washed with 10 ml. of water and 20 ml. of alcohol, and dried. After quantitatively freeing this of barium ions with sulfuric acid and removing barium sulfate, the solution was taken to dryness in a vacuum desiccator. The residue of 0.196 g. (0.0012 mole as tartaric acid monohydrate) was heated slowly with 0.85 g. (0.0059 mole) of benzoyl chloride to 150° over a period of three hours. The reaction mixture was extracted with 30 ml. of ether, the clear extract concentrated to 4 ml., and 10 ml. of petroleum ether, b. p. 60–70°, was added. Crystallization of dibenzoxysuccinic anhydride was promoted by scratching the sides of the vessel. The supernatant liquid was decanted, the solid was dissolved in 10 ml. of ether and then thrown down by the addition of 10 ml. of petroleum ether; recovery 0.23 g. (0.00068 mole), m. p., 206°.

Anal. Calcd. for $C_{18}H_{12}O_7$: saponification equiv., 85.0. Found: sapon. equiv., 86.1.

Summary

Alginic acid has been oxidized by means of periodic acid to a substance, presumably the corresponding polymeric dialdehyde acid, which undergoes hydrolysis in dilute acid. From the hydrolyzate glyoxal has been obtained in 42% yield.

The polymeric dialdehyde acid has been oxidized by bromine water. From the hydrolyzate of the resulting acid, *meso*-tartaric acid has been isolated in 25% yield.

Methyl alginate has been subjected to oxidation by periodic acid. Glyoxal in 30% yield has been isolated.

These results show that the scission of the mannuronic acid units of alginic acid takes place between the second and third carbon atoms. Therefore, hydroxyl groups are attached to C_2 and C_3, while bridge and ring linkages are attached to C_4 and C_5. The presence of other structural units in small amount is not excluded.

No conclusion has been drawn in regard to furanoside or pyranoside structure, or to alpha or beta configuration at C_1.

Pasadena, California Received April 15, 1940

[Contribution from the Department of Botany, University of Minnesota]

Linoleyl Alcohol. II. Preparation, Properties, and Rearrangement[1]

By J. P. Kass and G. O. Burr

In a previous communication[2] we have shown that the linoleyl alcohol prepared by the reduction of methyl linoleate with sodium in butyl alcohol, as described by Turpeinen,[3] is a mixture of the expected octadecadiene-9,12-ol-1 with the product of its rearrangement, octadecadiene-10,-12-ol-1, the anomalous properties of the alcohol being fully accounted for by the presence of the conjugated isomerides. The molecular rearrangement, accompanied by the appearance of typical absorption spectra in the ultraviolet,[4] is general among the polyenic acids[4] and has been found[5] to proceed much more rapidly in high-boiling anhydrous solvents than in aqueous alcohols. Preliminary determinations of the velocity of isomerization of linoleic and linolenic acids in 20% sodium ethoxide or in a 20% ethyl alcoholic solution of potassium hydroxide have shown only a negligible rise in the spectroscopic activities of the recovered acids at the end of one hour of boiling, and it was therefore correctly surmised that the reduction of the esters of these acids to the corresponding alcohols may be effected in ethyl alcohol without rearrangement, provided the time of heating in the anhydrous alkali was kept at a minimum. The physical and chemical properties of the alcohols prepared in this manner closely parallel those of the parent acids. Since these alcohols are of biological interest[6] as curative agents in the "fat deficiency" syndrome,[7] this paper describes the preparation and properties of the unconjugated linoleyl and linolenyl alcohols, and the rearrangement of the former to a mixture of octadecadiene-10,12-ols, the characteristics of which are essentially identical with those of the mixed alcohol prepared by the reduction of methyl linoleate with sodium in butanol.[2,3]

Experimental

Preparation of Linoleyl Alcohol.—A solution of 45 g. of methyl linoleate[8] in 300 cc. of anhydrous ethanol was treated at once with 18 g. of sodium cut in large pieces

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[1] This work was supported by grants from the Hormel Foundation and the Graduate School of the University of Minnesota. Presented before the American Chemical Society Convention in Cincinnati, April 9, 1940.

[2] Kass, Miller and Burr, This Journal, **61**, 482 (1939).

[3] Turpeinen, *ibid.*, **60**, 56 (1938).

[4] Moore, *Biochem. J.*, **31**, 138 (1937).

[5] Kass and Burr, This Journal, **61**, 3292 (1939).

[6] Burr and Kass, work in progress.

[7] Burr and Burr, *J. Biol. Chem.*, **86**, 587 (1930).

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

and the mixture left with adequate reflux, no external heating but frequent shaking. When the initially rapid reaction subsided at the end of half an hour, 150 cc. of ethanol was added and the mixture warmed gently to complete the dissolution of the sodium in one hour. Two hundred cc. of water was added immediately and the refluxing continued for one hour to saponify the unreduced ester. The solution was then diluted with 1200 cc. of water. (Dilution with more than four volumes of water causes emulsification due to the diminished solubility of the soaps.) The non-saponifiable fraction was extracted with ether, and the ether layer washed repeatedly with 1% potassium hydroxide and finally with water until free from alkali. After drying over sodium sulfate, the ether was removed under vacuum and the residue distilled from an alembic flask at 153–154° (3 mm.), with no fore-run and practically no residue; yield, 19.5 g., or 45%. The soap solution was acidified; the extracted acid after distillation was found to be essentially unchanged linoleic acid.

Properties.—The linoleyl alcohol was a colorless, fairly mobile oily liquid, f. p. below −16°, iodine value (rapid Wijs method[9]) 189.3 (theory, 190.7), $n^{23}\text{D}$ 1.4698, $E^{1\%}_{1\,\text{cm.}}$ at 2300 A. between 1.5 and 5.5.

On bromination in ligroin according to Brown and Frankel,[10] it produced a 48% yield of a tetrabromide, m. p. 87.5–88° from hexane, undoubtedly identical with the bromide, m. p. 87.3°, obtained by Turpeinen[3] in 5.8% yield. A sample of the tetrabromide was refluxed in acetone with potassium carbonate and potassium permanganate for eight hours, when the mixture was acidified and decolorized with sulfur dioxide to give a crystalline substance, m. p. 106–110°, from which tetrabromostearic acid, m. p. 112–114°, was obtained after fractional crystallization from hexane. A mixed melting point with authentic tetrabromostearic acid, m. p. 114.5°, produced no depression. Moreover, a blank oxidation of pure tetrabromostearic acid under similar conditions depressed its m. p. from 114.5 to 108–111°, with reduction of a considerable amount of permanganate.

The 3,5-dinitrobenzoate of the alcohol was an oil which remained liquid at 0°.

Isolation of Linoleyl Alcohol from Reduced Corn Oil Methyl Esters.—One-hundred grams of corn oil (Mazola) methyl esters dissolved in 650 cc. of absolute ethanol was treated with 40 g. of sodium, the metal dissolution being aided by the addition of 100 cc. of ethanol after one hour. The reaction was completed in one and one-quarter hours, and after saponification and dilution with a total of three volumes of water, the non-saponifiable portion was extracted with ligroin. The ligroin solution contained some soaps despite copious washing with dilute alkali and water. It was finally dried, filtered, made up to about one liter with additional ligroin, and then brominated at −5° with a slight excess of liquid bromine added dropwise with mechanical stirring. The bromides which precipitated immediately were left in contact with the mother liquor overnight, after which the excess bromine was removed with amylene and the bromides filtered; yield, 17.5 g. of white powder, m. p. 85–91° after a single crystallization from hexane. The mother liquor was evaporated and the liquid bromides were debrominated with zinc. Rebromination of the product yielded an additional 3 g. of bromide, m. p. 85–88°. The combined solid bromides, m. p. 86–91°, evidently a mixture of the tetrabromides of linoleyl alcohol and linoleic acid, were debrominated with an equal weight of zinc in ethanol, the reaction being accelerated by occasional additions of alcoholic hydrochloric acid. The reduction products were precipitated with water, extracted with ligroin, the solvent evaporated and the residue left overnight in a 5% solution of potassium hydroxide in 95% ethanol. After dilution with water and extraction with ligroin, which was in turn repeatedly extracted with dilute aqueous and alcoholic alkali, the washed and dried alcohol was distilled at 133° (2 mm.). The distillate was free from acid and had all the properties of linoleyl alcohol enumerated above, re-forming the bromide, m. p. 87.5–88°, in 50% yield. A total of 5 g. of alcohol was obtained.

Rearrangement of Linoleyl Alcohol.—Five grams of linoleyl alcohol was refluxed for five hours with 5 g. of potassium hydroxide in 25 cc. of anhydrous butanol. The alcohol was extracted with ligroin, washed free from alkali, the solvents removed *in vacuo*, and the residual alcohol distilled at 3 mm. The alcohol, recovered with practically no loss, was now viscous and solidified at about −5°. Its n^{23} rose to 1.4825 and its iodine number dropped to 165.2. Like other conjugated compounds,[11] the alcohol now liberated iodine from the Wijs reagent and exhibited an $E^{1\%}_{1\,\text{cm.}}$ of about 900 at 2300 Å.,[12] compared to *ca.* 1180 reported by Van der Hulst[13] for pure 9,11-linoleic acid.

On bromination as before, 0.438 g. of the isomerized alcohol precipitated ligroin-insoluble liquid bromides and only 0.024 g. of a solid of m. p. 61–71°.

Upon standing at −16° for several hours, a solution of 4 g. of the alcohol in 10 cc. of ligroin deposited 0.1 g. of a crystalline substance, m. p. 42.5–43.5° after one recrystallization from methanol. (The m. p. of this compound was previously[2] reported as 42.5°.) This had an $E^{1\%}_{1\,\text{cm.}}$ of 1200 at 2300 Å. and on oxidation with potassium permanganate in neutral acetone[14] produced a solid acid, m. p. 131°, no depression with authentic sebacic acid. It is therefore apparently an octadecadiene-10,12-ol-1. The liquid alcohol remaining after the removal of the solid still had an $E^{1\%}_{1\,\text{cm.}}$ of about 900 at 2300 Å. and on similar oxidation formed a solid acid which melted indefinitely at 123–130° after two crystallizations from water. This has been shown[2] to be impure sebacic acid, and the parent substance thus consists of one or more isomeric liquid octadecadiene-10,12-ols in an admixture with the incompletely removed solid alcohol and 25% of other alcohol. That the latter is the alpha-linoleyl alcohol appears improbable, since the characteristic bromide, m. p. 88°, is not formed at all after complete isomerization, although it may be obtained in low yields from the products of partial isomerization.

Preparation of Linolenyl Alcohol.—Forty-three grams of methyl linolenate was reduced in ethanol exactly as described above. Considerable difficulty was again encountered in removing the soaps from the non-saponifiable ex-

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[9] Hoffman and Green, *Oil and Soap*, **16**, 236 (1939).

[10] Brown and Frankel, This Journal, **60**, 55 (1938).

[11] Böeseken and Gelber, *Rec. trav. chim.*, **46**, 162 (1927).

[12] We wish to thank Dr. Elmer S. Miller for the spectrographic analyses. Complete ultraviolet absorption spectra of all unsaturated compounds described in this paper will be presented by Miller and co-workers in another communication.

[13] Van der Hulst, *Rec. trav. chim.*, **54**, 639 (1935).

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

tract. It was found necessary to wash the ether or ligroin solution with aqueous alcohol, although this caused some loss of linolenyl alcohol in the resulting emulsions. After copious washing, the dried alcohol was distilled at 133° (2 mm.). The distillate still contained 1.63% of free acid, which was removed with dilute alkali. The final yield of pure alcohol was 13 g.

Properties of Linolenyl Alcohol.—The linolenyl alcohol was a colorless, oily liquid. Its iodine value was 287.0 (calcd. 288.2); it had an $E^{1\%}_{1\,\text{cm.}}$ of less than 1 at 2700 Å. and about 6 at 2300 Å. Its $n^{23}\text{D}$ was 1.4792, compared to 1.4800 for linolenic acid. On bromination in ether, it produced an immediate precipitate of a granular bromide corresponding to approximately 25% of the theoretical yield. After one crystallization from benzene, the hexabromide sintered at 171° and melted sharply at 172°. An additional recrystallization did not alter the m. p. The alcohol thus closely resembles the corresponding acid.

Summary

Unconjugated alpha-linoleyl and alpha-linolenyl alcohols were prepared by the reduction of methyl linoleate and methyl linolenate with sodium in absolute ethanol.

The physical and chemical properties of the alcohols were shown to parallel closely the properties of the parent acids.

alpha-Linoleyl alcohol was characterized by its tetrabromide, m. p. 88°, while alpha-linolenyl alcohol formed a hexabromide, m. p. 172°.

alpha-Linoleyl alcohol was rearranged by potassium hydroxide in butanol to isomeric octadecadiene-10,12-ols, among them a solid 10,12-linoleyl alcohol, m. p. 43.5°. The properties of the isomerized alcohols were related to the characteristics of the products of reduction of methyl linoleate with sodium in butanol.

MINNEAPOLIS, MINNESOTA RECEIVED MAY 8, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of Tertiary Acetylenes[1]

BY KENNETH N. CAMPBELL AND LAWRENCE T. EBY

The catalytic reduction of acetylenes offers a good means of preparing olefins of known position of the double bond,[2] but so far this work has been confined to the straight chain compounds, as acetylenes containing branches near the triple bond have been difficult to prepare, and but few of them are known. In order to extend the reduction studies to this type of acetylene it therefore was necessary first to develop a method of preparing such compounds. The simplest method of making acetylenes, the reaction of an alkyl halide with a sodium acetylide, fails with secondary and tertiary halides.[3] *t*-Butylacetylene has been prepared[4] by treatment of 3,3-dimethyl-2,2-dichlorobutane with sodium hydroxide, and neopentylacetylene has been made by a similar produre.[5] This method is not, however, of general application, since in most cases the intermediate halide is difficult to prepare.

Attention was therefore turned to the Grignard reaction as a means of making the desired acetylenes. Just as neopentane can be made from methylmagnesium chloride and *t*-butyl chloride,[6] it was hoped that acetylenic hydrocarbons could be prepared from acetylenic Grignard reagents and tertiary alkyl halides. Although these Grignard reagents will couple with activated halides such as allyl bromide,[7] it was found in the present study that only poor yields of hydrocarbon were obtained when *t*-butyl or *t*-amyl bromides were used, and the method does not seem a promising one for the preparation of branched chain acetylenes.

The possibility of preparing such acetylenes from tertiary acetylenic chlorides and primary aliphatic Grignard reagents was then investigated. Tertiary acetylenic carbinols, which are easily prepared from sodium acetylide or a sodium alkylacetylide and a ketone in liquid ammonia,[8] can be readily converted to the corresponding chlorides by means of anhydrous hydrogen chloride at low temperatures. The chlorides are unstable, but can be distilled and kept without decomposition if reasonable care is used. They show the usual reactions of tertiary chlorides,

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[1] Paper XL on the chemistry of substituted acetylenes and their derivatives; previous paper, THIS JOURNAL, **62**, 1368 (1940). This material was presented before the Organic Division at the Cincinnati meeting, April, 1940.

[2] Campbell and O'Connor, *ibid.*, **61**, 2897 (1939).

[3] Picon, *Compt. rend.*, **168**, 825 (1919).

[4] Ivitsky, *Bull. soc. chim.*, [4] **35**, 357 (1924).

[5] Ozanne and Marvel, THIS JOURNAL, **52**, 5267 (1930).

[6] Whitmore and Fleming, *ibid.*, **55**, 3803 (1933).

[7] Danehy, Killian and Nieuwland, *ibid.*, **58**, 611 (1936).

[8] Campbell, Campbell and Eby, *ibid.*, **60**, 2882 (1938).