

by dissolving the glyoxal in a dioxane-water mixture and allowing it to cool and crystallize slowly. No attempt was made to obtain a completely pure compound, the highest melting point obtained being 89–91°.

The 2,4-dinitrophenylhydrazone crystallized from dioxane; m. p., 246.5–247.5°.

Anal. Calcd. for $C_{18}H_{12}O_8N_4$: N, 15.4. Found: N, 14.95.

2,4-Dimethylphenylglyoxal.—This glyoxal was prepared in 64% yield by the method just outlined for 2,4,6-triethylphenylglyoxal; b. p. 118–123° (13 mm.). The 2,4-dinitrophenylhydrazone after crystallization from ethyl acetate melted at 180–181°.

Anal. Calcd. for $C_{16}H_{14}O_2N_4$: N, 16.38. Found: N, 16.38.

TABLE I

| Arylglyoxal | Product | Color | M. p., °C. | |
|-------------------------------|--|-------|------------|--|
| | | | (corr.) | |
| 1 α -Naphthylglyoxal | α -Naphthylquinoxaline | Brown | 116–116.5 | |
| 2 2,4-Dimethylphenylglyoxal | 2,4-Dimethylphenylquinoxaline | White | 56–57 | |
| 3 Mesitylglyoxal | Di-(mesitylglyoxal)- <i>o</i> -phenylenediamine ⁸ | White | 183–184 | |
| 4 2,4,6-Triethylphenylglyoxal | Di-(2,4,6-triethylphenylglyoxal)- <i>o</i> -phenylenediamine | White | 136–136.5 | |

| Formula | Analyses, % | | | Found | | |
|------------------------|-------------|----------|-------|-------|------|-------|
| | C | Calcd. H | N | C | H | N |
| 1 $C_{18}H_{12}N_4$ | 84.35 | 4.72 | 10.93 | 84.44 | 4.91 | 10.84 |
| 2 $C_{16}H_{14}N_4$ | 82.02 | 6.02 | 11.96 | 82.15 | 5.93 | 12.07 |
| 3 $C_{18}H_{12}O_2N_4$ | 79.21 | 6.65 | 6.60 | 79.47 | 6.98 | 6.97 |
| 4 $C_{24}H_{40}O_2N_4$ | 80.27 | 7.93 | 5.51 | 80.30 | 7.88 | 5.80 |

(8) In one experiment a mixture of equimolecular amounts of the glyoxal and *o*-phenylenediamine was maintained for seven days at 95°. No quinoxaline was detected.

Reaction of the Glyoxals with *o*-Phenylenediamine.—The following general procedure was used in treating the glyoxals with *o*-phenylenediamine. To a boiling solution of 2.2 g. (0.02 mole) of *o*-phenylenediamine in 25 cc. of glacial acetic acid was added in small portions 0.01 mole of the glyoxal or its hydrate. The solution was refluxed for an hour and allowed to stand overnight at room temperature. Dilution with water gave a semi-solid precipitate. This material was recrystallized twice from aqueous alcohol. Table I shows the products obtained together with their colors, melting points and analyses.

Summary

o-Phenylenediamine reacts with α -naphthylglyoxal and 2,4-dimethylphenylglyoxal to give the corresponding quinoxalines. This reaction is inhibited, however, by introduction of extreme hindrance. Neither mesitylglyoxal nor 2,4,6-triethylphenylglyoxal forms a quinoxaline.

Mesitylglyoxal forms a stable ethyl hemiacetal which rearranges to mesitylglycolic acid when treated with sodium ethylate. Similarly mesitylglyoxal is transformed to isopropyl mesitylglycolate by aluminum isopropylate in isopropyl alcohol.

2,4,6-Triethylphenylglyoxal does not form a hydrate or hemiacetal but rearranges to 2,4,6-triethylphenylglycolic acid when heated with sodium ethylate.

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

A Note on the Constitution of Linoleyl Alcohol Prepared by the Sodium Reduction of Linoleic Acid¹

By J. P. KASS, E. S. MILLER AND G. O. BURR

Turpeinen² recently prepared linoleyl alcohol by the reduction of methyl linoleate with sodium in dry butanol according to the well-known method of Bouveault and Blanc³ as outlined by Reid and co-workers⁴ for the preparation of oleyl alcohol. The abnormal behavior of his product toward halogenating reagents led Turpeinen to infer possible contamination with saturated impurities. This supposition was shown to be untenable by the hydrogenation of the alcohol to octadecanol-1 after the consumption of practically the theoretical quantities of hydrogen.

(1) This work was supported by grants from the National Live Stock & Meat Board, the Rockefeller Foundation, and the Graduate School of the University of Minnesota.

(2) Turpeinen, *THIS JOURNAL*, **60**, 56 (1938).

(3) Bouveault and Blanc, *Compt. rend.*, **136**, 1676 (1903).

(4) Reid, *et al.*, *Org. Syntheses*, **15**, 51 (1935).

The molecular refraction of the alcohol, calculated by us on the basis of the constants reported by Turpeinen, is 87.24, while the calculated theoretical value is 85.69. This exaltation of 1.55 units is approximately one-half the difference reported by Böeseken⁵ and Smit⁶ between the observed and calculated molecular refractions of 9,11-linoleic acid. This, as well as the low iodine number and the peculiar behavior of the alcohol toward bromine, characteristic of the conjugated fatty acids,^{5,7} led us to believe that Turpeinen's product was a mixture of the expected octadecadiene-9,12-ol-1 and a conjugated alcohol, the shift in the position of un-

(5) Böeseken, *Chem. Zentr.*, **100**, II, 716 (1929).

(6) Smit, *Rec. trav. chim.*, **49**, 539 (1930).

(7) Böeseken and Gelber, *ibid.*, **46**, 162 (1927).

saturation being due to the action of the strong alkali. Spectroscopic examination of the alcohol produced an absorption curve with a characteristic peak at 2300–2350 Å., where the $E_{1\text{ cm.}}^{1\%}$ was 600. This value, again, is approximately one-half the maximum $E_{1\text{ cm.}}^{1\%}$ reported by Van Der Hulst⁸ for 9,11-linoleic acid, in contrast to the negligible absorptive power of 9,12-linoleic acid. Further confirmation of the presence of conjugation was obtained by oxidizing the alcohol with neutral potassium permanganate in acetone⁹ to caproic acid and approximately equal parts of azelaic and sebacic acids. It is therefore apparent that the substance is a mixture of octadecadiene-9,12-ol-1 and octadecadiene-10,12-ol-1.

On standing at ice-box temperatures in an evacuated and sealed tube for about a month, the liquid slowly deposited a small amount of a crystalline material melting at 41–42.5° after two crystallizations from methanol, while the freezing point of the mixture rose to 15°. Further investigation of the nature of the crystalline substance was prevented by its rapid conversion, even in highly evacuated containers, into a doughy material, m. p. 128°, insoluble in ligroin, ethyl ether, and methanol.

The effect of sodium butylate on linoleic acid, producing spectroscopic activity, conjugation, and isomerization to crystalline forms will be the subject of a future communication.

(8) Van Der Hulst, *Rec. trav. chim.*, **54**, 841 (1935).

(9) Armstrong and Hilditch, *J. Soc. Chem. Ind.*, **44**, 43T (1925).

Experimental

Eight grams of linoleyl alcohol, prepared essentially as directed by Turpeinen, was dissolved in 200 cc. of purified acetone; 120 g. of powdered potassium permanganate was added carefully, and the mixture finally refluxed on the water-bath for three hours. The acetone was then completely driven off and 450 g. of sodium bisulfite was added. Decolorization was effected by the addition of water and successive small portions of dilute sulfuric acid. The solution was extracted once with ethyl ether and the extract steam distilled. The distillate was extracted with ether, dried over sodium sulfate, and distilled. The volatile portion, weighing 0.8 g., boiled at 200° and had an equivalent of 115.2. (Caproic acid boils at 202°, equiv. 116.1.)

The residue from the steam distillation, after one crystallization from water and charcoal to remove a slight quantity of tarry material, weighed 1 g. and melted at 88–99°. Fractional crystallization yielded 0.2 g. of an acid, equivalent 102.7, m. p. 129–131°, no depression with a sample of authentic sebacic acid, m. p. 132°, equiv. 101.07; and 0.2 g. of azelaic acid, equivalent 95.2, m. p. 97–103°. The intermediate fraction melted at 105–125°.

Summary

1. Linoleyl alcohol prepared by the alcoholic sodium reduction of methyl linoleate was shown to consist of a mixture of octadecadiene-9,12-ol-1 and octadecadiene-10,12-ol-1.

2. The properties of the product were accounted for by the presence of conjugation.

3. The physical properties of the substance were observed to change on prolonged standing in the absence of oxygen.

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The Condensation of α -Keto Acids and Amides. II. Pyruvic Acid and Acetamide¹

BY ROBERT M. HERBST

When acetamide and pyruvic acid are condensed under the conditions described by Bergmann and Grafe,² the principal product is α,α -diacetaminopropionic acid. A small amount of α -acetaminoacrylic acid is also formed and may be separated from the former by its solubility in hot ethyl acetate. The ethyl acetate also removes from the reaction mixture a low melting component which has not been described previously.

By the interaction of benzoylformic acid and

(1) Previous paper, Shemin and Herbst, *THIS JOURNAL*, **60**, 1954 (1938).

(2) Bergmann and Grafe, *Z. physiol. Chem.*, **187**, 187 (1930)

acetamide, Shemin and Herbst¹ obtained, besides the expected α,α -diacetaminophenylacetic acid, small amounts of α -benzoylaminophenylacetic acid by a reaction apparently analogous to the formation of phenacetylphenylalanine³ or acetylalanine⁴ from ammonia and phenylpyruvic or pyruvic acids, respectively. The low melting by-product of the pyruvic acid-acetamide condensation was found to contain no acetylalanine, but yielded a compound which appeared to be a complex of one molecule of α -hydroxy- α -acet-

(3) Erlenmeyer and Kunlin, *Ann.*, **307**, 146 (1899); Erlenmeyer, *ibid.*, **337**, 205 (1904).

(4) De Jong, *Rec. trav. chim.*, **19**, 259 (1900).