PREPARATION OF BRANCHED-CHAIN NITRO AND AMINO SUGARS BY APPLICATION OF THE NITROMETHANE METHOD TO KETOSES[1]

GERHARDUS J. LOURENS

National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, Pretoria (South Africa)

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ABSTRACT

The addition of nitromethane to 1,2-*O*-isopropylidene-5-*O*-trityl-α-D-*erythro*-pentofuranos-3-ulose (**1**) and to the corresponding 5-*O*-*p*-tolylsulfonyl compound **2** to give branched-chain sugars **3** and **4** is described. The D-*ribo* configuration for **4** was established by reduction, followed by acetylation, to give 3-*O*-acetyl-5,1′-acetyl-epimino-5-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-D-ribofuranose (**5**). Acetylation of **3** and **4**, followed by base-catalyzed elimination of acetic acid, gave the corresponding nitro-olefins **9** and **8** (not isolated). Reduction of **8** with sodium borohydride readily gave 3-deoxy-1,2-*O*-isopropylidene-3-*C*-nitromethyl-5-*O*-*p*-tolylsulfonyl-α-D-ribofuranose (**10**). Catalytic hydrogenation of **10**, followed by benzoylation, gave the 3-*C*-benzamidomethyl compound **12** in 78% yield. 3-*C*-Acetamidomethyl-5-*O*-acetyl-3-deoxy-1,2-*O*-isopropylidene-α-D-ribofuranose (**13**) was similarly prepared from the nitro-olefin **9**. The 3-deoxy-D-*ribo* configuration for compounds **10**, **11**, **12**, and **13** was established by n.m.r. spectroscopy.

INTRODUCTION

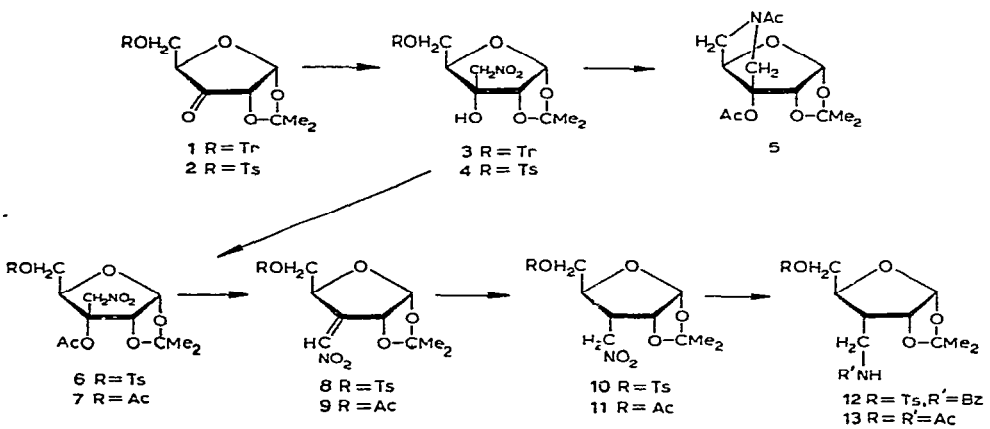
In recent years, several investigators have shown considerable interest in the chemical synthesis of various branched-chain carbohydrates[2,3]. Several methods for such syntheses have been developed which utilise oxo sugars as intermediates. These include the condensation of an appropriate oxo sugar with Grignard reagents[2,4,5], organolithium compounds[2,4], diazomethane[6], sulfur ylids[7], and phosphoranes[8,9].

Relatively few branched-chain amino sugars have been synthesized. The classical sugar dialdehyde–nitromethane route[10] for the synthesis of amino sugars has been modified[11a,b] by using nitroethane to give branched-chain, aminodeoxy sugars, where branching is on the carbon atom bearing the amino group. A branched chain could also be introduced into a nitrogenous, oxo sugar on a carbon atom not bearing the amino group[11c]. In addition, a recent method[9] described the synthesis of branched-chain, deoxy sugars containing a nitrile or an amino group on the branched chain. The addition of nitryl iodide to a branched-chain unsaturated sugar led to the synthesis of a branched-chain nitro sugar[12a], whereas Michael addition of nitroalkanes to unsaturated nitro sugars gave branched-chain dinitro sugar

derivatives[12b]. As has been described in a preliminary communication[1], the nitromethane method[10] has now been applied to oxo sugars to give branched-chain sugars having a nitro group on the branch. These could be readily converted into branched-chain, deoxy sugars containing a nitro or amino group on the branched chain. The method led to the direct introduction of a functionalized, one-carbon branch into carbohydrates. Recent reports[13] indicated that the nitromethane method has also been utilized independently in other laboratories to synthesize branched-chain carbohydrates.

RESULTS AND DISCUSSION

A suspension of the sodium salt of nitromethane in nitromethane was prepared by the careful addition of sodium hydride to nitromethane. Treatment of 1,2-*O*-isopropylidene-5-*O*-trityl-α-D-*erythro*-pentofuranos-3-ulose[14] (**1**) in nitromethane with this suspension gave compound **3** in 76% yield (after recrystallization). Similarly, **4** was prepared from the unpurified, oxo sugar[15] **2**, which was obtained by oxidation of 1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-xylofuranose[16] with methyl sulfoxide–acetic anhydride. The n.m.r. spectra of both **3** and **4** (see Experimental) showed the presence of an exchangeable proton (3-OH) and an AB quartet of the two methylene protons on C-1′. The presence of a nitro group in these two structures was indicated by their infrared spectra.



Although it was expected that the 1,2-*O*-isopropylidene group would control the addition sterically, the fact that **4** had the D-*ribo* configuration was deduced from the following evidence. Reduction with hydrogen over palladium-on-charcoal, and subsequent acetylation of the product obtained, gave crystalline 3-*O*-acetyl-5,1′-acetylepimino-5-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-D-ribofuranose (**5**), in 43% overall yield. The infrared spectrum of **5** showed bands at 1745 (ester C=O) and 1640 cm^{-1} (amide C=O), and the absence of a band at 1300–1400 cm^{-1} (SO_2). Structure **5** was further supported by elemental analyses and by mass-spectral data.

For this intramolecular displacement of the 5-*p*-tolylsulfonyl group, **4** must have had the D-*ribo* configuration.

The n.m.r. spectrum of **5** (see Fig. 1) in deuteriochloroform at room temperature was unusually complex, and suggested the presence of two isomers. Two pairs of overlapping doublets were present at τ 4.09 and 4.14 and at τ 4.99 and 5.05. In addition, there was a broadened, one-proton triplet at τ 5.40 and a four-proton multiplet at 5.92–6.57. The four signals at τ 7.90, 7.94, 7.98, and 8.02 could be assigned to the acetyl protons, and the isopropylidene methyl protons appeared as singlets at τ 8.50 and 8.68. However, in methyl sulfoxide-d_6, the ratio of the rotational isomers was significantly changed (see Fig. 2). This showed two doublets at τ 4.04 and 5.01 for H-1 and H-2, respectively, a broadened triplet at 5.41, a four-proton multiplet at 6.10–6.75, and three signals in the acetyl region at 7.95, 8.07, and 8.10. The isopropylidene methyl protons showed signals at τ 8.55, 8.61, and 8.73. At 100°, the acetyl signals collapsed into two signals at τ 7.95 and 8.08, while the methyl groups showed only two signals at 8.53 and 8.70. At this temperature, considerable broadening of the other signals was observed. The solvent and temperature dependence of the n.m.r. spectrum of **5** demonstrated the presence of two isomers in solution. Such isomerism, due to restricted rotation about the C–N bond, is expected from carbohydrates containing a nitrogen atom in the ring[17].

Acetylation of **4** with acetic anhydride and *p*-toluenesulfonic acid at room temperature gave **6** in 90% yield. Similar treatment of **3** not only acetylated the 3-hydroxyl group, but also caused acetolysis of the 5-trityl ether to give 3,5-di-*O*-acetyl-1,2-*O*-isopropylidene-3-*C*-nitromethyl-α-D-ribofuranose (**7**) in 95% yield.

β-Acetoxynitroalkanes are useful precursors for the synthesis of α-nitro-olefins, since they easily undergo base-catalyzed elimination of acetic acid[18]. Treatment of both **6** and **7** with anhydrous potassium carbonate in dry benzene readily afforded the corresponding nitro-olefins of uncertain structures. Without further purification, these nitro-olefins, which probably have structures **8** and **9**, respectively, were reduced with sodium borohydride in aqueous acetonitrile[19]. The corresponding, branched-chain, deoxy sugars **10** and **11** were obtained in good overall yields. As expected, the 1,2-*O*-isopropylidene group again controlled the reaction sterically. The configuration at C-3 of both **10** and **11** was deduced from their 100-MHz n.m.r. spectra. The n.m.r. spectrum of **10** showed a one-proton doublet at τ 4.24 (H-1), and a one-proton triplet at 5.22 (H-2); similarly, the n.m.r. spectrum of **11** showed a doublet at 4.14 and a triplet at 5.19 (see Experimental). The H-2 signal was a triplet in each case, showing that it was also coupled to H-3, and since there was no coupling between H-2 and H-3 in 1,2-*O*-isopropylidene-α-D-xylofuranose[20], C-3 must have had the deoxy D-*ribo* configuration.

Reduction of **10** with hydrogen over platinum, followed by benzoylation of the amine, gave the crystalline benzamido compound **12** in 78% yield. If **10** had the deoxy D-*xylo* configuration at C-3, one would expect the occurrence of an intramolecular displacement of the 5-*O*-*p*-tolylsulfonyl group, as was the case in the reduction of **4** to form **5**. Similarly, reduction of **11**, followed by acetylation, gave **13**

as a syrup in 82% yield. The n.m.r. spectra of both **12** and **13** confirmed the deoxy D-*ribo* configuration at C-3 (see Experimental).

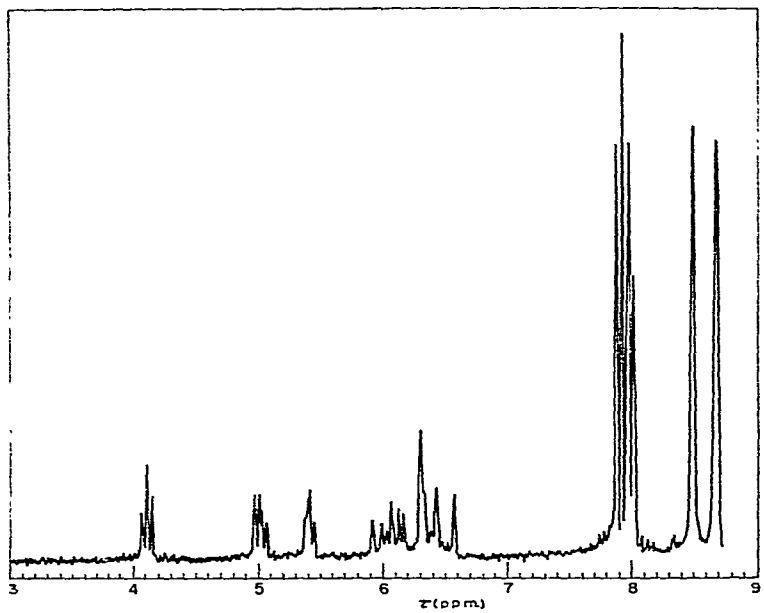


Fig. 1. The n.m.r. spectrum of 3-*O*-acetyl-5,1′-acetylepimo-5-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-D-ribofuranose (**5**) at 100 MHz in chloroform-*d*.

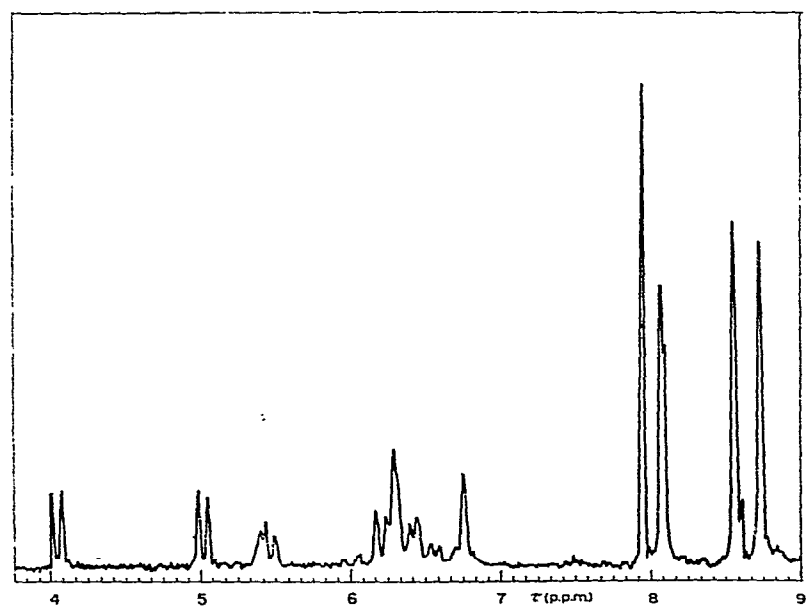


Fig. 2. The n.m.r. spectrum of 3-*O*-acetyl-5,1′-acetylepimino-5-deoxy-1,2-*O*-isopropylidene-3-*C*-methyl-α-D-ribofuranose (**5**) at 60 MHz in methyl sulfoxide-d_6

The series of reactions described above represents the synthesis of functionalized, branched-chain, deoxy sugars from a branched-chain sugar, with inversion of configuration at the point of branching; the inversion is achieved by the steric influence of the 1,2-*O*-isopropylidene group.

EXPERIMENTAL

General methods. — Melting points were determined in capillaries with a Gallenkamp apparatus. I.r. spectra were measured with a Perkin–Elmer Model 237 i.r. spectrophotometer. N.m.r. spectra were measured at 60 or 100 MHz with Varian A-60 or HA-100 n.m.r. spectrometers. Chemical shifts are given on the τ scale with tetramethylsilane as internal standard for chloroform-*d* or methyl sulfoxide-d_6 solutions. Optical rotations were measured at room temperature with a Bendix-NPL Automatic Polarimeter Type 143. Mass spectra were determined with an A.E.I. MS-9 spectrometer, using the direct-insertion technique and an ionizing voltage of 70 eV. T.l.c. was performed on silica gel GF_{254} (Merck), and spots were detected either under an ultraviolet lamp or with iodine vapour.

1,2-O-Isopropylidene-3-C-nitromethyl-5-O-trityl-α-D-ribofuranose (**3**). — To a magnetically stirred solution of 2.15 g (5 mmoles) of 1,2-*O*-isopropylidene-5-*O*-trityl-α-D-*erythro*-pentofuranos-3-ulose[14] (**1**) in 15 ml of nitromethane, cooled in a dry-ice bath below −20°, was added dropwise, over 5 min, a suspension of sodium hydride (50% dipersion in oil, 0.29 g, 6 mmoles) in 15 ml of nitromethane. After being stirred at room temperature for 1 h, the mixture was neutralized dropwise with glacial acetic acid. The solvent was evaporated *in vacuo*, water (100 ml) was added to the residue, and the mixture was extracted with chloroform (2 × 50 ml). The chloroform solution was washed with water (50 ml), dried (sodium sulfate), and evaporated to a syrup which crystallized on standing. Recrystallization from acetone–hexane gave **3**; yield 1.88 g (76%), m.p. 120–121.5°; $[\alpha]_D^{23}$ +28.6° (*c* 1.20, chloroform); $\nu_{max}^{CHCl_3}$ 3540 (OH), 1560 cm^{-1} (NO_2); n.m.r. data (60 MHz): τ 3.98 (H-1, doublet, $J_{1,2}$ 4.0 Hz); 5.13 (H-2, doublet); 5.88 (H-4, triplet, $J_{4,5}$ 5 Hz); 6.68 (H-5, multiplet); 5.59 (CH_2NO_2, quartet, $J_{a,b}$ 12.5 Hz); 8.40,8.60 (CMe_2, 2 singlets); 6.83 (OH-singlet, lost on addition of D_2O); *m/e* 491.

Anal. Calc. for $C_{28}H_{29}NO_7$: C, 68.42; H, 5.95; N, 2.85. Found: C, 68.42; H, 5.97; N, 2.45.

1,2-O-Isopropylidene-3-C-nitromethyl-5-O-p-tolylsulfonyl-α-D-ribofuranose (**4**). — A solution of 10.4 g (30 mmoles) of 1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-xylofuranose[16] and acetic anhydride (16 ml) in methy sulfoxide (60 ml) was kept at ambient temperature for 65 h, and then poured into a magnetically stirred mixture of sodium hydrogen carbonate (210 g) in water (2.4 l). After being stirred for 45 min, the mixture was extracted with chloroform (4 × 400 ml), and the chloroform solution was washed with water (1 litre), dried (magnesium sulfate), and evaporated to a syrup (10.5 g) containing the oxo sugar[15] **2**. To a magnetically stirred solution of this syrup in nitromethane (125 ml), cooled in a dry-ice bath below −20°, was added slowly

(10 min) a suspension prepared from sodium hydride (50% dispersion in mineral oil, 1.73 g, 36 mmoles) in 50 ml of nitromethane. After being stirred at room temperature for 1 h, the mixture was neutralized dropwise with glacial acetic acid and then treated as for the isolation of **3**. Recrystallization from methanol–water gave **4**; yield 5.59 g (45% overall), m.p. 131.5–132°, $[\alpha]_D^{23}$ +28.7° (*c* 1.23, chloroform); $\nu_{max}^{CHCl_3}$ 3550 (OH), 1615 (C=C), 1570 cm^{-1} (NO_2); n.m.r. data (60 MHz): τ 4.14 (H-1, doublet, $J_{1,2}$ 4.0 Hz); 5.17 (H-2, doublet); 5.78 (H-4, triplet, $J_{4,5}$ 4.0 Hz); 5.83 (H-5, multiplet); 5.46 (CH_2NO_2, quartet, $J_{a,b}$ 12.5 Hz); 8.45,8.61 (CMe_2, 2 singlets); 6.67 (OH-singlet, broad; lost on addition of D_2O); *m/e* 388 ($M^+ - 15$).

Anal. Calc. for $C_{16}H_{21}NO_9S$: C, 47.63; H, 5.25; N, 3.47. Found: C, 47.87; H, 5.27; N, 3.44.

3-O-Acetyl-5,1'-acetylepimino-5-deoxy-1,2-O-isopropylidene-3-C-methyl-α-D-ribofuranose (**5**). — A mixture of **4** (605 mg, 1.5 mmoles) and 10% palladium-on-charcoal (300 mg) in absolute ethanol (50 ml) was magnetically stirred under positive hydrogen pressure for 5 h, during which time the calculated amount of hydrogen was taken up. The mixture was filtered through a Celite pad, and the filtrate was evaporated to give a solid (514 mg). To this was added pyridine (5 ml) and acetic anhydride (4 ml), and the mixture was stirred at room temperature for 2.5 h, poured into 50 ml of ice–water, and extracted with chloroform (2 × 50 ml). The dried (sodium sulfate) chloroform solution was evaporated to give 310 mg of an oil which crystallized on standing. Two recrystallizations from acetone–hexane gave **5**, which moved as a single spot on t.l.c (ethyl acetate–hexane, 2:1); yield 185 mg (43%), m.p. 173–174°, $[\alpha]_D^{23}$ +87.1° (*c* 1.13, chloroform); $\nu_{max}^{CHCl_3}$ 1745 (ester C=O), 1640 cm^{-1} (amide C=O); *m/e* 270 ($M^+ - 15$).

Anal. Calc. for $C_{13}H_{19}NO_6$: C, 54.71; H, 6.71; N, 4.91. Found: C, 55.15; H, 6.57; N, 4.91.

3-O-Acetyl-1,2-O-isopropylidene-3-C-nitromethyl-5-O-p-tolylsulfonyl-α-D-ribofuranose (**6**). — A solution of **4** (1.01 g, 2.5 mmoles) and anhydrous *p*-toluenesulfonic acid (200 mg) in 6 ml of acetic anhydride was magnetically stirred at room temperature for 4.5 h. The solution was then added dropwise to a stirred mixture of sodium hydrogen carbonate (12 g) in 100 ml of water. After being stirred for 30 min, the aqueous layer was decanted, and the gummy residue was dissolved in chloroform (100 ml). The chloroform solution was washed with water (50 ml), dried (sodium sulfate), and evaporated to a syrup which moved as a single spot on t.l.c. (hexane–ethyl acetate, 2:1); yield 1.05 g (90%); $\nu_{max}^{CHCl_3}$ 1760 (OAc), 1615 (C=C), 1570 cm^{-1} (NO_2); n.m.r. data (60 MHz): τ 4.20 (H-1, doublet, $J_{1,2}$ 4.0 Hz); 4.90 (H-2, doublet); 5.41–5.78 (3-proton multiplet, H-4, H-5); 5.13 (CH_2NO_2, quartet, $J_{a,b}$ 12.5 Hz); 7.88 (Ac, singlet); 8.48,8.65 (CMe_2, 2 singlets).

Anal. Accurate determination of mass by mass spectrometry on base peak $M^+ - 15$: calc. for $C_{17}H_{20}NO_{10}S$: 430.080; found: 430.079.

3,5-Di-O-acetyl-1,2-O-isopropylidene-3-C-nitromethyl-α-D-ribofuranose (**7**). — A solution of **3** (1.23 g, 2.5 mmoles) and anhydrous *p*-toluenesulfonic acid (200 mg) in 10 ml of acetic anhydride was magnetically stirred at room temperature for 15 h.

The solution was slowly poured into a stirred solution of sodium hydrogen carbonate (30 g) in 200 ml of water. After being stirred for 30 min, the aqueous layer was decanted, and the gummy residue was dissolved in chloroform (100 ml). The chloroform solution was washed with water (100 ml), dried (sodium sulfate), and evaporated to gummy solid which moved as two spots on t.l.c. (benzene). This was applied to a column of silica gel and eluted with benzene and then with 5% methanol in benzene (monitoring by t.l.c.). The second fraction gave homogeneous (t.l.c.) **7** as a light-yellow syrup; yield 0.79 g (95%); $\nu_{max}^{CHCl_3}$: 1760 (OAc), 1570 cm^{-1} (NO_2); n.m.r. data (100 MHz): τ 4.22 (H-1, doublet, $J_{1,2}$ 4.0 Hz); 4.92 (H-2, doublet); 5.42–5.84 (3-proton multiplet, H-4,H-5); 5.14 (CH_2NO_2, quartet, $J_{a,b}$ 13.0 Hz); 8.48,8.68 (CMe_2, 2 singlets); 7.91,7.96 (Ac, 2 singlets).

Anal. Accurate determination of mass by mass spectrometry on base peak $M^+ - 15$: calc. for $C_{12}H_{16}NO_9$: 318·27; found: 318·8.

3-Deoxy-1,2-O-isopropylidene-3-C-nitromethyl-5-O-p-tolylsulfonyl-α-D-ribofuranose (**10**). — To a solution of **6** (2.1 g, prepared from 5 mmoles of **4**) in 25 ml of dry benzene was added powdered potassium carbonate (1.04 g, 7.5 mmoles), and the suspension was magnetically stirred at room temperature for 4.5 h. The mixture was filtered through a Celite pad, and the yellow filtrate was evaporated at 40° to give an oil **8**, molecular weight 385 (by mass spectrometry), which moved as two spots (presumably the *cis* and *trans* isomers) on t.l.c. (hexane–ethyl acetate, 5:2). A solution of this oil in 35 ml of acetonitrile was magnetically stirred with cooling in an ice bath, and a solution of sodium borohydride (400 mg) in 5 ml of water was added dropwise. After stirring had been continued for 30 min, 200 ml of water was added, and the mixture was extracted with chloroform (6 × 25 ml). The chloroform solution was washed with water (50 ml), dried (sodium sulfate), and evaporated to give a solid which was recrystallized from methanol–water; the product moved as a single spot on t.l.c. (hexane–ethyl acetate, 2:1); yield 1.12 g (58% overall from **4**), m.p. 96–97°, $[\alpha]_D^{23}$ +40.5° (*c* 1.02, chloroform); $\nu_{max}^{CHCl_3}$:1610 (C=C), 1565 cm^{-1} (NO_2); n.m.r. data (100 MHz): τ 4.24 (H-1, doublet, $J_{1,2}$ 4.0 Hz); 5.22 (H-2, triplet, $J_{2,3}$ 4.1 Hz); 5.80–6.08 (3-proton multiplet, H-4,H-5); 5.48 (CH_2NO_2, quartet, $J_{a,b}$ 13 Hz); 8.57,8.73 (CMe_2, two singlets); *m/e* 372 ($M^+ - 15$).

Anal. Calc. for $C_{16}H_{21}NO_8S$: C, 49.60; H, 5.46; N, 3.61. Found: C, 49.92; H, 5.35; N, 3.66.

5-O-Acetyl-3-deoxy-1,2-O-isopropylidene-3-C-nitromethyl-α-D-ribofuranose (**11**). — A solution of **7** (3.5 g, 10.05 mmoles) in benzene was treated with potassium carbonate for 5 h, as described for the preparation of **10**. A yellow syrup **9**, *m/e* 258 ($M^+ - 15$), was obtained which was reduced with sodium borohydride as described for the preparation of **10**. The solid obtained was recrystallized from acetone–hexane to give **11** which moved as a single spot on t.l.c. (chloroform); yield 1.61 g (58%), m.p. 127–128°, $[\alpha]_D^{23}$ +61.8° (*c* 1.04, chloroform); $\nu_{max}^{CHCl_3}$: 1750 (OAc), 1565 cm^{-1} (NO_2); n.m.r. data (100 MHz): τ 4.14 (H-1, doublet, $J_{1,2}$ 4.0 Hz); 5.14 (H-2, triplet); 7.32 (H-3, multiplet); 5.70–6.06 (3-proton multiplet, H-4,H-5); 5.39 (CH_2NO_2, quartet); 8.52,8.71 (CMe_2, 2 singlets); 7.95 (Ac, singlet); *m/e* 260 ($M^+ - 15$).

Anal. Calc. for $C_{11}H_{17}NO_7$: C, 48.00; H, 6.23; N, 5.09. Found: C, 48.30; H, 6.24; N, 4.82.

3-C-Benzamidomethyl-3-deoxy-1,2-O-isopropylidene-5-O-p-tolylsulfonyl-α-D-ribofuranose (**12**). — A mixture of **10** (194 mg, 0.5 mmole) and platinum oxide (100 mg) in absolute ethanol (20 ml) was magnetically stirred under a positive pressure of hydrogen for 1.5 h, during which time the calculated amount of hydrogen was consumed. The mixture was filtered through a Celite pad, and the filtrate was evaporated to give a syrup which was dissolved in 1.5 ml of dry pyridine. To this solution, cooled in an ice bath, was added slowly 105 mg (0.75 mmole) of benzoyl chloride. After 10 min, the mixture was poured into ice–water (50 ml) and processed in the usual manner, and the product was recrystallized from acetone–hexane (with charcoal treatment) to give **12**, which moved as a single spot on t.l.c. (chloroform); yield 180 mg (78%), m.p. 146–147°, $[\alpha]_D^{23}$ +23.7° (*c* 0.93, chloroform); $\nu_{max}^{CHCl_3}$: 3460 (NH), 1670 (amide I), 1530 (amide II), 1380 cm^{-1} (SO_2); n.m.r. data (100 MHz): τ 4.30 (H-1, doublet, $J_{1,2}$ 4.0 Hz); 5.31 (H-2, triplet); 3.20 (NH, triplet); 8.55,8.70 (CMe_2, 2 singlets); *m/e* 461 ($M^+ - 15$).

Anal. Calc. for $C_{23}H_{27}NO_7S$: C, 59.95; H, 5.91; N, 3.04. Found: C, 60.05; H, 5.71; N, 3.12.

3-O-Acetamidomethyl-5-O-acetyl-3-deoxy-1,2-O-isopropylidene-α-D-ribofuranose (**13**). — Reduction of **11** (275 mg, 1 mmole) was carried out as described for the reduction of **10**. The amine obtained was immediately stirred with acetic anhydride (2 ml) in pyridine (2.5 ml) for 30 min. The product was isolated as described for the isolation of **12**. The syrup obtained was dissolved in methanol and treated with charcoal. Evaporation of the solution gave a syrup which moved as a single spot on t.l.c. (ethyl acetate); yield 237 mg (82%); $[\alpha]_D^{23}$ +57.2° (*c* 1.34, chloroform); $\nu_{max}^{CHCl_3}$: 3460 (NH), 1750 (OAc), 1680 (amide I), 1525 cm^{-1} (amide II); n.m.r. data (100 MHz): τ 4.20 (H-1, doublet, $J_{1,2}$ 4.0 Hz); 5.34 (H-2, triplet); 3.74 (NH, broad); 7.94,8.05 (Ac, 2 singlets); 8.50,8.69 (CMe_2, 2 singlets); *m/e* 272 ($M^+ - 15$).

Anal. Calc. for $C_{13}H_{21}NO_6$: C, 54.33; H, 7.37; N, 4.87. Found: C, 54.50; H, 7.66; N, 4.80.

REFERENCES

1 Preliminary communication: G. J. LOURENS, *Tetrahedron Lett.*, (1969) 3733.
2 For a review see: W. G. OVEREND, *Chem. Ind.* (London), (1963) 342.
3 L. HOUGH AND A. C. RICHARDSON, in S. COFFEY (Ed.), *Rodd's Chemistry of Carbon Compounds*, Vol. I F, Elsevier, Amsterdam, 1967, pp. 529–543.
4 R. D. REES, K. JAMES, A. R. TATCHELL, AND R. H. WILLIAMS, *J. Chem. Soc.* (*C*), (1968) 2716; and references cited therein.
5 R. F. NUTT, M. J. DICKENSON, F. W. HOLLY, AND E. WALTON, *J. Org. Chem.*, 33 (1968) 1789.
6 R. J. FERRIER, W. G. OVEREND, G. A. RAFFERTY, H. M. WALL, AND N. R. WILLIAMS, *J. Chem. Soc.* (*C*), (1968) 1091; and references cited therein.
7 R. D. KING, W. G. OVEREND, AND N. R. WILLIAMS, *Chem. Commun.*, (1967) 726.
8 A. ROSENTHAL AND L. (BENZING) NGUYEN, *J. Org. Chem.*, 34 (1969) 1029; D. G. LANCE AND W. A. SZAREK, *Carbohyd. Res.*, 10 (1969) 306; A. ROSENTHAL AND M. SPRINGZL, *Can. J. Chem.*, 47 (1969) 3941.
9 A. ROSENTHAL AND D. A. BAKER, *Tetrahedron Lett.*, (1969) 397.

10 F. W. LICHTENTHALER, *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 211; H. H. BAER, *Advan. Carbohyd. Chem. Biochem.*, 24 (1969) 67.
11 (*a*) S. W. GUNNER, W. G. OVEREND, AND N. R. WILLIAMS, *Chem. Ind.* (London), (1964) 1523; (*b*) H. H. BAER, AND G. V. RAO, *Ann.*, 686 (1965) 210; (*c*) B. R. BAKER AND D. H. BUSS, *J. Org. Chem.*, 31 (1966) 217.
12 (*a*) W. A. SZAREK, J. S. JEWELL, I. SZCZEREK, AND J. K. N. JONES, *Can. J. Chem.*, 47 (1969) 4473; (*b*) H. H. BAER AND K.-S. ONG, *ibid.*, 46 (1968) 2511.
13 A. ROSENTHAL AND K.-S. ONG, *Tetrahedron Lett.*, (1969) 3981; H. P. ALBRECHT AND J. G. MOFFATT, *ibid.*, (1970) 1063; A. ROSENTHAL, K.-S. ONG, AND D. BAKER, *Carbohyd. Res.*, 13 (1970) 113.
14 W. SOWA, *Can. J. Chem.*, 46 (1968) 1586.
15 K. ONODERA, S. HIRANO, AND N. KASHIMURA, *Carbohyd. Res.*, 6 (1968) 276.
16 P. A. LEVENE, AND A. L. RAYMOND, *J. Biol. Chem.*, 102 (1933) 317.
17 W. A. SZAREK, S. WOLFE, AND J. K. N. JONES, *Tetrahedron Lett.*, (1964) 2743; H. PAULSEN AND K. TODT, *Ber.*, 100 (1967) 3385; M. H. HALFORD, D. H. BALL, AND L. LONG, *Chem. Commun.*, (1969) 255.
18 H. B. HASS, A. G. SUSIE, AND R. L. HEIDER, *J. Org. Chem.*, 15 (1950) 8; H. H. BAER, T. NEILSON, AND W. RANK, *Can. J. Chem.*, 45 (1967) 991.
19 A. I. MEYERS AND J. C. SIRCAR, *J. Org. Chem.*, 32 (1967) 4134.
20 R. J. ABRAHAM, L. D. HALL, L. HOUGH, AND K. A. MCLAUCHLAN, *J. Chem. Soc.*, (1962) 3699.