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CONVERSION OF D-FRUCTOSE INTO 4-AMINO, 4-AMINO-4-*C*-METHYL AND 3,4,5-TRIAMINO DERIVATIVES OF L-SORBOSE*,†

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ABSTRACT

The 1,5-dialdehydes generated *via* periodate cleavage of benzyl β-D-fructopyranoside (**1**) and 1,2-*O*-isopropylidene-D-fructopyranose (**10**) undergo cyclyzation with nitromethane with high stereoselectivity, yielding 4-deoxy-4-nitrohexulopyranoses of the α-L-*sorbo* (**2**, **11**) and α-L-*tagato* (**4**) configurations only, in 3:1 and 2:1 ratios, respectively. Nitroethane cyclization affords four methyl-branched 4-nitrohexuloses with a 12:6:2:1 stereoselectivity, of which the major three have been isolated and characterized to be the α-L-*sorbo* (**18**), β-D-*psico* (**20**), and α-L-*tagato* (**22**) isomers. Hydrogenation of the nitro function smoothly generated, in high yields, the respective 4-amino-4-deoxyhexulopyranoses of the α-L-*sorbo* (**14**, **23**), α-L-*tagato* (**9**), and β-D-*psico* (**24**) configurations. Subjection of the nitroacetates **2** and **11** to amination with methanolic ammonia — a double elimination-addition sequence — and, subsequently, to acetylation, furnished the 3,5-diacetamido-4-nitro-α-L-sorbopyranoses **7** and **15** in 53 and 64% yields, respectively, which were readily converted by hydrogenation into the respective 3,4,5-triamino-3,4,5-trideoxy-α-L-sorboses **6** and **16**, representing the first triaminosugars of this type. Structural and configurational assignments were based on conclusive ^{1}H-n.m.r. data, on rotational comparisons, and on stereochemical considerations, and were sustained by X-ray crystallographic analyses of benzyl 4-deoxy-4-nitro-α-L-tagatopyranoside (**5**) and its methyl-branched analog **22**.

INTRODUCTION

Nearly 30 years ago, after retirement from an illustrious career[2], H. O. L. Fischer extended the nitromethane addition to aldehydo sugars — a most useful method for ascending the sugar series when followed by the Nef reaction[3] — to the dialdehydes arising from the periodate oxidation of the common glycosides[4], and thus developed the "cyclization of dialdehydes with nitromethane" as a most efficient procedure for the preparation of 3-nitro- and, hence, 3-amino-3-deoxy

* Dedicated to the memory of Hermann O.L. Fischer on the centenary of his birth.
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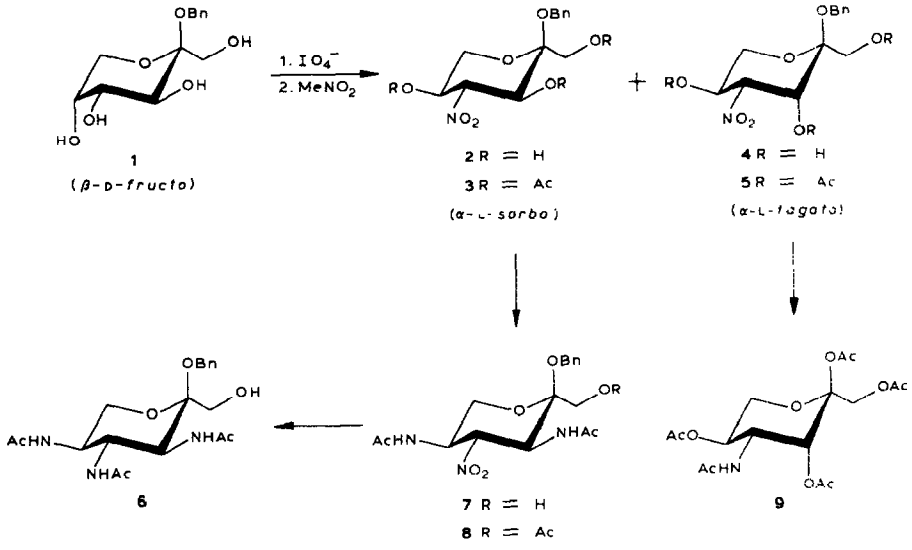
derivatives of pentoses, hexoses, and inositols[5-7].

Some 4-deoxy-4-nitro ketoses have also been prepared by nitromethane cyclization of the dialdehydes derived from benzyl β-D-fructopyranoside[8] (**1**), from sedoheptulose[9], and from sucrose[10], yet due to a tertiary anomeric centre in the products, proof of their configurations was less readily extractable from n.m.r. data than for standard aldopyranoses. This particularly holds for the 4-nitro-hexulosides originating from **1**, where affiliation to either the β-D- or the α-L-series is possible[8]. Twenty years ago this question was tackled using comparisons of rotational data from products having known *sorbo*[11] and *tagato*[12] configurations, but, particularly in the latter case, the data were encumbered with ambiguities as to the anomeric configurations of the reference compounds. These uncertainties as to the α-L or β-D affiliation of the products induced us to re-examine this issue, the results being reported herein together with investigations on the preparation of 4-C-methyl-4-aminohexuloses and 3,4,5-triamino analogs from simple fructose derivatives.

RESULTS AND DISCUSSION

4-Amino-4-deoxy hexuloses of α-L-sorbo *and* α-L-tagato *configurations.* — The base-catalyzed reaction between nitromethane and the dialdehyde generated by periodate oxidation of benzyl β-D-fructopyranoside[8] (**1**), as well as the ensuing acidification of the pyranoid *aci*-nitro salts formed, proceeded with high stereoselectivity. Of the eight stereoisomers possible, only *two* were obtained, viz. the C-3-epimeric 4-nitrohexulosides of the α-L-*sorbo* (**2**) and α-L-*tagato* (**4**) configurations in a ratio of 4:1. Whilst the major product **2** was readily isolated in pure form (36%, based on **1**), the minor component was not. It was best characterized as its tri-*O*-acetyl derivative **5**, which was highly crystalline and nicely separable from the



respective α-L-*sorbo* isomer **3** by fractional cystallization. The α-L-*sorbo* products **2** and **3** were readily converted into derivatives of 4-amino-4-deoxy-α-L-sorbopyranose which have been adequately characterized 20 years ago[8]. Similarly, the α-L-*tagato* isomer **5**, previously assigned the β-D-configuration[8] on the basis of invalid rotations attributed to tagatose derivatives in the literature[12], was convertible into the peracetate of 4-amino-4-deoxy-α-L-tagatopyranose (**9**) *via* hydrogenation and acetylation.

The relative stereochemical arrangements at C-3, C-4, and C-5 in both the *sorbo* and the *tagato* configurations could readily be derived from the coupling patterns of the respective ring protons. However, a decision whether the products obtained belonged to the α-L or the β-D series could not be reached on the basis of ^{1}H-n.m.r. data. The conclusion that both belong to the α-L series is based on the following pieces of evidence: (*i*) the operation of the anomeric effect in the dialdehyde-nitromethane cyclization is expected to highly favor the assumption by the benzyloxy group of an axial disposition as in **2** and **4** rather than equatorial arrangement (with an axially disposed hydroxymethyl moiety) characteristic of the respective β-D isomers; (*ii*) in the case of the *sorbo* isomer, sufficient and reliable rotational data on L-sorbose derivatives are available to allow, at the 4-amino-4-deoxy stage, an unequivocal conclusion in favor of the α-L-*sorbo* configuration for **2** and **3**; (*iii*) the scarce and not fully reliable rotational data for D-tagatose derivatives precluding similar unambiguous conclusions, a single-crystal structure determination of **5** was made, unequivocally establishing the α-L-*tagato* configuration and thereby also dispelling any uncertainties regarding the α-L affiliation of the *sorbo* products. A view of the structure is shown in Fig. 1, clearly revealing the benzyloxy and 3-acetoxy groups to be *trans* with a torsional angle deviating from a perfect antiparallel arran-

TABLE I

SELECTED TORSIONAL ANGLES IN BENZYL 1,3,5-TRI-*O*-ACETYL-4-DEOXY-4-NITRO-α-L-TAGATOPYRANOSIDE (**5**) AND 4-DEOXY-1,2-*O*-ISOPROPYLIDENE-4(*R*)-*C*-METHYL-4-NITRO-α-L-TAGATOPYRANOSE (**22**)

Description	*Angle (degrees)*		*Description*	*Angle (degrees)*	
	5	**22**		**5**	**22**
Pyranose ring			*Ring substituents*		
O-6-C-2-C-3-C-4	−53.1	−56.4	O-1-C-1-C-2-O-2	50.8	−31.6
C-2-C-3-C-4-C-5	51.5	50.5	O-1-C-1-C-2-O-6	175.4	86.0
C-3-C-4-C-5-C-6	−53.5	−48.8	C-1-C-2-C-3-O-3	−55.3	−58.2
C-4-C-5-C-6-O-6	54.8	55.8	O-2-C-2-C-3-O-3	−174.2	−174.2
C-5-C-6-O-6-C-2	−59.0	−63.9	O-3-C-3-C-4-N-4	57.7	49.1
C-6-O-6-C-2-C-3	58.7	62.8	O-3-C-3-C-4-C-41	—	164.1
			N-4-C-4-C-5-O-5	72.4	81.6
Ring protons					
H-3-C-3-C-4-H-4	69.7	—			
H-4-C-4-C-5-H-5	−157.7	—			
H-5-C-5-C-6-H-61	−176.0	176.2			
H-5-C-5-C-6-H-62	63.9	54.1			

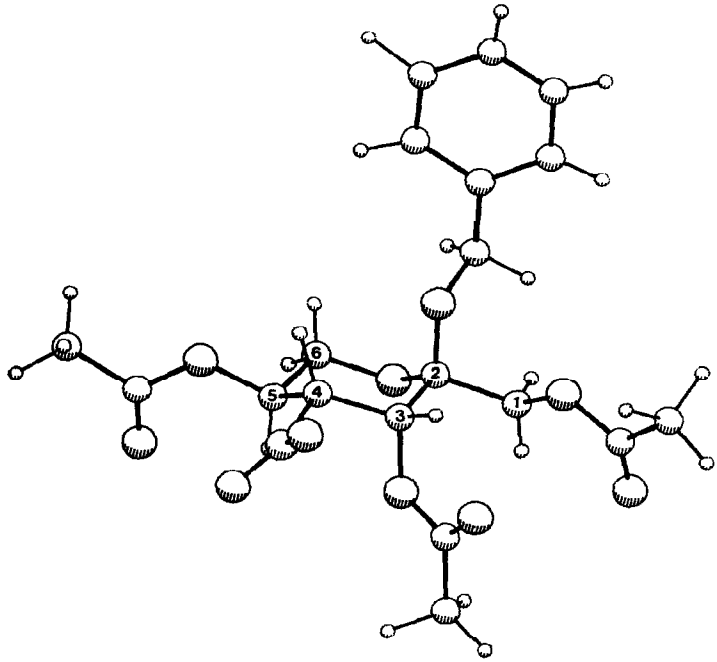
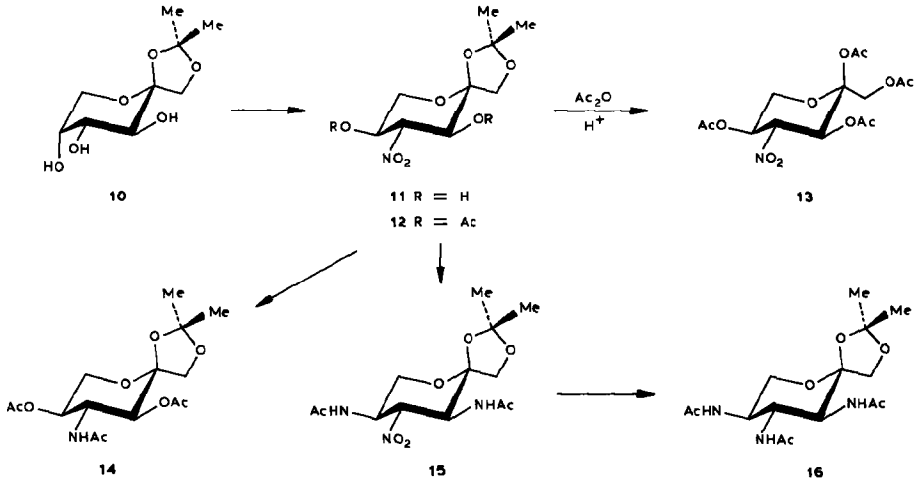


Fig. 1. Perspective view of the molecular structure of benzyl 1,3,5-tri-*O*-acetyl-4-deoxy-4-nitro-α-L-tagatopyranoside (**5**).

gement by less than 6° (*cf.* Table I). The bond lengths and bond angles are in the expected ranges[13]. The pyranoid ring adopts the expected $^2C_5$ conformation as evidenced by torsional angels of 51.5–59.0° (Table I).

When the more readily accessible[14] 1,2-*O*-isopropylidene-β-D-fructopyranose (**10**) was subjected to the sequence periodation–base-catalyzed nitromethane cyclization–acidification, a mixture of two 3-epimeric nitrodiols was again obtained, yet with a stereoselectivity of only 2:1 in favor of the α-L-*sorbo* isomer **11**. This was somewhat surprising, since in the cyclization step the sterically rigid and relatively bulky dimethyl-substituted dioxolane ring at one side of the dialdehyde would have been expected to exert an influence towards higher uniformity of the reaction in the cyclization step. The major product **11** was best isolated in the form of its highly crystalline diacetate **12**, which could be acetolyzed to give the α-L-*sorbo* peracetate **13**, or subjected to hydrogenation in the presence of acetic anhydride to smoothly afford the 4-acetamido-α-L-sorbose derivative **14**, both in good yields.

3,4,5-Triamino-3,4,5-trideoxy-α-L-sorbopyranose. — In view of the smooth replacement of acetoxy functions next to a nitro group by amino functions on simple treatment with ammonia[15], the nitroacetates **3** and **12** were regarded as susceptible to this simple one-pot elimination–addition sequence. And indeed when **3** and **12** were exposed to methanolic ammonia and subsequent *N*-acetylation, mixtures of 3,5-



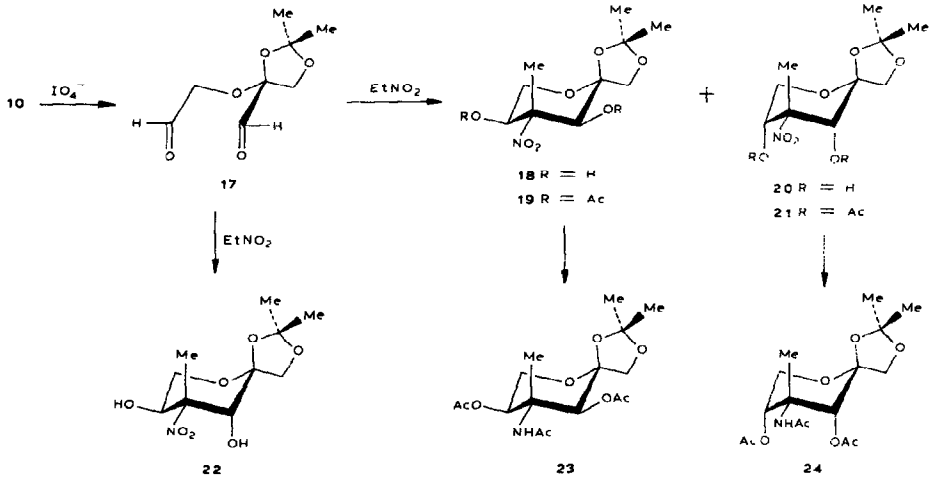
diacetamido-4-nitrohexulosides were obtained from which the major products (about 75% each on the basis of ^{1}H-n.m.r. data) could be isolated by crystallization in yields of 61 (**7**) and 65% (**15**). The nitro groups in **7** and **12** were readily hydrogenated over Raney nickel in an acidic medium, to afford, after *N*-acetylation, the 3,4,5-triacetamido-3,4,5-trideoxy-α-L-sorboses **6** and **16**, respectively, in yields over 80%.

The α-L-*sorbo* configuration for compounds **6**–**8**, **15**, and **16** clearly followed from the well resolved coupling patterns of the ring protons, analogous to those of the parent compounds **4** and **12** (*cf.* Experimental), and, as conclusively, from comparisons of the rotations of the 3,4,5-triacetamido derivatives with those fo their 4-acetamido analogoes, *e.g.* $[\alpha]_D^{20}$ −61° (methanol) for **14** *versus* −57° for **16**.

Methyl-branched 4-nitro- and 4-amino-4-deoxy hexuloses. — In view of the natural occurrence of several methyl-branched sugars bearing amino as well as nitro groups at the branch point[16] extension of the dialdehyde-nitromethane cyclizations described above to nitroethane[17] appeared desirable, since this provides a simple means for simultaneously introducing a nitro group and a methyl branch at C-4 of pyranoid hexuloses. It is known, though, that the stereoselectivity of the reaction decreases on replacement of nitromethane by other nitromethylene components, so that one obtains not only the four products having an equatorial nitro function, but also those having an axially disposed nitro group as well[17,18].

This pattern is exemplified by the nitroethane cyclization of the dialdehyde **17** derived from isopropylidene-β-D-fructose (**10**) by periodate cleavage: a mixture of four diastereomeric 4-*C*-methyl-4-nitrohexulosides was generated under standard conditions (nitroethane–sodium methoxide in methanol) in an approximate ratio of 12:6:2:1. As evidenced below, they constituted the 4(*R*)-methyl-4-nitro compounds of the α-L-*sorbo* (**18**), α-L-*psico* (**20**) (tentatively), and α-L-*tagato* (**22**) configurations, respectively, whilst the fourth product, least abundant, was not characterized. The

main component **18** crystallized on trituration of the mixture with chloroform giving a 38% yield, based on **10**, another 11% becoming available upon chromatography of the mother liquor on silica gel. This also provided the highly crystalline α-L-*tagato* isomer **22** (9%), and the second main component, of *psico* configuration **20** most probably (see below). The latter, however, was best characterized as the diacetate **21** (27%, based on **10**). Hydrogenation of either nitro diacetate, *i.e.* **19** or **21**, over Raney nickel in methanol–acetic anhydride smoothly afforded the respective per-acetylated 4-amino-4-*C*-methylhexuloses in crystalline form in yields of 91 and 86%;



they were fully characterized by 300-MHz n.m.r. data. Configurational assignments by ^{1}H-n.m.r. being impeded by the presence of two tertiary centers in the pyranoid ring, their deduction rests on the following considerations and pieces of evidence:

The α-L-*tagato* configuration for **22** was unequivocally revealed by X-ray crystal-structure analysis (Fig. 2), which demonstrates the anomeric and C-3 oxygen atoms to be *trans* with a torsional angle of 174.2° (Table I), *i.e.* exactly the same nearly antiparallel arrangement as in the unbranched benzyl 4-nitro-α-L-tagatoside **5**. The puckering of the pyranoid ring in the $^2C_5$ conformation is more pronounced in **22** than in **5**, as indicated by the comparatively small C-2–C-3–C-4–C-5 and C-3–C-4–C-5–C-6 torsional angles of 48.8 and 50.5° in the former, which undoubtedly is due to the *spiro*-anellated dioxolane ring.

That the major cyclization product **18** and its derivatives **19** and **23** possess the 4(*R*)-methyl-α-L-*sorbo* configuration is indicated by $J_{5,6}$ values of 5.7 and 10.8 Hz that are essentially the same as observed for the unbranched analogs **12** and **14**, as well as by the chemical shifts of the acetyl signals for **12**, **14**, **19**, and **23**, which are within the ranges expected[19] for equatorially disposed acetoxy and acetamido resonances. Additional persuasive evidence may be derived from stereochemical

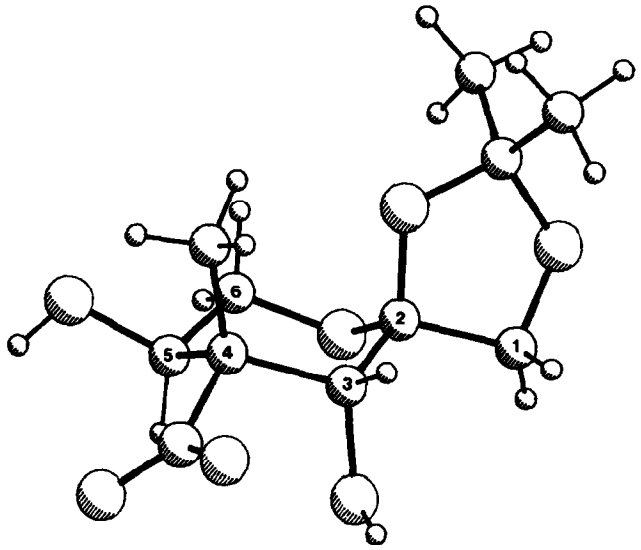


Fig. 2. Perspective view of the molecular structure of 1,2-*O*-isopropylidene-4(*R*)-*C*-methyl-4-nitro-α-L-tagatopyranose (**17**).

considerations: first, the cyclization of dialdehyde **17** with nitromethane and nitroethane would be surmised to yield the same major product, *i.e.* the α-L-*sorbo* isomers **11** and **18**, respectively; second, the β-D-*sorbo* or α-L-*psico* configuration for the main component would require highly unfavorable conformations, *i.e.* the $^5C_2$ form for the former with 1,3-diaxial repulsions between C-1(methylene) and the 4-*C*-methyl group, and an even less likely $^2C_5$ conformation for the latter with an axial 4-nitro function in contact with an axial anomeric oxygen.

The configuration for the second main component (about 30% of the cyclization mixture) must be either *psico* or *fructo*, whereby α-L as well as β-D affiliation is in principle possible. From the 5,6-coupling constants found ($J_{5,6}$ = 3.2 and 3.4 in **21** and 1.8 and 2.8 Hz, in **24**), an axial 5-oxygen can clearly be delineated, which would match with an α-L-*psico* isomer in the $^5C_2$-form (disfavored due to axially disposed C-1,3-OAc, and 3-Me, and an equatorial anomeric oxygen), an α-L-*fructo* configuration in the $^2C_5$ form (equally unlikely due to repulsion between axially disposed 2-OH and 4-nitro groups), and the 3-epimeric β-D-*psico* and β-D-*fructo* configurations. Either one, in its $^2C_5$-conformation, would give the small $J_{5,6}$ couplings observed; the decision in favor of the β-D-*psico* configuration rests on the long range coupling observed in **21** and **24** between H-3 and H-5, $J_{3,5}$ being of the order 0.7–0.8 Hz as expected for a W arrangement of these protons. This conclusion is substantiated by the chemical shifts of the acetyl-methyl signals in **21** (δ 2.14 and 2.18 in $CDCl_3$) and **24** (2.13 and 2.17, respectively), which clearly lie in the ranges observed[19] for axially oriented acetoxy groups.

EXPERIMENTAL

Melting points, determined on a Bock Monscop, are uncorrected. ^{1}H- And ^{13}C-n.m.r. spectra were measured on Varian XL 100 and Bruker WH 300 instruments with Me_4Si as internal standard. Rotations were determined with a Perkin-Elmer 141 polarimeter equipped with 10 cm cuvettes. T.l.c. was performed on Kieselgel 60 F-254 (Merck), and was used to monitor the reactions and ascertain the purity of the products. Useful solvent systems were: *A*, 10:1 chloroform–methanol; *B*, 10:1 benzene–ethyl acetate; and *C*, 20:2:1 *n*-hexane–ethyl acetate–ethanol. Detection was effected with light or by charring with 50% sulfuric acid. Column chromatography was done on Merck Kieselgel 60 (70–230 mesh).

*Benzyl 1,3,5-tri-*O*-acetyl-4-deoxy-4-nitro-α-*L*-sorbopyranoside* (**3**). — The sirupy nitrohexuloside mixture obtained on periodate oxidation of 13.5 g (50 mmol) of benzyl β-D-fructopyranoside[20] (**1**), and subsequent cyclization of the resulting dialdehyde with nitromethane according to the procedure given previously[8], consisted of a 4:1 mixture (^{1}H-n.m.r., t.l.c. in solvent *A*) of the α-L-*sorbo* (**2**) and α-L-*tagato* isomers (**4**). It was subjected to BF_3-catalyzed[21] acetylation by stirring with 60 mL of acetic anhydride at 0° with the addition of two 3 mL portions of BF_3-etherate in the course of 10 min. The precipitate that formed was collected (mother liquor see below) and recrystallized twice from methanol to give 6.7 g (32%, based on **1**) of **3** as wad-like needles, m.p. 147–148°, $[\alpha]_D^{25}$ −79.7° (*c* 1, chloroform); lit.[8] m.p. 138°, $[\alpha]_D^{20}$ −80.3° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 2.03, 2.08, 2.10 (9 H, 3 Ac–Me), 3.50 (t, 1 H, H-6a), 4.08 (q, 1 H, H-6b), 4.24 (q, 2 H, H-1a,b), 4.63 (q, 2 H, PhCH_2), 5.07 (t, 1 H, H-4), 5.47 (ddd, 1 H, H-5), and 5.66 (d, 1 H, H-3); $J_{1,1'}$ 11.9, $J_{3,4}$ 10.7, $J_{4,5}$ 10.5, $J_{5,6a}$ 6.0, $J_{5,6b}$ 10.7, $J_{6a,6b}$ 10.8 Hz; ^{13}C-n.m.r. (75.5 MHz, $CDCl_3$): δ 20.3, 20.6 (acetyl-CH_3), 59.5, 62.2, 63.7 (triplets, C-1, C-6, PhCH_2), 67.9, 69.3 (doublets, C-3, C-5), 85.8 (d, C-4), 98.4 (s, C-2), ~128, ~137 (arom. C), 168.8, 169.0, and 169.9 (3 acetyl-*C*O).

*Benzyl 1,3,5-tri-*O*-acetyl-4-deoxy-4-nitro-α-*L*-tagatopyranoside* (**5**). — The mother liquor remaining from the isolation of crystalline **3** was stirred into ice-water to give a precipitate consisting of **5** (R_F 0.48, solvent *B*) and **3** (R_F 0.40). The wad-like needles of **3** being more readily soluble in hot methanol (or ethanol) than **5**, which crystallizes in thick stapelets, their separation was effected by repeated fractional crystallization frome either of these solvents. This gave 1.91 (9%) of **5**, m.p. 161–162°, $[\alpha]_D^{22}$ −32° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 2.02, 2.03, 2.08 (q H, 3 Ac–Me), 3.45 (t, 1 H, H-6a), 4.13 (q, 1 H, H-6b), 4.60 (q_{AB}, 2 H, H-1a,b), 4.59 (q_{AB}, 2 H, PhCH_2), 5.10 (q, 1 H, H-4), 5.71 (sx, 1 H, H-5), 5.89 (d, 1 H, H-3), and 7.4 (m, 5 H, C_6H_5); $J_{3,4}$ 3.2, $J_{4,5}$ 10.9, $J_{5,6a}$ 6.1, $J_{5,6b}$ 10.7, $J_{6a,6b}$ 10.8 Hz; ^{13}C-n.m.r. (75.5 MHz, $CDCl_3$): δ 20.2, 20.4, 20.5 (3 acetyl-CH_3), 59.8, 58.6, 63.7 (triplets, C-1, C-6, PhCH_2), 64.4, 68.2 (doublets, C-3, C-5), 82.6 (d, C-4), 99.5 (s, C-2), ~128, ~136, (arom. C), 168, 169, and 170 (acetyl-CO).

The crystals of **5** were orthorhombic, space group $P2_12_12_1$, with cell constants a = 16.393, b = 14.892, c = 8.542 Å, V = 2085 (5) Å^3, Z = 4, D = 1.2848

TABLE II

ATOM POSITIONS FOR THE HEAVY ATOMS IN BENZYL 1,3,5-TRI-*O*-ACETYL-4-DEOXY-4-NITRO-α-L-TAGATOPYRANOSIDE (**5**)

Atom	x/a[a]	y/b[a]	z/c[a]
C-2	0.0934(04)	0.2614(04)	0.1001(10)
C-3	0.0223(04)	0.3053(05)	0.1924(11)
C-4	−0.0175(04)	0.3737(04)	0.0876(11)
C-5	−0.0403(04)	0.3376(04)	−0.0684(10)
C-6	0.0348(04)	0.2941(05)	−0.1439(10)
O-6	0.0694(03)	0.2275(03)	−0.0435(07)
C-1	0.1291(05)	0.1814(05)	0.1930(12)
O-1	0.1603(03)	0.2142(03)	0.3348(07)
C-11	0.1598(06)	0.1601(05)	0.4584(12)
C-12	0.2012(07)	0.2016(07)	0.5967(14)
O-11	0.1308(07)	0.0878(04)	0.4549(10)
O-3	−0.0361(03)	0.2343(03)	0.2262(07)
C-31	−0.0485(04)	0.2140(06)	0.3807(14)
C-32	−0.1049(06)	0.1356(07)	0.3947(15)
O-31	−0.0202(05)	0.2561(06)	0.4841(10)
N-4	−0.0945(06)	0.4066(05)	0.1786(12)
O-41	−0.1610(04)	0.3849(04)	0.1233(12)
O-42	−0.0794(06)	0.4513(06)	0.2926(10)
O-5	−0.0630(03)	0.4128(03)	−0.1669(07)
C-51	−0.1281(05)	0.4039(06)	−0.2615(12)
C-52	−0.1452(06)	0.4887(06)	−0.3480(13)
O-51	−0.1642(04)	0.3342(05)	−0.2723(12)
O-2	0.1501(02)	0.3344(03)	0.0885(06)
C-21	0.2262(05)	0.3113(06)	0.0159(14)
C-22	0.2818(04)	0.3932(04)	0.0276(10)
C-23	0.3478(04)	0.3920(05)	0.1282(11)
C-24	0.3991(05)	0.4665(07)	0.1304(14)
C-25	0.3865(06)	0.5383(07)	0.0426(14)
C-26	0.3220(07)	0.5411(06)	−0.0545(14)
C-27	0.2681(05)	0.4674(06)	−0.0643(13)

[a]Standard deviations in parentheses.

g. cm^{-3}, $\mu(CuK_\alpha)$ = 8.19 cm^{-1}. Intensities were collected on a Stoe two-circle diffractometer (CuK_α radiation) equipped with a graphite monochromator. Of the 2430 reflections measured, 1650 symmetry-independent reflections hk0–hk6 with $\vartheta < 62°$ and $|F| > 26$ were used for structure elucidation, which was effected with SHELX-76 (ref. 22). Anisotropic refinement of the carbon and oxygen atoms with fixed positions of H atoms converged to an R value of 0.074. None of the positional parameters* listed in Table II shifted more than 0.086.

*Supplementary material on the structural analysis of **5** and **22**, including the anisotropie thermal parameters of the heavy atoms, H-atom parameters, and observed and calculated structure factors has been deposited, and is available from Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/000/ *Carbohydr. Res.*, 164 (1987) 357–372.

Benzyl 3,4,5-triacetamido-3,4,5-trideoxy-α-L-sorbopyranoside (**6**). — A mixture of **7** (400 mg, 1 mmol), methanol (50 mL), acetic anhydride (5 mL), and freshly prepared Raney nickel (10 mL) was hydrogenated at room temperature for 12 h (uptake, 75 mL of H_2). Removal of the catalyst, evaporation to dryness, and purification of the residue by elution from a short silica gel column (2 × 10 cm) with 10:1 chloroform–methanol gave a syrup, which crystallized on trituration with a little chloroform furnishing 330 mg (81%) of **6** as needles of m.p. 121–123°, $[\alpha]_D^{25}$ −81° (*c* 1, methanol); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 1.92, 1.95, 1.99 (9 H, 3 Ac-Me), 3.0 (br m, 1 H, O*H*), 3.40 (t, 1 H, H-6a), 3.50, 3.7 (2 d, 2 H, AB system, H-1a,b), 3.95 (q, 1 H, H-6b), 4.10, 4.20 (2 m, 2 H, H-3, H-5), 4.37 (t, 1 H, H-4), 4.55 (q_{AB}, 2 H, PhCH_2), 6.55, 6.66, and 7.55 (3 d, 3 H, 3 N*H*), and 7.45 (m, 5 H, C_6H_5); $J_{3,4}$ 10.5, $J_{4,5}$ 9.4, $J_{5,6a}$ 4.7, $J_{5,6b}$ 10.6, $J_{6a,6b}$ −10.8, $J_{3,NH}$ 9.3 Hz.

Anal. Calc. for $C_{19}H_{27}N_3O_6$ (393.4): C, 58.0; H, 6.9, N, 10.7. Found: C, 57.9; H, 7.0; N, 10.6.

Benzyl 3,5-diacetamido-3,4,5-trideoxy-4-nitro-α-L-sorbopyranoside (**7**). — Ammonia gas was passed through a stirred and ice-cooled suspension of 4.5 g (10.6 mmol) of **3** in 100 mL of methanol for 4 h and the resulting mixture was then evaporated *in vacuo*, followed by several additions and reevaporations of the same solvent for complete removal of ammonia. The residual syrup was quickly dissolved in methanol (40 mL), acetic anhydride (8 mL) was added, and the mixture was kept overnight at ambient temperature. Evaporation *in vacuo* (40° bath temp.) with several additions and reevaporations of toluene left a residue that crystallized on trituration with ethyl acetate. Recrystallization from methanol with the addition of charcoal for decolorization gave, in two crops, 2.25 g (55%) of **7** needles, m.p. 260–261° (dec.), $[\alpha]_D^{20}$ −67.2° (*c* 0.5, methanol); ^{1}H-n.m.r. data [100 MHz, 1:1 $(CD_3)_2SO$–$CDCl_3$]: δ 1.78, 1.86 (6 H, 2 Ac-Me), 3.50 (m, 4 H, H-1a,b, H-6a,b), 4.41 (m, 1 H, H-5), 4.57 (m, 2 H, PhCH_2), 4.71 (m, 1 H, H-3), 4.90 (t, 1 H, H-4), 7.45 (m, 5 H, C_6H_5), 8.26, and 8.32 (2 d, 2 H, 2 N*H*); $J_{3,4}$ 10.5, $J_{3,NH}$ and $J_{5,NH}$ 8.5 Hz.

Anal. Calc. for $C_{17}H_{23}N_3O_7$ (381.4): C, 53.5; H, 6.1; N, 11.0. Found: C, 53.6; H, 6.0; N, 11.1.

Benzyl 3,5-diacetamido-1-O-acetyl-3,4,5-trideoxy-4-nitro-α-L-sorbopyranoside (**8**). — A mixture of **8** (640 mg, 1.7 mmol), acetic anhydride (5 mL), and BF_3 etherate (10 drops) was stirred for 15 min at room temperature. Evaporation *in vacuo* followed by treatment of the residual syrup with a little methanol gave 400 mg (53%) of **8**, m.p. 224–225°, $[\alpha]_D^{20}$ −57° (*c* 0.5, $CHCl_3$) and −63° (*c* 0.5, methanol). From the mother liquor a second crop (210 mg, 33%) was obtained; ^{1}H-n.m.r. [100 MHz, $(CD_3)_2SO$]: δ 1.77, 1.79 (6 H, 2 NAc-Me), 2.00 (s, 3 H, OAc-Me), 3.60 (m, 2 H, H-6a,b), 4.14 (q_{AB}, 2 H, H-1a,b), 4.5 (m, 1 H, H-5), 4.61 (AB, 2 H, PhCH_2), 4.75 (q, 1 H, H-3), 4.94 (t, 1 H, H-4), 7.4 (m, 5 H, C_6H_5), 8.26, and 8.35 (2 d, 2 H, 2 N*H*); $J_{3,4}$ 10, $J_{3,NH}$ and $J_{5,NH}$ 9 Hz.

Anal. Calc. for $C_{19}H_{25}N_3O_8$ (423.4): C, 53.9; H, 6.0; N, 9.9. Found: C, 53.7; H, 6.0; N, 10.0.

4-Acetamido-1,2,3,5-tetra-O-*acetyl-4-deoxy*-α-L-*tagatopyranose* (**9**). — A solution of 900 mg (2.3 mmole) of **5** in methanol (50 mL) was added to a prehydrogenated suspension of 10% Pd–C in 45 mL 0.1M methanolic HCl, and the hydrogenation was continued for 6 h. Removal of the catalyst, evaporation to dryness *in vacuo*, acetylation by keeping the residue in 10 mL of 5:3 pyridine–acetic anhydride overnight, and standard workup by evaporation *in vacuo* and trituration of the residual syrup with ethanol yielded 615 mg (69%) of **9**; m.p. 230–231°; $[\alpha]_D^{20}$ −45° (*c* 0.3, chloroform); lit.[8] m.p. 230°, $[\alpha]_D^{21}$ −42° (*c* 0.5, chloroform), there erroneously assigned the β-D-*tagato* configuration; ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 1.83 (3 H, NAc-Me), 1.93, 1.98, 2.07, 2.17 (12 H, 4 OAc-Me), 4.37 (dd, AB-system, 2 H, H-1a,b), 4.42 (AB system, 2 H, H-6a,b), 4.57 (dd, 1 H, H-3); $J_{3,4}$ 3.7, $J_{4,5}$ 8.9, $J_{5,6}$ 5.1 and 9.9, $J_{6,6}$ 10.9 Hz.

Anal. Calc. for $C_{16}H_{23}NO_{10}$ (389.4): C, 49.4; H, 6.0; N, 3.6. Found: C, 49.3; H, 5.9; N, 3.6.

3,5-Di-O-*acetyl-4-deoxy-1,2*-O-*isopropylidene-4-nitro*-α-L-*sorbopyranose* (**12**). — 1,2-*O*-Isopropylidene-β-D-fructopyranose[14] (**10**; 10.0 g, 45 mmol) was added in portions over 10 min to a stirred, cooled (5°) solution of 19.4 g (91 mmol) of sodium metaperiodate in 300 mL of water. The mixture was then allowed to warm to room temperature, the formic acid released being gradually neutralized by the addition of $NaHCO_3$ (3.5 g, 0.9 mol. equiv.). After 2 h, t.l.c. in solvent *A* showing absence of educt, 200 mL of methanol was added, and the sodium iodate was removed by filtration. The filtrate was concentrated *in vacuo* to a syrup, which was dissolved in ethyl acetate. After removal of insoluble material the solution was evaporated to dryness to yield 8.5 g (99%) of the syrupy dialdehyde.

Dissolution in methanol (60 mL), addition of nitromethane (2.6 g, 43 mmol), and chilling to 0° was followed by dropwise addition of M methanolic sodium methoxide (42 mL) over 15 min. After being stirred for 1 h at 0° and 30 min at ambient temperature the mixture was neutralized by the addition of 5 g of a strongly acidic cation-exchange resin (Amberlite IR-120, H^+ form) which, after 30 minutes stirring, was removed by filtration and thorough washing with methanol. The combined filtrate and washings were evaporated to dryness to yield 9.6 g of a yellowish syrup comprising an approximately 2:1 mixture of α-L-*sorbo* nitrodiol **11** and its α-L-*tagato* analog as evidenced by t.l.c. (solvent *A*) and ^{1}H-n.m.r. (H-3 for **11** at δ 5.49, versus 5.34 for the minor product), together with traces of two other products.

Separation of the nitrodiol mixture by column chromatography yielded amorphous products; these were subjected to acetylation with acetic anhydride (30 mL) to which, after cooling to 0°, a cold mixture of acetic anhydride (2 mL) and conc. sulfuric acid (3 drops) had been added. After 2 h at room temperature the mixture was stirred into ice-water followed by filtration and recrystallization of the precipitate from ethanol. This provided 5.6 g (37%, based on **10**) of **12** as fine needles of m.p. 178–179°, $[\alpha]_D^{20}$ −72° (*c* 1.0, chloroform); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 1.44, 1.48 (2 s, 6 H, CCH_3), 2.05, 2.09 (6 H, 2 Ac-Me), 3.72, 4.04 (2 dd, 2

H, H-6a,b), 3.98 (d, 1 H, H-1a,b), 4.99 (dd, 1 H, H-4), 5.40 (ddd, 1 H, H-5), and 5.49 (d, 1 H, H-3); $J_{3,4}$ and $J_{4,5}$ 10.4, $J_{5,6}$ 5.9 and 10.6, $J_{6,6}$ 10.8 Hz.

Anal. Calc. for $C_{13}H_{19}NO_9$ (333.3): C, 46.8; H, 5.8; N, 4.2. Found: C, 46.8; H, 5.8; N, 4.1.

*1,2,3,5-Tetra-*O*-acetyl-4-deoxy-4-nitro-α-*L*-sorbopyranose* (**13**). — On stirring **12** (500 mg) in acetic anhydride (3 mL) containing 3 drops of sulfuric acid for 6 h, the tetraacetate **13** was obtained by pouring the reaction mixture into ice-water, extracting with chloroform, and crystallizing the crude product from ethanol. This gave 490 mg (87%) of needles, m.p. 156°, $[\alpha]_D^{21}$ −32° (*c* 1, chloroform); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 2.97, 2.08, 2.09, 2.21 (4 s, 12 H, 4 OAc-Me), 3.48, 4.22 (2 dd, 2 H, H-6a,b), 4.54, 4.73 (2 d, 2 H, H-1a,b), 4.98 (dd, 1 H, H-4), 5.55 (ddd, 1 H, H-5), and 5.66 (d, 1 H, H-3); $J_{1,1}$ 12.0, $J_{3,4}$ 10.8, $J_{4,5}$ 10.4, $J_{5,6}$ 6.2 and 10.6, $J_{6,6}$ 11.2 Hz.

Anal. Calc. for $C_{14}H_{19}NO_{11}$ (377.3): C, 44.6; H, 5.1; N, 3.7. Found: C, 44.5; H, 5.1; N, 3.7.

*4-Acetamido-3,5-di-*O*-acetyl-4-deoxy-1,2-*O*-isopropylidene-α-*L*-sorbopyranose* (**14**). — Raney nickel T4 catalyst[23] (1.0 g) was added to a solution of 1.0 g (3 mmol) of **14** in 100 mL of methanol and 3 mL of acetic anhydride. The mixture was hydrogenated for 4 h whereupon t.l.c. in solvent *A* indicated absence of educt. Filtration and evaporation to dryness left a greenish residue which crystallized upon trituration with ethanol giving 0.88 g (85%) of **14**; m.p. 164°, $[\alpha]_D^{22}$ −77° (*c* 0.5, chloroform), −61° (*c* 0.3, methanol); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 1.43, 1.49 (2 s, 6 H, CC*H*$_3$), 1.91, 2.04, 2.09 (3 s, 9 H, 1 NAc-Me and 2 OAc-Me), 3.76, 3.87 (2 dd, 2 H, H-6a,b), 3.81, 3.95 (AB-system, 2 H, H-1a,b), 4.61 (dd, 1 H, H-4), 4.82 (d, 1 H, H-3), 4.89 (ddd, 1 H, H-5), and 5.45 (d, 1 H, N*H*); $J_{1,1}$ 9.2, $J_{3,4}$ 10.5, $J_{4,5}$10.4, $J_{4,NH}$ 10.0, $J_{5,6}$ 5.9 and 10.6, $J_{6,6}$ 10.8 Hz.

Anal. Calc. for $C_{15}H_{23}NO_8$ (345.3): C, 52.2; H, 6.7; N, 4.1. Found: C, 52.1; H, 6.7; N, 4.0.

*3,5-Diacetamido-3,4,5-trideoxy-1,2-*O*-isopropylidene-4-nitro-α-*L*-sorbopyranose* (**15**). — Ammonia gas was passed through a stirred and cooled (0°) suspension of 1.0 g (3 mmol) of **12** in methanol (100 mL) for 4 h, followed by evaporation to dryness *in vacuo* and repeated additions and reevaporations of methanol. The resulting syrup was dissolved in methanol (30 mL), acetic anhydride (3 mL) was added, and the mixture was kept overnight at ambient temperature. Evaporation *in vacuo* with several additions and reevaporations of toluene afforded a syrup which crystallized on trituration with ethanol–*n*-hexane to give 0.64 g (64%) of **15** as needles of m.p. 286°, $[\alpha]_D^{21}$ −63° (*c* 1, methanol); ^{1}H-n.m.r. [300 MHz, $(CD_3)_2SO$]: δ 1.38, 1.39 (2 s, 6 H, CC*H*$_3$), 1.78, 1.84 (2 s, 6 H, 2 NAc-Me), 3.61, 3.68 (2 dd, 2 H, H-6a,b), 3.81 (AB system, 2 H, H-1a,b), 4.35 (ddd, 1 H, H-5), 4.52 (dd, 1 H, H-3), 4.81 (dd, 1 H, H-4), 8.29, and 8.37 (2 d, 2 H, 2 N*H*); $J_{3,4}$ 11.2, $J_{3,NH}$ 9.3, $J_{4,5}$ 11.0, $J_{5,6}$ 6.4 and 10.1, $J_{5,NH}$ 9.0, $J_{6,6}$ 11.2 Hz.

Anal. Calc. for $C_{13}H_{21}N_3O_7$ (331.3): C, 47.1; H, 6.4; N, 12.7. Found: C, 47.1; H, 6.4; N, 12.6.

3,4,5-Triacetamido-3,4,5-trideoxy-1,2-O-isopropylidene-α-L-sorbopyranose (**16**). — Hydrogenation of **15** (300 mg) over Raney nickel T4 catalyst[23] (3 mL) in methanol (20 mL) containing 1 mL of acetic anhydride for 4 h and processing of the mixture as described for **12** → **14** afforded **16** (260 mg, 84%) as colorless needles of m.p. 143–144°, $[\alpha]_D^{21}$ −57° (*c* 0.3, methanol); ^{1}H-n.m.r. [300 MHz, $(CD_3)_2SO$]: δ 1.37, 1.39 (2 s, 6 H, CC*H*$_3$), 1.78, 1.79, 1.85 (3 s, 9 H, 3 NAc–Me), 3.60, 3.65 (2 dd, 2 H, H-6a,b), 3.85 (AB system, 2 H, H-1a,b), 4.30 (dddd, 1 H, H-5), 4.49 (dd, 1 H, H-3), 4.55 (ddd, 1 H, H-4), 8.29, 8.35, and 8.39 (3 d, 3 H, 3 N*H*); $J_{3,4}$ 11.1, $J_{3,NH}$ 9.3, $J_{4,5}$ 11.0, $J_{4,NH}$ 9.5, $J_{5,6}$ 6.3 and 10.2, $J_{5,NH}$ 9.1, $J_{6,6}$ 11.2 Hz.

Anal. Calc. for $C_{15}H_{25}N_3O_6$ (343.4): C, 52.5; H, 7.3; N, 12.2. Found: C, 52.4; H, 7.3; N, 12.2.

Nitroethane cyclization of the dialdehyde derived from 1,2-O-isopropylidene-β-D-fructopyranose (**10**) *by periodate cleavage.* — To a solution of the syrupy dialdehyde **17** [5.0 g, obtained from the periodate oxidation of 5.5 g (25 mmol) of **10** as described above for **10** → **11**] in methanol (50 mL) was added nitroethane (2.2 g, 30 mmol), and after chilling to 0°, M methanolic sodium methoxide solution (25 mL). After 1 h at 0° and 30 min at 25°, the mixture was stirred into a methanolic suspension of Amberlite IR-120 (5 g, H^+ form), and further stirred for 30 min. The resin was removed by filtration in a column having a glass frit and subsequently washed with methanol (3 × 50 mL). Evaporation of the filtrate and eluates to dryness *in vacuo* yielded 6.2 g (94%) of a nitrodiol mixture consisting of two major products [the α-L-*sorbo* (**18**) and β-D-*psico* (**20**) isomers] and two minor components [α-L-*tagato* (**22**) and β-D-*fructo* (tentatively) analogs] in the approximate ratio 12:6:2:1 (t.l.c. in solvents *A* or *C*).

4-Deoxy-1,2-O-isopropylidene-4(R)-C-*methyl-4-nitro-α-L-sorbopyranose* (**18**). — Dissolution of the sirupy nitrodiol mixture, as obtained above, in hot chloroform and standing overnight in a refrigerator yielded a precipitate of rod-shaped crystals which were essentially pyre **18** (mother liquor *vide infra*). The yield was 2.85 g (38%, based on **10**), m.p. 142°, $[\alpha]_D^{21}$ −88° (*c* 0.6, methanol). With a second crop from the column separation (see below) the total yield amounted to 49%. The ^{1}H-n.m.r. data [300 MHz, $(CD_3)_2SO$] were: δ 1.32, 1.39 (2 s, 6 H, CC*H*$_3$), 1.55 (s, 3 H, 4 Me), 3.34 (d, 1 H, H-3), 3.42, 3.60 (2 dd, 2 H, H-6a,b), 3.93 (dd, AB system, 2 H, H-1a,b), 4.18 (ddd, 1 H, H-5), 5.73, and 5.78 (2 d, 2 H, 2 O*H*); $J_{3,OH}$ 7.7, $J_{5,6}$ 5.5 and 10.8, $J_{5,OH}$ 5.7, $J_{6,6}$ 11.2 Hz.

Anal. Calc. for $C_{10}H_{17}NO_7$ (263.3): C, 45.6; H, 6.5; N, 5.3. Found: C, 45.6; H, 6.5; N, 5.2.

3,5-Di-O-acetyl-4-deoxy-1,2-O-isopropylidene-4(R)-C-*methyl-4-nitro-α-L-sorbopyranose* (**19**). — A cooled mixture of acetic anhydride (2 mL) and 3 drops of conc. H_2SO_4 was added to an equally cooled solution of nitrodiol **18** (530 mg, 2 mmol) in acetic anhydride (10 mL). After 3 h stirring at ambient temperature the mixture was poured into ice-water, and the solid formed thereby was separated and recrystallized from hexane–ethyl acetate. The yield was 620 mg (89%), m.p. 92°, $[\alpha]_D^{21}$ −83° (*c* 0.5, chloroform); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 1.41, 1.46 (2 s, 6 H,

CCH_3), 1.87 (s, 3 H, 4-Me), 2.06, 2.10 (2 s, 6 H, 2 OAc-Me), 3.68, 3.94 (2 dd, 2 H, H-6a,b), 3.69, 3.96 (2 d, 2 H, H-1a,b), 5.63 (s, 1 H, H-3), and 5.64 (dd, 1 H, H-5); $J_{1,1}$ 9.8, $J_{5,6}$ 5.7 and 10.6, $J_{6,6}$ 11.0 Hz.

*3,5-Di-*O*-acetyl-4-deoxy-1,2-*O*-isopropylidene-4*(R)*-*C*-methyl-4-nitro-β-*D*-psicopyranose* (**21**). — The nitrodiol **20**, being difficult to separate from traces of **18** as well as resisting attempts for crystallization, the mixture left after isolation of the major portion of **18** (above), acetylated as described for **18** → **19**. A 1.0 g portion of the mother-liquor fraction [after removal of the chloroform; according to t.l.c. in solvent *C* an approximately 2:1 mixture of **18** and **20**, with minor spots for **22** and another isomer] gave a mixture of diacetates, which was subjected to column separation on silica gel (2 × 20 cm) by elution with 20:2:1 *n*-hexane–ethyl acetate–ethanol. Evaporation of the major fraction, eluted second, afforded **21** (2.1 g; 24%, based on **10**) as a chromatographically homogeneous syrup, $[\alpha]_D^{20}$ −45° (*c* 0.3, chloroform); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 1.33, 1.45 (2 s, 2 H, CCH_3), 1.55 (s, 3 H, 4-Me), 2.14, 2.18 (2 s, 6 H, 2 OAc-Me), 3.73, 4.38 (2 dd, 2 H, H-6a,b), 3.98 (dd, AB system, 2 H, H-1a,b), 5.68 (dt, 1 H, H-5), and 5.77 (d, 1 H, H-3); $J_{1,1}$ 9.2, $J_{3,5}$ 0.8, $J_{5,6}$ 3.2 and 3.4, $J_{6,6}$ 13.3 Hz.

Anal. Calc. for $C_{14}H_{21}NO_9$ (347.3): C, 48.4; H, 6.1; N, 4.0. Found: C, 48.3; H, 6.1; N, 4.0.

*4-Deoxy-1,2-*O*-isopropylidene-4*(R)*-*C*-methyl-4-nitro-α-*L*-tagatopyranose* (**22**). — The chloroform mother liquor remaining after the isolation of **18** was taken

TABLE III

ATOM POSITIONS FOR THE HEAVY ATOMS IN 4-DEOXY-1,2-*O*-ISOPROPYLIDENE-4(*R*)-*C*-METHYL-4-NITRO-α-L-TAGATOPYRANOSE (**22**)

Atom	x/a[a]	y/b[a]	z/c[a]
C-1	0.6351(1)	0.1612(1)	−0.2829(3)
C-2	0.7181(1)	0.2002(1)	−0.2146(2)
C-3	0.7878(1)	0.1285(1)	−0.2976(2)
C-4	0.8693(1)	0.1731(1)	−0.2129(1)
C-5	0.8662(1)	0.1862(1)	0.0278(2)
C-6	0.7911(1)	0.2533(1)	0.0899(2)
O-6	0.7197(1)	0.1996(1)	0.0101(2)
O-1	0.5905(1)	0.2669(1)	−0.2803(2)
C-7	0.6435(1)	0.3594(1)	−0.3306(3)
C-8	0.6268(1)	0.4590(2)	−0.1821(4)
C-9	0.6384(1)	0.3925(2)	−0.5602(3)
O-2	0.7229(1)	0.3142(1)	−0.2940(2)
O-3	0.7744(1)	0.0117(1)	−0.2285(2)
C-41	0.9003(1)	0.2818(2)	−0.3233(3)
N-4	0.9288(1)	0.0795(1)	−0.2675(2)
O-41	0.9330(1)	0.0471(1)	−0.4534(2)
O-42	0.9700(1)	0.0335(1)	−0.1292(2)
O-5	0.9300(1)	0.2541(1)	0.1088(2)

[a]Standard deviations in parentheses.

to dryness, loaded onto a silica gel column (2 × 30 cm), and eluted with 10:1 toluene–ethanol. The fraction eluted first contained the *sorbo* isomer **18**, affording on evaporation and trituration with chloroform another 825 mg (11%) of **18** as described above. Evaporation of the minor fraction eluted next and recrystallization of the residue from chloroform yielded **22** (670 mg; 9%, based on **10**) as well developed crystals of m.p. 139–140°, $[\alpha]_D^{22}$ −80° (*c* 0.3, methanol); ^{1}H-n.m.r. [300 MHz, $(CD_3)_2SO$]: δ 1.34, 1.39 (2 s, 6 H, CC*H*$_3$), 1.59 (s, 3 H, 4-Me), 3.37, 3.63 (2 dd, 2 H, H-6a,b), 3.81 (d, 1 H, H-3), 3.83, 3.97 (2 d, 2 H, H-1a,b), 4.62 (ddd, 1 H, H-5), 5.44 (d, 1 H, 5-O*H*), and 6.12 (d, 1 H, 3-O*H*); $J_{1,1}$ 9.1, $J_{3,OH}$ 7.7, $J_{5,6}$ 6.0 and 11.1, $J_{5,OH}$ 5.4, $J_{6,6}$ 11.2 Hz.

Anal. Calc. for $C_{10}H_{17}NO_7$ (263.3): C, 45.6; H, 6.5; N, 5.3. Found: C, 45.6; H, 6.5; N, 5.3.

The crystals of **22** were orthorhombic, space group $P2_12_12_1$, with cell constants a = 16.677, b = 11.477, c = 6.360 Å, V = 1217 Å^3, Z = 4, D = 1.437 g. cm^{-3}, $\mu(MoK_\alpha)$ = 0.79 cm^{-1}. Intensities were collected on a Siemens–Stoe AED 2 diffractometer (MoK_α radiation) equipped with a graphite monochromator. Of the 2100 reflections measured, 1650 symmetry-independent reflections hk0–hk6 with $1.5° < \vartheta < 25°$ were used for structure elucidation, which was effected with SHELX-76 (ref. 22). Anisotropic refinement of the carbon and oxygen atoms with fixed positions of H atoms converged to an R value of 0.027. None of the positional parameters listed in Table III shifted more than 0.05.

*4-Acetamido-3,5-di-*O*-acetyl-4-deoxy-1,2-*O*-isopropylidene-4*(R)-C-*methyl-*α*-L-sorbopyranose* (**23**). — Hydrogenation of 200 mg of nitrodiacetate **19** in 20:1 methanol–acetic anhydride (20 mL) over Raney nickel T4 catalyst[23] overnight, and processing of the mixture as described for **12** → **14** (above) gave upon recrystallization from 1:10 ethanol-*n*-hexane 180 mg (91%) of **22**, m.p. 176°, $[\alpha]_D^{20}$ −74° (*c* 1, methanol); ^{1}H-n.m.r. [300 MHz, $(CD_3)_2SO$]: δ 1.28, 1.33 (2 s, 6 H, CC*H*$_3$), 1.40 (s, 3 H, 4-Me), 1.67 (s, 3 H, NAc-Me), 2.01, 2.08 (2 s, 6 H, 2 OAc-Me), 3.17 (s, 1 H, H-3), 3.58, 3.65 (2 dd, AB system, 2 H, H-6a,b), 3.77 (dd, AB system, 2 H, H-1a,b), 5.85 (s, 1 H, N*H*), and 6.02 (ddd, 1 H, H-5); $J_{5,6}$ 5.8 and 10.7, $J_{6,6}$ 11.0 Hz.

Anal. Calc. for $C_{16}H_{25}NO_8$ (359.4): C, 53.5; H, 7.0; N, 3.9. Found: C, 53.4; H, 7.0; N, 3.8.

*4-Acetamido-3,5-di-*O*-acetyl-4-deoxy-1,2-di-*O*-isopropylidene-4*(R)-C-*methyl-β-*D*-psicopyranose* (**24**). — Raney-nickel hydrogenation of **21** (300 mg) in methanol–acetic anhydride in a manner analogous to the conversion **19** → **23** (above) gave **24** (255 mg, 86%) as crytals, m.p. 167°, $[\alpha]_D^{20}$ −53° (*c* 0.2, chloroform); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 1.45, 1.53 (2 s, 6 H, CC*H*$_3$), 1.44 (s, 3 H, 4-Me), 1.96 (s, 3 H, NAc-Me), 2.13, 2.17 (2 s, 6 H, 2 OAc-Me), 3.83, 4.19 (2 dd, AB system, 2 H, H-6a,b), 3.89 (dd, AB system, 2 H, H-1a,b), 4.86 (d, 1 H, H-3), 5.38 (ddd, not fully resolved, 1 H, H-5), and 6.58 (s, 1 H, N*H*); $J_{3,5}$ 0.7, $J_{5,6}$ 1.8 and 2.8, $J_{6,6}$ 13.5 Hz.

Anal. Calc. for $C_{16}H_{25}NO_8$ (359.4): C, 53.5; H, 7.0; N, 3.9. Found: C, 53.5; H, 7.0; N, 3.8.

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