steam distillation 12.5 g. of the phenol; b. p. 148–152° (30 mm.).[14,15]

5-Hydroxy-6-nitrohydrindene.—(a) The above 5-aminohydrindene was diazotized and nitrated in one step according to Neunhoffer[16] but on steam distillation an impurity accompanied the product. This unknown material melted at 82–83°.

(b) Following Diepolder's general method,[17] 5-hydroxyhydrindene was nitrated directly. The impurity (m. p. 82–83°) was again obtained but it was found that the high solubility of the desired compound in petroleum ether (b. p. 60–68°) allowed it to be decanted away from the more insoluble impurity and then crystallized; m. p. 63.5–64.5°.

6-Hydroxy-7-nitrotetralin.—Raney nickel catalytic hydrogenation of β-naphthol gave 50–60% yields of 6-hydroxytetralin at 190° and 500 lb. pressure (33.3 atm.). This phenol was nitrated with nitrogen dioxide and after steam distillation gave a 21% yield of the product which was recrystallized from ethanol; m. p. 88.5–89°. The acetate prepared from acetyl chloride in pyridine melted at 100°.[10]

6-Methoxy-7-nitrotetralin.—Using two equivalents each of 2.0 *N* sodium hydroxide and methyl sulfate, we obtained from 3.05 g. of the phenol, 1.37 g. of the ether. The substance was pale yellow and melted at 50–51.5°.

Anal. Calcd. for $C_{11}H_{13}O_3N$: C, 63.73; H, 6.32. Found: C, 63.74; H, 6.54.

4,5-Dimethyl-2-nitrophenol.—This compound was prepared by the direct nitration of the phenol using Diepolder's method; m. p. 85–86°.[14]

5-Methyl-2-nitrophenol.—Technical *m*-cresol was nitrated in cooled glacial acetic acid with a small excess of nitric acid dissolved in glacial acetic acid. After steam distillation and recrystallization, it melted at 54.5–55°.[18]

4-Methyl-2-nitrophenol.—This substance was prepared in the usual manner from *p*-cresol.

(14) W. Baker, *J. Chem. Soc.*, 476 (1937).
(15) Smith and Haller, THIS JOURNAL, **61**, 143 (1939).
(16) Otto Neunhoffer, *Ber.*, **68**, 1774 (1935).
(17) Emil Diepolder, *Ibid.*, **42**, 2916 (1909).

Summary

1. In the light of recent structural studies on ethylene and tetramethylethylene, some of the original assumptions of the Mills–Nixon postulate are questionable.

2. A set of physical measurements on nitrophenols indicates no appreciable stabilization of double bonds caused by ring structures.

3. It has been pointed out that substitution reactions do not offer an acceptable method for locating double bonds.

(18) Staedel and Kolb, *Ann.*, **259**, 210 (1890).

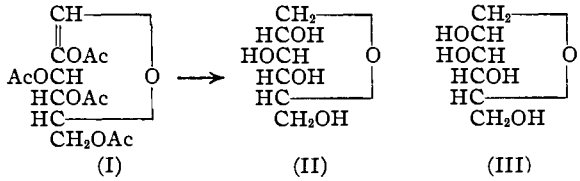
MINNEAPOLIS, MINNESOTA RECEIVED OCTOBER 23, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

The Chemistry of Naturally Occurring Monoanhydrohexitols. II. Synthetic Tetramethylstyracitol[1]

BY WERNER FREUDENBERG AND JOHN T. SHEEHAN

In 1930 Zervas[2] reported the synthesis of styracitol, the naturally occurring monoanhydrohexitol in *styrax obassia*. Tetraacetyl oxyglucal (I) was hydrogenated and subsequently deacetylated to 1,5-anhydro-*d*-sorbitol (II) or 1,5-anhydro-*d*-mannitol (III) depending on whether a *cis* or a *trans* addition occurred at the double bond.



(I) (II) (III)

The synthetic material was identical with the natural product. The question, however, if styracitol should be classified as a sorbitol or a mannitol derivative was not answered.

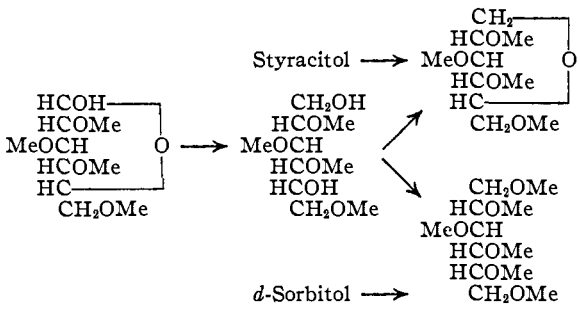
In a recent publication from this Laboratory we[3] attempted to ascertain the configuration of styracitol by a comparison of the rates of oxidation with lead tetraacetate and by an application of the isorotation rules to styracitol and its isomer polygalitol. These two substances were assumed to be epimeric since they formed on oxidation the same anhydrofructosazone[4] and glucosazone.[5] On the basis of this assumption the experimental results favored the mannitol structure for styracitol and the sorbitol structure for polygalitol.

To establish definitely the configuration of styracitol as a sorbitol or mannitol derivative, it was deemed necessary to devise a synthesis of a derivative of styracitol starting with glucose or mannose wherein all asymmetric centers are protected and remain unaltered throughout the series

(1) Reported before the Organic Division, A. C. S. Meeting, Boston, Mass., September, 1939.
(2) Zervas, *Ber.*, **63**, 1689 (1930).
(3) Freudenberg and Rogers, THIS JOURNAL, **59**, 1602 (1937).
(4) Bergmann and Zervas, *Ber.*, **64**, 2032 (1931).
(5) Shinoda, Sato and Sato, *Ibid.*, **65**, 1219 (1932).

of reactions. The tetramethyl ether of styracitol was the derivative chosen. It was synthesized from tetramethyl-*d*-glucopyranose by reducing the latter and then dehydrating the 2,3,4,5-tetramethylsorbitol obtained. The dehydrated product agreed in every respect with that obtained by methylating the natural styracitol isolated from the shells of *styrax obassia*. Styracitol therefore has the configuration of 1,5-anhydro-*d*-sorbitol as originally announced by Zervas.

To exclude the possibility of tetramethylmannitol being formed in the hydrogenation of tetramethylglucopyranose, the reduction was carried out in a neutral medium at high pressure. Furthermore a portion of the product obtained was completely methylated and its properties compared with an authentic sample of hexamethylsorbitol. The two compounds were found to agree completely, indicating that the hydrogenation and methylation had no racemizing or epimerizing effects.



When tetramethyl-*d*-mannopyranose was used as a starting material and methylated and dehydrated as described for the glucose derivative with the hope of synthesizing tetramethylpolygalitol, which as mentioned above was thought to be the epimer of tetramethylstyracitol, the resulting synthetic tetramethyl ether was not identical with that obtained from the natural product but differed considerably in physical properties. The configuration of 1,5-anhydro-*d*-mannitol therefore is excluded for polygalitol, and the two naturally occurring anhydro polyhydric alcohols are not epimeric.

The methylated derivatives herein described, while useful as reference compounds in establishing the presence of furanose and pyranose rings, may find other uses as they are high boiling limpid liquids quite soluble both in organic and inorganic solvents.

Experimental

Styracitol.—This compound was isolated from *styrax obassia* according to the method described by Asahina,[6] melting at 155°, $[\alpha]^{23}D$ −49.4° (H_2O, c = 1.6).

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.89; H, 7.37. Found: C, 43.90; H, 7.32.

Tetramethylstyracitol.—Ten grams of styracitol was methylated according to the method of West and Holden.[7] The product obtained was a limpid, colorless sirup which distilled at a bath temperature of 110° under 1.5 mm. pressure; $[\alpha]^{23}D$ −36.5° (no solvent), n^{25} 1.4520, d. 1.0849.

Anal. Calcd. for $C_{10}H_{20}O_5$: C, 54.54; H, 9.13; CH_3O, 56.31. Found: C, 54.62; H, 9.14; CH_3O, 56.72.

Tetramethylsorbitol.—A solution of 30 g. of tetramethylglucose in 75 cc. of water and 15 cc. of alcohol was reduced for seven hours at 135° under a pressure of 1300 pounds (85 atm.) of hydrogen in the presence of Raney nickel. The filtered solution was evaporated *in vacuo* to a clear sirup which did not reduce Fehling's solution. The sirup was purified by distillation at a bath temperature of 145° under 2 mm. pressure; $[\alpha]^{23}D$ +10.3° (EtOH, c = 6.3), $[\alpha]^{23}D$ +4.7° ($CHCl_3$, c = 10.5), n^{20} 1.4612.

Anal. Calcd. for $C_{10}H_{22}O_6$: C, 50.40; H, 9.32; CH_3O, 52.03. Found: C, 50.36; H, 9.36; CH_3O, 52.35.

Tetramethyl-1,5-anhydrosorbitol.—Fifteen grams of tetramethylsorbitol and 2 cc. of 13% sulfuric acid solution were heated *in vacuo* for half an hour at 140°. The solution was neutralized with 0.4 g. of anhydrous sodium carbonate after which a small amount of decolorizing charcoal and 50 cc. of ether were added. The solution was filtered and dried over anhydrous sodium sulfate. After filtering, the ether was removed leaving a sirup which distilled colorless at a bath temperature of 115° under 2 mm. pressure; $[\alpha]^{23}D$ −36.2° (no solvent), n^{25} 1.4518, d. 1.0876.

Anal. Calcd. for $C_{10}H_{20}O_5$: C, 54.54; H, 9.13; CH_3O, 56.31. Found: C, 54.29; H, 9.08; CH_3O, 56.58.

Hexamethylsorbitol.—Ten grams of tetramethylsorbitol was methylated according to the method of West and Holden. The product obtained was a colorless sirup which distilled at a bath temperature of 100° under 1.5 mm. pressure; $[\alpha]^{23.5}D$ 1.93° (no solvent), n^{22} 1.4370, d. 1.0476. For comparison 10 g. of sorbitol was methylated in the above fashion. The resulting product was found to distil at 100° under 1.5 mm. pressure; $[\alpha]^{24}D$ 1.97° (no solvent), n^{22} 1.4367, d. 1.0334.

Anal. Calcd. for $C_{12}H_{26}O_6$: C, 54.14; H, 9.77; CH_3O, 69.92. Found: C, 54.17; H, 9.75; CH_3O, 70.02 (product from tetramethylsorbitol); C, 54.07; H, 9.94; CH_3O, 69.80 (product from sorbitol).

Polygalitol.—This compound was isolated from *polygala amara*, according to the method described by Shinoda.[5] Briefly, the pulverized drug was repeatedly extracted with methyl alcohol and the extract, after the addition of water, neutralized with magnesia, filtered and the filtrate then taken to dryness in the air. The residue of dark brown gum was extracted with absolute methyl alcohol and the combined extract concentrated. Through the careful ad-

(6) Asahina, *Ber.*, **45**, 2365 (1912).
(7) West and Holden, THIS JOURNAL, **56**, 930 (1934).

dition of ether the bulk of the saponin present in the extract was removed. The filtrate was concentrated with removal of ether and, after standing a few days in the ice-box, crystals appeared. These were filtered off and recrystallized from methyl alcohol, forming colorless plates, melting at 142–143°; $[\alpha]^{21}D$ +42.0° (H_2O, c = 1.8).

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.89; H, 7.37. Found: C, 43.95; H, 7.44.

Tetramethylpolygalitol.—Ten grams of polygalitol was methylated according to the method of West and Holden. The product obtained was a limpid, colorless sirup which distilled at a bath temperature of 80° under 2 mm. pressure; $[\alpha]^{23}D$ +67.67° (no solvent); n^{22} 1.4444, d. 1.0571.

Anal. Calcd. for $C_{10}H_{20}O_5$: C, 54.54; H, 9.13; CH_3O, 56.31. Found: C, 54.54; H, 9.10; CH_3O, 56.55.

Tetramethylmannitol.—A solution of 30 g. of tetramethylmannose in 75 cc. of water and 15 cc. of alcohol was reduced for seven hours at 135° under a pressure of 1300 pounds (85 atm.) of hydrogen in the presence of Raney nickel. The filtered solution was evaporated *in vacuo* to a clear, thick sirup which did not reduce Fehling's solution. The sirup was purified by distillation at a bath temperature of 150° under 2 mm. pressure; $[\alpha]^{21}D$ +20.7° (EtOH, c = 10.15), $[\alpha]^{21}D$ +17.5° ($CHCl_3$, c = 10.6), n^{24} 1.4605.

Anal. Calcd. for $C_{10}H_{22}O_5$: C, 50.40; H, 9.32; CH_3O, 52.03. Found: C, 50.34; H, 9.27; CH_3O, 52.38.

Tetramethyl-1,5-anhydromannitol.—Fifteen grams of tetramethylsorbitol and 2 cc. of 13% sulfuric acid solution were heated *in vacuo* for a half hour at 140°. The solution was neutralized with 0.4 g. of anhydrous sodium carbonate, after which a small amount of decolorizing charcoal and 50 cc. of ether were added. The solution was filtered and dried over anhydrous sodium sulfate. After filtering off the sodium sulfate, the ether was removed leaving a limpid sirup which distilled colorless at a bath temperature of 95° under 2 mm. pressure; $[\alpha]^{22}D$ +30.6° (no solvent), n^{22} 1.4479, density 1.0435.

Anal. Calcd. for $C_{10}H_{20}O_6$: C, 54.54; H, 9.13; CH_3O, 56.31. Found: C, 54.21; H, 9.03; CH_3O, 56.24.

Hexamethylmannitol.—Ten grams of tetramethylmannitol was methylated according to the method of West and Holden. The product obtained was a colorless sirup which distilled at a bath temperature of 95° under 2 mm. pressure; $[\alpha]^{22}D$ +12.53° (no solvent), $n^{21}D$ 1.4403, density 1.0458. For comparison 10 g. of isolated mannitol was methylated in the above fashion. The resulting product was found to distil at 97° under 2 mm. pressure; $[\alpha]^{22}D$ +12.46° (no solvent), $n^{21}D$ 1.4400, d. 1.0410.

Anal. Calcd. for $C_{12}H_{26}O_6$: C, 54.14; H, 9.77; CH_3O, 69.92. Found: C, 54.28; H, 9.58; CH_3O, 69.90 (product from tetramethylmannitol); C, 54.28; H, 9.79; CH_3O, 70.07 (product from mannitol).

Acknowledgments.—The authors wish to express their thanks to Dr. P. A. Levene for permission to carry out the high pressure reductions in his laboratory, to Prof. S. Takei for the styrax used, and to the Atlas Powder Co. for a sample of natural mannitol. The microanalyses were made by J. F. Alicino of this Laboratory.

Summary

Styracitol has been proved to be 1,5-anhydro-*d*-sorbitol by the synthesis of its tetramethyl derivative.

Polygalitol has been shown not to be 1,5-anhydro-*d*-mannitol.

A new method is described for establishing the presence of furanose and pyranose rings by preparing the corresponding methylated anhydro sugar alcohols.

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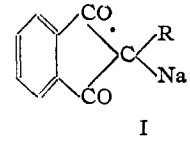
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A Synthesis of Substituted α-Naphthoquinones

BY C. F. KOELSCH AND D. J. BYERS

The recent discovery that vitamin K is a substituted α-naphthoquinone adds importance to all reactions leading to substances of this class. The research described in the present paper is an investigation of a series of reactions by means of which 2-alkyl, 2-alkyl-3-hydroxy-, and 2-alkyl-3-carbalkoxy-α-naphthoquinones and hydroquinones can be prepared. The reactions may be formulated as

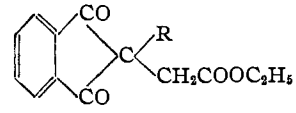
$$o\text{-}C_6H_4(COOC_2H_5)_2 + RCH_2COOC_2H_5 \xrightarrow{Na}$$



(1)

I

$$I + BrCH_2COOC_2H_5 \longrightarrow$$



(2)

II