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AMMONOLYSIS OF 1,6-ANHYDRO-2,4-DI-*O*-TOSYL-*β*-D-GLUCOPYRANOSE AND 1,6 3,4-DIANHYDRO-2-*O*-TOSYL-*β*-D-GALACTOPYRANOSE PREPARATION OF 4-AMINO-1,6-ANHYDRO-4-DEOXY-*β*-D-MANNO- AND -*β*-D-ALTRO-PYRANOSE*

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ABSTRACT

Treatment of the title ditosylate **1** or dianhydride **2** with methanolic ammonia afforded 1,6-anhydro-3,4-dideoxy-3,4-epimino-*β*-D-altropyranose (**5**) and 2,4-diamino-1,6-anhydro-2,4-dideoxy-*β*-D-glucopyranose *via* 4-amino-1,6 2,3-dianhydro-4-deoxy-*β*-D-mannopyranose Acid hydrolysis of **5** gave 4-amino-1,6-anhydro-4-deoxy-*β*-D-mannopyranose, and treatment of the diacetyl derivative of **5** with hydrochloric acid in moist chloroform yielded 4-acetamido-3-*O*-acetyl-1,6-anhydro-4-deoxy-*β*-D-mannopyranose Partial acylation of **5** with acetic anhydride or benzoyl chloride gave the *N*-acetyl or the *N*-benzoyl derivative, respectively The latter compound was isomerised with sodium iodide in acetone to an oxazoline derivative, alkaline hydrolysis of which yielded 4-amino-1,6-anhydro-4-deoxy-*β*-D-altropyranose (**18**) The hydrochloride of **18** was prepared by treatment of 4-acetamido-1,6 2,3-dianhydro-4-deoxy-*β*-D-mannopyranose with hydrochloric acid in ethanol

INTRODUCTION

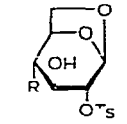
In continuing our study[1–3] of the isomerisation of *trans*-*α*-amino-oxirane derivatives of 1,6-anhydro-*β*-D-hexopyranoses into the corresponding *trans*-*α*-hydroxyaziridine derivatives, we have investigated the ammonolysis of 1,6-anhydro-2,4-di-*O*-toluene-*p*-sulphonyl-*β*-D-glucopyranose (**1**) and 1,6 3,4-dianhydro-2-*O*-toluene-*p*-sulphonyl-*β*-D-galactopyranose (**2**) Compounds **1** and **2** are readily available as potential starting materials for the preparation of some 4-amino-4-deoxy derivatives of hexoses related to naturally occurring aminodeoxy sugars[4 5] Furthermore, we report revision of some interpretations[6] of experimental data pertaining to the ammonolysis of **1**

*Syntheses with Anhydro Sugars Part XXIX For Part XXVIII, see J Pacak, M Braunova, D Štropova, and M Černy, *Collect Czech Chem Commun*, 42 (1977) 120–131

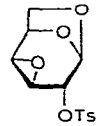
RESULTS AND DISCUSSION

Treatment of **1** or **2** with methanolic ammonia for 24 h at 100° gave, after chromatography, known[3] 1,6-anhydro-3,4-dideoxy-3,4-epimino-β-D-altropyranose (**5**) and 2,4-diamino-1,6-anhydro-2,4-dideoxy-β-D-glucopyranose[6,7] (**10**) in approximately equal amounts

The conversion of **1** → **2** with ammonia proceeds readily at room temperature, although more slowly than with sodium methoxide solution in chloroform[8] The conversion **2** → **5** involves the sequence **2** → **3** → **4** → **5** + **10** The highly regioselective reaction **2** → 4-amino-1,6-anhydro-4-deoxy-2-*O*-toluene-*p*-sulphonyl-β-D-glucopyranose (**3**) and the conversion of **3** → 4-amino-1,6:2,3-dianhydro-4-deoxy-β-D-mannopyranose (**4**) correlate with the general reactivity of **2** with other nucleophilic or electrophilic reagents[9] On treatment with ammonia, **4** partially isomerises[3] into epimine **5** and partially undergoes cleavage to give **10** T l c revealed that, in the first stages of ammonolysis of **2**, **3** and **4** are present, but gradually disappear with the simultaneous formation of **5** and **10** Authentic **3** was prepared by catalytic reduction of 1,6-anhydro-4-azido-4-deoxy-2-*O*-toluene-*p*-sulphonyl-β-D-glucopyranose[3] over palladium



1 R = OTs
3 R = NH_2



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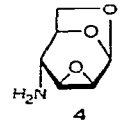

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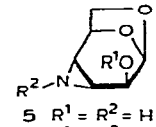
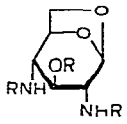
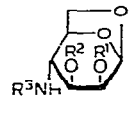


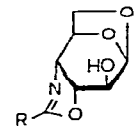
5 $R^1 = R^2 = H$
6 $R^1 = R^2 = Ac$
7 $R^1 = H$ $R^2 = Ac$
8 $R^1 = Ac$ $R^2 = H$
9 $R^1 = H$ $R^2 = Bz$



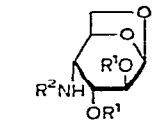
10 R = H
11 R = Ac



12 $R^1 = R^2 = R^3 = H$
13 $R^1 = R^2 = H$ $R^3 = H_2Cl$
14 $R^1 = R^2 = R^3 = Ac$
15 $R^1 = H$ $R^2 = R^3 = Ac$



16 R = Ph
17 R = Me



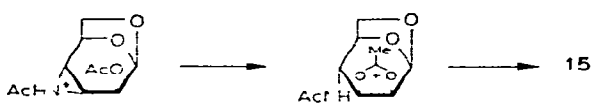
18 $R^1 = R^2 = H$
19 $R^1 = H$ $R^2 = H_2Cl$
20 $R^1 = R^2 = Ac$
21 $R^1 = H$ $R^2 = Ac$

Hydrolysis of the epimine **5** with 10% sulphuric acid at 100° yielded 4-amino-1,6-anhydro-4-deoxy-β-D-mannopyranose (**12**) isolated as the hydrochloride **13** and characterised as the triacetate **14** ^{1}H-N m r data for **13** in methyl sulphoxide established the $^1C_4$(D) conformation The presence of the amino group on C-4 is indicated by the low value (δ 3 40) of the chemical shift of H-4 The coupling constants $J_{4,5}$ 1 0, $J_{3,4}$ 1 2, and $J_{3,5}$ 1 2 Hz indicate an *eq,eq,eq* arrangement of H-3,4,5, and $J_{1,2}$ 2 0 and $J_{2,3}$ 5 4 Hz indicate an *eq,ax,eq* arrangement of H-1,2,3 The ^{1}H-n m r parameters of **13** and the $[M]_D$ value (−201° water) closely resemble those of 1,6-anhydro-β-D-mannopyranose[10] Acetylation of **13** afforded the known[11] triacetate **14**

Treatment of **5** with acetic anhydride in pyridine gave the diacetyl derivative **6**, whereas acetic anhydride in methanol gave the *N*-acetylepimine **7** Zemplén deacetylation[12] of **6** and **7** regenerated **5** The frequencies ν (N–C=O) for **6** and **7** are shifted $\sim 25\ cm^{-1}$ to higher values in comparison to those of the secondary amido groups for **14, 15,** and **20** (*cf* Ref 13)

Treatment of the diacetyl derivative **6** with a catalytic amount of hydrochloric acid in moist chloroform afforded 4-acetamido-3-*O*-acetyl-1,6-anhydro-4-deoxy-β-D-mannopyranose (**15**) in an almost quantitative yield The same compound was formed on storing a chloroform solution of **6** for several days in the presence of silica gel The D-*manno* configuration of **15** has been proved by its conversion into the triacetate **14** The position of the acetyl group at O-3 in **15** follows from the ^{1}H-n m r spectrum, which shows a downfield shift of 0 95 p p m for H-3 compared to the signal for H-3 in **13**

The formation of **15** involves protonation of **6** to give the epiminium ion **22** which rearranges into the 2-methyldioxolanylium ion **23** Regioselective cleavage[14–17] of **23** by water yields **15** Analogous reactions have been described for *O*-benzoyl derivatives of 1,6 2,3- and 1,6 3,4-dianhydro-β-D-hexopyranoses[18 19]

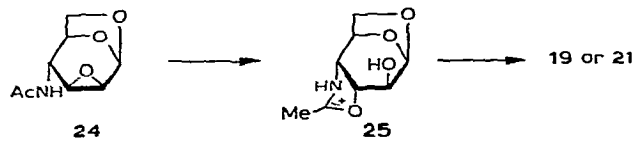


22 23

The epimine **5** readily afforded the *N*-benzoyl derivative **9**, which was isomerised by sodium iodide in acetone[20 21] to give a 90% yield of 2-phenyl-(1,6-anhydro-3,4-dideoxy-β-D-altropyrano) [4,3-*d*]-2-oxazoline (**16**) The structures of **9** and **16** were established by i r and ^{1}H-n m r spectroscopy

Alkaline hydrolysis of **16** gave the expected 4-amino-1,6-anhydro-4-deoxy-β-D-altropyranose (**18**) characterised as the hydrochloride **19** with an $[M]_D$ value (−334°, water) corresponding to those (−316°, −340°) for the hydrochlorides of 2-amino-2-deoxy[22] or 3-amino-3-deoxy derivatives[23] of 1 6-anhydro-β-D-altropyranose The ^{1}H-n m r spectrum of the triacetyl derivative (**20**) of **18** revealed the signal for H-4 to have a relatively low chemical shift, indicating the acetamido group to be at C-4, which is also verified by the disappearance of the $J_{4,NH}$ coupling on addition of deuterated acetic acid The couplings $J_{2,3}$ 9 7 and $J_{3,4}$ 5 3 Hz indicate *ax,ax* and *ax,eq* arrangements of H-2 3 and H-3 4, respectively and the D-*altro* configuration and $^1C_4$(D) conformation

An alternative route to **20** involved acid-catalysed conversion of 4-acetamido-1,6 2,3-dianhydro-4-deoxy-β-D-mannopyranose[3] (**24**) with participation of the neighbouring acetamido group (see **25**) However, the oxazoline **17** was not found in the reaction mixture and the principal, final product was 4-acetamido-1,6-anhydro-4-deoxy-β-D-altropyranose (**21**) Its structure was proved by acetylation and by hydrolysis which yielded **20** and **19**, respectively



24 25

The foregoing results indicate that the findings of Jeanloz and Rapin[6] on the ammonolysis of **1** require correction Their reaction was conducted under conditions very similar to those described herein, but the products were acetylated and subjected to chromatography on silica gel (elution with chloroform–ethyl acetate) Under these conditions, the formation of products due to acid catalysis can be anticipated Four products were described (*1*) the major product which was partially crystalline and was not further characterised (*2*) a compound {~5%, m p 203° $[\alpha]_D$ −95° (methanol)} which was identified as the 2- or 3-acetate of 4-acetamido-1 6-anhydro-4-deoxy-β-D-glucopyranose (*3*) the diamine acetate **11** (30%) and (*4*) partially crystalline material that was considered[6] to be an acetamido-1 6-anhydro-deoxy-β-D-hexopyranose

From the present study, it follows that product (*1*) contained mainly the epimine diacetate **6** Product (*2*) did not have the D-*gluco* configuration, but was 4-acetamido-3-*O*-acetyl-1 6-anhydro-4-deoxy-β-D-mannopyranose (**15**) since acetylation afforded the triacetyl derivative **14**, which was identical with an authentic sample prepared by acid hydrolysis of the epimine **5** followed by acetylation Compound **15** was formed by acid-catalysed cleavage of the diacetylepimine **6** during the isolation procedure We consider product (*4*) to be 4-acetamido-1 6-anhydro-4-deoxy-β-D-altropyranose (**21**), because on *N*-deacetylation by hydrochloric acid[6] it gave the hydrochloride **19** which in its physical properties, closely resembled the authentic sample prepared in the present work The formation of **19** by ammonolysis of **1** may be accounted for by conversion of the aminoepoxide **4** into the *N*-acetyl derivative **24** followed by acid-catalysed cleavage of the oxirane ring as described above

EXPERIMENTAL

General — Melting points were determined with a Boëtius micro melting-point apparatus and optical rotations with a Bendix–Ericsson ETL 143 A or Perkin–Elmer MC-141 polarimeter at 23–25° I r spectra were recorded with a Zeiss Jena UR 10 spectrophotometer (cell thickness 0 1 mm, unless stated o herwise), measurements of hydrogen-bonding were performed on a Unicam SP 700 spect ophotometer ^{1}H-N m r spectra [internal $(Me_3Si)_2O$] were recorded with a Varian HA-100 spectrometer Chemical shifts are given on the δ scale and are corrected for tetramethylsilane, *J* values are first-order spacings T l c was performed on Silica Gel G (Merck) with *A*, chloroform–propan-2-ol–25% ammonia–water–ethanol (20 20 2 2 1), *B*, benzene–acetone (2 1) and *C*, chloroform–methanol (10 1) Detection was effected with ninhydrin (for amines) or by charring with sulphuric acid Concentrations were conducted at <50°/~12 mmHg

*Ammonolysis of 1,6-anhydro-2,4-di-*O*-toluene-*p*-sulphonyl-β-*D*-glucopyranose* (**1**)

— A solution of **1** (1 2 g) in methanol (80 ml) saturated with ammonia at −10° was heated in a steel autoclave at 90–100° for 32 h After 3 h, t l c (solvent *A*) revealed 4-amino-1,6-anhydro-4-deoxy-2-*O*-toluene-*p*-sulphonyl-*β*-D-glucopyranose (**3**, R_F 0 59), 4-amino-1,6 2,3-dianhydro-4-deoxy-*β*-D-mannopyranose (**4**, R_F 0 46), 1,6-anhydro-3,4-dideoxy-3,4-epimino-*β*-D-altropyranose (**5**, R_F 0 31), and 2,4-diamino-1,6-anhydro-2,4-dideoxy-*β*-D-glucopyranose (**10**, R_F 0 17) As the reaction progressed, **3** and **4** gradually disappeared The mixture was concentrated to dryness, and the residue was crystallised from ethanol Sodium toluene-*p*-sulphonate was filtered off, and washed with cold ethanol, and the combined filtrates were evaporated with 2 g of silica gel and eluted from silica gel (30 g) with chloroform–propan-2-ol–25% ammonia (20 10 1) to yield a product (116 mg, 32%) that was recrystallised from ethanol–ether to give **5**[3] (78 mg, 21%), m p 147–148° (with sublimation), $[\alpha]_D$ −119° (*c* 0 56, water) Subsequent elution with chloroform–propan-2-ol–25% ammonia (10 10 1) yielded crude **10** (234 mg, 57%) containing traces of components having similar R_F values Recrystallisation from ethanol gave **10** (110 mg, 27%) m p 151–155° (dec) $[\alpha]_D$ −73° (*c* 0 95, methanol), lit [7] m p 152–155°, $[\alpha]_D$ −64° (*c* 2, methanol) The properties of the corresponding acetyl derivative **11** were in agreement with literature data[3 6 7]

*1,6 3,4-Dianhydro-2-O-toluene-*p*-sulphonyl-β-D-galactopyranose* (**2**) — A solution of **1** (300 mg) in methanol (20 ml) saturated with ammonia at −10° was stored for 30 h at room temperature and then concentrated to dryness A solution of the residue in water (15 ml) was extracted with chloroform (3 × 5 ml) The combined extracts were dried ($CaCl_2$) and concentrated to dryness, and the residue (177 mg, 93%) was recrystallised from chloroform–ethanol to give **2**[8] (134 mg, 71%), m p 149°, $[\alpha]_D$ −41° (*c* 1 35 chloroform)

4-Amino-1,6-anhydro-4-deoxy-β-D-mannopyranose (**12**) *and its hydrochloride* (**13**) — A solution of **5** (150 mg) in 5% sulphuric acid (10 ml) was heated in a sealed tube at 100° for 12 h little **5** then remained (t l c , solvent *A*) The solution was passed through a column of Dowex 50W (H^+) resin (5 g) which was washed with water to neutral reaction and then with 5% ammonia (50 ml) The ammoniacal solution was concentrated and the residue was eluted from a column of silica gel (15 g) with chloroform–propan-2-ol–25% ammonia–water–ethanol (10 10 1 1 1) to give **5** (25 mg, 17%) followed by **12** (144 mg, 85%) An ethanolic solution of **12** was treated with 7% hydrochloric acid in ethanol to give the hydrochloride **13** (136 mg 66%), m p 208–210° (dec), $[\alpha]_D$ −102° (*c* 0 75, water) ^{1}H-N m r data (100 MHz, Me_2SO-d_6) δ 3 40 ($J_{3,4}$ 1 2, $J_{4,5}$ 1 0 Hz, H-4) 3 66 ($J_{5,6exo}$ 6 2 $J_{6,6}$ 7 0 Hz H-6exo), 3 74 ($J_{1,2}$ 2 0, $J_{2,3}$ 5 4 Hz H-2), 3 90 ($J_{2,3}$ 5 4 $J_{3,4}$ 1 2 $J_{3,5}$ 1 2, $J_{1,3}$ 1 1 Hz H-3), 4 22 ($J_{5,6endo}$ 0 7, $J_{6endo,6exo}$ 7 0 Hz, H-6endo), 4 70 ($J_{4,5}$ 1 0, $J_{5,6endo}$ 0 7, $J_{5,6exo}$ 6 2, $J_{3,5}$ 1 2 Hz, H-5), and 5 25 ($J_{1,2}$ 2 0, $J_{1,3}$ 1 1 Hz, H-1)

Anal Calc for $C_6H_{12}ClNO_4$ C 36 47 H, 6 12, Cl, 17 94, N, 7 09 Found C, 37 03 H, 6 21 Cl, 17 80, N 7 51

Authentic **13** prepared[11] by ammonolysis of 1,6 3,4-dianhydro-*β*-D-talopyranose[2,4], had m p 175–180° (dec), $[\alpha]_D$ −100° (*c* 0 42, water)

4-Acetamido-2,3-di-O-acetyl-1,6-anhydro-4-deoxy-β-D-mannopyranose (**14**) — Treatment of **12** (100 mg) overnight at room temperature with pyridine (2 ml) containing acetic anhydride (0 3 ml), followed by concentration to dryness with methanol and crystallisation of the residue from ether–methanol, gave **14** (150 mg, 84%), m p 182–183°, $[\alpha]_D$ −84° (*c* 0 48, chloroform), −64° (*c* 0 6, methanol), $\nu_{max}^{CHCl_3}$ 3442 (NH), 1754 (O–C=O), 1682, and 1505 cm^{-1} (N–C=O)

Authentic **14**, prepared[11] by acetylation of **13**, had m p 182°, $[\alpha]_D$ −82° (*c* 0 48 chloroform)

Treatment of **15** (80 mg) with acetic anhydride (0 2 ml) and pyridine (1 ml) also gave **14** (89 mg, 95%), m p 181–183°, $[\alpha]_D$ −82° (*c* 0 88 chloroform)

Acetylation of 1,6-anhydro-3,4-dideoxy-3,4-epimino-β-D-altropyranose (**5**) — (*a*) To a solution of **5** (0 2 g) in pyridine (5 ml) was added acetic anhydride (0 3 ml), and the solution was left at room temperature for 20 h T l c (solvent *B*) then showed two spots having R_F 0 56 (main product) and 0 18 The mixture was treated with methanol (2 ml) and chloroform (5 ml), and extracted with aqueous 5% sodium hydrogen carbonate (10 ml) The water layer was re-extracted with chloroform (2 × 5 ml), and the combined chloroform solutions were dried ($MgSO_4$) and concentrated The residue was eluted from a column of silica gel (10 g) with benzene–acetone (5 1) to give first syrupy *N*-acetyl-2-*O*-acetyl-3 4-dideoxy-3 4-epimino-β-D-altropyranose (**6** 220 mg 70%), $[\alpha]_D$ −82° (*c* 0 95 chloroform), $\nu_{max}^{CHCl_3}$ 1745 (O–C=O) and 1710 cm^{-1} (N–C=O) ^{1}H-N m r data (Me_2SO-d_6) δ 2 09 (6 H, NAc and OAc), 2 58 ($J_{1,3}$ 2 0, $J_{2,3}$ ~0 $J_{3,4}$ 6 0 Hz, H-3), 2 88 ($J_{3,4}$ 6 0, $J_{4,5}$ 0 9, $J_{2,4}$ <0 2 Hz, H-4), 3 71 ($J_{1,6exo}$ <0 2, $J_{5,6exo}$ 4 4, $J_{6exo,6endo}$ 7 6 Hz, H-6exo), 4 05 ($J_{1,6endo}$ <0 2, $J_{5,6endo}$ 0 6, $J_{6endo,6exo}$ 7 6 Hz H-6endo), 4 68 ($J_{1,2}$ 3 0 $J_{2,3}$ ~0, $J_{2,4}$ <0 3 Hz, H-2) 4 81 ($J_{4,5}$ 0 9 $J_{5,6endo}$ 0 6 $J_{5,6exo}$ 4 4 Hz, H-5) and 5 29 ($J_{1,2}$ 3 0, $J_{1,3}$ 2 0, $J_{1,6endo}$ <0 2, $J_{1,6exo}$ <0 2 Hz, H-1)

Anal Calc for $C_{10}H_{13}NO_5$ C 52 86 H 5 77 N 6 17 Found C, 53 59 H, 6 14 N 6 49

Further 4-acetamido-3-*O*-acetyl-1 6-anhydro-4-deoxy-β-D-mannopyranose (**15** 37 mg 11%) was obtained, after crystallisation from methanol–acetone–light petroleum **15** gave material (27 mg, 8%), m p 193° (sublimation), $[\alpha]_D$ −102° (*c* 0 78, methanol) which was identical with the authentic sample prepared from the diacetylepimine **6** by the action of hydrochloric acid (see below)

(*b*) Epimine **5** (0 6 g) was treated with acetic anhydride (1 6 ml) in pyridine (10 ml) at room temperature for 2 h The solution was poured into water (100 ml) and the mixture was left overnight Extraction with an equal amount of benzene yielded **6** (~0 28 g) The aqueous solution was concentrated to dryness and the residue was eluted from a column of neutral silica gel (50 g Woelm) with benzene–acetone (85 15 and 70 30) to give **6** (0 2 g), followed by the *O*-acetylepimine **8** (80 mg) which was not pure and changed slowly, $\nu_{max}^{CHCl_3}$ 3320, 3280 (NH), and 1740 cm^{-1} (O–C=O) ^{1}H-N m r data (Me_2SO-d_6) δ 1 86 (m, H-3), 2 06 (3 H, OAc), ~2 20 (not separated, H-4), 3 70 ($J_{6exo,1}$ <0 3, $J_{6exo,5}$ 4 2, $J_{6exo,6endo}$ 7 0 Hz, H-6exo), 4 03 ($J_{6endo,1}$ <0 3, $J_{6endo,5}$ ~0 5, $J_{6endo,6exo}$ 6 8 Hz, H-6endo), 4 54 ($J_{2,1}$ 3 0, $J_{2,3}$ ~0 2 Hz, H-2),

4 64 ($J_{5\,6exo}$ 4 2, $J_{5\,6endo}$ ~0 5, $J_{5\,4}$ 0 9 Hz, H-5), and 5 22 ($J_{1\,2}$ 2 8, $J_{1\,3}$ 1 7 Hz, H-1) Traces of the *N*-acetylepimine **7** were also found

*N-Acetyl-1,6-anhydro-3,4-dideoxy-3,4-epimino-β-*D*-altropyranose* (**7**) — To a solution of **5** (100 mg) in methanol (2 ml) was added acetic anhydride (0 1 ml) After 1 h at room temperature, the solution was kept in a refrigerator overnight The crystals (113 mg, 87%) were collected, washed with light petroleum, and recrystallised from methanol–ether to give **7**, m p 171–173° (sublimation), $[\alpha]_D$ −102° (*c* 0 62, water), ν_{max}^{Nujol} 3100–3500 (OH) and 1660 cm^{-1} (N–C=O), $\nu_{max}^{CHCl_3}$ 3565 (OH) and 1705 cm^{-1} (N–C=O), $\nu_{max}^{CCl_4}$ 3566 cm^{-1} (OH O intramolecular) ^{1}H-N m r data (Me_2SO-d_6) δ 2 06 (3 H, NAc), 2 43 ($J_{3\,2}$ <0 5, $J_{3\,4}$ 6 2, $J_{3\,1}$ 2 0, $J_{3\,5}$ ~0 3 Hz, H-3), 2 82 ($J_{4\,3}$ 6 0, $J_{4\,5}$ 1 0, $J_{4\,2}$ <0 3 Hz, H-4), 3 67 ($J_{6exo\,5}$ 5 0, $J_{6exo\,6endo}$ 7 35 Hz, H-6exo), 3 67 ($J_{2\,1}$ ~3 0, $J_{2\,OH}$ ~7 0 Hz, H-2), 3 98 ($J_{6endo\,5}$ 0 6, $J_{6endo\,6exo}$ 7 25, $J_{6endo\,1}$ ~0 3 Hz, H-6endo), 4 75 ($J_{5\,6exo}$ 4 3 Hz, H-5), 5 11 ($J_{1\,2}$ ~2 9, $J_{1\,3}$ ~2 0, $J_{1\,6endo}$ ~0, $J_{1\,6exo}$ ~0 Hz, H-1), and 5 23 ($J_{OH,2}$ 6 95 Hz, OH)

Anal Calc for $C_8H_{11}NO_4$ C, 51 88, H, 5 99, N, 7 57, Found C, 52 16, H, 6 11, N, 7 87

*4-Acetamido-3-*O*-acetyl-1,6-anhydro-4-deoxy-β-*D*-mannopyranose* (**15**) — To a solution of **6** (270 mg) in chloroform (25 ml, saturated with water) was added ethanolic 5% hydrogen chloride (6 drops) at room temperature The reaction was monitored by t l c (solvent *B*, R_F 0 18 for **15**) After ~20 min, the solution was concentrated to dryness and the residue was treated with ether Recrystallisation of the product from methanol–ether gave **15** (282 mg, 96%), m p 191–193° (203–205° in a sealed capillary), $[\alpha]_D$ −101° (*c* 0 81, methanol), −62° (*c* 0 82, water), ν_{max}^{Nujol} 3350 (NH), 3200–3400 (OH), 1725 (O–C=O), 1640, and 1545 cm^{-1} (N–C=O) ^{1}H-N m r data (Me_2SO-d_6) δ 1 87 (3 H, NAc), 2 04 (3 H, OAc), 3 62 ($J_{6exo\,1}$ ~0, $J_{6exo\,5}$ 5 8, $J_{6exo\,6endo}$ 7 6 Hz, H-6exo), 3 71 ($J_{2\,1}$ 1 9, $J_{2\,3}$ 5 5, $J_{2\,OH}$ 8 3 Hz, H-2), 3 89 ($J_{4\,1}$ ~0, $J_{4\,3}$ ~1 4, $J_{4\,5}$ ~1 4, $J_{4\,NH}$ 8 0 Hz, H-4), 4 11 ($J_{6endo\,1}$ <0 2, $J_{6endo\,5}$ ~0 8, $J_{6endo\,6exo}$ 7 2 Hz, H-6endo), 4 34 ($J_{5\,4}$ ~1 4, $J_{5\,6exo}$ 5 8, $J_{5\,6endo}$ ~0 8 Hz, H-5), 4 85 ($J_{3\,2}$ 5 3, $J_{3\,4}$ ~1 4, $J_{3\,1}$ ~1 2, $J_{3\,5}$ ~1 4 Hz, H-3), 4 98 ($J_{OH\,2}$ 8 1 Hz, OH), 5 22 (w/2 3 6 Hz, H-1), and 8 21 ($J_{NH\,4}$ 8 0 Hz, NH)

Anal Calc for $C_{10}H_{15}NO_6$ C, 48 97, H, 6 17, N, 5 71 Found C, 49 25, H, 6 33, N, 6 09

*1,6-Anhydro-*N*-benzoyl-3 4-dideoxy-3,4-epimino-β-*D*-altropyranose* (**9**) — To a solution of **5** (500 mg) in aqueous 5% sodium hydrogen carbonate (25 ml) at 0° was added benzoyl chloride (0 5 ml) in three portions with vigorous shaking The mixture was shaken for a further 5 min, and then extracted with chloroform (3 × 10 ml) The combined organic layers were dried ($MgSO_4$), and concentrated to dryness Recrystallisation of the residue from ethanol gave **9** (827 mg, 96%), m p 137–138°, $[\alpha]_D$ −113° (*c* 0 63, chloroform), $\nu_{max}^{CHCl_3}$ 3550 (OH) and 1678 cm^{-1} (N–C=O) ^{1}H-N m r data (Me_2SO-d_6) δ 2 59 ($J_{3\,4}$ 6 2, $J_{3\,1}$ 1 9 Hz, H-3), 2 99 ($J_{4\,3}$ 6 0, $J_{4\,5}$ ~0 9 Hz, H-4), 3 72 ($J_{6exo\,5}$ 4 4, $J_{6exo\,6endo}$ 7 2 Hz, H-6exo), 3 87 ($J_{2,1}$ 3 0, $J_{2,3}$ <0 3 Hz, H-2), 4 02 ($J_{6endo,5}$ <0 5, $J_{6endo,6exo}$ 7 0 Hz, H-6endo), 4 84 ($J_{5\,6exo}$

~4 2 Hz, H-5), 5 21 ($J_{1,2}+J_{1,3}$ ~4 6 Hz, H-1), 7 40–7 72 (3 H, aromatic), and 7 84–8 05 (2 H, aromatic)

Anal Calc for $C_{13}H_{13}NO_4$ C, 63 15, H, 5 30, N, 5 66 Found C, 63 11 H, 5 38, N, 6 09

*2-Phenyl-(1,6-anhydro-3,4-dideoxy-β-*D*-altropyrano)-[4,3-*d*]-2-oxazoline* (**16**) — A mixture of **9** (500 mg), sodium iodide (3 g) and acetone (20 ml) was heated in a sealed tube at 100° for 8 h, and then concentrated to dryness The residue was extracted with ethyl acetate (3 × 10 ml) Concentration of the combined extracts and recrystallisation of the residue from ethanol gave **16** (430 mg, 86%) m p 225° (sublimes at 150°) $[\alpha]_D$ −90° (*c* 0 53, methanol) ν_{max}^{KBr} 3385, 3195 (OH) 1640 (C=N), 1603 1580, 1497, and 1452 cm^{-1} (aromatic ring) ^{1}H N m r data (Me_2SO-d_6) δ 3 36 ($J_{2,3}$ 5 3, $J_{2,4}$ <0 5 Hz, H-2), 3 73 ($J_{6exo,5}$ 5 3, $J_{6exo,6endo}$ 7 7 $J_{6exo,1}$ <0 2 Hz, H-6exo), 3 89 ($J_{6endo,5}$ 1 0, $J_{6endo,6exo}$ 7 7, $J_{6endo,1}$ <0 2 Hz H-6endo), 4 27 ($J_{4,5}$ ~1 0, $J_{4,3}$ 9 5, $J_{4,2}$ <0 5 Hz H-4), 4 73 ($J_{3,4}$ 9 5, $J_{3,2}$ 5 3 $J_{3,1}$ <0 2 Hz H-3), 4 94 ($J_{5,4}$ ~1 0 $J_{5,6endo}$ 1 0 $J_{5,6exo}$ 5 3 Hz, H-5), and 5 20 ($J_{1,2}$ 2 6, $J_{1,3}$ <0 2 Hz H-1)

Anal Calc for $C_{13}H_{13}NO_4$ C 63 15, H 5 30 N 5 66 Found C 62 88 H, 5 36, N, 6 17

*4-Amino-1,6-anhydro-4-deoxy-β-*D*-altropyranose* (**18**) *and its hydrochloride* **19** — A suspension of finely powdered **16** (250 mg) in aqueous 5% potassium hydroxide (15 ml) was heated in a sealed tube at 90–110° for 24 h with occasional shaking The hydrolysis was monitored by t l c (solvent *C*) The solution was then added to a column of Dowex 50W (H^+) resin and eluted with distilled water (500 ml) Elution with 5% ammonia gave **18**, which was recrystallised twice from methanol to give material (31 mg 19%) m p 162–163° $[\alpha]_D$ −203° (*c* 0 34 water) The combined mother liquors were neutralised with ethanolic 7% hydrochloric acid, and then concentrated to give **19** (81 mg, 45%) m p 190–230° (dec), $[\alpha]_D$ −169° (*c* 0 51 water) lit [6] for an unspecified 1 6-anhydro-aminodeoxy-β-D-hexopyranose hydrochloride, m p 221–225°, $[\alpha]_D$ −169 (*c* 1 1, water) ^{1}H-N m r data (Me_2SO-d_6) δ 3 40–3 90 (m, H-2 3 4 6endo,6exo), 4 83 ($J_{5,6exo}$ 5 5 Hz, H-5), and 5 23 ($J_{1,2}$ 1 3 Hz, H-1)

Anal Calc for $C_6H_{12}ClNO_4$ C 36 47 H, 6 12 Cl, 17 94 N, 7 09 Found C 36 80, H, 6 11, Cl, 18 06, N, 7 36

Compound **24**[3] {50 mg m p 145-149° (sublimes) $[\alpha]_D$ −29° (*c* 2, chloroform)} was heated with ethanol (2 ml) containing 6M hydrochloric acid (0 15 ml) in a sealed tube for 40 min at 100° The mixture was diluted with benzene and concentrated and an ethanolic solution of the residue was decolourised with charcoal, filtered, and concentrated Recrystallisation of the residue from ethanol gave **19** (32 mg, 60%) which was identical with the authentic sample described above

*4-Acetamido-2,3-di-*O*-acetyl-1,6-anhydro-4-deoxy-β-*D*-altropyranose* (**20**) — (*a*) Hydrochloride **19** (35 mg) was treated with acetic anhydride (3 ml) and anhydrous sodium acetate (0 2 g) at ~100° for 30 min Water (5 ml) and methanol (1 ml) were added to the cooled mixture which was concentrated to dryness A solution of the residue in methanol was concentrated and a solution of the residue in water (2 ml)

was extracted with chloroform (3 × 3 ml) The combined extracts were dried ($MgSO_4$), filtered, and concentrated to give **20** (47 mg, 92%), $[\alpha]_D$ −114° (*c* 0 53, chloroform), $\nu_{max}^{CHCl_3}$ 3443 (NH), 1748 (O–C=O), 1684, and 1510 cm^{-1} (N–C=O) ^{1}H-N m r data ($CDCl_3$) δ 1 99 (OAc), 2 05 (NAc), 2 10 (OAc), 3 83 ($J_{6exo\ 5}$ 5 4, $J_{6exo\ 6endo}$ 8 3 Hz, H-6exo), 4 03 ($J_{6endo\ 5}$ 0 8, $J_{6endo,6exo}$ 8 3 Hz, H-6endo), 4 57 ($J_{5,4}$ ~2 0, $J_{5\ 6endo}$ 0 8, $J_{5\ 6exo}$ 5 4 Hz, H-5), 4 64 ($J_{4,5}$ ~2 0, $J_{4,3}$ 5 3 $J_{4,NH}$ 8 0 Hz, H-4), 4 87 ($J_{2\ 3}$ 9 7, $J_{2\ 1}$ 1 5 Hz, H-2), 5 23 ($J_{3\ 4}$ 5 3, $J_{3\ 2}$ 9 7 Hz, H-3), and 6 21 ($J_{NH\ 4}$ ~8 0 Hz, NH)

(*b*) To a solution of **24**[3] (100 mg) in chloroform (10 ml) saturated with water, ethanolic 5% hydrochloric acid (0 4 ml) was added The mixture was left overnight with occasional shaking neutralised with a suspension of Amberlite IR-45 (HO^-) resin in ethanol and concentrated Residual crude **21** was dried over phosphorus pentaoxide and then acetylated as described in (*a*) to give syrupy **20** (135 mg 87%), $[\alpha]_D$ −112° (*c* 0 5 chloroform) Its identity with the authentic sample in (*a*) was proved by i r spectroscopy and g l c

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