crystals, mp 113–115° (lit.[4] mp 111–112°). A mixture melting point was only slightly depressed, and the infrared spectrum was identical with that of an authentic sample.

DL(123/45) **Diastereomer of 2,3,4,5-Tetrahydroxy-1-cyclohexanemethanol (Pseudo-α-DL-galactopyranose) (7).**—A 186-mg portion of the pentaacetate was dissolved in 5.0 ml of a 1 *M* solution of hydrochloric acid in 50% (by volume) aqueous ethanol, and the resulting solution was boiled under reflux for 6 hr, then evaporated. To the residual syrup 10-ml portions of 2-propanol were repeatedly added and evaporated. The crystalline residue was recrystallized from 3.0 ml of 2-propanol, giving 60 mg (71%) of the free pentol as colorless crystals, mp 173–174°. The melting point was not raised upon further recrystallization.

Anal. Calcd for $C_7H_{14}O_5$: C, 47.18; H, 7.92. Found: C, 46.97; H, 8.07.

The infrared spectrum (Nujol) contained absorption maxima at 3360, 3280, 1140, 1060, 1050, and 1030 cm^{-1}.

The proton magnetic resonance spectrum was recorded as noted previously in this article.

Registry No.—**2**, 10226-73-0; **7**, 16802-98-5; **8**, 16802-99-6.

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Synthesis of 3-*O*-(*p*-Tolylsulfonyl)-β-D-*altro*-heptulopyranose and Its Conversion into 2,7:3,4-Dianhydro-β-D-*allo*-heptulopyranose

EMMANUEL ZISSIS

National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Public Health Service, U. S. Department of Health, Education, and Welfare, Bethesda, Maryland 20014

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The oxidation of 2,7-anhydro-4,5-*O*-isopropylidene-β-D-*altro*-heptulopyranose (**1**) with methyl sulfoxide and acetic anhydride followed by reduction with sodium borohydride and subsequent hydrolysis with an acidic ion-exchange resin yielded two 2,7-anhydroheptuloses, namely, 2,7-anhydro-β-D-*altro*-heptulopyranose (sedoheptulosan, **2**) and the new anhydride, 2,7-anhydro-β-D-*allo*-heptulopyranose (**3**), isolated as its crystalline tetraacetate (**4**). These results confirmed the position of the isopropylidene group in compound **1** and, incidentally, demonstrated a simple method for the preparation of **3**. The 3-*O*-tosyl derivative of sedoheptulosan (**7**) was prepared by the selective tritylation of the primary hydroxyl group of **1**, tosylation of the remaining unsubstituted hydroxyl group at C-3, and removal of the isopropylidene and trityl groups. The only product of interest in the reaction of the monotosylate (**7**) with a slight excess of sodium methoxide in boiling methanol was a small amount of 2,7:3,4-dianhydro-β-D-*allo*-heptulopyranose (**9**) obtained as a crystalline diacetate (**10**). The structural assignment of compound **10** is based on its nmr spectrum and also the scission of its epoxide ring to give the expected 2,7-anhydro-β-D-*gluco*-heptulopyranose (**13**). 4,5-Di-*O*-acetyl-2,7-anhydro-1,3-di-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (**12**) was also prepared and, although found to be much more resistant than the 3-tosylate under the same conditions, presumably gave the same results when a large excess of sodium methoxide was employed. In conclusion the nmr spectrum of **10** is discussed briefly.

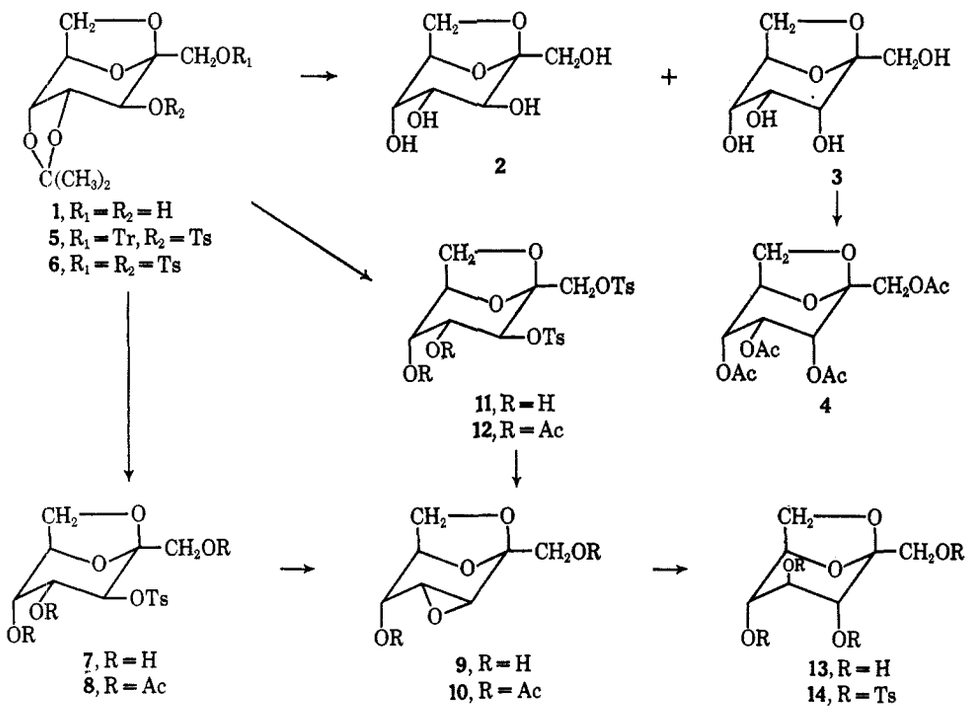
In 1967 the first epoxide in the 2,7-anhydroheptulose series, 2,7:3,4-dianhydro-β-D-*manno*-heptulopyranose,[1] anhydro-4-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose. The ease of reactivity of this monotosylate pyranose. The ease of reactivity of this monotosylate was in contrast to the behavior of the tosyl derivatives of the analogous 1,6-anhydro-β-D-altrose which were highly resistant to sodium methoxide.[2] The synthesis of 2,7-anhydro-3-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (**7**) seemed not only desirable for further study of these discrepant behaviors but also as a source for the preparation of another epoxide. 2,7-Anhydro-4,5-*O*-isopropylidene-β-D-*altro*-heptulopyranose (**1**) appeared to be a suitable intermediate for the synthesis of **7** (Scheme I).

Originally prepared in 1952[3] the structure of **1** has more recently[4] been confirmed through nmr studies. Further and unequivocal chemical confirmation has now been obtained in the course of the present research. The use of methyl sulfoxide–acetic anhydride[5] as a oxidizing agent for secondary hydroxyl groups is well known. Recently in this laboratory the structure of 1,3,5-tri-*O*-acetyl-β-D-*altro*-heptulopyranose was determined[1] by the oxidation of the unprotected hydroxyl group at C-4 with methyl sulfoxide–acetic anhydride. Reduction of the resulting keto derivative and removal of the acetyl groups yielded 2,7-anhydro-β-D-*altro*-heptulopyranose and 2,7-anhydro-β-D-*manno*-heptulopyranose. Horton and Jewell applied this method in obtaining 1,6-anhydro-β-D-talopyranose from 1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose[6] or from 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose.[7] The confirmation of the structure of **1** by this method seemed questionable owing to the unprotected hydroxyl group at C-1 which might result in other products. Nevertheless, oxidation of **1** by methyl sulfoxide–acetic anhydride, followed by reduction with sodium borohydride and then removal of the acetal group, yielded only two products, namely, 2,7-anhydro-β-D-*altro*-heptulopyranose (**2**) and 2,7-anhydro-β-D-*allo*-heptulopyranose (**3**). The former was isolated crystalline and the latter was shown to be the enantiomorph of the known 2,7-anhydro-β-L-*allo*-heptulopyranose[8] through a direct comparison of their crystalline tetraacetates.

The tritylation of **1** yielded a syrupy product which was subsequently tosylated to give crystalline 4,5-

(1) E. Zissis, *J. Org. Chem.*, **32**, 660 (1967).
(2) F. H. Newth, *J. Chem. Soc.*, 441 (1956).
(3) W. T. Haskins, R. M. Hann, and C. S. Hudson, *J. Amer. Chem. Soc.*, **74**, 2198 (1952).
(4) E. Zissis and N. K. Richtmyer, *J. Org. Chem.*, **30**, 462 (1965).
(5) J. D. Albright and L. Goldman, *J. Amer. Chem. Soc.*, **87**, 4214 (1965).
(6) D. Horton and J. S. Jewell, *Carbohyd. Res.*, **2**, 251 (1966).
(7) D. Horton and J. S. Jewell, *ibid.*, **5**, 149 (1967).
(8) J. W. Pratt and N. K. Richtmyer, Abstracts, the 126th National Meeting of the American Chemical Society, New York, N. Y., Sept 1954, p 22D.

SCHEME I



O-isopropylidene-3-*O*-(*p*-tolylsulfonyl)-1-*O*-(triphenylmethyl)-β-D-*altro*-heptulopyranose (**5**). Hydrolysis of **5** with hot 80% acetic acid gave the desired 2,7-anhydro-3-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (**7**).

In the preparation of 2,7:3,4-dianhydro-β-D-*manno*-heptulopyranose,[1] which was isolated as the crystalline diacetate in 43% yield, the 4-*O*-tosyl derivative of sedoheptulosan was allowed to react with excess sodium methoxide at room temperature for several days. The reaction of 3-*O*-tosylsedoheptulosan (**7**) under similar conditions was found to proceed with much degradation and to give a small amount of material which on a thin-layer plate sprayed with sodium iodide and methyl red in butyl alcohol solution developed as a yellow spot, characteristic of epoxides.[9] After variations of temperature and amount of reagent showed no improvement in the yield of the epoxide, the 3-monotosylate was refluxed with a slight excess of sodium methoxide in methanol for 1 hr; tlc then showed no evidence of any starting material. Acetylation of the isolated dianhydride yielded 6% of crystalline 1,5-di-*O*-acetyl-2,7:3,4-dianhydro-β-D-*allo*-heptulopyranose (**10**).

The only structural difference between the reactive 3- and 4-*O*-tosyl derivatives of sedoheptulosan and the resistant 2- and 3-*O*-tosyl derivatives of 1,6-anhydro-β-D-altropyranose is that the former compounds have a hydroxymethyl group at the anomeric carbon in place of a hydrogen atom. In view of this, it was decided to prepare 2,7-anhydro-1,3-di-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (**11**) and test its reactivity with alkoxide ion. Hydrolysis of the known[4] 2,7-anhydro-4,5-*O*-isopropylidene-1,3-di-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (**6**), prepared from **1**, afforded, however, a syrupy product and consequently was acetylated to give crystalline 4,5-di-*O*-acetyl-2,7-anhydro-1,3-di-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (**12**). Compound **12** heated overnight with about an equivalent amount of methoxide was not affected to any great extent. When a large excess of reagent was used it reacted quite readily with a high degree of degradation similar to that noted with 3-*O*-tosylsedoheptulosan (**7**). Investigation of the resulting syrup by tlc showed that the main product was again the dianhydride (**9**) and not the expected 1-*O*-tosyldianhydride.

The implications of these findings are not clear. The fact that the reaction is retarded until the tosyl group at C-1 is eliminated favors the possibility that the hydroxyl group at C-1 plays a direct role in the reaction. On the other hand, the isolation of dianhydride (**9**) does not support this theory since one would expect a different product. A simpler explanation for the slow reaction rate of **12** with methoxide might therefore be steric hindrance due to the presence of the tosyl group at C-1.

The structure of 1,5-di-*O*-acetyl-2,7:3,4-dianhydro-β-D-*allo*-heptulopyranose (**10**) was established by chemical means and substantiated by its nmr spectrum. According to the Fürst–Plattner rule,[10] scission of an epoxide ring in a rigid, six-membered ring should yield predominantly a *trans*-diaxial derivative; thus the anticipated product from **10** should be 2,7-anhydro-β-D-*gluco*-heptulopyranose ("D-*gluco*-heptulosan," **13**). An examination of the reaction of the dianhydride **10** with hot alkali by paper chromatography showed only one product, namely, "D-*gluco*-heptulosan" which was eventually isolated and identified through its crystalline tetratosylate (**14**). There was also evidence of **13** on acid treatment of the dianhydride **10**, although in this case, a second, more intense spot was observed and had a mobility similar to that of D-*gluco*-heptulose.

The structural assignment of **10**, based on the aforementioned results, was also in accordance with its nmr spectrum (Figure 1). The two hydrogen atoms at C-1 appeared as one sharp peak at δ 4.41 ppm. Furthest

(9) J. G. Buchanan and J. C. P. Schwarz, *J. Chem. Soc.*, 4770 (1962).

(10) A. Fürst and P. A. Plattner, *Intern. Congr. Pure Appl. Chem.*, 405 (1951).

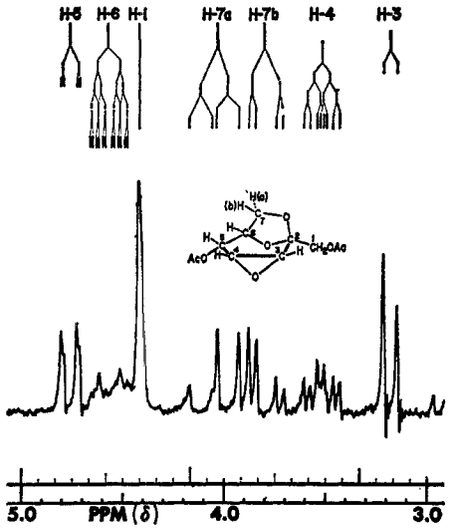


Figure 1.—The nmr spectrum of 1,5-di-*O*-acetyl-2,7:3,4-dianhydro-β-D-*allo*-heptulopyranose (10) at 60 MHz in deuteriochloroform.

downfield (δ 4.77 ppm) was H-5, a doublet ($J_{4,5}$ = 4.4 Hz) whose peaks were slightly split by a weak coupling between H-5 and H-6 ($J_{5,6}$ = 0.7 Hz). The geminal hydrogens at C-7 gave a well-resolved octet due to the A and B protons of an ABX system in the area of δ 3.70–4.18 ppm. The most complex pattern at δ 4.46–4.67 ppm was assigned to H-6. Signals for the protons of the epoxide ring were observed furthest upfield: H-3, δ 3.20; H-4, δ 3.52 ppm ($J_{3,4}$ = 3.8 Hz). These findings are in good agreement with other carbohydrate epoxides, episulfides, and epimines, studied by Buss, *et al.*,[11] in which case the δ values ranged from 2.3 to 3.6 ppm. In reference to a more specific example, H-3 and H-4 of 1,5-di-*O*-acetyl-2,7:3,4-dianhydro-β-D-*manno*-heptulopyranose[1] appeared as an AB quartet (δ 3.02 and 3.22 ppm, respectively ($J_{3,4}$ = 3.9 Hz)) where the two peaks assigned to H-4 were slightly broadened by coupling to H-5.

Although the sharp doublet (δ 3.20 ppm) was suitably assignable to H-3 in formula **10**, the unique features of the system for H-4 (δ 3.52 ppm) required a closer, more subtle evaluation of the structure and the necessity for several decoupling experiments. Since the hydrogen atoms at C-3 and C-5 have similar dihedral angles in relationship to the hydrogen atom at C-4 (about 0 and 10°, respectively), it is possible that the expected quartet for H-4 merges into a triplet. Its subsequent division ($J_{4,6}$ = 1.8 Hz) into a six-line pattern can then be accounted for by long-range coupling to H-6.

Various spin-decoupling experiments supported this theory. Irradiation of the regions assigned to H-3 and H-5 in either case collapsed the sextet of H-4 to a quartet which, without long range coupling, should otherwise have been a doublet. Several meaningful changes in the spectrum were also noted on irradiation of H-6. In this instance, the significant shoulders of the H-5 doublet disappeared, the octet of the geminal hydrogens at C-7 showed signs of converging into an AB quartet, and most importantly the sextet of H-4 had collapsed into a triplet.

(11) D. H. Buss, L. Hough, L. D. Hall, and J. F. Manville, *Tetrahedron*, **21**, 69 (1965).

Experimental Section

Confirmation of the Structure of 2,7-Anhydro-4,5-*O*-isopropylidene-β-D-*altro*-heptulopyranose (1).—Compound **1** (0.5 g) was oxidized overnight at room temperature with 6 ml of methyl sulfoxide and 4 ml of acetic anhydride. The reaction solution was then diluted with ice and concentrated *in vacuo* to a mobile syrup which was repeatedly taken up in toluene and concentrated *in vacuo* until a constant weight was obtained. The oxidation product was dissolved in 25 ml of aqueous ethyl alcohol and added dropwise to a stirred solution of 0.5 g of sodium borohydride in 20 ml of water. The solution was stirred an additional hr and then the excess of reagent was destroyed by the addition of 10 ml of acetone. The solution was then mixed with some Amberlite IR-120 ion-exchange resin, filtered, and concentrated *in vacuo* to a syrup. The syrup was taken up in methanol and concentrated on a steam bath by the passage of a stream of air across its surface. This procedure was repeated several times until boric acid could no longer be detected. An aqueous solution (20 ml) of the dionized product containing 2 g of Amberlite IR-120 ion-exchange resin was refluxed for 2 hr, the resin was removed by filtration, and the filtrate was concentrated *in vacuo* to a syrup (0.25 g). A paper chromatogram of the reaction mixture run in ethyl acetate–acetic acid–formic acid–water (18:3:1:4) and developed with orcinol–hydrochloric acid showed two blue spots. The lower one corresponded to sedoheptulosan (**2**) and the higher one corresponded to 2,7-anhydro-β-D-*manno*-heptulopyranose which has a mobility similar to that of 2,7-anhydro-β-D-*allo*-heptulopyranose (**3**) in the solvent system employed.[12] The two anhydrides were separated on several sheets of Whatman 3MM paper in the same system described above. Sedoheptulosan (**2**) was isolated in crystalline form but the other anhydride (**3**) was a syrup which was acetylated to give crystalline 1,3,4,5-tetra-*O*-acetyl-2,7-anhydro-β-D-*allo*-heptulopyranose (**4**). After one recrystallization from ethyl alcohol–pentane the prisms melted at 112–113° and showed $[\alpha]^{20}D$ −44.9° (*c* 0.25, chloroform). The ir spectra of **4** and of known 1,3,4,5-tetra-*O*-acetyl-2,7-anhydro-β-L-*allo*-heptulopyranose[8] (mp 116°, $[\alpha]^{20}D$ +46°) were compared and found to be identical.

Anal. Calcd for $C_{15}H_{20}O_{10}$: C, 50.00; H, 5.60. Found: C, 49.77; H, 5.44.

2,7-Anhydro-4,5-*O*-isopropylidene-3-*O*-(*p*-tolylsulfonyl)-1-*O*-(triphenylmethyl)-β-D-*altro*-heptulopyranose (5).—The optimum conditions for the tritylation of compound **1** were determined in a series of preliminary experiments. In each instance the progress of the reaction was followed by tlc as the temperature, concentration, and ratio of reagent were systematically varied. A small amount of the 1-*O*-trityl derivative of **1** was separated from the reaction mixture on a preparative tlc plate (Brinkman's silica gel F_{254}) run in benzene–ether (3:2). The desired product could not be crystallized and was finally tosylated to give crystalline 2,7-anhydro-4,5-*O*-isopropylidene-3-*O*-(*p*-tolylsulfonyl)-1-*O*-(triphenylmethyl)-β-D-*altro*-heptulopyranose (**5**).

After these preliminary experiments compound **5** was prepared on a large scale by the following method. Compound **1** (30 g) was partially dissolved in 150 ml of hot pyridine (60–70°). On the addition of 54 g of chlorotriphenylmethane and continued heating the remainder of **1** went into solution within 30 min. In the later stages of an additional hour of heating the pyridine hydrochloride began to crystallize out of the hot solution. When the reaction reached completion after 4 days at room temperature 60 g of tosyl chloride was added. Following another 4 days the reaction solution was filtered free of the pyridine hydrochloride and poured onto crushed ice. The resulting mixture of product and triphenylmethanol, filtered and washed with water and then ethyl alcohol, weighed 93 g. Recrystallization from six parts ethyl acetate afforded 55 g (68%) of product which was only slightly contaminated with triphenylmethanol. After a second recrystallization the prisms melted with decomposition at 177–179°, $[\alpha]^{20}D$ −7.3° (*c* 1, chloroform).

Anal. Calcd for $C_{38}H_{36}O_8S$: C, 68.77; H, 5.77; S, 5.10. Found: C, 68.97; H, 5.73; S, 5.10.

2,7-Anhydro-3-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (7).—A 30-g sample of **5** was dissolved in 240 ml of glacial

(12) According to Dr. R. Begbie of the Rowett Research Institute, Aberdeen, Scotland (personal communication, 1966), D-*allo*-heptulopyranose on acid treatment was partly converted into one product, presumably **3**. The mobility of this product on a paper chromatogram run in ethyl acetate–formic acid–water (18:3:1:4) was similar to that of 2,7-andro-β-D-*manno*-heptulopyranose.

acetic acid at 75–85°. The hot solution was then diluted slowly with 60 ml of water and held at the same temperature for 1 hr. After cooling overnight, the precipitated triphenylmethanol was removed by filtration and washed with 100 ml of 80% acetic acid. The combined filtrate and washing were concentrated *in vacuo* to a crystalline mass which was mixed with some chloroform, filtered, and washed with chloroform. The monotosylate (16 g, 97%) was successively recrystallized from acetone, ethyl alcohol, and ethyl acetate as prismatic needles: mp 163–164.5° dec; $[\alpha]^{20}D$ −115° (*c* 1.1, pyridine).

Anal. Calcd for $C_{14}H_{18}O_8S$: C, 48.55; H, 5.24; S, 9.26. Found: C, 48.41; H, 5.20; S, 9.32.

1,4,5-Tri-*O*-acetyl-2,7-anhydro-3-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (8).—Acetylation of 0.4 g of **7** yielded a syrup which crystallized during several months in the refrigerator (0.4 g, 73%). After two recrystallizations from ethyl alcohol–water the large prisms melted at 88–92° and showed $[\alpha]^{20}D$ −106° (*c* 0.9, chloroform).

Anal. Calcd for $C_{20}H_{24}O_{11}S$: C, 50.84; H, 5.12; S, 6.79. Found: C, 50.54; H, 5.41; S, 6.91.

1,5-Di-*O*-acetyl-2,7:3,4-dianhydro-β-D-*allo*-heptulopyranose (10).—The course of the reaction of 1 g of **7** in 20 ml of methanol and 12 ml of 2 *N* methanolic sodium methoxide was monitored by tlc using ethyl acetate–acetic acid–formic acid–water (18:3:1:4); after 17 days at room temperature there was no evidence of any remaining starting material. The dark reaction solution which had deposited a large amount of sediment was filtered, neutralized with some Amberlite IR-120 and Duolite A-4 ion-exchange resins, and refiltered, and the resins were washed thoroughly with methanol. The filtrate and washings were combined and concentrated *in vacuo* to a colored syrup (0.1 g). Examination (tlc) of the syrup showed only two well-defined spots, the faster, more predominant spot being the epoxide **9**. They were also observed as blue spots on Whatman No. 1 paper sprayed with orcinol–hydrochloric acid. The two products which were extracted from the syrup with chloroform were resolved on Whatman 3MM paper developed with butyl alcohol–ethyl alcohol–water (3:1:1). Acetylation of the amorphous epoxide (20 mg) yielded 17 mg of the crystalline diacetyl epoxide **10**.

In a final experiment a solution of 10 g of **7** in 60 ml of methanol and 25 ml of 2 *N* methanolic sodium methoxide was refluxed for 90 min resulting in a black solution containing sediment and practically no monotosylate. Following the same procedure described above, the final dark, viscous residue was shaken with 200 ml of chloroform for 2–3 hr and allowed to settle overnight, and the chloroform was decanted. This process was repeated several times until most of the epoxide had been extracted. The concentrated extracts weighed 0.9 g and were reextracted with chloroform which on concentration yielded 0.6 g of syrup highly enriched with epoxide. Acetylation of this final syrup produced 455 mg of **10** representing a 6% yield. Recrystallization from ethyl alcohol–pentane and finally from ethyl alcohol afforded stout prisms: mp 75–77°; $[\alpha]^{20}D$ +35.4° (*c* 1.1, chloroform).

Anal. Calcd for $C_{11}H_{14}O_7$: C, 51.16; H, 5.43. Found: C, 51.05; H, 5.42.

2,7-Anhydro-4,5-*O*-isopropylidene-1,3-di-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (6).—The ditosylate **6**, originally obtained as a by-product,[4] was prepared in high yield by the following procedure. An 8-g sample of **1** was almost completely dissolved in 75 ml of hot pyridine and following the introduction of 20 g of tosyl chloride the heating was continued for a short period of time until a clear reaction solution was obtained. It was then allowed to reach room temperature and after 3 days the pyridine solution was decanted from the pyridine hydrochloride which was washed with a small quantity of pyridine. The decantate and washing on being mixed with ice deposited 18 g (97%) of product. The ditosylate, recrystallized from 50 ml of ethyl alcohol, melted at 128–131°; the reported melting point is 131–132°.[4]

4,5-Di-*O*-acetyl-2,7-anhydro-1,3-di-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (12).—Hydrolysis of 8 g of **6** with 80 ml of 80% glacial acetic acid at 80–90° for 3 hr yielded 1,3-di-*O*-tosylsedoheptulosan (**11**) which could not be crystallized and consequently was acetylated. The crystalline diacetyl derivative (**12**) weighed 8.5 g (98%) and was recrystallized from ten parts ethyl alcohol and finally from chloroform–pentane. The physical constants of the prismatic needles were mp 137.5–138° and $[\alpha]^{20}D$ −71.3° (*c* 1, chloroform).

Anal. Calcd for $C_{25}H_{28}O_{12}S_2$: C, 51.36; H, 4.83; S, 10.97; CH_3CO, 14.38. Found: C, 51.10; H, 4.69; S, 11.08; CH_3CO, 14.25.

Reaction of 4,5-Di-*O*-acetyl-2,7-anhydro-1,3-di-*O*-(*p*-tolylsulfonyl)-β-D-*altro*-heptulopyranose (12) with Sodium Methoxide.—A solution of 1.1 g of **12** in 6 ml of methanol and 1.5 ml of 2 *N* methanolic sodium methoxide was refluxed overnight. A comparative examination (tlc) of the dark reaction solution with an aliquot which had been removed after the first 3 hr of refluxing showed no appreciable change. The only significant product was deacetylated starting material. An additional 6 ml of reagent was added to the reaction solution which was again heated overnight. During this time the deacetylated starting material had reacted yielding in small quantities two products which were isolated by tlc on a preparative plate (Brinkman's silica gel F_{254}) using butyl alcohol–ethyl alcohol–water (3:1:1). The faster moving fraction (15 mg) cochromatographed in two different systems with the dianhydride **9** produced from **7** and also developed as a yellow spot when sprayed with sodium iodide and methyl red in butyl alcohol.[9] This fraction was then acetylated and the resulting product found to have a mobility (tlc) similar to that of the diacetate **10**.

The other isolated fraction (10 mg) had the same mobility (tlc) in two different solvent systems as the secondary product observed in the reaction of 3-*O*-tosylsedoheptulosan (**7**) with sodium methoxide. Although this minor product was not definitely identified, it should be mentioned that it had a mobility similar to that of sedoheptulosan when cochromatographed on Whatman No. 1 paper in ethyl acetate–acetic acid–formic acid–water (18:3:1:4).

Alkaline and Acid Hydrolysis of 1,5-Di-*O*-acetyl-2,7:3,4-dianhydro-β-D-*allo*-heptulopyranose (10).—Investigation by tlc (ethyl acetate–acetic acid–formic acid–water, 18:3:1:4) of the reaction of **10** (62 mg) refluxed overnight (17 hr) in 6 ml of 3% potassium hydroxide solution showed only one significant spot with mobility similar to that of 2,7-anhydro-β-D-*gluco*-heptulopyranose ("D-*gluco*-heptulosan," **13**). After neutralization of the dark reaction solution with Amberlite IR-120 ion-exchange resin, it was filtered free of resin and concentrated *in vacuo* to a residue which was extracted with water. When the concentrated extract (5 mg) did not readily crystallize, it was tosylated to the crystalline tetratosylate of "D-*gluco*-heptulosan." After one recrystallization the tosyl derivative (**14**) melted at 130–136° and a mixture melting point with an authentic sample[13] (mp 138–139°) was not depressed.

A 10-mg sample of **10** in 1 ml of 0.1 *N* sulfuric acid was heated on a steam bath for 3 hr. A paper chromatogram of the neutralized solution run in ethyl acetate–acetic acid–formic acid–water (18:3:1:4) and sprayed with orcinol–hydrochloric acid developed three blue spots in addition to deacetylated **10**. Two of the spots had mobilities similar to those of "D-*gluco*-heptulosan" and D-*gluco*-heptulose; the third one was not identified.

Registry No.—**4,** 16526-57-1; **5,** 16526-58-2; **7,** 16526-59-3; **8,** 16526-60-6; **10,** 16526-61-7; **12,** 16526-62-8.

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(13) L. C. Stewart, E. Zissis, and N. K. Richtmyer, *Ber.*, **89**, 535 (1956).