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ORIGINAL PAPER

Octyl sinapate as a new antioxidant to improve oxidative stability and antioxidant activity of rapeseed oil during accelerated storage

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Abstract

The effect of the addition of a novel lipophilic antioxidant—octyl sinapate to refined rapeseed oil on its oxidative stability and antioxidant activity—was evaluated using the accelerated shelf-life test. The oxidation processes of rapeseed oils without and with octyl sinapate were analyzed as amounts of primary (peroxide values, conjugated diene) and secondary (anisidine values, conjugated triene) oxidation products and total oxidation (TOTOX) index. The synthesized antioxidant strongly inhibited the generation of secondary oxidation products during accelerated storage of rapeseed oil up to 4 weeks at 40 ± 1 °C under light (power of luminous flux = 385 lm). Moreover, antioxidant activity of rapeseed oil after enrichment with new antioxidant determined by four spectrophotometric methods: 2,2′-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid, 2,2-diphenyl-1-picrylhydrazyl, ferric reducing antioxidant power, and Folin–Ciocolteu were about 14, 14, 7, and 27 times higher in comparison with the refined oil without octyl sinapate. Antioxidant activity of the enriched rapeseed oil was reduced by about 20–40% during the accelerated storage period, while significantly higher decrease (55–70%) in antioxidant capacity of the refined rapeseed oil took place under these conditions. The addition of new lipophilic antioxidant to rapeseed oil effectively delayed secondary lipid oxidation processes and significantly increased its antioxidant activity under the accelerated conditions, which mimic the autoxidation process upon real storage conditions.

Keywords Rapeseed oil · Octyl sinapate · Oxidative stability · Antioxidant activity · Shelf life

Introduction

Rapeseed oil is a valuable source of compounds with health beneficial properties. Among them, sinapic acid (SA) and its derivatives: 4-vinylsyringol (canolol), sinapine, sinapoyl glucose, sinapoyl esters, and syringaldehyde are potent rapeseed antioxidants, which have different biological activities. Moreover, rapeseed oil contains high amounts of other bioactive components such as flavonoids, tocopherols, sterols, and optimal ratio of linoleic acid to linolenic acid (2:1) for human health [1]. However, each step of technological process affects the content of bioactive compounds causing generally their decrease in the final oil [2]. On the other hand, antioxidants are sensitive compounds to oxidation that can be degraded by destructive reactions during processing and storage. In addition, unsaturated fatty acids present in rapeseed oil are rather susceptible to oxidation through a reaction with air oxygen, especially during long storage period. Oxidation is the main reason of vegetable oil deterioration, which results in the changes of flavor, odor, color, and nutritive value, leads to formation of potentially toxic compounds for human health, and shortens a shelf-life of oils. Therefore, oxidation processes cause greater economic losses in the fat industry.

To retard, reduce, or prevent oxidative deterioration of vegetable oils, antioxidants should be added to enhance oxidative stability of oils by preventing the propagation of lipid peroxidation and/or removing the free radicals [3]. The effectiveness of different natural antioxidants present in plants, fruits, vegetables, cereals, seaweeds, macroalgae, essential oils, and by-products for the stabilization of rapeseed oils had been recently estimated [4–15]. The protective effect of these natural antioxidants in stabilizing rapeseed oils was evaluated by determining their peroxide values (PV), *p*-anisidine values (AV), carbonyl values, thiobarbituric acid-reactive substances (TBARS value), conjugated dienes (CD) and conjugated trienes (CT) amounts, TOTOX

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index, oxidative stability (Rancimat test), antioxidant activity (AA), total phenolic content (TPC), and amounts of volatile compounds during practical and accelerated storage conditions [4–15]. The addition of different plant extracts to rapeseed oils revealed efficacy in delaying both primary and secondary oxidative changes (PV = 0–450 and 0–350 meq O_2 kg^{-1}, CD = 0.3–22.5 and 0.3–20.0, AV = 3.4–216.9 and 3.4–160.3, CT = 1.1–4.8 and 1.1–4.5, TOTOX = 8.6–1049.6 and 8.6–924.7, induction period = 3.8–53.9 and 4.3–135.0 h for control and enriched oils, respectively) during storage under oxidation conditions [5, 8–12, 14].

Moreover, the supplemented rapeseed oil had higher ferric reducing antioxidant power (FRAP) (0.65–1.70 µmol Trolox (TE) g^{-1}) and TPC (0.062–0.11 mg SA g^{-1}) than the refined oil without addition of meal extracts (FRAP = 0.37–0.73 µmol TE g^{-1} and TPC = 0.0039–0.029 mg SA g^{-1}) [15].

In recent years, the modified extracts of the natural phenolic compounds present in rowanberry and Canadian crabapple were enzymatically obtained by lipophilization with octadecanol and octadecanoic acid and added to the refined rapeseed oils during accelerated storage [16, 17]. The esterification of the native phenolic compounds increased their lipophilicity, antioxidant properties, and stability of oil. The supplemented rapeseed oils with lipophilized extracts from rowanberry and Canadian crabapple revealed significantly higher storage stability during 7 days at 65 °C than the non-supplemented oil, causing above 40% decrease in PV. Furthermore, the synthesized novel dihydro-caffeic acid amides protected rapeseed oil triacylglycerols from oxidative degradation and the formation of rancidity. The level of hydroperoxides in the fortified rapeseed oil triacylglycerols after storage in darkness at 60 °C for up to 7 days was ten times lower than in unenhanced sample [18].

However, to the best of our knowledge, the effect of antioxidants addition to rapeseed oil stored under different conditions on its AA has rarely been studied. Therefore, it seems worth to consider the application of the novel lipophilic antioxidant—octyl sinapate (ester of sinapic acid predominant in rapeseed with 1-octanol)—to inhibit oxidative degradation of rapeseed oil and enhance its antioxidant potential during accelerated storage.

This work focused on the estimation of oxidative stability and AA of rapeseed oil supplemented for the first time with octyl sinapate during accelerated storage up to 4 weeks at 40 ± 1 °C under light to mimic the autoxidation process upon real storage conditions and define the oil shelf life. The oxidative stability of the studied rapeseed oils before and after addition of octyl sinapate was assessed by analysing of primary (PV, CD) and secondary (AV, CT) oxidation products and TOTOX index, whereas their AA was determined by means of four modified analytical methods: 2,2′-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS), 2,2-diphenyl-1-picrylhydrazyl (DPPH), FRAP, and Folin–Ciocolteu (FC). Moreover, possible relationships between oxidation parameters and the AA of rapeseed oils without and with a new antioxidant were compared, evaluated, and discussed.

Materials and methods

Reagents

All reagents of analytical or HPLC grade and 3 Å molecular sieves were purchased from Sigma-Aldrich (Poznań, Poland), whereas ethyl acetate (98%) and dichloromethane (98.5%) were provided by Chempur (Piekary Śląskie, Poland). All solutions were prepared with redistilled water.

Chemical synthesis, purification, and analysis of octyl sinapate

The novel lipophilic antioxidant—octyl sinapate—was synthesized, purified, and identified according to procedures and analytical methods described in our previous report [19]. Briefly, sinapic acid (SA) was lipophilized with 1-octanol in a two-neck flask equipped with a magnetic stirring bar, reflux condenser, and a thermometer according the modified procedure. To SA (6 mmoL) with 1-octanol (48 mmoL) (dried over 3 Å molecular sieves prior to reaction), 10 µL of the sulphuric acid solution in 1-octanol (10 mol L^{-1}) was added during stirring.

Next, activated molecular sieves (3 Å, 40 mg mL^{-1}) were introduced to the reaction mixture to remove water formed during esterification. The reaction mixture was stirred and incubated at 100 °C for 3 h.

The synthesized octyl sinapate was isolated in a pure form from an excess of 1-octanol by flash column chromatography on silica gel (pore size 60 Å, Kieselgel, Macherey-Nagel, Germany). Octyl sinapate was purified on silica gel using dichloromethane:ethyl acetate (90:10) as an eluent.

Qualitative analysis of the obtained octyl sinapate was carried out by thin-layer chromatography (TLC) on precoated TLC plates, silica gel 60 with fluorescent indicator UV254, trade name ALUGRAM R SIL G/UV_{254} (Macherey-Nagel, Germany), using the same eluent as for flash chromatography. The spots were visualized under a UV light (254 nm) detection. Then, TLC plates were sprayed with 5% ethanolic solution of molybdatophosphoric acid and heated at 150 °C to observe substrate and product.

Quantitative analysis of the obtained octyl sinapate was conducted by high-performance chromatography (HPLC) on C18 Kinetex column, particle size 5 µm, length 250 mm, diameter 4.60 mm (Phenomenex) using a Shimadzu LC-10AT system (Shimadzu Inc., Kyoto, Japan) with diode

array UV detector (254 nm). The mobile phase consisted of acetonitrile:water:trifluoroacetic acid (70:30:0.01) at a flow rate of 0.6 mL min^{-1}.

Structure of octyl sinapate was confirmed by nuclear magnetic resonance (NMR) spectroscopy. ^{1}H and ^{13}C NMR spectra of the purified octyl sinapate were recorded at 700 and 170 MHz, respectively, on a Bruker Avance III 700 MHz spectrometer (Bruker Corporation, Karlsruhe, Germany) at 298 ± 1 K. Ester was dissolved in deuterated chloroform containing tetramethylsilane as internal standard. Chemical shifts were recorded in δ values in parts per million (ppm) and coupling constant (J) was reported in Hertz (Hz).

The purified octyl sinapate was characterised by an attenuated total reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy. The ATR–FTIR spectrum of octyl sinapate was obtained on a Bruker VERTEX 70v FTIR spectrometer (Bruker Optics, Ettlingen, Germany) equipped with a diamond ATR cell. Ester was directly placed on the crystal surface of the ATR probe and analyzed from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

A light yellow liquid substance—octyl sinapate (octyl(E)-3-(4-hydroxy-3,5-dimethoxyphenyl)propenoate)—was obtained (Fig. 1). Yield: 83%. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 7.0 Hz, 3H), 1.23–1.36 (m, 8H), 1.37–1.43 (m, 2H), 1.66–1.73 (m, 2H), 3.91 (s, 6H), 4.19 (t, J = 6.8 Hz, 2H), 5.83 (br. s., 1H), 6.30 (d, J = 15.9 Hz, 1H), 6.77 (s, 2H), 7.58 (d, J = 15.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 13.80, 22.38, 25.75, 28.52, 29.01, 31.55, 56.02 (2xOCH_3), 64.38, 104.92 (2 × CH), 115.58, 125.59, 137.11, 144.70, 147.11 (2 × C), 167.09. IR: ν 3525, 3407, 3068, 2925, 2853, 1700, 1632, 1601, 1513, 1455, 1425, 1375, 1338, 1279, 1252, 1215, 1150, 1111, 978, 827, 620 cm^{-1}.

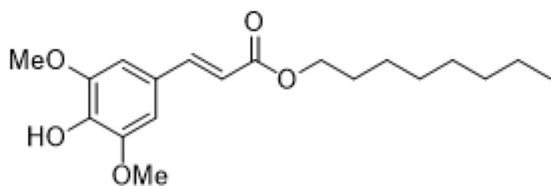


Fig. 1 Chemical structure of octyl sinapate

Samples and storage conditions

Samples

The refined rapeseed oil in the original packing (polypropylene containers) was kindly provided by a local vegetable oil factory and stored at 4 °C in the dark until the analysis.

Preparation of rapeseed oil enriched with octyl sinapate

The purified octyl sinapate (2.25 g) was added to the refined rapeseed oil (250 g) and stirred during 15 min to obtain a final concentration of 0.9%.

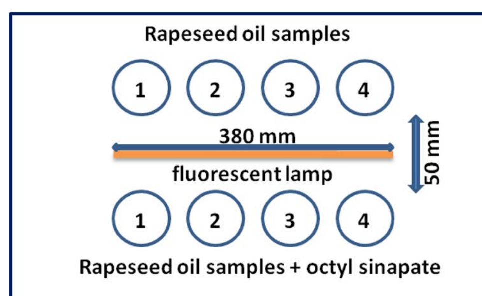
Storage of oil samples under accelerated oxidation conditions

Five samples (40 mL) of the refined rapeseed oil and five samples (40 mL) of rapeseed oil enriched with octyl sinapate were introduced in ten Duran glass bottles with blue screw caps (50 mL, 46 × 91 mm). Eight bottles (four with the refined rapeseed oil and four with the supplemented rapeseed oil) were placed in the incubator (Elkon CWE-2a, Łódź, Poland) at 40 ± 1 °C under light (fluorescent lamp T5 8W F8W/33 GE installed at a distance of 300 mm from the incubator shelf, power of luminous flux = 385 lm) for a period of 4 weeks. The position of bottles inside the incubator is presented in Fig. 2.

Oil samples were withdrawn at intervals of one week for analysis.

Sample preparation for determination of antioxidant activity

The extracts of refined and enriched rapeseed oils were obtained in methanol according to the procedure described previously [2]. Briefly, the test tubes with oils (2.00 g) and methanol (5 mL) were shaken for 30 min using a shaker SHKA 2508-1CE (Labo Plus, Warsaw, Poland) at room temperature in the dark. The extracts were then separated from oils in a freezer (− 20 °C, 30 min) and transferred quantitatively into glass bottles. Each oil sample was extracted in



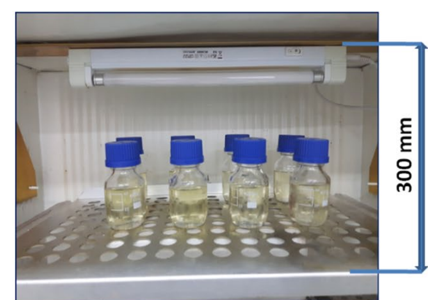


Fig. 2 Position of oil samples (blue color) in incubator with location of fluorescent lamp (orange color). The oil sample position in incubator relative to the light source was presented in photo

triplicate and the obtained extracts were stored in refrigerator, prior to AA analysis.

Moreover, the methanolic solution of octyl sinapate (69 µg mL^{-1}) was prepared for determination its antioxidant capacity.

Determination of oil antioxidant activity

The AA of rapeseed oils before and after enrichment with octyl sinapate was determined by four spectrophotometric methods: ABTS, DPPH, FRAP, and FC, described in our previous article [2]. The UV–Vis spectra were recorded using a Hitachi U-2900 spectrophotometer (Tokyo, Japan) in a 1 cm quartz cell.

The AA was expressed as µmol of Trolox equivalents per 1 g of sample (µmol TE g^{-1}).

Determination of oil oxidation

Peroxide value (PV) of the studied oil samples was determined iodometrically according to the official procedure ISO 3960:2017 [20]. The PV value was expressed as milliequivalents of active oxygen per kilogram of oil (meq O_2 kg^{-1}).

Anisidine value (AV) was analyzed as a measure of secondary oxidation products in the oil according the ISO 6885:2016 method [21].

The oxidation state of oil given by the TOTOX index was calculated according to the formula: (TOTOX = 2PV + AV).

Conjugated diene (CD) and triene (CT) values were measured by UV–Vis spectrophotometer (Hitachi U-2900, Tokyo, Japan) as the absorbance of 1% solution of each oil in hexane (no additional dilutions were made) at 233 and 268 nm, respectively, in a 1 cm quartz cell using hexane as blank according to ISO 3656:2011 method [22].

Statistical analysis

The oxidation parameters: PV, AV, TOTOX, and amounts of CD and CT in each oil sample were analyzed three times within 1 day, whereas the AA of non-supplemented and the supplemented rapeseed oils were evaluated by fivefold determination of each extract within the same day using the modified ABTS, DPPH, FRAP, and FC methods. The obtained results were presented as: mean (c) ± standard deviation (SD). One-way analysis of variance (ANOVA), followed by the Duncan test, was performed to analyze the significant differences between data ($p < 0.05$). The Pearson correlation coefficients between the AA results and oxidation parameters of the studied oils were evaluated.

Statistical analyses of data were performed using Statistica (Windows software package, version 8.0).

Results and discussion

Effect of new antioxidant on oxidative stability of rapeseed oil under accelerated conditions

The oxidative stability of a non-supplemented and octyl sinapate-supplemented rapeseed oils was analyzed during storage (4 weeks) at accelerated conditions ($T = 40$ °C, fluorescent lamp) to determine their shelf life. The mean concentrations of primary and secondary lipid oxidation products measured as PV and CD, as well as AV and CT in the refined rapeseed oil were compared with these determined for rapeseed oil fortified with a new antioxidant (Table 1).

As can be seen, PV and AV values of rapeseed oils in the absence and presence of lipophilic antioxidant—octyl sinapate—increased linearly with storage time (correlation coefficients, r ranged between 0.9691 and 0.9974). Therefore, PV values of all studied oil samples significantly differ from each other (Duncan test, Table 1). The increase in PV indicates the generation of hydroperoxides in rapeseed oils before and after addition of a new antioxidant during the accelerated storage. However, somewhat slower increase of PV for oils with octyl sinapate was observed (Table 1). A significantly higher PV results (14.96–99.87 meq O_2 kg^{-1}) for the stored oils than that recommended by ISO 3960 Standard (PV < 5 meq O_2 kg^{-1}) suggest quality degradation in terms of oxidative rancidity [20]. The PV > 5 meq O_2 kg^{-1} for the refined rapeseed oils without and with octyl sinapate after 1 week can be explained by the incubation of the relatively small volume (40 mL) of analyzed oils in 50-mL glass bottles at 40 °C under light. It is known that there are a faster and greater oxidative changes in small amounts of rapeseed oil under accelerated conditions.

On the contrary, there were no peroxides in the fresh refined rapeseed oil (PV = 0.02 meq O_2 kg^{-1}), whereas oil with octyl sinapate before acceleration test (0 week) revealed initial PV = 1.31 meq O_2 kg^{-1}, probably due to intensive mixing of oil with antioxidant during enrichment. It is noteworthy that the addition of octyl sinapate retarded the early stages of rapeseed oil oxidation. The amount of hydroperoxides in oil with octyl sinapate (PV = 93.13 meq O_2 kg^{-1}) was only slightly lower than PV for oil without antioxidant (99.87 meq O_2 kg^{-1}) after 28 days of storage. Although hydroperoxides content in the enriched rapeseed oil (PV = 14.96 meq O_2 kg^{-1}) was about 1.5 times lower than PV (22.79 meq O_2 kg^{-1}) of the control oil sample at the first week of storage (Table 1). This can be explained by the fact that a new lipophilic antioxidant had protective effect against primary oxidation of rapeseed oil specifically at early stage of the accelerated storage (7 days).

For comparison, the novel antioxidants such as dihydro-caffeic acid amides, phloridzyl octadecanoate and

Table 1 Oxidation parameters of the refined and enriched rapeseed oils under accelerated storage conditions

Storage time (weeks)	Oxidation parameters[a]				
	PV ± SD (meq O_2 kg^{-1})	AV ± SD	TOTOX	CD ± SD	CT ± SD
Refined rapeseed oil					
0	0.02 ± 0.00[a]	1.48 ± 0.06[a]	1.52[a]	2.678 ± 0.020[a]	0.589 ± 0.020[b]
1	22.79 ± 0.35[d]	2.08 ± 0.07[b]	47.66[d]	2.843 ± 0.033[b,c]	0.625 ± 0.014[b,c]
2	55.38 ± 0.66[f]	5.65 ± 0.21[d]	116.41[f]	2.769 ± 0.059[b]	0.679 ± 0.033[d]
3	74.65 ± 0.39[h]	9.11 ± 0.07[g]	158.41[h]	2.639 ± 0.063[a]	0.720 ± 0.010[e]
4	99.87 ± 0.60[j]	12.44 ± 0.14[h]	212.18[j]	3.089 ± 0.066[d]	0.969 ± 0.030[g]
Rapeseed oil enriched with octyl sinapate					
0	1.31 ± 0.05[b]	1.62 ± 0.01[a]	4.24[b]	2.799 ± 0.027[b]	0.532 ± 0.024[a]
1	14.96 ± 0.19[c]	1.94 ± 0.09[b]	31.86[c]	2.845 ± 0.079[b,c]	0.590 ± 0.019[b]
2	52.11 ± 0.23[e]	3.95 ± 0.09[c]	108.17[e]	2.889 ± 0.019[c]	0.597 ± 0.025[b]
3	73.42 ± 0.96[g]	7.22 ± 0.21[e]	154.06[g]	2.602 ± 0.019[a]	0.661 ± 0.020[c,d]
4	93.13 ± 0.31[i]	8.19 ± 0.23[f]	194.45[i]	3.014 ± 0.044[d]	0.772 ± 0.026[f]

Different letters (a–j) within the same column indicate significant differences between oxidation parameters of the stored oils during 4 weeks (one-way ANOVA and Duncan test, $p < 0.05$)

SD standard deviation

[a] $n = 3$

lipophilized extract from rowanberry had significantly higher protection against oxidative degradation of rapeseed oil during accelerated storage, inhibiting of hydroperoxides formation [16–18]. At the end of the accelerated storage in darkness at 60 °C for up to 7 days, the amount of hydroperoxides generated in canola oil triacylglycerols supplemented with 12 novel dihydro-caffeic acid amides was ten times lower than in control sample (without antioxidant) [18]. Moreover, the modified extracts prepared by enzymatic reaction between the native phloridzin in Canadian crabapple extract or phenolic compounds from rowanberry and octadecanoic acid added to rapeseed oil markedly decreased (above 40%) the formation of lipid hydroperoxides at the end of the 7 days storage [16, 17]. Although rapeseed oils with 0.02, 0.05, and 0.10% of sea buckthorn and Roman camomile extracts, as well as 0.02 and 0.05% of tansy extract exhibited higher PV (798.78–926.31 meq O_2 kg^{-1}) after 70 days of storage at 40 °C than unprotected oil sample (PV = 793.72 meq O_2 kg^{-1}) [6].

On the other hand, octyl sinapate reduced the content of secondary oxidation products in the supplemented rapeseed oils (AV = 1.62–8.19) compared with the refined oil (AV = 1.48–12.44). This suggests that a new antioxidant stabilizes hydroperoxides, initial products of lipid oxidation reactions and delays their decomposition to secondary products such as aldehydes, ketones, alcohols, acids, hydrocarbons, etc., which were determined by the AV.

The chemical structure of octyl sinapate added to oil contains two methoxyl groups and one phenolic hydroxyl group (Fig. 1), which can donate hydrogen atoms to active free radicals to interrupt the chain reaction of autooxidation.

It can be noted that AV of the refined and fortified oils increased significantly throughout the storage time, whereas the highest increase in the AV took place after 14 and 21 days, respectively. Moreover, the Duncan test indicated that fresh refined rapeseed oils without and with octyl sinapate did not differ significantly in AV. In addition, these oil samples had a similar content of secondary oxidation products after 1 week of storage at 40 °C under light (Table 1). As can be seen, at the end of the accelerated storage period, AV of rapeseed oil with phenolipid—octyl sinapate—decreased by approximately 34% compared with the control oil (without new antioxidant). The enriched rapeseed oil after 28 days of storage revealed somewhat higher content of secondary oxidation products than the prescribed limit of AV = 8, whereas AV = 9.11 of a non-supplemented rapeseed oil up to 21 days of storage was significantly higher than that recommended by ISO 6885 [21], reflecting the high level of carbonyls generation in oil without octyl sinapate. It is evident that the novel phenolipid added to oil inhibited the propagation chain during the oxidation process.

Similar effect of seaweeds, sage, mustard, and evening primrose extracts and essential oil on the evolution of secondary oxidation products in rapeseed oils during storage was observed by other authors [7, 9, 11, 12, 14]. The reported AV results suggest that natural and synthetic antioxidants provided protection against secondary lipid oxidation.

However, total oxidation (TOTOX) values of oil samples for the whole investigation period as a suitable indicator of their quality were calculated based on both PV and AV (Table 1). The changes in TOTOX values of rapeseed oils before and after supplementation with a new phenolipid

under accelerated conditions were very similar to those of PV. This quality factor was within the desirable level (< 10) only for the fresh rapeseed oil (TOTOX = 1.52 and 4.24 for oil without and with antioxidant, respectively). It is noteworthy that temperature (40 °C) and fluorescence light (385 lm) induced oxidation process in all oil samples. Although the Duncan test indicated that the overall oxidation in the fortified rapeseed oil (TOTOX 4.24–194.45) was significantly slower in comparison with the control oil sample (TOTOX 1.52–212.18).

Furthermore, CD and CT are also good parameters for the assessment of oxidative deterioration of oil. It is noteworthy that CD values (2.602–3.089) were consistently higher than CT results (0.532–0.969) for all analyzed oils. It is known that the CD formation is associated with the oxidation of polyunsaturated fatty acids (PUFA) and measures the degree of primary oxidation products, while generation of secondary oxidation products correlates with CT values. Unexpectedly, insignificant changes in CD values of oil samples without and with new antioxidant were observed during storage conditions up to 21 days (Duncan test, Table 1). However, the last 7 days of the accelerated storage of refined and fortified oils caused about 14% increase in CD amounts. This suggests that the rate of CD generation in the analyzed oils during oxidation time was higher than their decomposition rate, leading to the accumulation in each oil sample. Moreover, the addition of a novel antioxidant did not delay significantly primary oxidation of PUFA. For this reason, at the end of the oxidation period, similar CD amounts in rapeseed oils without (CD = 3.089) and with (CD = 3.014) antioxidant were found (Duncan test, Table 1).

On the contrary, the addition of seaweed extracts and butylated hydroxytoluene (BHT) caused significant decrease of CD amounts (66–68 and 36%, respectively) in rapeseed oils after 16 days of the accelerated storage at 60 °C in comparison with the non-supplemented oil [12]. However, CD levels in rapeseed oil treated with sage, savory, and borage extracts at 80 °C for 85 h were higher than in oil without antioxidants [5].

Furthermore, the control rapeseed oil samples had the higher CT content (0.589–0.969) than rapeseed oils with octyl sinapate (0.532–0.772) under accelerated storage. This indicates that new antioxidant inhibited the dehydration of CD hydroperoxides; thus, it revealed a good antioxidant properties. It can be noted that the absorbance at 268 nm of the 1% solutions of studied oils in hexane increases with the extension of storage time. Although lower increase in CT content was observed in the first weeks of rapeseed oils storage, however, oil with octyl sinapate started more intensively absorb at 268 nm after 21 days of storage, whereas CT amount in refined rapeseed oil increased significantly after 14 days (Duncan test, Table 1). The addition of 0.9% octyl sinapate to the refined rapeseed oil decreased CT accumulation by 20% with respect to control sample without antioxidant. This can be explained by the fact that a novel antioxidant reduces substantially the amounts of CT and other secondary oxidation products in the refined rapeseed oil. The obtained results are in agreement with those reported by Bandonienė et al., who noticed that plant extracts displayed the similar effectiveness in decrease of CT concentration in rapeseed oil during storage at 80 °C [5].

It is noteworthy that the calculated values of RSD = 0.33–3.82, 0.62–4.64, 0.66–2.78, and 1.39–4.86%, respectively, indicate reasonable repeatability of the ISO standard methods for PV, AV, CD, and CT determinations.

Effect of new antioxidant on antioxidant activity of rapeseed oil under accelerated conditions

The antioxidant capacity of the novel lipophilic antioxidant—octyl sinapate—and the AA of rapeseed oil before and after fortification during 4 weeks of storage at 40 °C under light were determined by the modified ABTS, DPPH, FRAP, and FC methods and the results are presented in Fig. 3 and Table 2.

The obtained ABTS, DPPH, FRAP, and FC results for octyl sinapate and oils in the absence and presence of 0.9% of new antioxidant differ significantly from each other (Duncan test). This variability can be explained by the influence of reaction conditions and mechanisms of the applied analytical methods.

As can be seen, ABTS, DPPH, FRAP, and FC values of the novel antioxidant—octyl sinapate—were about 125, 110, 80, and 60 times higher than the AA results for rapeseed oil treated with its addition (Fig. 3; Table 2). On the other hand, the supplementation of rapeseed oil with octyl sinapate caused approximately 14-, 14-, 7-, and 27-fold increase in

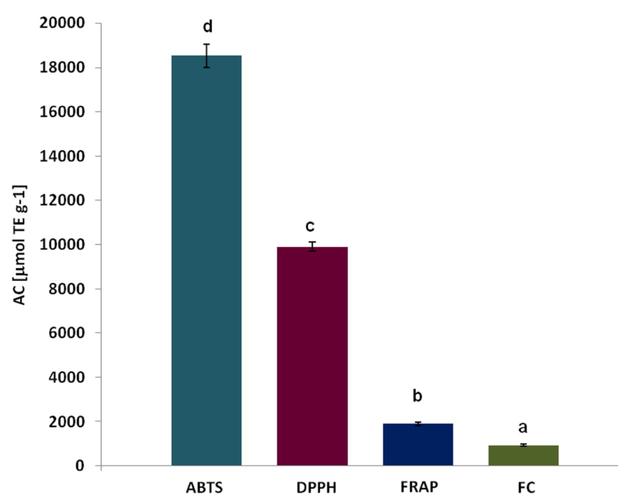


Fig. 3 Antioxidant capacity of octyl sinapate determined by ABTS, DPPH, FRAP and FC methods

Table 2 Antioxidant activity of the refined and enriched rapeseed oils under accelerated storage conditions

Storage time (weeks)	Antioxidant activity[a] (μmol TE g^{-1})			
	ABTS ± SD	DPPH ± SD	FRAP ± SD	FC ± SD
Refined rapeseed oil				
0	10.52 ± 0.41[d]	6.31 ± 0.17[d]	3.60 ± 0.16[c]	0.56 ± 0.01[d]
1	8.72 ± 0.30[c]	5.68 ± 0.23[c]	3.51 ± 0.17[c]	0.42 ± 0.02[c]
2	8.66 ± 0.35[c]	5.61 ± 0.11[c]	3.45 ± 0.11[c]	0.40 ± 0.02[c]
3	6.52 ± 0.31[b]	4.45 ± 0.20[b]	2.19 ± 0.09[b]	0.36 ± 0.01[b]
4	4.76 ± 0.16[a]	1.97 ± 0.05[a]	1.09 ± 0.04[a]	0.22 ± 0.01[a]
Rapeseed oil enriched with octyl sinapate				
0	147.89 ± 3.38[z]	88.95 ± 2.08[y]	24.07 ± 1.20[z]	15.30 ± 0.43[y]
1	134.78 ± 2.83[y]	86.27 ± 3.57[y]	22.49 ± 0.98[y]	13.54 ± 0.57[x]
2	126.53 ± 3.14[x]	80.53 ± 3.85[x]	16.44 ± 0.70[x]	13.17 ± 0.60[x]
3	123.67 ± 2.90[x]	80.22 ± 3.91[x]	15.80 ± 0.55[x]	13.01 ± 0.49[x]
4	114.48 ± 4.64[w]	64.77 ± 2.40[w]	13.83 ± 0.45[w]	12.22 ± 0.06[w]

Different letters within the same column indicate significant differences between antioxidant activity of the stored non-supplemented (a–d) and supplemented (w–z) oils during 4 weeks (one-way ANOVA and Duncan test, $p < 0.05$)

SD standard deviation

[a] $n = 5$

ABTS, DPPH, FRAP, and FC values, respectively (Table 2). Therefore, it can be stated that the synthesized phenolipid has significant antioxidant potential; hence, its addition to oil creates effective defense system against free radical attack.

However, during 4 week storage period at 40 °C under fluorescent lamp, the AA of the fortified and refined rapeseed oils decreased linearly ($r = 0.9176$–0.9784 and 0.9097–0.9736, respectively) with storage time, but the reduction rates of ABTS, DPPH, FRAP, and FC for oil with octyl sinapate were significantly lower than those for the control sample (without antioxidant). The changes of ABTS, DPPH, FRAP, and FC results for rapeseed oils after octyl sinapate addition during accelerated oxidation ranged between 114.48 and 147.89, 64.77–88.95, 13.83–24.07, and 12.22–15.30 μmol TE g^{-1}, respectively, whereas oils without phenolipid revealed lower ABTS = 4.76–10.52 μmol TE g^{-1}, DPPH = 1.97–6.31 μmol TE g^{-1}, FRAP = 1.09–3.60 μmol TE g^{-1}, and FC = 0.22–0.56 μmol TE g^{-1}. The highest ABTS values can be explained by the fact that this method measures both hydrophilic and lipophilic antioxidant compounds in the studied samples, whereas DPPH assay only considers lipophilic antioxidants. In contrast, FRAP and FC methods are inapplicable to lipophilic antioxidants; however, polar compounds like phenolics, proteins, but also aldehydes, ketones, and epoxides produced during lipid oxidation reactions can be found in rapeseed oil [1]. In addition, the antioxidant efficiency of polyphenols present in oil depends on the extent of hydroxylation and conjugation [23]. Thus, the significantly lower AA values were obtained using these two analytical methods. For these reasons, the AA of oil samples should be determined and compared by several analytical methods.

The initial AA of refined rapeseed oil decreased by about 55–70% after 28 days of the accelerated storage, indicating degradation of antioxidants naturally present in oil. However, octyl sinapate had important role in inhibiting these destructive reactions, because significantly lower losses of ABTS (23%), DPPH (27%), FRAP (43%), and FC (20%) were observed during the same period (Table 2). Furthermore, the AA of control oil sample (before supplementation with new phenolipid) exhibited the lowest degree of changes between 7 and 14 days of storage, whereas the AA of fortified rapeseed oils had reduced insignificantly in later stages (after 2 and 3 weeks) of oxidation (Duncan test, Table 2).

These losses of antioxidants may be due to the decomposition and oxidation of antioxidants in rapeseed oil, which undergoes qualitative and quantitative modifications during storage. However, the synthesized phenolipid is an active oil soluble component with one hydroxyl and two methoxyl groups (Fig. 1), which can act as an antioxidant by donating H-atom(s) to free radicals. The added octyl sinapate effectively prevents lipid oxidation in the refined rapeseed oil by significant increasing its AA and delaying the degradation of natural antioxidants.

However, the effect of antioxidants added to rapeseed oil on its AA under storage was rarely reported in the literature. Only decrease in FRAP (0.89–1.70 μmol TE g^{-1}) and TPC (0.09–0.11 mg SA g^{-1}) in rapeseed oil enriched with meal extract after 2 (FRAP = 0.66–1.37 μmol TE g^{-1}, TPC = 0.07–0.09 mg SA g^{-1}) and 4 (FRAP = 0.65–1.31 μmol

TE g^{-1}, TPC = 0.06–0.08 mg SA g^{-1}) weeks of storage was found previously [15].

Moreover, high amounts (above 75%) of a new caffeic acid amide antioxidants remained in canola triacylglycerols after 5 days of storage in darkness at 60 °C [18]. Similar changes in DPPH, ABTS, and FC values of soybean, rice bran, and cottonseed oils enriched with rosemary extract during storage at 62 °C for 24 days were found. Initially, oils with rosemary extract revealed higher DPPH (0.10 mg TE mL^{-1}), ABTS (0.50 mg TE mL^{-1}), and TPC [400–800 mg gallic acid (GA) kg^{-1}] than blank oils (DPPH = 0.07 mg TE mL^{-1}, ABTS = 0.20–0.40 mg TE mL^{-1}, TPC = 100–500 mg GA kg^{-1}), whereas the AA of non-supplemented oils (DPPH = 0.05–0.07 mg TE mL^{-1}, ABTS = 0.01–0.10 mg TE mL^{-1}, TPC = 20–400 mg GA kg^{-1}) and oils with rosemary extract (DPPH = 0.08 mg TE mL^{-1}, ABTS = 0.40 mg TE mL^{-1}, TPC = 300–700 mg GA kg^{-1}) decreased after the 24-day storage [24].

The RSD values of the AA determinations for all studied oils by a ABTS (2.10–4.75%), DPPH (1.96–4.87%), FRAP (3.19–4.99%), and FC (0.50–5.00%) methods indicate their good precisions.

Correlations between antioxidant activity and oxidative stability of rapeseed oil

Correlation analysis was conducted to explore the relationships between AA determined by ABTS, DPPH FRAP, and FC methods and oxidation parameters (PV, AV, TOTOX, CD, and CT) of rapeseed oils in the absence and presence of the novel antioxidant—octyl sinapate under accelerated storage for 4 weeks. The Pearson's correlation coefficients collected in Table 3 confirm linear and significant relationships (r = 0.9658–0.9994, $p < 0.0001$) between all analytical methods used for the AA determination of rapeseed oils without and with the synthesized phenolipid.

This fact indicates that the oxidation processes under accelerated conditions decreased the concentrations of hydrophilic and lipophilic antioxidants in the refined and enriched rapeseed oils.

However, somewhat lower correlation coefficients (r = 0.910–0.945, $p < 0.001$) were found for the relationship among FC and DPPH of cold pressed rapeseed oils from untreated and microwave-treated rapeseed stored at 60 °C in the dark for 10 weeks [25].

On the other hand, the AA of examined oil samples and their oxidation parameters such as PV (r = − 0.1264 to − 0.3304), AV (r = − 0.2727 to − 0.4337), TOTOX (r = − 0.1338 to − 0.3362), CD (r = 0.0057–0.0609), and CT (r = − 0.4142 to − 0.5397) were not correlated. Although the negative Pearson values suggest that antioxidants partially contribute to the decrease in oil oxidation during accelerated storage, thus, oils with lower AA revealed higher values of PV, AV, TOTOX, and CT. Therefore, the AA of rapeseed oils without and with octyl sinapate decreased during oxidation storage due to reactions of naturally present and added antioxidants with the generated lipid peroxyl radicals. However, positive very low Pearson coefficients for the relationship between AA and CD could be explained by inability of antioxidant compounds in rapeseed oil to inhibit double bound conjugation under accelerated storage conditions.

In addition, DPPH of cold pressed rapeseed oils after 6 months of storage at 4 °C did not correlate significantly with their PV (r = − 0.3012, p = 0.106) [26], although statistically significant correlation (r = − 0.6042, $p < 0.0001$) for relation DPPH–PV after 12 months of the same oils storage was reported by these authors.

Furthermore, there are significant ($p < 0.0001$), positive correlations between amounts of primary and secondary oxidation products (r = 0.9456 for PV–AV) in the studied rapeseed oils, and their total oxidation index (r = 0.9506 and 0.9999 for TOTOX–AV and TOTOX–PV, respectively). These high positive values of correlation coefficients suggest that formation of hydroperoxides in control and enriched rapeseed oils increased almost linearly with the increase in the oxidation time, but a maximum was not reached during the whole storage period. However, when lipid oxidation progressed, hydroperoxides were broken-down into secondary oxidation products that can be determined as AV. Probably a new lipophilic antioxidant—octyl

Table 3 Matrix of correlation between antioxidant activity of the refined rapeseed oils without and with octyl sinapate and their oxidation parameters

	DPPH	ABTS	FRAP	FC	PV	AV	TOTOX	CD
ABTS	0.9975***							
FRAP	0.9733***	0.9732***						
FC	0.9959***	0.9994***	0.9658***					
PV	− 0.1654	− 0.1527	− 0.3304	− 0.1264				
AV	− 0.3084	− 0.2959	− 0.4337	− 0.2727	0.9456***			
TOTOX	− 0.1728	− 0.1600	− 0.3362	− 0.1338	0.9999***	0.9506***		
CD	0.0177	0.0537	0.0057	0.0609	0.3585	0.3242	0.3577	
CT	− 0.4518	− 0.4329	− 0.5397	− 0.4142	0.8379*	0.9191**	0.8440*	0.5622

*$p < 0.05$, **$p < 0.001$, ***$p < 0.0001$

sinapate—had inhibitory effect on the secondary lipid oxidation. Similar, a highly positive correlation ($r = 0.977$, $p < 0.01$) between PV and AV of soybean oils fortified with potato peels and stored at 60 °C during 14 days was demonstrated by Franco et al. [27].

In addition, content of CT formed in all rapeseed oil samples under accelerated oxidation period significantly correlated with their AV ($r = 0.9191$, $p < 0.001$), PV ($r = 0.8379$, $p < 0.05$), and TOTOX ($r = 0.8440$, $p < 0.05$). The highest correlation coefficient among CT and AV can be explained as that the absorbance of oil solution in hexane at 268 nm also detects the secondary oxidation products in oil. For this reason, level of CT in rapeseed oils after addition of plant extracts and stored at 80 °C for 85 h was closely related to their AV [5].

On the contrary, PV of the analyzed rapeseed oils without and with octyl sinapate did not correlate significantly with CD level ($r = 0.3585$), which was measured as the absorbance at 233 nm. The lack of relation among PV and CD indicates that the absorbance around 233 nm for rapeseed oil solutions in hexane does not reflect only the amounts of primary oxidation products (conjugated hydroperoxides), but the overall spectral properties of these oils, including various absorbing species such as conjugated fatty chains. On the other hand, oleic and linoleic acids are two major unsaturated fatty acids in rapeseed oil, whereas only hydroperoxides from linoleic acid contribute to the increase in the CD values. Therefore, the increase in hydroperoxides from oleic acid causes increase of the PV, but this predominant monounsaturated fatty acid is not able to be oxidised to conjugated diene hydroperoxides, which absorb UV radiation at 233 nm [28]. The relationship between PV and CD in rapeseed oils without and with octyl sinapate during the accelerated oxidation was not found due to all hydroperoxides formed as the primary oxidation products does not simultaneously contain the conjugated diene structures. For comparison, PV of extra virgin olive oils (Bosana cv.) stored in hermetically sealed colourless transparent glass bottles at room temperature for 16 months did not directly correlate with CD content ($r = 0.3206$) [29]. Moreover, there were no correlations between PV and absorptivity at 232 nm for refined canola oil without and with antioxidants ($c_{BHA/BHT} = 200$ mg kg^{-1} and $c_{citric\ acid} = 100$ mg kg^{-1}) heated in a microwave oven (800 W) for 36 min ($r = 0.5131$–0.6129), as well as sunflower oil during microwave heating at power levels of 360, 600, and 900 W, respectively, for five consecutive days ($r = 0.2696$–0.4138) [30, 31], although high correlation coefficients ($r > 0.90$) for the relationship between PV and CD concentration in rapeseed oils fortified with herbs and macroalgae species extracts stored under different accelerated conditions (80 °C for 85 h and 60 °C for 16 days, respectively) and in soybean oils after addition of potato peels extract (60 °C, 14 days) were reported by other authors [5, 13, 27].

However, an insignificant positive correlation ($r = 0.5622$) was observed between CD and CT amounts in the studied rapeseed oils. It is known that CT may be produced by the dehydration of CD hydroperoxides, but lower increase in CD content was occurred in later stage of lipid oxidation.

Conclusions

Four analytical methods: ABTS, DPPH, FRAP, and FC assays demonstrated high antioxidant properties of a new synthetic compound—octyl sinapate.

The addition of a new lipophilic antioxidant improved storage stability of the refined rapeseed oil in terms of its antioxidant potential. The synthesized octyl sinapate significantly retarded secondary lipid oxidation under accelerated conditions decreasing the AV and CT contents in the fortified rapeseed oil by above 30 and 20%, respectively, in comparison with the control sample oil. Moreover, the enrichment of the refined rapeseed oil with octyl sinapate caused significant increase of its AA determined by ABTS, DPPH, FRAP, and FC methods. However, the initial AA of the supplemented refined rapeseed oil reduced by about 20–40% after 4 weeks of the accelerated storage, whereas a non-supplemented oil revealed higher losses of the AA (55–70%). Nevertheless, significant and linear correlations were found between the four analytical methods used to determine the AA and some oxidation parameters of the studied oils.

The synthesized octyl sinapate could be used as efficient antioxidant in the oil industry to delay oxidation reactions, although further studies are necessary to evaluate: (1) the effect of new antioxidant concentration on the AA of different vegetable oils as well as (2) the clinical efficacy and its dosage to ensure health benefits.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Compliance with ethics requirements This article does not contain any studies with human or animal subjects.

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