2-Anilinomethylnorvisnagin (II, R = NHC_6H_5).—A mixture of 1.0 g. of khellol tosylate, 2 ml. of purified aniline and 2 ml. of methanol was warmed until a clear solution resulted. Upon the addition of 10 ml. of ether and cooling the product separated as a crystalline powder. Recrystallized from glacial acetic acid, the compound forms tiny, nearly colorless prisms, m.p. 211–212°. The compound is insoluble in dilute aqueous acids, but when to a suspension of a small sample in methanol was added a drop of 6 *N* hydrochloride acid a clear solution resulted. This solution remained clear when diluted with water but became cloudy when a drop of dilute alkali was added.

Anal. Calcd. for $C_{19}H_{15}O_4N \cdot 0.5H_2O$: C, 69.07; H, 4.88; N, 4.24. Found: C, 68.97; H, 4.71; N, 4.70.

2-Iodomethylnorvisnagin (II, R = I).—To a warm solution of 1.0 g. of khellol tosylate in 20 ml. of dry acetone was added 2.0 g. of sodium iodide dissolved in 10 ml. of acetone. A thick crystalline magma formed at once. The mixture was warmed on the steam-bath for 5 min., allowed to stand overnight and poured into a water–ether mixture. The solid which separated (0.58 g.) and that recovered by evaporation of the ether layer (0.17 g.) were recrystallized from ethyl acetate. The tiny, pale yellow needles melted at 158–159° (dec.).

Anal. Calcd. for $C_{13}H_9O_4I$: C, 43.82; H, 2.55. Found: C, 43.95; H, 2.64.

Visnagin (II, R = H) (A) **from 2-Iodomethylnorvisnagin.**—To a solution of 280 mg. of the iodo compound in 5 ml. of glacial acetic acid, zinc dust was added in small portions while the solution was kept at the boiling point. The color of the solution went from yellow to brown and then to pale yellow. The zinc was removed by filtration, the filtrate poured into an ether–water mixture, and the ether solution separated, washed, dried and evaporated. The crystalline residue (155 mg.) was recrystallized from aqueous methanol and then from ethyl acetate–petroleum ether. The stout, colorless prisms melted at 139–140° alone or mixed with a sample of authentic visnagin. The absorption spectrum of the product showed maxima at 243 mμ (log ε 4.58) and 322.5 (log ε 3.71). A sample of synthetic visnagin (prepared from visnaginone) is reported to show a log ε of 4.59 at 244 mμ (the second maximum was not reported).[6] The absorption spectrum of khellol glucoside was determined for comparison, and showed maxima at 245 mμ (log ε 4.47) and 324 mμ (log ε 3.65).

(B) **From Khellol Tosylate.**—To a solution of 500 mg. of khellol tosylate in 5 ml. of acetic anhydride was added a hot solution of 1.0 g. of sodium iodide in 10 ml. of acetic anhydride. To the resulting brown solution (containing a colorless precipitate) was added zinc dust until the color changed to pale yellow. The mixture was filtered into a slurry of ice and water; as the acetic anhydride decomposed fine silky needles formed. After the mixture had stood overnight (at 5°) the product was collected and recrystallized from ethyl acetate–petroleum ether and from ethyl acetate. The colorless prisms melted at 138–140°, and did not depress the m.p. of authentic visnagin.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.80; H, 4.38. Found: C, 67.87, 67.70; H, 4.37, 4.67.

C-Methoxyacetylvisnaginone (III, R = $COCH_2OCH_3$).—To 2.0 g. of powdered sodium, covered with 20 ml. of dry ether, was added a solution of 3.0 g. of visnaginone in 10 ml. of methyl methoxyacetate. The vigorous reaction caused the ether to distil from the reaction flask, leaving a brown sirup. The addition of 20 ml. of dry ether to this sirup caused it to set to a yellow paste. After 12 hours at room temperature the reaction mixture was decomposed by the addition of ice, the aqueous layer was separated and washed with ether, and acidified. The mixture was extracted with ether and the ether solution dried and evaporated to 50 ml. Buff crystals separated on cooling, and a second crop was obtained by further concentration of the filtrate. The product was recrystallized from aqueous methanol (with the use of decolorizing carbon) and formed pale yellow, blunt needles, m.p. 127–128° (1.90 g.).

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 60.43; H, 5.02. Found: C, 60.20; H, 5.32.

Khellol Methyl Ether (I, R = CH).—To a suspension of 500 mg. of the above diketone in 5 ml. of methanol was added 0.5 ml. of concentrated hydrochloric acid. The compound dissolved on warming to give a clear orange-yellow solution which was heated to boiling for about 2 min., cooled, and diluted with water. The excess acid was neutralized with dilute alkali and the solution (*ca.* 15 ml.) cooled. The nearly colorless, soft needles (430 mg.) were collected and recrystallized from ethyl acetate–petroleum ether. The compound formed soft, white needles, m.p. 124–125°.

Anal. Calcd. for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65; OCH_3, 23.84. Found: C, 64.62; H, 4.76; OCH_3, 23.75.

Acknowledgment.—The author wishes to thank the Smith, Kline and French Laboratories and S. B. Penick and Company for financial assistance and for supplies of the khellol glucoside used in this work.

LOS ANGELES, CALIF. RECEIVED JANUARY 31, 1951

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[6] Private communication from Drs. G. E. Ullyot and P. N. Craig.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

A Dodecitol from the Alkaline Electroreduction of D-Glucose[1,2]

BY M. L. WOLFROM, W. W. BINKLEY, C. C. SPENCER AND B. W. LEW

A crystalline substance, designated atlitol and obtained as a by-product in the commercial alkaline electroreduction of D-glucose, has been characterized as an optically active unbranched dodecitol.

The Atlas Powder Co. of Wilmington, Delaware, operates a process for producing D-mannitol by the electroreduction of D-glucose.[3,4] In a factory run made in 1939 a high melting material was obtained from the centrifuge in a recrystallization of D-mannitol. The substance was sent to this Laboratory for characterization. It was a crystalline, non-reducing, optically active, high melting substance of low water solubility that was unchanged by acid treatment. It formed a crystalline acetate whose analysis (and that of the parent body) and molecular weight indicated a dodecitol. Periodate assay showed the consumption of essentially 11 moles (per mole of substance) of oxidant with the production of 10 moles of formic acid and 2 moles of formaldehyde; carbonic, oxalic or glycolic acids were not detected in the oxidation mixture. The substance showed a tendency to over-oxidize slightly and to analyze somewhat low on formic acid. Nevertheless, it is believed that the cited figures are essentially correct and it is to

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[1] A preliminary report of this work is recorded in *Abstracts Papers Am. Chem. Soc.*, **119**, 6Q (1951).

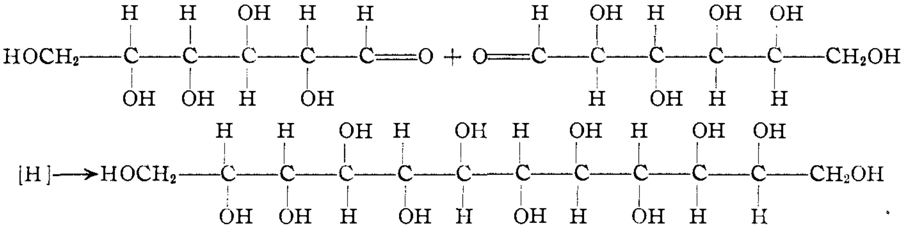
[2] Paper No. 5 in the series entitled "Sugar Interconversion under Reducing Conditions"; previous communication, M. L. Wolfrom, B. W. Lew, R. A. Hales and R. M. Goepp, Jr., THIS JOURNAL, **68**, 2342 (1946).

[3] H. J. Creighton, U. S. Patent 1,990,582 (1935).

[4] H. J. Creighton, *Trans. Electrochem. Soc.*, **75**, 289 (1939).

be noted that they must be evaluated to two significant figures whereas periodate values hitherto reported in work of this nature have been required to be defined to only one such figure. The substance is therefore in all probability an optically active unbranched dodecitol and is herein designated atlitol.

Unfortunately, the conditions for producing atlitol from D-glucose are not defined but it is probable that it is formed by the reductive coupling of two aldehyde groups. Had a ketose been involved, a branched chain dodecitol would have resulted. The alkaline electroreduction of D-glucose produces an exceedingly complex mixture of reduced alkali-interconversion products[5] but nevertheless the main component is sorbitol, obtained by the simple one-stage reduction of the aldehyde function of D-glucose. Thus D-glucose is the most probable aldose concerned in the coupling and if this union should occur in the predictable all-*trans*[6] manner, the product would have the configuration shown below.



$$HOCH_2-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{H}{C}{=}O + O{=}\overset{H}{C}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CH_2OH$$

$$[H]\longrightarrow HOCH_2-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-CH_2OH$$

It is to be emphasized that the most probable predictable product is not necessarily the one that would be isolated since low solubility was the main controlling factor. The number of sterically possible unbranched dodecitols can be calculated as 1024 less meso forms and identities.

Experimental

Atlitol.—A by-product from the manufacture of D-mannitol by the electroreduction of D-glucose (factory run November 22, 1939) below 30° and at *p*H 10–13[3] was received[7] for examination at this Laboratory from the Atlas Powder Co., Wilmington, Delaware. It was obtained from the factory centrifuge in a recrystallization of D-mannitol. A colorless crystalline solid was at hand in pure form after several recrystallizations from hot water; m.p. 233–235° (cor.), $[\alpha]^{29}D$ +212° (*c* 0.2, 0.04 *M* MoO_3, 6 dm. tube), Molisch (−), Fehling reduction before and after boiling (original material recovered) with mineral acid (−). It was soluble in hot water but was only slightly so at room temperature; it was insoluble in methanol, ethanol, ether, acetic acid and pyridine.

Anal. Calcd. for $C_{12}H_{26}O_{12}$: C, 39.77; H, 7.23. Found: C, 39.79; H, 6.98.

Periodate Assay of Atlitol.—An amount of 125 mg. of pure atlitol was dissolved in 100 ml. of hot water and the resulting solution was cooled to 3°. A volume of 125 ml. of 0.05 *M* sodium metaperiodate (previously cooled to 3°; 18 moles of oxidant per mole of substance) was added and the solution was adjusted to 250 ml. with cold distilled water. The reaction mixture was allowed to stand in the dark at 3°. The periodate consumption was determined as described by Jackson[8] and formaldehyde was assayed by the dimedon method of Vorländer.[9] Separate aliquots of the reaction mixture were allowed to react with ethylene glycol at 20–25° for 20–30 minutes. The formic acid content was then determined with 0.05 *N* NaOH using phenolphthalein[10] indicator. The reaction at this temperature was essentially complete in 24 hours or less but was observed for longer periods and time rate curves were determined. The final portions of the time curves were sufficiently flat that any extrapolation correction was essentially negligible. The substance consumed 11.5 moles of sodium metaperiodate (unbuffered or with acetate buffer at *p*H 4.5) and formed 9.5 moles of formic acid. Suitable methods applied to the reaction mixture failed to show the presence of carbonic, oxalic or glycolic[11] acids.

Atlitol Dodecaacetate.—Atlitol (500 mg.) was allowed to react with a solution of 0.3–0.4 g. of freshly fused zinc chloride in 10 ml. of acetic anhydride for 6 days at 26–27°. The reaction mixture was poured into 40 g. of ice and water and stirred for 1 hour. The resultant solution was adjusted to *p*H 5.5–6.0 with 15 g. of sodium bicarbonate and was extracted with chloroform. The sirup (1.17 g.) obtained on solvent removal from the dried extract was crystallized from ethanol–ether; yield 1.09 g. Pure material was obtained on further crystallization effected in the same manner; m. p. 69–70°, $[\alpha]^{30}D$ +18° (*c* 3, U. S. P. chloroform). The substance crystallized in colorless elongated prisms that were soluble in ethanol, ether, chloroform and benzene.

Anal. Calcd. for $C_{12}H_{14}O_{12}(CH_3CO)_{12}$: C, 49.89; H, 5.81; CH_3CO, 13.8 ml. 0.1 *N* NaOH per 100 mg.; mol. wt., 866.8. Found: C, 50.06; H, 5.85; CH_3CO, 13.8 ml.; mol. wt. (Rast), 849.

Columbus, Ohio Received February 12, 1951

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(5) See ref. 2 and previous papers in this series.

(6) M. L. Wolfrom, S. M. Olin and W. J. Polglase, This Journal, **72**, 1724 (1950).

(7) Forwarded by the late Dr. R. Max Goepp, Jr.

(8) E. L. Jackson, *Org. Reactions*, **2**, 361 (1944).

(9) D. Vorländer, *Z. anal. Chem.*, **77**, 241 (1929).

(10) Allene Jeanes and C. A. Wilham, This Journal, **72**, 2657 (1950).

(11) P. Fleury, G. Poirot and Y. Fiévet, *Ann. pharm. franç*, **5**, 209 (1947).