Antioxidant Effect of Soy Lecithins on Vegetable Oil Stability and Their Synergism with Tocopherols

Armelle Judde[a], Pierre Villeneuve[b,*], Anne Rossignol-Castera[a], and Anne Le Guillou[c]

[a]ITERG–Institut des Corps Gras, 33 600 Pessac,France, [b]CIRAD–AMIS, 34398 Montpellier Cedex 5, France, [c]Danone Vitapole 91767 Palaiseau Cedex, France

ABSTRACT: The antioxidant effect of lecithins was tested on several oils and fats varying in FA composition and tocopherol content. Standard lecithins, when added at a level of 1% w/w, exhibited a good protective effect against oxidation. This effect was observed to depend on the phospholipid content of the tested lecithins and the FA composition of the tested oils. Better results were obtained with lecithin samples containing high proportions of PC and PE. Indeed, the main antioxidant mechanism of lecithins was due to a synergistic effect between amino-alcohol phospholipids and γ- and δ-tocopherols. No synergism was observed with α-tocopherols, especially when the tested oil was rich in linoleic acid. Therefore, the antioxidant protection of lecithins was not effective for sunflower oil. Finally, the use of fractionated or enriched lecithins was not clearly advantageous compared to standard oil lecithins.

Paper no. J10410 in *JAOCS 80*, 1209–1215 (December 2003).

KEY WORDS: Antioxidant, phospholipids, soya lecithin, synergism, tocopherols.

Lecithins are well-known compounds that are used industrially for their emulsifying properties. In some cases, they can contribute to an improvement in the oxidative stability of oils and fats. This antioxidant effect has been attributed to phospholipids, the main components of lecithins, which represent about 60% of standard crude lecithins and more than 95% in enriched or fractionated lecithins. Various antioxidative mechanisms have been proposed for phospholipids. For example, the amino functions of PC, PS, or PE, or the sugar moiety of PI have been shown to have metal-chelating properties (1–3). An oxygen barrier effect also was observed when phospholipids were present at the oil/water interface and played a protective role for lipids against contact with atmospheric oxygen (4). Similarly, lecithins could favor the dispersion of other active antioxidants in emulsion systems and limit the propagation of free radicals in the medium (5). Moreover, when heating highly unsaturated oils at high temperatures, aldehydes can form complexes with phospholipids through carbonyl and amino group interactions and generate melanophosphatides, which themselves inactivate hydroperoxides (3,6). A synergistic effect of lecithins with phenolic antioxidants also has been observed. This property was attributed to the fact that phospholipids can donate a hydrogen atom of their amino function, regenerating the oxidized phenolic molecule of the true antioxidant (7). In such a case, PE exhibits its best synergist effect in the presence of α- or γ-tocopherols (7–9). Antiradical properties also have been described for lecithins, which could be due to the hydroxy amino function of PC and PE (10,11). Finally, the antioxidant properties of phospholipids are influenced by their thermodynamic characteristics, the types of phosphorylated groups present, and the nature of the FA (12–15).

The objective of this study was to evaluate the antioxidant capacity of various commercially available soy lecithins on refined oils, specifically high-linolenic oils such as refined rapeseed. Indeed, in most cases, native tocopherols are normally sufficient to protect the oil against oxidation during storage at ambient temperature. However, industrial applications with higher temperature treatments require the use of more efficient antioxidant systems to delay the oxidative degradation of the oil (16). Therefore, we studied the potential advantages of using lecithins and focused particularly on the mechanisms and synergism between phospholipids and different tocopherols (α-, γ-, δ-). Different crude soy lecithins were tested on commercially available oils or in model systems under either mild (40°C) or more drastic (110°C) oxidizing conditions.

MATERIALS AND METHODS

Materials. (i) Oils. Rapeseed, sunflower, soybean, and walnut oils were purchased from regular food stores. Oleic sunflower, palm, and fish oils and lard were obtained from industrial refiners of oils and fats.

(ii) Chemicals. Methyl oleate, methyl linoleate, and α- and γ-tocopherols were purchased from Sigma Chemical (St. Louis, MO). Methyl linolenate was from Cluzeau Info Labo (Bordeaux, France). Mixtures of γ- and δ-tocopherols were from Eastman Organic Chemicals (Rochester, NY). Prior to any trial, their purity and tocopherol composition were checked by HPLC.

(iii) Soy lecithins. Three standard soy lecithins from three different suppliers were tested, trade-named Vamothin S (Vamo-Fuji, Osaka, Japan), Sterncithin F10 (Stern, Hamburg, Germany), and Topcithin 50 (Lucas-Meyer, Atlanta, GA). Fractionated lecithins (Nathin 5KE, Nathin 3KE, and Nathin 140) were from Vamo-Fuji, and a deoiled lecithin (Sternpur E) was from Stern. The phospholipid compositions of the various lecithins are given in Table 1.

*To whom correspondence should be addressed at CIRAD–AMIS, TA 40/16, 73 rue Jean François Breton, 34398 Montpellier Cedex 5, France. E-mail: villeneuve@cirad.fr

Copyright © 2003 by AOCS Press

TABLE 1
Composition of the Phospholipid (PL) Fraction (molar %) of the Different Lecithins Tested

Molar % of PL	Vamothin S	Sterncithin F10	Topcithin 50	Nathin 5KE	Nathin 3KE	Nathin 140	Sternpur E
PC	28.8	28.0	28.0	16.9	12.5	74.6	32.9
PE	30.1	29.4	30.7	44.6	32.8	17.4	32.8
PI	26.0	25.6	26.6	16.8	28.1	3.1	20.0
PA	13.7	14.1	13.3	13.9	21.9	3.2	7.1
Other PL	1.3	2.5	1.3	7.7	4.7	1.6	7.1

[a]PA, phosphatidic acid. Vamothin S, Nathin 5KE, Nathin 3KE, and Nathin 140 were from Vamo-Fuji (Osaka, Japan); Sterncithin F10 and Sternpur E were from Stern (Hamburg, Germany); and Topcithin 50 was from Lucas-Meyer (Atlanta, GA).

Methods. (i) Accelerated oxidation test. A Rancimat apparatus (Rancimat 679, Metrohm) was used according to AOCS Method Cd 12b-92 (17) to determine the induction time of the tested oils and fats in the presence or absence of added lecithin samples and without the addition of any other antioxidants. The temperature was set at 110°C, the air flow was 20 L/h, and the fat or oil sample was 3 g.

(ii) Accelerated resistance test (Schaal oven test). Samples were placed in open vials and stored in a thermostated oven (Memmert, Paris, France) at 40°C (±2°C) for 2 to 5 wk. The oxidation status of the different samples was followed by PV measurements according to AOCS method Cd 23-93 (17). Results are given as meq of active oxygen/kg of fat.

The different antioxidant systems were classified according to their antioxidant power (AOP) (18), which corresponds to a value from 0 to 100 obtained from the following equation:

$$AOP = 100 - [(PV_a - PV_{a0})/(PV - PV_0) \times 100] \quad [1]$$

where PV_a = PV of a sample with added antioxidant at the time of measurement, PV_{a0} = PV of a sample with added antioxidant at time 0, PV = PV of a sample without antioxidant at the time of measurement, and PV_0 = PV of a sample without antioxidant at time 0. From this calculation, very efficient antioxidants have an AOP value close to 100, whereas weak ones have an AOP close to 0.

(iii) FA composition. FAME were obtained by AOCS method Ce 2-66 (17) and analyzed by GLC (Thermo Finnigan, Trace 200) using a BP 20 column (SGE, Courtaboeuf, France) with the following characteristics: length, 30 m; i.d., 0.22 mm; film thickness, 0.25 µm. FAME were injected directly into the gas chromatograph with heptadecanoic acid as internal standard. The carrier gas was hydrogen at a flow rate of 0.5 mL/min and a split ratio of 1:50. The injector temperature was 260°C, and the detector temperature was 260°C. The temperature settings were as follows: 10 min at 200°C, then 200–230°C at 5°C/min.

(iv) Tocopherol and tocotrienol content. The tocopherol and tocotrienol contents were determined according to AOCS Method Ce 8-89 (17) using a Kromasil 250 × 4.6 mm silica HPLC column (Kromasil Polymer Lab., Marseille, France) and detection by fluorescence spectrometry. Samples were dissolved in *n*-hexane. Concentrations of α-, γ-, and δ-tocopherols were determined with external standards.

Influence of the type of tocopherol and lecithin synergism. Experiments were carried out with refined lard containing no traces of tocopherols. The material was divided into six samples as follows: Sample 1: no addition of tocopherols or lecithins; Sample 2: addition of standard soy lecithins (1% w/w); Sample 3: addition of α-tocopherols (1000 ppm) + standard soy lecithins (1% w/w); Sample 4: addition of γ- and δ-tocopherol mixture (1000 ppm) + standard soy lecithins (1% w/w); Sample 5: addition of α-tocopherols (1000 ppm); Sample 6: addition of a γ- and δ-tocopherol mixture (1000 ppm). Each of these samples was placed in an open vial and stored at 40°C for 16 d. The PV was monitored regularly according to AOCS method Cd 23–93 (17).

(vi) Influence of the FA composition. Pure methyl ester samples of oleic, linoleic, or linolenic acid were stored in the presence of 1% (w/w) lecithin and/or α- or γ-/δ-tocopherols (1000 ppm) in open vials at 40°C. The oxidation kinetics of the different samples were followed by PV measurements according to AOCS method Cd 23–93 (17).

All assays of the accelerated oxidation test, the accelerated resistance test, and the evaluations of composition and tocopherol content were run in triplicate with less than 5% SD. Data presented in the tables correspond to the average values of three determinations. Study designs are presented in the Results and Discussion section.

RESULTS AND DISCUSSION

Antioxidant efficiency of standard soy lecithins, enriched (deoiled) soy lecithins, and fractionated lecithins. The antioxidant effects of various standard lecithins were first evaluated on refined rapeseed oil using the Rancimat test or the Schaal oven test (40°C) with PV measurements. The phospholipid compositions of these lecithins are given in Table 1. For these preliminary trials, each sample of standard lecithins was added to the oil at a level of 1% w/w with mechanical stirring at 35°C. Considering that standard oil lecithins have an acetone-insoluble fraction close to 60% and that their antioxidant effect is attributed to phospholipids, it was of interest to evaluate the AOP of enriched lecithins in which the acetone-insoluble fraction was increased. Finally, we tested fractionated lecithins, which exhibited specific types of phospholipids, depending on the fractionation process (Table 1). As in the preliminary tests carried out with standard lecithins, the enriched and fractionated

TABLE 2
Rancimat Induction Time (110°C) and PV Measurement (meq O_2/kg) During Storage in Open Vials at 40°C of Refined Rapeseed Oil (RRO) Supplemented with 1% (w/w) of the Different Lecithins Tested[a]

	Rancimat induction time (h)	PV (meq O_2/kg)					
		0 d	4 d	8 d	14 d	25 d	35 d
RRO	8.4	0.9	1.0	0.9	1.5	8.6	18.4
RRO + Vamothin S	13.5	0.9	1.1	1.3	1.5	2.6	3.8
RRO + Sterncithin F10	12.8	0.9	1.1	1.4	1.4	2.4	3.6
RRO + Topcithin 50	13.1	0.9	1.2	1.2	1.3	2.1	3.2
RRO + Nathin 5KE	13.1	1.1	1.3	1.6	4.0	4.3	10.0
RRO + Nathin 3KE	12.4	1.0	1.3	1.4	5.1	9.0	14.0
RRO + Nathin 140	14.1	1.1	1.4	1.3	1.8	1.9	3.1
RRO + Sternpur E	12.2	1.0	1.2	1.2	2.2	2.9	4.4

[a]See Table 1 for a list of suppliers of lecithins.

lecithins were also tested with rapeseed oil at a 1% w/w ratio using the same experimental procedure. All experiments were carried out in triplicate; the overall results given in Table 2 are averages of three determinations.

The oxidative resistance of rapeseed oil, as measured by PV, increased significantly with a 1% w/w addition of each of the lecithins. The refined rapeseed oil alone had a PV of 18.4 meq O_2/kg after 35 d. Comparatively, this value did not exceed 4 meq O_2/kg after the same time period when 1% w/w of lecithins was added to the oil. The three standard lecithins from the three different suppliers had very similar antioxidant activities. Concerning enriched or fractionated lecithins, the best results were obtained with Nathin 140 and Sternpur E, which contained 74.6 and 32.9%, respectively, of PC in the phospholipid fraction. Their antioxidant effect was very close to that of the standard oil lecithins. In contrast, lecithins presenting a lower amount of PC, namely, Nathin 3KE (12.5% of PC in the phospholipid fraction) and Nathin 5KE (16.9% of PC), showed a weaker antioxidant effect, which did not lead to satisfactory antioxidant protection of the oil after 35 d. In that case, PV were 10.0 and 14.0 meq O_2/kg, respectively, whereas the PV was 18.4 meq O_2/kg in the control experiment. Therefore, it seemed that the amount of PC was very important for the antioxidant effect and that the more of this specific phospholipid was present, the better was the antioxidant activity. In parallel, an insufficient quantity of PC would result in a insufficient protection of the refined rapeseed oil, as was the case for Nathin 5KE or Nathin 3KE.

Selection of treatment level. The experiments described above showed that standard, enriched, and fractionated lecithins had comparable antioxidant effects except for those with a low PC content in the phospholipid fraction. Considering that standard lecithins are much cheaper on the market, we decided to continue the study with only the latter lecithins, since they are the most economically attractive for a potential industrial application of these results. We then studied the relationship between the amount of added lecithins in the oil and the importance of the antioxidant effect. Vamothin S lecithin was used in these trials, from 1 to 5% w/w addition to rapeseed oil, and oxidation was monitored by PV while oxidative resistance was checked by the Rancimat method (Table 3). The results clearly showed that the antioxidant effect was better with increased addition of lecithins in the oil. This observation was clearly demonstrated with the Rancimat method, in which rapeseed oil alone had an 8.4-h induction time, and any addition of lecithins increased this value. The maximum was obtained with a 5% w/w addition, which resulted in an induction time of about 37.6 h. This conclusion was less evident with PV. Although the addition of lecithins resulted in a greater resistance to oxidation, the difference between a 1 and 5% w/w addition

TABLE 3
Rancimat Induction Time (110°C) and PV Measurement (meq O_2/kg) During Storage in Open Vials at 40°C of RRO Supplemented with Variable Amounts of Standard Soy Lecithins Tested[a]

	Rancimat induction time (h)	PV (meq O_2/kg)					
		0 d	4 d	8 d	14 d	25 d	35 d
Rapeseed oil	8.4	0.9	1.0	0.9	1.5	8.6	18.4
Rapeseed oil + 1% lecithin	15.2	0.9	1.1	1.3	1.5	2.6	3.8
Rapeseed oil + 1.5% lecithin	19.2	0.9	1.0	1.4	1.5	2.3	3.5
Rapeseed oil + 2% lecithin	21.6	0.9	0.9	1.2	1.4	2.1	3.0
Rapeseed oil + 5% lecithin	37.6	0.9	0.9	1.0	1.3	1.8	2.0

[a]For abbreviation see Table 2.

TABLE 4
FA Composition and Tocopherol Contents of the Different Oils Tested[a]

	FA composition (molar %)								Total tocopherols (ppm)	
Oil	16:0	18:0	18:1	18:2	18:3	20:5	22:6	Others	Tocopherols	Tocotrienols
Rapeseed	5.1	1.7	57.2	23.3	8.6	<DL	<DL	3.5	637	<DL
Soy	11.0	4.0	23.0	54.0	8.0	<DL	<DL	2.0	1106	<DL
Sunflower	6.0	4.0	21.0	67.0	<DL	<DL	<DL	2.0	656	<DL
Oleic sunflower	3.6	3.6	80.2	10.6	0.1	<DL	<DL	2.6	679	<DL
Lard	27.0	13.0	45.0	8.0	1.0	<DL	<DL	7.0	200	<DL
Palm	44.0	4.0	39.0	10.0	<DL	<DL	<DL	3.0	136	367
Fish	12.8	1.3	16.9	1.0	0.8	0.7	6.1	54.1(*)	<DL	<DL
Walnut	7.5	2.5	16.0	60.2	13.0	<DL	<DL	1.0	502	<DL

[a]DL, detection limit. (*) Includes 14:0 (6.4%), 16:1 (8.3%), 20:1 (12.7%), and 22:1 (16.6%).

was not as pronounced as with the Rancimat apparatus. From a practical point of view, however, it was difficult to obtain a homogeneous dispersion of lecithins in the oil when higher amounts were used. Therefore, considering that a 1% w/w addition of lecithins to the oil resulted in very satisfactory protection, we decided to continue our study with this amount.

From this point in the study, we concluded that the antioxidant properties of lecithins certainly could be attributed to an antiradical effect owing to the amino-alcohol groups present in some phospholipids. Moreover, as described in the literature, we suspected some synergism with the tocopherols naturally present in the rapeseed oil. It is worth noting that other mechanisms, such as metal-chelating properties, cannot be considered in such a case since the refined oil we used contained only very low traces of iron (<0.1 ppm) and copper (<0.05 ppm).

Antioxidant effect of standard oil lecithins on various oils and fats with or without tocopherols. We decided to extend our study to various oils that differed in their FA and tocopherol compositions. These oils were rapeseed, soy, sunflower, oleic sunflower, palm, walnut, and fish oils and lard (supplemented with 200 ppm of a mixture of γ- and δ-tocopherols). FA compositions as well as their tocopherol and tocotrienol contents and distributions are given in Tables 4 and 5. The same methodology as the one used previously was applied to evaluate the protective effect of standard soy lecithins against oxidative degradation. The results showed that, with the exception of sunflower oil, a 1% w/w addition of lecithins delayed the oxidation of all oils (Table 6). An AOP greater than 80 was observed after 35 d for standard oil lecithins added to rapeseed, walnut, and supplemented lard. For the same reaction time, the AOP was between 60 and 70 for oleic sunflower, soy, palm, and fish oils. In contrast, we observed that the oxidative stability of classical (linoleic) sunflower oil was not improved with the addition of lecithins. These results were also confirmed with the Rancimat test, which showed an increase in the induction time for every oil except sunflower oil.

These differences in the antioxidant effect of lecithins appeared to depend on the oil type and may have been due to the type of tocopherols present or the FA composition of the oil. Indeed, among the oils tested, sunflower oil contained mostly α-tocopherols. Therefore, it could be envisaged that the synergistic effect of lecithins with tocopherols occurred with only the γ- and δ- forms of tocopherols or tocotrienols that are naturally found in rapeseed, soy, palm, and walnut oils or that were artificially added to the lard used for this study (Table 5). However, a significant protective effect of lecithins was also observed with oleic sunflower oil, which also contains mostly α-tocopherols. Therefore, it seemed that the type of tocopherol present was not the only parameter influencing the synergism between tocopherols and lecithins but that the FA composition was also of paramount importance. Concerning sunflower oil, its high content of PUFA, and especially linoleic acid, was probably also a key parameter explaining the lack of an antioxidant effect of the lecithins. Finally, it is worth noting that since the protective effect of lecithins was also observed in fish oils, which naturally contain only traces of tocopherols, it is quite

TABLE 5
Relative Distribution of Tocopherols and Tocotrienols in the Different Oils Tested[a]

	Tocopherols (%)				Tocotrienols (%)			
Oil	α	β	γ	δ	α	β	γ	δ
Rapeseed	45.3	<DL	32.9	1.7	<DL	<DL	<DL	<DL
Soy	13.1	1.8	61.9	23.3	<DL	<DL	<DL	<DL
Sunflower	95.2	3.5	1.2	<DL	<DL	<DL	<DL	<DL
H.O. sunflower	94.6	2.8	0.7	<DL	<DL	<DL	<DL	<DL
Lard	<DL	<DL	51.7	48.3	<DL	<DL	<DL	<DL
Palm	92.6	<DL	7.4	<DL	40.9	<DL	49.3	9.8
Walnut	13.9	1.0	76.4	8.6	<DL	<DL	<DL	<DL

[a]H.O. sunflower, high-oleic sunflower; for other abbreviation see Table 4.

TABLE 6
Rancimat Induction Time (110°C) and PV Measurement (meq O_2/kg) During Storage in Open Vials at 40°C of Various Refined Oils Supplemented with 1% (w/w) of Standard Soy Lecithins

	Rancimat induction	PV (meq O_2/kg)				AOP[a]
	time (h)	0 d	9 d	29 d	35 d	(35 d)
Rapeseed oil	8.0	0.9	1.9	12.2	15.1	
Rapeseed oil + lecithin	14.0	0.9	1.2	2.5	3.3	83
Soy oil	7.0	1.2	1.8	8.0	13.0	
Soy oil + lecithin	12.0	1.8	2.4	3.3	5.5	69
Sunflower oil	5.0	1.2	4.0	19.0	23.2	
Sunflower oil + lecithin	6.0	1.2	2.4	18.0	22.4	5
Oleic sunflower oil	11.9	3.4	7.7	16.6	19.5	
Oleic sunflower oil + lecithin	22	3.3	5.9	7.7	8.7	60
Walnut oil	4.0	6.1	7.0	13.1	18.6	
Walnut oil + lecithin	7.1	5.8	6.3	7.1	7.8	84
Lard	13.0	0.4	1.3	6.4	7.6	
Lard + lecithin	32.0	0.6	0.7	1.1	1.2	92
Fish oil	1.0	2.8	17.8	21.0	24.0	
Fish oil + lecithin	2.5	2.9	5.9	8.7	9.4	70
Palm oil	24.0	0.7	0.9	1.8	3.3	
Palm oil + lecithin	43.0	0.7	1.0	1.1	1.5	69

[a]AOP, antioxidant power.

probable that the antioxidant properties of lecithins were due not only to their synergism with tocopherols but also to an antiradical effect that may also have occurred.

Validation of the antioxidant mechanism of lecithins in model systems. (i) Influence of the type of tocopherols. To verify the hypothesis of a synergistic effect between lecithins and tocopherols, refined lard containing no traces of tocopherols was used. The material was divided into six samples that were treated with various additions of different tocopherols and/or lecithins (see the Materials and Methods section). These samples were submitted to an accelerated resistance test for 16 d at 40°C, and the PV was monitored regularly (Table 7). We observed from these experiments that the addition of α-tocopherol alone did not result in an increased resistance of lard to oxidation. In fact, it seemed that α-tocopherol in such an amount (1000 ppm) had pro-oxidant activity. γ- and δ-Tocopherols did exhibit an antioxidant effect comparable to the one observed with the addition of 1% w/w standard soy lecithin alone. No synergistic effect was observed between α-tocopherol and lecithin, whereas a strong effect was evident when γ- and δ-tocopherols were mixed with the lecithin. In this case, the best AOP, a value close to 70, was obtained after 16 d. This synergistic effect can be explained by the role of the hydroxy amine functions of phosphatidylamino alcohols (PC and PE), which, as hydrogen providers, are able to regenerate active tocopherols. These phospholipids represent about 58% of the total phospholipid composition in the standard soy lecithin tested (Vamothin S).

(ii) Influence of the FA nature of FA composition. We decided to verify our hypothesis that, in the absence of δ- and γ-tocopherols, the lecithin could delay the oxidation of monounsaturated acids (as was observed for high-oleic sunflower oil) but not of PUFA (as found in linoleic sunflower oil). We stored pure methyl esters of oleic, linoleic, or linolenic acid in open vials at 40°C and followed their oxidation kinetics (PV measurements) in the presence of 1% w/w lecithin and/or α- or γ-/δ-tocopherols (Table 8). The addition of α- or δ-tocopherol resulted in slower oxidation kinetics for all methyl esters. Especially for linoleate and linolenate, these results confirmed the greater antioxidant efficiency of the γ-/δ- tocopherol mixture compared to α-tocopherol. For methyl oleate, such a statement was difficult to confirm since, in the presence of any kind of antioxidant tested (α-tocopherol, or γ-/δ- tocopherols, or lecithins), autooxidation of the monounsaturated methyl ester

TABLE 7
PV Measurement (meq O_2/kg) During Storage in Open Vials at 40°C of Refined Lard Supplemented with 1% (w/w) of Standard Lecithins and/or Tocopherols (1000 ppm)

	PV (meq O_2/kg)					AOP[a]
	0 d	2 d	6 d	12 d	16 d	(16 d)
Lard	5.4	8.0	11.8	18.6	30.0	
Lard + α-tocophenol (1000 ppm)	4.5	8.8	17.8	30.0	38.1	<0
Lard + γ-/δ-tocophenol (1000 ppm)	7.1	7.0	10.2	16.4	21.0	44
Lard + lecithin (1%)	5.5	5.0	8.6	12.6	19.0	45
Lard + α-tocophenol (1000 ppm) + lecithin (1%)	4.6	5.9	13.4	23.2	26.1	13
Lard + γ-/δ-tocophenol (1000 ppm) + lecithin (1%)	4.3	4.8	8.3	10.2	11.8	70

[a]For abbreviation see Table 6.

TABLE 8
PV Measurement (meq O_2/kg) During Storage in Open Vials at 40°C of Methyl Oleate, Methyl Linoleate, and Methyl Linolenate Supplemented with 1% (w/w) of Standard Lecithins and/or Tocopherols[a] (1000 ppm)

	PV (meq O_2/kg)					AOP
	0 d	3 d	7 d	14 d	21 d	(21 d)
Methyl oleate	1.8	1.9	3.9	29	83	
Methyl oleate + lecithin	1.7	3.3	5.4	7.4	8.7	91
Methyl oleate + α-tocophenol	1.9	1.4	2.7	2.2	2.9	99
Methyl oleate + γ-/δ-tocophenol	1.8	1.8	2.8	2.7	3.9	97
Methyl oleate + α-tocophenol + lecithin	1.7	1.8	3.3	3.6	4.9	96
Methyl oleate + γ-/δ-tocophenol + lecithin	1.7	2.4	3.6	5.1	6.4	94
Methyl linoleate	19.5	115.0	213.0	403.0	654.0	
Methyl linoleate + lecithin	17.7	35.0	33.0	110.0	338.0	50
Methyl linoleate + α-tocophenol	17.9	52.1	79.2	114.4	177.1	75
Methyl linoleate + γ-/δ-tocophenol	17.7	23.8	26.0	33.5	49.3	95
Methyl linoleate + α-tocophenol + lecithin	17.0	27.3	35.6	54.6	96.6	88
Methyl linoleate + γ-/δ-tocophenol + lecithin	17.6	18.7	19.5	24.0	33.0	98
Methyl linolenate	5.3	108.1	331.2	ND	722.5	
Methyl linolenate + lecithin	5.1	64.2	180.0	ND	424.8	42
Methyl linolenate + α-tocophenol	5.1	62.2	171.7	ND	298.8	59
Methyl linolenate + γ-/δ-tocophenol	4.4	37.0	122.4	ND	256.7	65
Methyl linolenate + α-tocophenol + lecithin	5.2	44.9	115.7	ND	213.0	71
Methyl linolenate + γ-/δ-tocophenol + lecithin	4.1	21.3	73.4	ND	156.9	79

[a]ND, not detected; for other abbreviation see Table 6.

sample was drastically reduced. Under such conditions, the oxidation kinetics were too slow to classify the antioxidant efficiency of γ-/δ-tocopherols vs. α-tocopherols. Consequently, the addition of 1% w/w lecithin by itself did not significantly improve the antioxidant effect of tocopherols (either α- or γ-/δ-) on methyl oleate. Concerning PUFA methyl esters, the AOP of γ-tocopherols for linoleate and linolenate esters were 96 and 65, respectively, after 21 d, whereas the AOP were 75 and 59 for α-tocopherols. Moreover, with such fatty esters, we observed that the addition of lecithin contributed to an improved efficiency of the tocopherols, especially γ-/δ-tocopherols. This model confirms our initial observations regarding linoleic or linolenic oils rich in γ- or δ-tocopherols such as rapeseed, soy, and walnut.

This study shows the potential of using standard lecithins to protect refined oils against oxidation. We showed that the antioxidant capacity of lecithin was influenced by the FA composition of the oil as well as the nature of its native tocopherols. We estimated that the main antioxidant mechanism of lecithin was due to a synergistic effect between amino-alcohol phospholipids and γ-/δ-tocopherols. The use of fractionated or enriched lecithins was not clearly advantageous compared to standard oil lecithins. Concerning rapeseed oil, it was shown that the addition of lecithins (1% w/w) allowed a doubling of its Rancimat induction time or a lowering of its PV by a factor 4 or 5 after 35 d at 40°C. For other linolenic oils such as soy or walnut, the addition of lecithins was also advantageous. In contrast, polyunsaturated oils rich in α-tocopherols were not sufficiently protected by lecithins.

ACKNOWLEDGMENTS

We would like to thank Laurence Lefébure, Danielle Mouginé, Loïc Lambert (Danone Vitapole), and Virginie Galan (ITERG) for their active participation and technical assistance.

REFERENCES

1. Zambiazi, R.C., and R. Przybylski, Effect of Endogenous Minor Components on the Oxidative Stability of Vegetable Oils, *Lipid Technol. 10*:58–62 (1998).
2. Pokorny, J., J. Davidek, M. Vierecklova, M. Ranny, and J. Sedlacek, Effect of Phosphorylated Acylglycerols on the Oxidative Stability of Oils, *Nahrung 34*:719–725 (1990).
3. Nasner, A., Antioxidizing Properties of Lecithin, in *Lipid Oxidation*: *Proceedings of Symposium LipidForum,* edited by R. Marcuse, Goteborg, Sweden, 1985, pp. 187–197.
4. Frankel, E.N., *Lipid Oxidation*, The Oily Press, Dundee, Scotland, 1998, pp. 56–57.
5. Hamilton, R.J., C. Kalu, G.P. McNeill, F.B. Padley, and J.H. Pierce, Effects of Tocopherols, Ascorbyl Palmitate, and Lecithin on Autoxidation of Fish Oil, *J. Am. Oil Chem. Soc. 75*:813–822 (1998).
6. King, M.F., L.C. Boyd, and B.W. Sheldon, Effects of Phospholipids on Lipid Peroxidation of a Salmon Oil Model System, *Ibid. 69*:237–242 (1992).
7. King, M.F., L.C. Boyd, and B.W. Sheldon, Antioxidant Properties of Individual Phospholipids in a Salmon Oil Model System, *Ibid 69*:545–551 (1992).
8. Ishikawa, Y., K. Sugiyama, and K. Nakabayashi, Stabilization of Tocopherols by Three Components. Synergism Involving Tocopherols, Phospholipids, and Amino Compounds, *Ibid. 61*: 950–954 (1984).
9. Hudson, B.J.F., and M. Ghavami, Phospholipids as Antioxidant Synergists for Tocopherols in the Autoxidation of Edible Oils, *Lebensm. Wiss. Technol. 17*:191–194 (1984).
10. Ohshima, T., Y. Fujita, and C. Koizumi, Oxidative Stability of Sardine and Mackerel Lipids with Reference to Synergism Between Phospholipids and a Tocopherol, *J. Am. Oil Chem. Soc. 70*:269–275 (1993).
11. Saito H., and K. Ishihara, Antioxidant Activity and Active Sites of Phospholipids as Antioxidants, *Ibid. 74*:1531–1536 (1997).
12. Pokorny, J., H. Poskocilova, and J. Davidek, Effect of Phospholipids on the Decomposition of Lipid Hydroperoxides, *Nahrung 25*:29–31 (1981).
13. Kashima, M., G.S. Cha, Y. Isoda, J. Hirano, and T. Miyazawa,

The Antioxidant Effects of Phospholipids on Perilla Oil, *J. Am. Oil Chem. Soc. 74*:1531–1536 (1997).
14. Nwosu, C.V., L.C. Boyd, and B. Sheldon, Effect of Fatty Acid Composition of Phospholipids on their Antioxidant Properties and Activity Index. *Ibid. 74*:293–297 (1997).
15. Chen, Z.Y., and W.W. Nawar, Prooxidative and Antioxidative Effects of Phospholipids on Milk Fat, *J. Am. Oil Chem. Soc. 68*: 938–940 (1991).
16. Rossignol-Castéra, A., and F. Bosque, Nouvelle Approche des Antioxydants, *Oleagineux Corps Gras Lipides 1*:10–15 (1994).
17. *Official Methods and Recommended Practices of the American Oil Chemists' Society,* 4th edn., edited by D. Firestone, American Oil Chemists' Society, Champaign, 1989, Methods Cd 23-93, Ce 2-66, and Ce 8-89.
18. Sugino, H., M. Ishikawa, T. Nitoda, M. Koketsu, L.R. Juneja, M. Kim, and T. Yamamoto, Antioxidative Activity of Egg Yolk Phospholipids, *J. Agric. Food Chem. 45*:551–554 (1997).

[Received October 14, 2002; accepted September 9, 2003]