alcohol. Stirring was continued at 25° for 5 days. On evaporation, a colorless syrup was obtained, and to it was added 6.0 ml of anhydrous pyridine and 6.0 ml of acetic anhydride. The mixture was kept at 25° for 1 day, then evaporated. The residual brown syrup was taken up in 15 ml of chloroform, and the chloroform solution processed in the usual manner, giving a pale yellow syrup. This syrup was crystallized from 2-propanol, giving 1.62 g of colorless crystals, mp 126–131°. This product was recrystallized, giving 1.19 g (38%) of the pure pentaacetate, mp 132–133°.

Anal. Calcd for $C_{17}H_{24}O_{10}$: C, 52.60; H, 6.23. Found: C, 52.45; H, 6.35.

The infrared spectrum (KBr) contained peaks at 3000, 1750, 1350, 1220, 1050, 900, and 820 cm^{-1}.

The nmr spectrum was recorded (see above).

B. From the Pentol Triacetate.—Acetylation of a 12-mg portion of the pentol triacetate with acetic anhydride and pyridine in the usual manner gave a 9-mg (58%) yield of the pentaacetate, mp 131–132°. A mixture melting point with a sample prepared by procedure A was not depressed, and the infrared spectra were identical.

DL(125/34) Diastereomer of 2,3,4,5-Tetrahydroxy-1-cyclohexanemethanol (Pseudo-β-DL-gulopyranose) (11).—To 175 mg of the pentaacetate was added 4.0 ml of a *M* solution of hydrogen chloride in ethanol–water (1:1). The resulting solution was boiled for 6 hr under reflux. The solution was then treated with decolorizing charcoal, and evaporated. The syrupy residue was repeatedly evaporated after additions of small volumes of absolute ethanol. The product (70 mg, 88%) was obtained as a colorless syrup; a correct microanalysis was obtained on the crystalline pentaacetate derivative (see above).

The same product was obtained by hydrolysis with hot sodium hydroxide (1 *M*) in ethanol–water (1:1), in somewhat lower yield.

The nmr spectrum was recorded (see above).

Registry No.—*cis,cis*-1,4-diacetoxy-1,3-butadiene, 10489-24-4; *trans,trans*-1,4-diacetoxy-1,3-butadiene, 15910-11-9; **5**, 16656-57-8; **6**, 16656-59-0; **8**, 16703-82-5; **11**, 16656-62-5.

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Alicyclic Carbohydrates. XXXIII. Epimerization of Pseudo-α-DL-talopyranose to Pseudo-α-DL-galactopyranose. Proton Magnetic Resonance Studies[1]

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The expression pseudo-sugar is used to denote an alicyclic analog of a cyclic monosaccharide. For example, a hydroxymethylcyclohexanetetrol (formula **1**) may be described as a "pseudo-hexose," or more explicitly, as a "pseudo-hexopyranose." When pseudo-α-DL-talopyranose (**2**) was heated with 95% acetic acid containing sulfuric acid, it underwent the expected epimerization at position 4 (position 2 by usual hexopyranose numbering). The crude product was treated with acetic anhydride. The yield of pure crystalline pentol pentaacetate (**8**, mp 147–148°) was less than 15%. This pentaacetate was readily converted in high yield by acidic hydrolysis into the desired free pentol, pseudo-α-DL-galactopyranose (**7**), mp 173–174°. The DL(123/45) or α-DL-galactopyranose configuration, **7**, which should exist in the (EAEEA) or side chain–equatorial favored conformation, **13**, was assigned for mechanistic reasons. Proton magnetic resonance studies on the pentol and its pentaacetate were consistent with this configuration and conformation. An improved preparation of pseudo-α-DL-talopyranose is described.

Recently we reported[3,4] the synthesis of pseudo-α-DL-talopyranose (**1** or **2**) (Scheme I). This was the first member of a new series of compounds which we propose to designate pseudo-sugars, *i.e.*, cyclic forms of monosaccharides in which the usual ring-oxygen atom is replaced by methylene.[3,4] It is hoped that pseudo-sugars will be found acceptable to some although not all enzymes or biological systems, and thus may have useful biological properties.

More recently, we reported the synthesis of a second pseudohexose, which had the β-DL-gulopyranose configuration.[1b]

We now wish to report synthesis and pmr characterization of a third diastereomer in the pseudo-hexopyranose (formula **1**) series, namely pseudo-α-DL-galactopyranose (**7**). In order to prepare this isomer, we utilized the valuable epimerization method recently developed by Angyal, Gorin, and Pitman.[5–7] Our starting material was the already available talopyranose isomer (**2**). This was heated for a prolonged period with the Angyal reagent,[5] 95% acetic acid (containing a little sulfuric acid). According to Angyal,[5] epimerization takes place most readily at a hydroxy or acetoxy group which has one *cis* and one *trans* neighboring functional group. Thus we predicted epimerization would take place at position 4 of formula **3** to give the acetylated α-DL-galactopyranose diastereomer **8**, and, in fact, the only new product isolated did have this configuration, as shown by pmr studies. The epimerization is believed to take place through the anchimeric effect of the neighboring *trans*-acetoxy group at position 5 of formula **3**, *via* the bicyclic acetoxonium intermediate **4**, which has not been isolated.

The yield of the α-DL-*galacto* pentaacetate product

(1) For the two preceding papers, see (a) G. E. McCasland, M. O. Naumann and L. J. Durham, *Carbohyd. Res.*, **4**, 516 (1967); (b) G. E. McCasland, S. Furuta, and L. J. Durham, *J. Org. Chem.*, **33**, 2835 (1968).

(2) To whom any correspondence should be addressed at the University of San Francisco.

(3) G. E. McCasland, S. Furuta, and L. J. Durham, *ibid.*, **31**, 1516 (1966).

(4) See also G. E. McCasland, *Advan. Carbohyd. Chem.*, **20**, 41 (1965).

(5) S. J. Angyal, P. A. J. Gorin, and M. E. Pitman, (a) *J. Chem. Soc.*, 1807 (1965); (b) *Proc. Chem. Soc.*, 337 (1962).

(6) P. A. J. Gorin, K. Horitsu, and J. F. T. Spencer, *Can. J. Chem.*, **43**, 2259 (1965).

(7) P. A. J. Gorin, *ibid.*, **41**, 2417 (1963).

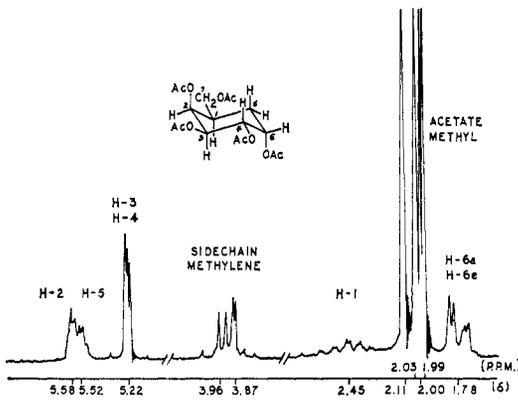
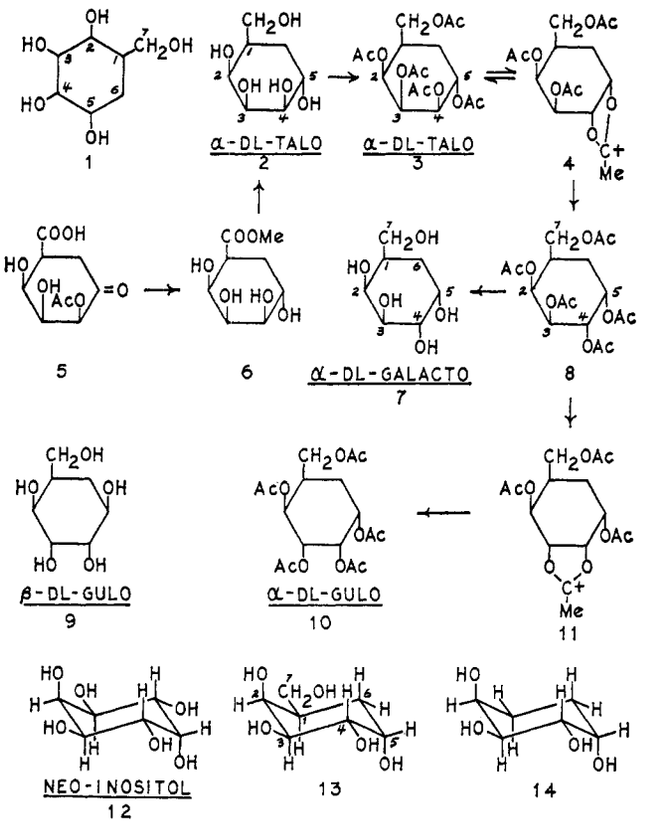


Figure 1.—Proton magnetic resonance spectrum of pseudo-α-DL-galactopyranose pentaacetate in chloroform-*d* at 100 MHz.

SCHEME I



was poor, only about 14%; nevertheless, the synthesis by epimerization is much more convenient (if one has the starting material) than a total synthesis of the pseudo-hexopyranose structure would be, and probably the over-all yield of any total synthesis would be less than 14%. Since the starting material was recovered from the mother liquors (as pentaacetate) in about 20% yield, the yield of *galacto* product could perhaps be increased by use of a longer reaction time (or higher temperature); however, some decomposition was noted after the reaction time of 90 hr actually used.

We anticipated that the α-DL-*galacto* product might itself undergo further epimerization. Such epimerization might be expected at position 4 (formula **8**), causing reversion to the starting material configuration. The recovery of starting material pentaacetate in 20% yield (see above) may well be due,[8] in part, to the reverse epimerization mentioned. Epimerization also might be expected at position 3 (formula **8**), since the group at position 3 also has one *cis* and one *trans* neighboring group. The product from this epimerization would be pseudo-α-DL-gulopyranose pentaacetate (**10**), formed *via* the acetoxonium intermediate (**11**). As yet we have no evidence for the formation of the α-DL-*gulo* product (**10**); however, no systematic effort to isolate this (unknown) isomer from the mother liquors has yet been made. The anomer, pseudo-β-DL-gulopyranose (**9**) recently has been prepared by us but will not epimerize to the α form in solution in the typical manner of *true* hexopyranose sugars.[9]

After the 90-hr heating period used in our epimerization reaction, we added acetic anhydride to ensure complete acetylation of the products (which might have one or more free hydroxyl groups), and isolated pseudo-α-DL-galactopyranose in the form of its pentaacetate **8**. This pentaacetate was readily converted by acidic aqueous hydrolysis into the desired free pentol (**7**) in high yield. The pentol and pentaacetate were both colorless, crystalline, sharp-melting substances with appropriate microanalyses and infrared and pmr spectra.

We previously[4] prepared pseudo-α-DL-talopyranose (**2**) by *lithium aluminum hydride* reduction of the tetrol methyl ester **6**, obtained by sodium borohydride reduction, and methylation, of the keto acid monoacetate[10] (**5**); the over-all yield was 23%. We now find it more convenient to carry out a second *borohydride* reduction on the crude tetrol methyl ester; the over-all yield is increased to 53%.

Pmr Evidence for the Configurations.—The spectrum (Figure 1) of the pentol pentaacetate (**8**) was recorded at 60 and 100 MHz using a chloroform-*d* solution. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane (TMS) used as an internal reference. The number of protons in each signal was confirmed by integration of the spectrum.

The one sidechain acetate methyl and two equatorial acetate methyl groups produced sharp singlets at 1.99, 2.00, and 2.03 ppm (three protons each). The two axial groups produced a sharp singlet at 2.11 ppm (six protons).

The side-chain methylene protons H-7 and H-7′ produced an eight-line pattern, each proton a perturbed pair of doublets, located at 3.87 and 3.96 ppm, with spacings indicative of a geminal coupling of about 11 Hz, and vicinal couplings of about 6 and 9 Hz. The ring-methylene protons H-6_a and H-6_e produced overlapping multiplets centered at about 1.78 ppm. The methine proton H-1 gave a complex, poorly resolved multiplet at about 2.45 ppm.

The remaining four (AcO–C**H**) ring protons produced two groups of signals. The first group, due to the two axial protons H-3 and H-4, consisted of a relatively sharp multiplet centered at 5.22 ppm. The second group, due to the two equatorial protons H-2 and H-5, was not completely separated but could be identified as a narrow tripletlike signal for H-2 at 5.58 ppm and a quartetlike signal for H-5 at 5.52 ppm. The

(8) It would be of interest to try the same epimerization procedure on pure pseudo-α-DL-galactopyranose to find out what products are actually formed from it. As yet we do not have a large enough quantity of the pseudo-galactose for such studies.

(9) We have recently completed the synthesis of pseudo-β-DL-gulopyranose and established its configuration by use of proton magnetic resonance and spin decoupling.[1b]

(10) M. M. Doshi, *Dissertation Abstr.*, **24**, 3998 (1964).

spacings of both these patterns were indicative of small coupling interactions, consistent with the equatorial orientations.[11,12]

The similarity of chemical shifts for H-2 and H-5, and especially for H-3 and H-4, results from the relatively high symmetry of the molecule in its favored chair conformation (**13**). Although the molecule (**13**) does not actually contain any symmetry element, its symmetry[13] approaches that of the tetrol (**14**), which has a twofold simple axis (symmetry point-group C_2), and the hexol (**12**), which has a center of symmetry (point-group C_{1h}).

The pmr results are consistent with the DL (123/45) or α-DL-*galacto* configuration (**7**), and the (EAEEA) or side-chain-equatorial favored conformation (**13**).

The spectrum (Figure 2) of the free pentol (**7** or **13**) was recorded at 60 and 100 MHz in deuterium oxide. Chemical shifts (δ) are recorded in parts per million downfield from the sodium 2,2-dimethyl-2-silapentane sulfonate (SDSS) internal reference. A large HDO peak (not shown in Figure 2) was observed at 4.70 ppm.

The side-chain methylene protons H-7 and H-7′ again showed up as an eight-line pattern, with components located this time at 3.50 and 3.64 ppm, and spacings indicative of a geminal coupling of 11 Hz and vicinal couplings of 6 and 7 Hz. The ring methylene protons H-6a and H-6e produced overlapping signals at about 1.6 ppm. The complex, poorly resolved multiplet of the methine proton H-1 this time was located at 2.0 ppm.

The remaining four (HO–CH) ring protons produced signals at 3.72 (axial, H-3 and H-4), and at 4.10 ppm (equatorial, H-2 and H-5). The outer lines of the presumed axial–axial coupling pattern of H-3 and H-4 were not visible because of the nearly equal chemical shifts of these two protons.

As with the pentaacetate, the relatively high symmetry of the pentol molecule (**13**) is reflected in its spectrum. The spectrum is consistent with the DL(123/45) or α-DL-*galacto* configuration (**7**), and the (EAEEA) or side-chain equatorial conformation (**13**).

Experimental Section

All melting points are corrected, and were measured on a Nalge-Axelrod micro hot-stage. Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill. Darco G-60 decolorizing charcoal[14] was used. All evaporations were performed under reduced pressure. Light petroleum of bp 60–100° was used. Infrared spectra were recorded on each intermediate and product with a Perkin-Elmer Model 421 or Model 137 (Infracord) spectrometer. Nuclear magnetic resonance spectra were recorded with Varian A-60 and HR-100 spectrometers.

DL(1234/5) Diastereomer of 2,3,4,5-Tetrahydroxy-1-cyclohexanemethanol (Pseudo-α-DL-Talopyranose) (2) (Improved Procedure Using Sodium Borohydride).—To a well-stirred solution of 2.32 g of the keto acid monoacetate[4,10] (**5**), mp 146–147°, in 20 ml of water was added dropwise a solution of 0.70 g of sodium borohydride in 20 ml of water. The resulting solution was stirred for 12 to 24 hr at 25°, then acidified with 12 *M* hydrochloric acid, and the solution was evaporated. To the residue portions of anhydrous methanol were repeatedly added and evaporated to dryness.

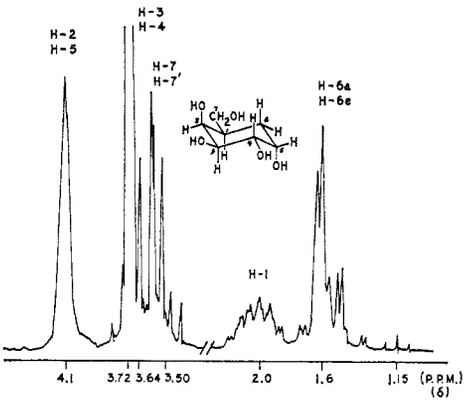


Figure 2.—Proton magnetic resonance spectrum of pseudo-α-DL-galactopyranose in deuterium oxide at 100 MHz.

To the residue was added 40 ml of a 2% solution of hydrogen chloride in anhydrous methanol, and the resulting mixture was boiled under reflux for 2 hr. After cooling, the mixture was filtered, and the filtrate was evaporated.

The residual crude methyl ester (a syrup) was dissolved in 15 ml of water, and the solution was added dropwise with stirring to a solution of 1.9 g of sodium borohydride in 20 ml of water. Stirring was continued for 12 to 24 hr at 25°. The mixture was then acidified with 12 *M* hydrochloric acid, and the solution was evaporated. To the residue portions of anhydrous methanol were repeatedly added and evaporated. Finally a 25-ml portion of methanol was added, the mixture was filtered, and the filtrate was evaporated.

The syrupy residue was dissolved in 15 ml of water, and the solution was decolorized with charcoal and passed through a 15-ml column of moist Amberlite MB-1 resin.[15] The column was eluted with 75 ml of water, and the eluate evaporated, giving 1.5 g of a colorless syrup. This syrup was crystallized from 2-propanol, giving 1.1 g of product, mp 159–161°. Recrystallization gave 0.93 g (52%) of pure pseudo-α-DL-talopyranose, mp 161–162° (lit.[4] mp 160–162°). We previously[4] obtained this pseudo-talose free pentol by the less convenient lithium aluminum hydride reduction of the tetrol methyl ester.

DL(123/45) Diastereomer of 2,3,4,5-Tetraacetoxy-1-cyclohexanemethanol Acetate (Pseudo-α-DL-galactopyranose pentaacetate) (8).—A solution of 0.534 g of pseudo-α-DL-talopyranose (free pentol, mp 161–162°) in 50 ml of 95% acetic acid (containing 1.5% by volume of 18 *M* sulfuric acid) was boiled under reflux for 90 hr (general procedure of Angyal[5]). The resulting brownish mixture, containing some charred particles, was treated with charcoal, and concentrated to about one-third volume.

Acetic anhydride (15 ml) was added, and the solution was kept at 25° for 2 days. Anhydrous sodium acetate (1.3 g) was added to neutralize the sulfuric acid, and the mixture was concentrated to one-third volume, and poured slowly into 50 ml of ice-cold water. The mixture was stirred for 30 min, then extracted repeatedly with chloroform. The chloroform extract was processed in the usual manner to give 0.87 g of a light orange syrup.

The syrup was dissolved in 3.0 ml of benzene, and the solution was transferred to a 150 × 10 mm column of basic Woelm aluminum oxide (Activity Grade I).[16] The column was eluted with 80 ml of benzene. The eluate on evaporation gave 0.63 g of a colorless syrup. This syrup was crystallized from a mixture of 2-propanol and light petroleum, giving 165 mg (14%) of colorless product, mp 145–148°. A sample was recrystallized for analysis from 2-propanol, mp 147–148°.

Anal. Calcd for $C_{17}H_{24}O_{10}$: C, 52.57; H, 6.23. Found: C, 52.69; H, 6.12.

The infrared spectrum (Nujol) contained absorption maxima at 1545, 1235, and 1050 cm^{-1}.

The proton magnetic resonance spectrum was recorded as noted in the beginning of the article.

When the original mother liquor was concentrated and then diluted with petroleum ether, a 225 mg (20%) yield of the starting material pentaacetate was obtained in the form of colorless

(11) (a) R. U. Lemieux and J. D. Stevens, *Can. J. Chem.*, **43**, 2059 (1966); (b) *ibid.*, **44**, 249 (1966).

(12) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 8.

(13) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 23–32.

(14) A product of the Darco Division, Atlas Powder Co., Wilmington, Del.

(15) A product of the Resinous Products Division, Rohm and Haas Co., Philadelphia, Pa.

(16) A product of Alupharm Chemicals, New Orleans, La.

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

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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.