Tetramethylguanidine Catalyzed Transesterification of Fats and Oils: A New Method for Rapid Determination of Their Composition

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A new method for the rapid preparation of methyl esters from vegetable oils and fats, using tetramethylguanidine as catalyst, has been developed. This method is compared with the traditional method (Ce 2-66, using 20% BF_3 in methanol) and that proposed by Hartman and Lago (using NH_4Cl/H_2SO_4 in methanol). It is shown that the new method produces the methyl esters in quantitative yields and has certain advantages, as it is simpler, cheaper and does not result in isomerization of the fatty acids.

TABLE 1

Percentages of Free Acids and Iodine Value of the Oils

Oil type	% Free acids	Iodine value
Degummed palm	6.70	75.2
Refined palm	0.28	59.2
Degummed soybean	1.11	133.1
Refined soybean	0.28	132.9
Degummed peanut	1.67	100.7
Refined peanut	0.21	101.1

The preparation of methyl esters for the determination of the fatty acid composition of fats and oils may be achieved by alkali or acid catalyzed methanolysis of the lipids or by their saponification, followed by esterification of the fatty acids (1). Alkali catalyzed methanolysis probably is the mildest method available, but it is limited to lipids with low acid values, while acid catalyzed methanolysis is a time consuming procedure (2). Saponification followed by acid catalyzed esterification with methanol is, therefore, considered to be the most suitable method (3), but may cause isomerization of the double bonds of unsaturated fatty acids (4).

Guanidines were shown to be excellent catalysts for the base catalyzed methanolysis and ethanolysis of lipids (5,6). They can be insolubilized on organic polymers, allowing the semicontinuous transesterification of vegetable oils in a fixed bed or fluidized bed reactor (7). Guanidine and its alkyl derivatives are also suitable for preparing the methyl esters of fatty acids for the rapid determination of the composition of fats and oils (8). In this paper we wish to describe the experimental procedure and show that the new method has certain advantages over the traditional method (Ce 2-66) (9) and that proposed by Hartman and Lago (2).

EXPERIMENTAL PROCEDURES

The percentages of the free acids and the iodine values of degummed and refined commercial palm, soybean and peanut oils were determined by AOCS methods Ca 2a-47 and Cd 1-25, respectively (9). The methanolysis reagent was prepared by dissolving one part of commercial tetramethylguanidine (Eastman Kodak) in four parts (v/v) of methanol (Merck, p.a.). The methanolysis was performed by mixing 250 mg of the oil with two ml of the transesterification reagent in a 30-ml test tube, which was closed and heated in a boiling water bath for two min. After the reaction, 20 ml of a saturated sodium chloride solution were added and the methyl esters extracted with six or eight ml of light petroleum ether (40/60). The organic phase was separated, and the petroleum ether was evaporated at room temperature in a stream of nitrogen.

The yield of the esters was calculated from the weight of the oil sample and its product, determined on an analytical balance. Its purity was examined by ^{1}H-NMR spectroscopy (Varian T60) in carbon tetrachloride (Merck, p.a.) with tetramethylsilane as internal standard. A possible *trans*-isomerization of the fatty acids during the methanolysis was investigated by infrared spectroscopy (Jasco A 202), using a 0.05-mm optical path liquid cell with potassium bromide windows. The gas chromatographic analysis was performed on a CG 35 (Instrumentos Cientificos) chromatograph, equipped with a thermal conductivity detector using a 2.2-m × 5-mm column of 17% DEGS on Chromosorb W 80-100 mesh. Helium at a rate of 50 ml min^{-1} was used as a carrier gas; the temperatures of the injection block, the column and the detector were 240, 190 and 270°C, respectively. The percentages of the fatty acids were determined with an automatic integrator, CG-100 (Instrumentos Cientificos).

RESULTS AND DISCUSSION

The percentages of the free acids and the iodine values of the oils are shown in Table 1. The degummed palm oil has a very high content of free acids and a low iodine value which is further reduced in the refined palm oil. The methanolysis of these oils in the presence of tetramethylguanidine is complete, furnishing the methyl esters in more than 99% yield. Their ^{1}H-NMR spectra show no impurities of glycerides between 4.02 and 4.40 ppm, even when amplified 100 times, which proves that their content is lower than 1% (w/w). The infrared spectra of the methyl esters show no absorption at 970 cm^{-1}, proving that tetramethylguanidine does not induce any *trans*-isomerization of the double bonds of the unsaturated fatty acids. This method can detect the methyl ester of elaidic acid in concentrations as low as 0.025 mol/l (0.75% w/w).

Gas chromatographic analysis of the methyl esters shows that tetramethylguanidine is not extracted to the organic phase. The percentages of the methyl esters obtained by the proposed method are compared, in Table 2, with those of the methyl esters obtained by the traditional method (Ce 2-66) (9) and by that used by Hartman and Lago (2). The values found for the proposed method and for the Ce 2-66 method are normally within ±0.3%, which is the standard deviation of the gas

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TABLE 2

Gas Chromatographic Analysis of the Methyl Esters[a]

		% Composition of fatty acids							
Oil type	Method[b]	12:0	14:0	16:0	18:0	18:1	18:2	20:0	18:3
Degummed palm	1	0.1	0.5	31.3	3.9	35.3	26.2	-	2.5
	2	0.1	0.4	30.7	3.8	37.9	24.8	-	2.3
	3	0.1	0.4	30.8	4.5	35.2	26.4	-	2.5
Refined palm	1	-	0.9	44.6	5.3	39.4	9.7	-	-
	2	-	0.8	44.3	5.4	39.9	9.4	-	-
	3	-	0.9	44.4	5.5	39.6	9.5	-	-
Degummed soybean	1	-	traces	12.7	3.6	22.5	54.7	traces	6.5
	2	-	-	12.9	3.8	22.7	53.4	-	7.1
	3	-	traces	12.4	3.5	22.4	55.2	traces	6.4
Refined soybean	1	-	traces	12.9	2.5	22.8	55.5	traces	6.3
	2	-	-	13.0	2.6	23.1	54.4	-	6.9
	3	-	traces	12.7	2.8	22.9	55.7	traces	5.8
Degummed peanut	1	-	-	13.3	2.9	43.8	38.4	1.5	-
	2	-	-	13.6	3.2	43.9	37.5	1.9	-
	3	-	-	13.6	3.1	43.3	38.1	1.9	-
Refined peanut	1	-	-	14.0	3.1	42.8	39.2	0.9	-
	2	-	-	14.1	3.2	42.6	39.0	1.0	-
	3	-	-	13.9	3.3	42.8	38.8	1.2	-

[a] Average of three independent determinations; standard deviation better than ± 0.3%.

[b] Method 1, Ce 2-66; Method 2, NH_4Cl/H_2SO_4 in methanol; Method 3, tetramethylguanidine in methanol.

chromatographic analysis under the conditions used. The method used by Hartman and Lago gives some slightly different values, mostly for linoleic acid, which may be due to some decomposition during the procedure.

The reaction conditions for the tetramethylguanidine catalyzed transesterification are not critical as long as a large excess of methanol is present to shift the equilibria to the methyl esters. The catalyst concentration may be lowered to 5% (v/v) without affecting the results, and the ester composition is not changed if the reaction is stopped after one min or extended to 60 min at 100°C. The reaction temperature may be lowered to 60°C with only small increases in reaction time. On the other hand, the reaction conditions given in the experimental section are the most secure to avoid errors by inexperienced operators.

Tetramethylguanidine is a strong organic base (pKa = 13.6) which catalyzes the transesterification by deprotonation of the reacting alcohol, forming the guanidinium ion in an equilibrium. Free acids react with the guanidine to give guanidinium carboxylate, which stays in solution and can be attacked by the alcohol, forming the corresponding ester. As the alcohol is used in excess the equilibria are dislocated to the esters, which are obtained in quantitative yield.

Other guanidines also show activity in the transesterification of fats and oils. The best catalyst is unsubstituted guanidine, but it has to be prepared from guanidinium chloride by reaction with stoichiometric amounts of sodium alcoxide in alcohol and is not very stable in alcoholic solution.

We, therefore, believe that tetramethylguanidine is most indicated for the rapid analysis of fats and oils, as it is commercially available and its solution in methanol is stable, under anhydrous conditions, for several years. It is inexpensive (the reagent used for each analysis costs approximately US$ 0.05). The reaction is rapid, with the total analysis done in approximately 10 min, and very mild, as no isomerization of the unsaturated fatty acids is observed. It is the first base which can be used for the complete methanolysis of oils with high acid values, as it forms a soluble acid-base complex with the free acids which reacts with the methanol to form the corresponding ester.

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