The Effect of Unsaponifiable Matter on the Properties of Coffee Seed Oil

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Abstract

The unsaponifiable matter of coffee seed oil has been shown to be responsible for the comparatively low melting-point (approximately 8C) of this oil. The melting point of coffee oil fatty acids, free of unsaponifiable matter, is 40–42C, and their esterification with glycerol produces an oil with a melting point of 34–36C. The unsaponifiable matter is probably responsible for high refining losses of coffee oil since the surface activity of its main constituents facilitates a partial saponification or emulsification of neutral oil during the treatment with alkalies, especially in oils with high acidity.

Introduction

THE OIL CONTENT of coffee seeds ranges from 7–16%, and with an annual world production of about 3,000,000 tons of coffee beans they are a potential source of some 300,000 tons of oil. Under present conditions nearly all of this oil is lost in the coffee grounds, however, and the recovery of oil from the residues of the soluble coffee manufacture offers technical difficulties. In Brazil a certain amount of low-grade beans (café expurgo) is processed for oil and fertilizer, and attempts are often made to convert the oil into an edible product. One problem encountered is the unusually high content of unsaponifiable matter in coffee oil, which according to the literature (1,2) may amount to some 12%. The main constituents of the unsaponifiable matter are two diterpenoid alcohols, cafestol $C_{20}H_{28}O_3$ and kahweol $C_{20}H_{24}O_3$, which differs from the former in having two more double bonds. Both are diols with one primary and one tertiary hydroxyl group. Their constitution has been investigated by a number of workers; a recent achievement has been the elucidation of the structure of kahweol by Djerassi and his school (3).

According to Kaufmann and Hamsagar (4), these alcohols are present in coffee oil in the form of monoesters of fatty acids, amounting to some 18.5% of the total oil. Cafestol and kahweol (about 1%) are present as free alcohols, and there are, in addition, phytosterol esters (1.5%), phosphatides (4%), and other minor components. The amount of triglycerides is about 75%.

The high content of unsaponifiable matter is accompanied by some other unusual features of coffee oil. Its low melting point is not in agreement with its fatty acid composition, and its refining loss is one of the highest observed in vegetable oils. The present investigation has been carried out to establish whether this behavior may be related to the unsaponifiable matter of coffee oil or not.

Materials and Methods

The five samples of coffee oil in this work were: 1 and 2 from commercial sources; 3, a sample extracted with solvent in the pilot plant of the Tropical Centre from a residue of "instant" coffee manufacture; 4, an oil extracted with hexane in the laboratory of the Tropical Centre from good-quality coffee beans; and 5, an oil extracted from low-quality coffee beans. A fraction of coffee oil with a high content of unsaponifiable matter obtained by molecular distillation was also examined.

Analytical work included determinations of a) FFA contents (expressed as % of oleic acid), b) unsaponifiable matter, c) iodine, and d) acetyl values (5). The contents of neutral oil were determined by the Wesson method, as described by Jamieson (6), and by the chromatographic method (7). The fatty acid composition of the various samples was obtained by gas chromatographic analysis of methyl esters by using Model C.G. 12 I.P. (Instrumentos Científicos Ltda., São Paulo), fitted with a thermoconductivity detector.

For the separation of polar and nonpolar constituents the countercurrent extraction method of Galanos and Kopoulas (8) was tentatively employed.

Effect on Melting Point

The two major fatty acids of coffee oil are palmitic and linoleic; there are lesser amounts of stearic, oleic, and higher molecular fatty acids, such as arachidic and behenic. The palmitic acid contents of samples examined in this laboratory were higher than reported in the literature (35–41% against 25–28%), but the over-all composition was similar (Table I). On the basis of the considerable proportions of saturated fatty acids, i.e., 40–45%, one would expect the coffee oil to be of solid or semisolid consistency at room temperature. In the literature (9) all samples examined were liquid oils.

To find out if the unsaponifiable matter were responsible for the low melting point of coffee oil, a 100-g sample of the oil 1 was saponified with ethanolic potassium hydroxide, and the unsaponifiable matter was extracted with diethyl ether. The fatty acids were recovered by acidification with hydrochloric acid, washed with water, and dried in vacuo. A sample (20 g) was re-esterified with a theoretical amount of glycerol (2 g) by heating at 180C for 5 hr in vacuo with 0.4% of stannous chloride as catalyst. The residual acidity of 13.7% was removed by washing the ethereal solution of the esterification product with 10% aqueous potassium carbonate solution,

TABLE I

Fatty Acids Composition of Coffee Seed Oils

Fatty acids	% Weight		
	Results obtained in the Tropical Centre	Results obtained by Kaufmann and Hamsagar (4)	Results quoted by Eckey (1)
Myristic	0.06– 0.14	....	3.10
Palmitic	35.44–41.35	25.30	28.20
Stearic	7.53–10.60	13.10	12.70
Oleic	8.07– 9.58	17.20	17.30
Linoleic	36.64–43.08	39.00	35.80
C_{20} and others	4.28– 6.43	5.20	2.90

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whereupon it was refluxed with activated carbon. After the filtering, removal of the solvent, and drying in vacuo the melting point of the bleached product was determined by the capillary method.

To establish whether the heating with stannous chloride and the resulting randomization had an effect on the melting point, a sample of the oil 1, neutralized with alkali, was heated with the same amount of catalyst and under the same conditions as the re-esterified product. Another sample of the neutralized oil 1 was heated at 90C for 2 hr in vacuo after the addition of 0.25% of sodium methylate to effect randomization.

Re-esterification experiments were also carried out with oils 2 and 3 by employing 2% of toluene-p-sulphonic acid as the re-esterification catalyst at 120–130C. The characteristics of the products obtained are shown in Table II. The re-esterified samples had a much higher melting point than both the original and the randomized products with the unsaponifiable matter. The reduction in iodine values after the removal of the unsaponifiable matter may be explained by the high iodine value of the diterpenoid alcohols (IV calculated for cafestol was 160.3, for kahweol 325.2). Thus the unsaponifiable matter appears responsible for the low melting-point of coffee oil. This effect might be analogous to that described in some recent patents, reporting that the addition of dextrin and disaccharide esters of fatty acids lowers the solidification point of oils (10).

Effect on Refining

The coffee oil extracted commercially in Brazil has been used mainly in the manufacture of soap. Attempts to convert it into an edible oil have encountered considerable difficulties. Besides the appreciable content of unsaponifiable matter which is undesirable in an edible oil, the refining loss of coffee oil is very high. Also the coffee beans used for oil extraction are usually poor in quality, and the free fatty acid content of the extracted oils is seldom below 10%. Such oils show high cup-refining losses, and occasionally there is hardly any separation of oil from soapstock.

To determine the amount of "neutral oil" or the minimum refining loss that could be expected in coffee oil, all five samples were subjected to the well known Wesson procedure (6). For comparison the amount of neutral oil was determined by the chromatographic procedure (7). The free fatty acid content, the amount of unsaponifiable matter, and the amount of neutral oil determined by these two methods are shown in Table III. Whereas the contents of neutral oil established by these methods are similar in common vegetable oils, data in Table III show that the Wesson method gives consistently lower results (i.e., higher losses) than does the chromatographic procedure with coffee oil. These differences seem to increase with the increased content of FFA. Soaps formed in the Wesson treatment might facilitate a partial saponification of neutral oil by the alkali employed in a large excess in the presence of cafestol and kahweol. This assumption was tested as follows.

TABLE II

Sample	FFA %	Iodine value (Wijs)	Melting point °C
1 (Neutralized)	0.8	101.1	8.5– 9
1 Fatty acids		89.3	41 –42
1 Re-esterified[a]	1.1	83.2	36.2
1 Randomized with $SnCl_2$			7 – 8
1 Randomized with NaOMe			7 – 8
2 (Original)	11.3	101.8	8 – 9
2 Fatty acids		87.2	40 –41
2 Re-esterified[b]	1.0	81.9	36.8
3 (Original)	9.8	100.8	7 – 8
3 Fatty acids		87.6	40 –41
3 Re-esterified[b]	0.9	81.7	35.4

[a] Re-esterification catalyst: stannous chloride.
[b] Re-esterification catalyst: toluene-p-sulphonic acid.

TABLE III

FFA, Unsaponifiable Matter, and Neutral Oil Contents of Coffee Oils

Sample	FFA %	Unsaponifiable matter %	Neutral oil %	
			Wesson method	Chromatographic method
1	13.3	10.9	77.8	82.8
2	11.3	9.4	84.5	87.7
3	9.8	7.9	86.9	88.8
4	2.6	9.6	93.8	94.3
5	18.6	10.8	68.3	75.9

a) The oil 4, which had the lowest FFA content (2.6%) and the smallest difference in the neutral oil yield obtained by the Wesson and chromatographic procedure was acidified with 8.0% of pure oleic acid, followed by the Wesson treatment. The neutral oil yield (without taking into account the added weight of oleic acid) was 92.3%. This is 1.5% lower than that of the original oil (cf. Table III).

b) The oil 1 was subjected to five consecutive Wesson treatments with restoration, after each treatment, of its original acidity by the addition of pure oleic acid. A continuous decrease of the neutral oil yield was noted; the amount of neutral oil after the fifth treatment was 68.4%, compared with 77.8% after the first treatment. A cottonseed oil subjected to treatment similar to that of oil 1 and 4 showed neutral oil losses amounting only to a few tenths of a per cent after each Wesson treatment.

c) The oil 1 was subjected to a modification of the Wesson procedure in substituting potassium hydroxide with potassium carbonate, which was expected to have little saponifying effect. The neutral oil yield was increased from 77.8% to 81.6%. The substitution of potassium hydroxide with potassium carbonate did not alter the results in other vegetable oils (11).

Accordingly the Wesson procedure has little significance with coffee oil; various amounts of neutral oil depending on acidity may be saponified or emulsified. This unusual behavior explains the excessive oil losses sustained in commercial refining with alkalies. This refining is carried out at elevated temperatures, which tend to increase losses owing to the saponification of neutral oil.

Attempts have been made to remove the monoesters of cafestol and kahweol from coffee oil without previous saponification by utilizing the polar character of these esters. To this end the countercurrent extraction procedure of Galanos and Kapoulas (8) was applied. It consists of the partition of polar and nonpolar lipids between 87% ethanol and light petroleum. The separation was carried out with coffee oil 2, previously neutralized, and a fraction rich in unsaponifiable matter (26.1%) which was obtained from it by molecular distillation in a laboratory falling-film still. The separations gave only 3.4% of the coffee oil 2, and 4.9% of the molecularly distilled fraction in the ethanolic phase consisted mainly of free alcohols and fatty acids. Similarly the unsaponifiable matter of the oil 1 was reduced from 10.9% only to 9.5% by the first Wesson treatment and remained practically unchanged after the fifth treatment. The unsaponifiable content of this oil increased from 10.9% to 12.7% in the "neutral oil" obtained by chromatographic procedure, demonstrating that activated alumina failed to adsorb the monoesters under the conditions of the experiment.

The weak polar character of these esters obviously results from the weak reactivity of their tertiary hydroxyl group. Thus Kaufmann and Gupta (12), on acetylation of pure kahweol at room temperature, obtained ca. 10% of diacetate and 90% of monoacetate. However the acetylation of the unsaponifiable matter obtained from oil 1, carried out according to AOCS official Method 5d, produced an acetyl value of 239.6 (acetyl value calculated for cafestol, 280.1) demonstrating the presence of diols.

Refining losses of coffee oil could be reduced by using sodium carbonate instead of sodium hydroxide as the refining agent. This would increase however the difficulty of obtained a satisfactory bleaching unless re-refining with caustic soda, with concomitant further neutral oil losses, was applied. The residual unsaponifiable matter in the refined oil presents more important nutritional problems which call for detailed investigation before the oil can be safely recommended for human consumption.

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