1,2-di-*O*-acetyl-3-bromo-1,2-propanediol with potassium thiolacetate.

Bis(2,3-diacetoxy-DL-propyl) Disulfide.—A solution of 1-thio-DL-glycerol[33] (20 g.) in water (50 ml.) was treated with 10% hydrogen peroxide (45 ml.), the exothermic reaction was moderated by cooling initially, and after 2 hr. excess peroxide was destroyed by adding manganese dioxide (0.1 g.). After 4 hr. effervescence ceased, and the solution was filtered, evaporated, freed from water by codistillation first with 1-propanol then acetic anhydride, and the crystalline residue was acetylated as in the above preparation. The acetylated product distilled as a yellow oil; yield 32.5 g. (92%), b.p. 200–210° (0.01 mm.), n^{25}D 1.4883, $\lambda_{\max(\mu)}^{\text{film}}$ 5.74 (OAc), no absorption at 5.8–6.0 μ (SAc).

Anal. Calcd. for $C_{14}H_{22}O_8S_2$: C, 43.95; H, 5.80; S, 16.70. Found: C, 43.66; H, 5.70; S, 17.09.

The sirupy unacetylated disulfide has been described as a reaction intermediate in the preparation of 1-thioglycerol,[35] but it was not characterized.

Acknowledgment.—The technical assistance of Miss Ramona Budd and Mr. A. Gardikes is gratefully acknowledged.

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The Reaction of Free Carbonyl Sugar Derivatives with Organometallic Reagents. I. 6-Deoxy-L-idose and Derivatives[1,2]

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Glycol cleavage of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (I) with lead tetraacetate produced a stable monomeric form of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (II). Catalytic debenzylation of the latter substance produced initially a monomeric product which has been previously known only as the dimer. Reaction of II with methylmagnesium iodide produced exclusively 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-*ido*(L-*glycero*-α-D-*xylo*-hexo)furanose (VII), the configuration of which was elucidated by conversion to derivatives of established structure. A mechanism is suggested to explain the exclusive production of the L-*ido*- configuration. It is shown that 6-deoxy-L-idose changes to 6-deoxy-L-sorbose (XIII) in the presence of acid.

The use of the Grignard reagent in reactions of acyclic aldoses has been quite limited.[3] The few recorded examples[4] of the application of this reaction have involved the use of *aldehydo*-D-(and L)-arabinose and *aldehydo*-D-xylose derivatives to produce the corresponding alditols. We wish to report herein the application of the Grignard reaction to suitably blocked dialdoses to produce terminal deoxyaldoses. 1,2-*O*-Isopropylidene-D-*xylo*-pentodialdo-1,4-furanose,[5] which appeared to be a suitable subject for the reaction, failed to condense with the Grignard reagent, probably beause the aldehyde group is masked in the dimeric structure[6] in which it is known to exist. It was found that dimerization was prevented by blocking participation of the hydroxyl on C-3 with an *O*-benzyl group, producing a monomeric pentodialdose with one true aldehyde group free to react with a Grignard reagent. Glycol cleavage of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (I)[7,8] produced 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (II) as a colorless sirup in good yield. The substance gave a positive Schiff aldehyde test. The infrared spectrum revealed essentially no hydroxyl peak but gave an intense carbonyl peak in the region of 5.8 μ. It was quite stable in the absence of moisture and formed a crystalline semicarbazone (V). Hydrogenolysis of the blocked pentodialdose (II) with palladium catalyst[9] produced 1,2,*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (III), which yielded a crystalline semicarbazone (VI) with constants identical with those reported by Iwadare[5] for the same derivative. Substance III also exhibited equal carbonyl and hydroxyl absorptions in the infrared spectrum. These diminished slowly with time. *p*-Nitrobenzoylation of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (I) produced a crystalline 5,6-di-*O*-(*p*-nitrobenzoyl) derivative (IV).

Treatment of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (II) with methylmagnesium iodide in ether solution produced a

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70% yield of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-*ido*(L-*glycero*-α-D-*xylo*-hexo)furanose (VII). The substance VII was converted to a crystalline-5-*O*-methylsulfonyl derivative (X). Since the reaction of II with the Grignard reagent produces a new asymmetric center at C-5, a second product, 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose, would also be expected. Extensive search of the mother liquors from the preparation of VII revealed only one product, the 6-deoxy-L-idose derivative, the identity of which was determined by conversion to known structures. Removal of the *O*-benzyl group by hydrogenolysis with palladium catalyst required both heat and pressure; milder conditions,[10] which are usually adequate, failed in this instance. The product, 6-deoxy-1,2-*O*-isopropylidene-β-L-*ido*-furanose (VIII), and its 3,5-diacetate (IX) were identical in properties with products described by Meyer and Reichstein.[11]

Cram and Abd Elhafez[12] have formulated a principle to correlate and predict in acyclic systems, the stereochemical direction in which a new asymmetric center is created adjacent to an existing one. This principle states essentially that that diastereomer will be favored which results from the approach of the entering group from the side least hindered by the groups on the existing adjacent asymmetric center. The principle is markedly altered[13] if the asymmetric center in the starting material carries a group, such as hydroxyl or amino, which is capable of complexing with the reagent, thus fixing the configuration.

An examination of the molecular model of 3-*O*-benzyl-1,2,-*O*-isopropylidene-α-D-*xylo*-pentodialdose-1,4-furanose (II), considering that the aldehyde group has possible free bond rotation shows that the L-*ido* and D-*gluco*-isomers are about equally sterically favored. The stereospecificity found is better accounted for by the alternate explanation[13] involving a participation in a polar sense. Because of the tendency of Grignard reagents to coordinate with the unshared electron pairs of oxygen or nitrogen,[14] one could postulate the formation of a precursor (XIV) having the geometry of a planar five-membered ring and which is sterically capable of existence. This system would fix the transition state in the L-*ido*-configuration. Such a coordinated cyclic precursor cannot be envisaged for the D-*gluco*-system.

It was shown by Vargha[15] that when 1,2-*O*-isopropylidene-β-L-idofuranose was hydrolyzed with dilute acid, a neutral sirup was obtained which showed a single spot on paper chromatograms. After storing for a few days, a second spot appeared which was identical with that of L-sorbose, and after 75 days α-L-sorbose crystallized from the sirup in good yield. In this laboratory it was observed that 6-deoxy-L-idose undergoes a similar change. Acid hydrolysis of 6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (VIII) yielded a sirup which produced three distinct spots, A, B, and C, on a paper chromatogram, the latter being most intense. The material in spot A was present in small quantities and was not positively identified. The material in spot C had the same mobility and was indistinguishable from a spot produced by known 6-deoxy-L-sorbose obtained from Prof. Reichstein.[16]

Hydrolysis of VII with sulfuric acid in aqueous methanol produced sirupy 3-*O*-benzyl-6-deoxy-L-idose (XI), which yielded a crystalline benzylphenylhydrazone and phenylosazone. Hydrogenolysis of XI yielded a colorless sirup which produced a distinct spot, presumably 6-deoxy-L-idose, corresponding to spot B of the hydrolyzate from VIII and a faint spot corresponding to spot C. The hydrogenolysis product of XI, when heated in water with Amberlite-IR-120 (H^+),[17] was rapidly equilibrated to material producing spots B and C in about equal intensities. The material in spot C, but not that in spot B, produced a red color when sprayed with resorcinol in hydrochloric acid or trichloracetic acid,[18,19] a specific reagent for ketoses. The R_f values for 6-deoxy-L-sorbose (XIII) in a number of solvent mixtures are recorded.[19] The material (XII) from the hydrogenolysis of XI, producing spot B, and material eluted from spot C of paper chromatograms produced 6-deoxy-L-*xylo*-hexose phenylosazone indicating a difference of configuration only on C-2. These data indicate that 6-deoxy-L-idose (XII) is partially converted to 6-deoxy-L-sorbose (XIII) in the presence of acid.

Experimental

3-*O*-Benzyl-1,2-*O*-isopropylidene-5,6-di-*O*-(*p*-nitrobenzoyl)-α-D-glucofuranose (IV).—*p*-Nitrobenzoyl chloride (4.3 g.) was added to a solution of 3.5 g. of sirupy 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (I)[7] in 25 ml. of dry pyridine and the mixture was allowed to stand at room temperature for 10 hr., whereupon it was poured into 200 ml. of ice and water and extracted with two 250-ml. portions of chloroform. The combined extracts were washed with water, aqueous sodium bicarbonate solution, and water, dried with anhydrous sodium sulfate, and evaporated to a pale yellow sirup which was crystallized from ethanol; yield 5 g. Two recrystallizations from acetone–petroleum ether gave pure material; yield 3.4 g., m.p. 116–117°,

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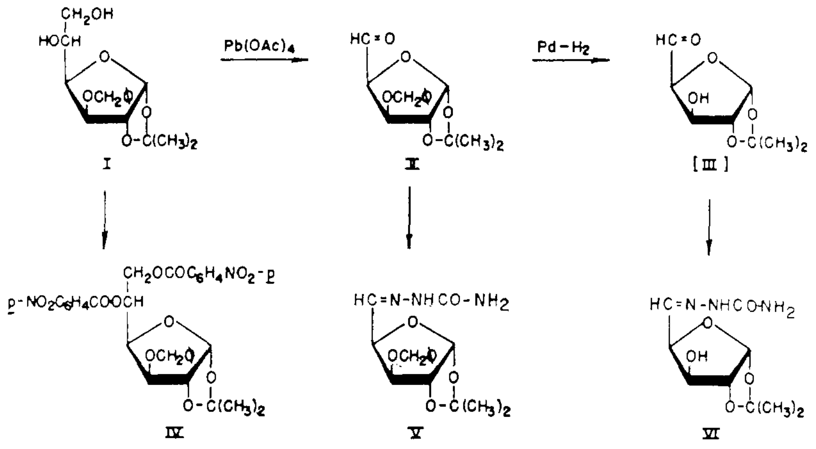

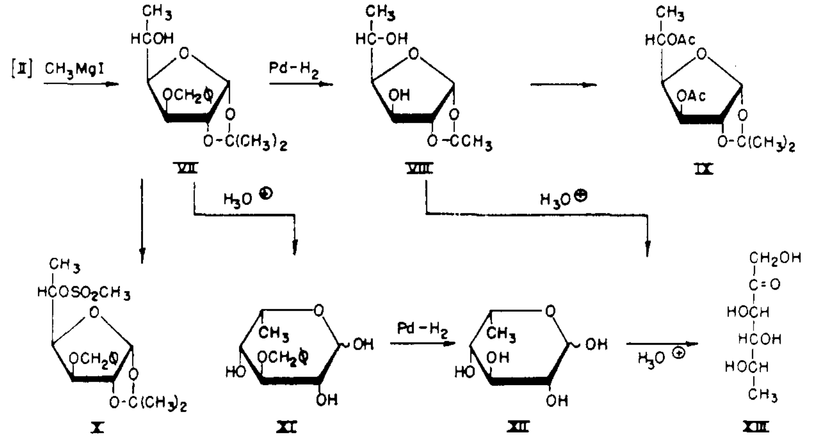

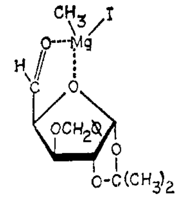

XIV

[α]^{25}D −22° (*c* 1.5, acetone), X-ray powder diffraction data[20]: 11.00 w, 6.68w, 6.15w, 5.68s(1), 5.12w, 4.82w, 4.52w, 4.28w, 4.21vw, 3.60m(2), 3.15vw.

Anal. Calcd. for $C_{30}H_{28}N_2O_{12}$: C, 59.20; H, 4.64; N, 4.61. Found: C, 59.05; H, 4.31; N, 4.83.

3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (II).—A suspension of 210 g. of lead tetraacetate in 1500 ml. of dry benzene was added gradually to a solution containing 94 g. of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (I)[7] in 100 ml. of dry benzene. The mixture was warmed for several minutes and then filtered. The filtrate was evaporated under reduced presssure, at a bath temperature below 30°, to a pale yellow sirup which was dissolved in 200 ml. of absolute ethanol and filtered. The filtrate was evaporated under reduced pressure to a sirup which was dissolved in ether and again concentrated to a sirup; yield 79 g. (92%). The sirup was further purified by distillation in a Hickman molecular pot still at 0.07 mm. and the fraction boiling at 150–155° was collected as a colorless viscous liquid; yield 55 g., [α]^{25}D −86.5° (*c* 2.7, ethanol-free chloroform); infrared absorption spectrum data: $\lambda_{\max}^{\text{film}}$ 5.8 μ (C=O), 9.35, 9.75 μ (C—O—C), 13.6, 14.9 μ (substituted phenyl). The sirup strongly reduced Fehling solution and gave an instantaneous positive Schiff reaction.

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52; mol. wt. 278. Found: C, 64.86; H, 6.55; mol. wt. (f.p. in benzene), 315.

3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose Semicarbazone (V).—3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (II) was converted to the crystalline semicarbazone in ethanol–water

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[20] Interplanar spacing, CuKα radiation. Relative intensity, estimated visually: s, strong; m, medium; w, weak; v, very. First few strongest lines are numbered (1, strongest).

solution; yield 0.6 g., m.p. 177–178°, $[\alpha]^{25}\text{D}$ −50° (*c* 1.48, ethanol), X-ray powder diffraction data[20]: 14.00vw, 8.06m, 6.44w, 6.20w, 5.64s(1), 5.27m(2), 4.92m, 4.45m(3), 4.23m, 3.98m, 3.60m, 3.22w, 2.97w.

Anal. Calcd. for $C_{16}H_{21}N_3O_5$: C, 57.30; H, 6.31; N, 12.53. Found: C, 57.41; H, 6.35; N, 12.37.

Preparation of 1,2-*O*-Isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (III).—Sirupy 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (II) was dissolved in 25 ml. of absolute ethanol and 0.1 g. of palladium-on-charcoal catalyst[9] was added. The mixture was hydrogenated at 65° under 400 p.s.i. for 4 hr. Filtration of the catalyst and evaporation of the filtrate under reduced pressure produced a colorless sirup; yield 0.94 g. The substance showed both hydroxyl and carbonyl infrared absorption but the characteristic phenyl absorption bands were missing. On standing for a week at room temperature, the carbonyl peak diminished slightly. The substance yielded a crystalline semicarbazone (VI) prepared according to Iwadare[5] for the corresponding 3-*O*-benzyl derivative; dec. 208–209°. Iwadare[5] reports m.p. 208–209.5° dec. for the same derivative.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-*ido*(L-*glycero*-α-D-*xylo*-hexo)furanose (VII).—A solution of 10.5 ml. of methyl iodide in 50 ml. of anhydrous ether was added dropwise to 4.5 g. of magnesium turnings suspended in 100 ml. of dry ether (distilled from lithium aluminum hydride directly into the reaction vessel under an atmosphere of dry nitrogen). After initiation of the reaction, a gentle reflux was maintained by regulation of the rate of addition of the halide. A solution of 10 g. of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (II) in 70 ml. of anhydrous ether was added dropwise to the refluxing Grignard solution over a period of 2 hr. The dropping funnel was rinsed with 50 ml. of ether, which was added to the reaction mixture, and the refluxing was continued for 30 min. The cooled, turbid solution gave a positive Gilman[21] Grignard test and was transferred to a separatory funnel and cautiously added dropwise to 200 ml. of a cold, saturated, aqueous solution of ammonium chloride under vigorous stirring. The aqueous layer was separated and washed with ether. The combined ether extracts were washed with a small quantity of saturated aqueous ammonium chloride solution, then with water, and dried over anhydrous sodium sulfate. The dry ether solution was evaporated under reduced pressure to a sirup which crystallized in a few minutes. The crystals were triturated with a small quantity of cold ether, filtered, and washed with cold ether–petroleum ether; yield 6.65 g., m.p. 85–86°. The aqueous solutions were evaporated under reduced pressure to a solid mass and exhaustively extracted with chloroform. The extracts upon concentration produced an additional 0.35 g. of material; combined yield 7 g. Recrystallization from hot petroleum ether containing a trace of methanol and again from ether–petroleum ether produced pure material; yield 6.2 g., m.p. 93–94°. $[\alpha]^{25}\text{D}$ −63.5° (*c* 1.3, chloroform), X-ray powder diffraction data[20]: 10.05m, 8.32m, 5.94m, 5.07s(1), 4.92w, 4.74w, 4.52m(2), 4.33w, 4.08m(3), 3.66w, 3.57vw, 3.50vw; infrared absorption spectrum data: $\lambda_{\max}^{\text{KBr}}$ 2.93 μ (OH), 7.27 μ (CH_3), 9.25, 9.50, 9.80 μ (C—O—C), 13.75, 14.50 μ (substituted phenyl).

Anal. Calcd. for $C_{16}H_{22}O_5$: C, 65.31; H, 7.50. Found: C, 65.14; H, 7.30.

This compound was identified as 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (VII) by derivatization to known substances as described below. An extensive search by chromatographic procedures failed to locate any accompanying 3-*O*-benzyl-6-deoxy-1,2- *O*-isopropylidene-α-D-glucofuranose.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-5-*O*-methylsulfonyl-β-L-*ido*-(L-*glycero*-α-D-*xylo*-hexo)furanose (X).—Methanesulfonyl chloride (0.2 ml.) and 2 ml. of chloroform were added successively to a cold solution of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (VII, 0.3 g.) in 2 ml. of dry pyridine and allowed to stand at room temperature for 16 hr. The mixture was poured into ice and water and stirred for 2 hr. The solid which separated was filtered and washed with ether–petroleum ether (1:5 by vol.) to produce colorless needles; yield 280 mg., m.p. 82–85°. Pure material was obtained on recrystallization from ether; m.p. 99–100°, $[\alpha]^{25}\text{D}$ −60° (*c* 1, chloroform), X-ray powder diffraction data[20]: 12.62vw, 10.85m, 8.88w, 7.44vw, 5.42m(2), 5.09s(1), 4.69m, 4.51m, 4.23m(2), 3.88vw, 3.80vw, 3.42w. The infrared spectrum showed no hydroxyl absorption.

Anal. Calcd. for $C_{17}H_{24}O_7S$: C, 54.82; H, 6.50; S, 8.61. Found: C, 54.34; H, 6.48; S, 8.47.

6-Deoxy-1,2-*O*-isopropylidene-β-L-*ido*-(L-*glycero*-α-D-*xylo*-hexo)furanose (VIII).—To 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (VII) 2.5 g. in 50 ml. of ethanol was added 0.25 g. of palladium-on-charcoal,[9] catalyst and the mixture was hydrogenated at 65–68° under 300 p.s.i. for 4 hr. (The reaction failed at room temperature and 28 p.s.i. for 24 hr.). After filtration and evaporation, under reduced pressure, a clear sirup was obtained which crystallized on standing. The crystals were filtered and washed with cold ether; yield 1.1 g., m.p. 88–89°, $[\alpha]^{25}\text{D}$ −7° (*c* 3.4, chloroform), infrared absorption data: $\lambda_{\max}^{\text{KBr}}$ 2.95 μ (OH), 7.25 μ (CH_3), 9.25, 9.50, 9.85 μ (C—O—C). The literature records: m.p. 90–91°, $[\alpha]^{21}\text{D}$ −12.9° (chloroform),[8,11] m.p. 88–90°, 84–88° and 90–92°, $[\alpha]^{25}\text{D}$ −7.1° (chloroform).[22]

3,5-Di-*O*-acetyl-6-deoxy-1,2-*O*-isopropylidene-β-L-*ido*-(L-*glycero*-α-D-*xylo*-hexo)furanose (IX).—An amount of 0.15 g. of 6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (VIII) was dissolved in 1 ml. of dry pyridine and 1 ml. of acetic anhydride was added. After standing at room temperature for 16 hr., the mixture was poured into ice and water and extracted with three 150-ml. portions of chloroform. The solution was evaporated under reduced pressure to a pale yellow sirup from which the last traces of pyridine were removed by repeated evaporation of its toluene solution. The resulting sirup crystallized and the crystals were triturated with ether–petroleum ether and filtered; yield 0.18 g., m.p. 122–123°, $[\alpha]^{23}\text{D}$ −27° (*c* 2, chloroform); recorded values[11]: m.p. 123–123.5°, $[\alpha]^{23}\text{D}$ −22.2° (chloroform).

3-*O*-Benzyl-6-deoxy-L-idose (XI).—3-*O*-Benzyl-1,2-*O*-isopropylidene-6-deoxy-β-L-idofuranose (VII, 2.94 g.) was dissolved in 12 ml. of methanol containing 4.41 ml. of *N* sulfuric acid. The solution was stirred at 70° for 4 hr. after which the methanol was removed by evaporation under reduced pressure and the residue was dissolved in 3 ml. of water. The solution was heated an additional hour, neutralized with barium carbonate, and filtered with decolorizing carbon. Evaporation under reduced pressure produced a colorless sirup which was dried at 60°; $[\alpha]^{23}\text{D}$ −11° (*c* 4, ethanol), infrared absorption data: $\lambda_{\max}^{\text{film}}$ 2.9 μ (OH), 13.5, 14.45 μ (substituted phenyl).

Anal. Calcd. for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14. Found: C, 61.00; H, 7.32.

On paper chromatograms using 1-butanol–ethanol–water (4:1:5 by vol.) a single spot having R_f 0.78 was obtained.

3-*O*-Benzyl-6-deoxy-L-idose benzylphenylhydrazone.—A solution containing 0.85 g. of 3-*O*-benzyl-6-deoxy-L-idose (XI), 0.3 g. of sodium acetate, and 0.76 g. of 1-benzyl-1-phenylhydrazine hydrochloride in 25 ml. of ethanol was refluxed 3 hr., treated with decolorizing carbon and filtered. The filtrate was evaporated under reduced pressure to dryness and extracted with chloroform. The chloroform

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(21) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(22) E. J. Reist, R. R. Spencer, and B. R. Baker, *J. Org. Chem.*, **23**, 1757 (1958).

solution was washed with water, dried with anhydrous sodium sulfate, and evaporated to a sirup which was crystallized from ether–petroleum ether; yield 1.1 g., m.p. 115–116°. Pure material was obtained on recrystallization from ethanol; m.p. 120–121°, $[\alpha]^{25}\text{D}$ +44° (*c* 1, ethanol), X-ray powder diffraction data[20]: 9.71m, 7.76w, 6.02m, 5.29s(1), 4.92 m(2), 4.37 m, 3.32 m(3), 3.56 w, 3.31 m, 2.98 m, 2.84 vw, 2.70 vw.

Anal. Calcd. for $C_{26}H_{30}N_2O_4$: C, 71.98; H, 6.93; N, 6.44. Found: C, 71.86; H, 7.05; N, 6.51.

3-*O*-Benzyl-6-deoxy-L-*xylo*-hexose phenylosazone.—3-*O*-Benzyl-6-deoxy-L-idose (XI, 0.5 g.) was heated with 1.5 g. of sodium acetate and 1.0 g. of phenylhydrazine hydrochloride in 10 ml. of water in a boiling water-bath for 2 hr. The solvent was decanted and the residue was dissolved in benzene which, upon dilution with petroleum ether, deposited crystals after a few hours. Pure material was obtained on recrystallization from ethanol–water; yield 0.6 g., m.p. 95–96°, $[\alpha]^{25}\text{D}$ +36° (*c* 0.3, pyridine–ethanol, 2:3 by vol.).

Anal. Calcd. for $C_{25}H_{28}N_4O_3$: C, 69.42; H, 6.53; N, 12.95. Found: C, 68.60; H, 6.46; N, 12.46.

6-Deoxy-L-idose (XII).—6-Deoxy-1,2-*O*-isopropylidene-L-idofuranose[11] (VIII, 0.13 g.) was dissolved in 1.4 ml. of 0.5% sulfuric acid and heated at 70° for 2 hr. The solution was neutralized with powdered barium carbonate, filtered with decolorizing carbon and evaporated, under reduced pressure, to a sirup. The material was chromatographed on paper using 1-butanol-ethanol-water (4:1:5 by vol.) as developer and ammoniacal silver nitrate[23] indicator. Three spots A, B, C, with R_f values 0.22, 0.32, and 0.44, respectively, were obtained.

Four chromatographs, each with 50 mg. of the sirupy hydrolyzate spread evenly on a line 8 cm. long on 12 × 42 cm. Whatman No. 1 paper, were developed for 42 hr. with 1-butanol–ethanol–water (4:1:5 by vol.) at room temperature. Guide strips were then cut from the ends of the lines and sprayed with ammonical silver nitrate indicator.[23] Three zones, A, B, and C, with R_f values 0.22, 0.32, and 0.44, respectively, appeared. The order of intensities was C>B>A. The zone materials were eluted with water and the solutions were freeze-dried. Zone A: yield 4.9 mg., dec. 60°, was not further studied; Zone B: yield 12.8 mg., very hygroscopic; Zone C: yield 70 mg., $[\alpha]^{25}\text{D}$ −24° (*c* 0.7, water) recorded value[16] for 6-deoxy-L-sorbose (XIII), $[\alpha]^{25}\text{D}$ −27.7° (water).

A preparation of 6-deoxy-L-idose (XII) was also made, under neutral conditions, by the reductive debenzylation of 0.1 g. of 3-*O*-benzyl-6-deoxy-L-idose (XI) in 25 ml. of absolute ethanol containing 10 mg. of palladium-on-carbon catalyst by hydrogenation at 500 p.s.i. and 65° for 4.5 hr. Filtration and concentration, under reduced pressure, gave a colorless sirup; yield 80 mg., $[\alpha]^{25}\text{D}$ −1.9° (*c* 2.5, water). This material showed, on paper chromatography, one distinct spot corresponding to Zone B, R_f 0.32, and a very faint spot at Zone C, R_f 0.44. An authentic sample of 6-deoxy-L-sorbose,[16] kindly furnished by Professor Reichstein, produced a spot identical with spot C.

Material from Zone C of the hydrolysis product of 6-deoxy-1,2,-*O*-isopropylidene-β-L-ido(L-*glycero*-α-D-*xylo*-hexo)furanose and from the hydrogenolysis of 3-*O*-benzyl-L-idose produced 6-deoxy-L-*xylo*-hexose phenylosazone by the conventional method of preparation: phenylosazone from Zone C of the hydrolyzate, dec. 182–184°; from the hydrogenolysis of XI, dec. 160–166°; (literature values: 6-deoxy-L-*xylo*-hexose phenylosazone from 6-deoxy sorbose,[16] dec. 184–185°; from 6-deoxy-L-gulose,[24] dec. 183–184°; from 6-deoxy-L-idose, dec. 184–185°,[11] 168–172° [25]); the products gave identical X-ray powder diffraction data[20]: 10.05w, 7.68vw, 4.98m(3), 4.67s(1), 4.10m(2), 3.80vw, 3.56vw, 3.47w, 3.19w, 3.05vw, 2.85w; the infrared absorption spectra of the phenylosazones were also identical.

The colorless sirupy hydrogenolysis product (15 mg., exhibiting essentially only one spot at Zone B), dissolved in water containing Amberlite IR-120 (H^+),[17] was heated on a steam bath for 3 hr. Samples were spotted on paper at intervals. Upon development and spraying the paper the second spot at Zone C had appeared with an intensity nearly equal to that in Zone B with as little as 5 min. of heating.

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Constitution of an Aldohexaouronic Acid Formed on Enzymatic Hydrolysis of a 4-*O*-Methylglucuronoxylan

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An aldohexaouronic acid has been isolated after enzymatic hydrolysis of a 4-*O*-methylglucuronoxylan from white birchwood. It has been identified as *O*-4-*O*-methyl-α-D-glucosyluronic acid-(1 → 2)-*O*-β-D-xylopyranosyl-(1 → 4)-*O*-β-D-xylosyl (1 → 4)-*O*-β-D-xylosyl-(1 → 4)-*O*-β-D-xylosyl-(1 → 4)-D-xylose.

When a 4-*O*-methylglucuronoxylan from white birch wood was treated with a commercial pectinase preparation, a series of oligosaccharides was obtained.[1,2] The xylan had previously been shown to contain a linear framework of (1→4)-linked β-D-xylose residues, every tenth of which, on the average, carried a (1→2)-linked 4-*O*-methyl-α-D-glucuronic acid residue.[3] The enzymic hydrolysis was carried out inside a semipermeable membrane surrounded by a large volume of water so that the sugars formed could diffuse rapidly through the membrane, thus escaping further hydrolysis.[4] High yields were obtained of a neutral and an acidic series of polysaccharides. This paper is concerned

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