Graham Smith,^{a*} Raymond C. Bott,^a Ian D. Jenkins^b and Urs D. Wermuth^b

^aCentre for Instrumental and Developmental Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane, Q4001, Australia, and ^bSchool of Science, Griffith University, Nathan, Q4111, Australia

Correspondence e-mail: g.smith@qut.edu.au

Key indicators

Single-crystal X-ray study

$T = 295\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.043

wR factor = 0.132

Data-to-parameter ratio = 12.1

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

Racemic 6-*exo*-hydroxybicyclo[2.2.1]heptane-2-*exo*-carboxylic acid

Received 6 June 2001

Accepted 18 July 2001

Online 27 July 2001

The crystal structure of the title cage hydroxy acid, $\text{C}_8\text{H}_{12}\text{O}_3$, has confirmed the *exo* configuration for both the carboxylic acid and hydroxy substituents, as previously determined from chemical and ^{13}C NMR evidence. Both the carboxylic acid and the hydroxy O atoms are involved in intermolecular hydrogen-bonding interactions, giving a centrosymmetric 12-membered cyclic ring system which extends *via* hydrogen bonding into an infinite two-dimensional network.

Comment

Racemic 6-*exo*-hydroxybicyclo[2.2.1]heptane-2-*exo*-carboxylic acid, (I), was first reported in 1969 together with the isomeric 5-*exo*-hydroxy isomer (Beckmann *et al.*, 1969) with which it forms in the normal synthetic route. The hydroboration procedure used here in the preparation (Fischer *et al.*, 1980) gives predominantly the 6-*exo*-hydroxy isomer, whereas the oxymercuration/demercuration procedure of Beckmann *et al.* (1969) gives predominantly the 5-*exo*-hydroxy isomer.

The crystal structure determination of (I) shows the relatively inflexible norbornane cage which is similar to other norbornane carboxylic acids (Apgar & Ludwig, 1972; Albinati *et al.*, 1973), with both the carboxylic acid and hydroxy groups *exo*-related (Fig. 1). The torsion angles $\text{C1}-\text{C2}-\text{C21}-\text{O212}$ and $\text{C2}-\text{C1}-\text{C6}-\text{O6}$ are $80.9(2)^\circ$ and $173.6(1)^\circ$, respectively. The carboxylic acid O atoms associate with the hydroxy groups of two different acids [$\text{O212}-\text{H212}\cdots\text{O6}^i$ $2.665(2)\text{ \AA}$ and $\text{O}-\text{H}\cdots\text{O}$ $167(2)^\circ$; $\text{O6}-\text{H6}\cdots\text{O211}^{ii}$, $2.752(2)\text{ \AA}$, $\text{O}-\text{H}\cdots\text{O}$, $170(2)^\circ$; symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1+z$; (ii) $\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$], forming cyclic centrosymmetric 12-membered $R_4^4(12)$ rings (Etter *et al.*, 1990) (Fig. 2). These then form into an infinite two-dimensional structure. This association is different from the common $R_2^2(8)$ cyclic *A-A* dimers or the more unusual catemer structures found among the monofunctional carboxylic acids (Leiserowitz, 1976).

Figure 1
The molecular configuration and atom-numbering scheme for the title compound. Atoms are shown as 30% probability ellipsoids (Spek, 1999).

Experimental

The title compound was synthesized using a modification of the method of Fischer *et al.* (1980) by the hydroboration of the unsaturated ester precursor followed by hydrolysis with sodium hydroxide. The modification (Vogel, 1989) involved the generation of diborane *in situ* by addition of the boron trifluoride–dietherate to a mixture of sodium borohydride and the ester precursor under a nitrogen atmosphere (Wermuth, 1995). Fractional crystallization of the isomeric mixture from acetone gave the 5-hydroxy and 6-hydroxy isomers. Crystals of the 6-hydroxy isomer (the title compound) suitable for X-ray analysis were obtained by slow evaporation from acetone.

Crystal data

$C_8H_{12}O_3$	$D_x = 1.320 \text{ Mg m}^{-3}$
$M_r = 156.18$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 25 reflections
$a = 11.821(2) \text{ \AA}$	$\theta = 13.1\text{--}16.3^\circ$
$b = 10.7618(18) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 6.3146(11) \text{ \AA}$	$T = 295(2) \text{ K}$
$\beta = 101.860(14)^\circ$	Prism, colourless
$V = 786.2(2) \text{ \AA}^3$	$0.50 \times 0.35 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-7R diffractometer	$h = -8 \rightarrow 15$
ω – 2θ scans	$k = 0 \rightarrow 13$
2170 measured reflections	$l = -8 \rightarrow 8$
1805 independent reflections	3 standard reflections
1216 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{\text{int}} = 0.033$	intensity decay: 1.2%
$\theta_{\text{max}} = 27.5^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.1309P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.132$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
1805 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
149 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	Extinction coefficient: 0.023 (5)

Figure 2
Perspective view of the two-dimensional polymer structure. Hydrogen bonds are shown as broken lines (Spek, 1999).

All H atoms were refined; the range of C–H distances was 0.95 (2)–1.03 (2) Å.

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*.

The authors acknowledge financial support from The Centre for Instrumental and Developmental Chemistry (Queensland University of Technology), The School of Science, Griffith University, and the Australian Research Council. Receipt of an ARC Scholarship by one of the authors (UDW) is also gratefully acknowledged. Dr Peter Healy is thanked for the collection of the diffraction data.

References

- Albinati, A., Zocchi, M., Germain, G. & Declercq, J. P. (1973). *Cryst. Struct. Commun.* **2**, 585–587.
- Apgar, P. A. & Ludwig, M. L. (1972). *J. Am. Chem. Soc.* **94**, 964–967.
- Beckmann, S., Eder, G. & Geiger, H. (1969). *Chem. Ber.* **102**, 815–819.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Fischer, W., Grob, C. A. & Sprecher, G. (1980). *Helv. Chim. Acta*, **63**, 806–815.
- Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–782.
- Molecular Structure Corporation (1999a). *MSC/AFC Diffractometer Control Software*. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1999b). *TEXSAN for Windows*. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Spek, A. L. (1999). *PLATON for Windows*. September 1999 version. University of Utrecht, The Netherlands.
- Vogel, A. I. (1989). *Textbook of Organic Chemistry*, 5th ed, p. 543. London: Longmans.
- Wermuth, U. D. (1995). PhD Thesis, Griffith University, Nathan 4111, Australia.