Effect of Possible Chlorophyll Breakdown Products on Canola Oil Stability

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Three model compounds, maleimide, dimethylpyrrole, and trimethylpyrrole, were chosen as possible chlorophyll breakdown products (CBP), and their effect on the stability of canola oil was investigated. Stability tests were carried out at 60 °C in a forced air oven. Addition of these compounds to canola oil either individually (0.05–10.0 ppm) or together (0.05–1.0 ppm) resulted in an oil of lower stability. Bleaching with clay (1–5% w/w of the oil) completely removed dimethylpyrrole and trimethylpyrrole, while maleimide was poorly adsorbed. Citric acid and phosphoric acid treatment did not result in an appreciable decrease in the concentration of any of the three compounds. Alkali refining resulted in complete removal of maleimide. Dimethylpyrrole and trimethylpyrrole were present in trace amounts in the bleached oil along with significant amounts of maleimide. The deodorized oil contained only trace levels of dimethylpyrrole. Trace amounts (<5% of the original concentration) of dimethylpyrrole remained in tricapryloylglycerol that had been degummed, refined, bleached, and deodorized.

Keywords: *Alkali refining; bleaching; canola oil; chlorophyll; chlorophyll breakdown products (CBP); degumming; deodorization; oxidative stability; pheophytin; processing*

INTRODUCTION

Chlorophyll breakdown is important, not only from the point of view of our understanding of fundamental biological processes but also in economic and environmental terms (Brown et al., 1991).

The level of pheophytin, a compound that is structurally similar to chlorophyll, is an important criteria in determining the quality of crude Canadian canola oil (Daun, 1982). The stability of canola oil obtained from green seed (seeds containing a high amount of chlorophyll) is under question. Since Coe (1938) reported the correlation between chlorophyll content and oxidative deterioration of oils, many researchers have shown that chlorophyll and some compounds derived from chlorophyll (such as pheophytin and pheophorbide) can act as prooxidants (Endo et al., 1984a,b; Usuki et al., 1984).

To bleach an oil from green seed, the oil processor uses higher amounts of clay to obtain a refined oil containing pheophytin in the parts per billion (ppb) range. Despite this, the stability of the refined oil is under question because of its origin. Tautorus and Low (1993) added known amounts of chlorophyll to canola oil and compared its stability to a control with no added chlorophyll. They observed that canola oil with added chlorophyll was less stable in comparison to the control, after subjection to identical processing steps. The same result was observed when they used pheophytin instead of chlorophyll in a fully saturated triacylglycerol (tricapryloylglycerol). They postulated that products (that are not removed by the oil refining process) resulting from breakdown of chlorophyll/pheophytin were prooxidant in nature. However, they were not able to isolate any compound that could be potentially responsible for decreased stability. If low molecular weight compounds are formed through degradation of chlorophyll/pheophytin, they must survive the processing steps (of degumming, alkali refining, bleaching, and deodorization) to have an effect on the oxidative stability of the oil. It is also possible that prooxidant compounds are formed during the processing of oils high in chlorophyll which reduce final oil stability. The lack of chemically characterized intermediates or products presents a major problem in understanding the role of the chlorophyll breakdown process at a chemical level.

Chlorophyll breakdown reactions have been classified as type I and type II reactions (Brown et al., 1991). Type I reaction include loss of magnesium, loss of phytol, and modification of the side chains of the chlorophyll nucleus but not the degradation of the tetrapyrrole nucleus itself. Type II reactions involve the cleavage of the macrocyclic ring system and subsequent degradation to smaller carbon- and/or nitrogen-containing fragments. For type II reactions, no degradation products are known with certainty to represent the fate of substantial quantities of chlorophyll (Brown et al., 1991). In addition, chlorophyll breakdown products (CBP) have not been isolated or identified.

A different approach was taken in this study in an attempt to understand the type of chlorophyll/pheophytin breakdown products that may cause decreased stability of canola oil. The effect of three model compounds, namely maleimide, dimethylpyrrole, and trimethylpyrrole, on the oxidative stability of canola oil was studied. Compounds such as ethylmethylmaleimide, hematinic acid, and *trans*-dihydrohematinic acid have been identified as products of chromic acid oxidation of chlorophyll *a* (Brown et al., 1991). It is quite possible that chlorophyll/pheophytin breakdown products through type II reactions could lead to the formation of similar low molecular weight compounds. The fate of the three model compounds in tricapryloylglycerol during degumming, alkali refining, bleaching, and deodorization was also studied to determine their fate during processing.

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MATERIALS AND METHODS

Fully processed canola oil was obtained from CanAmera Foods (Altona, MB). Tricapryloylglycerol (95%) was obtained from Sigma Chemical Co. (St. Louis, MO). Maleimide (99%), dimethylpyrrole (98%), and trimethylpyrrole (97%) were obtained from Aldrich Chemical Co. (Milwaukee, WI). Bleaching clay (Filtrol 105) was obtained from Engelhard Corp. (Jackson, MS).

Stability Assessment. Aliquots (0.1 g) of canola oil and canola oil containing various concentrations of maleimide, dimethylpyrrole, and trimethylpyrrole were weighed into a series of 13 × 100 mm disposable glass test tubes and placed in a forced air oven at 60 ± 1 °C in the dark. The extent of autoxidation was estimated by sampling two of the test tubes from each treatment at appropriate time intervals. Samples of oil (0.04 g) were taken from each tube for an eventual dilution of 1 in 2500 in hexane. Absorbance at 234 nm (indicative of conjugated diene content) was measured with a Milton Roy (Rochester, NY) Spectronic Model 1201 spectrophotometer. The presence of the three compounds did not interfere with the absorbance measurements when present at up to 2 ppm in the diluted sample. The maximum concentration of these compounds encountered during spectrometric analysis was 4 ppb in the diluted sample. Analysis of variance was performed using the StatView program (Abacus Concepts, 1992) on data collected at 211 h (leveling off of the curve for one or more of the samples was observed after 211 h). This time period was chosen as the data point included the effects of both the length of the induction period and the rate of buildup of primary oxidation products (Tautorus and Low, 1994).

Processing. Tricapryloylglycerol containing either 50 or 100 ppm each of maleimide, dimethylpyrrole, and trimethylpyrrole was used as the starting material to study the effect of processing. The mixture (typically 10 g) was subject to either degumming, alkali refining, bleaching, or deodorization individually (fresh starting material was taken for each step) and also in sequence (i.e., the degummed oil was taken through alkali refining and then followed by bleaching and deodorization). Samples were taken for the analysis of maleimide, dimethylpyrrole, and trimethylpyrrole by gas chromatography.

All processing steps were carried out in IKAMAG RET-G stirrer/heaters (Rose Scientific Ltd., Edmonton, AB). Degumming was carried out at 40 °C for 15 min by adding 0.2% (v/w of the oil) of citric acid (50% w/v aqueous solution). Deionized water (2% v/w of the oil) was added, and the resulting mixture was further heated at the same temperature for 15 min. The mixture was then centrifuged (4400*g*, 5 min) on a Sorvall Superspeed centrifuge (Newton, CT) followed by removal of the oil layer by pipetting. Phosphoric acid treatment involved heating the oil at 40 °C for 1 h with 0.015% (v/w of the oil) orthophosphoric acid. The resulting mixture was washed with deionized water and the oil phase separated by centrifugation (same as in the citric acid treatment step).

Alkali refining involved treatment of the oil at 40 °C for 15 min with sodium hydroxide (9.5% w/v; sufficient to neutralize 1.1% free fatty acid). The oil phase was separated by centrifugation (4400*g*, 5 min) and washed twice with deionized water (1:1 v/v of the oil, 70 °C).

Bleaching was accomplished by treating the oil with 5% (w/w) bleaching clay. The mixture was heated at 105 ± 1 °C for 30 min under vacuum (20 mmHg). The mixture was cooled to room temperature before the vacuum was released. The treated tricapryloylglycerol was separated from the clay by centrifugation (4400*g* for 15 min). To study only the effect of bleaching on the three compounds, experiments were carried out with 1–5% bleaching clay. Samples were taken for the analysis of maleimide, dimethylpyrrole, and trimethylpyrrole by gas chromatography.

Deodorization was carried out in a laboratory deodorizer as described by Moulton (1989). Tricapryloylglycerol (13 g) containing either 50 or 100 ppm each of maleimide, dimethylpyrrole, and trimethylpyrrole was deodorized at 250 °C for 1 h under 0.3 mmHg vacuum. The oil was cooled to room temperature under vacuum, and samples were analyzed for maleimide, dimethylpyrrole, and trimethylpyrrole by gas chromatography.

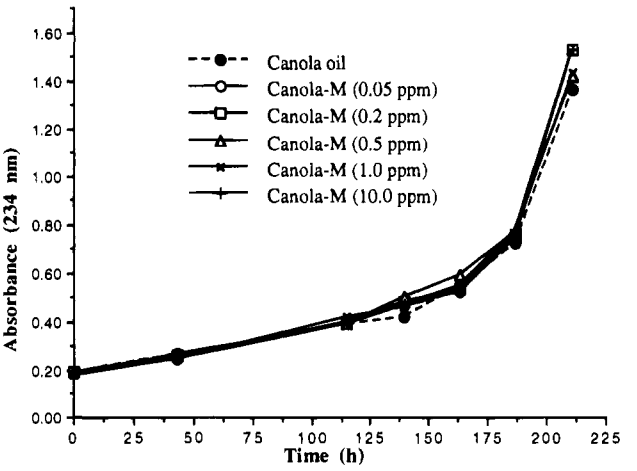

Figure 1. Storage stability at 60 ± 1 °C (measured as absorbance at 234 nm; indicative of conjugated dienes) of canola oil and canola oil containing 0.05, 0.2, 0.5, 1.0, and 10.0 ppm of maleimide (M).

Table 1. Average Absorbance at 234 nm after 211 h of Storage at 60 °C in the Dark of Canola Oil and Canola Oil Containing Various Amounts of Maleimide

sample	absorbance[a] at 234 nm
canola oil (control)	1.359 (0.023)A[b]
canola oil + 0.05 ppm of maleimide	1.526 (0.075)B
canola oil + 0.2 ppm of maleimide	1.528 (0.023)B
canola oil + 0.5 ppm of maleimide	1.460 (0.003)B
canola oil + 1.0 ppm of maleimide	1.468 (0.005)B
canola oil + 10.0 ppm of maleimide	1.532 (0.038)B

[a] Average of duplicates with standard deviation in parentheses. [b] Values within the column sharing the same letter are not significantly different at 5% level.

Gas Chromatography. A Varian Model 3400 gas chromatograph (GC) equipped with a flame ionization detector (FID) from Varian Canada Inc. (Georgetown, ON) was used for the analysis of maleimide, dimethylpyrrole, and trimethylpyrrole in tricapryloylglycerol.

Separation was achieved on an RTX-5 Amine column (15 m × 0.32 mm i.d., 1.0 μm film thickness) from Restek Corp. (Bellefonte, PA) under the following elution conditions: the column was initially held at 80 °C for 2 min, raised to 110 °C at a rate of 5 °C/min, and held for 1 min; the column was further raised to 250 °C at a rate of 10 °C/min, held for 5 min, raised to 300 °C at a rate of 10 °C/min, and held for 7 min. The injector and detector temperatures were maintained at 250 and 280 °C, respectively. Ultrapure helium was used as the carrier gas set at 1.0 mL/min, and the split ratio was 75:1. The samples (100 μL) were diluted 1:1 (v/v) in hexane, and an injection volume of 1–2 μL was employed.

RESULTS AND DISCUSSION

Stability test results at 60 °C for fully processed canola oil (control) and canola oil containing maleimide (0.05–10.0 ppm) are presented in Figure 1. The difference in stability of the various oils at different time periods was plotted as the amount of conjugated dienes measured as absorbance at 234 nm. The control, fully processed canola oil, was more stable than canola oil containing maleimide. The prooxidative effect of maleimide in canola oil was seen after 200 h of storage. Statistical analysis was performed on the data obtained at 211 h and is reported in Table 1. Analysis of variance revealed that the data obtained for canola oil containing all different concentrations of maleimide were significantly different from the control. From this it can be

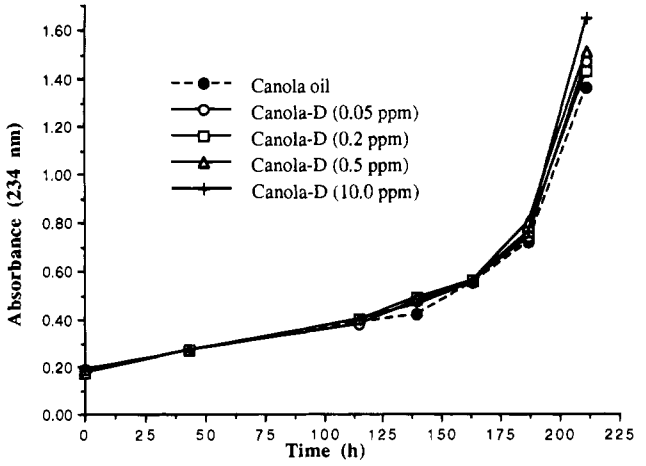

Figure 2. Storage stability at 60 ± 1 °C (measured as absorbance at 234 nm; indicative of conjugated dienes) of canola oil and canola oil containing 0.05, 0.2, 0.5, and 10.0 ppm of dimethylpyrrole (D).

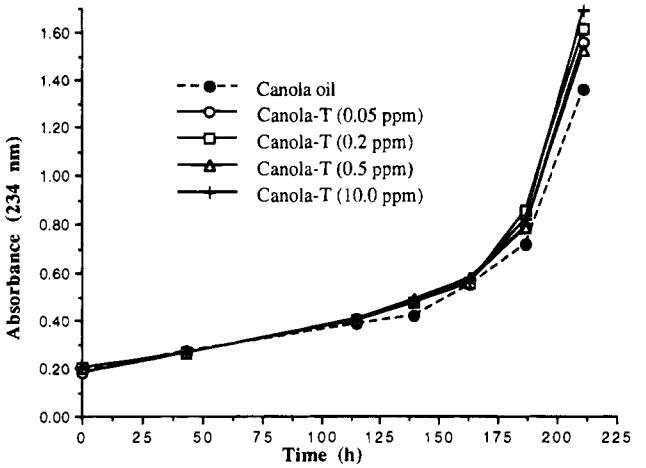

Figure 3. Storage stability at 60 ± 1 °C (measured as absorbance at 234 nm; indicative of conjugated dienes) of canola oil and canola oil containing 0.05, 0.2, 0.5, and 10.0 ppm of trimethylpyrrole (T).

concluded that maleimide acted as a prooxidant under the conditions used. However, an increase in the concentration of maleimide from 0.05 to 10.0 ppm did not result in a proportional increase in the instability effect as shown by the statistical analysis in Table 1.

Results obtained for stability tests at 60 °C for fully processed canola oil (control) and canola oil containing dimethylpyrrole and trimethylpyrrole (0.05–10.0 ppm) are presented in Figures 2 and 3. Canola oil containing either dimethylpyrrole or trimethylpyrrole was less stable than the control. Statistical analyses were performed in the same manner as for the previous data. It was observed (results not shown here) that the data obtained at 211 h for various concentrations of either dimethylpyrrole or trimethylpyrrole in canola oil were significantly higher than the control. From these results it can be concluded that dimethylpyrrole and trimethylpyrrole also acted as prooxidants in canola oil at the concentrations tested. While comparing different concentrations of dimethylpyrrole, statistical analysis revealed that the data for canola oil containing 10 ppm of dimethylpyrrole were significantly different from all other concentrations. A similar result was seen for canola oil containing 10 ppm of trimethylpyrrole. Also, data for canola oil containing 0.5 ppm of trimethylpyrrole was significantly different from those for canola oil

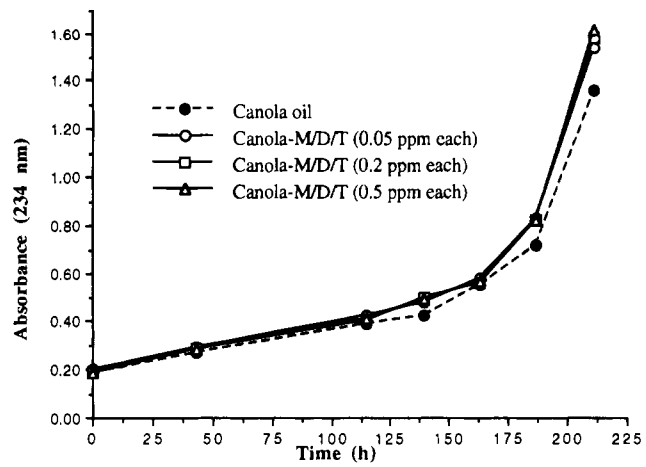

Figure 4. Storage stability at 60 ± 1 °C (measured as absorbance at 234 nm; indicative of conjugated dienes) of canola oil and canola oil containing 0.05, 0.2, and 0.5 ppm each of maleimide(M), dimethylpyrrole (D), and trimethylpyrrole (T).

containing 0.05 ppm. Thus, the prooxidative effect of dimethylpyrrole and trimethylpyrrole in canola oil was dependent on their concentration, which was not the case for maleimide for the concentrations studied here. The exact reason for this behavior is not known.

Since neither the chlorophyll degradation pathway nor its breakdown products are presently known, it may be assumed that more than one CBP formed would be responsible for the instability of the final processed oil. Three model compounds chosen in this study were added to canola oil at concentrations of 0.05, 0.2, and 0.5 ppm each. The results of stability tests at 60 °C for fully processed canola oil and canola oil containing all three compounds, maleimide, dimethylpyrrole, and trimethylpyrrole together, are presented in Figure 4. For all three concentrations, canola oils containing maleimide, dimethylpyrrole, and trimethylpyrrole were less stable than fully processed canola oil. Statistical analysis confirmed the cumulative prooxidant effect of the three compounds. The prooxidative effect of the three compounds at the 0.5 ppm level was significantly higher than at the 0.05 ppm level, while the effect at the 0.2 ppm level was not significantly different from either at 0.05 or 0.5 ppm.

A bleaching step is employed in the refining process of oils to remove pigments and trace compounds by adsorption (Taylor et al., 1989). Formation of some unknown chlorophyll-derived green compounds has been observed during hydrogenation of canola oil (Mag, 1983). These compounds were found to adsorb less on the bleaching clay in comparison to chlorophyll. Experiments were conducted to examine the ability of these three compounds to survive the bleaching step. A mixture containing 50 ppm each of maleimide, dimethylpyrrole, and trimethylpyrrole in tricapryloylglycerol was used. This mixture was subjected to bleaching conditions in the presence of 1, 2, 3, 4, and 5% (w/w) bleaching clay. Controls for this experiment included tricapryloylglycerol heated at 105 °C for 30 min, tricapryloylglycerol heated at 105 °C for 30 min under vacuum (20 mmHg), tricapryloylglycerol heated at 105 °C for 30 min under vacuum with 5% bleaching clay, and tricapryloylglycerol under vacuum with 5% bleaching clay without heating. The mixture was also subjected to heating at 105 °C for 30 min under atmospheric pressure.

Table 2. Effect of Bleaching on the Residual Concentration of Maleimide, Dimethylpyrrole, and Trimethylpyrrole in Tricapryloylglycerol

processing condition	concn[a] (ppm) M[b]	D[c]	T[d]
TC (M,D,T-50 ppm), 105 °C	49.7 (1.2)[f]	47.9 (1.4)	49.3 (1.0)
TC (M,D,T-50 ppm), 105 °C/ vacuum	48.2 (1.4)	49.6 (0.9)	49.7 (1.7)
TC (M,D,T-50 ppm), 105 °C/ vacuum/1% bleaching clay	48.1 (2.2)	2.4 (0.4)	2.9 (0.4)
TC (M,D,T-50 ppm), 105 °C/ vacuum/2% bleaching clay	39.5 (2.1)	bdl[g]	1.0 (0.3)
TC (M,D,T-50 ppm), 105 °C/ vacuum/3% bleaching clay	26.9 (0.5)	bdl	bdl
TC (M,D,T-50 ppm), 105 °C/ vacuum/4% bleaching clay	30.0 (2.8)	bdl	bdl
TC (M,D,T-50 ppm), 105 °C/ vacuum/5% bleaching clay	24.8 (3.9)	bdl	bdl

[a] Values reported are average of duplicates. [b] M, maleimide. [c] D, dimethylpyrrole. [d] T, trimethylpyrrole. [e] TC, tricapryloylglycerol. [f] Standard deviation. [g] bdl, below detection limit of 1.0 ppm (by GLC).

The results from these experiments are presented in Table 2. No decrease in the concentration of maleimide, dimethylpyrrole, and trimethylpyrrole was observed either on heating at 105 °C or on heating at 105 °C under vacuum. These results show that these three compounds are stable to heat and are not destroyed under bleaching conditions. Use of 1% (w/w) clay was sufficient to reduce the concentration of dimethylpyrrole and trimethylpyrrole to 2 and 3 ppm, respectively, while maleimide was not adsorbed by the bleaching clay. Use of 2% (w/w) clay resulted in nearly complete adsorption of dimethylpyrrole and trimethylpyrrole on the clay. Only 20% of maleimide was adsorbed on the clay under the same conditions. More than 45% of maleimide was retained in the tricapryloylglycerol mixture even after treatment with 5% clay. These results clearly showed that maleimide was not adsorbed efficiently by the bleaching clay. During bleaching of oils, pigments and several other trace compounds compete for adsorption sites on the bleaching clay surface (Patterson, 1976). Maleimide may have a slightly lower affinity for the absorption site than dimethylpyrrole and trimethylpyrrole. Thus, if maleimide or any structurally related compound were present in the oil entering the bleaching step, a large percentage would not be adsorbed and, hence, be left behind in the bleached oil.

Experiments were also conducted to determine the fate of maleimide, dimethylpyrrole, and trimethylpyrrole, during degumming, alkali refining, bleaching, and deodorization. The individual and combined effects of each step on each of the three compounds were studied. The result of each individual step is presented in Table 3. Treatment with citric acid and phosphoric acid did not appreciably reduce the concentration of maleimide, dimethylpyrrole, and trimethylpyrrole in tricapryloylglycerol. Alkali refining resulted in the complete elimination of maleimide from the 50 and 100 ppm starting levels, while there was no substantial loss of dimethylpyrrole and trimethylpyrrole. Bleaching was performed with an excess of clay (5%) to approximate the amounts used to treat oils containing high chlorophyll levels. Bleaching resulted in residual levels of less than 8 ppm of dimethylpyrrole and trimethylpyrrole at both initial concentrations, while 36–42% of maleimide was retained in bleached tricapryloylglycerol. Deodorization resulted in complete removal of both maleimide and trimethylpyrrole, while trace amounts of dimethylpyrrole were retained in the deodorized oil. These results indicate that alkali refining would eliminate compounds similar in structure to maleimide but not those similar to dimethylpyrrole and trimethylpyrrole. Deodorization was the most effective processing step for removal of these compounds, leaving behind only trace amounts of dimethylpyrrole. When these compounds are initially present at relatively high concentrations, as tested here, even deodorization does not ensure complete removal of dimethylpyrrole. Bleaching was only partially effective, as a significant amount of maleimide and trace amounts of dimethylpyrrole and trimethylpyrrole are left behind in the bleached oil. Since the presence of these compounds at low levels (<1 ppm) in canola oil has been shown in this study to lower oil stability, it can be postulated that CBP similar in structure could be responsible for the decreased stability of oil from green seed.

Table 3. Effect of Individual Processing Steps on Residual Concentration of Maleimide, Dimethylpyrrole, and Trimethylpyrrole in Tricapryloylglycerol

processing condition	% recovery[a] of M[b]	D[c]	T[d]
TC[e]/M,D,T (50 ppm each)			
citric acid	92.4 (3.9)	95.2 (1.0)	96.7 (0.2)
phosphoric acid	94.6 (1.5)	94.7 (1.4)	95.6 (1.8)
alkali	bdl[f]	88.4 (1.3)	90.1 (2.2)
bleaching (5% bleaching clay)	36.3 (1.1)	7.1 (0.3)	5.9 (0.6)
deodorization	bdl	2.1 (0.4)	bdl
TC/M,D,T (100 ppm each)			
citric acid	100	88.4 (1.0)	91.0 (2.5)
phosphoric acid	95.8 (3.6)	99.1 (0.9)	94.9 (1.6)
alkali	bdl	97.1 (1.4)	95.9 (2.5)
bleaching (5% bleaching clay)	41.7 (4.0)	5.3 (1.1)	6.2 (0.9)
deodorization	bdl	5.0 (0.1)	bdl

[a] % recovery = (ppm of component after processing step)/(ppm of component before processing step) × 100. Results provided are average of duplicates with standard deviation in parentheses. [b] M, maleimide. [c] D, dimethylpyrrole. [d] T, trimethylpyrrole. [e] TC, tricapryloylglycerol. [f] bdl, below detection limit of 1.0 ppm (by GLC).

Table 4. Effect of Processing Steps in Sequence on Residual Concentration of Maleimide, Dimethylpyrrole, and Trimethylpyrrole in Tricapryloylglycerol

processing condition	% recovery[a] of M[b]	D[c]	T[d]
TC[e]/M,D,T (50 ppm each)			
citric acid	97.6 (2.3)	97.9 (2.1)	94.3 (0.9)
phosphoric acid	92.8 (2.0)	98.0 (2.0)	93.6 (0.5)
alkali	bdl[f]	83.9 (2.3)	76.8 (3.6)
bleaching (5% bleaching clay)	bdl	5.6 (0.4)	1.7 (0.5)
deodorization	bdl	2.9 (0.2)	bdl
TC/M,D,T (100 ppm each)			
citric acid	98.9 (1.0)	97.5 (1.7)	98.6 (0.9)
phosphoric acid	95.3 (0.5)	95.5 (0.3)	94.4 (0.9)
alkali	bdl	83.1 (1.2)	82.2 (0.9)
bleaching (5% bleaching clay)	bdl	4.9 (0.2)	3.8 (0.1)
deodorization	bdl	3.5 (0.2)	bdl

[a] % recovery = (ppm of component after processing step)/(ppm of component in the original starting material) × 100. Results provided are average of duplicates with standard deviation in parentheses. [b] M, maleimide. [c] D, dimethylpyrrole. [d] T, trimethylpyrrole. [e] TC, tricapryloylglycerol. [f] bdl, below detection limit of 1.0 ppm (by GLC).

The effect of processing steps in sequence on the final concentration of maleimide, dimethylpyrrole, and trimethylpyrrole in tricapryloylglycerol is presented in Table 4. Treatment with citric acid followed by phosphoric acid did not substantially reduce the concentration of maleimide, dimethylpyrrole, and trimethylpyr-

role in tricapryloylglycerol. Alkali refining of the degummed oil resulted in complete elimination of maleimide at both the 50 and 100 ppm starting levels, with losses of 17–23% for dimethylpyrrole and trimethylpyrrole. The concentration of dimethylpyrrole and trimethylpyrrole was substantially reduced (>90%) during bleaching. Further, on deodorization, trimethylpyrrole was completely removed. Only trace amounts of dimethylpyrrole survived the complete processing. However, it is possible that these compounds could have escaped detection by the method used in this study as the detection limit for these compounds in tricapryloylglycerol was 1 ppm.

CONCLUSION

From this study it has been shown that maleimide, dimethylpyrrole, and trimethylpyrrole act as prooxidants and reduce the stability of canola oil. This is important because CBP could be similar in structure to these heterocyclic compounds. These compounds act as prooxidants at low concentrations (even below 1 ppm), either alone or in combination. These results are significant to the canola industry because high-chlorophyll seed is frequently encountered. Even though green seed canola oil is processed to remove all chlorophyll/pheophytin, the formation and fate of CBP remain a mystery.

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