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Antioxidant Activity of Soybean Oil Containing 4-Vinylsyringol Obtained from Decarboxylated Sinapic Acid

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Abstract 4-Vinylsyringol was produced by decarboxylation from sinapic acid. To evaluate the antioxidant activity of 4-vinylsyringol, 500 ppm of 4-vinylsyringol, sinapic acid, or α-tocopherol was added to soybean oil and the oxidation processes were monitored by the peroxide value (PV), the thiobarbituric acid reactive substances value (TBARS) assay, and ^{1}H-NMR spectroscopy. The results obtained by PV and TBARS indicated that soybean oil containing 4-vinylsyringol (SBO-VS) showed the highest oxidative stability. ^{1}H-NMR analysis also showed concurring results. After 19 days of oxidation, the degradation rates of linoleic acid (4.2 %) and linolenic acid (4.4 %) in SBO-VS were significantly lower than those in other oils. Secondary oxidation products (i.e. aldehydes) were undetectable in SBO-VS by ^{1}H NMR, whereas concentrations of such compounds in soybean oils containing α-tocopherol or sinapic acid were 38.0 ± 0.4 and 2.75 ± 0.2 mM oil, respectively. In addition, synergistic antioxidant effect between any two antioxidants was not observed.

Keywords ^{1}H NMR · 4-Vinylsyringol · Decarboxylation · Sinapic acid · Oxidative stability

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Introduction

Oils and fats are important ingredients of the human diet. They not only influence the organoleptic and textural properties of foods, but they also play important roles in human health. However, lipids that contain unsaturated fatty acids are prone to oxidation. The secondary oxidation products, especially 4-hydroxy-(*E*)-2-alkenal, have been proven to be related to atherosclerosis, cancer, and cardiovascular disease [1, 2]. Hence, antioxidants have been employed for inhibiting lipid oxidation in the food industry.

Polar phenolics, which are abundant in plant tissues, are an important class of antioxidants and much attention has been paid to the antioxidant activities of these compounds in crude oils. For example, Baldioli *et al*. [3] suggested that total polar phenolic levels were well correlated with the oxidative stability of crude olive oil, whereas tocopherols correlated poorly. Crude rapeseed oil, which contains a high concentration of polar phenols, has been reported to be more stable than refined oils [4, 5]. Besides, other researchers have reported that polar phenols, such as hydroxycinnamates and flavonoids, have higher antioxidant activities than tocopherols [6, 7].

However, the limited solubility of polar phenolics in lipids inhibits their application as antioxidants in foods. Recently, researchers have examined the use of nonpolar-derivatives of hydroxycinnamic acids as potential antioxidants. For example, vinylguaiacol (extracted from coffee) has been reported to have a greater antioxidant effect than α-tocopherol [8], and vinylsyringol (produced from sinapic acid by a pressing and roasting procedure) improved the oxidative stabilities of protein and lipids in cooked pork [9, 10]. Furthermore, according to Terpinc *et al*. [11], decarboxylation products of hydroxycinnamic acids were more

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efficient at inhibiting oxidation in emulsion systems than their parent compounds.

However, little research has been performed on the oxidation of bulk oils with hydroxycinnamic acids and their decarboxylated products as antioxidants. Sinapic acid (3,5-dimethoxy-4-hydroxycinnamic acid) and its decarboxylated product 4-vinylsyringol are good examples of such antioxidant compounds. In the present study, the peroxide value (PV) and thiobarbituric acid reactive substances (TBARS) assay were performed to measure the concentrations of hydroperoxides and malondialdehydes in soybean oils containing different antioxidants (α-tocopherol, sinapic acid, or 4-vinylsyringol). The effect of synergistically inhibiting oxidation between any two antioxidants was also determined. Furthermore, ^{1}H NMR was used to compare the antioxidant activities of α-tocopherol, sinapic acid, and 4-vinylsyringol in stripped soybean oil by monitoring the degradation of polyunsaturated fatty acids (PUFA), the evolution of conjugated forms, and the formation of aldehydes during oxidation.

Experimental Procedures

Materials

Soybean oil was purchased from a local market (Daejeon, South Korea). Silicic acid, deuterated chloroform (99.9 atom % D, containing 0.1 % v/v TMS) and dimethyl sulfoxide-d_6 (99.9 at.% D, contains 0.03 % (v/v) TMS) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Activated charcoal for column chromatography was obtained from Daejung Chemical Reagent (Daejung Chemicals & Metals Co., Ltd). *N*,*N*-Dimethylformamide (DMF) was purchased from TCI (Tokyo Chemical Industry Co., Ltd).

Preparation of Stripped Soybean Oil

Stripped soybean oil (SSO) was obtained by passing soybean oil through a vacuum liquid chromatographic column (3.5 cm diameter, 20 cm length) [12]. Samples were prepared by diluting 120 g of soybean oil with 120 mL of *n*-hexane. The lower layer of the column was packed with 15 g of silicic acid to remove minor diacylglycerol (DAG), monoacylglycerol (MAG), and free fatty acid (FFA) in soybean oil, and an upper layer of 30 g of active charcoal was used to remove tocopherols. After eluting the oil with 300 mL of *n*-hexane, the solvent was removed using a vacuum rotary unit (RE 111, Büchi, Flawil, Switzerland) at 40 °C. Traces of *n*-hexane were removed by flushing with nitrogen. Stripped soybean oil was stored at −70 °C prior to the oxidation study. The tocopherol contents of stripped soybean oil were determined as described previously [13].

Synthesis of 4-Vinylsyringol

4-Vinylsyringol (4-VS) was synthesized by a modified method described in previous study [11]. Sinapic acid (100 mg) was dissolved in 2 mL of *N*,*N*-dimethylformamide (DMF) containing 20 mg of sodium acetate as a catalyst for the decarboxylation reaction. The reaction was carried out at 130 °C in an oil bath for 15 min. After cooling to room temperature, 4-VS was extracted with *n*-hexane (2 mL each time) several times. The solvent was removed by flushing with nitrogen, and 4-VS obtained was stored at −70 °C for further experiments.

Oxidation Process

Different antioxidants, namely α-tocopherol, sinapic acid, or 4-VS, were added to 10 g of SSO at a concentration of 500 ppm. In order to determine synergistic antioxidant effect between two antioxidants, soybean oil containing 250 ppm of α-tocopherol and 250 ppm of sinapic acid (SBO-toco + SA), 250 ppm of α-tocopherol and 250 ppm of 4-VS (SBO-toco + VS), or 250 ppm of sinapic acid and 250 ppm of 4-VS (SBO-SA + VS) were submitted to oxidation. The oil (6 g) was placed into a Petri dish (35 × 10 mm) and exposed to air for 19 days in an oven at 60 °C in the dark. Oxidized samples were flushed with nitrogen and frozen at −70 °C until required for analysis.

Peroxide Value (PV) and Thiobarbituric Acid Reactive Substances Value (TBARS Value)

Peroxide values of oxidized oils were measured using the IDF method described in the previous study [14]. TBARS values were determined as described previously [15].

^{1}H-NMR Experiment

^{1}H-NMR experiments were carried out using a Bruker Avance III 600 spectrometer operated at 600.23 MHz. Typically, 200 mg of oil was mixed with 400 μL of $CDCl_3$ containing 0.1 % tetramethylsilane as an internal standard, and this mixture was placed in a 5-mm diameter NMR tube. The acquisition parameters used were: spectral width 12,335.5 Hz, number of scans 16, and acquisition time 2.656 s. The experiment was carried out at 28 °C. All spectra were processed using ACD labs NMR Processor, version 10.0. Chemical shifts (δ) were referred to the TMS at $\delta = 0$ ppm. Conjugated forms (–C<u>H</u>=CH–CH=CH–), hydroperoxides (–OO<u>H</u>), and aldehydes (–C<u>H</u>O) can be presented in mol/mol oil directly by normalizing the peak

area of β hydrogen atom (>CHOCOR) in the glycerol backbone to 1. For recalculating the amounts of above oxidation products in mmol/L of oil, the molecular weights of oils were considered.

Statistical Analysis

Oxidation reactions were conducted in duplicate and results are presented as averages. Analysis of variance (ANOVA) was performed using SPSS 16.0 (SPSS Inc., Chicago, IL). Statistical significance was accepted for $p < 0.05$ [16].

Results and Discussion

Identification of 4-Vinylsyringol

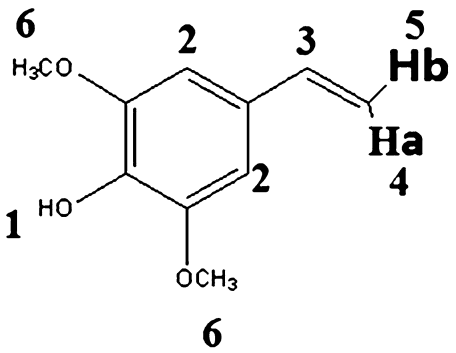
The ^{1}H-NMR spectroscopic data of 4-vinylsyringol (4-VS) is shown in Table 1. The structure of 4-VS was confirmed by comparison with previous studies [11, 17, 18].

Peroxide Value (PV) and Thiobarbituric Acid Reactive Substances Value (TBARS Value)

Peroxide values (PV) and TBARS assays were used to monitor the oxidation processes of SBO-control (soybean oil without antioxidant), SBO-toco (soybean oil containing 500 ppm α-tocopherol), SBO-SA (soybean oil containing 500 ppm sinapic acid), and SBO-VS (soybean oil containing 500 ppm 4-VS) as described previously [14, 15]. It is worth mentioning that 500 ppm of 4-VS or α-tocopherol was easily dissolved in soybean oil while heating (in boiling water for 5 min) and sonication (50 °C for 15 min) were performed for dissolving 500 ppm of sinapic acid. Furthermore, to accurately determine the antioxidant activity of 4-VS, the main antioxidants (tocopherols) in soybean oil were removed by a vacuum liquid chromatographic column (yield: 84.6 %, by weight). The total tocopherol content of stripped soybean oil was 9.2 ppm. As shown in Fig. 1a, among the soybean oils containing single antioxidant, SBO-VS showed the lowest evolution rate of peroxides. On day 3, the concentrations of peroxides in SBO-VS (11.5 ± 0.3 milliequivalents/kg oil) were significantly lower than that in the SBO-control (355.2 ± 21.8 milliequivalents/kg oil), SBO-toco (55.9 ± 1.1 milliequivalents/kg oil) and SBO-SA (23.0 ± 0.2 milliequivalents/kg oil) ($p < 0.05$). Thereafter, from day 3 to day 10, 619.7, 289.7, and 103.8 milliequivalents/kg oil of peroxides were respectively increased in SBO-control, SBO-toco, and SBO-SA while only 31.3 milliequivalents/kg oil of peroxides were generated in SBO-VS over the same period. After day 10, the concentrations of peroxides in SBO-control showed a gradual decrease due to conversion from primary to secondary oxidation products [19]. Furthermore, from day 10 to day 19, SBO-VS showed less peroxides formation than SBO-toco or SBO-SA, and the final concentrations of peroxides in SBO-VS (326.9 ± 26.0 milliequivalents/kg oil) on day 19 were significantly lower than that in SBO-toco (884.9 ± 22.6 milliequivalents/kg oil) and SBO-SA (424.4 ± 19.3 milliequivalents/kg oil) ($p < 0.05$). According to the above results, although the long time (19 days) accelerated oxidation process (exposed to air in an oven at 60 °C) led to a high concentration of peroxide in SBO-VS for consumption, 4-VS still showed higher antioxidant activity in oil system than sinapic acid and α-tocopherol.

TBARS values of SBO-control, SBO-toco, SBO-SA, and SBO-VS are shown in Fig. 1b. The results indicated that SBO-control and SBO-toco were more susceptible to oxidation than SBO-SA and SBO-VS. On the other hand, although TBARS value of SBO-SA and SBO-VS increased

Table 1 Assignments and the ^{1}H-NMR spectroscopic data of 4-vinylsyringol (4-VS)

	Position	Chemical shift[a] (ppm)
	1	8.47 (1H, s, –OH)
	2	6.75 (2H, s, Ar–H)
	3	6.60 (1H, dd, $J_{34} = 17.50$, $J_{35} = 10.73$, –CH=)
	4	5.69 (1H, d, $J_{34} = 17.50$, $J_{45} = 0.94$, =CH_2)
	5	5.10 (1H, d, $J_{35} = 10.73$, $J_{45} = 0.94$, =CH_2)
	6	3.79 (6H, S, –OCH_3)

[a] *s* singlet, *d* doublet, *dd* doublet of doublets

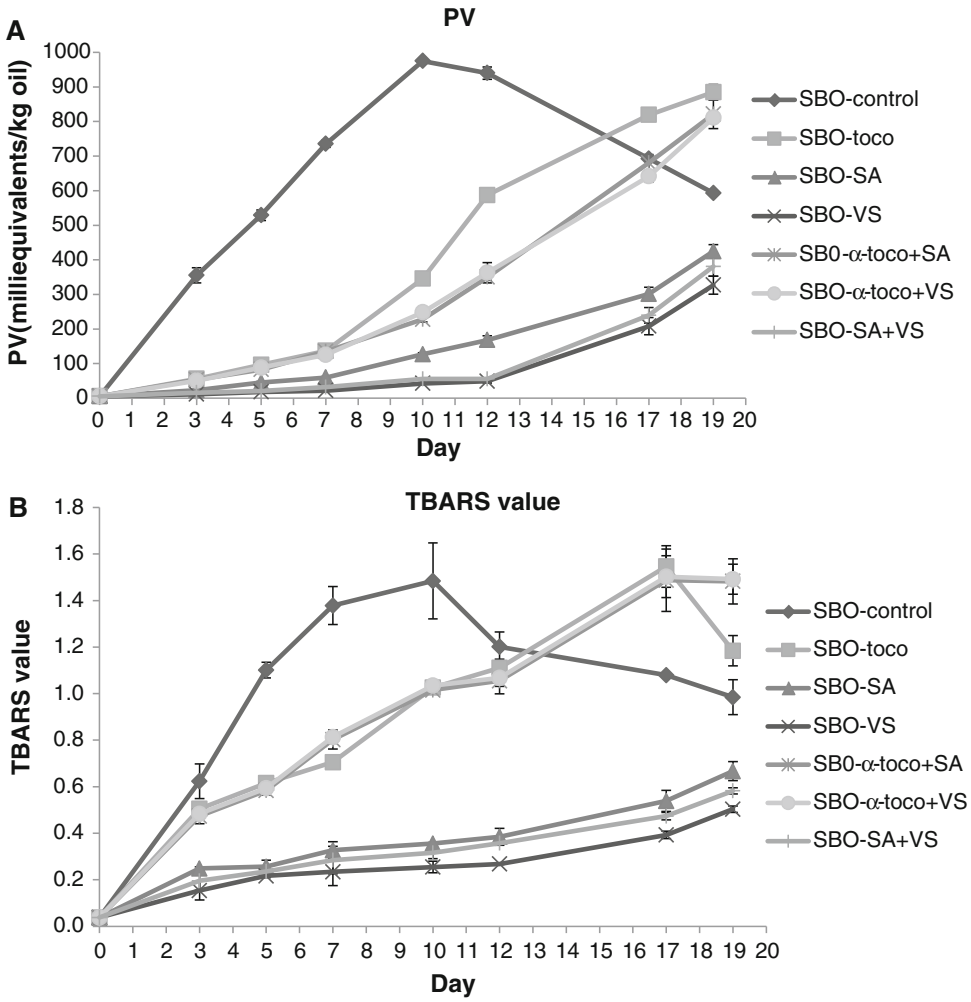


Fig. 1 Peroxide value (PV) and TBARS value of soybean oils containing different antioxidants [control, α-tocopherol (500 ppm), sinapic acid(500 ppm), 4-VS(500 ppm), α-tocopherol (250 ppm) + sinapic acid (250 ppm), α-tocopherol (250 ppm) + 4-VS (250 ppm), 4-VS (250 ppm) + sinapic acid (250 ppm),] during oxidation at 60 °C in the dark. **a** PV and **b** TBARS value

slightly, SBO-VS showed consistently lower TBARS value than SBO-SA throughout the oxidation process, and the final TBARS value of SBO-VS (0.5 ± 0.0 mg^{-1}) was lower than that of SBO-SA (0.7 ± 0.0 mg^{-1}).

In addition, in Fig. 1a, b, the synergistic antioxidant effects of two antioxidants were also determined. Among the combinations of each two antioxidants, sinapic acid with 4-VS showed the highest antioxidant activity. On day 19, both PV and TBARS values of SBO-SA + VS (PV: 380.6 ± 27.7 milliequivalents/kg oil; TBARS values: 0.6 ± 0.0 mg^{-1}) were significantly lower than those of SBO-toco + SA (PV: 821.3 ± 42.0 milliequivalents/kg oil; TBARS value: 1.5 ± 0.0 mg^{-1}) and SBO-toco + VS (PV: 810.9 ± 9.8 milliequivalents/kg oil; TBARS values: 1.5 ± 0.1 mg^{-1}) ($p < 0.05$). However, compared with SBO-VS (PV: 326.9 ± 26.0 milliequivalents/kg oil; TBARS value: 0.5 ± 0.0 mg^{-1}) on day 19, SBO-SA + VS showed higher peroxide and malondialdehyde formation, indicating that combination of sinapic acid (250 ppm) and 4-VS (250 ppm) was less effective on retarding the oxidation than 4-VS (500 ppm) in soybean oil. Similar results were observed in the other combinations of antioxidants. The antioxidant activity of tocopherol (250 ppm) with either sinapic acid (250 ppm) or 4-VS (250 ppm) was lower than 500 ppm of either sinapic acid or 4-VS, although such combinations showed higher antioxidant activity than 500 ppm of α-tocopherol. Thus, the synergistic antioxidant effect of tocopherol with sinapic acid or 4-VS was not distinctly observed in this study.

Monitoring the Oxidation Process by ^{1}H NMR

To further confirm the antioxidant activity of 4-VS, ^{1}H NMR was performed to investigate the degradation of PUFA (polyunsaturated fatty acids), the evolution of primary oxidation products (conjugated forms), and the formation of secondary oxidation products (aldehydes) in soybean oil. ^{1}H-NMR signals are directly proportional to proton numbers. By adopting this principle, ^{1}H NMR was able to quantify amounts of linolenic acid (C18:3) and linoleic acid (C18:2) as previously described [20] and the results are presented in Fig. 2. Figure 2a shows obvious

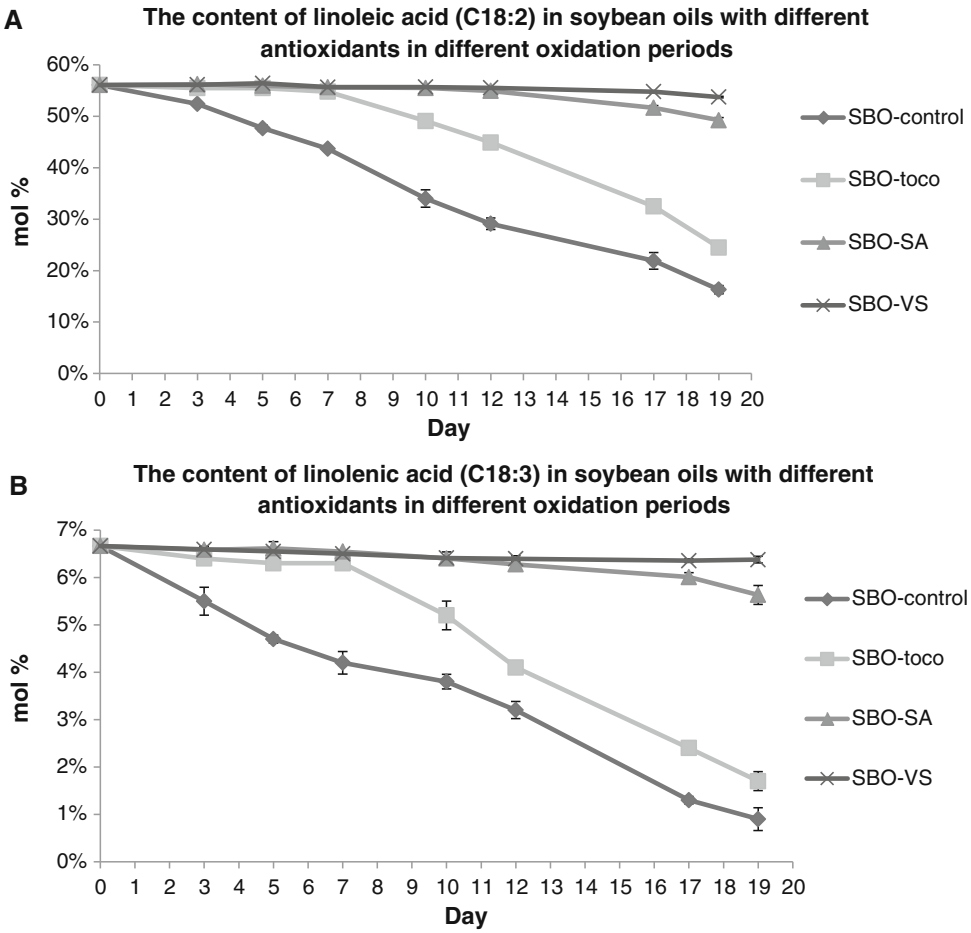


Fig. 2 **a** The content (molar percentage) of linoleic acid (C18:2) in soybean oils containing different antioxidants [control, α-tocopherol(500 ppm), sinapic acid(500 ppm) and 4-VS(500 ppm)] in different oxidation periods. **b** Contents (molar percentage) of linolenic acid (C18:3) in soybean oils containing different antioxidants [control, α-tocopherol(500 ppm), sinapic acid(500 ppm) and 4-VS(500 ppm)] in different oxidation periods

decreases in C18:2 levels in the SBO-control and SBO-toco while SBO-SA and SBO-VS showed only slight degradation of C18:2 throughout the oxidation process. After 19 days of oxidation at 60 °C in dark, 70.9, 56.3, and 12.2 % of C18:2 were lost in the SBO-control, SBO-toco, and SBO-SA, respectively. Meanwhile, only 4.2 % of C18:2 decreased in SBO-VS. On the other hand, the decomposition of C18:3 in these soybean oils (Fig. 2b) showed that 86.5, 74.5, 15.4, and 4.4 % of C18:3 were degraded after 19 days of oxidation in the SBO-control, SBO-toco, SBO-SA, and SBO-VS, respectively. The significantly lower degradation rate of PUFA in SBO-VS showed that soybean oil containing 4-VS was more resistant to autoxidation than soybean oil containing α-tocopherol or sinapic acid.

Furthermore, the peroxidation of PUFA is accompanied by the formation of conjugated diene structures [21]. Thus, several signals in the region between 5.4 and 6.7 ppm newly appeared in the ^{1}H-NMR spectra. As Fig. 3a shows, *Z*,*E*-conjugated form and *E*,*E*-conjugated form were identified in oxidized soybean oils, as has been previously reported [22, 23]. In addition, ^{1}H-NMR quantitative analysis of conjugated forms was performed to evaluate levels of oxidation. Figure 3b shows that the concentrations of conjugated forms in SBO-control and SBO-toco decreased after 7 and 12 days of storage, respectively. However, both SBO-SA and SBO-VS showed gradual increases in conjugated forms until the 19 days of the oxidation. These results suggest that conjugated forms in SBO-control and SBO-toco decomposed into secondary oxidation products [24] while SBO-SA and SBO-VS still in the primary oxidation stage by 19 days of oxidation. Compared with sinapic acid, its decarboxylation product (4-VS) was more useful at preventing the formation of conjugated forms. From day 0 to day 5, 13.6 ± 0.4 mM oil of the conjugated forms were formed in SBO-SA, while the conjugated forms in SBO-VS remained undetectable by ^{1}H NMR over the same period. From day 5 to day 19, conjugated forms increased consistently in SBO-SA and SBO-VS, but the formation rate in SBO-VS was lower. On day 19, the concentration of conjugated forms in SBO-VS (44.9 ± 3.0 mM oil) was significantly lower than that in SBO-SA (111.4 ± 2.5 mM oil) ($p < 0.05$).

Finally, although the TBARS assay was used to evaluate amounts of secondary oxidation products, it can only detect malondialdehyde generated during lipid

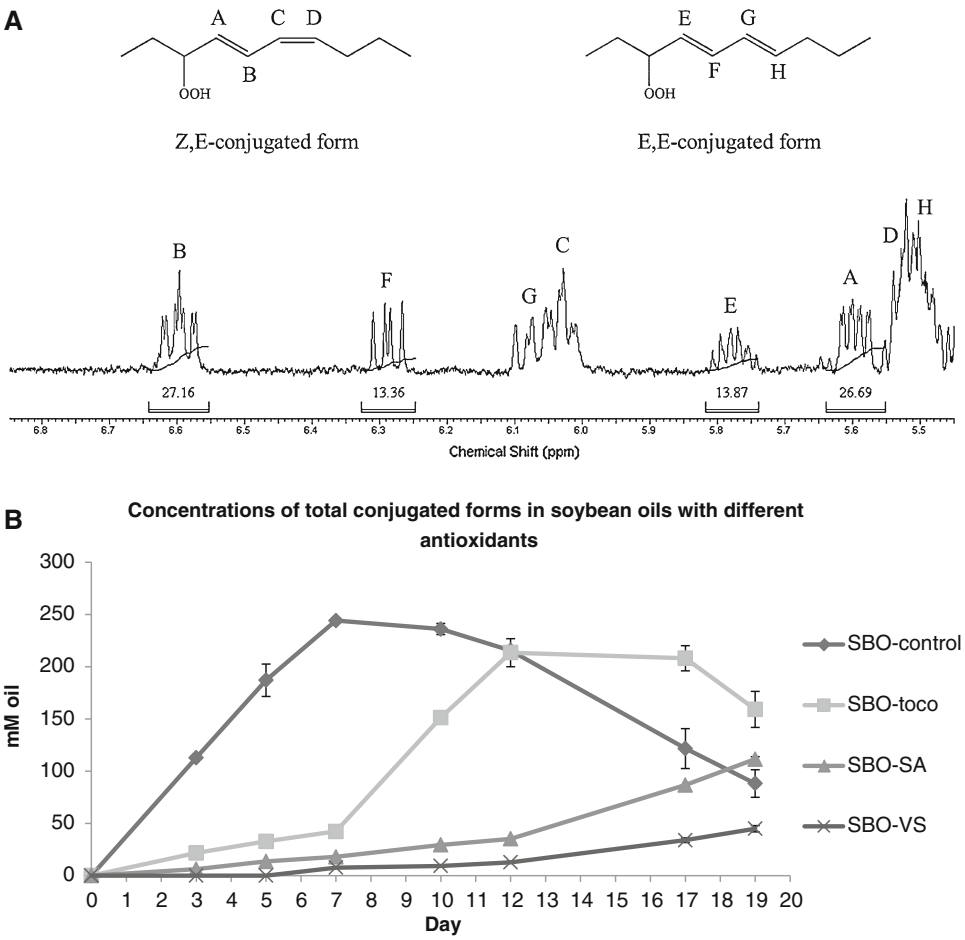


Fig. 3 Primary oxidation products (conjugated forms): **a** assignments and the ^{1}H-NMR spectra of conjugated forms (obtained from soybean oil containing α-tocopherol after 7 days of oxidation). **b** The concentrations of total conjugated forms in soybean oils containing different antioxidants [control, α-tocopherol (500 ppm), sinapic acid (500 ppm), or 4-VS (500 ppm)] after oxidation at 60 °C in the dark

oxidation, and malondialdehyde is neither the sole end product nor a substance generated exclusively by lipid oxidation [25]. Therefore, the molar concentrations of total aldehydes in soybean oils containing different antioxidants were also determined by ^{1}H NMR. In this study, six types of aldehydes, namely (I) *n*-alkanal, (II) 4-hydroperoxy-(*E*)-2-alkenal, (III) 4-hydroxy-(*E*)-2-alkenal, (IV) 4,5-epoxy-(*E*)-2-alkenal, (V) (*E*,*E*)-2,4-alkadienal, and (VI) (*E*)-2-alkenal, were identified (Fig. 4a) [22, 26]. As is shown in the Fig. 4b, 4-VS and its corresponding hydroxycinnamic acid (sinapic acid) showed obviously higher antioxidant activity than α-tocopherol. After 19 days of oxidation, aldehydes were not detectable in SBO-VS and only *n*-alkanal and (*E*)-2-alkenal were generated in SBO-SA. However, in SBO-control and SBO-toco, all six aldehydes were detected. On day 19, the concentrations of total aldehydes in SBO-control, SBO-toco, and SBO-SA were 52.0 ± 3.7, 38.0 ± 0.4, and 2.7 ± 0.2 mM oil, respectively (Fig. 4b). Furthermore, Figs. 2, 3 and 4 suggest that the degradation of PUFA, the evolution of conjugated forms, and the formation of aldehydes in soybean oils are somewhat related. In SBO-toco, for example, the obvious increase of aldehydes was first observed between day 7 and 10 (Fig. 4), during which PUFA degradation (Fig. 2) and formation of conjugated forms (Fig. 3) were obviously fast. In SBO-SA, this phenomenon may be observed between day 12 and day 17. These results suggest that significant oxidation of SBO-toco, and SBO-SA started after 10 days, and 17 days of storage, respectively. However, changes in fatty acid composition and primary and secondary oxidation products were almost undetectable in SBO-VS even after 19 days of oxidation.

Conclusion

Generally, 4-VS exists in small amounts in crude rapeseed oil [27] and no side-effects on human health have been reported. Our results are in agreement with previous studies [9, 11], in which 4-VS showed greater antioxidant activity than sinapic acid in meat and emulsion oxidation. In the present study, 4-VS was obtained from decarboxylated sinapic acid, and exhibited the highest antioxidant activity in bulk oil, followed by sinapic acid and α-tocopherol. The results indicated that 4-VS appears to have potential as an antioxidant for oil applications. Furthermore, as compared with sinapic acid, 4-VS (the decarboxylation product of

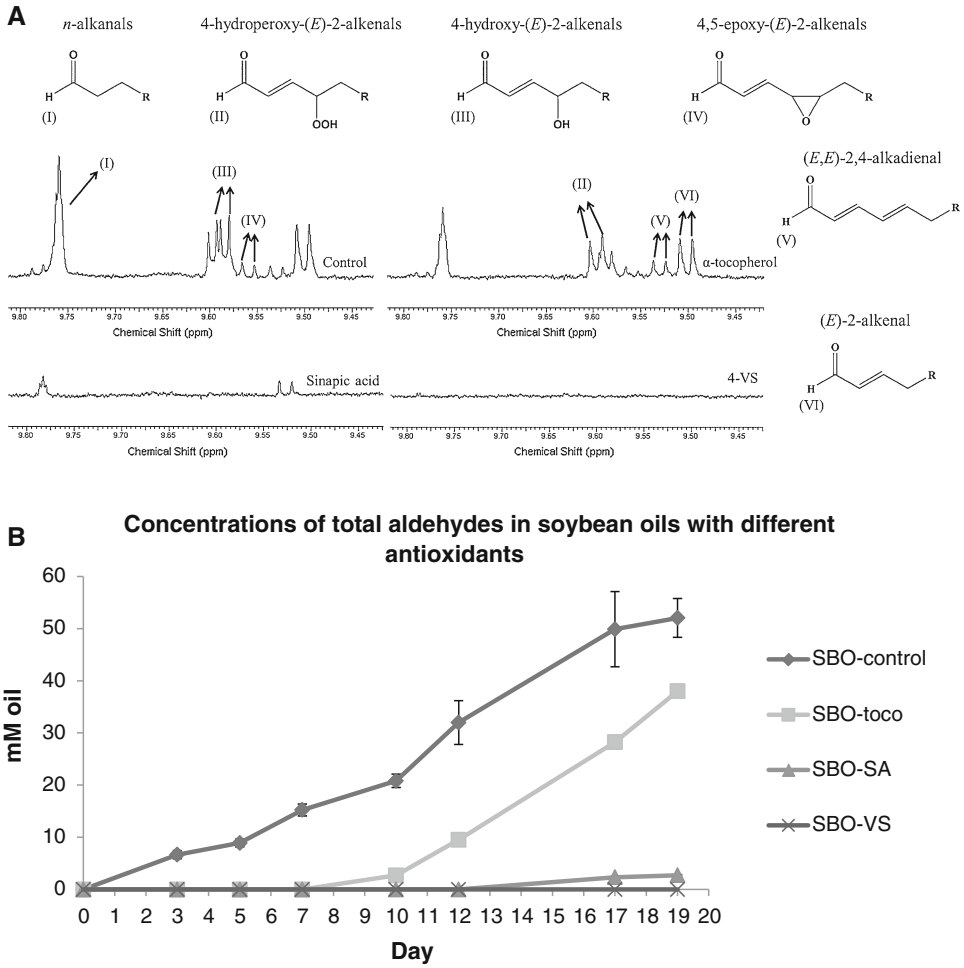


Fig. 4 Secondary oxidation products (aldehydes): **a** assignments and the ^{1}H-NMR spectra of aldehydes obtained from soybean oil containing different antioxidants after oxidation for 19 days. **b** Concentrations of total aldehydes in soybean oils containing different antioxidants [control, α-tocopherol(500 ppm), sinapic acid (500 ppm), or 4-VS (500 ppm)] after oxidation at 60 °C in the dark

sinapic acid) had higher solubility in oil. All the above findings imply that there is a possibility of further utilization of sinapic acid which was abundant in rapeseed oil cake. To the best of our knowledge, the use of rapeseed oil cake has been limited due to the antinutritional effects of compounds such as glucosinolates [28]. Therefore, the potential antioxidant activity of 4-VS in this study may allow us to extend the applications of the by-products of rapeseed oil processing. Further studies on the antioxidant activities of 4-VS at different concentrations will be performed.

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