Reductive debenzylation of this material as described above produced a sirup; $[\alpha]^{25}\text{D}$ −19° (*c* 1.5, chloroform). Baker and co-workers[17] record for 6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose; m.p. 92°, $[\alpha]^{20}\text{D}$ −26.3° (chloroform). Acetylation of the sirup with acetic anhydride and pyridine as described above produced crystalline material (VI); m.p. 87–88°, $[\alpha]^{22}\text{D}$ +20° (*c* 2, chloroform). Freudenberg and associates[14] record for 3,5-di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (VI): m.p. 96°, $[\alpha]^{20}\text{D}$ +23° (chloroform); Meyer and Reichstein[15] report m.p. 88–89°.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-5-methyl-α-D-*xylo*-hexofuranose (III).—A solution of 1 g. of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose (II) was added dropwise with stirring over a period of 30 min. to 30 ml. of an ether solution of methylmagnesium iodide (0.375 g. of magnesium turnings and 5 ml. of methyl iodide). The mixture was refluxed gently 1.5 hr., cooled, and added dropwise with vigorous stirring to a cold saturated solution of ammonium chloride (50.ml.). The organic layer was separated and washed with water. The aqueous solutions were washed with ether and the combined ether extract was dried with anhydrous sodium sulfate and evaporated under reduced pressure to a sirup which was crystallized from 2 ml. of ether; yield, 0.5 g., m.p. 78–80°. Further processing the mother liquor gave an additional amount; total yield, 0.75 g. Three recrystallizations from petroleum ether produced pure material (III); m.p. 91–92°, $[\alpha]^{25}\text{D}$ −49° (*c* 2, chloroform), infrared absorption spectral data: $\lambda_{\max}^{\text{KBr}}$ 2.9 μ (OH), 13.75, 14.5 μ (substituted phenyl), no carbonyl absorption, X-ray powder diffraction data[16]: 10.62 s (1), 7.46 m, 6.20 m, 5.34 m, 5.12 m, 4.65 m (3), 4.42 m (2), 4.02 w, 3.73 w, 3.60 w, 3.41 vw, 3.24 vw.

Anal. Calcd. for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.43; H, 7.88.

Attempts to acetylate this compound resulted in recovery of the starting product or very incompletely acetylated material.

6-Deoxy-1,2-*O*-isopropylidene-5-methyl-α-D-*xylo*-hexofuranose (IV).—A solution of 0.4 g. of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-5-methyl-α-D-*xylo*-hexofuranose (III) was reductively debenzylated with hydrogen and palladium catalyst as described above. The solution was filtered and evaporated to dryness under reduced pressure. Trituration with petroleum ether gave colorless needles; yield, 0.22 g., m.p. 113–115°. Recrystallization from ether–petroleum ether gave a pure material (IV); m.p. 115–116°, $[\alpha]^{25}\text{D}$ −21° (*c* 2, water), infrared absorption spectral data: $\lambda_{\max}^{\text{KBr}}$ 2.9 μ (OH), no substituted phenyl absorption in the region 13–15 μ, X-ray powder diffraction data[16]: 11.30 m, 9.60 m, 7.74 m, 7.08 m, 6.18 m, 5.59 m, 5.29 s (1), 4.95 m (2), 4.30 m (3), 3.52 vw, 3.16 vw.

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.06; H, 8.32.

6-Deoxy-5-methyl-D-*threo*-hexose Phenylosazone.—1,2-*O*-Isopropylidene-5-methyl-α-D-*xylo*-hexofuranose (IV, 0.57 g.) was heated 2 hr. at 70° in 1.5 ml. of 0.05% sulfuric acid. The solution was then neutralized with powdered barium carbonate, filtered, and the filtrate evaporated to a sirup (6-deoxy-5-methyl-D-*xylo*-hexose, VII); yield, 45 mg., $[\alpha]^{25}\text{D}$ −10.5° (*c* 0.9, water). The sirup was strongly reducing in warm Fehling solution. It was soluble in water, alcohol, and acetone but was insoluble in ether. It did not restore the color of Schiff reagent and was quite stable at room temperature. On paper chromatograms, using the solvent system 1-butanol–ethanol–water (4:1:5) a single spot having an R_{Rf} value of 1.18 was obtained. Another hydrolyzate of IV, obtained in the same manner and containing about 150 mg. of the sugar, was neutralized with 2 *N* sodium hydroxide and allowed to evaporate slowly to 3 ml. Phenylhydrazine acetate (300 mg.) in 3 ml. of aqueous solution was added, and the mixture was heated on a boiling water bath. The crystalline phenylosazone which formed in 15 min. was filtered and washed successively with water, dilute acetic acid, and ethanol–petroleum ether; yield, 64 mg., 185–187° dec. Pure 6-deoxy-5-methyl-D-*threo*-hexose phenylosazone was obtained on crystallization from ethanol–water; 188–190° dec.

Anal. Calcd. for $C_{19}H_{24}N_4O_3$: C, 64.02; H, 6.79; N, 15.72. Found: C, 64.27; H, 6.82; N, 15.61.

5-*S*-Ethyl-5-thio-L-arabinose Diethyl Dithioacetal

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Treatment of tetra-*O*-acetyl-α-L-arabinopyranose (I) with ethanethiol in the presence of boron trifluoride resulted, after saponification, in crystalline 5-*S*-ethyl-5-thio-L-arabinose diethyl dithioacetal (IV), whose structure was established by hydrogenolysis with Raney nickel followed by oxidative degradation of the sirupy pentanetriol obtained.

It has been reported by Wolfrom and Thompson[2] that the treatment of hexa-*O*-acetyl-D-*gluco*-heptulose with ethanethiol in the presence of zinc chloride and Drierite[3] results in the replacement of two acetoxy groups with thioethyl groups. It was demonstrated that only one thioethyl function occupied a glycosidic position. No attempt was made to locate the second thioethyl moiety. It was later demonstrated by Lemieux[4] that penta-*O*-acetyl-β-D-glucopyranose reacted with ethanethiol under these conditions to yield, after deacetylation, 2-*S*-ethyl-2-thio-D-glucose(mannose) diethyl dithioacetal. This latter observation led to the conjecture that these reaction conditions might have value in the synthesis of 2-deoxy sugar precursors.

Since tetra-*O*-acetyl-α-L-arabinopyranose (I) has the same stereochemistry on carbon atoms C-1–C-3 as penta-*O*-acetyl-β-D-glucopyranose, reactions

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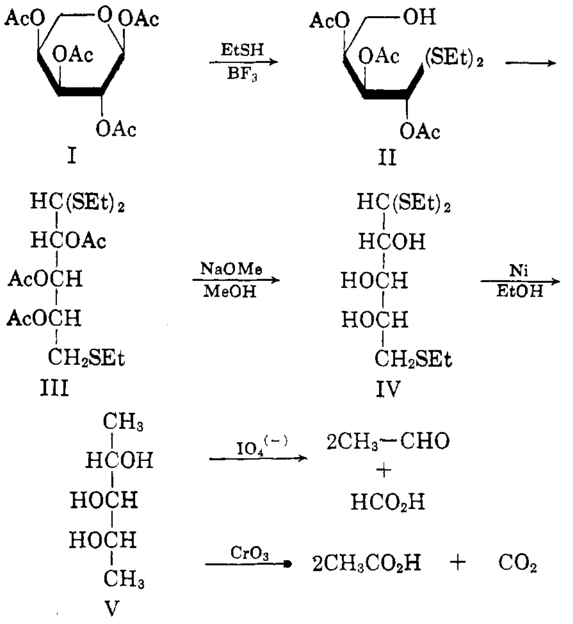
(2) M. L. Wolfrom and A. Thompson, *J. Am. Chem. Soc.*, **56**, 1804 (1934).

(3) Anhydrous calcium sulfate, a product of the W. A. Hammond Drierite Co., Xenia, Ohio.

(4) R. U. Lemieux, *Can. J. Chem.*, **29**, 1079 (1951).

which depend on this configuration might be expected to be common to both. We report herein, however, the reaction of tetra-*O*-acetyl-α-L-arabinopyranose with ethanethiol in the presence of zinc chloride or boron trifluoride–etherate to yield, after deacetylation, not the expected 2-*S*-ethyl-2-thio-L-arabinose(ribose) diethyl dithioacetal but rather crystalline 5-*S*-ethyl-5-thio-L-arabinose diethyl dithioacetal (IV). The structure of IV was proved by reductive desulfurization with Raney nickel to sirupy 1,5-dideoxy-L-arabinitol(L-lyxitol) [pentane-L-*arabino*(L-*lyxitol*)-2,3,4-triol] (V) which was characterized by periodate and chromic acid oxidation (CH_3—C assay). Acetaldehyde was identified as a product of periodate oxidation, in the course of which an unstable dimorph of acetaldehyde "dimedon" was encountered.



It is possible that α-L-arabinopyranose tetraacetate (I) undergoes ring-opening on formation of the dithioacetal with the resultant liberation of a free hydroxyl group on C-5 (II). The C-5 hydroxyl is then replaced by the thioethyl function. That a free hydroxyl is replaceable under these conditions is demonstrated by the formation of the 2-*S*-ethyl group on similar treatment of 3,4,5,6-tetra-*O*-benzoyl-D-glucose diethyl dithioacetal[5] and 3,4,5-tri-*O*-benzoyl-D-xylose diethyl dithioacetal.[6] In the case of β-D-glucopyranose pentaacetate,[4] acetyl migration down the chain is probably faster than hydroxyl replacement on C-5 and the thioethyl group finally enters the C-2 position.

Experimental

5-*S*-Ethyl-5-thio-L-arabinose Diethyl Dithioacetal (IV).—To a suspension of 20 g. of tetra-*O*-acetyl-α-L-arabinopyranose[7] and 20 g. of soluble anhydrite (Drierite)[8] in 100 ml. of ethanethiol was added 25 g. of freshly distilled boron trifluoride etherate, in small portions. When the initial exothermic reaction had subsided, the flask was sealed and the reaction mixture was stirred (magnetic stirrer) for 4 days. At the end of this time the flask was opened, and the mixture was poured slowly into a saturated aqueous sodium bicarbonate solution. Chloroform (100 ml.) was added and the mixture was heated on a steam bath until the chloroform had boiled away. An additional 200 ml. of chloroform was added to the cooled solution, and the mixture was filtered under reduced pressure. The chloroform layer was separated, dried with sodium sulfate, and evaporated to a clear sirup. The sirup was dissolved in 75 ml. of methanol and 1 g. of sodium methoxide was added after which the solution was heated to the boiling point and an additional 0.65 g. of sodium methoxide added. After 1 hr. the solution was neutralized by stirring with an excess of IR-120 ion exchange resin,[8] and the solvent was removed under reduced pressure. The sirupy residue was dissolved in heptane and diluted with petroleum ether (b.p. 30–60°) to incipient cloudiness. Crystallization was spontaneous and was completed by adding further amounts of petroleum ether. The crystalline material was filtered and washed with petroleum ether; yield 7.3 g. Purification was effected by recrystallization from hexane (decolorizing carbon) or by sublimation at 50 microns pressure and 70° bath temperature; m.p. 65–67°, $[\alpha]^{24}\text{D}$ −16° (*c* 3.4, pyridine), X-ray powder diffraction data[9]: 4.14 s (3), 10.57 s (1), 7.64 vw, 6.97 vw, 5.39 vw, 4.85 m, 4.53 m, 4.15 s (2), 3.75 w, 3.21 w, 2.32 w.

Anal. Calcd. for $C_{11}H_{24}O_3S_3$: C, 43.96; H, 8.05; S, 32.01. Found: C, 44.3; H, 8.03; S, 32.2 (Parr bomb).

Similar results but with a lower yield were obtained on using zinc chloride (12 g.) as a catalyst in place of the boron trifluoride.

To a solution of 1.0 g. of the above substance (IV) in 75 ml. of absolute ethanol was added 15–20 g. of neutral Raney nickel. The solution was heated 48 hr. under reflux and with stirring. The nickel was extracted with ethanol in a Soxhlet apparatus, the ethanol removed under reduced pressure, and the resultant sirup was dissolved in water and stirred with a mixture of IR-120(H^+) and IR-45(OH^-) ion exchange resins.[8] The water was removed by evaporation under reduced pressure and the colorless sirup obtained was dried under reduced pressure; yield 160 mg., $[\alpha]^{26}\text{D}$ +5.5° (*c* 1, H_2O).

Anal. Calcd. for CH_3—$(CHOH)_3$—CH_3: CH_3—C, 2.0; IO_4 oxidation (moles per mole reducant): oxidant consumed 2.0; HCO_2H, 1.0. Found: CH_3—C, 1.9; IO_4 consumed, 1.7; HCO_2H, 0.9; S, 0.00.

Acetaldehyde formed by the periodate oxidation was swept into a solution of 5,5-dimethyl-1,3-cyclohexanedione (dimedon) in water. The resulting dimedon derivative was filtered and dried; m.p. 140–142°, X-ray diffraction data of an unstable dimorph[9]: 13.60 m, 8.59 m, 7.63 w (2), 6.92 w, 6.13 s (3), 5.85 s (1), 4.91 m, 4.62 m, 4.22 m, 3.87 w, 3.50 w, 3.41 vw, 3.05 vw, 2.93 vw. Recrystallization and seeding with an authentic sample of acetaldehyde dimedon resulted in material identical with authentic acetaldehyde dimedon, X-ray diffraction data[9]: 9.12 m (2,2), 6.92 m (2,2), 5.34 m (3), 5.13 s (1), 4.70 vw, 4.06 vw, 3.65 vw, 3.46 vw, 3.35 vw, 3.00 vw.

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[5] P. Brigl, H. Mühlschlegel, and R. Schinle, *Ber.*, **64**, 2921 (1931).

[6] M. L. Wolfrom and W. von Bebenburg, *J. Am. Chem. Soc.*, **82**, 2817 (1960).

[7] C. S. Hudson and J. K. Dale, *ibid.*, **40**, 992 (1918).

[8] A product of the Rohm and Haas Co., Philadelphia, Pa.

[9] Interplanar spacing, CuKα radiation. Relative intensity, estimated visually: s, strong; m, medium; w, weak; v, very. Three strongest lines are numbered, (1, strongest); double numbers indicate approximately equal intensities.