

Crystal Structure of the Self Condensation Product of (3*R*,4*R*)-3,4-Dihydroxyhexane-2,5-dione

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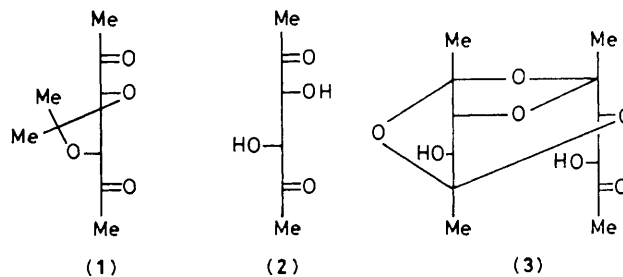
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Two molecules of (3*R*,4*R*)-3,4-dihydroxyhexane-2,5-dione condense to afford a novel, tricyclic acetal whose structure has been determined by X-ray crystallography.

We recently required 3,4-dihydroxyhexane-2,5-dione, and developed a synthesis of 3,4-*O*-isopropylidene-(3*R*,4*R*)-3,4-dihydroxyhexane-2,5-dione (1), which appeared to be a reasonable precursor of a chiral form (2)[†] of the dihydroxydione.

Treatment³ of the acetal (1) with trifluoroacetic acid-water (9:1 v/v) for 10 min, followed by evaporation of the aqueous acid under reduced pressure (bath temperature ≤ 30 °C), and crystallisation of the residue from ethyl acetate or methanol gave, however, not compound (2), but a crystalline solid m.p. 199–201 °C; $[\alpha]_D^{25} - 1.4^\circ$ (*c* 1.0, Me₂SO); M^+ 274; ¹H n.m.r. [200 MHz, (CD₃)₂SO] δ 1.24, 1.48, 1.53 (3 \times 3H, 3 \times s, 3 \times Me-C), 2.11 (3H, s, MeCO), 3.95 [1H, d, *J* 4 Hz, -CH(OH)-],



[†] Racemic 3,4-dihydroxyhexane-2,5-dione has been prepared¹ by hydrodimerization of methyl glyoxal, and a preparation of a 3,4-dihydroxyhexane-2,5-dione from D-mannitol has been described² which, presumably, afforded the (3*S*,4*S*)-isomer.

4.00 [1H, s, -CH(OR)-], 4.07 [1H, dd, *J* 2 and 8 Hz, -CH(OH)-], 4.15 [1H, d, *J* 2 Hz, -CH(OR)-], 4.78 [1H, d, *J* 8 Hz, -CH(OH)-], and 5.52 [1H, d, *J* 4 Hz, -CH(OH)-]; ¹³C n.m.r. [25 MHz, (CD₃)₂SO] δ 19.6, 20.6, 21.4 (3 \times Me-C), 26.0 (Me-CO-), 77.1, 77.7 [2 \times -CH(OH)-], 80.6, 86.7 [2 \times

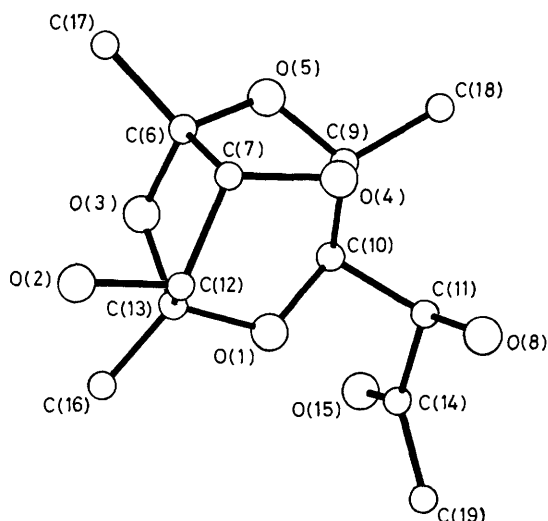


Figure 1. Crystal structure of the condensation product (3). The absolute configuration of the molecule is represented.

$-\text{CH}(\text{OR})-$, 108.6, 109.9, 112.4 ($3 \times -\text{OCR}_2\text{O}-$), and 208.9 p.p.m. ($\text{C}=\text{O}$); ν_{max} (Nujol) 3510, 3470 (OH), and 1700 cm^{-1} ($\text{C}=\text{O}$).

The analytical and physical data clearly suggested the compound to have been formed from two molecules of (2) with elimination of water, to have an acetal-type structure, and to contain two hydroxy groups and one acetyl group. However, a considerable number of structures may be envisaged which satisfy these criteria, and, therefore, an X-ray crystallographic analysis was undertaken. These revealed the novel tricyclic structure shown in Figure 1 and in formula (3).

Crystal data: compound (3), $\text{C}_{12}\text{H}_{18}\text{O}_7$, $M = 274.3$, from methanol, monoclinic, space group $P2_1$, $a = 12.458(1)$, $b = 5.314(1)$, $c = 9.561(1) \text{ \AA}$, $\beta = 90.02(1)^\circ$, $U = 632.9 \text{ \AA}^3$, $D_c = 1.449 \text{ cm}^{-3}$, $D_m = 1.439 \text{ cm}^{-3}$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 1.26 \text{ cm}^{-1}$.

Cell dimensions were determined and refined from the setting angles of 23 reflections found on the Hilger-Watt Y290 diffractometer using Mo-K α radiation (graphite monochromator). Intensities were measured for reflections with $\theta \leq 30^\circ$ and of the 2026 scanned, 1828 had $I \geq 3\sigma(I)$ and were deemed 'observed' and used in the refinement. The structure was solved using MULTAN 78 and refined by full matrix least squares. Hydrogen atoms were all found from a difference map, and in the final stages of refinement were included in calculated positions where possible (the two hydroxy hydrogens and one of the acetyl methyl hydrogens were included in

found positions), but not refined.† The final conventional R value was 3.9%. The standard deviation for lengths not involving hydrogen lay in the range 0.002–0.004 Å and for angles 0.14–0.22°.

The two six-carbon units in (3) are linked by oxygen bridges connecting C(2), C(3), and C(5) in the first chain to C(2), C(2), and C(3), respectively, in the second chain. The seven membered ring defined by O(1), C(10), C(9), O(5), C(6), O(3), and C(13) (see Figure 1) exists in a near ${}^{\text{C}(13)}, {}^{\text{O}(1)}\text{C}_{\text{O}(5)}$ chair conformation.⁴ A consideration of Dreiding and Corey–Pauling–Koltun molecular models suggests that the tricyclic ring system may contain considerable strain, and it is noteworthy that two of the bond angles within this framework, C(10)–O(1)–C(13) at 120.8° and C(7)–C(12)–C(13) at 100.6° , represent, respectively, the upper and lower extreme value for bond angles at oxygen and tetrahedral carbon in this structure.

It is interesting to compare this crystal structure with the quite different tricyclic spiran structure reported for a related compound D-threo-2,5-hexodiulose, which dimerizes in the crystal state,⁵ and in solution in dimethyl sulphoxide.^{6,7}

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The structure factor table is available as a Supplementary Publication No. SUP 23674 (15 pp.) from the British Library Lending Division. For details of how to obtain this material, see Instructions to Authors, *J. Chem. Soc., Perkin Trans.*, 1983, Issue 1.