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Note

The reaction of 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose with diazomethane*

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The reaction of diazomethane with aldoketoses and diketoses has been extensively used in the synthesis of branched-chain sugars[2] *via spiro*-epoxides. Sometimes, this reaction proceeds with ring expansion[3], giving a deoxyaldoketose which, with diazomethane, yields the corresponding *spiro*-epoxides. In an application[5] of this method to the title compound[4] (**1**), the *spiro*-epoxide **2** was not isolated but transformed into the corresponding 3-*C*-hydroxymethyl derivative. We now report on the reaction of **1** with diazomethane and describe some ring-expansion products.

The reaction of **1** with diazomethane gave a mixture of *spiro*-epoxides that could be partially resolved by column chromatography. The compound of higher mobility was identified as 3,3^1-anhydro-3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**), and transformed into 1,2:5,6-di-*O*-isopropylidene-3-*C*-methyl-α-D-glucofuranose[6] (**6**) by treatment with lithium aluminium hydride. The second component eluted was a crystalline 1:2 mixture of two compounds having retention times (*T*) in g.l.c. of 248 and 390 s. The major component was isolated from this mixture and identified as 3,3^1-anhydro-4,5-dideoxy-3-*C*-hydroxymethyl-1,2:7,8-di-*O*-isopropylidene-α-D-octoseptanose (**5**). The component (**3**) having *T* 248 s could not be isolated, but reduction of the mixture allowed its identification as a 3-epimer of **4**. The third component was isolated crystalline and, on the basis of its analytical and spectroscopic data, identified as 3,3^1-anhydro-4-deoxy-3-*C*-hydroxymethyl-1,2:6,7-di-*O*-isopropylidene-α-D-heptopyranose (**4**).

The formation of **3**–**5** could involve ring expansion of **1** *via A* and *B*. Reaction of *B* (not isolated) with diazomethane would give **3** and **4**. Ring expansion of *B* to give *C* (not isolated) followed by reaction with diazomethane would give **5**. The ^{1}H-n.m.r. spectra of **4**, **5**, and the *C*-methyl derivative (**7**) of **3** contained doublets for H-2 at δ 3.80, 3.68, and 4.11 (assignments based on double-resonance experiments), respectively, indicating coupling only with the anomeric proton, in accord with the proposed ring-expansion. (*cf.* ref. 3).

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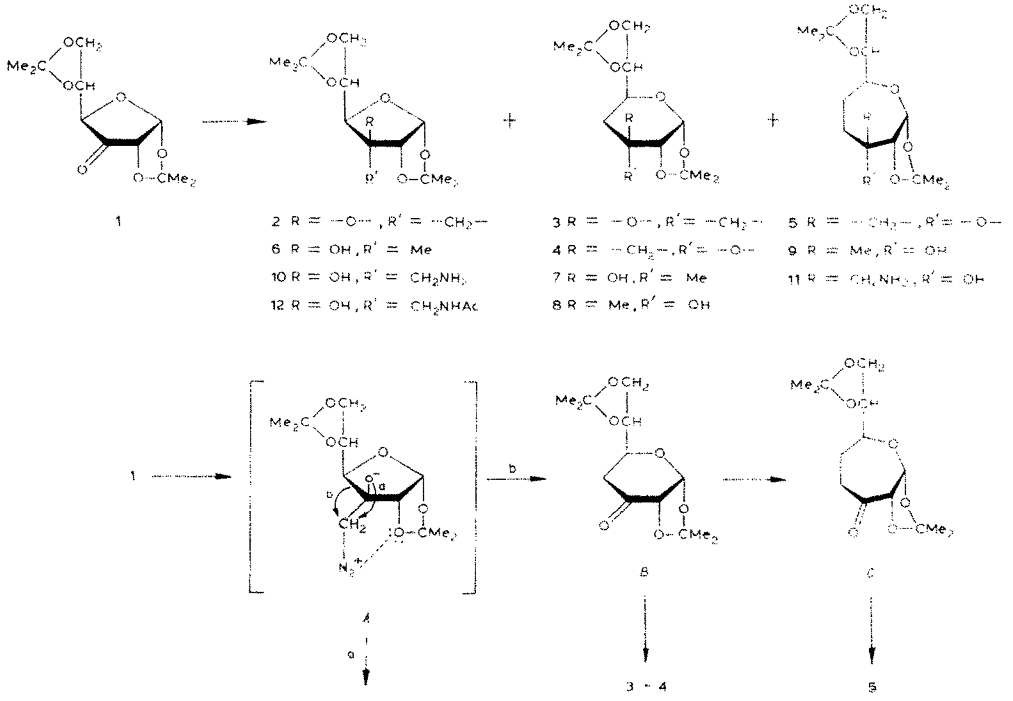
*Branched-chain Sugars, Part IV. For Part III, see ref. 1.

The reaction of **3**–**5** severally with lithium aluminium hydride in ether gave the corresponding 3-*C*-methyl derivatives **7**–**9**. The configurations of **3**–**5** and **7**–**9** have not been established, but some spectroscopic data suggest that **7** and **8** have D-*gluco* and D-*allo* configurations, respectively. Thus, the ^{1}H-n.m.r. spectrum of **7** contained signals for H-1 and H-2 at δ 5.67 and 4.11, whereas, for **8**, these signals were shifted upfield by 0.09 and 0.11 p.p.m.; this could reflect a deshielding by HO-3 in the D-*gluco* compound **7**, which must adopt a distorted $^1C_4$(D) conformation (due to the presence of a 1,2-*cis*-fused ring[7]), in which the bulky group at C-5 and Me-3 must occupy *quasi*-equatorial positions and bring HO-3 close to H-1,2. A similar effect was also observed in **6**, where the signals for H-1 and H-2 were shifted downfield by 0.08 and 0.11 p.p.m., respectively, in comparison with the corresponding signals for the D-*allo* isomer[8]. The chemical shift of the signal for the *endo* methyl group attached to the 1,2-dioxolane ring in **7** and **8** (δ 1.54 and 1.60) accorded with literature data[9]. This difference (0.06 p.p.m.) in chemical shifts could be due to a deshielding effect of HO-3 in the D-*allo* compound.

The configurations of **5** and **9** were not established, but D-*allo* configurations would be expected on the basis of previous results[3a]. A dilute solution of **9** in carbon tetrachloride showed an i.r. band at 3570 cm^{-1} (HO-3), which is shifted by 50 cm^{-1} from the position of the normal absorption (3620 cm^{-1}) of a tertiary hydroxyl group



2 R = —O—, R′ = —CH$_2$—
6 R = OH, R′ = Me
10 R = OH, R′ = CH$_2$NH$_2$
12 R = OH, R′ = CH$_2$NHAc

3 R = —O—, R′ = —CH$_2$—
4 R = —CH$_2$—, R′ = —O—
7 R = OH, R′ = Me
8 R = Me, R′ = OH

5 R = —CH$_2$—, R′ = —O—
9 R = Me, R′ = OH
11 R = CH$_2$NH$_2$, R′ = OH

Scheme 1

and which may reflect intramolecular hydrogen-bonding[10] between HO-3 and O-2, as would be expected for the D-*allo* compound.

The high stereoselectivity of the reaction of diazomethane with **1** to give **2** may be explained[11] by the stabilisation of the diazomethyl cation-intermediate *A* by O-2 (Scheme 1).

The reaction of **2** and **5** with ammonia in methanol opened the oxirane ring[10,12] at C-3 to give **10** and **11** in quantitative yield. Acetylation of **10** gave the known[5] *N*-acetyl derivative **12**.

The mass-spectral data for the compounds described accorded with those reported[13] for compounds of similar structure.

EXPERIMENTAL

General methods. — Melting points were determined with a Reichter hotplate microscope and are uncorrected. Solutions were concentrated, after drying over $MgSO_4$, under diminished pressure. ^1H-N.m.r. spectra (60 MHz, internal Me_4Si) were recorded with a Perkin–Elmer R-20B spectrometer for solutions in $CDCl_3$. I.r. spectra were recorded with a Pye–Unicam SP 1000 spectrophotometer, and mass spectra with a Hewlett–Packard 5930A instrument. Optical rotations were measured for solutions in chloroform (1-dm tube) with a Perkin–Elmer 141 polarimeter. G.l.c. was performed with a Carlo–Erba Fractovap G gas chromatograph equipped with a flame-ionisation detector and a glass column (2 m × 1.75 mm i.d.) packed with 3% of SE-52 on Chromosorb G (100–120 mesh) and kept at 180°; *T* values are reported in s. The N_2 flow-rate was 30 mL/min, the injection-port temperature 200°, and the zone-detector temperature 210°. R_F values are reported for t.l.c. performed on Silica Gel G (Merck) with ether–hexane (1 : 1) and detection by charring with sulfuric acid. Column chromatography was performed on silica gel (Merck, 7734). Microanalyses were performed with a Carlo–Erba Elemental Analyzer Model 1106.

*Reaction of 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose* (**1**) *with diazomethane.* — To a solution of **1** (3.5 g, 13.6 mmol) in methanol (50 mL) at room temperature was added ethereal 2.8% diazomethane, portionwise, until the mixture remained yellow (50 mL). The solution was stored overnight at room temperature. T.l.c. then revealed three components, R_F 0.40, 0.34, and 0.23. Evaporation of the solvent gave a residue (4 g) that was subjected to column chromatography (ether–hexane 1:5→1:3), to give, first, $3,3^1$-anhydro-3-*C*-hydroxymethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**; 1.5 g, 40.3%), $[\alpha]_D$ +42° (*c* 1.6), +52° (*c* 1.7, methanol); lit.[4] $[\alpha]_D$ +55° (methanol); R_F 0.40, *T* 148, ν_{max}^{film} 1370 and 1380 cm^{-1} (CMe_2). N.m.r. data: δ 5.97 (d, $J_{1,2}$ 4 Hz, H-1), 3.41 (m, 1 H, H-5), 4.29 (d, 1 H, H-2), 4.06 (s, 2 H, H-6,6′), 4.00 (d, 1 H, $J_{4,5}$ 1.3 Hz, H-4), 3.19 (d, 1 H, $J_{3^1a,3^1b}$ 4.5 Hz, H-3^1a), 3.08 (d, 1 H, H-3^1b), and 1.58, 1.42, and 1.34 (3 s, 12 H, intensity ratios 1 : 1 : 2, 2 CMe_2). Mass spectrum: *m/z* 272 ($M^{+\cdot}$), 257 (M^+ − Me), 199 (M^+ − Me − Me_2CO), 139 (M^+ − Me − Me_2CO − AcOH), 101 ($C_5H_9O_2^+$), 85 ($C_4H_5O_2^+$), 59 (Me_2COH^+), and 43 (Ac^+).

Eluted second was a semicrystalline residue (0.9 g), $[\alpha]_D$ −25° (*c* 1.7), R_F 0.34, *T* 248 (**3**, minor) and 390 (**5**, major). Two recrystallisations from hexane gave 3,3^1-anhydro-4,5-dideoxy-3-*C*-hydroxymethyl-1,2:7,8-di-*O*-isopropylidene-α-D-octoseptanose (**5**, 340 mg), m.p. 94–95°, $[\alpha]_D$ −36° (*c* 1); ν_{max}^{KBr} 1365, 1375, and 1380 cm^{-1} (CMe_2). N.m.r. data: δ 5.56 (d, 1 H, $J_{1,2}$ 5.3 Hz, H-1), 4.26–3.62 (m, 4 H, H-6,7,8,8′), 3.68 (d, 1 H, H-2), 2.78 (s, 2 H, H-3^{1}a,3^{1}b), 2.58–1.25 (m, 4 H, H-4,5,4′,5′), and 1.75, 1.48, and 1.41 (3 s, 12 H, intensity ratios 1:1:2, 2 CMe_2). Mass spectrum: *m/z* 285 (M^+ − Me), 227 (M^+ − Me − Me_2CO), 199 (M^+ − $C_5H_9O_2$), 184 (M^+ − Me − $C_5H_9O_2$), 167 (M^+ − Me − Me_2CO − AcOH), 101 ($C_5H_9O_2^+$), 85 ($C_4H_8O_2^+$), 59 (Me_2COH^+), and 43 (Ac^+).

Anal. Calc. for $C_{15}H_{26}O_6$: C, 59.99; H, 8.05. Found: C, 60.23; H, 8.15.

Eluted third was a compound (0.2 g, 5.2%) that was recrystallised from hexane, to give 3,3^1-anhydro-4-deoxy-3-*C*-hydroxymethyl-1,2:6,7-di-*O*-isopropylidene-α-D-*allo*-heptopyranose (**4**), m.p. 119–120°, $[\alpha]_D$ −26° (*c* 1.7), R_F 0.23, *T* 295, ν_{max}^{KBr} 1380 and 1395 cm^{-1} (CMe_2). N.m.r. data: δ 5.66 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 4.30–3.70 (m, 4 H, H-5,6,7,7′), 3.80 (d, 1 H, H-2), 2.77 (s, 2 H, H-3^{1}a,3^{1}b), 1.36 (dd, 1 H, $J_{4,5}$ 6, $J_{4,4'}$ 12 Hz, H-4), 1.74 (dd, 1 H, $J_{4',5}$ 3.0 Hz, H-4′), and 1.62, 1.43, and 1.35 (3 s, 12 H, intensity ratios 1:1:2, 2 CMe_2). Mass spectrum: *m/z* 271 (M^+ − Me), 213 (M^+ − Me − Me_2CO), 167 (M^+ − Me − Me_2CO − AcOH), 101 ($C_5H_9O_2^+$), 85 ($C_4H_8O_2^+$), 59 (Me_2COH^+), and 43 (Ac^+).

Anal. Calc. for $C_{14}H_{22}O_6$: C, 58.72; H, 7.75. Found: C, 58.97, H, 7.78.

*1,2:5,6-Di-*O*-isopropylidene-3-*C*-methyl-α-D-glucofuranose* (**6**). — To a stirred suspension of lithium aluminium hydride (0.2 g) in anhydrous ether (10 mL) was added a solution of **2** (272 mg, 1 mmol) in the same solvent (10 mL), and the mixture was heated under reflux for 3 h. T.l.c. then revealed the absence of **2** and the presence of a new compound, R_F 0.34. The excess of hydride was decomposed with aqueous ammonium chloride, the ethereal layer was separated, and the aqueous phase was extracted with ether (2 × 10 mL). The combined ether solutions were concentrated, to give **6** (260 mg, 95%), m.p. 65–66° (from hexane), $[\alpha]_D$ +22° (*c* 1.1, acetone); lit.^{4} m.p. 66–67°, $[\alpha]_D$ +23° (*c* 1, acetone); R_F 0.34, *T* 148; ν_{max}^{KBr} 3440 (OH), 1385, and 1370 cm^{-1} (CMe_2). N.m.r. data: δ 5.88 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.24 (d, 1 H, H-2), 4.54–3.70 (m, 4 H, H-4,5,6,6′), 2.53 (s, 1 H, HO-3), and 1.52, 1.47, 1.39, and 1.36 (4 s, 15 H, intensity ratios 1:2:1:1, Me-3 and 2 CMe_2). Mass spectrum: *m/z* 274 (M^+), 259 (M^+ − Me), 220, 201 (M^+ − Me − Me_2CO), 173 (M^+ − $C_5H_9O_2$), 159 (M^+ − Me − Me_2CO − AcOH), 143 ($C_7H_{11}O_3^+$), 141, 131 ($C_6H_{11}O_3^+$), 101 ($C_5H_9O_2^+$), 100 ($C_5H_8O_2^+$), 85 ($C_4H_5O_2^+$), 59 (Me_2COH^+), and 43 (Ac^+).

Anal. Calc. for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 57.07; H, 8.44.

*4-Deoxy-1,2:6,7-di-*O*-isopropylidene-3-*C*-methyl-α-D-*allo*-heptopyranose* (**8**). — Reduction of **4** (50 mg, 0.17 mmol) in anhydrous ether (10 mL) with lithium aluminium hydride (100 mg), as described above, gave **8** (50 mg, quantitative), m.p. 123–124° (from hexane), $[\alpha]_D$ −20.5° (*c* 1.15), R_F 0.15; ν_{max}^{KBr} 3500 (OH), 1385, and 1375 cm^{-1} (CMe_2). N.m.r. data: δ 5.58 (d, 1 H, $J_{1,2}$ 5.3 Hz, H-1), 4.29–3.70 (m, 4 H, H-5,6,7,7′), 4.00 (d, 1 H, H-2), 2.48 (s, 1 H, HO-3), 2.00–1.75 (m, 2 H, H-4,4′), and 1.60, 1.47, 1.44, 1.36, and 1.31 (5 s, 15 H, Me-3 and 2 CMe$_2$). Mass spectrum: *m/z* 272 (M^+ − Me), 259, 215 (M^+ − Me − Me$_2$CO), 187 (M^+ − $C_5H_9O_2$), 162 (M^+ − Me − $C_5H_9O_2$), 155 (M^+ − Me − Me$_2$CO − AcOH), 129, 101 ($C_5H_9O_2^+$), 85 ($C_4H_5O_2^+$), 59 (Me$_2$COH$^+$), and 43 (Ac$^+$).

Anal. Calc. for $C_{14}H_{24}O_6$: C, 58.31; H, 8.39. Found: C, 58.94; H, 8.25.

Reduction of a mixture of 3 *and* 5. — Reduction of the mixture of **3** and **5** (550 mg) described above with lithium aluminium hydride (0.2 g) in anhydrous ether (20 mL), as described above, gave a mixture of two substances, R_F 0.20 and 0.10. Column chromatography of this mixture (ether–hexane 1:2→1:1) gave, first, 4,5-dideoxy-1,2:7,8-di-*O*-isopropylidene-3-*C*-methyl-α-D-octoseptanose (**9**, 290 mg), m.p. 83–85° (from hexane), $[\alpha]_D$ −35° (*c* 1.34), R_F 0.20, *T* 155; ν_{max}^{KBr} 3430 (OH), 1390, 1385, and 1380 cm^{-1} (CMe$_2$). N.m.r. data: δ 5.48 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 4.11–3.64 (m, 4 H, H-6,7,8,8′), 4.04 (d, 1 H, H-2), 2.64 (s, 1 H, HO-3), 2.20–1.50 (m, 4 H, H-4,5,4′,5′), and 1.61 and 1.36 (2 s, 15 H, intensity ratio 1:4, Me-3 and 2 CMe$_2$). Mass spectrum: *m/z* 287 (M^+ − Me), 234, 229 (M^+ − Me − Me$_2$CO), 187 (M^+ − Me − $C_5H_8O_2$), 186 (M^+ − Me − $C_5H_9O_2$), 169 (M^+ − Me − Me$_2$CO − AcOH), 151, 143, 101 ($C_5H_9O_2^+$), 100 ($C_5H_8O_2^+$), 85 ($C_4H_5O_2^+$), and 43 (Ac$^+$).

Anal. Calc. for $C_{15}H_{26}O_6$: C, 59.58; H, 8.57. Found: C, 59.94; H, 9.05.

Eluted second was syrupy 4-deoxy-1,2:6,7-di-*O*-isopropylidene-3-*C*-methyl-α-D-*gluco*-heptopyranose (**7**, 231 mg), $[\alpha]_D$ −23° (*c* 1.16), R_F 0.10, *T* 130; ν_{max}^{film} 3490 (OH), 1385, and 1370 cm^{-1} (CMe$_2$). N.m.r. data: δ 5.67 (d, 1 H, $J_{1,2}$ 5.3 Hz, H-1), 4.36–3.59 (m, 4 H, H-5,6,7,7′), 4.11 (d, 1 H, H-2), 2.60 (s, 1 H, HO-3), 2.00–1.78 (m, 2 H, H-4,4′) and 1.54, 1.48, 1.36, and 1.32 (4 s, 15 H, intensity ratios 1:1:2:1, Me-3 and 2 CMe$_2$). Mass spectrum: *m/z* 287 (M^+ − 1), 273 (M^+ − Me), 215 (M^+ − Me − Me$_2$CO), 213 (M^+ − Me − AcOH), 187 (M^+ − $C_5H_9O_2$), 173 (M^+ − Me − $C_5H_8O_2$), 155 (M^+ − Me − Me$_2$CO − AcOH), 129, 101 ($C_5H_9O_2^+$), 100 ($C_5H_8O_2^+$), 85 ($C_4H_5O_2^+$), 59 (Me$_2$COH$^+$), and 43 (Ac$^+$).

Anal. Calc. for $C_{14}H_{24}O_6$: C, 58.31; H, 8.39. Found: C, 58.24; H, 8.02.

3-C-Aminomethyl-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (**10**) *and 3-C-aminomethyl-4,5-dideoxy-1,2:7,8-di-O-isopropylidene-α-D-octoseptanose* (**11**). — A solution of **2** (544 mg, 2 mmol) in methanol (3 mL) containing ammonia (3%) was heated in a sealed tube at 100° for 1 h. T.l.c. then revealed the absence of **2**, and an immobile substance. Evaporation of the solvent gave a crystalline residue (560 mg, quantitative) that was recrystallised from ether, to yield **10** (430 mg, 74%), m.p. 113–114°, $[\alpha]_D$ +20° (*c* 1.3), $[\alpha]_D$ +31° (*c* 1.24, methanol); lit.[4] m.p. 114–115°, $[\alpha]_D$ +28.8° (*c* 1, methanol); ν_{max}^{KBr} 3480 (OH), 3320 and 3260 (NH$_2$), 1615 (NH$_2$), and 1380 and 1365 cm^{-1} (CMe$_2$). N.m.r. data: δ 5.91 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.41–3.62 (m, 4 H, H-4,5,6,6′), 3.34 (d, 1 H, H-2), 3.19 (d, 1 H, $J_{3^1a,3^1b}$ 12 Hz, H-3^{1}a), 2.92 (d, 1 H, H-3^{1}b), 2.48 (s, 3 H, HO-3, NH$_2$), and 1.52, 1.43, 1.38, and 1.33 (4 s, 12 H, intensity ratios 1:1:1:1, 2 CMe$_2$). Mass spectrum: *m/z* 290 (M^+ − 1), 274 (M^+ − Me), 216 (M^+ − Me − Me$_2$CO), 214 (M^+ − Me − AcOH), 188

$(M^+ - C_5H_9O_2)$, 158 $(M^+ - C_7H_{12}NO_3)$, 156 $(M^+ - Me - Me_2CO - AcOH)$, 101 $(C_5H_9O_2^+)$, 100 $(C_5H_8O_2^+)$, 85 $(C_4H_5O_2^+)$, 59 (Me_2COH^+), and 43 (Ac^+).

Anal. Calc. for $C_{13}H_{23}NO_6$: C, 53.94; H, 8.02; N, 4.84. Found: C, 54.14; H, 8.10; N, 4.73.

Acetylation of **10** (100 mg, 0.35 mmol) in the usual manner gave the 3-*C*-acetamidomethyl derivative **12** (85 mg, 74%), m.p. 119–120° (from hexane), $[\alpha]_D$ +65° (*c* 1.5), $[\alpha]_D$ +62° (*c* 1.15, ethanol); lit.[4] m.p. 120–121°, $[\alpha]_D$ −63.8° (ethanol); ν_{max}^{KBr} 3300 (OH), 3100 (NH), 1660 and 1575 (NHAc), and 1385 and 1380 cm^{-1} (CMe_2). N.m.r. data: δ 6.60 (bs, 1 H, NH), 5.83 (d, 1 H, $J_{1,2}$ 3.75 Hz, H-1), 4.77 (bs, 1 H, HO-3), 4.43 (d, 1 H, H-2), 4.47–3.46 (m, 6 H, H-3^1a,3^1b,4,5,6,6′), 2.00 (s, 3 H, AcN), 1.45, 1.36, 1.31, and 1.28 (4 s, 12 H, intensity ratios 1:1:1:1, 2 CMe_2). Mass spectrum: *m/z* 332 (M^+), 316 $(M^+ - Me)$, 258 $(M^+ - Me - Me_2CO)$, 216 $(M^+ - Me - C_5H_8O_2)$, 200 $(C_9H_{14}NO_4^+)$, 100 $(C_5H_8O_2^+)$, 85 $(C_4H_5O_2^+)$, 59 (Me_2COH^+), and 43 (Ac^+).

Anal. Calc. for $C_{15}H_{25}NO_7$: C, 54.37; H, 7.61; N, 4.23. Found: C, 54.45; H, 7.60; N, 3.96.

Compound **5** (160 mg, 0.3 mmol) was transformed into the 3-*C*-aminomethyl derivative as described above for **2**. Evaporation of the solvent gave **11** as a syrup (160 mg), $[\alpha]_D$ 29° (*c* 1.1). N.m.r. data: δ 5.54 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 4.41–3.41 (m, 5 H, H-2,6,7,8,8′), 2.78 (s, 2 H, H-3^1a,3^1b), 2.47 (s, HO-3 and NH_2), 2.26–1.19 (m, 4 H, H-4,5,4′,5′), and 1.57, 1.36, and 1.30 (3 s, 12 H, intensity ratios 1:1:2, 2 CMe_2). Mass spectrum: *m/z* 317 (M^+), 302 $(M^+ - Me)$, 244 $(M^+ - Me - Me_2CO)$, 242 $(M^+ - Me - AcOH)$, 229, 184 $(M^+ - Me - Me_2CO - AcOH)$, 166, 129, 101 $(C_5H_9O_2^+)$, 100 $(C_5H_8O_2^+)$, 85 $(C_4H_5O_2^+)$, 59 (Me_2COH^+), and 43 (Ac^+).

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