Royal Society for a grant which defrayed part of the cost of the investigation.[4]

Summary

1. Crystalline compounds containing mercury are produced by the action of mercuric acetate in acetic acid solution upon dehydroundecylenic and 9–10 undecinolic acids and upon their ethyl esters.

2. The mercury compounds yield, after treatment with hydrochloric acid, saturated ketonic acids or esters free from mercury. Hydration at the triple bond has thus been effected.

3. Hydration in the case of dehydroundecylenic acid takes place in one direction, but in the case of 9–10 undecinolic acid in the two theoretically possible directions with formation of two isomeric ketonic acids. The ethyl esters behave in the same manner.

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UNSATURATION PHENOMENA OF ACETYLENIC ACIDS AND ESTERS

II. THE REACTION BETWEEN MERCURIC ACETATE AND SOME ACETYLENIC ACIDS AND ESTERS

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RECEIVED MAY 16, 1927 PUBLISHED SEPTEMBER 2, 1927

Two of the present authors have described the isolation of mercury compounds resulting from the action of mercuric acetate upon dehydroundecylenic acid and 9,10-undecinolic acid.[1]

These examples include one case in which the acetylenic bond is at the end of a carbon chain and one in which it occurs along the chain and without any associated hydrogen atom.

In the present investigation we have varied the type of acetylenic acid by studying the action of mercuric acetate upon (a) stearolic acid, (b) ricinolic acid, (c) behenolic acid, (d) methyl behenolate, (e) γ-butinene-α,α-dicarboxylic acid, (f) γ-butinene-α-carboxylic acid.

Preparation of the Acetylenic Acids

A preliminary investigation of the methods of preparation of stearolic, ricinolic and behenolic acids was considered desirable. They are obtained by brominating oleic, ricinoleic and erucic acids, respectively, the

[4] Since this work was completed the authors have noted that Chuit, Boelsing, Hausser and Malet [*Helv. chim. Acta*, 9, 1074 (1926)] describe the preparation of 2-keto-11-undecylic acid by oxidation of undecane-2,11-diol. The melting point recorded by these investigators is 58.5–59.5°.

[1] Myddleton and Barrett, THIS JOURNAL, 49, 2258 (1927).

dibromo acids so formed being then heated with concd. alcoholic or aqueous potassium hydroxide at temperatures between 150 and 180°. The purification of oleic acid and ricinoleic acid is extremely tedious, but it was found unnecessary to arrive at extreme purity in order to obtain the pure acetylenic acids.

(a) **Stearolic Acid.**—The oleic acid for this preparation was derived from olive oil. Analysis had shown that the mixed fatty acids from this oil contain 14.6% of palmitic acid, 10% of linoleic acid and 75.4% of oleic acid.[2]

It was found sufficient to remove all but traces of palmitic acid by converting the total mixed acids into lead salts and extracting the lead oleate and linoleate with ice-cold ether. The acids regenerated by dil. sulfuric acid were converted into the lithium salts by boiling with an excess of lithium carbonate suspended in water. The lithium salts were recrystallized once from dil. alcohol. Oleic acid of sufficient purity was obtained from the less soluble fraction.

(b) **Ricinolic Acid.**—Castor oil used for the preparation of ricinoleic acid was found to contain 8% of stearic acid, 1% of dihydroxy-stearic acid, 7% of linolenic acid and 84% of ricinoleic acid. In view of this analysis the preparation of ricinolic acid employed by Mangold[3] by direct bromination of castor oil followed by treatment of the bromo-glycerides with alkalies was considered unsound.

Stearic acid, therefore, was separated, together with the dihydroxy acid, through the insolubility of their lead salts in dry ether. Ricinoleic and linolenic acids were regenerated from the soluble lead salts and were either converted into lithium salts and recrystallized or into methyl esters and fractionally distilled. The less soluble lithium salt and the methyl ester fraction boiling at 225–227° (10 mm.) gave a sufficiently pure ricinoleic acid.

(c) **Behenolic Acid.**—Rape oil gave a mixture of fatty acids containing 98.8% of erucic acid and traces of lignoceric and arachidic acids. In this case it was found sufficient to brominate the whole of the mixed acids after hydrolysis or to brominate the oil without prior treatment.

(d) **and (e) γ-Butinene-carboxylic Acids.**—γ-Butinene-α,α-dicarboxylic acid and γ-butinene-α-carboxylic acid were prepared in a pure condition by the method described by Perkin and Simonsen.[4]

Action of Mercuric Acetate

The acetylenic compounds were dissolved in glacial acetic acid and warmed on the water-bath with a solution of mercuric oxide in the same

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[2] Myddleton and Barry, "Fats, Natural and Synthetic," Benn, London, **1924**, p. 107.

[3] Mangold, *Monatsh.*, **15**, 307 (1894).

[4] Perkin and Simonsen, *J. Chem. Soc.*, **91**, 821 (1907).

solvent. Reaction proceeded at temperatures between 70 and 100° with deposition of small amounts of mercurous acetate.

The mercury compounds were isolated by cooling the filtered solution and diluting with water. The butinene derivatives were exceptional in yielding relatively large amounts of mercurous acetate and a further product which proved to be a mixture of mercurous and mercuric salts of indefinite composition and from which no ketonic acid could be obtained. The acetylenic acids of higher molecular weight gave mercuric salts of diacetoxymercuri-ketonic acids in the form of microcrystalline needles. These salts were recrystallized from dil. acetic acid. They were found to be decomposed by hydrogen sulfide and hydrochloric acid with formation of ketonic acids.

Methyl behenolate gave the ester of a diacetoxymercuri-ketobehenic acid and this, after being shaken with cold dil. hydrochloric acid, gave a methyl ketobehenate.

In the preparation of ketonic acids it was found unnecessary to isolate the mercury compound. The whole of the acetic acid solution was treated with an excess of concd. hydrochloric acid and the mixture poured into water. The ketonic acid separated in good yield.

Analysis of the Mercuric Compounds

The method employed in the analysis of the mercury compounds is described in detail in the first paper.[1] The results obtained were as follows.

TABLE I

ANALYSES

Acetylenic compound	Mercury compound		
	Hg, %	CH_3COO, %	Ketonic acid or ester, %
Stearolic acid	54.77	12.68	32.3 $C_{18}H_{34}O_3$
Calcd. for a mercuric diacetoxymercuri-ketostearate	54.81	12.90	32.6 $C_{18}H_{34}O_3$
Ricinolic acid	53.81	12.6	33.3 $C_{18}H_{34}O_4$
Calcd. for a mercuric diacetoxymercuri-hydroxyketostearate	53.87	12.69	33.7 $C_{18}H_{34}O_4$
Behenolic acid	51.58	11.89	35.9 $C_{22}H_{42}O_3$
Required for a mercuric diacetoxymercuri-ketobehenate	51.65	12.16	36.5 $C_{22}H_{42}O_3$
Methyl behenolate	45.21	13.27	41.3 $C_{22}H_{41}O_3CH_3$
Required for a methyl diacetoxymercuri-ketobehenate	45.30	13.33	41.59 $C_{22}H_{41}O_3CH_3$

The Ketonic Acids Derived from the Mercury Compounds

Baruch,[5] Goldsobel[6] and Holt[7] have investigated the action of concd.

[5] Baruch, *Ber.*, **27**, 172 (1894).

[6] Goldsobel, *Ber.*, **27**, 3121 (1894).

[7] Holt, *Ber.*, **25**, 962 (1892).

sulfuric acid upon stearolic, ricinolic and behenolic acids and have described the isolation of ketonic acids as products of the reaction. The constitution of the ketonic acid was in each case established by forming the oxime and effecting scission through the Beckmann transformation. Stearolic acid gave 10-ketostearic acid, ricinolic acid gave 10-keto-12-hydroxystearic acid and behenolic acid gave 14-ketobehenic acid.

We have prepared the ketonic acids by this method as well as by intermediate formation of acetoxymercuri compounds and find that the products are identical. The melting points of the ketonic acids and the parent acetylenic acids are given in Table II.

TABLE II

MELTING POINTS OF KETONIC ACIDS

Acetylenic acid	M. p., °C.	Ketonic acid, m. p., °C.	Method of formation or observer
Stearolic acid	48.0	75–76	Mercury compd.
	48.0	76	Baruch
Ricinolic acid	53.5	84–85	Mercury compd.
	53.0	84–85	Goldsobel
	51.0	78–80	Mangold
Behenolic acid	57.5	83–84	Mercury compd.
	57.5	83	Holt and Baruch

In view of the observation of Myddleton and Barrett[1] that 9,10-undecinolic acid yields a mixture of two ketonic acids, and considering also the suggestion of Robinson and Robinson[8] that hydration of a triple bond may take place in each of the two possible directions, we submitted the ketonic acids prepared from the mercury compounds to the process of purification described by Robinson and Robinson. The melting points of the purified acids were as follows: 10-ketostearic acid, 76°; 10-keto-12-hydroxystearic acid, 85.6°; 14-ketobehenic acid, 84.5°.

The last two observers we have mentioned found that by treating stearolic acid with concd. sulfuric acid and then pouring into water, according to the method of Baruch, they obtained a mixture of ketonic acids from which, after a troublesome and wasteful process of purification, it was possible to isolate a small amount of a ketostearic acid melting at 83°. The high-melting acid was obtained in better yield by dissolving stearolic acid in concd. sulfuric acid and exposing the solution to moist air in an open vessel. They assume that the acid they have isolated is 10-ketostearic acid because it is indistinguishable from the product of a synthesis which seems capable of yielding only 10-ketostearic acid. We were not able to raise the melting point of our ketostearic acid above 76° by careful purification. This fact, together with the observation of Behrend[9] that a ketostearic acid whose oxime yields scission products indicative of

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[8] Robinson and Robinson, *J. Chem. Soc.*, **127**, 176 (1925); **128**, 2204 (1926).

[9] Behrend, *Ber.*, **29**, 806 (1896).

the constitution 9-ketostearic acid melts at 83°, suggests the advisability of studying the oximes of the acids described by Robinson and Robinson. They have themselves suggested that 9-ketostearic acid is one of the products of hydration of stearolic acid.

According to the constitutions assigned to the ketonic acids under discussion by Baruch, Goldsobel and Holt the keto group occurs at carbon atoms of even number, counting the carboxyl carbon atom as one. The position of the acetylenic bond before hydration is thus fixed to two possible positions, either immediately preceding or following the keto group.

In the case of stearolic, ricinolic and behenolic acids we have found it impossible to isolate from each more than one ketonic acid after hydration but it is possible that very small amounts of a second may be formed. Myddleton and Barrett have found evidence of hydration in two directions in the case of 9,10-undecinolic acid. In such a case the constitution of the two ketonic acids would afford conclusive evidence of the position of the triple bond in the parent acid, but in this instance simpler and equally convincing evidence is found in the fact that dehydro-undecylenic acid which has the triple bond in the ultimate position yields the same ketonic acid.

It is in most cases impossible to determine the position of the original triple bond by reference to the constitution of one ketonic acid derived from the acetylenic compound. Account must necessarily be taken of the nature of the dibasic acid produced by oxidation of the acetylenic acid with such reagents as nitric acid and alkaline potassium permanganate, although this is decidedly unsatisfactory because the dibasic acid is usually formed in small amount.

It is probably safer to derive supporting evidence from the nature of the scission products of the ozonides of the ethylenic acid which may readily be prepared by reducing the acetylenic compound with zinc in the presence of titanous chloride.

We propose to continue the investigation of the mercury compounds we have described to ascertain the position of the acetoxymercuri groups. If this is achieved another method of deciding the position of triple bonds in acetylenic acids and esters will be available.

Experimental Part

Bromination of Oleic, Ricinoleic and Erucic Acids.—The procedure was the same in the three cases. The acid was dissolved in a small volume of glacial acetic acid and a solution of bromine in acetic acid was stirred in at a temperature of 5° until excess bromine was indicated by starch-iodide paper after an hour's interval. The solution was allowed to stand overnight in the ice chest, after which it was poured into a large volume of water. The oily layer was washed with cold water and then with warm water and finally with a dilute solution of sodium thiosulfate. After a final washing, the product was dried over calcium chloride. In the case of erucic acid the drying was omitted and the semi-solid product recrystallized from alcohol. Rape oil brominated in a similar manner gave a viscous oil which was dried over calcium chloride.

The characteristics of the products were as follows: oleic acid and ricinoleic acid gave a viscous oil; erucic acid gave a solid which after recrystallization from alcohol melted at 42–43°.

Conversion of Dibromo Acids into Acetylenic Acids.—Each dibromo acid was heated to gentle boiling in a solution of twice its weight of potassium hydroxide in eight times its weight of alcohol. For the treatment of brominated rape oil twice the proportion of alkali and alcohol was used. The reaction was complete after seven or eight hours' refluxing in a capacious flask heated in an oil-bath.

The bulk of the alcohol was then slowly distilled, the residue dissolved in water and the solution acidified with hydrochloric acid. The oily layer which separated was induced to crystallize by skimming off and stirring with fresh water.

Action of Mercuric Acetate upon the Acetylenic Acids.—The reaction was carried out as already described with the following amounts of reactants and solvent: acetylenic acid, 1 mole; mercuric oxide, 2.6 moles dissolved in five times the total weight of acetic acid. Methyl behenolate required the following proportions: ester, 1 mole; mercuric oxide, 2.1 moles dissolved in five times the total weight of acetic acid.

The products were recrystallized from 75 to 50% acetic acid.

The authors are indebted to the Government Grant Committee of the Royal Society for a grant which defrayed part of the cost of the investigation.

Summary

1. Mercuric acetate reacts with stearolic, ricinolic and behenolic acids in acetic acid solution to form crystalline mercuric salts of diacetoxymercuri-ketonic acid.
2. The mercury compounds yield saturated ketonic acids after treatment with hydrochloric acids.
3. When mercuric acetate reacts with γ-butinene-α,α-dicarboxylic acid and with γ-butinene-α-carboxylic acid a mixture of mercuric and mercurous salts of indefinite composition results. No ketonic acid has been isolated after treating the mercury compounds with hydrochloric acid.
4. Methyl behenolate gives rise to a crystalline ester of a diacetoxy mercuri keto-behenic acid. Hydrochloric acid liberates from this methyl 14-ketobehenate.

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