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

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 13C 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 BF₃-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).
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 C−H⋅⋅⋅O21′ (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″ 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]heptane-5-exo-bromo-6-endo-hydroxy-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 BF₃·OEt₂ 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, lactone), 1190.0 (C−O stretch, lactone), 1022.7 (C−O stretch, ether bridge); ¹H NMR (200 MHz, CDCl₃, 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, J₁₆=5 Hz), 5.34 (1H, t, H-1, J₁₂=5 Hz); ¹³C NMR (CDCl₃, p.p.m.): δ 30.02 (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); ¹³C NMR (DEPT, p.p.m.): δ 25.02 (CH), 36.13 (CH₂), 38.06 (CH), 81.87 (CH), 84.21 (CH), 87.52 (CH).

**Crystal data**

C₇H₇IO₃

Mₐ = 260.04

Monoclinic, P2₁/c

a = 5.9896 (11) Å

b = 15.5307 (15) Å

c = 8.8471 (11) Å

β = 106.934 (12)°

V = 1787.3 (2) Å³

Z = 4

Dᵣ = 2.244 Mg m⁻³

Mo Kα radiation

Cell parameters from 25 reflections

θ = 19.5–20.0°

μ = 4.02 mm⁻¹

T = 295 (2) K

Prism, colourless

0.30 × 0.25 × 0.25 mm

**Data collection**

Rigaku AFC-7R diffractometer

ω-2θ scans

Absorption correction: ϕ scan

(TEXSAN for Windows; Molecular Structure Corporation, 1999b)

Tmin = 0.379, Tmax = 0.433

2170 measured reflections

1787 independent reflections

Reflinement

Reflinement on F²

R[F² > 2σ(F²)] = 0.029

wR(F²) = 0.077

S = 1.06

1787 reflections

101 parameters

H-atom parameters constrained

Extinction correction: SHELX97

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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**References**


Molecular Structure Corporation (1999a). MSC/AFC Diffractometer Control Software. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.


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