

TABLE IV
FRACTIONAL CRYSTALLIZATION OF LITHIUM AND POTASSIUM SOAPS

Soap	Solvent	Temp., °C.	% total wt.	Iod. no.	% linoleic
Lithium	Butyl alcohol	Ppt. 30	3
		Ppt. 0	41	82.4	..
		Ppt. -20	41	144.0	60
		Filtrate -20	15	164.5	82
Potassium	Ethyl alcohol	Ppt. 30	1
		Ppt. 0	34	49.2	..
		Ppt. -20	26	134.8	49
		Filtrate -20	39	157.8	74.3

of the more useful methods of fatty acid separation involve differences of soap solubility. Early in this work we were hopeful of finding some suitable soaps of oleic and linoleic acids which would exhibit wide enough difference in solubility to be useful in their separation. Only a few of our more promising results will be reported here. Starting with cottonseed oil fatty acids, crystallization of the potassium soaps from a 10% solution in absolute alcohol at 0° gave 45% insoluble soaps and 55% soluble soaps, containing 68% linoleic acid. The lithium soaps, prepared by neutralizing a solution of the acids in alcohol with lithium hydroxide, removing the alcohol and water under reduced pressure and taking up the soaps in butyl alcohol, were fractionally crystallized from that solvent; also the potassium soaps from absolute alcohol with the results in Table IV.

When the fact is considered that we began here with a mixture of cottonseed oil fatty acids, it is clear that either of the separations in Table IV has possibilities. In the former case, a comparatively small amount of the acids comes out as 82% linoleic, while in the latter a much larger portion came out 74% linoleic acid.

Summary

1. The saturated and unsaturated fatty acids of cottonseed and corn oils may be separated conveniently by crystallization of the mixed acids from a 10% solution in acetone at -20°.
2. Linoleic acid preparations containing up to 93% of the acid were obtained by fractional crystallization of the unsaturated acids (and methyl esters) of these oils from acetone and methyl alcohol at low temperatures.
3. Fractional crystallization of the lithium soaps from *n*-butyl alcohol and of the potassium soaps from absolute alcohol may also be used in obtaining linoleic acid concentrates.
4. Crystallization of unsaturated fatty acids from appropriate solvents at low temperatures is a useful procedure for their separation.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY]

Studies on the Chemistry of the Fatty Acids. II. The Preparation of Pure Oleic Acid by a Simplified Method¹

BY J. B. BROWN AND G. Y. SHINOWARA

Although oleic acid (*cis*-9,10-octadecenoic) is perhaps the most common of the naturally occurring fatty acids, the pure acid is still one of the rare chemicals. The reason for this state of affairs is that oleic acid always occurs in fats and oils associated with saturated acids and usually with varying amounts of linoleic acid and other acids of higher unsaturation. The methods for separating these impurities are only semi-quantitative so that purification of oleic acid is extremely tedious. Olive oil is usually employed as a source of the acid. The saturated acids, mostly palmitic, are removed by the lead soap separation

in alcohol or ether; the unsaturated acids are then converted into barium soaps which are repeatedly crystallized from moist benzene to remove linoleic acids.

Excellent reviews of work previous to 1925 are given by Lewkowitsch² and by Lapworth, Pearson and Mottram.³

These investigators prepared the pure acid by a procedure which included the lead salt treatment, distillation, barium soap crystallization and finally distillation. Holde and Gorgas⁴ claimed

(2) J. Lewkowitsch, "Technology of Oils, Fats and Waxes," Macmillan and Co., Ltd., London, Vol. I, 1921, p. 182.

(3) A. Lapworth, L. K. Pearson and E. N. Mottram, *Biochem. J.*, **19**, 7 (1925).

(4) D. Holde and A. Gorgas, *Z. angew. Chem.*, **39**, 1443 (1926).

(1) Presented at the Pittsburgh Meeting of the American Chemical Society, September, 1936.

the preparation of a pure product through reduction of dibromostearic acid. Bertram⁵ prepared 99.5% oleic acid by use of the Twitchell⁶ lead salt-alcohol procedure, formation of the silver salt and crystallization of the acid three times from acetone. Raymond⁷ modified the Bertram method by eliminating the use of a silver salt, and crystallizing the acid from cold alcohol in a special apparatus. Shelton⁸ likewise used the Twitchell separation and in addition crystallized the barium or lithium salts and distilled the methyl esters of the resulting product.

All procedures so far used that have resulted in satisfactory products have been tedious and have employed a combination of methods to attain the desired results. As a result of experience gained in the course of the preceding work⁹ it seemed likely that we could obtain oleic acid of a high degree of purity by direct crystallization of the acids of olive oil from acetone. Our method in brief involves removal of the saturated acids by the -20° acetone precipitation, crystallization of the resultant unsaturated acids from acetone at -60° four or more times, followed by a partial crystallization of the resultant product from acetone at -35° to remove small amounts of palmitic acid not taken out by the original treatment at -20° . Three preparations are described and compared with other preparations reported in the literature. The multifarious operations of previously reported methods are replaced by seven or more crystallizations from the same solvent. No soap preparations are involved after the original saponification.

Experimental Part

Equipment.—For low temperature work we had available the special equipment described previously, namely, a room in which a temperature of -20 to -25° was maintained and a well insulated dry ice-alcohol apparatus designed to accommodate a 2-liter Erlenmeyer flask. All filtrations were carried out by suction in the -20° room.

Procedures.—(1) One kilogram of olive oil (iodine number 85.5; saponification number, 190.1) was saponified and the soaps converted into fatty acids (iodine number 84.5). Two hundred and twenty-five grams of the acids was dissolved in 3450 cc. of c. p. acetone in a 4-liter flask and allowed to stand in the cold room overnight. The precipitate was removed by suction on a large Büchner funnel. The filtrate (3000 cc.) was cooled to -60° with

continuous stirring. After filtering, the precipitate was allowed to melt and was made up to 2000 cc. with acetone, and again brought to -60° and filtered. After two more crystallizations at this temperature, the final precipitate was melted and made up to 1250 cc. with acetone and cooled slowly with stirring to the point of first appearance of crystals, about -35° . These, consisting of some oleic acid and any saturated acids which may have escaped the first crystallization, were filtered off in the cold room. The acetone was removed from the filtrate by warming under reduced pressure. The residual product was distilled at 15 mm. pressure in an entire glass apparatus. It was water-white and odorless; yield 90 g. Other constants are in Table I.

TABLE I

ANALYSIS OF OLEIC ACID PREPARATIONS IN COMPARISON WITH THOSE REPORTED IN THE LITERATURE

	M. p., °C.	Mean mol. wt.	Iodine number	n_D^{20}	Purity, %
Calcd.	...	282.3	89.93	
Specimen (1)	13.0	282.2	90.03	1.4585	
Specimen (2)	13.0	282.4	89.63	1.4586	
Specimen (3)	13.0	282.5	90.04	1.4585	
Bertram	13.2	1.4582	99.5
Shelton	13-14	282.5	90.6	1.4610	

(2) Four hundred and fifty grams of the mixed acids, as above, was treated as before, except that six -60° crystallizations, instead of four, were made; yield 135 g.

(3) The -60° filtrates from the two preceding experiments were combined; the acetone was removed. Two hundred and fifty grams of these acids was made up to 1500 cc. in acetone and crystallized four times at -60° ; crystals were washed each time with 200 cc. of acetone cooled to -70° ; yield 74 g.

All three of these preparations were practically constant boiling. The boiling point of No. 2 oleic acid was determined accurately at several pressures, using a micro-gage with the following results.

Pressure	Obsd.	B. p., °C.	Corr.
15	228-229		234-235
10	219-220		225-226
5	209-210		215-216
1.2	194-195		200-201

Criteria of Purity.—We have employed the following criteria of purity, actual data being given in Table I. (1) Mean molecular weight: The principal saturated acid of olive oil is palmitic. Five per cent. contamination with this acid would lower this value 1.4 points. No appreciable lowering was observed. (2) Iodine number: Method used, Wijs thirty minutes. Palmitic and linoleic acids must be present in equal amounts to maintain the theoretical value. (3) Melting point: Specimens, frozen in a special tube and held overnight. All three preparations melted sharply at 13° . Difference between softening and melting point was less than 0.1° . (4) Oxidation products: Dihydroxystearic acids were prepared from each product by the method of Lapworth and Mottram;¹⁰ yield, 95-96%; molecular weight 315.6-316.0 (calcd. 316.3).

The data are summarized in Table I.

(10) A. Lapworth and E. N. Mottram, *J. Chem. Soc.*, 1628 (1926).

(5) S. H. Bertram, *Rec. trav. chim.*, **46**, 397 (1927).

(6) E. Twitchell, *J. Ind. Eng. Chem.*, **13**, 806 (1921).

(7) E. Raymond, *Chimie et Industrie*, Feb., 523 (1929).

(8) J. H. Shelton, *J. Soc. Chem. Ind.*, **50T**, 131 (1931).

(9) J. B. Brown and G. G. Stoner, *THIS JOURNAL*, **58**, 3 (1936).

Summary

1. A simplified procedure for preparing oleic acid of high purity is described.

2. The constants of three specimens of oleic acid, prepared by slight modifications of the procedure, are described.

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A Method for the Synthesis of Phenanthridine Derivatives by an Application of the Stieglitz Rearrangement

BY LOUIS A. PINCK AND GUIDO E. HILBERT

The rearrangements of hypothetical intermediates $\begin{matrix} R_1 \\ R_2 \\ R_3 \end{matrix} \text{C}-\text{N}$: resulting from appropriate treatment of tertiary methyl nitrogen substituted compounds of the type $\begin{matrix} R_1 \\ R_2 \\ R_3 \end{matrix} \text{C}-\text{N} \begin{matrix} \text{X} \\ \text{Y} \end{matrix}$ where R_1 , R_2 and R_3 usually have been aromatic groups and where $-\text{N} \begin{matrix} \text{X} \\ \text{Y} \end{matrix}$ may be $-\text{N} \begin{matrix} \text{H} \\ \text{Br} \end{matrix}$,¹ $-\text{N} \begin{matrix} \text{Cl} \\ \text{Cl} \end{matrix}$,¹ $-\text{N} \begin{matrix} \text{H} \\ \text{OH} \end{matrix}$,² $-\text{N}(\text{N}_2)$,³ etc.,⁴ have been studied extensively by Stieglitz and co-workers.⁵ When R_1 is aliphatic in nature and R_2 and R_3 are aromatic, it was noted that either R_2 or R_3 rather than R_1 migrated to

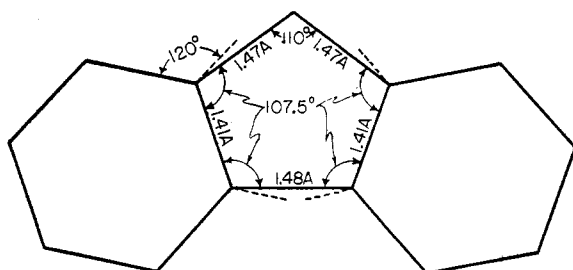
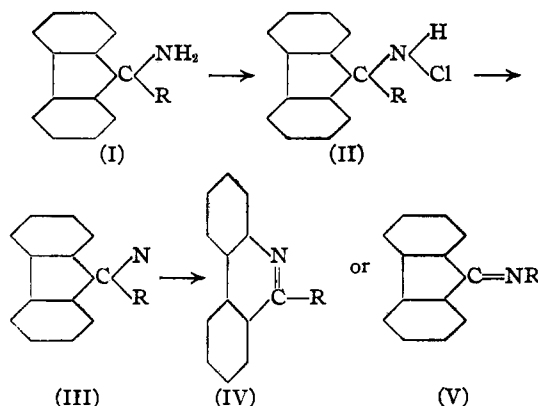


Fig. 1.—Structural formula of fluorene.

the nitrogen atom and largely on the basis of this fact it has been suggested⁵ that the migration of the most electronegative group attached to the carbon atom would in general be favored. The rearrangement of intermediates formed from tertiary methyl nitrogen derivatives, where two of the groups attached to the tertiary carbon atom are linked together, as for example in a 9-substituted 9-fluorylchloroamine (II), has not pre-

viously been studied. Here the situation is more complicated, since the possible influence that the five-membered ring might have on the rearrangement must be considered in addition to the electronegativities of the radicals. From the general results of recent x-ray and electron diffraction studies⁶ fluorene would be expected to have the configuration shown in Fig. 1.⁷ In order that the C-C distances be those shown in the figure the normal valence angle from the benzene ring must be distorted approximately 12 to 13°. Since the linkages attached to the benzene ring are known to be quite rigid the five-membered ring in fluorene, because of the considerable distortion of the normal valence angles, must be appreciably strained. Theoretically a 9-substituted fluoryl nitrogen (III) can be stabilized by undergoing two possible types of rearrangement: (1) opening of



(6) Robertson, *Chem. Rev.*, **16**, 417 (1935); Hendricks, *ibid.*, **7**, 341 (1930).

- (1) Vosburgh, *THIS JOURNAL*, **38**, 2081 (1916).
 (2) Stieglitz and Leech, *ibid.*, **36**, 272 (1914).
 (3) Senior, *ibid.*, **38**, 2718 (1916).
 (4) Stieglitz and Stagner, *ibid.*, **38**, 2046 (1916); Stieglitz and Senior, *ibid.*, **38**, 2727 (1916); Guthmann and Stieglitz, *J. Org. Chem.*, **1**, 31 (1936).
 (5) For a review, which also includes unpublished results, see Porter, "Molecular Rearrangements," Chemical Catalog Co., Inc., New York, 1928, pp. 30-33.

(7) Stuart "Molekülstruktur," Verlag von Julius Springer, Berlin, 1934, p. 76, has interpreted the results obtained in an x-ray examination of fluorene by Hengstenberg and Mark, *Z. Krist.*, **70**, 283 (1929), as favoring a planar configuration of the molecule. Since this manuscript was written, additional articles on the configuration of fluorene have appeared. Cook and Iball, *Chemistry and Industry*, **55**, 467 (1936), on the basis of crystallographic data consider it to be a non-planar molecule, whereas dipole moment measurements by Hughes, LeFevre and LeFevre, *ibid.*, **55**, 545 and 561 (1936), suggest that fluorene is a flat molecule.