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(1*R*,3*S*)-1-Monoamidocamphoric acid

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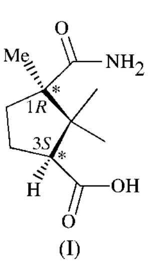
The title compound, (1*S*,3*R*)-3-carbamoyl-2,2,3-trimethylcyclopentane-1-carboxylic acid, $C_{10}H_{17}NO_3$, was synthesized and characterized by IR, EA, ES–MS (electrospray ionization mass spectra), ^{1}H NMR, ^{13}C NMR and X-ray diffraction techniques. The two independent molecules form a two-dimensional network *via* O—H···O and N—H···O hydrogen-bonding interactions between their carboxylic acid and carbamoyl groups.

Comment

Camphoric acids and their derivatives, especially those having specific absolute configurations, are very useful intermediates in organic synthesis (Nieto *et al.*, 1998), and can be used as building blocks in self-assembly studies *via* coordinative and hydrogen bonds, thus generating interesting topologies and functions. For example, D-(+)-camphoric acid has been used in self-assembly with certain organic acids (Hu *et al.*, 2001) and polyamines (Goswami *et al.*, 2000; Zakaria *et al.*, 2003) by means of hydrogen-bonding interactions.



(I)

While racemic 3-monoamidocamphoric acid can be obtained from camphoric anhydride, racemic 1-monoamidocamphoric acid can be prepared from camphoric imide (Noyes, 1894) by a method which has been improved, simplified and further characterized in our experiments. The crystallographic data of the title compound [also known as (1*R*,3*S*)-*β*-camphoramic acid], (I), is different to that of (1*R*,3*S*)-3-monoamidocamphoric acid [or (1*R*,3*S*)-*α*-camphoramic acid], synthesized *via* an alternative method from (1*R*,3*S*)-camphoric acid (Nie *et al.*, 2002). The results of the IR, microanalytical, ES–MS, ^{1}H NMR and ^{13}C NMR analyses of (1*R*,3*S*)-*β*-camphoramic acid and its optical rotation value confirm the formulation and absolute configuration.

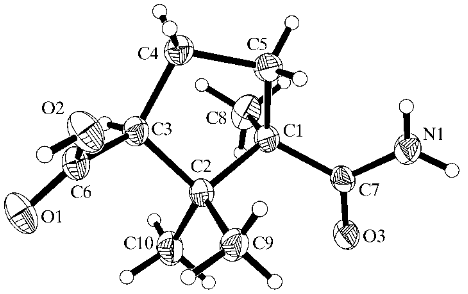


Figure 1
A view of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level.

There are two crystallographically independent molecules per asymmetric unit in the orthorhombic chiral space group $P2_12_12_1$. The absolute configuration shown is that determined by the optical rotation value $[\alpha]_D^{20} = +73.3°$ ($c = 1$, C_2H_5OH), which is consistent with the value in the literature (*CRC Handbook of Chemistry and Physics*, 1988–1989). The ring geometries are similar to those of (1*R*,3*S*)-3-monoamidocamphoric acid reported by Nie *et al.* (2002), with elongation of the C—C bonds and C—C—C bond-angle contractions of the 'flap' quaternary atoms in the five-membered rings (C2 and C12). Bond lengths related to the carboxylic acid groups also exhibit electron delocalization because of their conjugate interactions. Changing the positions of the carboxyl and carbamoyl groups leads to higher values of *R*1 and *wR*2 (0.065 and 0.146, respectively), and of the displacement parameters, thus confirming the (1*R*,3*S*)-1-monoamidocamphoric acid formulation.

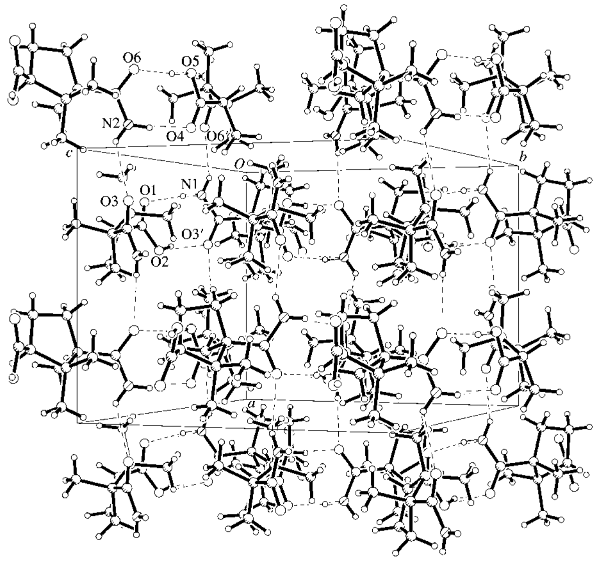


Figure 2
A perspective view of the crystal packing of (I), approximately along the *b* axis. For clarity, labels are given only once for the hydrogen-bond contacts (see Table 2).

The crystal packing involves three kinds of traditional hydrogen-bonding interactions, as well as weak C—H···O interactions (Table 2). Hydrogen-bonding interactions between the carboxyl and carbamoyl groups (O2—H1···O3, O5—H2···O6, N1—H1*A*···O1 and N2—H2*A*···O4) form eight-membered rings along the *c* axis. Hydrogen bonds associated with the N and O atoms of adjacent carbamoyl groups (N1—H1*B*···O6 and N2—H2*B*···O3) along the *a* axis are also observed. The resulting two-dimensional layers formed are not planar, but form a ripple along the *c* direction. This is different from the crystal packing of (1*R*,3*S*)-3-monoamidocamphoric acid, in which a three-dimensional hydrogen-bond-supported framework is found.

Experimental

(1*R*,3*S*)-1-Monoamidocamphoric acid was synthesized successfully from D-(+)-camphoric imide *via* a simplified version of the method reported by Noyes (1894). Treatment of D-(+)-camphoric imide (1.81 g, 10 mmol) with sodium hydroxide (2.0 g, 50 mmol) in water under reflux for 2 h gave a solution of the sodium salt of (1*R*,3*S*)-1-monoamidocamphoric acid. After cooling to room temperature, the mixture was carefully acidified with hydrochloric acid (2 mol l^{-1}), and the resulting white precipitates [(1*R*,3*S*)-1-monoamidocamphoric acid] were collected and recrystallized from ethanol/water (yield 1.22 g, 61.3%; m.p. 452–454 K). Analysis calculated for $C_{10}H_{17}NO_3$: C 60.28, H 8.60, N 7.03%; found: C 59.91, H 8.60, N 6.93%. Main FT–IR (KBr plates, cm^{-1}): 3475, 3415, 3224, 3235, 3195, 2982, 2971, 1709, 1693, 1644 and 1389 (all strong peaks); ^{1}H NMR (d_6-DMSO): δ 0.74 (*s*, 3H, Me), 1.08 (*s*, 3H, Me), 1.18 (*s*, 3H, Me), 1.43 (*m*, 1H, CH_2), 1.65 (*m*, 1H, CH_2), 1.98 (*t*, 1H, CH_2), 2.39 (*t*, 1H, CH_2), 2.63 (*t*, 1H, CH), 3.29 (*s*, 2H, $CONH_2$), 6.65 (*s*, 1H, COOH); ^{13}C NMR (d_6-DMSO): δ 26.36, 26.94, 27.68, 28.48, 37.86, 51.39, 57.70, 60.77, 180.83, 182.85; ES–MS: *m*/*z* $[C_{10}H_{17}NO_3H]^+$ 200 (100%). $[\alpha]_D^{20}$ = + 73.3° (*c* = 1 g per 100 ml, C_2H_5OH). Elemental analysis was performed with a Perkin–Elmer 1400C analyzer, IR spectra (4000–400 cm^{-1}) were recorded on a Nicolet FT–IR 170X spectrophotometer, NMR spectra were obtained with a Bruker 500 MHz NMR spectrometer, electrospray ionization mass spectra were obtained with a Finnigan MAT SSQ 710 mass spectrometer in the scan range 300–1200 a.m.u. and the optical rotation values were determined with a WZZ-115 digital autopolarimeter.

Crystal data

$C_{10}H_{17}NO_3$
M_r = 199.25
Orthorhombic, $P2_12_12_1$
a = 10.400 (2) Å
b = 12.810 (3) Å
c = 16.000 (3) Å
V = 2131.6 (8) Å^3
Z = 8
D_x = 1.242 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 871 reflections
θ = 2.8–20.1°
μ = 0.09 mm^{-1}
T = 293 (2) K
Slab, colorless
0.40 × 0.30 × 0.20 mm

Table 1
Selected geometric parameters (Å, °).

C6—O1	1.199 (3)	C7—O3	1.234 (3)
C6—O2	1.311 (3)	C7—N1	1.323 (3)
O1—C6—O2	122.1 (3)	O3—C7—N1	120.0 (2)
O1—C6—C3	123.2 (2)	O3—C7—C1	121.1 (2)
O2—C6—C3	114.7 (2)	N1—C7—C1	118.8 (2)

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.968, T_{max} = 0.982
12 841 measured reflections

2873 independent reflections
1653 reflections with $I > 2\sigma(I)$
R_{int} = 0.078
θ_{max} = 28.1°
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -14 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.096
S = 0.87
2873 reflections
253 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1···O3^{i}	0.85	1.83	2.619 (3)	155
N1—H1*A*···O1^{ii}	0.86	2.09	2.902 (3)	158
N1—H1*B*···O6	0.86	2.23	2.978 (3)	145
O5—H2···O6^{iii}	0.97	1.70	2.657 (3)	170
N2—H2*A*···O4^{iv}	0.86	2.12	2.920 (3)	155
N2—H2*B*···O3^{v}	0.86	2.41	3.037 (3)	130
C4—H4*B*···O2	0.97	2.30	2.769 (3)	109
C14—H14*B*···O4	0.97	2.39	2.836 (4)	107
C20—H20*A*···O5	0.96	2.48	3.071 (3)	119
C20—H20*B*···O2^{iii}	0.96	2.58	3.391 (4)	142

Symmetry codes: (i) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$; (ii) $\frac{3}{2}-x, 1-y, z-\frac{1}{2}$; (iii) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (iv) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (v) $x-1, y, z$.

The positions of all H atoms were fixed geometrically, with C—H = 0.96 Å, N—H = 0.86 Å and O—H = 0.85 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1021). Services for accessing these data are described at the back of the journal.

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