Racemic 7-oxabicyclo[2.2.1]heptane-5-*exo*-iodo-6-*endo*-hydroxy-2-*endo*-carboxylic acid- γ -lactone

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Key indicators

Single-crystal X-ray study

$T = 295\text{ K}$

Mean $\sigma(\text{C}—\text{C}) = 0.007\text{ \AA}$

R factor = 0.029

wR factor = 0.077

Data-to-parameter ratio = 17.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the γ -lactone of racemic 7-oxabicyclo[2.2.1]heptane-5-*exo*-iodo-6-*endo*-hydroxy-2-*endo*-carboxylic acid has confirmed the position of the lactone bridge as 2–6 and the *exo*-iodo substituent configuration as previously proposed from chemical and ^{13}C NMR evidence. The iodo substituent is also involved in a short non-bonding intermolecular interaction [$\text{I} \cdots \text{O}$ 3.289 (5) $\text{\AA}$] with the non-bridging lactone oxygen giving polymeric chains which link weakly hydrogen-bonded ($\text{C}—\text{H} \cdots \text{O}$) centrosymmetric dimer units.

Comment

The γ -lactone of racemic 7-oxabicyclo[2.2.1]heptane-5-*exo*-iodo-6-*endo*-hydroxy-2-*endo*-carboxylic acid was first reported by van Tamelen & Shamma (1954). A modification of the standard Diels–Alder procedure for the synthesis of the 7-oxabicyclo[2.2.1]heptenes using furan with ethyl acrylate rather than maleic anhydride (Kunstmann *et al.*, 1962) gave rise to a series of 2-substituted derivatives (both *exo*- and *endo*-isomers) and the title compound, (I), was prepared by these authors from the 2-*endo* isomer by treatment with iodine/potassium iodide. Later procedures (Kotsuki *et al.*, 1984) employing furan with methyl acrylate in the presence of $\text{BF}_3\text{—OEt}$ catalyst gave high *endo*-isomer selectivity (*ca* 75%). The analogous optically active (+)-5-bromo compound has also been resolved and its crystal structure determined (Ogawa *et al.*, 1985).

The crystal structure of the iodo lactone (I) prepared from the alkene synthesized by the method of Kotsuki *et al.* (1984) has confirmed the *exo*-configuration of the 5-iodo substituent, as well as the siting of the 2–6 lactone bridge (Fig. 1). The torsion angles $\text{C3}—\text{C4}—\text{C5}—\text{I5}$ and $\text{C1}—\text{C2}—\text{C21}—\text{O21}$ are $-172.0(3)^\circ$ and $-159.1(5)^\circ$, respectively. The relatively inflexible oxabicyclo cage together with its associated lactone bridge is not as common structurally as the corresponding norbornane cage lactone structures (Moriarty *et al.*, 1972; Singh *et al.*, 1974) or the more comparable *exo*-5-iodo-bi-

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Figure 1
The molecular configuration and atom-numbering scheme. Non-H atoms are shown as 30% probability ellipsoids.

cyclo[2.2.2]octane cage lactone structure (Carman *et al.*, 1982). However, the molecular cage in (I) is similar to both these cage structural units and more so to the analogous optically active bromo compound, (+)-7-oxabicyclo[2.2.1]heptane-5-*exo*-bromo-6-*endo*-hydroxy-2-*endo*-carboxylic acid γ -lactone (Ogawa *et al.*, 1985) (comparative torsion angles: -174.5 and -161.7°).

In the packing of the compound in the unit cell, although no formal hydrogen bonds may exist, weak C5—H5...O21ⁱ (lactone) interactions [$C \cdots O$ 3.350 (6) Å; symmetry code: (i) $-x, -y, 2 - z$] join the molecules into centrosymmetric dimers. These are then linked across a *b*-face diagonal by relatively short intermolecular associations between the iodo substituent and the non-bridging lactone oxygen [I5...O21ⁱⁱ 3.289 (5) Å; symmetry code: (ii) $-1 + x, y, -1 + z$].

Experimental

The title compound was synthesized using a variation of the method of Kunstmann *et al.* (1962) by the room-temperature reaction of the unsaturated carboxylic acid, racemic 7-oxabicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid with iodine/potassium iodide for 4 h (72% yield). The acid was prepared from the methyl ester by hydrolysis with 10% aqueous NaOH (room temperature, 1 d). This ester precursor was synthesized using the method of Kotsuki *et al.* (1984) by a Diels–Alder addition reaction of methyl acrylate with furan in the presence of $BF_3 \cdot OEt_2$ catalyst (253 K, then 277 K for 10 h). After extraction of the final iodolactone into chloroform, data crystals were obtained by recrystallization from acetone. Spectroscopic data, FT-IR (cm^{-1}): 2996.3 (C—H stretch, aliphatic), 1786.2 (C=O stretch), 1190.0 (C—O stretch, lactone), 1022.7 (C—O stretch, ether bridge); 1H NMR (200 MHz, $CDCl_3$, p.p.m.): δ 2.00–2.30 (2H, *m*, C-3 methylene), 2.65–2.85 (1H, *m*, H-2), 3.29 (1H, *s*, H-5), 4.77 (1H, *m*, H-4), 5.08 (1H, *d*, H-6, $J_{1,6} = 5$ Hz), 5.34 (1H, *t*, H-1, $J_{1,2} = 5$ Hz); ^{13}C NMR ($CDCl_3$, p.p.m.): δ 25.02 (C-5), 36.13 (C-3), 38.06 (C-2), 81.87 (C-6), 84.21 (C-4), 87.52 (C-1), 175.76 (C=O); ^{13}C NMR (DEPT, p.p.m.): δ 25.02 (CH), 36.13 (CH_2), 38.06 (CH), 81.87 (CH), 84.21 (CH), 87.52 (CH).

Crystal data

$C_7H_7IO_3$
 $M_r = 266.04$
Monoclinic, $P2_1/c$
 $a = 5.9896$ (11) Å
 $b = 15.5307$ (15) Å
 $c = 8.8471$ (11) Å
 $\beta = 106.934$ (12) $^\circ$
 $V = 787.3$ (2) Å³
 $Z = 4$

$D_x = 2.244$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 19.5$ – 20.0°
 $\mu = 4.02$ mm⁻¹
 $T = 295$ (2) K
Prism, colourless
 $0.30 \times 0.25 \times 0.25$ mm

Data collection

Rigaku AFC-7R diffractometer
 ω - 2θ scans
Absorption correction: ψ scan
(*TEXSAN for Windows*; Molecular Structure Corporation, 1999b)
 $T_{min} = 0.379$, $T_{max} = 0.433$
2170 measured reflections
1787 independent reflections

1470 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$
 $\theta_{max} = 27.5^\circ$
 $h = 0 \rightarrow 7$
 $k = 0 \rightarrow 18$
 $l = -11 \rightarrow 11$
3 standard reflections every 150 reflections
intensity decay: 1.2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.077$
 $S = 1.06$
1787 reflections
101 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2 + 2.3302P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.43$ e Å⁻³
 $\Delta\rho_{min} = -0.35$ e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0208 (9)

All H atoms were included at calculated positions with their positional and isotropic displacement parameters constrained.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999a); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999b); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *TEXSAN for Windows*.

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