unit too high. While this error may be considered negligible for high concentrations of epoxy and cyclopropenoid materials, it assumes major significance at low concentrations. Further investigation is being directed toward the elimination of the effect of these trace interfering substances so that the stepwise titration method may be applied to the accurate determination of the cyclopropenoid constituents in cottonseed oils.

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Methyl Azelaaldehydate Purification Via the Bisulfite Compound

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Abstract

Methyl azelaaldehydate was obtained at 99.8% purity with 82.5% recovery from the ozonolysis products of commercial methyl oleate by separation as the sodium bisulfite addition compound, regeneration with 10% NaOH, and distillation.

Introduction

PREVIOUS PAPERS from this laboratory (2) have reported the ozonolysis of unsaturated fatty acid derivatives. Separation and purification of individual aldehydic ozonolysis products from certain impurities have presented difficulties because of similarity in physical properties, particularly boiling points. Methyl azelaaldehydate (MAZ) can be obtained in high yield and is an especially versatile intermediate (3). It was sought in a high state of purity for certain studies now under way in this laboratory. Purification of aldehydes through their sodium bisulfite addition compounds is a useful procedure (1) because of the ease of separation of the derivative and of subsequent regeneration of the aldehyde. This paper reports the application of this method to the purification of MAZ from the complex mixture obtained by the ozonolysis of commercial methyl oleate.

Experimental

Reductive decomposition of the ozonolysis product from pure methyl oleate gives two compounds, MAZ and pelargonaldehyde. These compounds are easily separable by simple distillation because the difference in boiling points is about 50°. However, commercial methyl oleate contains a number of other components (Table I), so that the ozonolysis mixture contains saturated esters—methyl laurate, myristate, palmitate, and stearate—as well as aldehydes and aldehyde esters derived from the unsaturated esters. Positional isomers of the unsaturated esters like palmitoleic, give rise to homologs of the desired products. In addition,

TABLE I

Typical Analysis of Commercial Methyl Oleate [a]

Methyl ester	Percentage
Laurate	Trace
Myristate	2.5
Palmitate	5.0
Palmitoleate	3.5
Stearate	1.0
Oleate	79.0
Linoleate	8.0
Linolenate	1.0

[a] Swift and Company, Technical Products Department, Hammond, Ind.

[1] No. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.

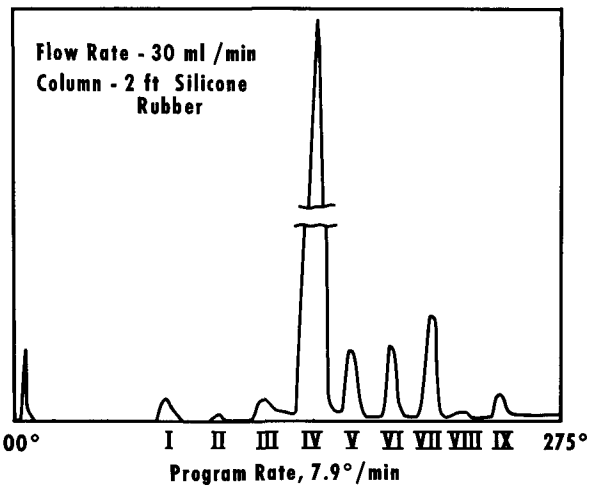

FIG. 1. GLC of Fraction 2, crude methyl azelaaldehydate.

there are present acetals, condensation and oxidation products, and esters like dimethyl azelate, which are formed by decomposition of methoxy hydroperoxides over certain hydrogenation catalysts (2c).

Distillation through a simple Vigreux column of the products obtained from commercial methyl oleate gave three fractions. Fraction 1 consisted of pelargonaldehyde, homologous aldehydes, their acetals, and lower esters. Fraction 2 contained crude MAZ, some homologous aldehyde esters, dimethyl azelate and some of its homologs, acetals, and esters of myristic and palmitic acids. The residue contained esters of higher fatty acids and condensation products. A typical GLC analysis is shown in Figure 1. The identity of the main peaks and the relative quantities are shown in Table II. Fraction 2 contained 79% MAZ and its dimethyl acetal, 4.4% dimethyl azelate and C_{10} aldehyde ester, 4.7% C_{11} aldehyde ester, 6.9% methyl myristate, and lesser quantities of other compounds.

Isolation of MAZ was effected by treatment of Fraction 2 with an aqueous-methanolic saturated solution of sodium bisulfite. The crude crystalline addition compound was removed by filtration and washed with ether to remove C_{14} and C_{16} fatty acid methyl esters, diesters, and acetals. Ether was more effective than ethanol, pentane-hexane, or methylene chloride for washing the adduct. The purified adduct was treated with 10% NaOH solution and the regenerated aldehyde ester distilled. Figure 2 depicts the GLC of the regenerated MAZ. The analyses of regenerated MAZ and of distilled product, 99.8% pure, are

also shown in Table II. In a typical experiment, 692 g of Fraction 2 gave 448 g of pure MAZ, representing a recovery of 82.5%. The overall yield of MAZ depends on the ozonolysis procedure and subsequent treatment before distillation. In the laboratory we have realized yields of 88% C_9 aldehyde ester and acetal ester, corresponding to peak IV in Figure 2 and Table II, based on C_9 double bonds and assuming the absence of oleate positional isomers. Thus a 73% overall yield of pure MAZ from commercial methyl oleate is possible.

Commercial methyl oleate was ozonized, and the products were reductively decomposed in the pilot plant and will be reported elsewhere. The product was distilled through a Vigreux column to give Fraction 1, boiling range 28–94C at 3 mm, and Fraction 2, boiling range 65–118C at 0.5 mm. Fraction 2 (692 g, 79% MAZ) was added slowly with vigorous stirring to a saturated solution of sodium bisulfite: 576 g sodium metabisulfite dissolved in 1,000 ml of water to which 840 ml of absolute methanol was added (4). After stirring 3 hr at room temp, the addition compound was removed by filtration. The adduct was slurried with ether three times and filtered. MAZ was regenerated by shaking the bisulfite adduct with 1 liter each of ether and 10% NaOH solution. The ether removed the MAZ from the aqueous layer, displacing the equilibrium in the direction of the free aldehyde and minimizing possible saponification of the ester and condensation of the aldehyde functions. The basic solution was extracted several times to remove all the aldehyde ester. The combined ether extracts were washed with water until neutral and dried over anhydrous calcium sulfate. The solvent was then stripped off and the residue distilled through a 15-cm helix-packed column. The yield of MAZ was 448 g, 82.5% recovery, 99.8% purity by GLC analysis.

TABLE II
GLC Analyses of Methyl Azelaaldehydate Fractions

Peak	Compound	Product analyzed, wt %		
		Fraction 2	Regenerated MAZ	Distilled MAZ
I	Pelargonaldehyde	1.4	2.3	0.0
II, III	Unknowns	2.4	0.2	0.0
IV	MAZ	79.0[a]	90.3	99.8
V	Dimethyl azelate, C-10 aldehyde ester	4.4	1.5	0.2
VI	C-11 aldehyde ester	4.7	5.6	0.0
VII	Methyl myristate	6.9	0.0	0.0
VIII	C-13 aldehyde ester	0.3	0.0	0.0
IX	Methyl palmitate	1.0	0.0	0.0

[a] This figure includes MAZ dimethyl acetal.

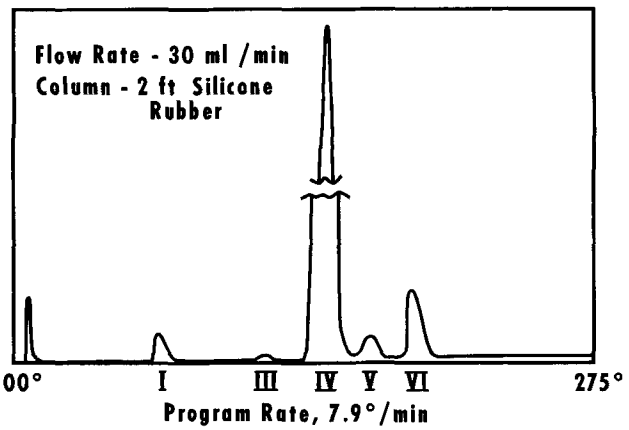

FIG. 2. GLC of regenerated methyl azelaaldehydate.

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Chemical Reactions Involved in the Catalytic Hydrogenation of Oils. I. Characteristics of the Volatile By-Products

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Abstract

The gas chromatogram of the isolated volatile by-products I, which were produced during catalytic hydrogenation of soybean oil is quite different from that of the isolated volatile by-products II, which were produced by a duplicate sample of the same oil subjected to the same conditions of hydrogenation with no nickel catalyst. Many of the peaks on these two gas chromatograms had different retention times. Furthermore, catalytic hydrogenation of I did not alter its gas chromatogram to equal that of II. The side reactions which may take place when an oil is treated under hydrogenation conditions are, therefore, affected by the presence of nickel catalyst.

The carbonyl compounds in the volatile by-products which were formed during catalytic hydrogenation were converted into their 2,4-dinitrophenylhydrazones and then fractionated into dicarbonyls, saturated aldehydes, methyl ketones, 2-enals, and 2,4-dienals. Upon regeneration, the dicarbonyls, 2-enals, and 2,4-dienals did not yield the characteristic hydrogenation flavor, while the saturated aldehydes and methyl ketones did. The characteristic hydrogenation flavor would seem to be at least partially contributed by saturated aldehydes and methyl ketones.

Introduction

CATALYTIC HYDROGENATION is considered by many oil chemists as the most outstanding discovery in oil and fat processing during the past sixty years (1). It is estimated that 3 billion lb of hydrogenated fats are consumed in foods each year in the U.S. The main chemical reactions involved in hydrogenation, such as

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