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Note

A new synthesis of 3,4,6-trideoxy-DL-hex-3-enopyranosides

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The title compounds are useful intermediates in the total synthesis of various monosaccharides. The first synthesis[1] of the isomeric methyl 3,4,6-trideoxy-DL-hex-3-enopyranosides involved 5 steps starting from *trans*-5,6-dihydro-2-methoxy-6-methyl-2*H*-pyran. Additions to their double bond made possible the synthesis of 6-deoxyhexoses[2].

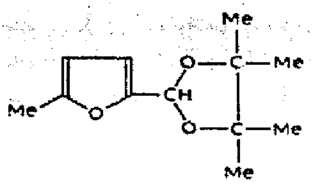
We have described[3] a method for the synthesis of racemic pentoses from 2-furaldehyde. We now report the synthesis of racemic methyl 3,4,6-trideoxy-DL-*threo*- and -DL-*erythro*-hex-3-enopyranosides from 5-methyl-2-furaldehyde (**1**)

The formyl group of **1** was protected[3] by condensation with 2,3-dimethylbutane-2,3-diol to give the dioxolane **2**. The high stability of **2** in acidic conditions permitted oxidation with bromine water at pH 3–4. The resulting unsaturated dioxo-compound **3** was not isolated, but was reduced immediately with sodium borohydride to give a mixture of **4** and **5**, which was fractionated by chromatography: **4** and **5** were characterised as the dibenzoates. The fundamental structure of **4** and **5** was proved by n.m.r. spectroscopy. The value (11 Hz) of $J_{3,4}$ shows that the double bond has a *cis* configuration, but, because of the rotation of the open chain, it was not possible to assign *erythro* and *threo* configurations to the isomers of DL-2-(1,4-dihydroxy-*cis*-pent-2-enyl)-4,4,5,5-tetramethyl-1,3-dioxolane. However, methanolysis of **4** and **5** gave known[1] methyl 3,4,6-trideoxy-α-DL-*threo*-hex-3-enopyranoside (**6**) and methyl 3,4,6-trideoxy-β-DL-*erythro*-hex-3-enopyranoside (**7**), respectively, which were identified by n.m.r. spectroscopy.

EXPERIMENTAL

General methods. — Melting points, which are uncorrected, were determined on a Kofler block. I.r. spectra were recorded with a Unicam SP 200 spectrophotometer, and n.m.r. spectra with a JEOL JNM-100 spectrometer.

4,4,5,5-Tetramethyl-2-(5-methyl-2-furyl)-1,3-dioxolane (**2**). — A mixture of 5-methyl-2-furaldehyde (21.2 g, 0.192 mol), 2,3-dimethylbutane-2,3-diol (22.6 g,



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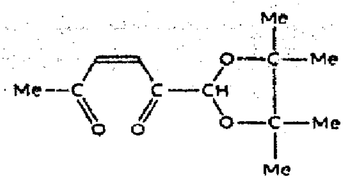

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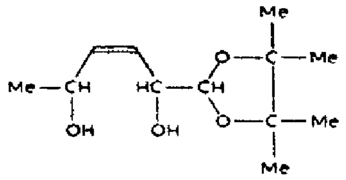
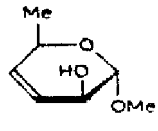


4 + 5



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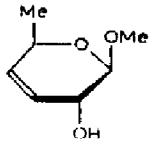

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0.192 mol), and dry benzene (200 ml) was boiled under reflux in the presence of toluene-*p*-sulphonic acid (500 mg) for 5 h with removal of water by azeotropic distillation. The mixture was then successively washed with 10% aqueous sodium carbonate and water, dried, and concentrated to dryness. The residue was distilled to give **2** (27.5 g, 68%), b.p. 92°/0.5 mmHg.

Anal. Calc. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.62. Found: C, 68.15; H, 8.75.

2-(DL-erythro-*1,4-Dihydroxy-*cis*-pent-2-enyl)-4,4,5,5-tetramethyl-1,3-dioxolane* (**5**) *and its* threo *isomer* (**4**). — Compound **2** (10.5 g, 0.05 mol) was oxidized with bromine water, and the product was reduced with sodium borohydride as described earlier[3] for 2-(2-furyl)-4,4,5,5-tetramethyl-1,3-dioxolane. The crude product contained two components (t.l.c.; light petroleum–acetone, 95:5), which were separated by elution from silica gel with light petroleum–acetone (9:1) to give first the *threo* isomer **4** as a syrup (3.55 g). N.m.r. data ($CDCl_3$): δ 4.88 (d, 1 H, $J_{1,2}$ 5.6 Hz, H-2), 4.38 (q, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 5.71 (q, 1 H, $J_{2',3'}$ 11 Hz, H-2'), 5.45 (q, 1 H, H-3'), 4.65 (octet, 1 H, $J_{3',4'}$ 7.7 Hz, H-4'), 1.31 (d, 3 H, $J_{4',5'}$ 6.3 Hz, Me-5'), 1.20 (s, 12 H, Me-4,4,5,5).

Anal. Calc. for $C_{11}H_{22}O_4$: C, 62.53; H, 9.63. Found: C, 62.70; H, 9.69.

The dibenzoate of **4**, prepared conventionally with benzoyl chloride–pyridine, was a syrup.

Eluted second was the *erythro* isomer **5** which was also a syrup (3.25 g). N.m.r. data: δ 4.85 (d, 1 H, $J_{1',2'}$ 6.2 Hz, H-2), 4.50 (q, 1 H, $J_{1',2'}$ 7.9 Hz, H-1'), 4.50 (octet, 1 H, H-4'), 5.70 (q, 1 H, H-2'), 5.50 (q, 1 H, $J_{2',3'}$ 11.1 Hz, H-3'), 1.25 (d, 3 H, $J_{4',5'}$ 7.9 Hz, Me-5'), 1.20 (s, 12 H, Me-4,4,5,5).

Anal. Found: C, 62.04; H, 9.67.

The dibenzoate of **5** had m.p. 103–104° (from ethanol).

Anal. Calc. for $C_{26}H_{30}O_6$: C, 71.25; H, 6.89. Found: C, 71.69; H, 6.93.

*Methyl 3,4,6-trideoxy-α-*DL-threo-*hex-3-enopyranoside* (**6**). — A solution of

4 (2 g) in 1% methanolic hydrogen chloride was boiled under reflux for 8 h, then neutralized with Dowex-1 (HCO_3^-) resin, and concentrated. The residue was eluted from silica gel with benzene–ether (1:1) to give **6** (712 mg). The n m r. spectrum was the same as that recorded in Ref 1.

*Methyl 3,4,6-trideoxy-β-*DL-erythro-*hex-3-enopyranoside* (**7**) — Treatment of **5** (2 g) by the procedure described for **4** gave **7** (708 mg) The n m.r. spectrum was the same as that recorded in Ref 1

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