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Acta Cryst. (1990). C**46**, 156–158

Structure of (1*R*,5*S*,8*R*)-8-Methoxy-3,3-dimethyl-2,4,7-trioxabicyclo-[3.3.0]octan-6-one

By Dionissios Papaioannou,* George W. Francis and Knut Maartmann-Moe

Department of Chemistry, University of Bergen, Allégaten 41, *N*-5007 *Bergen, Norway*

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Abstract. $C_8H_{12}O_5$, $M_r = 188{\cdot}18$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}164\,(2)$, $b = 9{\cdot}388\,(3)$, $c = 13{\cdot}813\,(3)$ Å, $V = 928{\cdot}9\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}345$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}06$ cm^{-1}, $F(000) = 400$, $T = 90$ K, final $R = 0{\cdot}024$ for 1474 unique observed reflections with $I > 2\sigma(I)$ and 167 variables. The determination was carried out to establish unambiguously the structure of an unexpected reaction by-product. The lactone ring is nearly planar, while the acetonide ring has an envelope conformation with the C atom carrying the *gem*-methyl substituents lying out of plane. The angle between the ring planes is 109·15°. Bond distances and angles are unexceptional.

Experimental. The title compound was isolated as a by-product of oxidation of methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside with pyridinium dichromate. The by-product was obtained after flash chromatography and fractional distillation. The compound was recrystallized as colourless prisms, m.p. 352–353 K (sealed tube), $[\alpha]_D^{25^\circ\text{C}}$ $-53{\cdot}3$ ($c = 1$, $CHCl_3$). The X-ray diffraction measurements were made on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The crystal used was cut to an approximate size 0·34 × 0·31 × 0·39 mm. The temperature at the crystal site was 90 K. Cell parameters were based on a least-squares fit of 25 independent reflections with $28 < 2\theta < 40°$. The intensity data were recorded using the ω-scan technique with a constant scan speed of 2·7° min^{-1}. The crystal orientation was checked every 200 recordings. Three standard reflections were measured every hour. They varied by less than 2%, the variations being irregular with respect to time. The data were corrected for Lp and absorption effects. The latter correction was empirical (Walker & Stewart, 1983); minimum correction factor was 0·94 and maximum 1·05. 1567 independent reflections were recorded ($2\theta < 60°$), h 0–10, k 0–13, l 0–19, 93 reflections with $I < 2{\cdot}0\sigma(I)$ were regarded as unobserved. The structure was solved by *MULTAN*80 (Main *et al.*, 1980) and refined by full-matrix least-squares minimization of $\sum w(\Delta F)^2$, where $w^{-1} = \sigma^2(I)/4\text{Lp}I$, $\sigma^2(I) = \sigma^2(I_c) + 0{\cdot}02(I_c)^2$ and $I_c = I_{\text{count}}$. Non-H atoms were refined with anisotropic and H atoms with isotropic thermal parameters. The final shift-to-e.s.d. ratio was $\leq 0{\cdot}01$. The difference Fourier map after final least-squares

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* On leave from the Department of Chemistry, University of Patras, Patras, Greece.

iteration showed maximum and minimum residual electron densities of 0·25 and 0·00 e Å^{-3}. The refinement converged to a conventional R = 0·024, wR = 0·032 and S = 1·30.* Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974). The computer programs used are part of the Enraf–Nonius *SDP-Plus* package (Frenz, 1985). The absolute configuration was determined by means of refinement of the chirality parameter η (Rogers, 1984). The configuration found (Fig. 1), which is in accord with expectation, was clearly indicated irrespective of whether the correct or antipodal structure was used as a starting point for the calculation. Atomic parameters are listed in Table 1, and bond distances and selected bond angles in Table 2.

Related literature. Although pyridinium dichromate has been widely used to oxidize alcohols to carbonyl compounds (Corey & Schmidt, 1979) successful application to sugar alcohols requires the presence of molecular sieves (Herscovici, Egron & Antonakis, 1982; Czernecki, Georgoulis, Stevens & Vijayakumaran, 1985). The structure compares well with those already determined for 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose (Poppleton, 1976), 2,3-di-*O*-acetyl-2-*C*-methylerythrono-1,4-lactone (Conde, Moreno & Marquez, 1980) and of nucleosides bearing an isopropylidene substituent (Mande, Sheshadri & Viswamitra, 1989).

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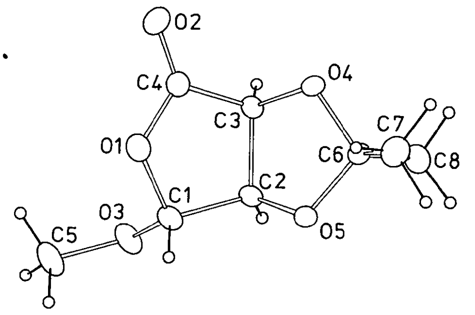

Fig. 1. *ORTEP* (Johnson, 1965) drawing of (1*R*,5*S*,8*R*)-8-methoxy-3,3-dimethyl-2,4,7-trioxabicyclo[3.3.0]octan-6-one.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}].$$

	x	y	z	B_{eq}(Å^2)
O(1)	0·4412 (1)	0·29544 (9)	0·70054 (5)	1·72 (1)
O(2)	0·2481 (1)	0·12996 (9)	0·64235 (7)	2·48 (2)
O(3)	0·7407 (1)	0·35549 (8)	0·65201 (5)	1·75 (1)
O(4)	0·1790 (1)	0·38170 (8)	0·51836 (6)	1·37 (1)
O(5)	0·3627 (1)	0·56285 (7)	0·56817 (6)	1·57 (1)
C(1)	0·5617 (2)	0·4073 (1)	0·66287 (7)	1·39 (2)
C(2)	0·4856 (1)	0·4441 (1)	0·56274 (7)	1·28 (1)
C(3)	0·3574 (1)	0·3199 (1)	0·53623 (7)	1·18 (1)
C(4)	0·3411 (2)	0·2341 (1)	0·62885 (8)	1·53 (2)
C(5)	0·8274 (2)	0·3139 (1)	0·74136 (9)	2·23 (2)
C(6)	0·2101 (2)	0·5312 (1)	0·50491 (8)	1·45 (2)
C(7)	0·0405 (2)	0·6111 (1)	0·5383 (1)	2·33 (2)
C(8)	0·2611 (2)	0·5589 (1)	0·39955 (9)	2·38 (2)
H(1)	0·555 (2)	0·484 (1)	0·7081 (9)	1·4 (3)
H(2)	0·587 (2)	0·456 (2)	0·515 (1)	2·0 (3)
H(3)	0·402 (2)	0·262 (1)	0·4826 (9)	1·2 (2)
H(5–1)	0·757 (3)	0·232 (2)	0·775 (1)	3·9 (4)
H(5–2)	0·827 (3)	0·395 (2)	0·788 (1)	3·1 (4)
H(5–3)	0·954 (3)	0·283 (2)	0·728 (1)	3·8 (4)
H(7–1)	0·011 (3)	0·589 (2)	0·607 (1)	3·4 (4)
H(7–2)	–0·071 (3)	0·582 (2)	0·497 (1)	3·0 (3)
H(7–3)	0·068 (3)	0·717 (2)	0·532 (1)	3·3 (4)
H(8–1)	0·385 (3)	0·501 (2)	0·379 (1)	3·9 (4)
H(8–2)	0·160 (3)	0·526 (2)	0·358 (1)	3·1 (4)
H(8–3)	0·274 (3)	0·659 (2)	0·390 (1)	3·7 (4)

Table 2. *Bond distances* (Å) *and angles* (°)

O(1)—C(1)	1·455 (1)	O(4)—C(3)	1·425 (1)	C(2)—C(3)	1·529 (1)
O(1)—C(4)	1·352 (1)	O(4)—C(6)	1·433 (1)	C(3)—C(4)	1·516 (1)
O(2)—C(4)	1·198 (1)	O(5)—C(2)	1·422 (1)	C(6)—C(7)	1·501 (2)
O(3)—C(1)	1·380 (1)	O(5)—C(6)	1·430 (1)	C(6)—C(8)	1·523 (2)
O(3)—C(5)	1·436 (1)	C(1)—C(2)	1·526 (1)		

C(1)—O(1)—C(4)	111·11 (7)	O(4)—C(3)—C(4)	107·04 (8)
C(1)—O(3)—C(5)	113·85 (8)	C(2)—C(3)—C(4)	104·45 (8)
C(3)—O(4)—C(6)	106·38 (7)	O(1)—C(4)—O(2)	121·9 (1)
C(2)—O(5)—C(6)	106·15 (7)	O(1)—C(4)—C(3)	110·54 (8)
O(1)—C(1)—O(3)	109·62 (8)	O(2)—C(4)—C(3)	127·4 (1)
O(1)—C(1)—C(2)	105·99 (8)	O(4)—C(6)—O(5)	104·05 (7)
O(3)—C(1)—C(2)	108·26 (8)	O(4)—C(6)—C(7)	108·88 (8)
O(5)—C(2)—C(1)	110·54 (7)	O(4)—C(6)—C(8)	109·16 (9)
O(5)—C(2)—C(3)	103·82 (6)	O(5)—C(6)—C(7)	109·13 (8)
C(1)—C(2)—C(3)	105·00 (8)	O(5)—C(6)—C(8)	111·40 (8)
O(4)—C(3)—C(2)	105·62 (7)	C(7)—C(6)—C(8)	113·8 (1)

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* Lists of structure factors, anisotropic thermal parameters, torsional angles, least-squares planes, and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52226 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Benzopyranopyranooxazepinone

By Jochen Antel and George M. Sheldrick

Institute für Anorganische Chemie der Universität, Tammannstrasse 4, *D*-3400 *Göttingen, Federal Republic of Germany*

and Thomas Pfeiffer and Lutz-F. Tietze

Institut für Organische Chemie der Universität, Tammannstrasse 2, *D*-3400 *Göttingen, Federal Republic of Germany*

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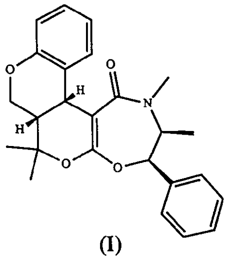
Abstract. *cis*-(+)-(3*S*,4*R*,7a*S*,13b*R*)-2,3,7,7-Tetramethyl-4-phenyl-1,2,3,4,7,7a,8,13b-octahydro-8*H*-[1]-benzopyrano[4′,3′:4,5]pyrano[3,2-*f*][1,4]oxazepin-1-one monohydrate, $C_{25}H_{27}NO_4.H_2O$, $M_r = 423{\cdot}49$, monoclinic, $P2_1$, $a = 6{\cdot}563\,(1)$, $b = 7{\cdot}922\,(2)$, $c = 20{\cdot}877\,(4)$ Å, $\beta = 94{\cdot}32\,(2)°$, $V = 1082{\cdot}46$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 448$, $T = 298$ K, $R = 0{\cdot}057$ for 2256 observed reflections. The structure was investigated to determine the relative configuration at C(7a) and C(13b), which could not be established unambiguously by NMR. The absolute configuration at C(3) and C(4) was already known from the educt L-ephedrine. The seven-membered oxazepine ring shows a pseudo-boat conformation. The two dihydropyran rings adopt a half-chair conformation. The title compound cocrystallized with one molecule of water, which forms a weak hydrogen bond [O(6)···O(90) = 2·84 Å].

Experimental. (I): crystal size 0·4 × 0·6 × 0·1 mm. Stoe–Siemens four-circle diffractometer, monochromated Mo $K\alpha$ radiation, profile-fitting mode involving variable scan width and speed (Clegg, 1981). 2814 reflections measured, $2\theta_{\max}$ 45°, $\pm h + k + l$, three check reflections with no significant intensity change. 2814 unique reflections, of which 2256 with $F > 4\sigma(F)$ were used for all calculations (*SHELXS*86, Sheldrick, 1985; *SHELX*76, Sheldrick, 1976). Cell constants refined from $\pm 2\theta$ values of 32 reflections in the range 20–25°. Absorption correction was deemed unnecessary. Extinction correction was applied yielding a secondary-extinction coefficient x of 0·0049 (8), where $F_c^* = F_c(1 + 0{\cdot}002xF_c^2/\sin2\theta)^{-0{\cdot}25}$. Structure solution by direct methods. Refinement on F to $R = 0{\cdot}057$, $wR = 0{\cdot}062$; all non-H atoms anisotropic, H atoms were refined using a riding model [C—H 0·96 Å, U(H) = 0·08 Å^2, except for methyl protons U(H) = 0·12 Å^2]. H atoms attached to water O(90) were not located. 280 parameters were refined, $S = 1{\cdot}47$, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0006F^2$ which led to a featureless analysis of variance in terms of $\sin\theta$ and F_o, max. $\Delta/\sigma = 0{\cdot}55$ for U_{23} of O(90), max. and min. heights in final $\Delta\rho$ map 0·31 and $-0{\cdot}43$ e Å^{-3} respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).



(I)

Atomic parameters are given in Table 1, selected bond distances and angles in Table 2.* Fig. 1 shows a thermal ellipsoid plot with the atom numbering.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52146 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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