Carbohydrate Research, 59 (1977) 103–110

THE PREPARATION OF 6-DEOXY-3-*O*-METHYL-6-NITRO-D-ALTROSE*

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(Received January 24th, 1977; accepted for publication, February 17th, 1977)

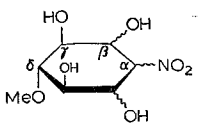
ABSTRACT

The title compound (**9**), a new nitro sugar and potential starting-point for the synthesis of hitherto unknown stereoisomers in the deoxynitroinositol series, was prepared by a sequence of high-yielding reactions. Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside was converted into methyl 3-*O*-methyl-α-D-altropyranoside (**3**) by the action of sodium methoxide followed by debenzylidenation essentially according to established procedures. Acetolysis of **3** and subsequent Zemplén transesterification gave syrupy 3-*O*-methyl-D-altrose, from which the furanoid 1,2:5,6-di-*O*-isopropylidene and 1,2-*O*-isopropylidene (**7**) derivatives were prepared by standard acetonation and partial hydrolysis. Periodate oxidation of **7**, and addition of nitromethane to the product, furnished crystalline 6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-6-nitro-β-D-altrofuranose (**8**) as the chief epimer. Deacetonation of **8** by trifluoroacetic acid gave **9** in crystalline form.

INTRODUCTION AND RESULTS

In preceding work[1,2] on conformational analysis of nitro inositols, we have studied epimeric equilibria and conformational preferences in two series of δ-*O*-methylated derivatives† represented by formulas A and B. Compounds of this type readily undergo base-catalyzed epimerization at the nitromethine carbon atom, as well as at the two vicinal carbinol groups (*i.e.*, in the α, β, and β′ positions), whereas the γ, γ′, and δ positions are configurationally stable. The studies have led to a refined assessment of nonbonded substituent interactions in these systems and, in particular, have provided new insights in the conformational requirements of nitro and nitronate groups in relation to the spatial disposition of neighboring hydroxyl substituents. The two series of stereoisomers in which the investigations were performed differed with respect to their configurationally fixed *trans,trans* (A) and *cis,cis* (B) arrangements. In order to test the data obtained, and the conformational concepts derived, it was of

*This work was supported by the National Research Council of Canada (Grant A1350 to H. H. B.).
†The methyl substituent primarily served to facilitate product identification by n.m.r. spectroscopy.



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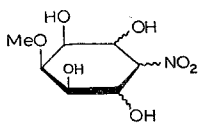

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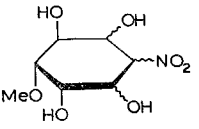
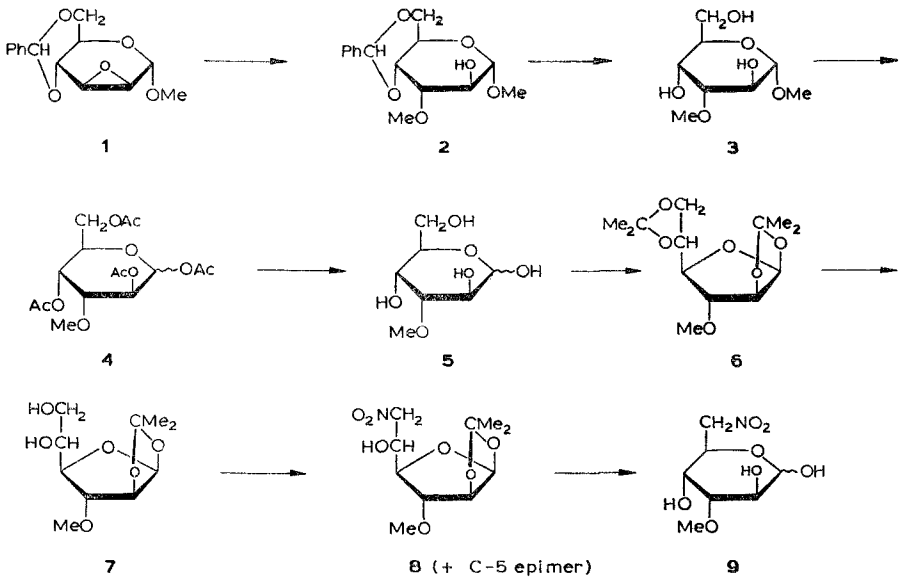


C

interest to examine in like manner a third, independent family of stereoisomers, namely, compounds having the corresponding *cis,trans* arrangement, as in C. No representatives of this group are known, but some should be accessible through Fischer cyclization[3] of any 6-deoxy-3-*O*-methyl-6-nitrohexose having the (D or L) *altro*, *galacto*, *gulo*, or *manno* configuration. In this article, we report the synthesis of the D-altrose derivative (**9**) which should lend itself to the purpose stated.

Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside[4] (**1**) was converted in high yield into methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-altropyranoside (**2**) by the action of sodium methoxide, according to Robertson and Griffith[5], but with a procedural modification allowing scaled-up operation (see Experimental). As immediate acid hydrolysis of **2** to produce the reducing sugar seemed inadvisable, because formation of the 1,6-anhydride could be expected to interfere, the deprotection of **2** was performed in three consecutive, almost quantitative steps imitating the classical synthesis of altrose[6]. These comprised removal of the benzylidene acetal group by mild, acid hydrolysis, to give methyl 3-*O*-methyl-α-D-altropyranoside[7] (**3**), acetolysis of the crude product to 3-*O*-methyl-α,β-D-altrose tetraacetate (**4**), and, finally, Zemplén transesterification to afford free 3-*O*-methyl-D-altrose (**5**). The tetraacetate **4** was obtained (and used) as a syrupy mixture containing the anomers in the ratio of ~1:1 (according to n.m.r. data). The syrup ($[\alpha]_D$ +34° in chloroform) eventually crystallized, and recrystallization gave a product ($[\alpha]_D$ +66°) that was probably the α anomer, but whose anomeric purity was not ascertained. The free sugar **5**, characterized by optical rotation data only, was acetonated in the usual way by catalysis with cupric sulfate and sulfuric acid. It furnished 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-β-D-altrofuranose (**6**) as an analytically pure liquid in 77% yield after distillation. The compound, whose structure was supported by n.m.r. data, had previously been obtained[8] by Purdie methylation of 1,2:5,6-di-*O*-isopropylidene-β-D-altrofuranose which, however, arises together with the pyranoid 1,2:3,4-diacetal in the acetonation of D-altrose, and was isolated in only moderate yield[9]. The present reaction-sequence therefore constitutes an advantageous route to **6**. Graded, acid hydrolysis of **6** readily afforded 1,2-*O*-isopropylidene-3-*O*-methyl-β-D-altrofuranose (**7**), likewise as an analytically pure, distillable liquid. Its structure was confirmed by a quantitative, periodate-oxidation assay in which it consumed 1 mole of oxidant per mole (in accord with the lead tetraacetate oxidation previously reported[8]), and by a complete, first-order analysis of the well resolved, n.m.r. spectrum of its 5,6-diacetate.

Preparative oxidation of **7** with sodium metaperiodate was followed by reaction of the resultant dialdose derivative with nitromethane in a weakly basic, methanolic medium at 0°, to give a mixture of 6-deoxy-6-nitro sugars. The conditions chosen for



the nitromethane addition favor kinetic control[10], and one of the C-5 epimeric products strongly preponderated and could be isolated crystalline in 70% yield. From the trend of its o.r.d. curve, it was determined, by application of Satoh's rule[11,12], to possess the *R* configuration at C-5, allowing its formulation as 6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-6-nitro-β-D-altrofuranose (**8**). A small amount of a crystalline material showing an opposite Cotton effect was isolated from the mother liquor; it was judged to consist mainly of the α-L-*galacto* epimer, but was not available in quantities sufficient for purification and definitive characterization.

Deacetonation of **8** with 90% trifluoroacetic acid[13] at room temperature yielded 6-deoxy-3-*O*-methyl-6-nitro-D-altrose (**9**) quantitatively in a crystalline form (m.p. 109–110°) that, prior to recrystallization, showed upward mutarotation. Recrystallization gave a form (m.p. 130–131°) that mutarotated downward. It may be noted that, for the proposed utilization of the sugar in an inositol synthesis, its anomeric composition would play no role.

EXPERIMENTAL

General methods. — Melting points were determined with an electrically heated, aluminium-block apparatus and are uncorrected. Optical rotations refer to room temperature and were obtained in a Perkin–Elmer automatic polarimeter equipped with sodium and mercury lamps. Unless otherwise specified, n.m.r. data were recorded, for $CDCl_3$ solutions, with a Varian HA 100 instrument (Me_4Si lock signal). Thin-layer chromatography was performed on silica gel G plates (7.5 cm), and the spots were made visible by heating the plates after spraying with 1% ceric sulfate in 10% sulfuric acid. Chromatographic solvents were 1:1 (v/v) chloroform–ethyl acetate

(solvent *A*) or 1:1 (v/v) carbon tetrachloride–ethyl acetate (solvent *B*), unless indicated otherwise.

Methyl 4,6-O-benzylidene-3-O-methyl-α-D-altropyranoside (**2**). — A fresh solution of sodium (2.6 g) in methanol (50 ml) was added to the anhydromannoside[4] **1** (5.58 g, crystallized from methanol, m.p. 150–151°, $[\alpha]_D$ +106° in $CHCl_3$) contained in a 100-ml, stainless-steel flask, and the sealed flask was heated for 45 h at 100 ±1°. After being cooled, the solution was saturated with carbon dioxide, and filtered, and the filtrate was evaporated to give a syrup which was distributed between chloroform (20 ml) and water (20 ml). The aqueous phase was extracted with additional chloroform (4 × 10 ml), and the combined chloroform solution was dried ($MgSO_4$), and evaporated. Trituration of the residue with carbon tetrachloride gave crude, crystalline **2** which, after being dried *in vacuo*, weighed 6.20 g (99%), melted at 124–127°, gave a single spot (R_F 0.50–0.52) in t.l.c. (solvent *A*), and showed an n.m.r. spectrum normally indistinguishable from that of purified **2**. The material was usable for the next preparative step, although a faint odor of benzaldehyde was present. Recrystallized from carbon tetrachloride (30 ml), **2** showed m.p. 127–130°, $[\alpha]_D$ +103.3° (*c* 0.4, chloroform); reported[5]: m.p. 130–131°, $[\alpha]_D$ +103° and[7] m.p. 132–133°, $[\alpha]_D$ +103 ±2° (chloroform). The n.m.r. data for **2** were in excellent agreement with those reported by Coxon[14], except for the phenyl proton signal, which we found to be centered at δ 7.12 (reported[14], 7.40).

Methyl 3-O-methyl-α-D-altropyranoside (**3**). — A solution of the acetal **2** (5.24 g) in methanol (90 ml) was acidified with 0.05M sulfuric acid (10 ml), and boiled under reflux for 45 min. According to t.l.c. with solvent *A*, the debenzylidenation of **2** (R_F 0.5) to give **3** (R_F 0.05) was virtually complete after 40 min. The pH of the cooled reaction-solution was brought to 7 (indicator paper) by stirring for 5 min with 4 ml of Dowex-1 X8 resin (HCO_3^- form, prewashed with methanol). The solution was then passed through layers of Celite and the same resin (1 cm each) contained in a small tube, with methanol (10 ml) and water (10 ml) used for final washing. The solution was evaporated, and several portions of water, ethyl acetate, and ethanol were successively added to, and evaporated from the residual syrup, which was finally dried to constant weight (3.8 g) in an oil-pump vacuum. The colorless, glassy material had $[\alpha]_D$ +117.5° (*c* 0.95, water) and $[\alpha]_{578}$ +121°, $[\alpha]_{546}$ +133°, $[\alpha]_{436}$ +220°, $[\alpha]_{365}$ +334° (*c* 0.5, water). Reported[7]: $[\alpha]_D$ +139.5 ±2° (*c* 3.5, water).

1,2,4,6-Tetra-O-acetyl-3-O-methyl-α,β-D-altropyranose (**4**). — A solution of altroside **3** (3.8 g) in ice-cooled acetic anhydride (20 ml) containing conc. sulfuric acid (0.2 ml) was kept for 24 h at 0° under protection from moisture. Processing by treatment of the reaction mixture with crushed ice (200 g) and sodium hydrogencarbonate (30 g), followed by extraction of the product into dichloromethane (4 × 30 ml), yielded **4** as a colorless syrup (6.6 g, dried at the oil pump) giving a single spot (R_F 0.72–0.75) in t.l.c. with solvent *A*; $[\alpha]_D$ +34° (with minor variations in different runs; *c* 0.7, chloroform). The n.m.r. spectrum of a solution in $CDCl_3$ showed a singlet at δ 5.95 and a narrow doublet at δ 6.10 with approximately equal intensities, attributable to H-1 of two anomers. Other n.m.r. signals occurred at

δ 4.9–5.3 (m, 2 H, H-2,4), 4.2–4.5 (m, 3 H, H-3 or -5, and H-6,6'), 3.6–3.8 (m, H-5 or -3), 3.50 (s, 3 H, OMe), 1.98, 1.99, 2.01, 2 02, 2.07, and 2.08 (s, 12 H, 4 OAc of two anomers).

The syrup crystallized upon refrigeration for 2 days. A sample (118 mg) was recrystallized from methanol, to give well-developed crystals (70 mg) of what appeared to be the α anomer, m.p. 105–108°, $[\alpha]_D$ +66.2° (*c* 0.4, chloroform). However, the substance was not checked for anomeric homogeneity, nor was isolation of the other anomer attempted.

3-O-Methyl-D-altrose (**5**). — A chilled solution of crude tetraacetate **4** (6.6 g) in methanol (66 ml) was basified with 1 ml of 3.3M methanolic sodium methoxide, and kept in a closed flask for 3 h at 0°. It was then made neutral by adding a small amount of Rexyn 101 (H^+) cation-exchange resin, the suspension was filtered, and the filtrate evaporated. The residue was stirred with 1 ml of Dowex 1 X2 (acetate form) resin and some activated charcoal in water (10 ml), and this mixture was filtered through layers of (from top to bottom) 1.5 ml of Rexyn 101 (H^+), 1.5 ml of Dowex 1 X2 (acetate form), and 0.5 ml of Celite contained in a 25-ml burette. The packing was thereafter eluted with water (50 ml), and evaporation of the colorless effluent gave 3.20 g (93%) of syrupy **5**, $[\alpha]_D$ +30.6° (*c* 6.4, water) and $[\alpha]_{578}$ +36°, $[\alpha]_{546}$ +35°, $[\alpha]_{436}$ +56°, $[\alpha]_{365}$ +83° (*c* 7.2, water).

1,2:5,6-Di-O-isopropylidene-3-O-methyl-β-D-altrofuranose (**6**). — A suspension of anhydrous cupric sulfate (3.5 g) in dry acetone (32 ml) containing the sugar **5** (3.2 g) was cooled with Dry Ice and mixed with a similarly cooled solution of conc. sulfuric acid (2.56 ml) in dry acetone (32 ml). Protected from moist air, the mixture was allowed to warm to 25° and stirred magnetically for 3.5 h. Recooled as before, the pH was then brought to 7–7.5 by careful addition of aqueous ammonia, the end point being indicated by the appearance of a blue precipitate. The suspension was filtered through sintered glass, the precipitate was washed with acetone, and the solution was concentrated *in vacuo*. To the two-phase, liquid concentrate were added chloroform (15 ml) and water (5 ml). After separation, the aqueous phase was extracted with three 5-ml portions of chloroform, and each extract was washed once with water (5 ml). The chloroform solutions were combined, dried ($MgSO_4$), and evaporated, to give a yellow syrup (4.23 g) which was distilled at 0.08 torr. A forerun (0.3 g) distilling at 30–40° (bath temp.) was discarded, and the main product (3.45 g, 77%) was collected at 110–120°. It was homogeneous in t.l.c. (R_F 0.90 with solvent *A*), and showed $[\alpha]_D$ +11.6°, $[\alpha]_{578}$ +12°, $[\alpha]_{546}$ +12.9°, $[\alpha]_{436}$ +22.6°, $[\alpha]_{365}$ +37.7° (*c* 0.6, chloroform); reported[8]: b.p.$_{0.05}$ 102°, $[\alpha]_D$ +4.0° (chloroform); n.m.r. data: δ 5.85 (d, $J_{1,2}$ 4 Hz, H-1), 4.57 (d, $J_{1,2}$ 4, $J_{2,3}$ <1 Hz, H-2), 4.4–3.9 (m, 5 H, H-3,4,5,6,6'), 3.41 (s, 3 H, OMe), 1.55, 1.47, 1.40, and 1.35 (4 s, 12 H, 2 Me_2C).

Anal. Calc. for $C_{13}H_{22}O_6$ (274.3): C, 56.92; H, 8.08. Found: C, 56.99; H, 8.01.

1,2-O-Isopropylidene-3-O-methyl-β-D-altrofuranose (**7**). — Partial hydrolysis of the diacetone derivative **6** (2.86 g) was performed by heating it in acetic acid (15 ml) and water (2.25 ml) for 2 h at 50–60°, with the formation of **7** (R_F 0.17) being monitored by t.l.c. (solvent *A*). Removal of the acid by evaporation, and coevapora-

tion of added water, gave **7** as a syrup (2.49 g) that was directly usable for preparation of **8**. A sample (0.7 g) of the crude **7** was subjected to short-path distillation using a cold-finger condenser, and the fraction boiling at 90–100° (bath temp.)/0.03–0.05 torr was collected as a colorless, very viscous syrup; $[\alpha]_D$ +12.0°, $[\alpha]_{578}$ +12.6°, $[\alpha]_{546}$ +14.6°, $[\alpha]_{436}$ +23.9°, $[\alpha]_{365}$ +36.8° (*c* 0.6, methanol); reported[8]: b.p.$_{0.04}$ 145°, $[\alpha]_D$ +10.2° (methanol); n.m.r. data: δ 5.88 (d, $J_{1,2}$ 4 Hz, H-1), 4.59 (d, $J_{1,2}$ 4, $J_{2,3}$ 0 Hz, H-2), 4.0–3.6 (m, 5 H, H-3 to -6′), 3.43 (s, 3 H, OMe), 3.2 and 2.95 (broad peaks, disappearing on D_2O exchange, OH), 1.53 and 1.35 (s, 6 H, Me_2C).

Anal. Calc. for $C_{10}H_{18}O_6$ (234.2): C, 51.27; H, 7.74. Found: C, 51.16; H, 7.84.

A sample of **7** (20.85 mg, 89.0 μmol) in water (3.0 ml) containing 105 μmol of sodium metaperiodate consumed 83.8 (94%), 85.3 (96%), and 89.5 μmol (100.5%) of the oxidant during 10 min, 36 min, and 21 h, respectively, as determined by polarography.

A sample of **7** (30 mg) in chloroform (0.5 ml) was treated for 4 h with acetic anhydride (0.1 ml) and pyridine (0.2 ml). Evaporation produced the syrupy *5,6-diacetate*, the n.m.r. spectrum of which, in $CDCl_3$, was in complete accord with the structure: δ 5.89 (d, $J_{1,2}$ 4.2 Hz, H-1), 5.30 (o, $J_{4,5}$ 9.5, $J_{5,6}$ 5, $J_{5,6'}$ 2.7 Hz, H-5), 4.58 (d, $J_{1,2}$ 4.2, $J_{2,3}$ 0 Hz, H-2), 4.55 (q, $J_{5,6'}$ 2.7, $J_{6,6'}$ 12 Hz, H-6′), 4.18 (q, $J_{5,6}$ 5, $J_{6,6'}$ 12 Hz, H-6), 4.13 (q, $J_{3,4}$ 2, $J_{4,5}$ 9.5 Hz, H-4), 3.74 (d, $J_{3,4}$ 2, $J_{2,3}$ 0 Hz, H-3), 3.39 (s, 3 H, OMe), 2.09 and 2.06 (s, 6 H, 2 OAc), 1.55 and 1.32 (s, 6 H, Me_2C).

*6-Deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-6-nitro-β-*D*-altrofuranose* (**8**). — For the example here described, undistilled **7**, slightly contaminated by its precursor **6**, was used. Therefore, a solution of the crude compound (3.38 g) in water (10 ml) was first extracted with two 5-ml portions of petroleum ether (b.p. 30–60°), which removed the contaminant (90 mg; weighed, and identified by t.l.c., after evaporation of the extract). The aqueous solution was then briefly agitated *in vacuo* to drive off remnant petroleum ether, and the volume was adjusted to 15 ml. Aqueous 0.5M sodium metaperiodate solution (30 ml) was added dropwise, with stirring, during 15 min to the cooled (0°) sugar solution, and stirring was thereafter continued for 1 h at room temperature. The excess of oxidant was decomposed with ethylene glycol (15 drops), and ethanol (50 ml) was added to the mixture, which was chilled (0°) for some time before the inorganic precipitate was filtered off with suction, and washed thoroughly with cold ethanol. The filtrate was evaporated to give a residue that was taken up in ethanol (10 ml). Removal of insoluble matter, evaporation, and dissolution in fresh ethanol were repeated. Finally, the product was brought to dryness *in vacuo*, dissolved in chloroform (15 ml), and recovered by evaporation of the solution which had been refrigerated overnight and filtered through Celite. The dialdose derivative was obtained as a yellowish syrup (~3 g, vacuum-dried) that was used without delay for the subsequent operation.

The dialdose syrup resulting from 2.85 g (12.2 mmol) of **7** was dissolved in a mixture of methanol (13 ml) and nitromethane (13 ml) which was chilled (0°), agitated by passing through it a stream of pure nitrogen, and rendered alkaline (pH 8.5–9, wet indicator paper) by the addition of 0.40 ml of 3.3M sodium methoxide

in methanol. A voluminous precipitate formed initially, but disappeared within 10–15 min. The vessel was then stoppered, and the clear solution was kept for 140 min at 0°. It was thereafter acidified to pH 5–6 with glacial acetic acid (0.5 ml), and evaporated to give a syrup that crystallized on subsequent evaporation of added chloroform. The dry mixture of products (3.76 g) was systematically partitioned between chloroform (30+10+10+5 ml) and water (3×10 ml) by use of separatory funnels. The chloroform solution was dried ($MgSO_4$), filtered, and concentrated to incipient crystallization. The crystals were redissolved by heating the remaining liquid (8–10 ml), petroleum ether (2 ml) was added, and crystallization was allowed to proceed. There was obtained 2.08 g (7.9 mmol, 65%) of quite pure **8**, m.p. 144–145°, $[\alpha]_{365}$ −157° (*c* 0.8, chloroform), and a second crop (0.20 g, 6%) of slightly less-pure product was recovered from the mother liquor. Recrystallization from chloroform–ligroin resulted in a very sharp melting point, 145–145.2° (with resolidification on slight cooling); $[\alpha]_D$ +2°, $[\alpha]_{578}$ +1.6°, $[\alpha]_{546}$ 0°, $[\alpha]_{436}$ −19.9°, $[\alpha]_{365}$ −164.2° (*c* 0.3, chloroform). The trend of the optical rotatory dispersion indicated the Cotton effect due to the nitro group chromophore to be negative, and thus identified[11,12] the C-5 configuration as *R*.

Compound **8** showed the following n.m.r. data (60 MHz): δ 5.83 (d, $J_{1,2}$ 4 Hz, H-1), 4.8–4.3 and 4.1–3.8 (m, 4+2H, unresolved, H-2 to -6′), 3.40 (s, 3 H, OMe), 1.53 and 1.33 (s, 6 H, Me_2C).

Anal. Calc. for $C_{10}H_{17}NO_7$ (263.2): C, 45.62; H, 6.51; N, 5.32. Found: C, 45.48; H, 6.47; N, 5.16.

The mother liquor remaining after isolation of the aforementioned second crop of **8** was evaporated, to give a semi-crystalline residue (0.5 g) which showed five distinct spots in t.l.c. (solvent *B*): R_F 0.11, 0.36, 0.58 (main spot), 0.77, and 0.93. A similarly obtained material (250 mg, from another run) was chromatographed on a column of silica gel (10 g, with 1 ml of water added) by use of 5:1 carbon tetrachloride–ethyl acetate as the eluant. The main component (R_F 0.58) appeared in 10-ml fractions Nos. 4–7, and amounted to 136 mg of crystals, m.p. 75–100°. Recrystallization from carbon tetrachloride gave 40 mg of crystals, m.p. 80–83°; $[\alpha]_{578}$ +27°, $[\alpha]_{546}$ +29°, $[\alpha]_{436}$ +51°, $[\alpha]_{365}$ +115° (*c* 0.3, chloroform). The n.m.r. spectrum was very similar to that of **8**, especially as regards the H-1 and substituent-group resonances, but the pattern of the remaining (unresolved) signals in the δ 3.8–4.8 region was clearly not identical. From the opposite trend of the optical rotatory dispersion, the substance was concluded to be rich in the α-L-*galacto* epimer of **8**.

*6-Deoxy-3-*O*-methyl-6-nitro-*D*-altrose* (**9**). — A solution of **8** (106 mg) in 90% trifluoroacetic acid (1.1 ml) was kept for 20 min at room temperature, and then evaporated with several additions of water and, finally, of ethyl acetate. The powdery, crystalline residue (**9**) obtained in quantitative yield (90 mg) had m.p. 109–110°, $[\alpha]_{436}$ +2→+17° (equil.) and $[\alpha]_{365}$ −105→−97° (equil.; *c* 0.5, 0.1M acetic acid). Recrystallization from ethyl acetate gave crystals (40 mg) that melted at 130–131° and showed $[\alpha]_{436}$ +29→+17° (equil.) and $[\alpha]_{365}$ −69→−98° (equil.; *c* 0.2, 0.1M

acetic acid). The mutarotation was complex. The microanalytical data refer to the high-melting form.

Anal. Calc. for $C_7H_{13}NO_7$ (223.2): C, 37.66; H, 5.87; N, 6.28. Found: C, 37.74; H, 5.86; N, 6.14.

REFERENCES

1 J. KOVÁŘ AND H. H. BAER, *Can. J. Chem.*, 51 (1973) 3373–3379.
2 H. H. BAER AND J. KOVÁŘ, *Can. J. Chem.*, 54 (1976) 2038–2044.
3 J. M. GROSHEINTZ AND H. O. L. FISCHER, *J. Am. Chem. Soc.*, 70 (1948) 1479–1484; J. KOVÁŘ AND H. H. BAER, *Can. J. Chem.*, 51 (1973) 1801–1811, 2836–2842; *Carbohydr. Res.*, 45 (1975) 161–180.
4 L. F. WIGGINS, *Methods Carbohydr. Chem.*, 2 (1963) 188–191.
5 G. J. ROBERTSON AND C. E. GRIFFITH, *J. Chem. Soc.*, (1935) 1193–1201.
6 N. K. RICHTMYER, *Methods Carbohydr. Chem.*, 1 (1962) 107–113.
7 C. A. GROB AND D. A. PRINS, *Helv. Chim. Acta*, 28 (1945) 840–850.
8 F. H. NEWTH, *J. Chem. Soc.*, (1953) 2504–2505.
9 M. STEIGER AND T. REICHSTEIN, *Helv. Chim. Acta*, 19 (1936) 1011–1016; J. S. BRIMACOMBE AND P. A. GENT, *Carbohydr. Res.*, 12 (1970) 1–8.
10 J. KOVÁŘ AND H. H. BAER, *Carbohydr. Res.*, 39 (1975) 19–32.
11 C. SATOH, A. KIYOMOTO, AND T. OKUDA, *Carbohydr. Res.*, 5 (1967) 140–148; C. SATOH AND A. KIYOMOTO, *ibid.*, 7 (1968) 138–145.
12 W. RANK AND H. H. BAER, *Carbohydr. Res.*, 35 (1974) 65–72.
13 J. E. CHRISTENSEN AND L. GOODMAN, *Carbohydr. Res.*, 7 (1968) 510–512.
14 B. COXON, *Tetrahedron*, 21 (1965) 3481–3503.