Anal. Calcd for $C_{18}H_{32}O_{16}$: C, 42.86; H, 6.39; mol wt, 504. Found: C, 42.45; H, 6.63; mol wt (by osmometry), 501.

This substance, the isomeric trisaccharide V, was cleaved by β-D-glucosidase[20] to D-glucose and maltose, identified by paper chromatography.

B. From the Reaction of 3,4,6-Tri-*O*-acetyl-2-*O*-nitro-β-D-glucosyl Chloride (III) and *O*-(2,3,4-Tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-tetra-*O*-acetyl-β-D-glucopyranose (I-6′-OH).—*O*-(2,3,4-Tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-tetra-*O*-acetyl-β-D-glucopyranose (I, 6′-OH; 1.17 g, 1.84 mmoles), Drierite (1.5 g), silver carbonate[12] (1 g), and silver perchlorate (50 mg) were stirred in 50 ml of anhydrous ether for 30 min in the absence of light. To this mixture was then added 0.55 g (1.50 mmoles) of 3,4,6-tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl chloride[12] (III). The reaction mixture was stirred for 6 hr at room temperature, after which time no chloride ion was detectable. The mixture was filtered through a carbon-precoated filter and washed with 50 ml of ether. The combined filtrate and washings were concentrated to a syrup which was dissolved in 100 ml of absolute ethanol, and the solution was denitrated by hydrogenolysis, deacetylated, and chromatographed on carbon as described above for the previous synthesis of panose, which was isolated and identified in crystalline form: yield 43 mg (5.7%), mp 220–221° dec.

The eluates obtained with 15 and 30% aqueous ethanol were combined. They contained the trisaccharide (V) isomeric with panose (IV) and a small proportion of higher saccharide, separated by chromatography on thick filter paper (Whatman No. 3MM) with 1-butanol–pyridine–water (6:4:3, v/v) as developer; yield of amorphous V was 19 mg (2.5%), $[\alpha]^{20}D$ +70° (*c* 0.6, water).

β-Isomaltose Octaacetate and β-Gentiobiose Octaacetate from Tetra-*O*-acetyl-6-*O*-trityl-β-D-glucopyranose and III.—Tetra-*O*-acetyl-6-*O*-trityl-β-D-glucopyranose[21] (1.69 g) was treated with an equimolar amount (1 g) of III in nitromethane containing silver perchlorate (0.7 g) as described above for the panose synthesis. The syrup obtained after reductive removal of the nitrate group was acetylated for 30 min at 130° with 0.5 g of of sodium acetate and 7 ml of acetic anhydride. The cooled reaction mixture was poured into 30 ml of ice and water and stirred for 18 hr. The resultant solution was extracted with chloroform, and the extract was washed successively with aqueous sodium hydrogen carbonate and water, and concentrated to a syrup. The syrup was dissolved in 24 ml of benzene and chromatographed in two equal parts on Magnesol–Celite as described by Wolfrom and Lineback.[13] The mother liquors from the crystallizations of the material in the two zones obtained were rechromatographed in the same manner, and there was so obtained a total of 304 mg (16.6%) of β-isomaltose octaacetate, mp and mmp 146–147°, and 332 mg (18.1%) of β-gentiobiose octaacetate, mp and mmp 193–194°.

Registry No.—IV, 490-40-4; I-6-OTr, 7482-59-9; I, 7485-48-5; I-6′-OH, 7482-60-2; II, 6748-75-0; II, 1-β-*O*-OAc, 7482-62-4; V, 7485-51-0; β-isomaltose octaacetate, 4627-41-2; β-gentiobiose octaacetate, 4613-78-9.

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(20) "Emulsin" of Worthington Biochemical Co., Freehold, N. J. The preparation hydrolyzed gentiobiose but not isomaltose.

(21) B. Helferich, L. Moog, and A. Jünger, *Ber.*, **58**, 872 (1925).

Confirmation of the Structure of 1,3,5-Tri-*O*-acetyl-2,7-anhydro-β-D-*altro*-heptulopyranose and Its Conversion *via* an Epoxy Intermediate into 2,7-Anhydro-3-*S*-methyl-3-thio-β-D-*gluco*-heptulopyranose

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The structure of 1,3,5-tri-*O*-acetyl-2,7-anhydro-β-D-*altro*-heptulopyranose (II) has been confirmed by the oxidation of the free hydroxyl group at C-4 with dimethyl sulfoxide and acetic anhydride, followed by reduction of the resulting keto group with sodium borohydride and the isolation of 2,7-anhydro-β-D-*manno*-heptulopyranose as one of the products. The tosylate of II slowly reacted with sodium methoxide at room temperature to yield 2,7:3,4-dianhydro-β-D-*manno*-heptulopyranose (VI) isolated as the crystalline diacetate (VII). Epoxide scission of VII by sodium thiomethoxide proceeded in concurrence with the Fürst–Plattner rule yielding 2,7-anhydro-3-*S*-methyl-3-thio-β-D-*gluco*-heptulopyranose (VIII). Desulfurization of VIII with Raney nickel afforded 2,7-anhydro-3-deoxy-β-D-*arabino*-heptulopyranose (X) which was resistant to sodium periodate but not to lead tertaacetate–pyridine. The configurations assigned to these new compounds are based on the fact that any alternative pathway of the reactions described above, including possible epoxide migration, would not produce a deoxyheptulosan which would comply with these specific oxidation results.

Recently in this laboratory during the preparation of the tetraacetate of sedoheptulosan (2,7-anhydro-β-D-*altro*-heptulopyranose, I), known only as a levorotatory syrup,[1] a small amount (4%) of a crystalline triacetate[2] was isolated from the main product. On the basis of its nmr spectrum,[2] this new compound was designated 1,3,5-tri-*O*-acetylsedoheptulosan (II). The presence of an unacetylated, equatorial hydroxyl group at C-4 in compound II seemed rather unusual and is contrary at least to the results of sulfonation reactions[3,4] where preferential tosylation of equatorial hydroxyl groups in locked ring systems has been demonstrated. The selective tosylation[5] of 1,6-anhydro-2-*O*-benzoyl-β-D-altropyranose was of special interest. In this compound, which is structurally analogous to II, Newth[5] successfully tosylated the equatorial hydroxyl group at C-3 in preference to the axial hydroxyl group at C-4. Furthermore, the possibility that the triacetate II resulted from partial hydrolysis of the syrupy tetraacetate seemed very unlikely since the yield of the former compound has now been increased

(1) N. K. Richtmyer and J. W. Pratt, *J. Am. Chem. Soc.*, **78**, 4717 (1956).
(2) E. Zissis and N. K. Richtmyer, *J. Org. Chem.*, **30**, 462 (1965).
(3) G. O. Aspinall and G. Zweifel, *J. Chem. Soc.*, 2271 (1957).
(4) J. G. Buchanan and J. C. P. Schwarz, *ibid.*, 4770 (1962).
(5) F. H. Newth, *ibid.*, 441 (1956).

to 21% by acetylating sedoheptulosan at a lower temperature. In view of these observations it was deemed necessary to verify further the structure of II.

The proof of its structure was accomplished by oxidizing the free hydroxyl group at C-4 with dimethyl sulfoxide and acetic anhydride, a reagent first described by Albright and Goldman.[6] The resultant syrup (V) was reduced with sodium borohydride, with simultaneous deacetylation, to two products identified by paper chromatography as 2,7-anhydro-β-D-*manno*-heptulopyranose and sedoheptulosan (I). A mixture melting point of the 2,7-anhydro-β-D-*manno*-heptulopyranose, isolated by fractional crystallization, with an authentic sample was not depressed and their infrared spectra were identical. Further proof was the tosylation of II to III and its deacetylation to the monotosylate IV which was not oxidized by either sodium periodate or lead tetraacetate–pyridine. The resistance of IV to oxidation would be indicative only of a 4-tosyl derivative.

The verification of the structure of 1,3,5-tri-*O*-acetylsedoheptulosan and its greater accessibility, owing to improved yield, prompted an interest in preparing an epoxy derivative of a 2,7-anhydroheptulose. In 1942 Hann and Hudson[7,8] prepared the 3,4- and the 2,3-anhydrides of 1,6-anhydro-β-D-talose and in recent years similar dianhydrides in the hexose series have been synthesized.[5,9-11] Since epoxides in the heptulosan series are still unknown to the best knowledge of the author, the synthesis of such a compound would not only be unique in itself but would be also ideal for the preparation of variously substituted derivatives by scission of the epoxide ring.

Compound III was allowed to react with sodium methoxide at 20° for 18 days. Paper chromatography of the syrupy product indicated that it consisted chiefly of an epoxy derivative plus minor amounts of starting material and two other uncharacterized products. The new epoxide was obtained as a crystalline acetate and based on results described below was assigned the structure of 1,5-di-*O*-acetyl-2,7:3,4-dianhydro-β-D-*manno*-heptulopyranose (VII). The nmr spectrum of VII showed a well-resolved AB quartet at τ = 6.78 and 6.98 ppm with a spacing of 3.9 cps (J_{AB}) which is in good agreement with other epoxides. For example, Buss, *et al.*,[12] in a study of carbohydrate epoxides, have assigned similar values for the proton–proton coupling of C-2 and C-3 in methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (τ = 6.56 and 6.88 ppm, J = 4.0 cps).

In 1956 Newth[5] found that the 2-tosyl and the 3,4-ditosyl derivatives of 1,6-anhydro-β-D-altrose were resistant to hot sodium methoxide. The 1,6-anhydro-3-*O*-tosyl-β-D-altrose, analogous to IV, was also unreactive but at a higher alkoxide concentration a small yield of a dianhydride was obtained and its structure established as 1,6:3,4-dianhydro-β-D-altrose; this unexpected product was explained by the phenomenon of epoxide migration. Lake and Peat[13] had also observed a small amount of methyl 3,4-anhydro-β-D-altropyranoside in the reaction of methyl 2-*O*-tosyl-β-D-glucopyranoside with sodium methoxide; however, the main product was the expected methyl 2,3-anhydro-β-D-mannopyranoside. Despite this, it was strongly believed that under these milder conditions the reaction of 1,3,5-tri-*O*-acetyl-4-*O*-tosylsedoheptulosan (III) proceeds normally and the resulting epoxide is rightfully named 2,7:3,4-dianhydro-β-D-*manno*-heptulopyranose (VI). This view is supported by the work of Buchanan and Schwarz,[4] who clearly demonstrated in a study of the interconversion of methyl 2,3-anhydro-α-D-mannoside and methyl 3,4-anhydro-α-D-altroside in alkali that the equilibrium favored the former isomer.

These conclusions were substantiated by the scission of the epoxide ring of VII with thiomethoxide ion yielding a crystalline methylthio derivative (VIII), desulfurization of VIII with Raney nickel to a crystalline deoxy derivative (X), and the behavior of X to specific oxidizing reagents (see Scheme I).

According to the Fürst–Plattner rule,[14] nucleophilic rearside attack of epoxide rings in rigid, six-membered rings generally produces *trans*-diaxially substituted derivatives. This rule of preferential scission has been well established even with the more uncommon, nucleophilic methanethiolate anion.[15-17] Diacetate VII was allowed to react with sodium thiomethoxide and in accordance with the Fürst–Plattner rule afforded a 65% yield of crystalline 2,7-anhydro-3-*S*-methyl-3-thio-β-D-*gluco*-heptulopyranose (VIII) with the methylthio group on C-3 and the hydroxyl group on C-4 *trans*-diaxially oriented. The proof of the structure of compound VIII was its desulfurization with Raney nickel to a crystalline deoxy derivative X, 2,7-anhydro-3-deoxy-β-D-*arabino*-heptulopyranose, which was unaffected by sodium periodate but oxidized by lead tetraacetate–pyridine.

A pair of vicinal, *trans*-diaxial hydroxyl groups in a fused ring system will not be oxidized by sodium periodate; such known compounds in carbohydrate chemistry are 1,6-anhydro-β-D-glucofuranose and -α-D-galactofuranose,[18] 2,7-anhydro-β-D-*altro*-heptulofuranose,[1] methyl 4,6-*O*-benzylidene-α-D-altropyranoside and its anomer,[19] 2,6-anhydro-β-D-fructofuranose,[20] and 2,7-anhydro-α-L-*galacto*-heptulofuranose.[21] However, lead tetraacetate in pyridine solution has been found by Goldschmid and Perlin[22] to readily oxidize such aforementioned compounds although overoxidation is evident. From methyl 4,6-*O*-benzylidene-α-D-altropyranoside, the expected dialdehyde was isolated as the hemialdal hydrate when the reaction was stopped at the appropriate time.[22]

(6) J. D. Albright and L. Goldman, *J. Am. Chem. Soc.*, **87**, 4214 (1965).
(7) R. M. Hann and C. S. Hudson, *ibid.*, **64**, 925 (1942).
(8) R. M. Hann and C. S. Hudson, *ibid.*, **64**, 2435 (1942); S. P. James, F. Smith, M. Stacey, and L. F. Wiggins, *J. Chem. Soc.*, 625 (1946).
(9) M. Černý, V. Gut, and J. Pacák, *Collection Czech. Chem. Commun.*, **26**, 2542 (1961).
(10) M. Černý and J. Pacák, *ibid.*, **27**, 94 (1962).
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(16) H. R. Bolliger and D. A. Prins, *ibid.*, **29**, 1061 (1946).
(17) A. C. Maehly and T. Reichstein, *ibid.*, **30**, 496 (1947).
(18) R. J. Dimler, H. A. Davis, and G. E. Hilbert, *J. Am. Chem. Soc.*, **68**, 1377 (1946); B. H. Alexander, R. J. Dimler, and C. L. Mehltretter, *ibid.*, **73**, 4658 (1951).
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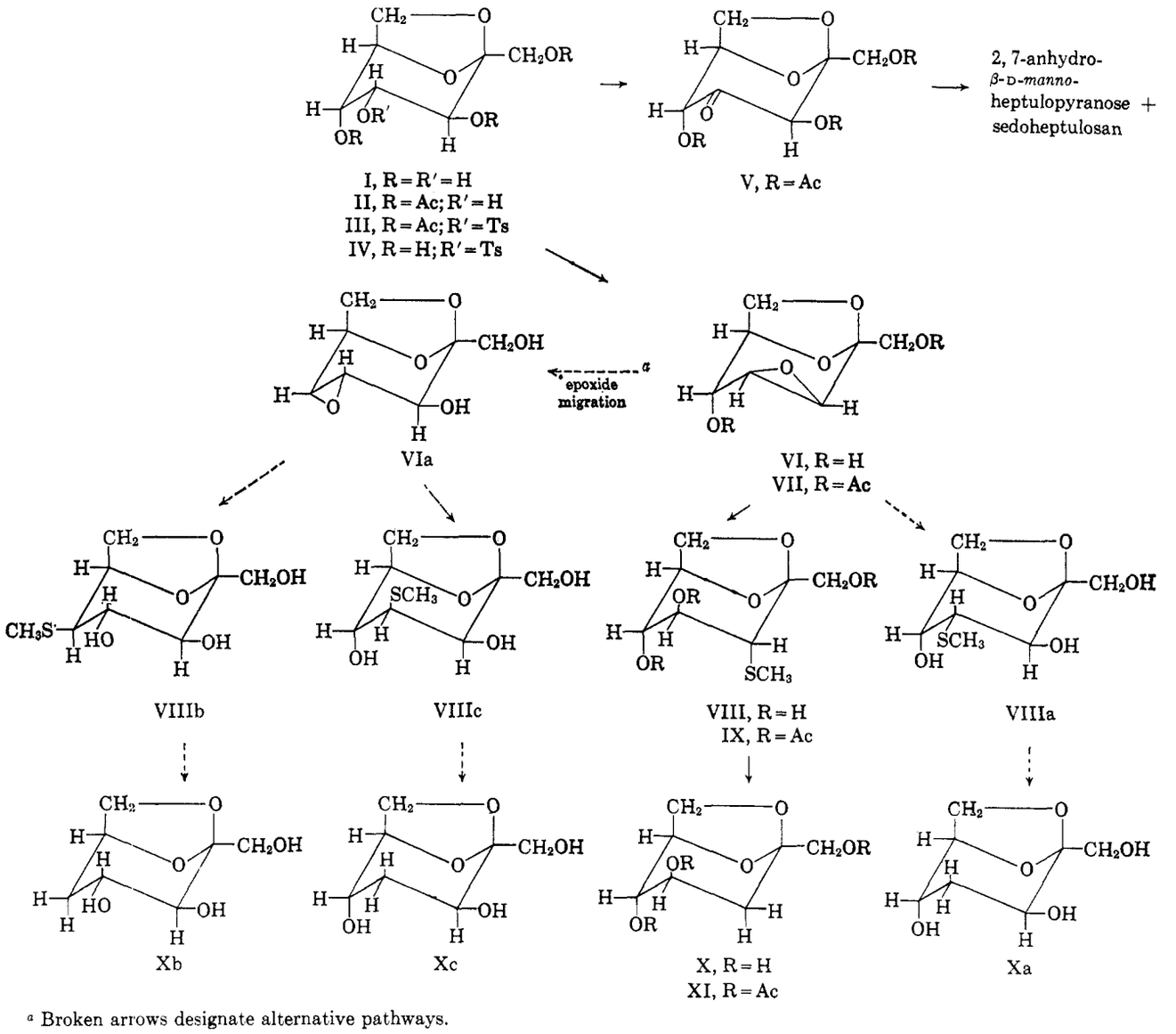
(20) H. R. Goldschmid and A. S. Perlin, *Can. J. Chem.*, **38**, 2178 (1960).
(21) L. C. Stewart, E. Zissis, and N. K. Richtmyer, *J. Org. Chem.*, **28**, 1842 (1963).
(22) H. R. Goldschmid and A. S. Perlin, *Can. J. Chem.*, **38**, 2280 (1960).

SCHEME I



[a] Broken arrows designate alternative pathways.

The specific oxidation results observed in the deoxyheptulosan therefore indicate the presence of adjacent hydroxyl groups *trans*-diaxially oriented, and compound X is the only one which can fulfill these requirements. If the epoxide scission of VI had occurred by nucleophilic attack at C-4, the resulting deoxy derivative (Xa) would not be attacked by either oxidant owing to the absence of adjacent hydroxyl groups. Furthermore, the possibility of epoxide migration can also be disregarded. Such an isomerization product (VIa) can yield two possible deoxy derivatives (Xb, Xc) dependent on the process of the rupture of the epoxide ring. The one possibility, Xc, having no adjacent hydroxyl groups, will not react with either oxidizing reagent. In Xb, containing equatorial-, equatorial-hydroxyl groups at C-3 and C-4, sodium periodate should be consumed at a slow rate. Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside of similar structure, that is, with e,e-hydroxyl groups at C-2 and C-3, was observed by Honeyman and Shaw[19] to be oxidized slowly by periodate, whereas methyl 4,6-*O*-benzylidene-α-D-altropyranoside with *trans*-diaxial hydroxyl groups at C-2 and C-3 was unreactive. When 2,7-anhydro-3-deoxy-β-D-*arabino*-heptulopyranose (X) was subjected to sodium periodate for about 4 days with no consumption of oxidant, a sample of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside under similar conditions had consumed 0.67 mole of periodate.

Experimental Section

Partial Acetylation of Sedoheptulosan (2,7-Anhydro-β-D-*altro*-heptulopyranose, I) to the 1,3,5-Triacetate (II).—To a chilled solution of 101 g of sedoheptulosan monohydrate in 1 l. of pyridine was added 200 ml of acetic anhydride and the mixture was kept in the refrigerator for 6 days. The reaction solution was then poured onto crushed ice, neutralized with sodium bicarbonate, and concentrated *in vacuo* to a residue which was extracted with chloroform. The extract, dried with sodium sulfate and decolorized with carbon, was concentrated *in vacuo* to a syrup, which was diluted with methanol and reconcentrated overnight by blowing a stream of air over the surface of the solution. The deposited crystals of triacetate were removed by filtration and washed with methanol in the cold. After recrystallization of the 25.6 g of product from two parts of methanol, the prismatic needles, dried overnight in a vacuum oven at 80°, melted at 116–119°. Analytically pure triacetate[2] melts at 119–120°, $[\alpha]^{20}D$ −155° (*c* 1, chloroform). The syrupy mother liquor after several months' duration deposited an additional 6.8 g, the total (32.4 g) representing a 21% yield.

Oxidation of 1,3,5-Tri-*O*-acetyl-2,7-anhyro-β-D-*altro*-heptulopyranose (II) with Dimethyl Sulfoxide and Acetic Anhydride to (V) and Subsequent Reduction with Sodium Borohydride.—A mixture of 0.3 g of II, 3 ml of dimethyl sulfoxide, and 2 ml of acetic anhydride allowed to stand overnight at room temperature was diluted with ice and concentrated *in vacuo* to a small volume. It was then repeatedly taken up in toluene and reconcentrated *in vacuo* until a stiff syrup of constant weight (0.25 g) was obtained. An aqueous ethyl alcohol solution (10 ml) of the syrup was added dropwise to a stirred solution of 0.25 g of sodium borohydride in 10 ml of water. After 2 hr 5 ml of acetone was added dropwise to destroy the excess of reagent and then the solution was concentrated *in vacuo* to a water-soluble syrup. An aqueous solution of the product was stirred with some Amberlite IR-120 and after removal of the resin by filtration reconcentrated to a residue. Removal of the borate ion was accomplished by repeatedly dissolving the syrup in hot methanol and concentrating on a steam bath by the passage of a stream of air across its surface. The product was finally deionized by a mixture of Amberlite IR-120 and Duolite A-4 and concentrated *in vacuo* to a syrup weighing 0.1 g. A paper chromatogram showed two main spots with mobilities similar to those of 2,7-anhydro-β-D-*manno*-heptulopyranose and sedoheptulosan. The former compound was isolated crystalline (21 mg), melted at 157–159°, and a mixture melting point with authentic 2,7-anhydro-β-D-*manno*-heptulopyranose (159–160°) was not depressed. In addition, their infrared spectra were identical and their mobilities on Whatman No. 1 paper in two different systems were also the same.

1,3,5-Tri-*O*-acetyl-2,7-anhydro-4-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (III).—After 4 days at room temperature a solution of 1.2 g of II and 1.8 g of tosyl chloride in 50 ml of pyridine was poured onto crushed ice, depositing 1.6 g (90%) of the tosyl derivative. Two recrystallizations from 3.5 parts of ethyl alcohol yielded clusters of rods: mp 119–120°, $[\alpha]^{20}D$ −112° (*c* 1.7, chloroform).

Anal. Calcd for $C_{20}H_{24}O_{11}S$: C, 50.84; H, 5.12; S, 6.79; CH_3CO, 27.3. Found: C, 50.93, H, 4.88; S, 6.66; CH_3CO, 27.7.

2,7-Anhydro-4-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (IV).—Catalytic deacetylation of 1.3 g of III with sodium methoxide was carried out in the usual manner. The monotosylate crystallized as a hydrate from an aqueous acetone solution allowed to evaporate slowly overnight at room temperature. The 0.9 g of crude product (88%) was dissolved in a few milliliters of 85% ethyl alcohol, chilled in an ice bath, and deposited as square prisms on the addition of ethyl ether. A constant melting point of 47–52° was obtained after a second recrystallization and the specific rotation of the monotosylate was $[\alpha]^{20}D$ −102° (*c* 1, acetone).

Anal. Calcd for $C_{14}H_{18}O_8S \cdot 1.5\ H_2O$: C, 45.03; H, 5.67; S, 8.59. Found: C, 45.52; H, 5.70; S, 8.53. Calcd for $C_{14}H_{18}O_8S$ (dehydrated to syrup): C, 48.55; H, 5.24. Found: C, 48.80, 48.28; H, 5.27, 5.50.

1,5-Di-*O*-acetyl-2,7:3,4-dianhydro-β-D-*manno*-heptulopyranose (VII).—The course of the reaction of III with sodium methoxide, in preliminary experiments, was followed by paper chromatography. At 5° only deacetylation was observed. At 20° the reaction solution slowly darkened and after several days the main component was the epoxide VI plus a small amount of starting material and two minor products. On further standing, the amount of starting material decreased but the two minor products seemed to have increased proportionally faster than the epoxide.

In a final experiment, 20 g of III in 400 ml of methanol was allowed to react with 250 ml of 2 *N* sodium methoxide for 3 days at 5° and then for 15 days at room temperature. Amberlite IR-120 resin was added, and the solution was filtered with carbon and concentrated *in vacuo* to a syrup. Four extractions with 200-ml portions of hot ethyl acetate and a final extraction with 200 ml of hot ethyl alcohol left a residue containing a negligible amount of epoxide. The combined, concentrated ethyl acetate extracts weighed 4.4 g. The ethanolic extract was concentrated to a small volume and filtered free of undesirable material which had deposited. Further concentration yielded a syrup which was digested with hot ethyl acetate and the decantate on evaporation furnished an additional 1.0 g of syrup. The total amount of syrup (5.4 g) was reextracted several times with hot ethyl acetate and the combined, concentrated extracts yielded 4.6 g of reasonably pure, amorphous epoxide. On acetylation of this material with pyridine and acetic anhydride, 0.8 g of starting material was recovered when the reaction solution was poured onto crushed ice. The filtrate was then neutralized with sodium bicarbonate and concentrated *in vacuo* to a residue which was extracted several times with chloroform. Evaporation of the chloroform solution yielded a mobile syrup crystallizing completely overnight. The 4.7 g (43%) of crude diacetate was crystallized twice from three parts of ethyl alcohol as clusters of thick prisms: mp 101–102°, $[\alpha]^{20}D$ −54.7° (*c* 1, chloroform).

Anal. Calcd for $C_{11}H_{14}O_7$: C, 51.16; H, 5.43; CH_3CO, 33.3. Found: C, 51.26; H, 5.43; CH_3CO, 33.2.

2,7-Anhydro-3-*S*-methyl-3-thio-β-D-*gluco*-heptulopyranose (VIII).—According to the procedure of Jeanloz, *et al.*,[15] 2.8 g of liquid methanethiol and 2.5 g of VII were successively added to a chilled solution (0°) of 1 g of sodium in 20 ml of methanol. The reaction mixture was then refluxed for 2 hr and the resulting pale yellow solution was concentrated by a stream of air to about half its volume, diluted with 10 ml of water, and mixed with Amberlite IR-120 resin to destroy the excess of reagent. When the evolution of methanethiol had subsided, the resin was filtered off and washed thoroughly with 50% methanol. The combined filtrate and washings, concentrated *in vacuo* to a colorless syrup, weighed 2.0 g and its nmr spectrum showed a sharp peak equivalent to three protons at τ = 7.83 ppm; the range of the chemical shifts of methylthio protons is τ = 7.6–8.6 ppm. A portion of the syrup was extracted with hot ethyl acetate and the extract, left in the refrigerator over a weekend, deposited a gum which had partly crystallized. A second sample of syrup crystallized slowly in the cold from ethyl alcohol–pentane as elongated prisms melting at 70–75°; however, on being recrystallized from the same solvents the product readily deposited overnight as rosette clusters of chunky prisms, mp 106–108°. The main portion of product also in ethyl alcohol–pentane, which had been in the refrigerator for over 1 week, suddenly crystallized completely overnight yielding the higher melting form. The first crop of crystals weighed 1.2 g and an additional 0.2 g was obtained from the mother liquor; the total represented a 65% yield. The methylthio derivative, recrystallized twice from ethyl alcohol–pentane, melted at 107–108.5°, $[\alpha]^{20}D$ −80.0° (*c* 0.6, water).

Anal. Calcd for $C_8H_{14}O_5S$: C, 43.23; H, 6.35; S, 14.43. Found: C, 43.10; H, 6.28; S, 14.42.

1,4,5-Tri-*O*-acetyl-2,7-anhydro-3-*S*-methyl-3-thio-β-D-*gluco*-heptulopyranose (IX).—A solution of 0.3 g of VIII in 6 ml of pyridine containing 3 ml of acetic anhydride, after 2 days at room temperature, was diluted with crushed ice, neutralized with sodium bicarbonate, and concentrated *in vacuo* to a residue which was extracted with chloroform. The concentrated extract, dissolved in a small amount of ethyl alcohol, evaporated overnight to a crystalline mass. The acetate, filtered and washed with pentane, weighed 0.4 g (85%). The product, dissolved in a small amount of hot ethyl alcohol and allowed to stand overnight at 0°, recrystallized as rectangular prisms which were rapidly filtered and washed with pentane. After a second recrystallization the acetate melted at 73.5–74.5°, $[\alpha]^{20}D$ −40.1° (*c* 0.8, chloroform).

Anal. Calcd for $C_{14}H_{20}O_8S$: C, 48.27; H, 5.79; S, 9.20; CH_3CO, 37.1. Found: C, 48.39; H, 5.99; S, 9.04; CH_3CO, 37.1.

2,7-Anhydro-3-deoxy-β-D-*arabino*-heptulopyranose (X).—The preparation[23] of Raney nickel was slightly modified[24] by heating the final reaction mixture at 50° for only 1 hr. Freshly prepared Raney nickel from 20 g of the nickel aluminum alloy was added to 0.2 g of VIII dissolved in 15 ml of ethyl alcohol. After dilution with 5 ml of water, the stirred reaction mixture was refluxed for 2.5 hr. The catalyst was removed by filtration and washed thoroughly with 80% ethyl alcohol, and the combined filtrate and washings were concentrated *in vacuo* to a syrup. The syrup was digested with a small amount of hot ethyl acetate and the chilled extract, on being concentrated by a stream of air, partly crystallized. Complete crystallization was obtained by the addition of a few drops of ethyl alcohol. The deoxy derivative, redissolved in warm ethyl alcohol, formed elongated prisms on cooling. It weighed 76 mg (48%) and on being recrystallized melted at 139–142°, $[\alpha]^{20}D$ −90.2° (*c* 1, water).

(23) R. Mozingo, *Org. Syn.*, **21**, 15 (1941).

(24) R. Mozingo, D. E. Wolf, S. A. Harris, and K. Folkers, *J. Am. Chem. Soc.*, **65**, 1013 (1943).

Anal. Calcd for $C_7H_{12}O_5$: C, 47.72; H, 6.87. Found: C, 47.70; H, 7.11.

1,4,5-Tri-*O*-acetyl-2,7-anhydro-3-deoxy-β-D-*arabino*-heptulopyranose (XI).—Acetylation of X (36 mg) gave a 62% yield of crystalline triacetate. The long needles, recrystallized twice from chloroform–pentane, melted at 63–65°, $[\alpha]^{20}D$ −98.3° (*c* 0.3, chloroform).

Anal. Calcd for $C_{13}H_{18}O_8$: C, 51.65; H, 6.00. Found: C, 51.74; H, 6.13.

Sodium Periodate Oxidations.—The sodium periodate oxidations were carried out on a microscale employing the method described by Dixon and Lipkin.[25] A Beckman DU spectrophotometer was used to determine the amount of oxidant consumed by the measurement of the absorption of periodate ion at a wavelength of 222.5 mμ. Methyl 4,6-*O*-benzylidine-α-D-glucopyranoside consumed 0.32 and 0.67 mole of periodate per mole of compound in 18 and 88 hr, respectively, whereas 4-*O*-tosylsedoheptulosan (IV) and 2,7-anhydro-3-deoxy-β-D-*arabino*-heptulopyranose (X) were not oxidized under similar conditions.

Lead Tetraacetate–Pyridine Oxidations.—The method of Goldschmid and Perlin[22] was slightly modified by using a commercial grade of lead tetraacetate which was merely dried by being pressed between layers of filter paper until the first signs of decomposition were observed. It was then immediately dissolved in a minimum amount (about 65 parts) of dry pyridine forming a very dark solution. This reagent was tested on 10-mg samples of the triacetate (II) and montosylate (IV) of sedoheptulosan and on 2,7-anhydro-3-deoxy-β-D-*arabino*-heptulopyranose (X) at 5°. Only X reacted, consuming 0.76 mole of oxidant within 6.5 hr. After 24 hr, overoxidation was noted but the other two compounds were still unreactive.

Reaction of 2,7-Anhydro-3-*S*-methyl-3-thio-β-D-*gluco*-heptulopyranose (VIII) with Acid.—Paper chromatography of the reaction of 170 mg of VIII in 5 ml of 0.2 *N* sulfuric acid at 85° for 7 hr indicated the formation of a new compound whose mobility was slightly slower than that of the starting material. The resulting syrup reduced Fehling solution and upon acetylation yielded a crystalline product which could not be purified. After several recrystallizations from ethyl alcohol–pentane, the needles melted at 112–123°. Although decomposition was not evident, the compound on being heated at various high temperatures gave erratic carbon analyses and weight losses ranged as high as 33%. Elemental analysis of a sample dried at 80° overnight (25% weight loss) indicated that the compound might be the penta-acetate of 3-*S*-methyl-3-thio-D-*gluco*-heptulopyranose contaminated with some starting material.

Anal. Calcd for $C_{18}H_{26}O_{11}S$: C, 47.99; H, 5.82; S, 7.12. Found: C, 48.30; H, 5.87; S, 7.77.

Registry No.—II, 7540-81-0; VIII, 7485-52-1; 2,7-anhydro-β-D-mannoheptulopyranose, 7739-21-1; III, 7785-14-0; IV, 10026-48-9; VII, 7739-22-2; IX, 7739-23-3; X, 7782-05-0; XI, 7739-24-4.

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Syntheses with Partially Benzylated Sugars. VII.[1] The Anomeric Vinyl D-Glucopyranosides

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Two synthetic pathways to the synthesis of vinyl D-glucopyranosides have been explored. In the first pathway, 2-chloroethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside was converted into *N*-(2-β-D-glucopyranosyloxyethyl)dimethylammonium chloride (I) and thence into 2-dimethylaminoethyl β-D-glucopyranoside (V). The latter base was quaternized with methyl iodide and the resulting iodide (VI), after conversion into the hydroxide, was subjected to a Hofmann degradation. Acetylation of the crude product afforded crystalline vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (VIII). Hydrogenation of VIII gave the known ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (XII). An attempted synthesis of vinyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (VIII) through the Cope degradation of the *N*-oxide of 2-dimethylaminoethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (III) was unsuccessful. The second pathway to the synthesis of the vinyl D-glucopyranosides began with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (IX); an improved preparation of this substance from methyl α-D-glucopyranoside is described. Transvinylation of IX with isobutyl vinyl ether in the presence of mercuric acetate readily gives the anomeric vinyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosides (X and XI) separable by chromatography. The structures of these substances were demonstrated by conversion into the known ethyl 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosides (XII and XIII). The rates of hydrolysis of the two vinyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosides (X and XI) under acidic conditions were measured and the axial anomer was found to be cleaved more rapidly than the equatorial anomer. The benzyl groups of X and XI were removed through the action of sodium in liquid ammonia and the immediate products were acetylated to give the anomeric vinyl 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosides (VIII and XIV), both in crystalline form. From these, the two anomeric vinyl D-glucopyranosides (XV and XVI) were prepared, only the α anomer (XVI) being obtained in crystalline form. Like phenyl α-D-glucopyranoside, vinyl α-D-glucopyranoside (XVI) is comparatively stable to alkali; its anomer (XV) resembles phenyl β-D-glucopyranoside in that it is converted into 1,6-anhydro-β-D-glucopyranose (XVII) when treated with alkali.

In view of the number and diversity of the D-glucose derivatives which have been described in the literature, it may seem, *a priori*, somewhat surprising that one of the simplest of these, vinyl D-glucopyranoside, has not, apparently, attracted the attention of organic chemists. However, when one considers, on the one hand, the nature of the conventional procedure for the vinylation of alcohols (*i.e.*, acetylene or vinyl chloride with an alkali at elevated temperatures and pressures[4-6]) and, on the other hand, the well-known

(1) Paper VI of this series: T. D. Inch and H. G. Fletcher, Jr., *J. Org. Chem.*, **31**, 1810 (1966).

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(3) The initial portion of the investigation described in this paper was undertaken by two of us (T. D. P. and J. K.) while at the Rocky Mountain Laboratory of the National Institute of Allergy and Infectious Diseases, Hamilton, Mont.

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