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Note

Loss or transfer of an acetyl group during Knoevenagel reactions of aldehydo sugars with acetylacetone

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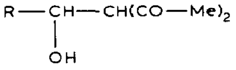
The reaction of aldehydo-sugar derivatives with acetylacetone (2,4-pentanedione) has been widely studied. Although the products (**1**–**3**) of aldol addition and subsequent dehydration were obtained[1–4] from acetylacetone, more complex products were isolated when ethyl acetoacetate was used. Thus, diethyl 2,4-diacetyl-3-(D-*gluco*-penta-acetoxypentyl)glutarate was obtained[5] from penta-*O*-acetyl-*aldehydo*-D-glucose. This glutarate derivative could have been formed from the intermediate corresponding to **2**, *via* a Michael addition of ethyl acetoacetate. Aldehydes related to glycolaldehyde react with acetylacetone to give[6,7] compounds of type **4** or **5**.



$R—\underset{OH}{CH}—CH(CO—Me)_2$

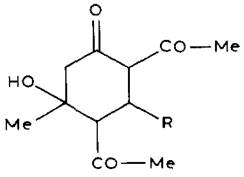
1

$R—CH=C(CO—Me)_2$

2

$R—CH=CH—CH(CO—Me)_2$

3



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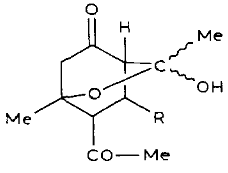

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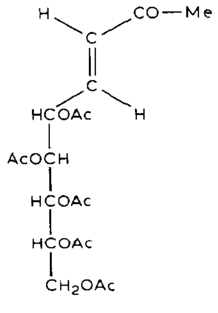

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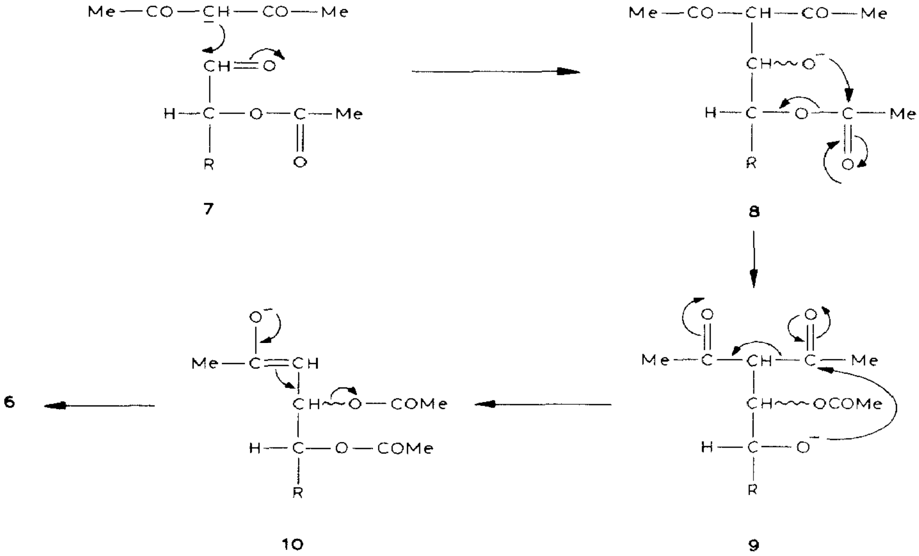
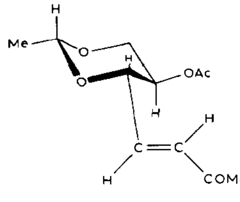
We now report on the reactions of acetylacetone with penta-*O*-acetyl-*aldehydo*-D-glucose, 2,4-*O*-ethylidene-*aldehydo*-D-erythrose, and 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose in ethanol using piperidine as catalyst.

The reaction of penta-*O*-acetyl-*aldehydo*-D-glucose and acetylacetone was carried out at room temperature to give *trans*-4-(D-*gluco*-penta-acetoxypentyl)-3-buten-2-one (**6**, 33.2%), which had λ_{max}^{MeOH} 217 nm (ε 892) and ν_{max} 1745 (CH_3COO), 1680 (C=C-CO), and 977 cm^{-1} (C=C-H) in accord with the proposed structure. On the other hand, the n.m.r. signals at δ 6.72 (dd, *J* 16 and 4.8 Hz) and 6.17 (bd, *J* 16 Hz) indicated a *trans* configuration. A possible mechanism for this reaction is shown in the sequence **7**→**8**→**9**→**10**→**6**.



The reaction of acetylacetone with 2,4-*O*-ethylidene-*aldehydo*-D-erythrose gave several products. Column chromatography of the mixture gave, first, (2*R*,4*S*,5*R*)-5-acetoxy-2-methyl-4-(*trans*-3-oxobutenyl)-1,3-dioxane (**11**, 24%); second, a mixture (14.6%) tentatively considered to contain (2*R*,4*S*,5*R*)-4-(3,5-diacetyl-2,6-dioxohept-4-yl)-5-hydroxy-2-methyl-1,3-dioxane (**12**) and (2*R*,4*S*,5*R*)-5-acetoxy-4-(3-acetyl-2,6-dioxohept-4-yl)-2-methyl-1,3-dioxane (**13**); third, (2*R*,4*S*,5*R*)-5-acetoxy-4-[(*S*)-1-hydroxy-3-oxobutyl]-2-methyl-1,3-dioxane (**14**, 15%); and fourth, (2*R*,4*S*,5*R*)-5-hydroxy-2-methyl-4-{(1*S*,3*R*,4*R*,5*R*,6*S* or 1*R*,3*S*,4*S*,5*S*,6*R*)-6-acetyl-3-hydroxy-1,3-dimethyl-8-oxo-2-oxabicyclo[2.2.2]oct-5-yl}-1,3-dioxane (**15** or **16**, 1.7%).

Compound **11** showed absorption bands typical for α,β-unsaturated ketones, namely, λ_{max}^{MeOH} 220 nm (ε 12,303) and ν_{max} 1760 (CH_3-COO), 1704 and 1686 (C=C-C=O), 1640 (C=C), 1224 (acetate), and 968 cm^{-1} (=C-H). The ^{1}H-n.m.r. spectrum contained signals at δ 6.62 (dd, *J* 16.1 and 5.2 Hz) and 6.26 (dd, *J* 16.1 and



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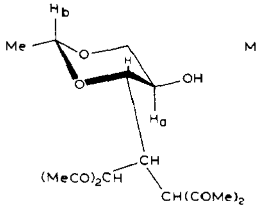

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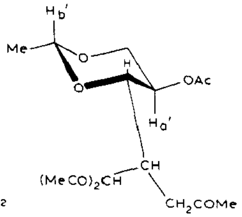

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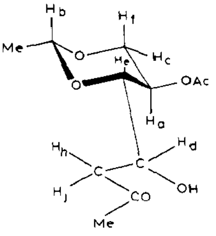

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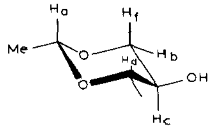

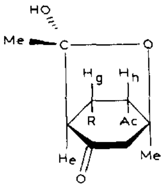

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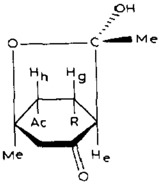


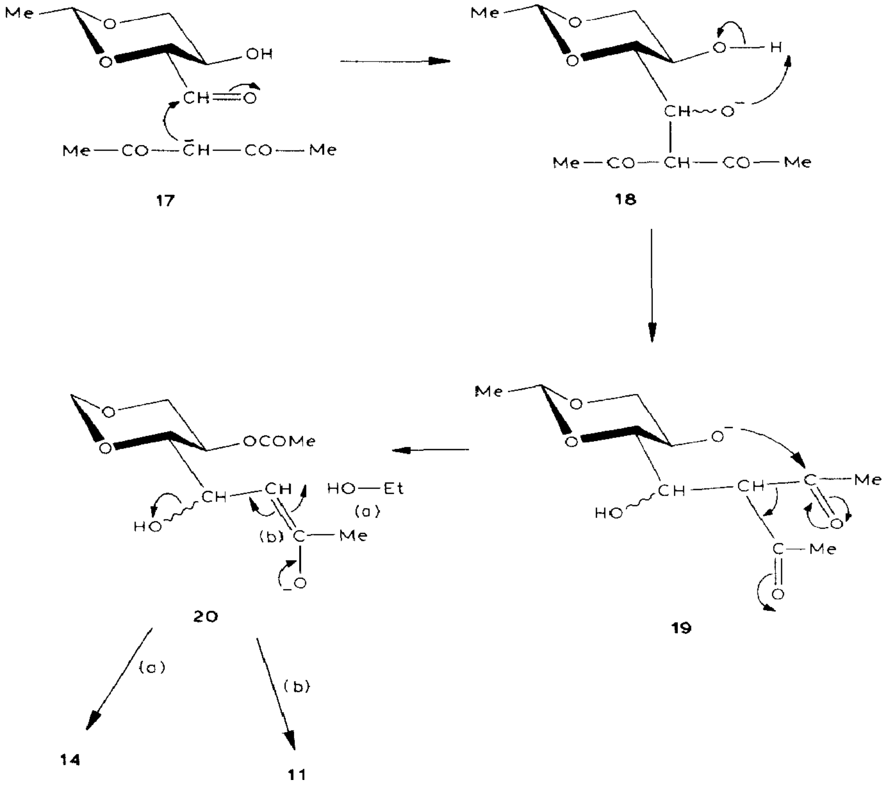
16

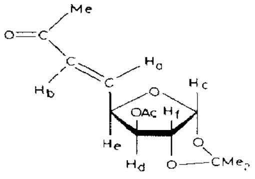
1.4 Hz), indicative of *trans* configuration. An antiperiplanar relationship between H-4 and H-5 is assumed ($J_{a,b}$ 10.2 Hz) and an equatorial disposition for Me-2 is proposed based on the configuration of the starting aldehyde.

Compound **14** showed i.r. absorptions at 3450 (OH), 1748 (acetate), 1718 (CH_3CO-R), and 1236 cm^{-1} (acetate). The ^1H-n.m.r. spectrum contained eight peaks at δ 4.92 ($J_{a,f}$ 10.5, $J_{a,e}$ 9.6, and $J_{a,c}$ 5.4 Hz) for H_a, and a signal at δ 3.41 (dd, $J_{a,e}$ 9.6 and $J_{d,e}$ 1.9 Hz) for H_e which accord with an antiperiplanar relationship of H_a and H_e. On the other hand, the resonance for H_d appeared as a set of eight peaks at δ 4.08 ($J_{d,h}$ 8.3, $J_{d,j}$ 4.5, and $J_{d,e}$ 1.9 Hz) which indicated the dihedral angle between H_e and H_d to be close to 90° and that a quasi-antiperiplanar relationship between H_d and H_j should be assumed, which would be favoured by hydrogen-bonding between the CH_3COCH_2 and OH groups. In this connexion, a broad i.r. band at 3200–2800 cm^{-1} was observed for a solution of **14** in CCl_4.

In **11** and **14**, the acetyl group has migrated to the free hydroxyl group in the starting aldehyde as shown in the sequence **17**→**18**→**19**→**20**→**11** or **14**. The remaining products **12**, **13**, and **15** or **16** apparently arise from further reaction of **11**, or intermediates in the sequence, with acetylacetone[6,7].

The reaction of 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose with acetylacetone gave (after chromatography) 3-*O*-acetyl-1,2-*O*-isopropylidene-4-(*trans*-3-oxobutenyl)-α-D-threofuranose (**21**, 26.8%), 3-*O*-acetyl-4-[(4*R*)-3-acetyl-2,6-dioxohept-4-yl]-1,2-*O*-isopropylidene-α-D-threofuranose (**22**, 15.1%), 3-*O*-acetyl-4-[(4*S*)-3-acetyl-2,6-dioxohept-4-yl]-1,2-*O*-isopropylidene-α-D-threofuranose (**23**, 20.5%), a mixture (tentatively identified on the basis of spectroscopic data) of two stereoisomers of 4-(3-hydroxy-1,3-dimethyl-8-oxo-2-oxabicyclo[2.2.2]-oct-5-yl)-1,2-*O*-isopropylidene-α-D-threofuranose (**24** or **25**, and **26** or **27**, 6.2%), and 3-*O*-acetyl-4-(6-acetyl-5-hydroxy-5-methyl-3-oxocyclohexyl)-1,2-*O*-isopropylidene-α-D-threofuranose (**28**, 4.6%).





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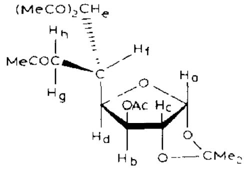

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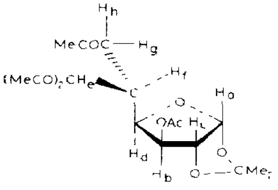

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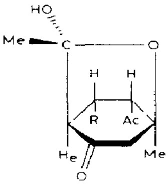

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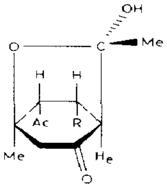

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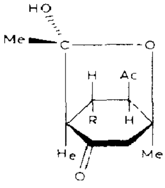

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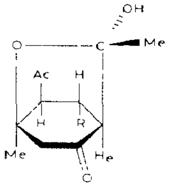

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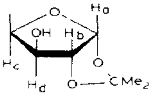
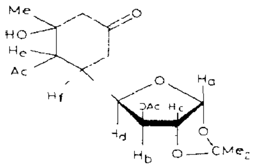
R =





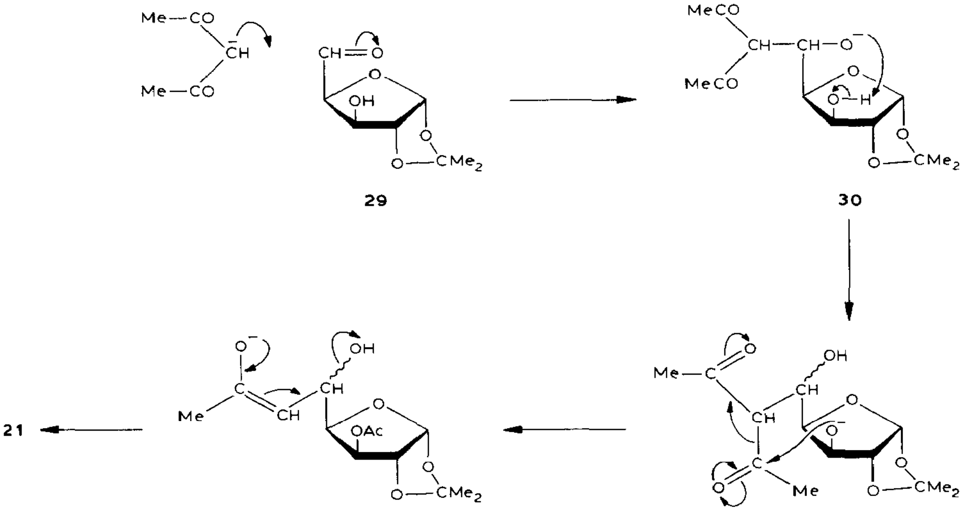
28

Compound **21** had λ_{max}^{MeOH} 220 nm (ε 13,183) consistent with a C=C-C=O group, and i.r. bands at 1748 (acetate), 1677 (C=C-C=O), 1635 (C=C), 1230 (acetate), and 986 cm^{-1} (=C-H). In accord with the configuration assigned around the C=C bond were the ^{1}H-n.m.r. signals at δ 6.60 (dd, $J_{a,b}$ 16 and $J_{a,e}$ 4.4 Hz, H_a) and 6.34 (dd, $J_{a,b}$ 16 and $J_{b,e}$ 1.6 Hz, H_b). Compound **22** had i.r. bands at 1748 (acetate), 1715 and 1700 (CH_3CO-R), and 1230 cm^{-1} (acetate), but none for enolic forms. The ^{1}H-n.m.r. signals for H_b and H_e appeared at δ 5.14 (d, $J_{b,d}$ 2.7 and $J_{b,c}$ ~0 Hz) and 4.16 (d, $J_{e,f}$ 4.4 Hz), respectively, and H_f gave a multiplet at δ 3.06–2.88. Two dd for CH_3-CO-CH_2 at δ 2.8 (J 19.3 and 6 Hz) and 2.32 (J 19.3 and 3.1 Hz) were also observed.

The *R* configuration was assigned to C-5 in **22** after considering molecular models for stereoisomers **22** and **23**. For **22**, a dihedral angle between H_f and H_d close to 180° would be expected, but this angle could be lower in **23** because of the higher repulsive interaction of the acetoxy and diacetylmethyl groups. Therefore, the highest value (10.8 Hz) for $J_{d,f}$ was tentatively associated with **22** and the lowest (8.8 Hz) with **23**, with the *R* and *S* configurations at C-5, respectively.

Compound **23** showed i.r. bands at 1742 (acetate), 1730 and 1718 (CH_3-CO-R), and 1241 cm^{-1} (acetate), but none for enolic forms. In the ^{1}H-n.m.r. spectrum, the signal for H_b was a doublet at δ 5 ($J_{b,d}$ 2.6 and $J_{b,c}$ ~0 Hz), and another doublet at 3.77 ($J_{e,f}$ 4.4 Hz) for H_e was observed. A multiplet at δ 3.02 for H_f and two double-doublets at δ 2.91 (J 18.5 and 4.8 Hz) and 2.62 (J 18.5 and 5.3 Hz) were observed for CH_3COCH_2.

Compound **28** showed i.r. bands at 3400 (OH), 1740 (acetate), 1715 (CH_3CO-R), and 1240 cm^{-1} (acetate). The configurations at the chiral carbon atoms in the cyclohexanone ring could not be deduced from the ^{1}H-n.m.r. spectrum, but the signal for H_e (bs at δ 2.86) indicated a dihedral angle close to 90° for H_e and H_f.



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21

The structure depicted was assigned after considering the signals at δ 2.38 (s, 3 H, AcO), 2.04 (s, 3 H, AcR), 1.45 (s, 3 H, MeC), 1.22 (s, 3 H, MeC), 1.21 (s, 3 H, MeC), and 1.15 (bs, 1 H, exchangeable with D_2O). As in the previous case, acetyl transfer occurred to give **21** *via* the sequence **29**→**30**→**31**→**32**→**21**. Products **22**–**28** result from further reaction of **21** with acetylacetone[6,7].

EXPERIMENTAL

General methods. — Organic solutions were dried over anhydrous Na_2SO_4. Solvents were evaporaed under diminished pressure at <40°. Column chromatography was carried out on Silica Gel 60 (Merck, 70–230 mesh, ASTM). Melting points (uncorrected) were obtained with an Electrothermal apparatus. Optical rotations were measured with a Perkin–Elmer 141 automatic polarimeter. U.v. spectra were recorded with a Perkin–Elmer 124 spectrophotometer and i.r. spectra with a Pye–Unicam SP 1000 spectrometer. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Perkin–Elmer–Hitachi R-20 B (60 MHz) spectrometer or a 200-MHz spectrometer of the University of Barcelona. Mass spectra were determined with a Hewlett–Packard model 5930 A spectrometer.

*Reaction of 2,3,4,5,6-penta-O-acetyl-*aldehydo-D-*glucose*[8] *and 2,4-pentanedione.* — A mixture of starting aldehyde (2 g), 2,4-pentanedione (1.5 g), ethanol (10 mL), and piperidine (0.25 mL) was left at room temperature for 2 days and then concentrated. The crude product was purified by column chromatography (1:1 hexane–ether) to give *trans*-4-(D-*gluco*-penta-acetoxypentyl)-3-buten-2-one (**6**; 0.7 g, 33.2%), m.p. 117–118° (from ethanol–water), $[\alpha]_D^{18}$ +24° (*c* 0.6, chloroform); λ_{max}^{MeOH} 217 nm (ε 892); ν_{max}^{KBr} 1745, 1680, 1375, 1222, 1082, 1050, 1020, 977, 958, and 830 cm^{-1}. ^{1}H-N.m.r. data (60 MHz): δ 6.72 (dd, 1 H, *J* 16 and 4.8 Hz, H-4), 6.17 (d, 1 H, *J* 16 Hz, H-3), 5.67–4.9 (m, 4 H, H-5,6,7,8), 4.16 (m, 2 H, H-9,9′), 2.27 (s, 3 H, Ac), and 2.07 (m, 15 H, 5 AcO). Mass spectrum: *m/z* 420 (M^+, absent), 387, 372, 370, 328, 313, 289, 269, 268, 250, 227, 208, 187, 143, 127, 100, and 43 (100%) (Found: C, 53.3; H, 6.1. $C_{19}H_{16}O_{11}$ calc.: C, 53.0; H, 6.1%).

*Reaction of 2,4-O-ethylidene-*aldehydo-D-*erythrose*[9] *and 2,4-pentanedione.* — A mixture of starting aldehyde (2.5 g), 2,4-pentanedione (4 g), ethanol (10 mL), and piperidine (0.3 mL) was left at room temperature for 8 days and then concentrated. Column chromatography (1:1 hexane–ether) of the crude material gave, first, (2*R*,4*S*,5*R*)-5-acetoxy-2-methyl-4-(*trans*-3-oxobutenyl)-1,3-dioxane (**11**; 0.94 g, 24%) as a syrup, $[\alpha]_D^{22}$ −41° (*c* 0.8, chloroform); λ_{max}^{MeOH} 220 nm (ε 12,303); $\nu_{max}^{CCl_4}$ 1760, 1704, 1686, 1640, 1404, 1364, 1224, 1155, 1140, 1110, 1044, 968, 920, 900, 878, and 847 cm^{-1}. ^{1}H-N.m.r. data (200 MHz): δ 6.62 (dd, 1 H, *J* 16.1 and 5.2 Hz, H-1′), 6.26 (dd, 1 H, *J* 16.1 and 1.4 Hz, H-2′), 4.72 (q, 1 H, *J* 5 Hz, H-2), 4.67–4.55 (m, 1 H, H-5), 4.19 (dd, 1 H, *J* 10.4 and 5.2 Hz, H-6), 4.18–4.1 (octet, 1 H, *J* 10.2, 5.2, and 1.4 Hz, H-4), 3.41 (dd, 1 H, *J* 10.4 and 10.1 Hz, H-6′), 2.2 (s, 3 H, Ac), 2 (s, 3 H, AcO), and 1.32 (d, 3 H, *J* 5 Hz, Me-2) (Found: C, 57.6; H, 6.9. $C_{11}H_{16}O_5$ calc.: C, 57.9; H, 7.0%).

Eluted second was a liquid mixture (0.82 g, 14.6%) probably of (2*R*,4*S*,5*R*)-4-(3,5-diacetyl-2,6-dioxohept-4-yl)-5-hydroxy-2-methyl-1,3-dioxane (**12**) and (2*R*,4*S*,5*R*)-5-acetoxy-4-(3-acetyl-2,6-dioxohept-4-yl)-2-methyl-1,3-dioxane (**13**), which had $[\alpha]_D^{22}$ −45° (*c* 0.8, chloroform); $\nu_{max}^{CCl_4}$ 3300–2800, 1744, 1722, 1708, 1357, 1228, 1150, 1112, and 1042 cm^{-1}. ^{1}H-N.m.r. data (200 MHz): δ 4.8 (m, 0.33 H, $H_{a'}$), 4.45 (m, 1 H, H_b,$H_{b'}$), 4.15–2.3 (m, 7 H), 2.28 (s, 1 H, AcO), 2.17, 2.12, 2.10, 2.09, 2.05, and 2.03 (7 s, 11 H, Ac), 1.52 (bs, 0.66 H, exchangeable with D_2O, OH), and 1.21 (d, 3 H, *J* 5.1 Hz, Me-2) (Found: C, 58.3; H, 7.5. $C_{16}H_{24}O_7$ calc.: C, 58.5; H, 7.3%).

Eluted third was (2*R*,4*S*,5*R*)-5-acetoxy-4-[(*S*)-1-hydroxy-3-oxobutyl]-2-methyl-1,3-dioxane (**14**; 0.6 g, 15%) as a syrup, $[\alpha]_D^{22}$ −30° (*c* 0.78, chloroform); ν_{max}^{film} 3450, 1748, 1718, 1365, 1236, 1144, 1112, 1087, 1038, 912, and 830 cm^{-1}; $\nu_{max}^{CCl_4}$ 3200–2800 cm^{-1}. ^{1}H-N.m.r. data (200 MHz): δ 4.92 (m, 1 H, H_a), 4.63 (q, 1 H, *J* 5 Hz, H_b), 4.18 (dd, 1 H, *J* 10.6 and 5.4 Hz, H_c), 4.08 (m, 1 H, H_d), 3.41 (dd, 1 H, *J* 9.6 and 1.9 Hz, H_e), 3.38 (dd, 1 H, *J* 10.6 and 10.5 Hz, H_f), 2.86 (dd, 1 H, *J* 17.1 and 8.3 Hz, H_h), 2.81 (bs, 1 H, exchangeable with D_2O, OH), 2.53 (dd, 1 H, *J* 17.1 and 4.5 Hz, H_j), 2.15 (s, 3 H, AcO), 2.01 (s, 3 H, Ac), and 1.28 (d, 3 H, *J* 5 Hz, Me-2) (Found: C, 53.5; H, 7.1. $C_{11}H_{18}O_6$ calc.: C, 53.6; H, 7.3%).

Eluted fourth was (2*R*,4*S*,5*R*)-5-hydroxy-2-methyl-4-{(1*S*,3*R*,4*R*,5*R*,6*S* or 1*R*,3*S*,4*S*,5*S*,6*R*)-6-acetyl-3-hydroxy-1,3-dimethyl-8-oxo-2-oxabicyclo[2.2.2]oct-5-yl}-1,3-dioxane (**15** or **16**; 0.095 g, 1.7%), m.p. 173–174° (from ether), $[\alpha]_D^{21}$ +5° (*c* 0.5, chloroform); ν_{max}^{KBr} 3430, 1705, 1693, 1366, 1154, 1116, 1097, 1060, 1022, and 878 cm^{-1}. ^{1}H-N.m.r. data (200 MHz): δ 4.63 (q, 1 H, *J* 5.1 Hz, H_a), 4.02 (dd, 1 H, *J* 10.1 and 5 Hz, H_b), 4.01–3.84 (m, 2 H, H_c,H_d), 3.6 (bs, 1 H, exchangeable with D_2O, OH), 3.4 (d, 1 H, *J* 9.6 Hz, H_e), 3.27 (dd, 1 H, *J* 10.1 and 10 Hz, H_f), 2.94–2.7 (m, 2 H, H_g,H_h), 2.46–2.37 (m, 3 H, one exchangeable with D_2O, OH, CH_2CO), 2.26 (s, 3 H, Ac), 1.38 (s, 3 H, MeC), 1.21 (d, 3 H, *J* 5.1 Hz, Me-2), and 1.2 (s, 3 H, MeC) (Found: C, 58.5; H, 7.2. $C_{16}H_{24}O_7$ calc.: C, 58.5; H, 7.3%).

*Reaction of 1,2-*O*-isopropylidene-α-*D-xylo*-pentodialdo-1,4-furanose and 2,4-pentanedione.* — A solution of 1,2-*O*-isopropylidene-α-D-glucofuranose[10] (5.5 g) in water (40 mL) was treated with $NaIO_4$ (5.5 g), and the crude product[11] was kept *in vacuo* over sulfuric acid for 24 h. A mixture of this anhydrous material, 2,4-pentanedione (6.5 g), and piperidine (0.6 mL) was left at room temperature for 17 days and then concentrated. Column chromatography (1:3 hexane–ether) of the crude material gave, first, 3-*O*-acetyl-1,2-*O*-isopropylidene-4-(*trans*-3-oxobutenyl)-α-D-threofuranose (**21**; 1.8 g, 26.8%), m.p. 75–76° (from hexane–ether), $[\alpha]_D^{17}$ +9° (*c* 0.9, chloroform); λ_{max}^{MeOH} 220 nm (ε 13,183); ν_{max}^{KBr} 1748, 1677, 1635, 1370, 1260, 1230, 1160, 1092, 1070, 1056, 1017, 986, 880, 860, and 848 cm^{-1}. ^{1}H-N.m.r. data (200 MHz): δ 6.6 (dd, 1 H, *J* 16 and 4.4 Hz, H_a), 6.34 (dd, 1 H, *J* 16 and 1.6 Hz, H_b), 5.93 (d, 1 H, *J* 3.6 Hz, H_c), 5.23 (d, 1 H, *J* 3.2 Hz, H_d), 4.91–4.86 (m, 1 H, H_e), 4.54 (d, 1 H, *J* 3.6 Hz, H_f), 2.19 (s, 3 H, Ac), 1.96 (s, 3 H, AcO), 1.47 (s, 3 H, MeC), and 1.27 (s, 3 H, MeC) (Found: C, 57.7; H, 6.6. $C_{13}H_{16}O_6$ calc.: C, 57.7; H, 6.7%).

Eluted second was 3-*O*-acetyl-4-[(4*R*)-3-acetyl-2,6-dioxohept-4-yl]-1,2-*O*-isopropylidene-α-D-threofuranose (**22**; 1.4 g, 15.1%), m.p. 127–128° (from hexane–ether), $[\alpha]_D^{17}$ −87° (*c* 0.9, chloroform); ν_{max}^{KBr} 1748, 1715, 1700, 1368, 1230, 1210, 1152, 1055, 1010, and 840 cm^{-1}. ^{1}H-N.m.r. data (200 MHz): δ 5.79 (d, 1 H, *J* 3.8 Hz, H_a), 5.14 (d, 1 H, *J* 2.7 Hz, H_b), 4.4 (d, 1 H, *J* 3.8 Hz, H_c), 4.29 (dd, 1 H, *J* 10.8 and 2.7 Hz, H_d), 4.16 (d, 1 H, *J* 4.4 Hz, H_e), 3.06–2.88 (m, 1 H, H_f), 2.8 (dd, 1 H, *J* 19.3 and 6 Hz, H_g), 2.32 (dd, 1 H, *J* 19.3 and 3.1 Hz, H_h), 2.25 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 2.03 (s, 3 H, AcO), 1.97 (s, 3 H, Ac), 1.39 (s, 3 H, MeC), and 1.22 (s, 3 H, MeC) (Found: C, 58.1; H, 7.0. $C_{18}H_{26}O_8$ calc.: C, 58.3; H, 7.1%).

Eluted third was 3-*O*-acetyl-4-[(4*S*)-3-acetyl-2,6-dioxohept-4-yl]-1,2-*O*-isopropylidene-α-D-threofuranose (**23**; 1.73 g, 20.5%), m.p. 122–123° (from hexane–ether), $[\alpha]_D^{17}$ +45° (*c* 1, chloroform); ν_{max}^{KBr} 1742, 1730, 1718, 1372, 1241, 1154, 1144, 1082, 1070, and 1010 cm^{-1}. ^{1}H-N.m.r. data (200 MHz): δ 5.76 (d, 1 H, *J* 3.8 Hz, H_a), 5.0 (d, 1 H, *J* 2.6 Hz, H_b), 4.41 (d, 1 H, *J* 3.8 Hz, H_c), 4.32 (dd, 1 H, *J* 8.8 and 2.6 Hz, H_d), 3.77 (d, 1 H, *J* 4.4 Hz, H_e), 3.02 (m, 1 H, H_f), 2.91 (dd, 1 H, *J* 18.5 and 4.8 Hz, H_g), 2.62 (dd, 1 H, *J* 18.5 and 5.3 Hz, H_h), 2.18 (s, 3 H, Ac), 2.1 (s, 3 H, Ac), 2.08 (s, 3 H, AcO), 2.05 (s, 3 H, Ac), 1.43 (s, 3 H, MeC), and 1.22 (s, 3 H, MeC) (Found: C, 58.6; H, 6.9. $C_{18}H_{26}O_8$ calc.: C, 58.3; H, 7.1%).

Eluted fourth was 4-(3-hydroxy-1,3-dimethyl-8-oxo-2-oxabicyclo[2.2.2]oct-5-yl)-1,2-*O*-isopropylidene-α-D-threofuranose (probably a mixture of **24** or **25**, and **26** or **27**; 0.58 g, 6.2%), m.p. 184–185° (from hexane–ether), $[\alpha]_D^{19}$ +28° (*c* 0.8, chloroform); ν_{max}^{KBr} 3460, 1718, 1707, 1370, 1080, and 1010 cm^{-1}. ^{1}H-N.m.r. data (200 MHz): δ 5.84 (d, 0.66 H, *J* 3.2 Hz, H_a), 5.8 (d, 0.33 H, *J* 3.7 Hz, H_a), 4.43 (dd, 0.66 H, *J* 3.2 and 0.4 Hz, H_b), 4.4 (d, 0.33 H, *J* 3.7 Hz, H_b), 4.21 (d, 0.66 H, *J* 1.2 Hz, H_c), 4.17 (dd, 0.33 H, *J* 1.2 and 0.7 Hz, H_c), 3.97 (m, 0.33 H, H_d), 3.84 (m, 0.66 H, H_d), 3.48 (d, 0.33 H, *J* 11.4 Hz, H_e), 3.32 (d, 0.66 H, *J* 11.4 Hz, H_e), 2.9–2.33 (m, 5 H, one exchangeable with D_2O, OH, CH_2CO, CHR, CHAc), 2.42 (s, 2.1 H, Ac), 2.34 (s, 0.9 H, Ac), 1.41, 1.36, 1.24, 1.23, and 1.13 (5 s, 12 H, MeC), and 1.39 (bs, 1 H, exchangeable with D_2O, OH) (Found: C, 58.3; H, 7.1. $C_{18}H_{26}O_8$ calc.: C, 58.3; H, 7.1%).

Eluted fifth was 3-*O*-acetyl-4-(6-acetyl-5-hydroxy-5-methyl-3-oxocyclohexyl)-1,2-*O*-isopropylidene-α-D-threofuranose (**28**; 0.43 g, 4.6%), m.p. 153–154° (from ether), $[\alpha]_D^{18}$ −29° (*c* 0.7, chloroform); ν_{max}^{KBr} 3400, 1740, 1715, 1370, 1240, 1160, 1085, and 1012 cm^{-1}. ^{1}H-N.m.r. data (200 MHz): δ 5.76 (d, 1 H, *J* 3.8 Hz, H_a), 4.96 (d, 1 H, *J* 2.6 Hz, H_b), 4.37 (d, 1 H, *J* 3.8 Hz, H_c), 4 (m, 1 H, H_d), 2.86 (m, 1 H, H_e), 2.5–1.8 (m, 5 H, H_f, CH_2COCH_2), 2.38 (s, 3 H, AcO), 2.04 (s, 3 H, AcR), 1.45 (s, 3 H, MeC), 1.22 (s, 3 H, MeC), 1.21 (s, 3 H, MeC), and 1.15 (bs, 1 H, exchangeable with D_2O, OH) (Found: C, 58.6; H, 7.3. $C_{18}H_{26}O_6$ calc.: C, 58.3; H, 7.1%).

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