

[CONTRIBUTION FROM THE DEPARTMENT OF BOTANY, UNIVERSITY OF MINNESOTA]

Certain Derivatives of the Octadecenoic Acids. I. The *p*-Phenylphenacyl Esters. II. The S-Benzylthiuronium Salts¹

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The pronounced solubility and low melting points of most unsaturated fatty acids present considerable difficulty in the separation of their mixtures to a stage permitting the identification of the individual components by means of their physical constants. Final characterization is usually based upon the conversion of the unsaturated acid to the bromo- or hydroxy- derivatives of the corresponding saturated acid. However, aside from requiring sizable quantities of starting material, both of these derivatives involve as yet unsolved problems of isomerism,^{3,4} and neither is suitable for the conjugated acids or for mixtures containing only minor proportions of any one component.⁵ Too, the bromination procedure is limited to the very few acids which form crystalline bromides, while it is well-nigh impossible to separate the hydroxy derivatives obtained from even a binary mixture of geometrically isomeric di- or trienoic acids, each of which forms two or more pairs of enantiomorphous polyhydroxy acids.⁶ The advantages of relatively insoluble, high-melting derivatives which leave the double bonds unaffected are obvious.

Among such derivatives recently suggested are the *p*-phenylphenacyl esters and the S-benzylthiuronium salts. Drake and Bronitsky⁷ prepared *p*-phenylphenacyl oleate, m. p. 60.5°, while Kimura⁸ reported a m. p. of 73.5° for the elaidate. Donleavy⁹ confined his work on the S-benzylthiuronium salts to the saturated fatty acids.

Extending these studies to the linoleic, linolenic, and eleostearic acids and their geometric isomers, we were indeed sorry to find that while all formed derivatives with satisfactory melting points, only the *p*-phenylphenacyl oleate and elaidate already

reported in the literature showed iodine numbers corresponding with the calculated values. No difficulty was encountered in reproducing the constants of these two and several other control derivatives prepared by the previous workers and it therefore appeared that the *p*-phenylphenacyl esters of the di- and trienoic acids were contaminated with impurities impossible to remove by repeated crystallizations, while the S-benzylthiuronium salts of all the unsaturated acids investigated proved to be highly unstable. The recovery of the free acids from these salts by an improved procedure which avoided the contamination with mercaptans noted by Anderson¹⁰ indicated considerable decomposition to products possessing a very rancid odor, although due precaution against oxidation was observed throughout our work.¹¹ Despite the disappointing results of our efforts, it was considered that the properties of the various derivatives were sufficiently interesting to be reported.

Experimental

I. The *p*-Phenylphenacyl Esters.—The procedure of Drake and Bronitsky⁷ was followed throughout. A weighed quantity of the fatty acid in a 95% alcoholic solution was neutralized to phenolphthalein with 1 *N* alcoholic potassium hydroxide and a few drops of 1 *N* hydrochloric acid was then added. The solution was boiled for one hour under nitrogen with a slight excess of *p*-phenylphenacyl bromide. After cooling and filtering in an inert atmosphere, the derivative was recrystallized three to seven times for acetone, dried in a vacuum and its m. p. and I. V. determined as shown in Table I. The linoleate and linolenate appeared to have the properties of liquid crystals.

II. The S-Benzylthiuronium Salts.—These were made according to the directions of Donleavy.⁹ To an alcoholic solution of the potassium salt prepared as above was added with stirring a slight excess of a warm absolute alcoholic solution of the S-benzylthiuronium chloride. The salt precipitated almost immediately. It was dissolved with slight warming, the insoluble potassium chloride was removed, and the fatty acid derivative recrystallized several times from absolute alcohol in a stream of carbon dioxide. It was finally dried in an Abderhalden apparatus.

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(3) Matthews, Brode and Brown, *THIS JOURNAL*, **63**, 1064 (1941).

(4) Kass and Burr, *ibid.*, **61**, 1062 (1939).

(4a) Kass, Nichols and Burr, *ibid.*, **63**, 1060 (1941).

(5) Kass, Lundberg and Burr, *Oil and Soap*, **17**, 50 (1940).

(6) Kass, A. C. S. Meeting, Memphis, Tenn., April, 1942.

(7) Drake and Bronitsky, *THIS JOURNAL*, **62**, 3715 (1930).

(8) Kimura, *J. Soc. Chem. Ind., Japan*, **37**, 154B (1934).

(9) Donleavy, *THIS JOURNAL*, **68**, 1004 (1936).

(10) Anderson, *J. Biol. Chem.*, **74**, 548 (1927).

(11) It is noteworthy that Dewey and Sperry [*THIS JOURNAL*, **61**, 3251 (1939)] prepared *p*-chlorobenzyl pseudothiuronium oleate and, without presenting their analytical data, stated that the analysis by the Kjeldahl method showed good agreement with the calculated values.

TABLE I
 PROPERTIES OF THE *p*-PHENYLPHENACYL ESTERS AND S-BENZYLTHIURONIUM SALTS OF THE OCTADECENOIC ACIDS

	<i>p</i> -Phenylphenacyl ester			S-Benzylthiuronium salt			Appearance
	M. p., °C.	Found	I. V. Calcd.	M. p., °C.	Found	I. V. Calcd.	
<i>p</i> -Phenylphenacyl bromide	125	0	0				
S-Benzylthiuronium chloride				172-174	0	0	Crystalline
Oleic ^a	61 - 62	52.5	53.3	134-134.5	59.7	56.1	Intermediate
Elaidic ^b	72 - 73	52.8	53.3	125-125.5	66.6	56.1	Crystalline
Linoleic ^c	37 - 37.5 ^f 46.5- 47	99.6	107.0	123.5-125	108.2	113.7	Non-crystalline
Linolelaidic ⁴	73 - 75						
Linolenic ^d	37.5- 38 ^{f,g} 38 - 39	140.4	161.2	122-124 ^h	160.2	171.4	Non-crystalline
β -Eleostearic ^e	89 - 90						
9,10,12,13-Tetrabromostearic ^c	107 -108	0	0	129-130	0	Crystalline

^a Wheeler and Riemenschneider, *Oil and Soap*, **16**, 207 (1939). ^b Bertram, *Chem. Weekblad*, **33**, 3 (1936). ^c Rollett, *Z. physiol. Chem.*, **62**, 410 (1909). ^d Kass, Loeb, Norris and Burr, *Oil and Soap*, **17**, 118 (1940). ^e Meyers, Kass and Burr, *ibid.*, **18**, 107 (1941). ^f Melts sharply to opaque liquid at lower temperature, clears suddenly at higher temperature indicated. ^g Mixed m. p. with linoleate, 38.5° and 44-46°. ^h Mixed m. p. with linoleate, 120-123°.

All the derivatives adhered tenaciously to the solvent, and the β -eleostearate decomposed upon prolonged heating at 100° even in a high vacuum. The stability of the others was in approximately the same order as their parent acids. The appearance of the salts depended on the melting point of the parent acid, the higher the melting point the more nearly crystalline was the derivative. The non-crystalline appearance of the salts of the linoleic and linolenic acids may possibly point to the multiple nature of the debromination acids used by us.³ Every one of the thiuronium salts was insoluble in petroleum ether. None melted quickly, all requiring considerable time to soften and melt, the di- and trienoic acids decomposing below their true melting point when the temperature of the bath was raised too slowly. The melting point bath was therefore preheated to within a few degrees of the approximate melting point, when the capillary was inserted and the heating continued cautiously. The melts of the di- and trienoic acids quickly turned brown, while the β -eleostearate, despite its crystalline appearance, decomposed at 115-116° to a brown gel which did not liquefy until 130°. The properties of the derivatives are listed in Table I.

Since the thiuronium salts of the weak acids decompose easily in water with the formation of mercaptans, the recovery of the fatty acids was effected through their esters. S-Benzylthiuronium linoleate was warmed gently with a solution of gaseous hydrogen chloride in absolute alcohol and then left at room temperature for several hours, when the solution turned dark brown. It was then thoroughly extracted with petroleum ether and the extract washed with the acid alcohol and then with water. Evaporation of the dried solution left a light yellow residue with a pro-

nounced odor characteristic of oxidized fats, but not of mercaptans. Distillation removed the color but not all traces of the odor. The I. V. of the distillate was 145 (calcd. for ethyl linoleate, I. V. 165). Spectrographic examination yielded no significant data beyond indicating absence of conjugation.

Summary

1. The *p*-phenylphenacyl esters of oleic, elaidic, linoleic, linolelaidic, linolenic, β -eleostearic, and α -tetrabromostearic acids were prepared. Although all had good melting points, only the esters of the first two acids, already known, were found to have the calculated I. V. among the unsaturated derivatives.

2. The S-benzylthiuronium salts of the above unsaturated acids were found unsuited for purposes of identification because of impurity, instability, similarity of melting point and dependence of the melting point on rate of heating. The appearance of these derivatives varied from crystalline to non-crystalline with the diminishing melting point of the parent acid.

3. An improved procedure, avoiding formation of mercaptans, was given for the recovery of the acids from the thiuronium salts.

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