for estimating linoleic acid, we wish to present data based on the following procedure for determination of tetrabromide number. Weigh a 1.5–2.0 g. sample of fatty acids into a tared 50-cc. centrifuge tube. Add at once 30–35 cc. of low-boiling petroleum ether. Place the tube in an ice-salt bath and, with constant stirring, add dropwise an excess of bromine. Allow to stand at 0° for at least four hours and centrifuge. Add 30 cc. of cold petroleum ether, disintegrate the bromides and stir for five to ten minutes in an ice-water bath. Repeat this washing three times. Dry the resultant tetrabromides to constant weight, and weigh. The results obtained are given in Table II.

Summary

1. A procedure for the preparation of linoleic acid by fractional crystallization of the fatty acids of corn oil is described.

2. The properties of the acid prepared by crystallization are compared with those of pure α-linoleic acid.

3. A method of quantitative estimation of linoleic acid, based on the determination of its tetrabromide number, is proposed and discussed.

COLUMBUS, OHIO RECEIVED NOVEMBER 8, 1937

[CONTRIBUTION FROM THE INSTITUTE OF EXPERIMENTAL BIOLOGY, UNIVERSITY OF CALIFORNIA]

Linoleyl Alcohol: Preparation and Some Properties

BY OSMO TURPEINEN[1]

During the course of a recent work on the "essential unsaturated fatty acids"[2] it became desirable also to test the biological effectiveness of the alcohol corresponding to linoleic acid, linoleyl alcohol. It was found that this alcohol could be prepared easily from methyl linoleate by means of the reduction method of Bouveault and Blanc.[3] Since linoleyl alcohol evidently has never before been synthesized or isolated, it seems proper to report briefly on the preparation and some properties of this compound.

Preparation.—The starting material was methyl linoleate prepared from corn oil according to Rollet.[4] This ester was reduced with sodium in dry butanol. The procedure was principally the same as that suggested by Reid and co-workers[5] for the preparation of oleyl alcohol. The only points of difference were: (1) the methyl ester was used as starting material, and (2) the drying of the oil before the final distillation was done (in order to minimize the risk of oxidation) under reduced pressure in a large flask on a steam-bath. The final distillation was carried out under a pressure of approximately 1 mm., at which the main fraction boiled at 148–150°. The yields were comparatively good; 70–72% of the theoretical.

Properties.—Linoleyl alcohol is a colorless, oily liquid without a distinct odor or taste. Exposed to the air in a thin layer, it shows a tendency to "dry." Some of its characteristics were found to be as follows: specific gravity, d^{20}_{4} 0.8612; refractive index, n^{20}_{D} 1.4782; melting point, −5–−2°.

Halogen Addition.—The attempts to determine the iodine number of linoleyl alcohol resulted in only a partial addition of iodine. The Hanus method gave the following results: 152 (one hour), 160 (three hours), 158 (twenty-four hours), the theoretical value being 190.7.

For bromination 6.4 g. of linoleyl alcohol was dissolved in 20 cc. of carbon tetrachloride, the solution was cooled to 0°, and a 5% solution of bromine in the same solvent was added slowly. The reaction was rapid in the beginning, but languished later, and when about 80% of the theoretical amount of bromine had been added, the uptake of bromine was very slow. The bromination was stopped at this point without trying to force it farther. The solvent was evaporated, and the remainder, a yellow oil, was chilled at 0° overnight, at which it partially crystallized. The yield of the crystalline substance was, however, very small, only 0.95 g. After three recrystallizations from petroleum ether, the substance showed a constant melting point of 87–87,3°. The bromine content was: calculated for tetrabromooctadecanol ($C_{18}H_{34}OBr_4$), 54.56%, found, 54.2, 53.9%.

It is known that linoleic acid can be halogenated easily and completely. Since it would seem unlikely that the corresponding alcohol could show any considerably different behavior in this respect, the most natural conclusion to be drawn from the results reported above would be that the present preparation is contaminated with some less unsaturated impurities, which bring its mean degree of unsaturation down to 80–85% of the theoretical. That this conclusion is not, however, correct is shown by the following hydrogenation experiment.

Hydrogenation.—The reaction was carried out in Smith's micro hydrogenation apparatus.[6] The solvent was glacial

---

[1] Rockefeller Foundation Fellow.

[2] The results of this work will be published in the *Journal of Nutrition*.

[3] L. Bouveault and G. Blanc, *Compt. rend.*, **136**, 1676 (1903).

[4] A. Rollet, *Z. physiol. Chem.*, **62**, 410 (1909).

[5] E. E. Reid, F. O. Cockerille, J. D. Meyer, W. M. Cox, Jr., and J. R. Ruhoff, *Org. Syntheses*, **15**, 51 (1935).

[6] J. H. C. Smith, *J. Biol. Chem.*, **96**, 35 (1932).

acetic acid, and platinum oxide[7] was used as the catalyst. The substance took up hydrogen readily, and the procedure was finished in about thirty minutes. The following results were obtained:

Substance		Hydrogen absorbed		Hydrogenation ratio
Mg.	Millimoles	Cc.	Millimoles	
19.9	0.0747	3.68 (757 mm., 21°)	0.152	2.03
23.9	.0898	4.41 (756.5 mm., 23°)	.181	2.01

These results are in excellent accordance with the theory, which requires a hydrogenation ratio of 2 for linoleyl alcohol.

The hydrogenation product was isolated by diluting the acetic acid solution with several volumes of distilled water, filtering the precipitate, redissolving it on the filter in a few drops of methanol, and evaporating the solvent. It was a white, crystalline substance which, without further purification, melted at 57.5–58° (reported for octadecanol-1 58.5°).[8]

p-Nitrophenylurethan.—Linoleyl-p-nitrophenylurethan was prepared by means of p-nitrophenyl isocyanate in benzene solution.[9] After several recrystallizations from methanol, it showed a constant melting point of 91–92°. The analysis[10] gave the following results: Calcd. for $C_{25}H_{38}O_4N_2$: C, 69.71; H, 8.90; N, 6.51. Found: C, 68.95, 69.10; H, 8.73, 8.67; N, 6.38, 6.42.

I wish to acknowledge my indebtedness to Professor Herbert M. Evans for the facilities afforded for this work and for his help and advice.

Summary

Linoleyl alcohol, a compound not previously described, has been prepared from methyl linoleate. Some of its properties are given, and its behavior with halogens and catalytically activated hydrogen is described. The alcohol has also been converted into linoleyl-p-nitrophenylurethan.

---

[7] V. Voorhees and R. Adams, This Journal, **44**, 1397 (1922).

[8] P. A. Levene, C. J. West and J. van der Scheer, *J. Biol. Chem.*, **20**, 521 (1915).

[9] R. L. Shriner and R. F. B. Cox, This Journal, **53**, 1601 (1931).

[10] I am obliged to Merck & Co., Inc., Rahway, New Jersey, for this analysis.

BERKELEY, CALIF. RECEIVED NOVEMBER 16, 1937

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

Reductions of Benzil

BY IRWIN A. PEARL AND WILLIAM M. DEHN

Benzil is unique because it yields a large number of reduction products. Without additions of hydrogen to the rings there are fourteen monomolecular reduction products of benzil, namely, *d*- and *l*-benzoin, *cis*- and *trans*-dihydroxystilbene, *cis*- and *trans*-stilbene, *d*-, *l*- and *meso*-hydrobenzoin, *d*- and *l*-phenylbenzylcarbinol, tolane, desoxybenzoin, and dibenzyl. In addition to these there is one split reduction product, toluene, and numerous bimolecular products including well-known compounds such as didesyl, benzoin pinacone and desoxybenzoin pinacone. The number of geometric and stereoisomers of the bimolecular products makes a list too large to recite here. However, only sixteen reduction products of benzil are known, and of these only six have been prepared directly from benzil, namely, benzoin,[1–5] hydrobenzoin,[1,2] isohydrobenzoin,[3] dibenzyl,[1,6] desoxybenzoin[1] and benzoin pinacone.[1] We have prepared six others from benzil, namely, stilbene, isostilbene, phenylbenzylcarbinol, didesyl, isodidesyl, and β-desoxybenzoin pinacone. Also most of these twelve reduction products have been prepared in greatly improved yields.

Because different reducing agents and modifications of conditions used with one reducing agent yield varied products, benzil itself is, perhaps, the most interesting compound for purposes of study of reduction.

Experimental

Preparation of Benzil.—Benzil was prepared from benzoin[7] by oxidation with copper hydroxide in water solution. Clark and Dreger[8] oxidized benzoin to benzil with copper hydroxide in pyridine solution. The disadvantages accompanying the use of pyridine are overcome in the following method.

A concentrated solution of 125 g. of hydrated copper sulfate was stirred mechanically while a 20% solution of 40 g. of sodium hydroxide was added. The mixture was heated to boiling and 40 g. of powdered benzoin was added slowly. The boiling and stirring were continued for

---

[1] Beilstein, Fourth Ed., VII, p. 748.

[2] Kubota and Hayashi, *Bull. Chem. Soc.* (*Japan*), **1**, 14 (1926).

[3] Gomberg and Bachmann, This Journal, **49**, 2584 (1927).

[4] Buck and Jenkins, *ibid.*, **51**, 2163 (1929).

[5] Bachmann, *ibid.*, **53**, 2758 (1931).

[6] Clemmensen, *Ber.*, **47**, 683 (1914).

[7] Benzoin was prepared by the method of Adams and Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. (1932), p. 88.

[8] Clark and Dreger, *ibid.*, p. 81.