Further Observations Concerning Effects of Unsaponifiable Constituents on the Properties of Coffee Seed Oil

ABSTRACT

The addition of monoesters of cafestol to triglycerides obtained by re-esterification of coffee oil fatty acids resulted in a behavior similar to that of the original coffee oil when subjecting the mixture to the Wesson procedure, a test for predicting refining losses. Contrary to expectation, the softening point of the triglycerides remained practically unaffected by the above addition.

INTRODUCTION

In a previous communication (1) the assumption was made that the presence of cafestol monoesters in coffee seed oil, demonstrated by Kaufmann and Hamsagar (2), was responsible for certain unusual properties of this oil, viz., its low melting point, which is not in agreement with its fatty acid composition, and its refining loss, one of the highest observed in vegetable oils. It was considered of interest to test the above assumption by incorporating into triglycerides prepared from coffee oil fatty acids esters of cafestol and of other alcoholic components of unsaponifiable matter of this oil, and by studying the behavior of the resulting mixtures.

EXPERIMENTAL PROCEDURES AND DISCUSSION

Two hundred grams of a commercial coffee seed oil with 9.6% free fatty acids and 10.2% unsaponifiable matter was saponified with ethanolic potassium hydroxide in a nitrogen atmosphere, diluted with water and the unsaponifiable matter extracted with diethyl ether. The liberated fatty acids were extracted with light petroleum and refluxed with activated carbon, whereupon the solvent was removed in a rotary evaporator in vacuo. One hundred grams of the fatty acids thus obtained was re-esterified with 10% of glycerol using toluene-*p*-sulphonic acid as catalyst. The resulting product was subjected to the Wesson treatment (3) and purified further by passing through a silica gel column.

The absence of free fatty acids and partial glycerides was verified by thin layer chromatography. The softening point of the triglycerides was 37.0 C.

The unsaponifiable matter (19.5 g) was divided into two parts. Ten grams was crystallized from light petroleum and diethyl ether, and 5 g of a relatively pure cafestol (mp found 150 C, lit. 152-155 C) was obtained. Then 1.05 g (0.0033 mol) of the above product was esterified with 1 g (0.0033 mol) fatty acid chlorides following the procedure described by Kaufmann and Hamsagar (2). The fatty acid chlorides were prepared from coffee oil fatty acids using phosphorus trichloride according to the procedure of Dufek et al. (4). Another 1 g sample of cafestol was esterified with 2 g fatty acid chlorides to obtain a "diester." Similarly 1 g samples of the total unsaponifiable matter were esterified with 1 g and 2 g fatty acid chlorides, respectively. Preliminary tests have shown that an esterification time of 72 hr at room temperature resulted in the formation of a monoester containing less than 5% free fatty acids. The formation of a "diester" with less than 10% free fatty acids required an incubation at 40 C during 120 hr. All these experiments were carried out in a nitrogen atmosphere.

The various esters thus obtained were added to the triglycerides prepared from coffee oil fatty acids in a proportion of 1:5, and the softening points of the mixtures were determined (5). The results are shown in Table I.

It may be seen that none of the additions produced an appreciable effect on the softening point of the mixtures. It appears therefore that the low softening point of the original coffee oil is due to some other factor or to a combination of several factors. One of these may be the presence of carbohydrate compounds in the coffee oil, indicated by the detection of small amounts of reducing sugars in the aqueous phase remaining after the saponification of the oil and extraction of the liberated fatty acids. In view of the complex composition of the coffee oil, a reproduction of the original mixture would obviously be rather difficult.

On the other hand a mixture of re-esterified fatty acids and monoesters of cafestol showed, when subjected to the Wesson treatment, a behavior similar to that of the original coffee oil. This was demonstrated as follows: To 10 g of the triglycerides, 20% of the monoester of cafestol was added and the Wesson procedure applied to the mixture. To 9 g of the resulting "neutral oil" 1 g pure oleic acid was added and the Wesson treatment repeated three times, restoring the initial acidity after each treatment by the addition of oleic acid. There was a successive decrease of the "neutral oil" yield amounting each time to 1.8-2%. Similar results were obtained when employing mixtures of triglycerides and 20% of the esterified total unsaponifiable matter. As pointed out in our previous communication (1), a cottonseed oil with 10% free fatty acids subjected to a similar procedure showed neutral oil losses amounting only to a few tenths of a per cent after each Wesson treatment.

The above results seem to corroborate our earlier assumption that the presence of the monoesters of cafestol and of other alcoholic components of the unsaponifiable

TABLE I

Softening Points of Mixtures of Triglycerides of Coffee Oil Fatty Acids and Added Compounds

Sample	Softening point, C
Original coffee oil	9.5
Triglycerides of coffee oil fatty acids-triglycerides	37.0
Triglycerides + 20% of cafestol monoester	36.0-36.5
Triglycerides + 25% of cafestol monoester	35.5-36.0
Triglycerides + 20% of cafestol "diester"	36.0-36.2
Triglycerides + 20% of "monoester" of total unsaponifiable matter	34.5-35.0
Triglycerides + 20% of "diester" of total unsaponifiable matter	36.2-36.5
Triglycerides + 10% of total unsaponifiable matter	36.0

matter is responsible for the high refining loss of the coffee seed oil. The soap formed during the Wesson treatment facilitates a partial saponification or emulsification of the neutral oil by the excess alkali in the presence of cafestol monoesters, which is still more pronounced during the commercial refining process.

The effect of the unsaponifiable matter on the softening point of the coffee oil could not be substantiated, and the reason for its low softening point remains unexplained.

LEOPOLD HARTMAN
Faculty of Food Technology
State University of Campinas
Campinas, SP, Brazil
REGINA C.A. LAGO
Centro de Tecnologia Agrícola e Alimentar
Rio de Janeiro, GB, Brazil

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Erratum

In Appendix II to the "Report of the Instrumental Techniques Committee, AOCS, 1971-72" (*JAOCS*, 49:431A [1972]), a sentence is missing in the first complete paragraph on p. 436A. The entire paragraph is printed correctly below.

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Filter the melted fat if it is not clear. Fill the sample tubes with fat (1.5-1.8 g) and place them in the metal block in a bath of 60 C. After 30 min at 60 C, the first tube (reference oil) is placed in the magnet, through which air of 60 C is blown. The average of two readings at the digital voltmeter is used for the calculation. At 60 C the reference oil is measured twice at the beginning and the end of the series. When two values deviate less than 1.5% the average is taken for the calculation. At a higher value all the measurements at 60 C must be repeated (instrumental instability). After the first measurement of the reference oil the other samples (including again the reference oil) are measured in a fixed sequence and placed in a bath of 0 C every minute and a half. After 90 min stabilization, the sample tubes are transferred every minute and a half in the same sequence as before in a bath at the first measuring temperature (10 C) (Note 7). After 30 min the signals are measured at 10 C (air through the magnet also 10 C) and the samples are then placed in a bath at the next measuring temperature. Repeat the procedure for all the measuring temperatures. If by mistake the temperature of the bath exceeds the required temperature, it must not be cooled because the melted part of the fat will not crystallize again. Maintain the wrong temperature and report the NMR values at that temperature.