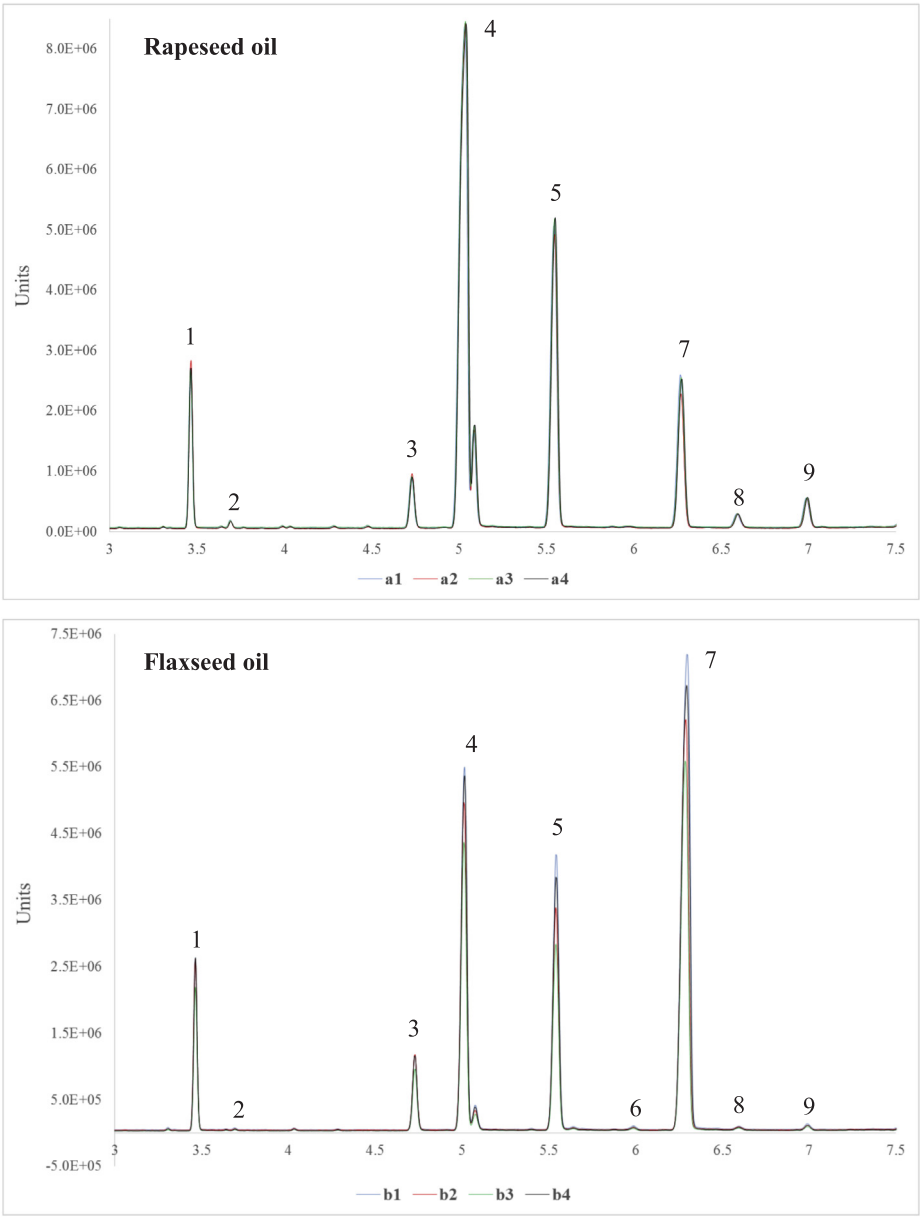


Fig. 2. GC chromatograms of fatty acids of studied oils: a1) fresh rapeseed without additives, a2) oxidized rapeseed without additives, a3) oxidized rapeseed with 4-vinylsyringol, a4) oxidized rapeseed with 4-vinylguaiacol, b1) fresh flaxseed without additives, b2) oxidized flaxseed without additives, b3) oxidized flaxseed with 4-vinylsyringol, b4) oxidized flaxseed with 4-vinylguaiacol. Peak identification: 1. palmitic acid, 2. palmitoleic acid, 3. stearic acid, 4. oleic acids, 5. linoleic acid, 6. γ-linolenic acid, 7. α-linolenic acid, 8. arachidic acid, 9. eicosenoic acid.

retained after oxidation.

Tocopherol stability during oxidation in the TAGs matrix depends mainly on their concentration, homologues composition, temperature of reaction, oxygen availability, degree of TAGs unsaturation and the position of the unsaturated fatty acid within the TAG molecule. In our study, determined tocopherol depletion in rapeseed oil ranged from 17.3% (oxidized control oil) to 74.5% (oil with 4-VS). In general, tocopherols are efficient antioxidants at low concentrations, for example 60–100 mg/kg for α-tocopherol in olive oil (more data in Kamal-Eldin, 2006). In used oils, their content was relatively high; at such concentrations, tocopherols can compete with unsaturated fatty acids in reactions with alkoxyl radicals that lead to increased rates of initiation (Verleyen et al., 2002). However, tocopherol decay can be substantially diminished by the addition of phenolic acids like, for example, gallic acid, which prolonged ca. 4-fold half-life of α-tocopherol in sunflower oil oxidized in 120 °C (Reblova, Fisnar, Tichovska, Dolezal, & Joudalova, 2012). Used rapeseed oil contained small amount of natural phenolic acids (21 μg/100 g) and other phenolic compounds (ca. 1 mg/100 g), which could protect α-tocopherol decay. On the other hand, the addition of vinyl derivatives (especially 4-VS) increased its decay. It can be related to the greater topological polar surface area of 4-VS (38.70) than of 4-VQ (29.46). It seems that α-tocopherol can be exhausted in oil as a result of the protection of the more polar 4-VS. Additionally, in the case of rapeseed oil overall content and share of main tocopherol homologues was important, since at a concentration of α-tocopherol above 100 mg/kg (like in our study) this compound is less stable than γ-tocopherol (Lampi, Kataja, Kamal-Eldin, & Vieno, 1999).

However, the observed phenomenon of the destructive effect of vinyl derivatives of ferulic and sinapic acids on tocols during thermal oxidation needs further investigations. Both of these compounds differ in affinity to active site of oxidation in bulk oil, and probably differ in the BDE value of O—H group (Choe & Min, 2009). Up to-date, the

Table 3
Content of terpenoids (mg/100 g) in fresh and oxidized rapeseed and flaxseed oils.

Compounds	Rapeseed oil				Flaxseed oil			
	Fresh*	Oxidized	4-VS	4-VQ	Fresh*	Oxidized	4-VS	4-VQ
Campesterol	261.00^{a}	144.50^{b}	204.00^{c}	242.00^{d}	62.50^{a}	42.15^{b}	60.00^{c}	58.50^{d}
β-Sitosterol	351.00^{a}	205.50^{b}	317.00^{c}	342.00^{a}	192.50^{a}	91.50^{b}	160.50^{c}	157.50^{c}
Brassicasterol	79.00^{a}	39.10^{b}	61.00^{c}	73.50^{d}	0.00^{a}	0.00^{a}	0.00^{a}	0.00^{a}
Δ5-avenasterol	9.05^{a}	5.40^{b}	8.15^{c}	8.20^{c}	28.65^{a}	20.15^{b}	25.80^{c}	26.75^{d}
Total sterols	700.00^{a}	394.50^{b}	590.50^{c}	665.50^{d}	283.50^{a}	153.50^{b}	246.50^{c}	242.50^{c}
α-Tocopherol	26.60^{a}	22.00^{b}	6.78^{c}	16.20^{d}	0.00^{a}	0.00^{a}	0.00^{a}	0.00^{a}
γ-Tocopherol	39.80^{a}	39.50^{a}	21.10^{b}	34.40^{c}	35.30^{a}	34.30^{b}	32.20^{c}	35.20^{a}
δ-Tocopherol	2.33^{a}	1.97^{b}	2.19^{c}	1.79^{d}	0.20^{a}	0.12^{bc}	0.14^{b}	0.11^{c}
Plastochromanol-8	3.06^{a}	1.53^{b}	1.02^{c}	1.62^{b}	11.90^{a}	11.30^{b}	11.90^{a}	11.70^{a}
Total tocols	71.80^{a}	65.00^{b}	31.10^{c}	54.00^{d}	47.40^{a}	45.70^{b}	44.20^{c}	47.00^{a}
Lutein	3.26^{a}	0.69^{b}	3.05^{a}	2.53^{c}	1.16^{a}	0.14^{b}	1.09^{c}	0.98^{c}
Zeaxanthin	0.12^{a}	0.10^{ab}	0.08^{b}	0.04^{c}	0.11^{a}	0.06^{b}	0.08^{c}	0.08^{c}
β-Carotene	1.45^{a}	1.29^{b}	1.21^{b}	1.02^{c}	3.35^{a}	1.23^{b}	2.44^{c}	2.22^{c}
9-cis-β-Carotene	0.43^{a}	0.34^{b}	0.42^{a}	0.38^{c}	0.14^{a}	0.25^{b}	0.25^{b}	0.21^{b}
Total carotenoids	5.26^{a}	2.42^{b}	4.75^{c}	3.97^{d}	4.76^{a}	1.67^{b}	3.86^{c}	3.49^{d}
Squalene	2.18^{a}	0.41^{b}	1.92^{c}	1.99^{c}	2.39^{a}	0.51^{b}	2.31^{c}	2.36^{ac}

a, b, c, … Mean values in the same line separately for each oil type followed by different letters are significantly different ($p \leq 0.05$).
* Results of fresh oils are taken from the study of Tańska et al. (2018).

studied phenolic acid derivatives have not yet been tested in this respect.

3.5. Carotenoid retention during oil oxidation

The initial content of carotenoids was similar in both oils and equalled 5.26 and 4.76 mg/100 g in rapeseed and flaxseed oil, respectively (Table 3). For rapeseed oil, this value was relatively low, since cold-pressed oils can contain up to 27 mg/100 g of carotenoids (Roszkowska et al., 2015). In contrast, flaxseed oil was rich in these compounds, since in typical oil, the carotenoid content did not exceed 3 mg/100 g (Tańska et al., 2016). Significantly higher values can be found only in oils from genetically modified seeds, with a possible 7.8 to 18.6-fold increase in carotenoid content (Fujisawa et al., 2008). The used types of oils differed in carotenoid composition. In rapeseed oil, lutein prevailed (62%), followed by β-carotene (27.6%), 9-cis-β-carotene (8.2%) and zeaxanthin (2.3%), while in flaxseed oil, β-carotene was the most abundant (70.4%) and was accompanied by lutein (24.4%) and aligned shares of 9-cis-β-carotene and zeaxanthin (each of ca. 2.5%). The stated high share of β-carotene in this oil can be a premise that used flaxseed oil could be produced from seeds of modified genotypes with substantially increased contents of β-carotene in seeds (Fujisawa et al., 2008).

The majority of intact forms of carotenoids were destroyed during oil oxidation. This mainly concerned lutein, which was 79% destroyed in rapeseed oil and 88% destroyed in flaxseed oil. The high decay was also stated for β-carotene in flaxseed oil, with only 37% retention of intact form. Such high decomposition was unexpected in thermally oxidized oils, since carotenoids generally act as singlet oxygen quenchers and protect oils against photooxidation (Ahmad, Atta, Zeb, & Gul, 2011). However, carotenoids can also be donors of hydrogen atoms (Choe & Min, 2009) and it is likely this mechanism was displayed in the current study. Added derivatives of phenolic acids efficiently protected lutein and β-carotene, with relatively higher impact of 4-VS. In summary, after the addition of vinyl derivatives at least 75% carotenoids in rapeseed oil and 73% in flaxseed oil survived, with the highest retention of lutein in both oils and, additionally, β-carotene in flaxseed oil.

3.6. Squalene retention during oil oxidation

Squalene was a minor oil component and constituted only 2.18 and 2.39 mg/100 g in rapeseed and flaxseed oil, respectively (Table 3). This compound can range in flaxseed oil from 1.01 to 4.29 mg/100 g (Tańska et al., 2016) and the highest values can be found in oils extracted from not fully ripened seeds (Herchi et al., 2009). Data on squalene content in rapeseed oil are not available, but this compound occurs in it, since it is found as an important component in deodorizer distillate (Saba, Sherazi, Talpur, Talpur, & Kara, 2012).

Significant degradation of squalene was noted during oxidation, which resulted in retention of an intact form equal to 19% in rapeseed oil and to 22% in flaxseed oil. The main oxidation products of squalene are hydroperoxides, ranging from squalene monohydroperoxide (squalene-[OOH]) to squalene-$[OOH]_5$ and squalene epoxide (Mountfort, Bronstein, Archer, & Jickells, 2007). Although squalene may exert a weak antioxidant activity, its oxidation products have a pro-oxidant activity that can be suppressed only in the presence of primary antioxidants (Naziri, Consonni, & Tsimidou, 2014). Vinyl derivatives of sinapic and ferulic acid protected squalene against oxidative degradation. For rapeseed oil, retention of this compound ranged from 88 to 92%, while in flaxseed oil it ranged from 97 to 99%. In both oils, 4-VQ was more efficient.

4. Conclusions

Most studies on the impact of selected antioxidants on oils oxidation were conducted using purified TAGs matrices. However, oxidation of plant oils, especially unrefined ones, is a much more complex phenomenon. In such oils, TAGs, primary and secondary antioxidants interact with traces of water, ions of transition metals, chlorophylls, phospholipids, free fatty acids, etc. Oxidative stability of oils results from the synergism, antagonism or additive action of all antioxidants, superimposed by interaction with primary and secondary (radicals) pro-oxidants (Choe & Min, 2009). This particularly applies to cold-pressed oils, in which the content of non-triacylglycerol components can reach up to 5% (Mińkowski, Zawaka, Ptasznik, & Kalinowski, 2013). The present study showed that in control oils (without the addition of 4-VQ or 4-VS), bioactive compounds were highly destroyed (only 54–56% of sterols, 35–46% of carotenoids, 19–22% of squalene, and 78–84% of α-linolenic acid survived oxidation during the induction period). Surprisingly, the loss of tocols was minor, reaching 9% in rapeseed oil and 4% in flaxseed oil. Added vinyl derivatives of ferulic and sinapic acids were almost entirely consumed during the induction time of accelerated oxidation test, which resulted in a ca. 80% and 95% decrease in 4-VS and 4-VQ content, respectively. However, their use increased the retention of intact forms of most of the determined compounds. The use of 4-VS preserved at least 81% of squalene, sterols

and carotenoids in both oils. Unfortunately, this compound favoured the loss of tocopherols in rapeseed oil (mainly of α-tocopherol) and α-linolenic acid in flaxseed oil. For 4-VQ, the retention of squalene was 92–99%, sterols 86–95% and carotenoids 73–75%. This additive also effectively inhibited the loss of α-linolenic acid in both oils (ca. 4-fold in rapeseed oil and ca. 3-fold in flaxseed oil) and tocopherols in flaxseed oil (99% of retained forms). The only adverse effect of this additive was the increased decay of α-tocopherol, but this impact was above 2-fold lower than found for 4-VS. Based on these results and the results presented in our previous study (Tańska et al., 2018), it can be generalized that a vinyl derivative of ferulic acid is a good antioxidant for both types of oil and can be proposed as a food additive. The better antioxidant properties of 4-VQ than 4-VS result from the higher topological polar surface area of the former (which is similar to that of tocopherols).

Conflict of interest statement

The authors have declared no conflict of interest.

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