Improvement of Foaming Tendency of Kapok Seed Oil by Catalytic Hydrogenation

YOSHIYUKI KAWASE, HARUMI NIIZUMA and KOSAKU YASUDA,
Research Laboratory, The Nisshin Oil Mills, Ltd., Chiwakacho, Kanagawaku, Yokohama, Japan

Abstract

Deodorized kapok seed oil foams vigorously when used for deep fat frying at a temperature around 180 C. This foaming tendency is due to the presence of cyclopropenoid in the oil. It was found that this foaming tendency can be greatly reduced by catalytic hydrogenation provided the cyclopropene ring is not cleaved by deodorization or bleaching prior to hydrogenation. Infrared spectrum of the refined and hydrogenated kapok seed oil showed absorption at 1020 cm^{-1} which is associated with the formation of the cyclopropane ring during the hydrogenation.

Introduction

The annual production of kapok seed oil in Japan has risen steadily to 10,000 tons. The oil is being used not only in margarine and shortening industries as an oil component but also for commercial deep fat frying. This oil is obtained from the seed of the *Eriodendron anfractuosum* tree which grows in many tropical countries. Jamieson and McKinney found that a sample of kapok seed oil with iodine value 96 contained 19.0% of saturated acids and 74.3% of unsaturated acids. Kapok seed oil is known to contain cyclopropene fatty acid (2). In a previous paper (3) the authors reported that the content of cyclopropene fatty acid in crude kapok seed oil varied from 12% to 14% as determined by the back titration method with 0.1 N-HBr acetic acid solution. More recently, Reiser and Raju (5) reported a gas chromatographic method for the quantitative analyses of cyclopropene fatty acids as their methyl mercaptan derivatives. According to them, there are two kinds of cyclopropene fatty acids in crude kapok seed oil, malvalic and sterculic acids.

In Japan, the crude kapok seed oil obtained by screw pressing-solvent extraction is usually refined continuously with 20° Be sodium hydroxide. Refined-dried kapok seed oil is then treated with 2% of bleaching clay at 105 C under vacuum and then deodorized at 220 C for 1.5 hr. We reported previously (3) that bleaching and deodorization of kapok seed oil tend to reduce cyclopropene fatty acids to some extent with simultaneous increase of conjugated diene contents. Cyclopropene ring could be easily cleaved between one of the olefinic carbons and the methylene carbon in the ring during bleaching with an adequate amount of clay or during deodorization at a high temperature (3).

In the present work the foaming tendency of hydrogenated kapok seed oil was compared with that of soybean oil during deep fat frying at 180 C. It is known that deodorized kapok seed oil foams vigorously during deep fat frying. This strong foaming tendency is attributed to the presence of the cyclopropenoid in the oil.

Cyclopropene fatty acids are unstable even at room temperature and polymerize with apparent destruction of the cyclopropene ring (4). To reduce the high reactivity of cyclopropene fatty acids in kapok seed oil, hydrogenation was applied at the various processing steps of the oil. According to Nunn (4) hydrogenation of sterculic acid in ethanol with palladium catalyst causes the formation of dihydrosterculic acid. Dihydrosterculic acid was reduced to a mixture of n-nonadecanoic acid and two methyl substituted octadecanoic acids in the presence of Adams' platinum catalyst (4). Those hydrogenated products were expected to be more stable than the original cyclopropene fatty acids.

Experimental Procedures

Deep Fat Frying With Kapok Seed Oil

An 800 g sample of deodorized kapok seed oil was heated to 180 C in a deep fat frying pan of 25 cm ID by 4 cm depth. Sixty-gram portions of potato cubes were fried for 2 min, at 30 min intervals.

Determination of Viscosity and Foaming of Kapok Seed Oil

Each 150 g of kapok seed oil used for deep fat frying experiments was filtered through filter paper and then heated again at 230 C for 5 hr in a 200 ml beaker. Twenty grams of the heated oil were then transferred to a 3 cm ID test tube. The temperature of the oil in the test tube was kept at 150 C. A fresh potato cube of $1 \times 1 \times 1$ cm was then dropped into the test tube. Foaming was determined by measuring the height of the foam and viscosity was determined at 30 C with an Ostowald Viscometer.

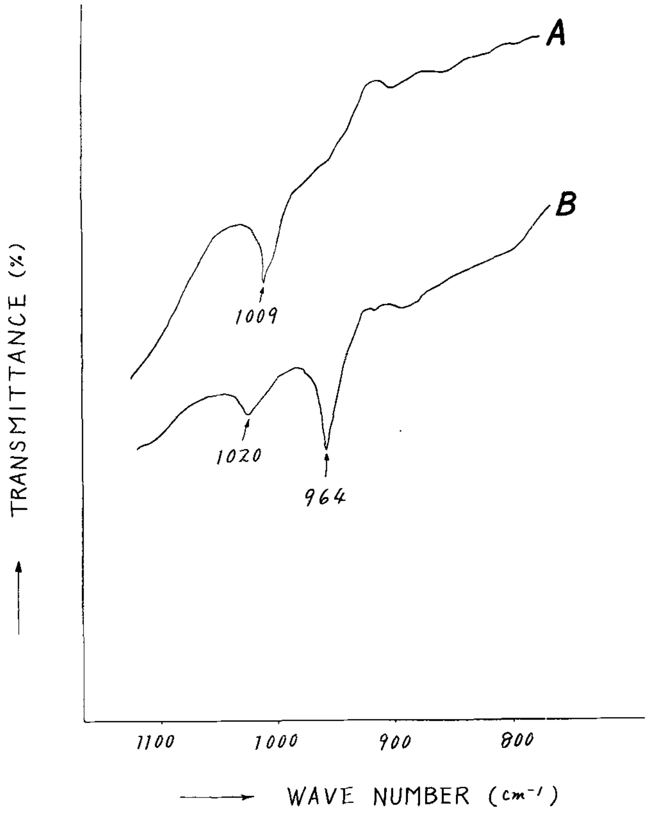

FIG. 1. Infrared absorption spectra of kapok seed oil in carbon tetrachoride. A. Refined kapok seed oil. B. Refined and hydrogenated kapok seed oil.

TABLE I

Characteristics of Deodorized Kapok Seed Oil and Soybean Oil

Oil	IV	Cyclo-propenoid %	Conj. diene %	*Trans* acid %	Viscosity (cp at 30 C)
Deodorized kapok seed	102.0	3.8	2.1	2.3	59
Deodorized soybean	133.1	0.0	0.3	0.0	30

Hydrogenation of Kapok Seed Oil

An amount of 1500 g of kapok seed oil was hydrogenated at 180 C under 2.0 kg/cm^2 of hydrogen pressure, in a stainless steel reaction apparatus of 3000 ml with 0.06% flake nickel as a catalyst. The apparatus was fitted with an electric heater and cooling coil. The catalyst, flake nickel (Nikki Kagaku Co., Japan), contains 25% nickel in hydrogenated cotton seed oil.

The reactants were stirred at 600 rpm. Periodical measurements of refractive index of samples were carried out to follow the extent of hydrogenation.

Winterization

The hydrogenated samples were slowly cooled in a 3000-ml Erlenmeyer flask to 8 C and kept at this temperature for 48 hr. The oils were then filtered with suction using Buchner funnels.

Analyses

Cyclopropene fatty acids were determined by modified HBr titration methods (3). *Trans* acids were determined by the method of the Spectroscopy Committee (6). Infrared spectra of the kapok seed oil were determined with a Hitachi EPI spectrophotometer.

Results and Discussion

The foaming tendency of deodorized kapok seed oil when used for deep fat frying was compared with that of soybean oil. Characteristics and foaming tendency of both oils are shown in Tables I and II, respectively. In a previous paper (3) the authors reported that both bleaching and deodorization processes tended to decrease cyclopropene fatty acids to some extent with an increase of conjugated diene. As shown in Table I, the deodorized kapok seed oil contained 3.8% of cyclopropenoid, significantly less than crude kapok seed oil. Vigorous foaming was observed when the deodorized kapok seed oil was used for deep fat frying (Table II). This strong foaming tendency of deodorized kapok seed oil was attributed to the cleavage of the cyclopropene ring during processing. The authors therefore postulated that, to prevent foaming of kapok seed oil during deep fat frying, cyclopropene fatty acid should be hydrogenated to more stable products before being cleaved by bleaching or deodorization. The following samples of kapok seed oil were hydrogenated and the foaming tendency of the products was determined: Refined kapok seed oil; bleached kapok seed oil (refined kapok seed oil treated with 2.5% of clay at 105 C for 10 min under vacuum); slightly bleached kapok seed oil (refined kapok seed oil treated with 1.0% of clay at 80 C under vacuum); deodorized kapok seed oil (bleached kapok seed oil deodorized at 240 C for 1.5 hr under vacuum of 4 mm Hg).

TABLE II

Comparison of Foaming Height and Viscosity of Kapok Seed Oil, Hydrogenated Kapok Seed Oil and Soybean Oil After Deep Fat Frying

Oil	Foaming height (mm)	Viscosity (cp at 30 C)
Deodorized kapok seed	75	82
Deodorized soybean	6	46
Refined and hydrogenated	5	54
Bleached and hydrogenated	76	73
Slightly bleached and hydrogenated	13	59
Deodorized and hydrogenated	88	82

TABLE III

Characteristics of Kapok Seed Oil

Oil seed	I.V.	Cyclo-propenoid %	Conj. diene %	*Trans* acid %	Viscosity (cp at 30 C)
Refined kapok	97.2	13.0	0.3	0	42
Bleached kapok	97.5	6.2	1.4	0	47
Slightly bleached kapok	97.3	12.8	0.4	0	42
Deodorized kapok	102.0	3.8	2.1	2.3	59

Table III shows that the content of cyclopropene fatty acid significantly decreased during bleaching and deodorization. It also demonstrates that the bleaching process with a smaller amount of clay at a lower temperature resulted in less destruction of the cyclopropene ring. It also shows that deodorized kapok seed oil had slightly higher iodine value and *trans* acid content. This is probably due to the introduction of a new double bond in the molecule by way of the cyclopropene ring cleavage (3). The deodorized kapok seed oil also had higher viscosity than nondeodorized oil. The high temperature treatment of cyclopropene during deodorization apparently caused the ring cleavage to form polymers (1). Decrease of cyclopropene fatty acid during hydrogenation of slightly bleached kapok seed oil is not linearly correlated with the degree of hydrogenation (Table IV). The infrared spectrum of the refined oil showed the characteristic absorption band of the cyclopropene ring at 1009 cm^{-1}. Both bleached oil and deodorized oil had much weaker absorption at this region, indicating the ring cleavage (3). When refined oil was hydrogenated, the absorption band at 1009 cm^{-1} disappeared and a new absorption band at 1020 cm^{-1} appeared, which corresponds to the cyclopropane ring. The absorption band at 964 cm^{-1} is attributed to the *trans* double bond formed during hydrogenation. Characteristics of the four hydrogenated kapok seed oils after winterization and deodorization are shown in Table V. Foaming of these hydrogenated kapok seed oils after being used for deep fat frying at 180 C

TABLE IV

Hydrogenation of Slightly Bleached Kapok Seed Oil

Reaction time min	I.V.	Cyclo-propenoid %	Conj. diene %
0	97.3	12.8	0.4
10	95.4	8.2	0.5
20	93.1	4.1	0.7
30	85.2	3.5	0.7

TABLE V

Characteristics of Hydrogenated Winterized-Deodorized Kapok Seed Oil

Oil	I.V.	Cyclo-propenoid %	Conj. diene %	*Trans* acid %	Viscosity (cp at 30 C)
Refined and hydrogenated	89.3	2.3	1.2	10.1	52
Bleached and hydrogenated	84.7	2.1	1.2	11.6	55
Slightly bleached and hydrogenated	86.3	2.5	1.1	10.3	52
Deodorized and hydrogenated	91.3	1.9	0.7	11.9	65

for 3 hr and heating at 230 C for 5 hr are shown in Table II. When kapok seed oils were hydrogenated after bleaching or deodorization, there was no improvement in the foaming tendency. Furthermore, the amount of cyclopropene fatty acid in the oil, prior to hydrogenation, was closely related to the foaming tendency of the hydrogenated oil (Tables III and V). Foaming of kapok seed oil can be greatly improved by catalytic hydrogenation if the cyclopropene ring is not cleaved by heat treatment during deodorization or by the catalytic action of clay during bleaching before the oil is hydrogenated.

ACKNOWLEDGMENT

The authors appreciate the advice given by Y. Toyama, Toyo University and S. S. Chang, Rutgers The State University.

REFERENCES

1. Faure, P. K., and J. C. Smith, J. Chem. Soc., 1818 (1956).
2. Jamieson, G. S., "Vegetable Fats and Oils," Reinhold Publishing Corporation, New York, 1943, p. 85.
3. Kawase, Y., H. Nizuma, K. Yasuda and K. Yoshitomi, Yukagaku *9*, 506 (1965).
4. Nunn, J. R., J. Chem. Soc., 313 (1952).
5. Raju, P. K. and R. Reiser, Lipids *1*, 10 (1966).
6. Report of the Spectroscopy Committee, JAOCS *36*, 627 (1959).

[Received April 2, 1968]