cyclopentylamine from the corresponding β-keto esters are described.

Seven of these have been coupled with 2-methoxy-6,9-dichloroacridine to form analogs of atabrine.

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[Contribution from the Eastern Regional Research Laboratory[1]]

Formation of Isomeric Hydroxy Acids by Sulfation of Oleic Acid

By B. B. Schaeffer, E. T. Roe, J. A. Dixon and W. C. Ault

During sulfation of oleic acid and hydrolysis of the resulting product, formation of monohydroxy acids with the hydroxyl group attached at either the 9- or the 10-carbon position would normally be expected. A study of the sulfation reaction led us to suspect, however, that the mixture of hydroxy acids obtained was considerably more complex than previously indicated.

It has been established[2] that under certain conditions of sulfation the gamma stearolactone is formed. This would seem to be conclusive evidence that during the process the substituent group has migrated to the gamma position with respect to the carboxyl group. Our investigation did not disclose any definite information regarding the mechanism involved in the shift. While this work was in progress, a paper[3] dealing with olefins came to our attention which reports that mixed alcohols are formed by sulfation, indicating probable migration of the hydroxyl group.

To determine whether hydroxy acids other than those formed by substitution in the 9- and 10-carbon positions are obtained by the sulfation and hydrolysis of purified oleic acid, the oxidation products of the mixed hydroxy acids were investigated.

It is difficult to separate monohydroxy acids from unreacted oleic acid by crystallization without removing isomeric hydroxy acids during purification. To avoid these losses, the acids in the crude reaction product were converted to methyl esters, and the mixed methyl hydroxystearates thus obtained were fractionally distilled under high vacuum. The esters were oxidized with nitric acid and steam distilled yielding volatile and non-volatile fractions.

Obviously, if only 9- and 10-monohydroxystearic acids were present in the hydrolysis product, oxidation would produce 8-, 9- and 10-carbon monobasic acids and the 8-, 9- and 10-carbon dibasic acids. If the hydroxyl group were closer to the carboxyl group, longer-chain monobasic acids and shorter-chain dibasic acids would result. On the other hand, if the hydroxyl group were located farther away from the carboxyl group than the 10-carbon position, oxidation would produce shorter-chain monobasic acids and longer-chain dibasic acids.

Fractionation of the methyl esters prepared from the non-volatile, water-insoluble portion of the oxidation products showed that this portion had contained 14-, 15- and 16-carbon dibasic acids, the chain lengths of which were estimated from refractive index data, saponification equivalents and cryoscopic molecular weights given in Table I. The dimethyl ester of 1,14-tetradecanedicarboxylic acid was isolated from one of these fractions. This compound could have been formed only as the result of a shift away from the carboxyl group. The possibility of its formation from a saturated acid need not be considered because such acids were removed by fractional distillation before the material was oxidized. Cleavage of a hydroxy acid at the 16-carbon position without shifting would have given a hydroxy dibasic acid instead of the unsubstituted compound.

Table I

Distillation of Methyl Esters of Steam-nonvolatile Water-insoluble Fatty Acids

Fraction No.	Range b. p., °C. at 1.5–2 mm.	Distilland 35.6 g. Recovery, g.	$n^{50}D$	Sapn. equiv.	Mol. wt., cryoscopic	No. C atoms in acid calcd. from Sapn. equiv.	Mol. wt.
I	58–80	2.0	1.4147	181.8	183.0	9.7	9.8
II	80–105	4.1	1.4190	177.7	196.0	..	..
III	105–120	6.4	1.4255	140.7	223.0	..	..
IV	120–140	9.2	1.4317	133.6	244.5	..	..
						twice the sapn. equiv.	
V	140–159	5.1	1.4352	145.7	281.0	14.4	13.7
VI	159–171	6.5	1.4377	153.4	297.0	15.5	14.7
Residue	.....	2.1	1.4462	146.7	322.0	..	..

Experimental

Oleic Acid.—A purified oleic acid was prepared by fractional distillation and crystallization of commercial oleic acid.[4] The iodine value (Wijs, one-half hr.) of this material was 88.2. Its melting point was 11.9–12.4°. Spectrophotometric examination showed 0.2% linoleic acid, 0.1% linolenic acid, 0.005% arachidonic acid, 0.3% diene conjugated acids and 0.006% triene conjugated acids. Calculations based on these data indicate the product to be approximately 97% oleic acid.

Methyl Monohydroxystearate.—The oleic acid was sulfated at 10° with a three-to-one molar ratio of sulfuric

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

(2) A. A. Shukoff and P. I. Schestakoff, *J. Russ. Phys.-Chem. Soc.*, **35**, 1 (1903); *ibid.*, **40,** 830–839 (1908); P. W. Clutterbuck, *J. Chem. Soc.*, **125,** 2330–2333 (1924).

(3) P. Baumgarten, *Ber.*, **76B**, 213–218 (1943); **75B**, 977–983 (1942).

(4) J. B. Brown and G. Y. Shinowara, This Journal, **59**, 6 (1937).

acid (95.5%) to oleic acid.[5] The sulfated product was hydrolyzed with alcoholic potassium hydroxide, reacidified with dilute sulfuric acid, and converted to methyl esters. The yield was 86.2%. These esters were distilled under reduced pressure through a twelve-inch Vigreux column. The methyl monohydroxystearate fraction (yield, 34.9% of theoretical), which distilled at 170°, and a pressure of 0.22 mm., solidified to a white crystalline material having the following properties: melting point, 29–31°; iodine value, 2.3; acid value, 2.6; saponification value, 179.4 (theoretical, 178.4); hydroxyl, 4.88% (theoretical, 5.41%).

Oxidation.—The methyl monohydroxystearate (70 g.) was oxidized by the method described by Hall and Reid[6] using 280 cc. of concentrated nitric acid and 0.07 g. of ammonium vanadate (*meta*). Subsequent steam distillation yielded two main fractions, a volatile portion containing most of the monobasic acids and a non-volatile portion containing the dibasic acids and the longer-chain monobasic acids. Each of these fractions was further divided into water-soluble and water-insoluble portions.

All of these fractions were examined and evidence was found for the presence of considerable quantities of short chain monobasic and dibasic acids, but these could conceivably have been formed by oxidative degradation. Consequently only the results obtained by the detailed examination of the non-volatile, water-insoluble portion are presented.

Non-volatile, Water-insoluble Portion.—The solid acids were filtered from the cold solution and washed, yielding 34.5 g. of air-dried solid. This was converted to the methyl esters, and distilled at 1.5–2 mm. Six fractions were taken. Data regarding the recovery of the fractions and their analyses are shown in Table I. Comparison of saponification equivalents with molecular weights obtained by the cryoscopic method indicates that the composition of the higher boiling fractions was quite different from that of the lower boiling fractions. For example, fraction I was essentially monobasic, whereas fractions V and VI were composed almost completely of dibasic material. Since fraction I consisted almost exclusively of monobasic esters derived from acids having an average chain length of nearly 10 carbon atoms, it seems reasonable to assume that fractions III and IV contained appreciable amounts of monobasic acids having a chain length above 10 carbon atoms.

The data indicate that fractions V and VI consisted almost exclusively of dibasic acids having a chain length of about 14 to 16 carbon atoms. This was confirmed by the isolation of the dimethyl ester of 1,14-tetradecanedicarboxylic acid from fraction VI. After two crystallizations from petroleum ether, 4.9 g. of this fraction yielded 1.8 g. of a white crystalline solid, m. p. 49.5–50.3°. The dimethyl ester of 1,14-tetradecanedicarboxylic acid is reported to melt at 51.6°.[7] *Anal.* Calcd. for $C_{18}H_{34}O_4$: C, 68.74; H, 10.89; mol. wt., 314.4. Found: C, 69.06; H, 10.81; saponification equivalent, 157.2, corresponding to a mol. wt. of 314.4.

The close agreement of the saponification equivalent and cryoscopic molecular weight of fraction I indicates that this material is the corresponding methyl ester of a C_{10} monocarboxylic acid. The refractive index, $n^{20}\text{D}$ 1.4268, of this fraction plotted on a curve for the normal methyl esters of the acetic acid series gives a value in close agreement with the number of carbon atoms determined by saponification equivalent and cryoscopic molecular weight.

The intermediate fractions, II, III and IV are evidently mixtures of methyl esters of mono- and dicarboxylic acids, corresponding to monocarboxylic acids of 10 carbon atoms or higher and dicarboxylic acids of 13 carbon atoms or lower. The distillation temperature and the values for saponification equivalents and cryoscopic molecular weights of these fractions support this statement. Attempts to separate the fractions further by crystallization were not successful.

Summary

Hydroxy acids resulting from the sulfation and subsequent hydrolysis of oleic acid were oxidized with nitric acid. Esters of dibasic acids having more than 10 carbon atoms were found by fractionation of the methyl esters of the steam-non-volatile, water-insoluble portion. The dimethyl ester of 1,14-tetradecanedicarboxylic acid was isolated and identified. Esters of monobasic acids longer than decanoic appeared to be present. The sulfation of oleic acid leads not only to 9- and 10-hydroxystearic acids but also to other isomeric hydroxy acids.

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(5) Complete details of the sulfation procedure are described in a paper now in preparation on the sulfation of oleic and linoleic acids.

(6) W. P. Hall and E. E. Reid, THIS JOURNAL, **65**, 1468 (1943).

(7) P. Chuit, *Helv. Chim. Acta*, **9**, 264–278 (1926).

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY,[1] PHILADELPHIA, PENNSYLVANIA]

Epoxidation of Oleic Acid, Methyl Oleate and Oleyl Alcohol with Perbenzoic Acid

BY DANIEL SWERN, THOMAS W. FINDLEY AND JOHN T. SCANLAN

The best procedure available for the preparation of 9,10-epoxystearic acid is the reaction of oleic acid with perbenzoic acid.[1a] The perbenzoic acid is usually prepared from benzoyl peroxide, which is not only expensive but inconvenient to use for the preparation of large quantities of perbenzoic acid in the laboratory. Search of the literature revealed a more promising method, namely, the preparation of perbenzoic acid by air or oxygen oxidation of benzaldehyde. Jorissen and his co-workers[2] prepared perbenzoic acid on a small scale in 63% yield by the air or oxygen oxidation of benzaldehyde. Raymond,[3] in a study of the effect of various unsaturated compounds on the inhibition of oxidation of benzaldehyde, demonstrated that pure oleic acid dissolved in a large excess of benzaldehyde could be oxidized by oxygen in the presence of ultraviolet light to form 9,10-epoxystearic acid in good yield. Perbenzoic acid was undoubtedly the oxidizing agent although it was not actually isolated.

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(1a) Bauer and Bähr *J. prakt. Chem.*, **122**, 201 (1929).

(2) Jorissen and van der Beek, *Rec. trav. chim.*, **45**, 245 (1926); **46**, 42 (1927); van der Beek, *ibid.*, **47**, 286 (1928).

(3) Raymond, *J. chim. phys.*, **28**, 480 (1931).