

Effect of Processing on the Composition and Oxidative Stability of Coconut Oil

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The effect of various processing procedures on the composition and oxidative stability of coconut oil has been studied. The crude oil is relatively stable but major reductions in oxidative stability occur during the bleaching of oil degummed with phosphoric acid; during alkali refining; during the deodorization of oil degummed with citric acid and bleached; and during the deodorization of oil processed with a combined phosphoric acid degumming and bleaching operation. The reasons for the loss of oxidative stability during processing are discussed with reference to changes in the composition of the oil. Residual traces of citric acid or phosphoric acid play an important role in stabilizing processed oils. The tocopherol content is also important, although no additional stabilization of the oil occurs on adding levels of tocopherol above those present naturally in the crude oil. A combined phosphoric acid degumming and bleaching process leads to smaller losses of tocopherols than sequential treatments.

KEY WORDS: Coconut oil, composition, oxidation, processing, refining.

Crude edible oils may be processed by various procedures in order to obtain an oil of optimum quality in high yield. Degumming, alkali refining, bleaching and deodorizing have traditionally been used for many oils with wide variations in processing conditions and procedures, including the replacement of alkali refining by physical refining.

It is known that refining has a strong effect on the oxidative stability of oils. Jung *et al.* (1) found that crude soybean oil became less stable during processing with the order of stability being crude > deodorized > degummed > alkali refined > bleached oil. Other studies have also shown that crude oil is more stable than processed oil (2,3). The stability of the oil is dependent on the presence of minor components including tocopherols, metal ions and phospholipids, which are partly removed during processing. Tocopherols, which act as natural antioxidants, are lost at each stage of processing with total losses of 31–47% being reported during the processing of soybean oil (1,4) and 94% during the processing of coconut oil (5). Phospholipids and metal ions are mainly removed during degumming (6) with further losses during subsequent steps (1). Bleaching removes pigments including chlorophyll and carotenoids, but the hydroperoxide level may also be reduced at this stage (7) with residual hydroperoxides decomposing during deodorization (1).

This study was concerned with a detailed investigation of the effect of variations in processing conditions on the composition and oxidative stability of crude coconut oil.

EXPERIMENTAL PROCEDURES

Crude coconut oil supplied by Van den Berghs & Jurgens, Purfleet, U.K., was processed in the laboratory on a scale of 0.5–1 kg. Fuller's earth for bleaching was purchased from BDH Chemicals Ltd, Poole, U.K. Degumming and bleaching operations were performed at 80°C under nitrogen and vacuum. Alkali refining of selected samples was performed at 70° by addition of sodium hydroxide solution (0.8M, 10% excess of that required to neutralize the free fatty acids) under nitrogen and vacuum. The oil was separated by centrifugation, washed with water and dried under vacuum at 90°C. Deodorization was performed at 240°C for 4 hr with a vacuum of 2–4 mm mercury. Analyses of phosphorus content, free fatty acids, copper, iron and tocopherols were performed on selected samples where processing might cause changes in composition relevant to oil stability. Phosphorus content and free fatty acids were determined by the IUPAC methods (8). Fatty acid methyl ester analysis was performed by British Standard Method BS 684, 2.34 (1980) with methanolic sodium hydroxide and boron trifluoride followed by gas chromatographic analysis on a diethylene glycol succinate column with temperature programming from 100°C after 3 min to 200°C at 12°C/min. Copper and iron were determined by atomic absorption spectrophotometry with a Pye Unicam SP9 spectrometer. Tocopherols were determined by high performance liquid chromatography following the method of Carpenter (9). Oxidative stability was determined in triplicate in a Metrohm Rancimat Model 617 (Herisau, Switzerland) as described in the literature (10). The Rancimat tubes were cleaned thoroughly before use by washing with detergent and water; boiling with aqueous sodium hydroxide (5%) for 1 hr; boiling with concentrated hydrochloric acid (15 min) and washing with water before drying.

All analyses were performed in duplicate, or in triplicate where standard deviations are quoted.

Phospholipids were separated and collected from the crude gum obtained by phosphoric acid degumming of crude coconut oil by using a silica gel column and eluting with 10 column volumes of chloroform to remove the neutral lipids, followed by 10 column volumes of methanol to elute the phospholipids.

RESULTS AND DISCUSSION

Crude coconut oil is a stable oil due mainly to the high content of saturated fatty acids in the triacylglycerols (Table 1).

Degumming crude coconut oil either with citric acid or with phosphoric acid caused a slight increase in the oxidative stability of the oil (Table 2, samples S1, S2 and S6) despite the large reduction in phosphorus, iron and copper evident in sample S6 (Table 3). However, bleaching the phosphoric acid-degummed sample caused a strong reduction in stability (S6,S7), which did not occur during the bleaching of the citric acid-degummed sample (S2,S3).

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EFFECT OF PROCESSING ON COCONUT OIL

TABLE 1

Fatty Acid Composition of Crude Coconut Oil

Fatty acid	Area (%)
6:0	0.4
8:0	5.2
10:0	4.5
12:0	48.9
14:0	17.7
16:0	9.1
18:0	3.0
18:1	7.7
18:2	2.3

A reduction in iron and copper content should increase oxidative stability but a reduction in phosphorus content should reduce the stability because phospholipids are known antioxidants (11,12). A balance between these effects may contribute to the small change in stability on degumming. However, it is likely that the 4.7 ppm phosphorus in sample S6 indicates that phosphoric acid remains in this sample and is removed on bleaching, thereby causing a large reduction in stability.

Citric acid is more soluble in oil than phosphoric acid, and hence, residual acid is removed less completely by bleaching. Thus, the stability of sample S3 is partly due to the presence of residual citric acid in the oil.

When bleaching earth was added to oil containing added phosphoric acid (S14), the loss of oil stability on bleaching was less than that when the phosphoric acid was removed before bleaching (S7). The combined degumming and bleaching operation led to reduced losses of tocopherols (7.4%) compared with sequential degumming and bleaching where the losses were 45.6% for citric acid-degummed and bleached sample (S3) and 58.1% for the phosphoric acid-degummed and bleached sample (S7).

The increased retention of tocopherols in sample S14 may contribute to its stability, although it is also likely that this process is less effective at removing residual traces of phosphoric acid, which may chelate metal ions, than the sequential process. The phosphorus content in sample S6 was 4.7 ppm, and this is consistent with the presence of residual traces of phosphoric acid after the phosphoric acid degumming. The phosphorus content of the degummed and bleached sample S7 was only 0.04 ppm, and this sample had very low oxidative stability. Alkali refining was also effective in reducing the phosphorus content of the oil (S10) with 39.4% loss of tocopherols, and this sample had very low oxidative stability, despite the large reduction in the levels of iron and copper, which were similar after alkali refining (sample S10) to the levels in the phosphoric acid-degummed oil (S6). This loss of stability on alkali refining indicates the important role of phospholipids in improving the oxidative stability of crude oils either by complexing metal ions (11) or by other secondary antioxidant action (12). In order to confirm this effect, the phospholipids were isolated from crude coconut oil by column chromatography and added back to a sample of oil that had been degummed, bleached and deodorized.

The Rancimat induction period at 120°C increased from 5.1 to 32.3 hr, which is a value close to that of the crude oil, on adding the phospholipids, thus confirming the effect of these components.

Deodorization of the oil was accompanied by relatively small losses of tocopherols (S4, S12, S15 compared with S3, S11 and S14 respectively). Bleached oils S7 and S11 used for deodorization had low oxidative stability and there was little change after deodorization. However, the oxidative stability of the citric acid-degummed and bleached sample S3 fell considerably on deodorization with the induction period falling from 37.4 hr to 4.9 hr. This confirms the presence of citric acid in the bleached

TABLE 2

Effect of Processing on the Rancimat Induction Period of Coconut Oil at 120°C

Sample no.	Processing	Mean induction period (hr)	s.d. ^a
S1	Crude	36.9	0.5
S2	Citric acid (C.A.)-degummed	43.2	2.2
S3	C.A.-degummed, bleached	37.4	1.3
S4	C.A.-degummed, bleached, deodorized	4.9	0.5
S5	C.A.-degummed, bleached, deodorized + C.A. (0.01%)	19.8	1.7
S6	Phosphoric acid (P.A.)-degummed	39.5	0.2
S7	P.A.-degummed, bleached	0.2	0.05
S8	P.A.-degummed, bleached, deodorized	0.2	0
S9	P.A.-degummed, bleached, deodorized + C.A. (0.01%)	16.4	0.3
S10	Alkali-refined	4.2	0.1
S11	Refined, bleached	5.8	0.1
S12	Refined, bleached, deodorized	8.0	0.2
S13	Refined, bleached, deodorized + C.A. (0.01%)	34.4	0.4
S14	Combined P.A.-degummed + bleached	22.3	0.1
S15	Combined P.A.-degummed and bleached; deodorized	8.7	0.7
S16	Combined P.A.-degummed and bleached; deodorized + C.A. (0.01%)	30.7	0.3

^as.d. = standard deviation.

TABLE 3

Effect of Processing on the Composition of Coconut Oil

Sample ^a no.	Phosphorus (ppm)	Iron (ppm)	Copper (ppm)	FFA (%)	PV (meq/kg)	Tocopherols (ppm)
S1	22.2	1.06	0.35	2.03	1.45	55.0
S2	— ^b	—	—	—	—	46.9
S3	—	—	—	—	—	30.0
S4	—	—	—	—	—	23.8
S5	—	—	—	—	—	—
S6	4.7	0.09	0.03	1.97	2.2	53.9
S7	0.04	0.02	0.01	1.95	1.0	23.1
S8	—	—	—	0.12	6.02	25.3
S9	—	—	—	—	—	—
S10	0.3	0.16	0.02	0.01	2.5	33.4
S11	0.0	0.02	0.02	0.12	1.9	8.7
S12	—	—	—	0.06	2.45	4.2
S13	—	—	—	—	—	—
S14	—	—	—	—	—	51.0
S15	—	—	—	—	—	38.1
S16	—	—	—	—	—	—

^aSee Table 2 for processing of each sample.

^b— indicates "not determined."

TABLE 4

Effect of Added α -Tocopherol on the Rancimat Induction Period of Crude Coconut Oil^a at 120°C

Added α -tocopherol (ppm)	Induction period (hr)
0	36.9
50	33.6
100	35.3
200	36.5

^aCrude coconut oil contained 55.0 ppm total tocopherols comprising 40.7 ppm α -tocopherol, 3.3 ppm β -tocopherol and 11.0 ppm γ -tocopherol.

oil, because it is known that citric acid decomposes at the high temperatures used for deodorization. The oil sample that had been degummed and bleached in a single operation (S14) was also reduced in oxidative stability from 22.3 hr to 8.7 hr on deodorization, although the fall in tocopherols was modest. It is likely that residual traces of phosphoric acid were lost under deodorization conditions.

The effect of adding tocopherols on the stability of crude coconut oil was investigated. However, addition of 50–200 ppm α -tocopherol did not cause any increase in stability (Table 4). Therefore, it appears that the natural level of tocopherols in the oil are approximately the optimum concentration for stabilization of the oil. This observation has also been made for other oils (13). α -Tocopherol was found to be the major natural tocopherol in crude coconut oil (Table 4). This contrasts with the report of Taylor and

Barnes (14) who found δ -tocotrienol to be the major tocopherol.

Addition of citric acid at the end of the deodorization process when the oil had cooled to 100°C was effective in regaining considerable oxidative stability in the oil. This effect is well known since citric acid is a metal-chelating agent. Samples S13 and S16 in particular were similar in oxidative stability to the crude oil.

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[Received December 6, 1990; accepted May 27, 1991]