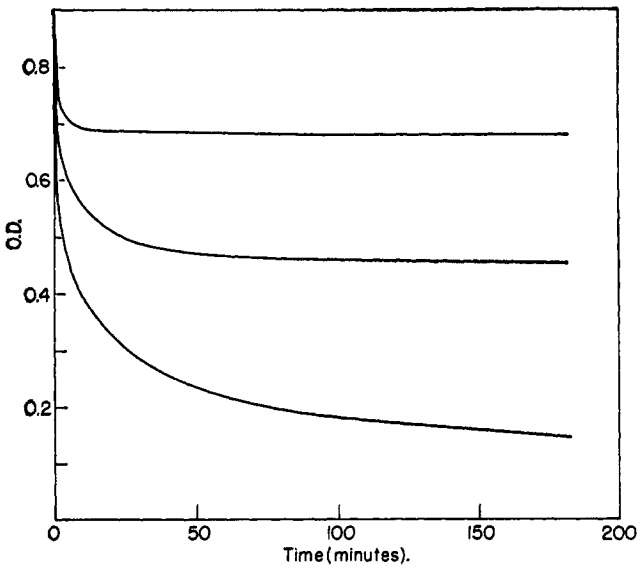

Fig. 2.—Reaction of galvinoxyl with trihydrogalvinoxyl in benzene at 25°; initial concentration of galvinoxyl, 10^{-3} M (O.D., 0.90). Initial concentration of trihydrogalvinoxyl: upper curve, 1.25×10^{-4} M; middle curve, 2.50×10^{-4} M; lower curve, 5×10^{-4} M.

TABLE I

INHIBITION OF THE AUTOXIDATION OF GALVINOXYL BY HYDROGALVINOXYL IN BENZENE AT 30°

Hydrogalvinoxyl, % added	Inhibition time, min.	Δt
0	59	59
4	117	58
8	171	54
12	277	56

bility of solutions of galvinoxyl with varying solvents has not been investigated. Qualitatively, the results of Fig. 1 are observed with both benzene and carbon tetrachloride.[5]

It is of interest that this hindered phenoxyl radical, galvinoxyl, a type of compound usually considered as an inhibitor of autoxidation, is itself susceptible to autoxidative destruction.[6]

Experimental

Galvinoxyl was prepared by the procedure of G. M. Coppinger.[2a] The method of Greene, Adam, and Cantrill[3c] was used for its purification and titrimetric analysis.

Autoxidation of Galvinoxyl.—A stream of oxygen was passed through a solution of 1 g. (2.37 mmoles) of galvinoxyl in 500 ml. of carbon tetrachloride. After 24 hr. the initial dark reddish brown solution decolorized to a pale reddish orange solution. The solvent was removed under reduced pressure and the residue chromatographed on an alumina column, eluting with *n*-pentane. The first ten fractions contained an intensely yellow solid, 2,6-di-*t*-butyl-1,4-benzoquinone, 0.2613 g., m.p. 64.5–65.5° (lit.[7] m.p. 65–66°), identical in infrared spectrum with that reported in the literature[7]; mol. wt.: calcd., 220; found, 214 (Rast). The next compound eluted from the column was a white solid, 41 mg., m.p. 185–186°. Two recrystallizations from an ether–pentane mixture afforded 3,5-di-*t*-butyl-4-hydroxybenzaldehyde, m.p. 186–188° (lit.[8] m.p. 187–188°), m.m.p. 186–188°, and identical in ultraviolet and infrared spectra with an authentic sample. No other discrete compound could be isolated from the alumina column. An autoxidation in benzene gave similar results.

Reaction of Galvinoxyl with Trihydrogalvinoxyl.—To a dry constricted test tube, flushed with nitrogen, was added 0.844 g. (2 mmoles) of galvinoxyl and 0.425 g. (1.0 mmole) of trihydrogalvinoxyl, followed by 30 ml. of freshly distilled benzene (deaerated with nitrogen). The solution was degassed, sealed, and left for 3 days at 25°. The ultraviolet absorption of the resulting solution at 385 mμ showed an ϵ of 32,000; for pure hydrogalvinoxyl at λ 385 mμ, ϵ is 33,800. Removal of solvent afforded material identical in infrared spectrum with hydrogalvinoxyl. Several recrystallizations of the product from methanol–water afforded pure hydrogalvinoxyl, m.p. 158–159° (lit.[2] m.p. 158–159°).

Spectrophotometric and Volumetric Determination of the Rate of Autoxidation of Galvinoxyl.—For the spectrophotometric rate a 0.001 M solution of galvinoxyl in benzene (reagent grade, distilled from sodium) was prepared. Readings of optical density *vs.* time were made at 530 mμ in a stoppered quartz cell in a Beckman DU spectrophotometer.

The rate of oxygen absorption was measured by the procedures normally employed in catalytic hydrogenations. Concurrent changes in optical density were followed by periodic removal of a sample by a syringe inserted through a rubber stopple. Representative data are summarized in Fig. 1.

(5) A $\sim 10^{-4}$ M solution of galvinoxyl in undegassed isooctane (spectral grade) in quartz showed no change in the intensity of the electron spin resonance signal (the normal 10-line spectrum of galvinoxyl is changed to a broad band in the presence of oxygen) over a period of hours (private communication from G. M. Coppinger).

(6) A number of chain branching steps may be envisioned to describe the autocatalysis. Some of these are outlined in the Ph.D. thesis of W. Adam: M. I. T., February, 1961.

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Hydroboration in the Sugar Series[1a]

M. L. WOLFROM, K. MATSUDA, F. KOMITSKY, JR.,[1b] AND T. E. WHITELEY[1c]

Department of Chemistry, The Ohio State University, Columbus 10, Ohio

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Brown and Subba Rao[2] observed that terminal olefins were smoothly converted into trialkylboranes in the presence of a solution of aluminum chloride and sodium borohydride in bis(2-methoxyethyl) ether (diglyme). These trialkylboranes were readily converted into the corresponding alcohols by subsequent oxidation with hydrogen peroxide. The procedure has been improved[3] by the use of different solvents, hydrides, and Lewis acids. It was of interest to apply this hydroxylation reaction to the sugar series. An available terminal olefin is I which may be designated 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuran-5-enose. This substance is obtainable from 1,2-*O*-isopropylidene-α-D-glucofuranose by treatment of its 5,6-di-*O*-*p*-toluenesulfonate with sodium iodide.[4]

Three possible products could be obtained from the hydroboration of I: 6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose, the C-5 epimeric 6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose, and 5-deoxy-1,2-*O*-iso-

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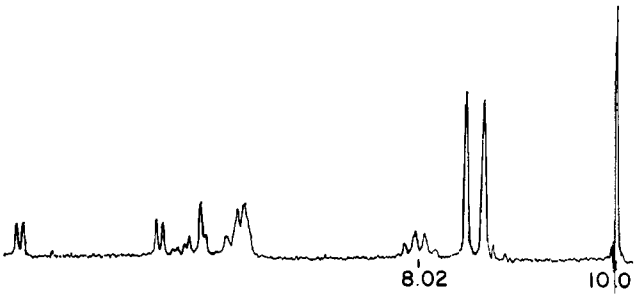


Fig. 1.—N.m.r. spectrum of 5-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose in deuteriochloroform with a tetramethylsilane internal reference standard. Varian A-60 nuclear magnetic resonance spectrometer.

propylidene-α-D-*xylo*-hexofuranose (II), the last being the expected product of the normal, non-Markovnikov hydroboration.[2,3] In fact, a single product was obtained and it was assigned the structure II on the following evidence. First, although their melting points correspond, the difference in rotations between our compound and the known[5] 6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose precludes their identity (Table I). Further, direct comparison with a sample of the known[6] 6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose, which possesses very similar properties (Table I) showed the product of hydroboration to be different by definitive melting point depression.

TABLE I

PHYSICAL CONSTANTS OF DEOXY SUGARS

Substance	$[\alpha]_D$, $CHCl_3$	M.p., °C.
5-Deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (II)	−10.6°	94–96
6-Deoxy-1,2-*O*-isopropylidene-β-L-idofuranose[a]	− 7.0°	88–89
6-Deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose[b]	−26.3°	95

[a] Ref. 6. [b] Ref. 5.

Subsequent to our preliminary communication[1a] on the work herein reported, Overend and co-workers, in a preliminary communication,[7] also reported the synthesis of II by the reductive ring opening of 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose with Raney nickel at elevated temperature and pressure. Separation from accompanying 6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose, the product of the alternate mode of ring cleavage, and hydrolysis of the isopropylidene group with a cation-exchange resin was reported to yield crystalline 5-deoxy-D-*xylo*-hexose (III, "5-deoxy-D-glucose"). Although we have been informed that this crystalline material is not 5-deoxy-D-*xylo*-hexose,[8] a sample of the *O*-isopropylidene precursor (II) furnished by Professor Overend was found to be identical with our sample of II obtained from the hydroboration of I.

The nuclear magnetic resonance spectrum of II (Fig. 1), when compared with the spectra of various 6-deoxyhexose derivatives, for example, that of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose[6] (Fig. 2), conclusively shows that the hydroxyl group is attached to position 6, yielding the 5-deoxy derivative. If the hydroboration had proceeded in such a manner as to insert the hydroxyl at C-5 yielding a 6-deoxy derivative, the protons at C-6 would have appeared as a doublet at about τ 8.9 (tetramethylsilane = 10.00), as in Fig. 2, where they appear at τ 8.89 ($J_{5,6}$ = 5.9 c.p.s.). Also the 6-deoxy group protons of 6-deoxy-α-L-galactose tetraacetate[9] give a doublet at τ 8.88 ($J_{5,6}$ = 6.3 c.p.s.), and the same protons in 6-deoxy-*aldehydo*-L-mannose hexaacetate[10] give a doublet at τ 8.87 ($J_{5,6}$ = 5.8 c.p.s.). Instead, the 5-deoxy protons of II give a multiplet at τ 8.02 (Fig. 1). The absence of any signals in the region around 8.9 τ in the spectrum of our product demonstrates that it contains no 6-deoxy derivative.

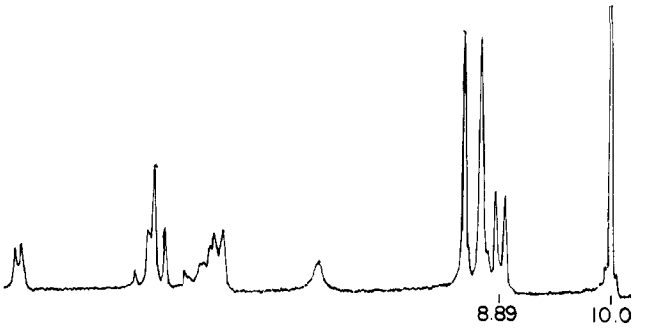
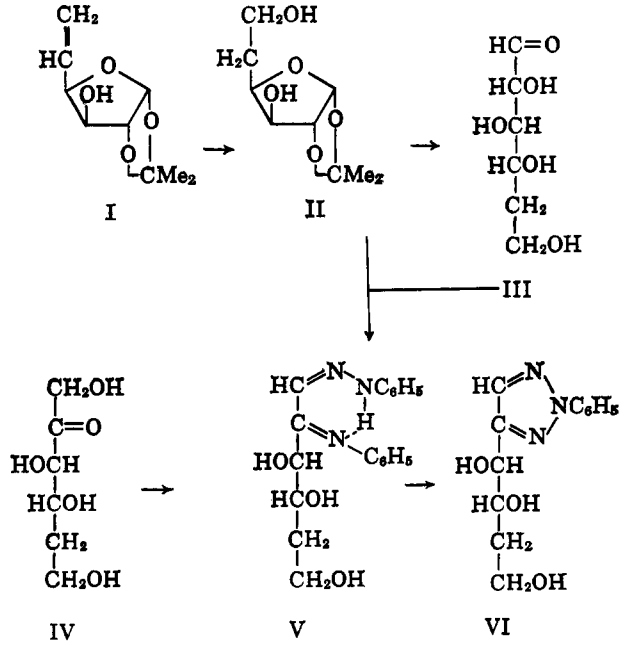


Fig. 2.—N.m.r. spectrum of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose in deuteriochloroform with a tetramethylsilane internal reference standard. Aromatic signals are not shown. Varian A-60 nuclear magnetic resonance spectrometer.

The isopropylidene group was removed from II by hydrolysis with an acid ion-exchange resin. A chromatographically homogeneous, colorless sirup was obtained upon processing the aqueous hydrolysis reaction. This sirup failed to crystallize even when nucleated with a sample of the aforementioned "5-deoxy-D-glucose" furnished by Professor Overend.[8]



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The sirupy 5-deoxy-D-*xylo*-hexose (III) formed a crystalline phenylosazone (V) and phenylosatriazole (VI) identical with those produced from 5-deoxy-D-*threo*-hexose (IV, "5-deoxy-L-sorbose")[11] of established structure. Thus the sirupy free sugar is established as 5-deoxy-D-*xylo*-hexose.

Experimental

5-Deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (II).—A solution of 3 g. of 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuran-5-enose (I)[4] and 0.93 g. of lithium borohydride in 50 ml. of tetrahydrofuran was treated dropwise, under a stream of nitrogen gas, with 2.5 g. of concentrated sulfuric acid and the resulting solution stirred for 2 hr. at room temperature. The excess reagent was destroyed by adding methanol and the solution was evaporated under reduced pressure. The residue was dissolved in 50 ml. of chloroform, washed twice with water, dried over sodium sulfate, and the solvent removed under reduced pressure to yield a sirup. The sirup was dissolved in 10 ml. of absolute ethanol, 2 g. of pulverized sodium hydroxide was added and the alkaline ethanol solution was treated dropwise, with stirring, with 1.5 ml. of 30% hydrogen peroxide. After stirring for 1 hr. at room temperature, the mixture was filtered. The filtrate was neutralized with Amberlite[12] IR-120 (H^+) resin and evaporated to a sirup under reduced pressure following removal of the resin by filtration. The sirup was extracted with ether and the solvent removed under reduced pressure to yield a sirup which crystallized from ether–petroleum ether (b.p. 30–60°) yield 0.74 g., m.p. 88–92°. A second recrystallization from the same solvent yielded pure product, m.p. 94–96°, $[\alpha]^{24}D$ −10.6° (*c* 2.0, chloroform). The aforementioned sample and a sample furnished by Professor Overend evidenced identical X-ray powder diffraction patterns[13]: 9.41 vw, 8.30 s (2), 5.68 s (3), 4.72 vs (1), 4.21 vw, 3.92 w, 3.72 w, 3.53 w, 3.29 vw. A mixture melting point of the sample with an authentic sample of 6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose[6] (m.p. 89–91°) was 70–80°.

5-Deoxy-D-*xylo*-hexose (III).—A solution of 0.5 g. of II in 10 ml. of water was heated on a steam bath for 3 hr. with 2.0 g. of Amberlite[12] IR-120 (H^+) resin. The mixture was then filtered and the solvent removed from the filtrate under reduced pressure to yield a sirup. This sirup was dried by repeated evaporation with methanol under reduced pressure, $[\alpha]^{24}D$ +38° (*c* 2.1, water).[14]

This sirupy free sugar was chromatographed on Whatman No. 1 filter paper using an upper layer of 1-butanol–ethanol–water (4:1:5 by vol.) as developer. A single spot, $R_{glucose}$ 2.59, was obtained by spraying with aniline hydrogen phthalate reagent.[15]

5-Deoxy-D-*threo*-hexose Phenylosazone (V).—A solution of 0.5 g. of II in 5 ml. of 0.1 *N* hydrochloric acid was heated on a steam bath for 1.5 hr. to hydrolyze the isopropylidene group. The solution was neutralized with 5 ml. of 0.1 *N* sodium hydroxide solution. To this solution was added 5 ml. of a solution of phenylhydrazine prepared from 1 g. of phenylhydrazine hydrochloride and 1.5 g. of sodium acetate. The solution was heated on a steam bath for 0.5 hr. and cooled in a refrigerator overnight. The crude osazone was removed by filtration, triturated with chloroform, and dried; yield, 0.12 g. Recrystallization from 60% ethanol gave a pure product, m.p. 151° (lit.[11] m.p. 153°); X-ray powder diffraction pattern[13]: 10.53 m, 8.42 w, 6.92 vw, 5.55 m (3), 4.80 m (2), 4.56 s (1), 4.27 m, 3.87 vw, 3.38 vw, 3.33 m, 3.23 vw, 3.09 w.

5-Deoxy-D-*threo*-hexose Phenylosotriazole (VI).—A solution of crude 5-deoxy-D-*threo*-hexose phenylosazone (0.1 g.) in 6 ml. of isopropyl alcohol was mixed with a solution of 0.3 g. of cupric sulfate pentahydrate in 9 ml. of water and refluxed for 1 hr. on a steam bath. The reaction mixture was treated with a small amount of carbon and filtered while warm. The filtrate was concentrated, under reduced pressure, to a volume of about 3 ml. and kept in a refrigerator overnight. The brown precipitate obtained on filtration was dissolved in a minimal amount of hot water, decolorized with carbon, and again placed in the cold. Colorless crystals were obtained upon filtration; yield, a few mg.; m.p. 140–140.5°; X-ray powder diffraction pattern[13]: 13.00 w, 7.53 m, 6.49 s (3), 4.93 s (1), 4.53 w, 4.33 w, 4.05 w, 3.88 vw, 3.60 vw, 3.44 s (2), 3.23 m, 2.96 vw, 2.88 vw, 2.69 vw, 2.53 vw, 2.44 w. These physical constants are identical with those of the phenylosotriazole produced from a sample of 5-deoxy-D-*threo*-hexose (5-deoxy-L-sorbose) kindly provided by Dr. P. Regna.

Acknowledgment.—It is a pleasure to acknowledge the assistance of Dr. G. Fraenkel and Mr. Byron Bossenbroek of this department in obtaining and interpreting the n.m.r. spectrum. The assistance and counsel of the late Dr. Alva Thompson is also acknowledged.

(11) P. P. Regna, *J. Am. Chem. Soc.*, **69**, 246 (1947).

(12) A product of the Rohm and Haas Co., Philadelphia, Pa.

(13) Interplanar spacing, Å., CuKα radiation. Relative intensities, estimated visually; s, strong; m, medium; w, weak; v, very. Strongest lines numbered, 1 strongest.

(14) This value supersedes that previously reported[1a] although since the product was a sirup no high accuracy is claimed.

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Amino Derivatives of Starches. Amination of Amylose[1]

M. L. WOLFROM, MAHMOUD I. TAHA, AND D. HORTON

Department of Chemistry, The Ohio State University, Columbus 10, Ohio

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It was of interest to perform chemical modifications on the amylose molecule with a view to the replacement of secondary hydroxyl by amino groups while maintaining polymeric structure. Such a cationic polymer might be expected to possess physical and chemical properties which could offer possibilities for increased utilization of starch. A polymer modified by amination at C-2 might possess the high stability toward hydrolysis exhibited by chitosan; the acetamido analog would be analogous to chitin, a polysaccharide whose high degree of intermolecular hydrogen bonding[2] affords great physical stability. The present work describes the conversion of a sulfonylated amylose by hydrazinolysis, followed by reduction, to give a product which in all probability has had a considerable proportion of its secondary hydroxyls replaced by amino groups.

Amylose was treated portionwise with a total of 2.2 molar equivalents of *p*-toluenesulfonyl chloride in pyridine to yield a *p*-toluenesulfonate ester derivative with a degree of substitution of 1.7. Esterification of amylose with *p*-toluenesulfonyl chloride has been shown[3] to take place selectively and readily at the C-6 position of the D-glucose units. Further reaction would presumably occur selectively, though probably not exclusively, at the C-2 hydroxyl group.[4]

The 2(3),6-di-*O*-*p*-tolylsulfonylamylose was then refluxed with hydrazine and the resulting hydrazino derivative was reduced by Raney nickel to yield an aminated derivative with a degree of substitution of 1.4. The amino groups of the aminated amylose were selectively acetylated with aqueous acetic anhydride. The

(1) Supported by Contract No. 12-14-100-5760(71) (Research Foundation Project 1301) from the U. S. Department of Agriculture, Northern Utilization Research Bureau, Peoria 5, Ill. The opinions expressed in this article are those of the authors, and not necessarily those of the sponsoring agency.

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