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Note

Reductive opening of 2,3-unsaturated aldopyranosides*

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2,3-Unsaturated aldopyranosides are attractive carbohydrate synthons[1]. Neutral hydrolysis of these compounds leads to the corresponding unstable sugars, the acyclic forms of which, in the presence of weak acid catalysts[2], elevated temperature[3], mercury ions[4], or light[5], undergo rapid $Z \rightarrow E$ isomerisation of the double bond to form E-α,β-unsaturated aldehydes. Acid-catalysed hydrolysis of 2,3-unsaturated glycosides directly affords the corresponding E-α,β-unsaturated aldehydes[6].

Owing to the easy isomerisation of the double bond, only E-α,β-unsaturated aldehydes of this type have been widely investigated[1]. We now describe a method for opening the 5,6-dihydro-2*H*-pyran ring with preservation of the *Z* configuration of the double bond[7], based on an approach to the synthesis of α,β-unsaturated δ-lactones[8].

The 2,3-unsaturated glycosides **1–7** were studied. Compound **1** was obtained in racemic form by the (4 + 2)cycloaddition of 1-methoxybuta-1,3-diene to butyl glyoxylate[9], the ethyl glycosides **2** and **3** were obtained from 3,4,6-tri-*O*-acetyl-D-glucal and 3,4,6-tri-*O*-acetyl-D-galactal[10], respectively, and **4–7** were prepared by high-pressure (4 + 2)cycloaddition of 1-methoxybuta-1,3-diene to 2,3-di-*O*-acetyl- and 2,3-di-*O*-benzyl-D-glyceraldehyde[11].

The oxidation of **1–7** severally with hydrogen peroxide, catalysed by molybdenum trioxide, afforded the corresponding hydroperoxides **8** which were not purified but reduced with sodium borohydride in 2-propanol. Under these conditions, the corresponding alditols were formed without isomerisation of the double bond and, after acetylation, **9–15** were formed in good yields.

The configuration of the double bond in **9–15** was assigned on the basis of the

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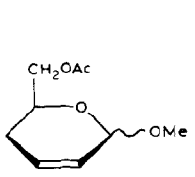

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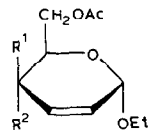
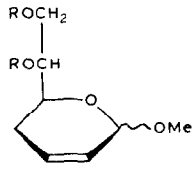


2 R^1 = H, R^2 = OAc
3 R^1 = OAc, R^2 = H



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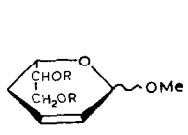
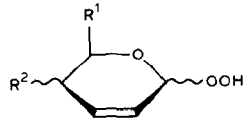
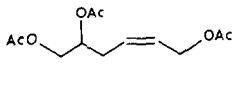


6 R = Ac
7 R = Bzl



8 R^1 = H, Me, CH_2OAc
R^2 = OAc



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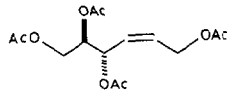

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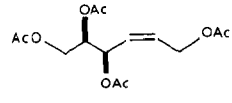

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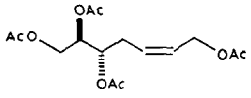

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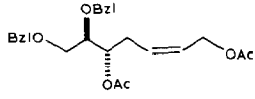

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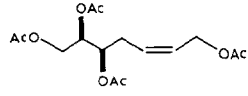

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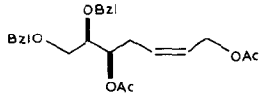

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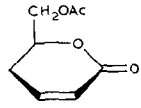

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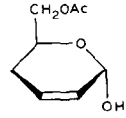

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^{1}H-n.m.r. data. The $J_{2,3}$ values (10.7–12.5 Hz) were typical of a *Z*-double bond. The structures of **9–15** were proved unequivocally by 2D-COSY spectra, of which that for **12** in Fig. 1 is illustrative.

The lactone **16**[8] was unaffected under the conditions used to reduce the hydroperoxides **8**, and the 2,3-unsaturated sugar **17**[6] afforded a complex mixture of products.

The method described above can be used to prepare optically pure synthons of potential value in the synthesis of natural products.

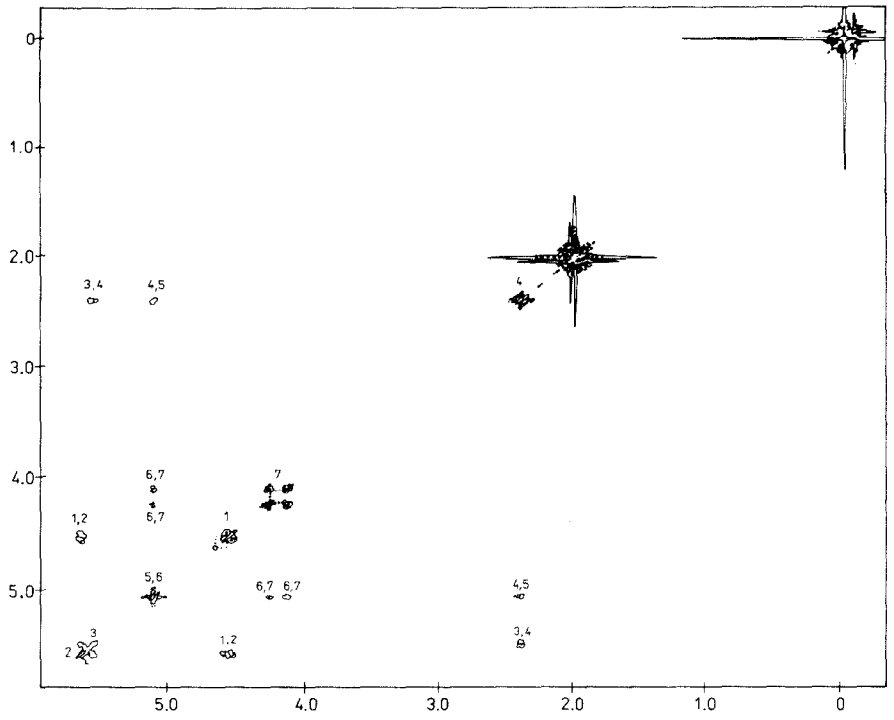

Fig. 1. The COSY spectrum of **12** in $CDCl_3$ obtained at 500 MHz.

EXPERIMENTAL

General methods. — Optical rotations were measured with a Perkin–Elmer 141 automatic polarimeter. ^{1}H-N.m.r. spectra were recorded with Bruker AM 500 (500 MHz) and Varian EM 360 (60 MHz) spectrometers on solutions in $CDCl_3$ (internal Me_4Si). I.r. spectra (films) were recorded with a Beckman IR-4240 spectrophotometer. The progress of all reactions was monitored by t.l.c. on Silica Gel 60 (Merck). Column chromatography was performed with Kieselgel 60 (230–400 mesh, Merck).

Z-(R,S)-*Tri*-O-*acetylhex-2-ene-1,5,6-triol* (**9**). — To a suspension of **1** (260 mg, 1.4 mmol) in aqueous 30% hydrogen peroxide (3 mL) was added molybdenum trioxide (2 mg). The mixture was stirred for 6 days at room temperature, water (3 mL) was then added, and the product was extracted with dichloromethane (4 × 5 mL). The combined extracts were concentrated and to a solution of the residue containing the hydroperoxide in 2-propanol (10 mL) at 0° was added sodium borohydride (114 mg). The mixture was stirred for 3 h and then concentrated to dryness, and a solution of the residue in ether (25 mL) was washed with brine, dried, passed through a pad of silica gel, and concentrated. To a solution of the residue in dichloromethane (5 mL) were added triethylamine (1 mL), acetic

anhydride (1 mL), and a catalytic amount of 4-dimethylaminopyridine. The mixture was kept for 6 h at room temperature and then concentrated. Column chromatography (hexane–ethyl acetate, 1:1) of the residue gave **9** (206 mg, 57%), isolated as a colourless oil; ν_{max} 1740, 1370, 1230, 1040 cm^{-1}. ^{1}H-N.m.r. data (60 MHz): δ 5.6 (m, 2 H, H-2,3), 5.1 (m, 1 H, H-5), 4.6 (m, 2 H, H-1,1′), 4.1 (m, 2 H, H-6,6′), 2.7–2.3 (m, 2 H, H-4,4′), 2.1 (s, 9 H, 3 OAc); $J_{2,3}$ 11.9 Hz.

Anal. Calc. for $C_{12}H_{18}O_6$: C, 55.8; H, 7.0. Found: C, 55.5; H, 7.3.

Z-*(4*S*,5*R*)-Tetra*-O-*acetylhex-2-ene-1,4,5,6-tetraol* (**10**). — Using the above procedure, **2** was converted into **10** (59%), isolated as a colourless oil, $[\alpha]_D^{25}$ −8° (*c* 2.6, chloroform); ν_{max} 1740, 1440, 1370, 1220, 1040 cm^{-1}. ^{1}H-N.m.r. data (500 MHz): δ 5.83 (m, 1 H, H-2), 5.73 (m, 1 H, H-4), 5.54 (m, 1 H, H-3), 5.21 (m, 1 H, H-5), 4.75 (m, 2 H, H-1,1′), 4.20 (m, 2 H, H-6,6′), 2.09–2.06 (4 s, 12 H, 4 OAc); $J_{2,3}$ 10.7 Hz.

Anal. Calc. for $C_{14}H_{20}O_8$: C, 53.2; H, 6.3. Found: C, 53.2; H, 6.6.

Z-*(4*R*,5*R*)-Tetra*-O-*acetylhex-2-ene-1,4,5,6-tetraol* (**11**). — Compound **11** (47%), obtained from **3** according to the above procedure, was isolated as a colourless oil, $[\alpha]_D^{25}$ +49.5° (*c* 1, chloroform); ν_{max} 1740, 1430, 1370, 1220, 1040 cm^{-1}. ^{1}H-N.m.r. data (500 MHz): δ 5.82 (m, 1 H, H-2), 5.73 (m, 1 H, H-4), 5.50 (m, 1 H, H-3), 5.22 (m, 1 H, H-5), 4.77 (m, 2 H, H-1,1′), 4.36 (dd, 1 H, H-6), 4.00 (dd, 1 H, H-6′), 2.10–2.06 (4 s, 12 H, 4 OAc); $J_{2,3}$ 11.1 Hz.

Anal. Calc. for $C_{14}H_{20}O_8$: C, 53.2; H, 6.3. Found: C, 53.5; H, 6.7.

Z-*(5*S*,6*R*)-Tetra*-O-*acetylhept-2-ene-1,5,6,7-tetraol* (**12**). — Compound **12** (81%), obtained from **4** according to the above procedure, was isolated as a colourless oil, $[\alpha]_D^{25}$ +19.5° (*c* 1, chloroform); ν_{max} 1740, 1440, 1230, 1030, 700 cm^{-1}. ^{1}H-N.m.r. data (500 MHz): δ 5.66 (m, 1 H, H-2), 5.60 (m, 1 H, H-3), 5.14 (m, 2 H, H-5,6), 4.60 (m, 2 H, H-1,1′), 4.24 (m, 2 H, H-7,7′), 2.46 (m, 2 H, H-4,4′), 2.09–2.05 (4 s, 12 H, 4 OAc); $J_{2,3}$ 11.0 Hz.

Anal. Calc. for $C_{15}H_{22}O_8$: C, 54.5; H, 6.7. Found: C, 54.5; H, 6.6.

Z-*(5*S*,6*R*)-1,5-Di-*O-*acetyl-6,7-di-*O-*benzylhept-2-ene-1,5,6,7-tetraol* (**13**). — Compound **13** (75%), obtained from **5** according to the above procedure, was isolated as a colourless oil, $[\alpha]_D^{25}$ +8° (*c* 1.1, chloroform); ν_{max} 1740, 1450, 1230, 1030, 700 cm^{-1}. ^{1}H-N.m.r. data (500 MHz): δ 7.32 (m, 10 H, 2 Ph), 5.60 (m, 2 H, H-2,3), 5.13 (m, 1 H, H-5), 4.52 (m, 6 H, H-1,1′, 2 CH_2Ph), 3.70 (m, 1 H, H-6), 3.58 (m, 2 H, H-7,7′), 2.48 (m, 2 H, H-4,4′), 2.03 (s, 3 H, OAc), 1.98 (s, 3 H, OAc); $J_{2,3}$ 11.2 Hz.

Anal. Calc. for $C_{25}H_{30}O_6$: C, 70.4; H, 7.0. Found: C, 70.9; H, 7.4.

Z-*(5*R*,6*R*)-Tetra*-O-*acetylhept-2-ene-1,5,6,7-tetraol* (**14**). — Compound **14** (57%), obtained from **6** according to the above procedure, was isolated as a colourless oil, $[\alpha]_D^{25}$ −7° (*c* 0.7, chloroform); ν_{max} 1740, 1440, 1230, 1030, 695 cm^{-1}. ^{1}H-N.m.r. data (500 MHz): δ 5.69 (m, 1 H, H-2), 5.60 (m, 1 H, H-3), 5.21 (m, 1 H, H-6), 5.14 (m, 1 H, H-5), 4.59 (m, 2 H, H-1,1′), 4.29 (m, 1 H, H-7), 4.03 (m, 1 H, H-7′), 2.42 (m, 2 H, H-4,4′), 2.10–2.05 (4 s, 12 H, 4 OAc); $J_{2,3}$ 12.5 Hz.

Anal. Calc. for $C_{15}H_{22}O_8$: C, 54.5; H, 6.7. Found: C, 54.9; H, 6.6.

Z-(5R,6R)-1,5-Di-O-acetyl-6,7-di-O-benzylhept-2-ene-1,5,6,7-tetraol (**15**). — Compound **15** (58%), obtained from **7** according to the above procedure, was isolated as a colourless oil, $[\alpha]_D^{25}$ −22° (*c* 0.5, chloroform); ν_{max} 1740, 1450, 1240, 1030, 700 cm^{-1}. ^{1}H-N.m.r. data (500 MHz): δ 7.33 (m, 10 H, 2 Ph), 5.60 (m, 1 H, H-2), 5.52 (m, 1 H, H-3), 5.11 (m, 1 H, H-5), 4.64–4.50 (m, 6 H, H-1,1′, 2 CH_2Ph), 3.68 (m, 1 H, H-6), 3.58 (m, 2 H, H-7,7′), 2.50 (m, 2 H, H-4,4′), 2.03 (s, 3 H, OAc), 2.00 (s, 3 H, OAc); $J_{2,3}$ 10.8 Hz.

Anal. Calc. for $C_{25}H_{30}O_6$: C, 70.4; H, 7.0. Found: C, 70.3; H, 7.4.

ACKNOWLEDGMENT

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