Effects of Minor Components on the Crystallization of Coconut Oil

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Variations in the crystallization behavior of fats have important consequences for the processing of fatty foods.

This paper is concerned with the changes in the crystallization of coconut oil due to refining, and the effects of diacylglycerols, free fatty acids and phospholipids on oil crystallization.

The changes in coconut oil crystallization due to changes in oil composition have been studied by pulsed nuclear magnetic resonance spectroscopy. Bleaching or neutralization of crude coconut oil caused a dramatic reduction in the induction time before the onset of detectable crystallization at 15°C. The addition of oleic and lauric acid caused a large increase in the induction time of refined coconut oil whereas palmitic acid had a smaller effect. However, the changes in coconut oil crystallization during refining are not completely explained by the removal of free fatty acids. Dilaurin retarded the nucleation of coconut oil whereas diolein did not have any significant effect. Phosphatidylcholine also retarded the nucleation of coconut oil at 15°C, but this effect is not significant in practice for coconut oil because of the low levels of phospholipids present in the crude oil.

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

The crystallization behavior of edible fats is important in a wide variety of food applications including confectionary, margarines, spreads and bakery products. Coconut oil or modified coconut oil is commonly applied in several food products such as biscuit filling creams and chocolate-flavored coatings in which its crystallization behavior is important. Although there have been many studies of the polymorphism and phase behavior of fats, factors affecting the rate of fat crystallization have not been widely investigated. Rapid cooling of coconut oil causes crystallization into an α polymorph, which rapidly transforms to a β'-2 polymorph. The latter is quite stable (1) although a β polymorph may develop after several months (2). The effect of oil components on the crystallization of coconut oil has not been reported in the literature, but the effects of diacylglycerols on the crystallization of other fats have been studied by several groups. 1,2-Dipalmitylglycerol has a strong stabilizing effect on the β' polymorph of hydrogenated rapeseed oil, whereas the 1,3 isomer does not have this effect (3). Diacylglycerols isolated from palm oil retard the β'_2 to α and the α to β'_1 polymorphic transformations of palm oil (4). Whereas diacylglycerols retard crystal growth of sheanut oil, removal of surface-active agents (presumably phospholipids) by washing accelerates the formation of β'_1 crystals in the oil (5). This paper is concerned with the changes in the crystallization of coconut oil due to refining and the effects of diacylglycerols, free fatty acids and phosphatidylcholine.

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EXPERIMENTAL PROCEDURES

Crude coconut oil supplied by Van den Berghs & Jurgens Ltd., Purfleet, U.K., was refined in the laboratory by two procedures. One sample was neutralized, bleached and deodorized for 4 hr at 240°C under a vacuum of 2–4 mm Hg, and a second sample was degummed, bleached and deodorized under the same deodorization conditions. Phosphorus and free fatty acid content of oil samples were determined according to IUPAC (6). Oleic acid, lauric acid, palmitic acid, dioleylglycerol, dilaurylglycerol and phosphatidylcholine (from egg yolk) were purchased from Sigma Chemical Co. Ltd., Poole, U.K. Crystallization studies were performed in duplicate on unstirred samples in glass tubes 0.75 cm i.d. Samples were heated at 70°C for 30 min and then transferred to a water bath at the temperature of interest. The solid fat content was determined with a Bruker Minispec PC120 (Bruker Spectrospin Ltd., Coventry, U.K.) by the direct method (7).

RESULTS AND DISCUSSION

The solid fat content (SFC) of each coconut oil sample remained close to zero for a period at 15°C before increasing rapidly as shown in Figure 1. The curves have been analyzed by extrapolating the line of maximum gradient back to the x-axis and determining at which point this line cuts a line drawn through the initial SFC values (see Fig. 1). The induction time is the time before this intercept and is mainly dependent on the rate of nucleation of the fat. The maximum rate of solids increase, which is dependent both on the surface area of nuclei formed in the induction period and on the rates of nucleation and crystal growth, corresponds to the maximum gradient. Six crystallization experiments with degummed, bleached, deodorized coconut oil give a mean induction period of 8.4 min with standard deviation 1.3 min (15.1%). The mean value of the maximum rate of solids increase was 3.66% min^{-1} with standard deviation 0.42% min^{-1} (11.4%).

A control sample of degummed, bleached, deodorized coconut oil was included in each set of crystallization experiments. Degumming of coconut oil had a minor effect on the induction time, but bleaching caused a dramatic reduction in this parameter from 42.0 to 7.5 min at 15°C (Table 1). Neutralization of the crude oil also caused a large reduction in the induction time from 46.0 min to 5.0 min at this temperature. Deodorization of the degummed bleached oil did not cause a significant change in induction period despite the removal of 1.85% free fatty acids, which are later shown to extend the induction period. This

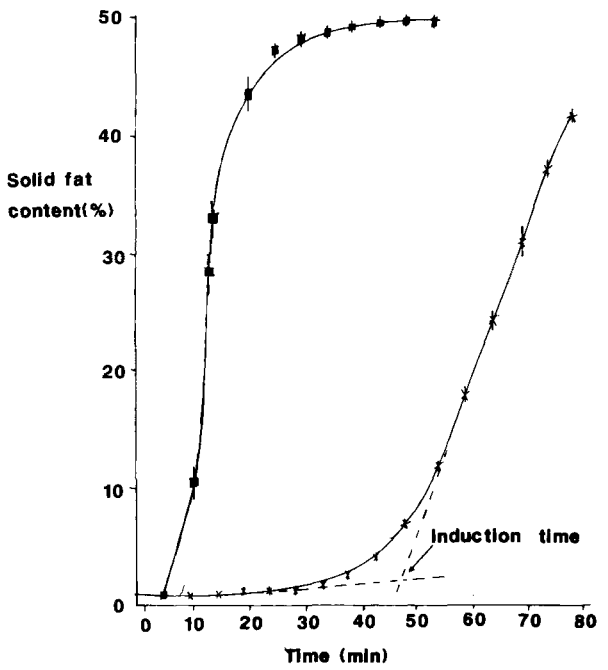

FIG. 1. Crystallization of crude (■) and degummed, bleached, deodorized coconut oil (×) at 15°C. The range of the duplicate determinations is indicated.

observation together with the fact that deodorization of neutralized, bleached oil extended the induction period from 5.0 min to 13.5 min, despite the free fatty acid level remaining constant, suggests that some change on deodorization tended to increase the induction period. The reason for this is unclear but a very small amount of transesterification may be occurring. However, no significant change in carbon number of the triacylglycerols could be detected by gas chromatography.

In order to clarify the effects of minor components, pure lipids were added to neutralized, bleached, deodorized coconut oil and crystallization was studied.

Effects of fatty acids on coconut oil crystallization. The effect of fatty acids is clearly dependent on the identity of the fatty acids (Table 2). The addition of the distilled fatty acids isolated during the deodorization of degummed and bleached coconut oil extended the oil induction time dramatically. Addition of 4% mixed fatty acids gave an induction period close to that of the crude oil containing 2.0% free fatty acids. However, the addition of 2% mixed fatty acids only raised the induction period from 8.0 min to 16.5 min compared with 44 min for the crude oil. Clearly, part of the change in crystallization rate on refining is due to the removal of free fatty acids but other minor components are also affecting the crystallization rate. It appears that other components that retard crystallization are removed during neutralization or the bleaching of a degummed oil.

Oleic acid was most effective at retarding nucleation at low levels, although lauric acid had a similar effect to oleic acid at the 5% level (Table 2). Palmitic acid was relatively ineffective at retarding nucleation at both the 2.5% and 5% levels. The effects on nucleation at 15°C were much greater than at lower temperatures (Table 3, Fig. 2). Application of the Arrhenius equation showed that the activation energy was considerably increased by both lauric acid and oleic acid (Table 3). It was found that the solubility of lauric acid in sunflower oil at 15°C was 8%, whereas the solubility of palmitic acid was 1%. Therefore, it is likely that palmitic acid precipitates out of coconut oil on cooling and initiates nucleation. Lauric acid, however, is likely to be incorporated into the growing embryo prior to nucleation and thereby retards formation of a nucleus. Oleic acid may be more effective than lauric acid at the 2.5% level, because the disorder introduced into the growing embryo is greater due to the difference in the shape of oleic acid and the fatty acid chains of the triacylglycerols.

Since there is no strong increase in induction time with oleic acid concentration, it may be that the oleic acid molecules associate together in solution at higher concentrations whereas lauric acid molecules are incorporated into the embryo at higher levels.

Effects of diacylglycerols and phosphatidylcholine on coconut oil crystallization. The effect of diacylglycerols was investigated by adding dilaurin and diolein to refined coconut oil. The refined coconut oil contained 2.0% diacylglycerols. Diolein had no significant effect on the induction time but dilaurin retarded nucleation with its effect increasing with concentration (Table 4). The effect

TABLE 1

Effect of Processing on Induction Time, Crystallization and Composition of Coconut Oil at 15°C

Sample	Induction time (min)	Maximum crystallization rate (% solids/min)	Free fatty acids (%)	Phosphorus (ppm)
Crude	46.0	1.3	2.0	22.2
Degummed	42.0	0.9	2.0	4.7
Degummed, bleached	7.5	3.4	1.95	0.04
Degummed, bleached deodorized	8.0	4.4	0.1	—
Neutralized	5.0	4.4	0.0	0.4
Neutralized, bleached	5.0	4.1	0.1	0.0
Neutralized, bleached deodorized	13.5	1.7	0.1	—

TABLE 2

The Effect of Fatty Acids on the Crystallization of Degummed, Bleached, Deodorized Coconut Oil at 15°C

Fatty acids (%)	Induction time (min)	Maximum rate of solidification (%/min)
Control (0.1)	7.6	3.3
Lauric (2.5)	35.5	1.0
Lauric (5.0)	53.1	0.8
Palmitic (2.5)	12.4	2.4
Palmitic (5.0)	13.6	2.2
Oleic (2.5)	52.2	1.7
Oleic (5.0)	59.8	1.1
Distilled coconut fatty acids (2.0)	16.5	1.2
Distilled coconut fatty acids (4.0)	41.0	1.0
Crude oil (1.8% fatty acids)	44.0	1.4

TABLE 3

Effect of Fatty Acids on the Induction Time of Degummed, Bleached, Deodorized Coconut Oil at Various Temperatures

Fatty acid (%)	Induction time (min) at 6°C	9°C	12°C	15°C	Activation energy(E)[a] ($kJ \cdot mol^{-1}$)
Control (0.1)	2.5	4.2	6.7	7.9	87 (r^b = 0.98)
Lauric (2.5)	3.3	3.9	5.5	36.6	174 (r = 0.95)
Lauric (5.0)	3.1	8.7	16.9	50.8	203 (r = 0.99)
Palmitic (2.5)	3.3	5.4	7.4	12.3	95 (r = 0.99)
Palmitic (5.0)	3.3	4.6	7.4	13.3	105 (r = 1.00)
Oleic (2.5)	4.2	9.5	16.2	49.8	178 (r = 0.99)
Oleic (5.0)	4.2	11.3	16.5	57.2	184 (r = 0.99)

[a] Activation energy calculated from equation: −ln(induction time) = C−E/RT.

[b] r = correlation coefficient for plot of ln(induction time) against 1/T. (Fig. 2).

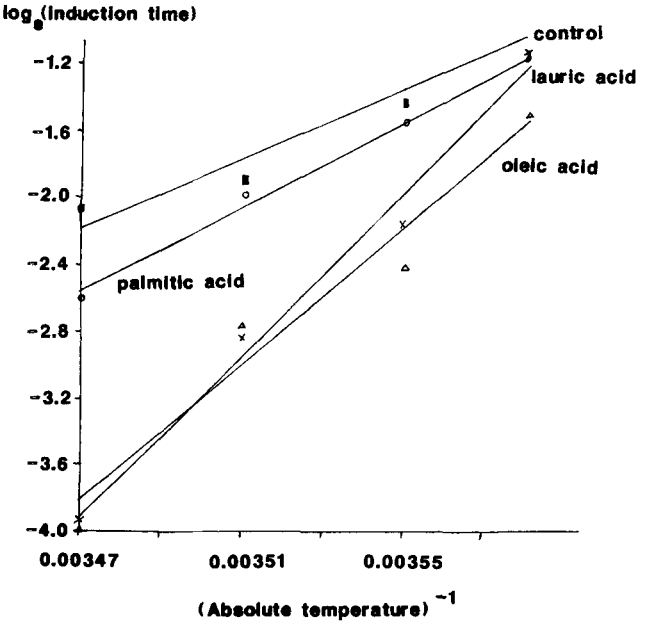

FIG. 2. Plot of ln(induction time) against 1/T for degummed, bleached, deodorized coconut oil (control (■)), and control with added lauric acid (5.0%) (×), palmitic acid (5.0%)(○),or oleic acid (5.0%)(△).

TABLE 4

Effect of Diacylglycerols and Phosphatidylcholine (PC) on the Crystallization of Degummed, Bleached, Deodorized Coconut Oil at 15°C

Additive (%)	Induction time (min)	Maximum crystallization rate (% solids/min)
—	8.0	3.4
Dilaurin (5)	11.5	3.7
Dilaurin (10)	19.0	2.5
Diolein (5)	8.0	4.6
Diolein (10)	8.0	2.5
PC (0.25)	14.0	1.4
PC (0.5)	27.0	0.7

of diacylglycerols is much less than that of free fatty acids, and this must reflect the greater loss of entropy on incorporating a diacylglycerol molecule into the nucleus. Earlier studies demonstrating large effects of diacylglycerols on the rates of polymorphic transformations of fats have used dipalmitylglycerol or fat isolates rich in this component (3,4). However, dipalmitylglycerol has a lower solubility in oil than the dilaurylglycerol used in this study. The effects of dilaurylglycerol on coconut oil crystallization rate are quite small, although the effects on polymorphic transformations have not been studied.

Phosphatidylcholine (PC) was found to extend the induction period for coconut oil crystallization at 15°C, with an increase in the induction period from 8 min to 27 min at an addition of 0.5%. It is notable that the maximum crystallization rate is considerably reduced by the phosphatidylcholine. In general, a low value for the maximum crystallization rate is found for samples with a long induction period, due to the rate being dependent on the number of nuclei available for crystal growth. However, the large reduction in maximum crystallization rate caused by PC accompanies only a moderate increase in induction time, and this may indicate that PC reduces the rate of crystal growth. In practice the levels of phospholipids in crude coconut oil are low, with only 0.05% typically being present (8), and therefore, natural phospholipids are unlikely to have a significant effect on the crystallization of this oil. However, they may have a greater effect in other oils where they are present at higher levels, or when used as a food additive.

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