Effect of Heat Treatments on Canola Press Oils. II. Oxidative Stability

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Oxidative stability of the canola press oils increased with increasing heat treatment to the seed, and decreased on refining. The tocopherol content of the press oils was relatively uniform and could not account for the observed variations in oxidative stability. The variation in stability corresponded to variations in the content of other non-triglyceride components. In general, the greater the initial quality of the oils, *i.e.*, the lower the content of non-triglyceride material, the lower their oxidative stability. Oxidative stability was found to be significantly correlated to phosphorus content (R^2>0.99). This could be explained by synergism between tocopherols and phospholipids, in the range from 0.025% to 0.22% phospholipid. Above this level increasing the phosholipid content did not significantly improve the oxidative stability. After oxidation the oils were "bleached", *i.e.*, there was a loss of color bodies. This loss was related to both the original content of color bodies in the oil and the degree of oxidation of the oil.

KEY WORDS: Canola, heat treatment, oxidative stability, phospholipids, press oils, refining, tocopherols.

The degree of heat treatment and refining that the seed receives before, during and after pressing affects the content of non-triglyceride components in the press oil (1). The content of tocopherols is relatively uniform, but there are considerable increases in phosphorus content as the degree of heat treatment to the seed is increased. These nontriglyceride components are removed during refining. Crude oils have good oxidative stability while refined oils are less stable and are subject to deterioration (2). Kwon *et al.* (3) found that oxidative stability of soybean oil decreased with increasing degree of refining—soybean triglyceride was the least stable and crude soybean oil was the most stable. Adding back phospholipids and tocopherols to the refined oil improved the stability. Hildebrand *et al.* (4) also found that phospholipids and tocopherols increased soybean oil stability.

Vegetable oil is frequently stored for some time after extraction and before use. The stability of the press oils obtained with varying pretreatments described in the first part of this research (1), and the effects of the increase in non-triglyceride components with degree of heat treatment on the oxidative stability are thus of interest.

EXPERIMENTAL PROCEDURES

Canola press oils, previously prepared from Westar seed after a variety of seed pretreatments and with differing degrees of refining, were used (1). A commercial canola oil (crude, non-degummed) was obtained from CSP Foods (Nipawin, Saskatchewan, Canada). It was a blend of prepress and solvent-extracted oils, predominantly from Westar. Non-triglyceride components were analyzed as given previously (1). Sample characteristics are given in Table 1.

Oxidation of oils. Oxidation experiments were carried out on 100 g oil at 60°C in an air-oven (Model 18, Precision Scientific Corporation, Chicago, IL) in the dark. This was a modification of the Schaal Oven Test (5). Oils were oxidized in 250-mL Erlenmeyer flasks with rubber stoppers. Samples were taken at regular intervals over a period of 0–500 hr. The samples were stored in 3.5-mL screw-capped vials at −20°C. Peroxide values (PV) of the sample taken during oxidation were determined spectrophotometrically at 350 nm according to the micromethod of Swoboda and Lea (6). The PV at 300 hr was taken as a measure of the oxidative stability of the oils.

Oil analysis after oxidation. After completion of oxidation, chlorophyll and color values of the remaining oil were determined as before.

RESULTS

Effect of treatment on oxidative stability. The oxidative stability increased with increasing pretreatment and with increase in barrel temperature during pressing, and decreased progressively as the oil was refined. The effect of seed treatment prior to pressing on the degree of oxidation occurring in main-run oils is shown in Figure 1. The peroxide value (PV) after 300 hr, *i.e.*, the final PV, decreased with increasing heat treatment given to the seeds: The cold press oil (oil 2) had the highest final PV and the flaked-seed oil (oil 6) the lowest final PV. The effect of barrel temperature during pressing on degree of oxidation occurring in the oils is shown in Figure 2. Oils 1 and 4, expelled at lower barrel temperatures, had higher final PV than oils 2 and 5. Both the oils expelled from cold seed had a higher final PV compared to the oils expelled from heated seed. The effect of degumming and bleaching treatments given to the press oil on degree of oxidation occurring in the oils is shown in Figure 3. Final PV of the oils increased in the order crude < degummed < bleached (oils 5, 7 and 8, respectively).

Effect of non-triglyceride components on oxidative stability. There was no direct linear relationship between PV at 300 hr and total tocopherol content of the nine oils; instead the oils showed three groupings (Fig. 4). Bleached oil (oil 8) was in a low tocopherol, high PV group; cold press oil (oil 1) to 100°C-heated seed oil (oil 4) and degummed oil (oil 7) were in an intermediate group; and the rest, 100°C-heated oil (oil 5), flaked seed oil (oil 6) and the commercial oil (oil 9), were in a high tocopherol, low PV group.

The non-triglyceride component most closely related to oxidative stability was phosphorus (Fig. 5). There was a direct relationship between PV at 300 hr and phosphorus

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TABLE 1

Sample Characteristics

Source	Treatment			Total tocopherols[b] (mg/100 g)	Phosphorus[c] (ppm)	Oil
	Pre	BT(°C)[a]	Post			
Seed	none	80-90	none	57.4	12.6	1
Seed	none	90-100	none	58.4	16.2	2
Seed	80°C	105-110	none	52.1	22.1	3
Seed	100°C	<105	none	47.2	41.7	4
Seed	100°C	105-127	none	64.2	89.2	5
Flakes	100°C	124-127	none	59.3	82.5	6
Oil 5			degummed	51.6	19.3	7
Oil 5			degummed, refined bleached	30.8	4.3	8
Commercial oil			none	66.4	176.7	9

[a]BT, barrel temperature.

[b]CV = 2.0-2.7%.

[c]CV = 6.6%.

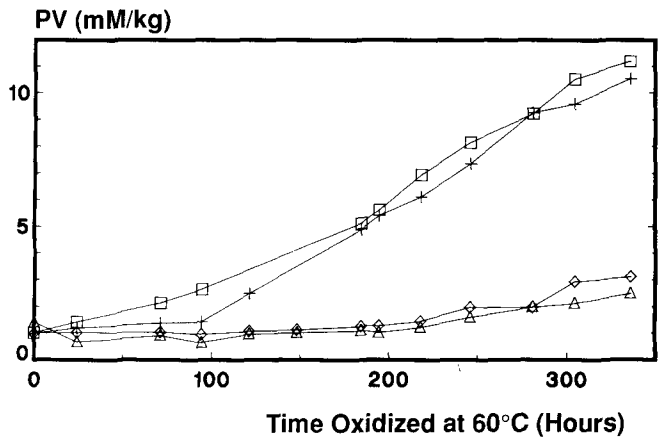

FIG. 1. Effect of seed treatment on oxidative stability of press oils: Oil 2 (□), oil 3 (+), oil 5 (◇) and oil 6 (△). Peroxide value ± 0.6%.

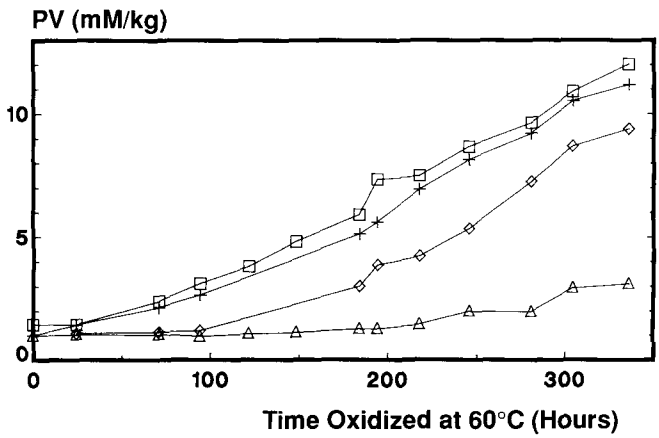

FIG. 2. Effect of increase in barrel temperature during pressing on oxidative stability of press oils: Oil 1 (□), oil 2 (+), oil 4 (◇) and oil 5 (△). Peroxide value ± 0.6%.

content of the oils. For oils 1 to 5 this relationship had an R^2 of 0.997. The commercial oil (oil 9), which had a substantially higher phosphorus content compared to the laboratory-prepared oils, did not have a significantly improved oxidative stability. (Phosphorus content corresponds to phospholipid content, *e.g.*, phosphorus × *ca.* 25 = phospholipid).

The degummed oil (oil 7) had a lower final PV, and the bleached oil (oil 8) had a higher final PV than indicated by their phosphorus contents, as compared to the crude oils. The degummed oil was more stable than could be predicted from either phospholipid or tocopherol contents.

Effect of oxidation on press oils. During oxidation the press oils were significantly reduced in color, *i.e.*, bleached (Table 2). For the pressed crude oils, color value L was greater in the oxidized oils. The magnitude of this increase, *ca.* 5-18 units, was directly related to the PV, *i.e.*, degree of oxidation that had occurred. The bleached oil (oil 8) showed a much smaller increase, 3.3 units, and the L value of the commercial oil (oil 9) decreased by 1 unit. There was no consistent trend in color values a and b. Chlorophyll content was reduced in all samples after oxidation. The magnitude of the loss, *ca.* 26-96% remaining, was related to the final PV, *i.e.*, degree of oxidation that had occurred. Degummed and bleached oils showed a similar trend to the crude oils, but at higher residual chlorophyll percentages.

DISCUSSION

Non-triglyceride components—tocopherols. The oxidative stability of an oil is dependent on its fatty acid composition and its content of non-triglyceride components. The seven press oils had similar fatty acid compositions (*ca.* 59.8% oleic, 19.8% linoleic and 9.0% linolenic acids), and thus the changes in oxidative stability could be attributed to differences in non-triglyceride components. Tocopherols are primary antioxidants and the oxidative stability of vegetable oils has been attributed to their presence (7). However, the press oils in this experiment had a relatively uniform level of tocopherols, which could not

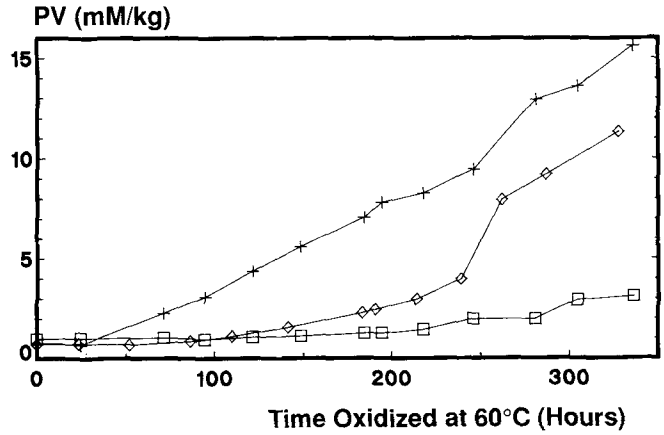

FIG. 3. Effect of oil processing on oxidative stability of press oils: Oil 5 (□), oil 7 (◇) and oil 8 (+). Peroxide value ± 0.6%.

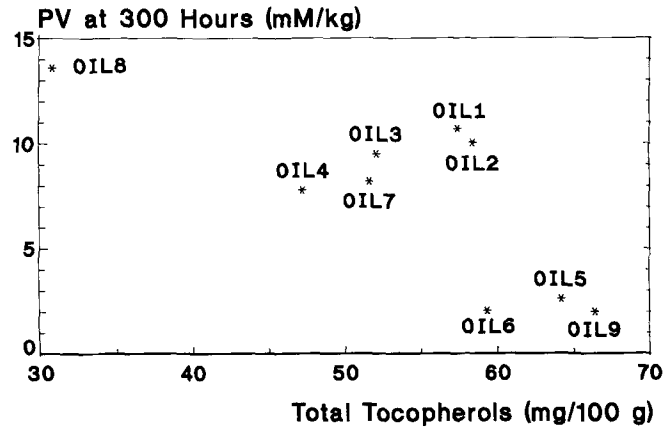

FIG. 4. Effect of total tocopherols content on stability of oils oxidized at 60°C. Tocopherols ± 2.0-2.7%, peroxide value ± 0.6%.

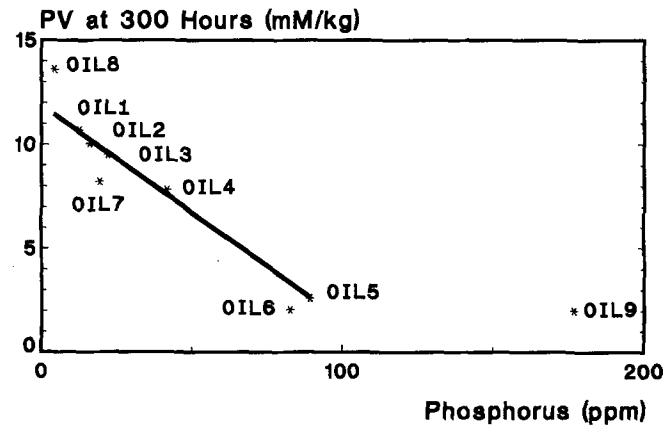

FIG. 5. Effect of phosphorus content on stability of oils oxidized at 60°C. Phosphorus ± 6.6%, peroxide value ± 0.6%. Regression equation: $Y = -0.1034X + 11.89$, $R^2 = 0.997$, N=5.

account for the observed variations in oxidative stability (Fig. 4). As a general rule, tocopherols have their greatest antioxidative effect at ca. 20-50 mg/100 g, the effect diminishes at increasing concentrations and becomes pro-oxidative at *ca.* 150-200 mg/100 g (8), the precise values depend on the particular oil. Vgetable oils naturally have optimum, or near optimum, tocopherol contents and thus supplementation with tocopherols will not significantly improve their oxidative stability. This was confirmed by Kwon *et al.* (3) who found that supplementation of soybean oil containing 60 mg/100 g tocopherols to 120 mg/100 g tocopherols did not significantly improve the stability. The tocopherols content of the present experimental oils was at the upper end of the most effective concentration, *ca.* 50-60 mg/100 g, and it is likely that concentration increases in this range have little effect on oxidative stability. However, the decreased oxidative stability of the bleached oil, which contained *ca.* 30 mg/100 g as compared to *ca.* 60 mg/100 g in the press oils, can be explained, in part, by its lower tocopherol content.

Non-triglyceride components—phospholipids. Phospholipids have been extensively studied as antioxidants because many crude oils are more stable than refined oils (9). However, there has been some confusion in the literature as to the pro-oxidant or antioxidant activity of phospholipids (10). A number of studies (3,4,11,12) have shown that, while having no antioxidant activity *per se*, phospholipids act as potent synergists with primary antioxidants, such as tocopherols. The present experimental results showed that, at *ca.* 60 mg/100 g tocopherol, there was a direct linear relationship between phospholipid content, in the range 0.025-0.22%, and oxidative stability. The maximum effective level was extrapolated to *ca.* 0.27%. The solvent-extracted oil (oil 9), with *ca.* 0.44% phospholipid, did not have a significantly improved oxidative stability, as compared to the oil from heated seed (oil 5), which contained *ca.* 0.22% phospholipid. This agrees well with results obtained by Hudson and Ghavami (12) who found that the synergistic effect of dipalmitoylphosphatidylethanolamine (DPE) was a function of its concentration and that for a given substrate and tocopherol concentration, the induction period increased approximately linearly over the range 0.025-0.25% DPE.

However, the experimental results, in which a considerable degree of synergism was observed at 60°C, do not agree with results obtained by Dziedzic and Hudson (13). They found that synergistic activity of DPE in refined rapeseed oil increased with oxidation temperature in the range 80°C to 140°C and was slightly pro-oxidative at 60°C. Subsequent analysis of thin film oxidation of rapeseed oil at room temperature showed that 0.1% DPE showed very slight synergism. Explanations for the differences in synergism could lie in the composition of the phospholipids and in alterations in the mechanism of autoxidation and antioxidation at elevated temperatures.

Autoxidation and antioxidation are known to proceed by different mechanisms at elevated temperatures (14) and, thus, explanations for antioxidant effects observed at oxidation temperatures greater than 60°C probably cannot be applied to lower temperatures. Dziedzic and Hudson (13) attributed the greater effectiveness of DPE at elevated temperatures to a change in the autoxidation mechanism, the high temperature mechanism permitting

TABLE 2

Color and Chlorophyll Levels in Oil Samples After 14 Days at 60°C, and Change in these Values upon Oxidation[a,b]

Oil	Color			Color change			Chl (ppm)	Chl (% left)	PV (mM/kg)
	L	a	b	L	a	b			
1	54.8	13.8	37.5	+16.7	−0.7	+11.7	1.9	29	12.02
2	52.1	14.5	34.7	+17.8	+4.2	+11.7	2.6	26	11.19
3	34.6	11.2	23.1	+17.7	+10.2	+13.0	16.6	35	10.53
4	31.3	10.1	21.0	+15.4	+8.6	+11.1	24.7	52	9.39
5	20.2	7.3	12.9	+11.7	+3.9	+9.3	48.9	72	3.11
6	19.3	7.1	12.3	+5.4	+5.1	+4.5	52.1	93	2.48
7	21.6	6.2	14.0	—	—	—	52.4	87	11.31
8	43.6	4.2	29.3	+3.3	−4.9	+2.1	8.4	78	15.61
9	29.4	10.6	19.6	−1.0	−1.4	+0.9	24.1	96	2.36
CV	<1	<1	<1	—	—	—	2.5	—	0.6

[a]Abbreviations: Chl, chlorophyll as chlorophyll a; Color, L, a, b, Hunter Lab colorimeter readings; PV, peroxide value; CV, coefficient of variations.

[b]Codes explained in Table 1.

the intervention of the synergist. The mechanism of phospholipid synergism is not known, but both Hildebrand *et al.* (4) and Hudson and Ghavami (12) concluded that it could not be accounted for by trace metal chelation. Hildebrand *et al.* (4) suggested that the amino group of PE and PC and the reducing sugar of PI could facilitate hydrogen, or electron, donation to tocopherols. In this way the phospholipids would extend the effectiveness of the tocopherols, and hence the induction period.

It is possible that the mechanism of phospholipid synergism is different at 60°C than the elevated temperatures used in the other studies. It is also possible that the synergistic activity exhibited by a particular phospholipid class is affected by oxidation temperature. Consequently, particular phospholipids may be more effective at 60°C and below than at higher temperatures. This has considerable implications, as vegetable oils are only held above 60°C for a short time during processing and are stored at much lower temperatures. Several of the authors quoted above have suggested adding phospholipids back to refined oils to improve their oxidative stability, but antioxidant additions based on studies carried out at elevated temperatures, particularly above 60°C, may be ineffective at preventing oxidation during storage.

Phospholipid synergism is also dependent on substrate, *e.g.*, fatty acid composition of the oil, and primary antioxidant content. Both of these must be important considerations in any recommendations concerning addition of phospholipids to oils.

The oil from the flaked seed (oil 6) was more stable than could be explained by either tocopherol or phospholipid contents. This may have been due to its elevated sterol content, 773 mg/100 g as compared to *ca.* 620–690 mg/100 g for the other oils. Sterols have been characterized as antioxidants. Johansson and Appelqvist (15) found that low erucic acid rapeseed oils similar in fatty acid composition and tocopherol content varied in oxidative stability. They attributed this to the sterol content. The increased stability of the degummed oil, as regards to its tocopherol and phospholipid contents, could have been due to reduced initial FFA and PV contents, or reduced contents of prooxidants, such as trace metals, removed during degumming. Relative composition of phospholipid classes could have been altered by degumming to produce a more effective synergist. The decreased stability of the bleached oil was a result of its decreased tocopherol and phospholipid contents.

Effect of oxidation on press oils. The magnitude of bleaching was related to the degree of oxidation undergone by the oil, and to the initial color and chlorophyll content of the oil. Chlorophyll is convertd to colorless derivatives by reaction with peroxy radicals produced during oxidation (16). Chlorophylls and pheophytins are also bleached by heat. Endo *et al.* (17) found that at 30°C chlorophylls were bleached, but at 50°C both chlorophylls and pheophytins were bleached. Therefore, it is likely that some of the chlorophyll loss was caused not by oxidation, but by the temperature used in this study. Although carotenoid contents of the oxidized oils were not determined, the oils were considerably less yellow, and destruction of carotenoids, by co-oxidation, had probably taken place. β-Carotene is easily oxidized to epoxycarotenoids, which are colorless (18). Oxidation products of β-carotene can induce autocatalytic oxidation in oils.

The commercial oil, however, became darker on oxidation. This is probably due to its higher phospholipid content. During heating of oil for extended lengths of time or at elevated temperatures, phospholipids can turn brown and discolor the oil (19).

These results show that differing treatments, to both seed and oil do not only have significant effects on the nontriglyceride components, but also have a considerable influence on the oxidative stability of the resultant oil. In order for a crude oil to have an acceptable oxidative stability it is probably desirable for it to have a certain minimum phospholipid content.

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