Phenylstearic Acids and Related Compounds

Isolation of 17-, 16-, 15- and 13-Phenyl Isomers[1]

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ABSTRACT

Alternate use of acetone and hexane as crystallizing solvents permitted the isolation of the 17-, 16-, 15- and 13-phenyl isomers of phenylstearic acid and related compounds made by the Friedel-Crafts reaction. The pure crystalline isomers were used as reference compounds to correct the distribution curve based on alkyl aryl ketones formed by chromic acid oxidation.

INTRODUCTION

Phenylstearic acid made from oleic acid and benzene by the Friedel-Crafts reaction is a viscous oil. It has been shown by gas liquid chromatography (GLC) of the alkyl aryl ketones obtained by chromic acid oxidation to be a mixture of 12 positional isomers. Some of these isomers of phenylstearic acid, and of related compounds, were isolated in a crystalline state, in small amount (2).

The composition of phenylundecanoic acid obtained by the Friedel-Crafts reaction of benzene with 10-undecylenic acid has been investigated by capillary gas chromatography and mass spectrometry of the methyl ester. It was found to consist of 11.6% of a mixture of the 5- and 6-phenyl isomers, and 15.1%, 17.0%, 21.0% and 35.3% of the 7-, 8-, 9- and 10-isomers, respectively (5). In contrast methyl phenylstearate is of higher molecular weight (375 compared to 276), contains 12 rather than 6 isomers and separation by GLC has been possible only to a limited extent (2).

An improvement in the factional crystallization process, the alternate use of acetone and hexane as crystallizing solvents, facilitated the isolation of the 17-, 16- and 13-phenyl isomers of phenylstearic acid. The pure crystalline isomers were used as reference compounds to correct the distribution curve based on alkyl aryl ketones formed by chronic acid oxidation (1). A discrepancy between the relative amounts of isomeric phenylstearic acids and the relative amounts of alkyl aryl ketones derived therefrom by chromic acid oxidation might be expected as was observed in the case of phenyldodecanes (3,4).

EXPERIMENTAL PROCEDURES

Phenylstearic acid, phenyloctadecanol and phenylstearonitrile were prepared from oleic acid, oleyl alcohol and oleonitrile as previously described (2). Methyl phenylstearate and phenyloctadecyl acetate were made by esterification of phenylstearic acid and phenyloctadecanol, respectively.

Isolation of Crystalline Isomers

The scheme for the isolation of crystalline isomers is shown in Figure 1. It differs from a previous one (2) and features alternate use of acetone and hexane as the solvent in the fractionation of methyl phenylstearate. Steps in the separation were followed directly by GLC. This procedure was used also with phenyloctadecyl acetate. It was not very successful with phenylstearonitrile. In most cases the yield of isolated crystalline isomer was 50-80%, based on the amount of the isomer present in the original mixture.

Methyl 17-Phenylstearate

A solution of 100 g of methyl phenylstearate in 400 ml of acetone crystallized twice from acetone at -28 C and twice again from 400 ml of hexane at -28 C gave 3.6 g methyl 17-phenylstearate mp 42.2-42.9 C, yield 59%, purity by GLC analysis 99.8%.

Methyl 16-Phenylstearate

The acetone filtrates from the isolation of methyl 17-phenylstearate were evaporated to dryness. Five crystal-

TABLE I

Chromic Acid Oxidation of Mixtures of Crystalline Isomers

Mixture	Composition by weight, %	Composition by GLC: Esters, mole %	Composition by GLC: Acetophenone homologs, mole %
Phenyloctadecyl acetate			
13-phenyl		62.4	$63.2C_6H_{13}COPh$
15-phenyl		37.6	$36.8C_4H_9COPh$
Methyl phenylstearate			
13-phenyl		36.7	$36.5C_6H_{13}COPh$
15-phenyl		63.3	$63.5C_4H_9COPh$
Methyl phenylstearate			
17-phenyl	46.53	45.8	$69.8CH_3COPh$
15-phenyl	53.47	54.2	$30.2C_4H_9COPh$
Methyl phenylstearate			
17-phenyl	31.34	31.2	$58.4CH_3COPh$
16-phenyl	32.65	31.1	$17.4C_3H_7COPh$
15-phenyl	36.01	37.8	$24.3C_4H_9COPh$

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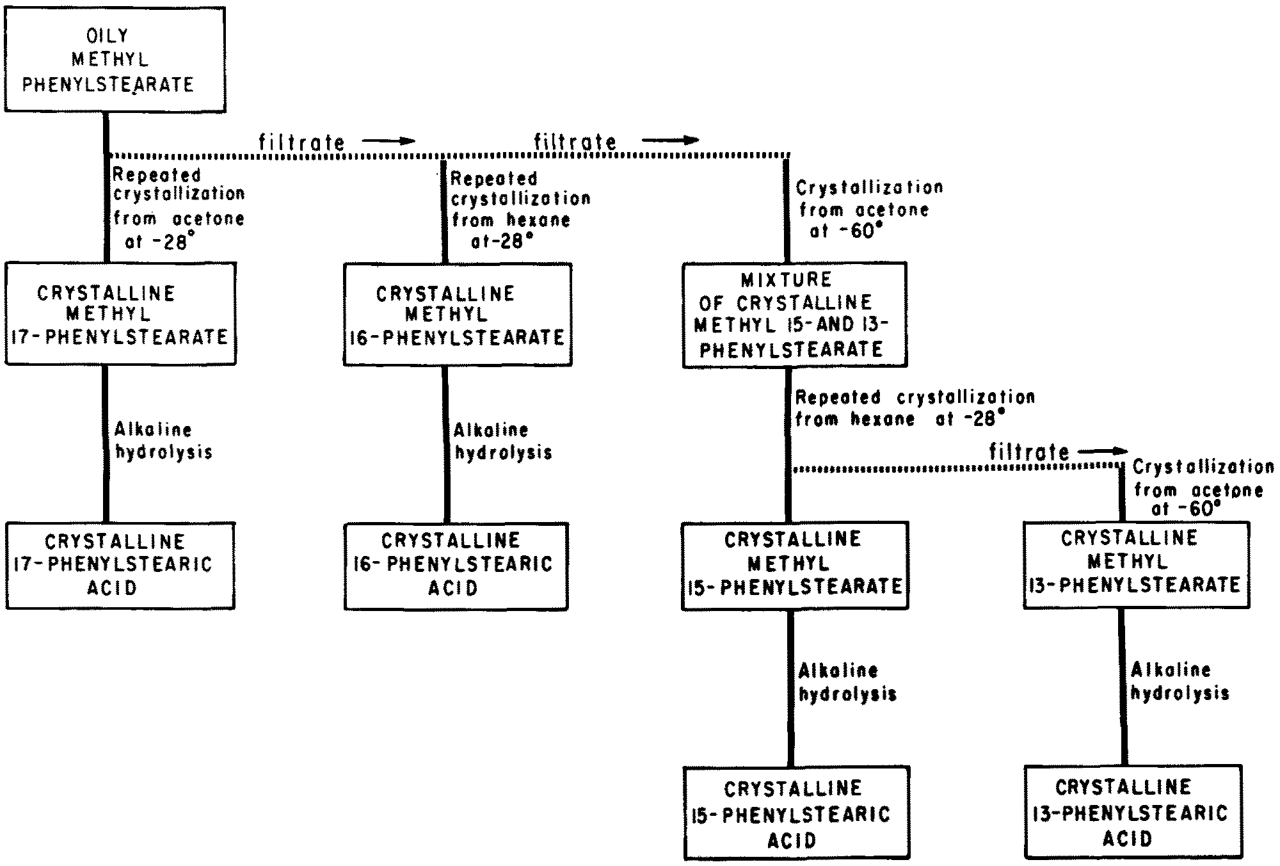

FIG. 1. Separation of crystalline isomers.

lizations from 300 ml of hexane at -28 C gave 2.3 g methyl 16-phenylstearate mp 30.8-31.5 C, yield 64%, purity 98.9%.

Methyl 13- and 15-Phenylstearate

The hexane filtrates from the isolation of methyl 16-phenylstearate were evaporated to dryness. Crystallization from 400 ml of acetone at -60 C gave the crystalline mixture indicated in Figure 1.

Methyl 15-Phenylstearate

The above mixture containing principally the 13- and 15-phenyl isomers, crystallized eight times from 200 ml of hexane at -28 C gave 2.6 g methyl 15-phenylstearate mp 43.6-44.5 C, yield 55%, purity 98.5%.

Methyl 13-Phenylstearate

The first four filtrates from the isolation of methyl 15-phenylstearate were combined and evaporated to dryness. The residue, crystallized 15 times from acetone at -60 C at 100:1 solvent ratio gave 1.5 g methyl 13-phenylstearate mp 25-26.1 C, yield 17%, purity 98.6%. Alkaline saponification gave 13-phenylstearic acid, mp 43.6-45.0 C.

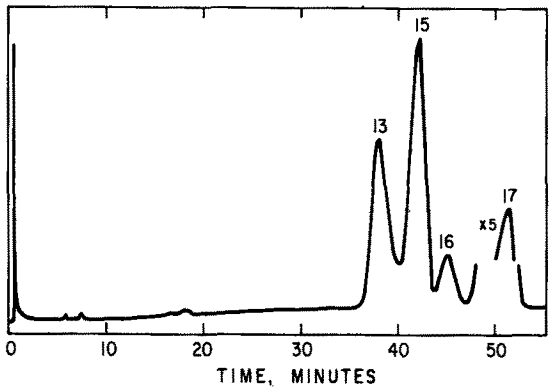

FIG. 2. Chromatogram, first crystallization of methyl phenylstearate from acetone. Numbered peaks indicate position of phenyl group.

17-Phenyloctadecyl Acetate

A solution of 100 g of phenyloctadecyl acetate in 400 ml of acetone crystallized four times at -60 C and four times at -28 C gave 3.1 g 17-phenyloctadecyl acetate mp 34.9-35 C, yield 79%, purity 99.6%.

16-Phenyloctadecyl Acetate

Filtrates from the isolation of the 17-phenyl isomer were combined and evaporated to dryness. Crystallization of the residue eight times from 200 ml of hexane at -28 C gave

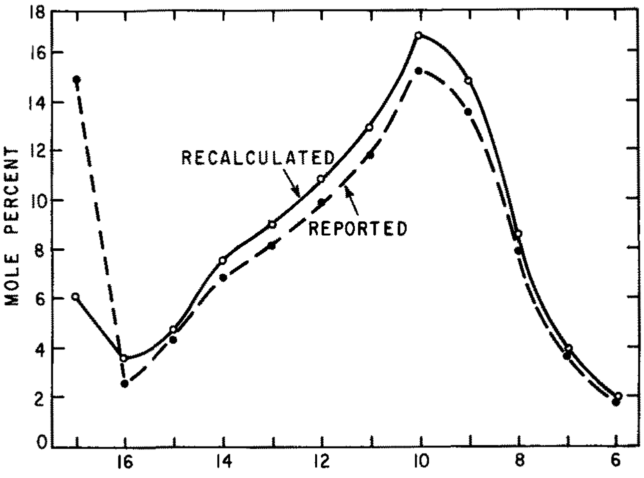

FIG. 3. Distribution of isomeric phenylstearic acids.

TABLE II

Distribution of Isomeric Phenylstearic Acids

Position isomer	Reported	Recalculated	Position isomer	Reported	Recalculated
17	14.9	6.1	11	11.7	12.8
16	2.6	3.6	10	15.1	16.5
15	4.3	4.7	9	13.4	14.7
14	6.8	7.5	8	7.8	8.5
13	8.1	8.9	7	3.6	3.9
12	9.8	10.7	6	1.8	2.0

2.7 g 16-phenyloctadecyl acetate, mp 31.3-31.9 C, yield 61%, purity 98.9%.

15-Phenyloctadecyl Acetate

Filtrates from the isolation of the 16-phenyl isomer were evaporated to dryness. Crystallization of the residue from 400 ml of acetone at -60 C and further crystallization eight times from 200 ml of hexane at -60 C gave 2.8 g of 15-phenyloctadecyl acetate, mp 15.4-16.3 C, yield 51%, purity 99.5%. Alkaline saponification gave 15-phenyloctadecanol, mp 34.4-35.2 C.

13-Phenyloctadecyl Acetate

Filtrates from the isolation of the 15-phenyl isomer were combined and evaporated to dryness. Crystallization of the residue 17 times from 100 ml of acetone at -60 C gave 1.0 g of 13-phenyloctadecyl acetate, mp 5.0-6.1 C, yield 12%, purity 97.8%. Alkaline saponification gave 13-phenyloctadecanol, mp 24.8-25.6 C.

CHROMIC ACID OXIDATION

Chromic acid oxidation of individual isomers or mixtures of isomers obtained in the course of the separation process was carried out as described previously (2).

Gas Liquid Chromatography

The instrument was an F & M Model 810 dual column chromatograph fitted with a commercial 8 ft x 0.25 in. o.d. stainless steel column with 20% silicone gum rubber (SE-30) on Chromasorb P, 60-80 mesh. It was connected to a digital integrator, Model CRS-11 HSB (Infotronics) and printer (Victor Digit-matic). The instrument was operated isothermally at 220 C with a helium flow rate of 60 ml/min. The alkyl aryl ketones were recognized by comparison of their gas liquid chromatography (GLC) retention times with those of reference alkyl aryl ketones.

RESULTS AND DISCUSSION

Acetone as a solvent favored the isolation of the odd isomers, the 17-, 15- and 13-phenyl isomers with the phenyl group located at the odd-numbered C atoms of the fatty acid chain. Figure 2 is the chromatogram of the crude crystals obtained in the first crystallization of the oily methyl phenylstearate from acetone at -28 C, showing how the odd isomers crystallize together. To a lesser extent hexane favored the isolation of the even isomers.

Results from the oxidation of known mixtures of crystalline isomers are shown in Table I. Since binary mixtures of 13- and 15-phenyloctadecyl acetate and methyl 13- and 15-phenylstearate are isolated en route to isolation of the individual isomers it was convenient to compare the composition determined by GLC to the relative amounts of the acetophenone homologs. In both of the cases of Table I there was good agreement. From this evidence it was concluded that acetophenone homologs derived from oxidation of position isomers 6 to 15 inclusive are obtained in amounts proportional to the amounts of parent compounds in the mixture.

Oxidation of the binary mixture of pure crystalline methyl esters 46.53% 17-phenyl, 53.47% 15-phenyl, ratio 0.870 to 1, gave an acetophenone to butyrophenone ratio of 2.31 to 1. The correction factor, converting acetophenone found to methyl 17-phenylstearate present was therefore 0.870/2.31 or 0.377. Similarly the ratio of methyl 16-phenylstearate to methyl 15-phenylstearate in the ternary mixture was 32.65% to 36.01% or 0.907, the propiophenone to butyrophenone ratio 0.716, and the correction factor converting propiophenone found to methyl 16-phenylstearate present was 0.907/0.716 or 1.27. These factors were used to correct the reported values for the 17- and 16-isomers of Table II. All reported values were corrected again to total 100 and then listed as recalculated values.

The previously reported (1) and recalculated values for the distribution of position isomers in oily phenylstearic acid are listed in Table II and graphed in Figure 3.

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