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Activity and thermal stability of antioxidants by differential scanning calorimetry and electron spin resonance spectroscopy

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Abstract

Heat flux differential scanning calorimetry (DSC) and electron spin resonance spectroscopy (ESR) were used to assess the activity and the thermal stability of antioxidants in four vegetable oils. Sunflower oil (SO) and high oleic sunflower oil (HOSO), both rich in diunsaturated fatty acids (FA), low trans oil (LT) and partially hydrogenated palm oil (PHPO), both containing monounsaturated FA, were analyzed by isothermal heat flux DSC, with or without 300 mg/kg of antioxidant: ascorbyl palmitate (AP), α-tocopherol (αT), δ-tocopherol (δT) and propyl gallate (PG). DSC experiments showed that δT is the most effective antioxidant for SO and PG for the less unsaturated oils. SO and PHPO were also analyzed by ESR at 120 and 145 °C, respectively. ESR results confirm the strongest antioxidant activity of δT and PG for SO and PHPO, respectively. Therefore, the present study demonstrates that DSC and ESR are valuable technologies to study activity and stability of antioxidants at high temperature. Moreover, experiments performed in the presence of the spin-trap *N-tert*-butyl-α-phenylnitrone (PBN), suggest that δT delay lipid oxidation through a different reaction mechanism when compared to αT. A different mechanism between tocopherols isomers in delaying lipid oxidation has been hypotized.

Keywords: Antioxidant; Differential scanning calorimetry; Electron spin resonance spectroscopy; Oxidation; Thermal analysis; Vegetable oils

1. Introduction

Oil quality and stability are principally affected by lipid oxidation, a general term for a complex process that results in generation of off-flavour and reduction in nutritional value. To delay oxidation in food systems natural antioxidants, such as tocopherols and the fatty acid ester ascorbyl palmitate (AP), and synthetic antioxidants such as propyl gallate (PG) are employed. Primary or "chain-breaking" antioxidants such as α-tocopherol (αT) and PG inhibit or retard lipid oxidation by interfering with either chain initiation or propagation by readily donating hydrogen atoms to lipid peroxyl and alkoxyl radicals (Frankel, 1996). AP acts in different way, it can scavenge oxygen, shift the redox potential of a food system to the reducing range and regenerate primary antioxidants (Frankel, 1996).

Generally αT is found to be better antioxidant in vivo than δT and vice versa in vitro (Kamal-Eldin and Appelqvist, 1996). Latest studies (Isnardy, Wagner, and Elmadfa, 2003; Mäkinen, Kamal-Eldin, Lampi, and Hopia, 2004; Wagner, Isnardy, and Elmadfa, 2004) reported that δT is a more powerful antioxidant than αT, in oils and in oil/water emulsions. When present at high concentrations a prooxidant effect of α-tocopherol has been observed (Huang, Frankel, and German, 1994; Huang, Frankel, and German, 1995; Jung and Min, 1990). Recent studies suggest that αT does not behave as prooxidant but rather lose efficacy at a high concentrations due to its participation in side reactions (Fuster, Lampi, Hopia, and Kamal-Eldin, 1998; Lampi, Kataja, Kamal-Eldin, and Piironen,

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1999; Mäkinen, Kamal-Eldin, Lampi, and Hopia, 2000; Yanishilieva, Kamal-Eldin, Marinova, and Toneva, 2002).

The Rancimat method and electron spin resonance spectroscopy (ESR), both using accelerated oxidation conditions, have been developed for the evaluation of oxidative stability (AOCS, 1992; Thomsen et al., 2000). Differential scanning calorimetry (DSC) has also been employed for establishing the oxidative stability of oils and fats, as well as for characterization of their physical properties (Cross, 1970; Hassel, 1975; Raemy et al., 1987; Raemy, 2003; Velasco et al., 2004). This isothermal calorimetric technique has shown very good correlation with other methods such as Rancimat or ESR (Thomsen et al., 2000; Velasco et al., 2004).

Published studies related to thermal properties and activities of antioxidants in vegetable oils by DSC are limited (Kowalski, 1993; Pereira and Das, 1990; Tan et al., 2001). The present study aims at evaluating the potential of heat flux DSC techniques to measure both thermal stability and activity of antioxidants in vegetable oils and at comparing DSC to ESR. Ascorbyl palmitate (AP), α-tocopherol (αT), δ-tocopherol (δT) and propyl gallate (PG) were selected as antioxidants. Tocopherols represents natural antioxidants with different antioxidant mechanism of reaction; while AP and PG are synthetic antioxidants widely employed in culinary products.

2. Materials and methods

2.1. Chemicals and samples

N-tert-butyl-α-phenylnitrone (PBN) (purity ⩾ 99%) was obtained from Fluka (Buchs, Switzerland). All other chemicals and reagents were of analytical grade and were used without further purification. AP, αT, δT, and PG were purchased from Sigma (Steinheim, Germany), and added (300 mg/kg) to sunflower (SO), high oleic sunflower oil (HOSO), low trans oil made from palm oil (LT) and partially hydrogenated palm oil (PHPO) obtained from a local supplier.

2.2. Fatty acid composition

Fatty acid composition was analyzed by gas–liquid chromatography after derivatization to fatty acid methyl esters with a methanolic solution of potassium hydroxide according to an official method (IUPAC).

2.3. Analysis of natural antioxidants

Tocopherols and tocotrienols in oils were quantified by reverse-phase liquid chromatography according to Dionisi, Prodolliet, and Tagliaferri (1995).

2.4. Differential scanning calorimetry (DSC)

Data were recorded on a Mettler Toledo DSC821e apparatus (Schwerzenbach, Switzerland). The induction period (IP) of pure and spiked oils (1 mg) was analyzed by isothermal heat flux at 120, 125, 130 and 135 °C for SO and HOSO and at 145, 150, 155 and 160 °C for LT and PHPO, under constant oxygen flow (100 ml/min). Pure antioxidant samples were analyzed by dynamic DSC at 2 and 5 °C/min rates under both oxygen atmosphere and in sealed crucibles, i.e. in a N_2 atmosphere.

2.5. Electron spin resonance spectroscopy (ESR)

The spin trapping method was applied to monitor the formation of free radicals. PBN, dissolved in the oils (1 mg/g oil) by stirring, was used as spin trap. Twelve aliquots of SO and PHPO containing AP, αT, δT, PG and PBN were weighed (1.00 ± 0.05 g) into ESR tubes (700-PQ-7, heavy wall, Wilmad Glass, Buena, NJ) and placed in an oven at 120 °C for SO and at 145 °C for PHPO. The tubes were successively taken from the oven every 5 min and immediately placed in an ECS 106 ESR spectrometer (Bruker, Rheinstetten, Germany) to be analyzed in real time. ESR measurements were performed according to Thomsen et al. (2000) and formation of PBN-adducts was monitored by the peak-to-peak amplitude of the first line of the ESR signal. Signals were monitored by Winepr software (Bruker, Rheinstetten, Germany).

3. Results and discussion

3.1. Characterization of oils

SO, HOSO, LT and PHPO were analyzed for their content in FA and natural antioxidants. Their FA composition is given in Table 1. SO, HOSO, LT and PHPO showed all typical FA profiles. The content of natural antioxidants was within the normal range for these oils (Firestone, 1999).

3.2. Oxidative stability by DSC

Four different vegetable oils, i.e. SO, HOSO, LT and PHPO, were used in order to evaluate the activity of differ-

Table 1
Fatty acid contents of the oil samples (mean of duplicate analysis)

Fatty acid (g/100 g of FA)	SO	HOSO	LT	PHPO
–				
12:0	–	–	0.19	0.30
14:0	–	0.03	1.20	1.14
16:0	6.48	4.01	52.72	47.91
16:1	0.04	0.10	0.10	–
17:0	–	–	0.11	–
18:0	4.34	3.33	8.87	7.36
18:1 *n*-9 (*cis* and *trans*)	25.60	80.33	32.38	42.09
18:2 *n*-6 (*cis* and *trans*)	62.35	11.28	3.90	1.10
18:3 *n*-3	0.46	0.29	–	–
20:0	0.18	0.28	0.38	–
20:1	0.24	0.30	0.09	–
20:2	0.06	–	–	–
20:3	0.01	–	–	–
Other	0.24	0.06	0.06	0.09

ent antioxidants by DSC. Evaluation of oxidative stability by DSC was based on the measurement of the induction period (IP). SO and HOSO have a higher content of polyunsaturated FA than LT and PHPO, therefore they should be more sensitive towards oxidation. For this reason the IP for SO and HOSO should be monitored at lower temperatures than for LT and PHPO. Results for IP measured in the presence or absence of added antioxidants are given in Table 2. Moreover the effectiveness of the antioxidants was expressed as the inhibitor effect of AP, αT, δT, PG on the oxidation of oils. The effectiveness represents the possibility of blocking the chain radical process by interaction with the peroxyl radicals, which are responsible for the duration of the IP (Yanishilieva et al., 2002). The effectiveness expressed as the stabilization factor F (F = IPinh/IPo). Where IPinh is the induction period in the presence of inhibitor, and IPo is the induction period of an uninhibited oxidation (Yanishilieva et al., 2002). Therefore, F is 1 in the absence of antioxidant, higher than 1 in the presence of an added antioxidant and lower than 1 in the presence of a prooxidant.

Significance testing ($p < 0.05$) (Table 2) indicated that δT was effective for SO and PG for HOSO, LT and PHPO stabilization. AP exhibits a low antioxidant activity in all of oils. The poor antioxidant activity of AP could be due to the high oxygen partial pressure and temperature employed during measurements. AP is readily and reversibly oxidized to dehydroascorbic palmitate. When the dehydroascorbic lactone ring is irreversibly opened, giving rise to 2,3-diketo-gulonic palmitate, the antioxidant activity is lost (Fig. 1) (Belitz and Grosch, 1987). Both high oxygen partial pressure and higher temperature enhance AP oxidation and its further degradation (Belitz and Grosch, 1987). Thermograms of SO with and without tocopherols (Fig. 2) showed that δT exhibits a stronger antioxidant activity than αT. This observation based on the hydrogen-atom donator capacities of αT and δT, has been previous reported (Cetin, 1989; Isnardy et al., 2003; Yanishlieva-Maslarova, 2001). δT exhibited significant antioxidant activities on LT; none of the tested tocopherols (α T and δT) showed significant antioxidant activities on PHPO. These findings are in accordance with previous results (Jorge, Marquez-Ruiz, Martin-Polvillo, Ruiz-Mendez, and Dobarganes, 1996; Verleyen et al., 2002) reporting that tocopherol antioxidant activity depends on the degree of triacylglycerol unsaturation, with lower tocopherol antioxidant activity in the less unsaturated oils.

Non-isothermal DSC experiments were performed on αT and δT to study their thermal degradation. Results obtained for tocopherols showed that αT was more susceptible to thermo-oxidative degradation than δT. The temperature at which the degradation process starts was 165.1 and 179.2 °C for αT and δT, respectively (Fig. 3), therefore tocopherols did not degrade at experimental tem-

Table 2
Induction period (IP) and stabilization factor (F) determined by differential scanning calorimetry (DSC) of the oil samples with and without antioxidants (300 ppm)

Oil	135 °C		130 °C		125 °C		120 °C	
	IP (min)	F	IP (min)	F	IP (min)	F	IP (min)	F
SO	9.33	1.00C	13.62	1.00C	23.82	1.00C	21.24	1.00C
SO + α-toc	45.62	4.89A	39.92	2.93A	93.39	3.92A	104.89	4.94A
SO + δ-toc	47.75	5.12B	99.76	7.33B	120.89	5.07B	203.70	9.59B
SO + AP	30.09	3.23C	21.98	1.61C	24.46	1.03C	56.59	2.66C
SO + PG	20.57	2.21C	23.19	1.70C	41.15	1.73C	39.23	1.85C
HOSO	62.91	1.00D	75.99	1.00D	96.93	1.00D	153.57	1.00D
HOSO + α-toc	51.36	0.82C	79.86	1.05C	121.52	1.25C	154.48	1.01C
HOSO + δ-toc	74.86	1.19B	111.25	1.46B	129.33	1.33B	213.87	1.39B
HOSO + AP	65.96	1.05C	90.44	1.19C	119.08	1.23C	173.36	1.13C
HOSO + PG	102.39	1.63A	132.75	1.75A	176.44	1.82A	240.21	1.56A
	160 °C		155 °C		150 °C		145 °C	
	IP (min)	F	IP (min)	F	IP (min)	F	IP (min)	F
LT	12.06	1.00C	18.70	1.00C	21.98	1.00C	32.18	1.00C
LT + α-toc	11.47	0.95C	11.70	0.63C	25.96	1.18C	26.06	0.81C
LT + δ-toc	18.09	1.50B	24.39	1.30B	31.22	1.42B	47.39	1.47B
LT + AP	17.22	1.43B	23.16	1.24B	35.18	1.6B	40.88	1.27B
LT + PG	37.46	3.11A	53.50	2.86A	70.17	3.19A	81.02	2.52A
PHPO	15.59	1.00C	21.13	1.00C	35.68	1.00C	39.44	1.00C
PHPO + α-toc	23.44	1.50B	28.93	1.37B	47.91	1.34B	53.48	1.36B
PHPO + δ-toc	19.22	1.23B	25.43	1.20B	33.29	0.93B	50.48	1.28B
PHPO + AP	19.38	1.24B	37.66	1.78B	56.67	1.59B	59.19	1.5B
PHPO + PG	61.64	3.95A	97.79	4.63A	120.37	3.37A	167.43	4.24A

Mean within each column (for the same oil) with same letters are no significantly ($p < 0.05$) different.

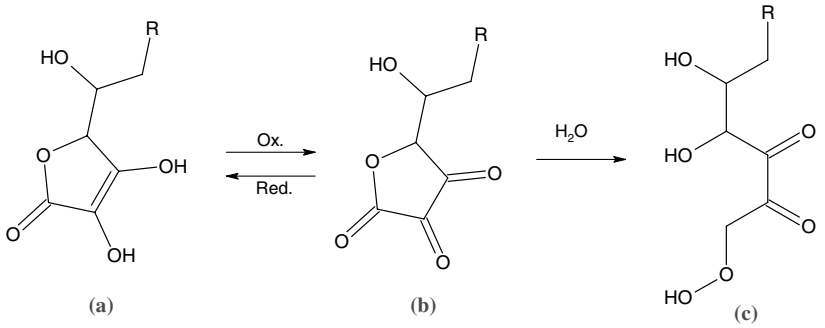

Fig. 1. Degradation of ascorbyl palmitate (a) into dehydroascorbic acid (b) and 2,3-diketo-gulonic acid (c). R represents the palmitoyl residue.

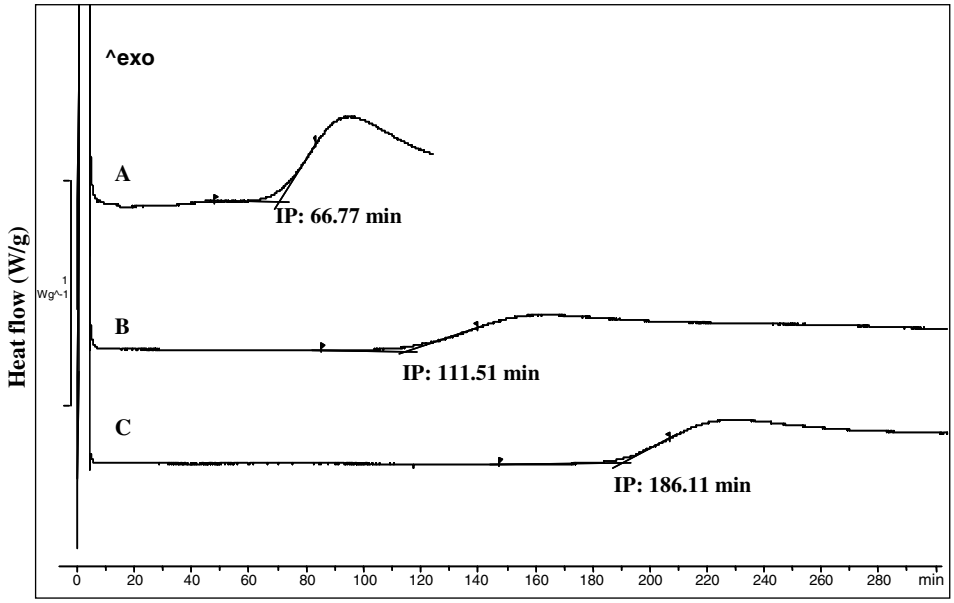

Fig. 2. Themograms obtained by isothermal DSC analysis at 120 °C of (A) sunflower oil, (B) sunflower oil plus 300 mg/kg of α-tocopherol and (C) sunflower oil plus 300 mg/kg of δ-tocopherol.

peratures. Analyses performed under inert conditions did not show any baseline variations confirming that the observed IPs indicate, unambiguously, that we have observed oxidative degradation of tocopherols.

In conclusion isothermal DSC experiments showed that tocopherols were good antioxidants for SO and PG for less unsaturated oils. Moreover, δT was more effective than αT in delaying lipid oxidation in unsaturated oils. A greater thermo-oxidative stability of δT compared to αT was observed in non-isothermal DSC measurements. These results demonstrate the efficacy of DSC for studying thermal stability and activity of antioxidants in vegetable oils.

3.3. Oxidative stability by ESR

To compare DSC with ESR technique, SO and PHPO were analyzed by ESR in order to further evaluate the activity of different antioxidants. Evaluation of oxidative stability by ESR was based on measurement of the free radicals formed in the early stages of oxidation. Radicals are very reactive species with very short life time, and usually the use of spin trapping agents, which react with free radicals to form more stable radicals (spin adducts), is necessary to detect radicals (Velasco et al., 2004). In the present study, PBN was used as spin trap and the formation of spin-adducts was monitored by ESR to evaluate the activity of the antioxidants.

ESR results showed that PG had the strongest antioxidant activity ($p < 0.05$) in PHPO (Fig. 4). Tocopherols were the most effective antioxidants ($p < 0.05$) in retarding oxidation in SO during the first stages of oxidation (results not shown). No significant differences ($p > 0.05$) in delaying lipid oxidation were detected between IP of αT and δT in contrast to previous findings. The fact that no difference in antioxidation activity between αT and δT was observed could be attributed to the presence of PBN. It was reported (Frankel, 1996) that α-tocopherol is a chain-breaking antioxidant that inhibits or retards lipid oxidation by interfer-

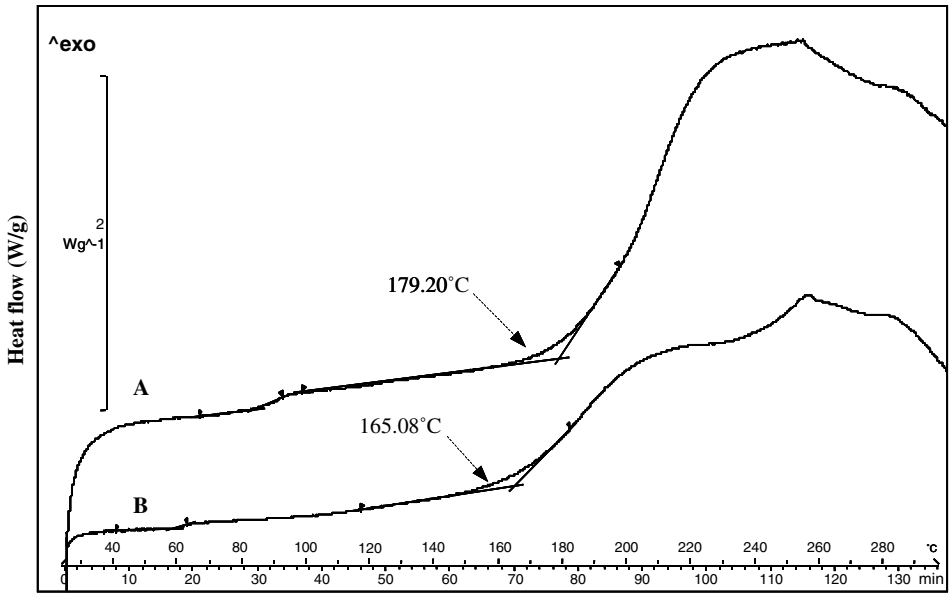

Fig. 3. Thermograms obtained by dynamic DSC analysis at 2 °C/min of (A) δ-tocopherol and (B) α-tocopherol.

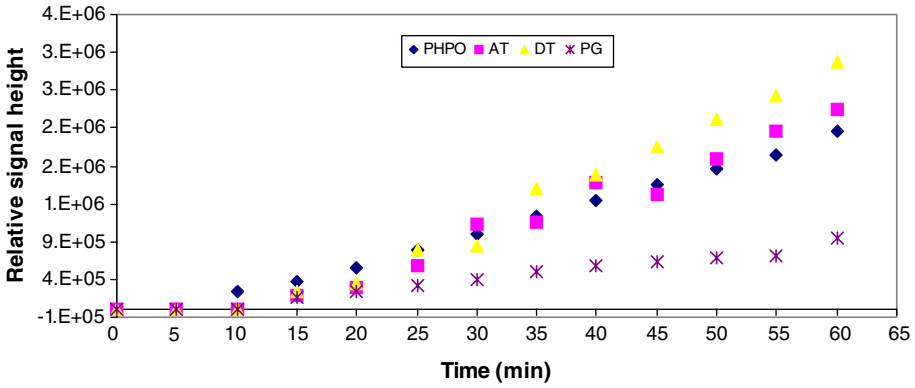

Fig. 4. Determination of free radical content by electron spin resonance spectroscopy (ESR) in PHPO.

ing with either chain propagation or initiation by donating hydrogen atom to lipid peroxyl and alkoxyl radicals. PBN does not act as a chain-breaking antioxidant but traps peroxyl radicals (Barclay and Vinqvist, 2000). It has been suggested that PBN reacts with peroxyl radicals (ROO•) very slowly to form spin adducts (PBN/ROO•) which are known to be very unstable and rapidly decompose to form alkoxyl radical RO• (Chiba and Kaneda, 1984; Janzen et al., 1990; Pfab, 1978). As a consequence, in presence of PBN the rate of RO• formation increases. Because no difference between αT and δT in delaying lipid oxidation was detected in the presence of PBN, we can suppose that δT and αT have different reaction affinities to alkoxyl and peroxyl radicals. To verify our hypothesis, pure and spiked SO samples were analyzed by DSC, under air, in the presence and the absence of PBN (Table 3). According to the results from DSC, tocopherols retarded oxidation in SO, nevertheless in the presence of PBN measurements, δT was less effective in delaying oxidation than in the absence of PBN, as a consequence α T and δT showed the same antioxidant power when PBN was added. PBN did not influence αT antioxidant activity. These results allowed us to suppose that PBN competes with δT for reaction with ROO•, but not with αT, probably because of the different hydrogen-atom donator capacities of α T and δT, demonstrating that αT and δT could delay lipid oxidation through different reaction mechanisms.

Table 3
Induction period (IP) determined at 120 °C by differential scanning calorimetry (DSC) and stabilization factor (*F*) of the oil samples with and without PBN (*N-tert*-Butyl-α-phenylnitrone)

Vegetable oil	Without PBN		With PBN	
	IP (min)	*F*	IP (min)	*F*
SO	203	1.00	219	1.00
SO + α-toc	380	1.87	382	1.74
SO + δ-toc	482	2.37	372	1.70

4. Conclusion

In this study DSC and ESR have been employed to study the oxidative stability of saturated and unsaturated oils spiked with different antioxidants. We showed that DSC and ESR are valuable tools to study oxidative stability of oils with and without antioxidants, and to better understand antioxidant activity and stability at higher temperature in vegetable oils. Furthermore, the obtained data suggest that αT and δT could delay lipid oxidation through different reaction pathways. Anyway, this hypothesis needs to be confirmed with further experiments.

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