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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

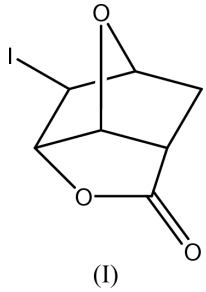
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.007 Å
R factor = 0.029
wR factor = 0.077
Data-to-parameter ratio = 17.7

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 [I···O 3.289 (5) Å] with the non-bridging lactone oxygen giving polymeric chains which link weakly hydrogen-bonded (C—H···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 BF_3–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).



(I)

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 C3—C4—C5—I5 and C1—C2—C21—O21 are −172.0 (3) and −159.1 (5)°, 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-

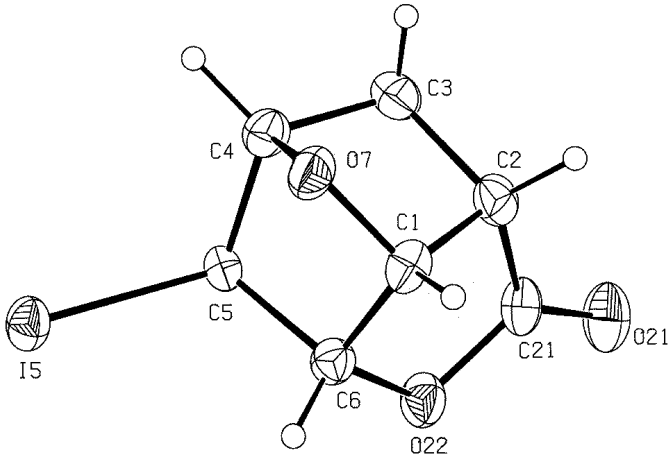


Figure 1
The molecular configuration and atom-numbering scheme. Non-H atoms are shown as 30% probability ellipsoids.

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···O21^{i} (lactone) interactions [C···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···O21^{ii} 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); ^{1}H 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

$C_7H_7IO_3$	D_x = 2.244 Mg m^{-3}
M_r = 266.04	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
a = 5.9896 (11) Å	θ = 19.5–20.0°
b = 15.5307 (15) Å	μ = 4.02 mm^{-1}
c = 8.8471 (11) Å	T = 295 (2) K
β = 106.934 (12)°	Prism, colourless
V = 787.3 (2) Å^3	0.30 × 0.25 × 0.25 mm
Z = 4	

Data collection

Rigaku AFC-7*R* diffractometer	1470 reflections with $I > 2\sigma(I)$
ω–2θ scans	R_{int} = 0.024
Absorption correction: ψ scan (*TEXSAN for Windows*; Molecular Structure Corporation, 1999*b*)	θ_{max} = 27.5°
	$h = 0 \rightarrow 7$
	$k = 0 \rightarrow 18$
T_{min} = 0.379, T_{max} = 0.433	$l = -11 \rightarrow 11$
2170 measured reflections	3 standard reflections
1787 independent reflections	every 150 reflections
	intensity decay: 1.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0265P)^2 + 2.3302P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.029	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.077	$\Delta\rho_{max}$ = 0.43 e Å^{-3}
S = 1.06	$\Delta\rho_{min}$ = −0.35 e Å^{-3}
1787 reflections	Extinction correction: *SHELXL*97
101 parameters	Extinction coefficient: 0.0208 (9)
H-atom parameters constrained	

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, 1999*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *TEXSAN for Windows*.

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