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

Jing-Jing Nie,[a] Duan-Jun Xu,[a]* Zi-Qiang Hu,[a] Yuan-Zhi Xu,[a] Jing-Yun Wu[b] and Michael Y. Chiang[b]

[a]Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China, and [b]Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan
Correspondence e-mail: xudj@mail.hz.zj.cn

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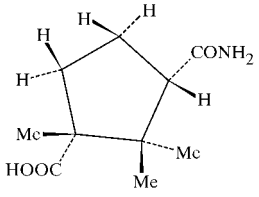
The title chiral compound, 3-aminocarbonyl-1,2,2-trimethylcyclopentane-1-carboxylic acid, $C_{10}H_{17}NO_3$, was prepared from (1*R*,3*S*)-camphoric acid. The five-membered ring adopts a conformation which is intermediate between a twist and an envelope. Elongations of the C—C bonds and contractions of the C—C—C bond angles are observed within the five-membered ring. A ^{1}H NMR spectrum was recorded to assist in distinguishing the amide group from the carboxyl group.

Comment

The title compound, (I), was prepared from (1*R*,3*S*)-camphoric acid and used in our laboratory as a chiral agent to separate racemic mandelic acid (Hu *et al.*, 2002). In order to compare possible structural variations of (I) between its free and complexed states, we have determined its structure and the results are presented here.



(I)

The absolute configuration of (I) could not be determined reliably. Since the specific optical rotation $[\alpha]_D^{20}$ value of 24.96° agrees with that reported previously for (1*R*,3*S*)-camphoramic acid (Faigle & Karrer, 1962), the present refinements were performed assuming the 1*R*,3*S*-configuration, the same as the camphoric acid starting material.

A perspective molecular view of (I) is presented in Fig. 1 and selected geometric parameters are listed in Table 1. All bond distances and angles agree well with those found in a molecular complex of camphoramic acid with mandelic acid (Hu *et al.*, 2002). Thus, (I) shows little or no structural change upon forming complexes with other molecules.

Compound (I) can be viewed as a cyclopentane derivative with methyl and carboxyl groups on C1, two methyl groups on C2 and an amide group on C3. In order to establish the conformation of the five-membered ring, the ring-puckering coordinates and internal Cartesian coordinates (Cremer & Pople, 1975) were calculated. With atom C4 at the apex, the puckering coordinates q_2 and φ_2 are 0.434 (3) Å and −98.8 (4)°, respectively. This φ_2 value of near to −90° suggests a twist conformation of the ring, with the twist axis through C4. The conformation of the five-membered ring is also close to an envelope, with atom C1 at the flap position; C1 lies 0.653 (3) Å from the best plane of the other four atoms, which exhibit a maximum deviation of −0.040 (3) Å (C4).

Two somewhat elongated C—C distances [C1—C2 1.568 (4) Å and C2—C3 1.574 (4) Å] and one contracted bond angle [C1—C2—C3 100.9 (2)°] are observed within the five-membered ring. They agree well with the corresponding values [1.561 (7) and 1.580 (7) Å, and 101.6 (4)°] found in a molecular complex of (I) with mandelic acid (Hu *et al.*, 2002). As the structurally similar camphoric acid differs from (I) by having a carboxylic acid group on C3 instead of an amino-carbonyl group, camphoric acid structures can also be used for comparing the above-mentioned structural features. Similar elongation of C—C distances involving atoms C1, C2 and C3 was also found in several (1*R*,3*S*)-camphoric acid structures (Santis *et al.*, 1997; Goswami *et al.*, 2000; Barnes *et al.*, 1991; Calderon *et al.*, 1994). These deformations may be explained by intramolecular repulsion between the closely situated methyl and carboxyl groups.

The C10—N1 distance of 1.326 (4) Å shows the existence of electron delocalization within the amide moiety.

Hydrogen-bond parameters for (I) are listed in Table 2. Adjacent molecules are linked by hydrogen bonds between the amide and carboxyl groups to form a supramolecular structure. Weak intramolecular C—H···O bonding interactions involving the carbonyl O atoms are also observed, which seem to affect the conformation of the carboxyl and amide groups.

Although elemental analysis of C, H and N is consistent with the fact that only one carboxyl group of camphoric acid has been transformed into an amide group in the present synthesis, it is still necessary to distinguish the amide group

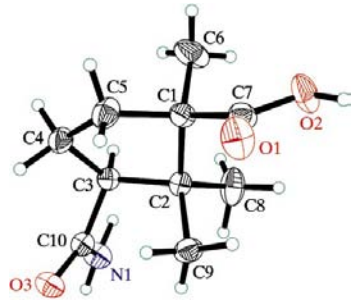


Figure 1
A view of the molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

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from the carboxyl group. The reasonable isotropic displacement parameters on the N and O atoms confirmed the present 1*R*,3*S*-configuration for (I). Inverting the N,O assignment gave unusually large and small displacement parameters, and a higher *R* factor of 0.054.

Experimental

A mixture of (1*R*,3*S*)-camphoric acid (20 g) and thionyl chloride (25 ml) was heated at 348 K with stirring for 4 h. Once the camphoric acid had completely dissolved, the excess thionyl chloride was removed under reduced pressure in a rotary evaporator to give a white intermediate, camphoryl chloride. The camphoryl chloride was treated with saturated aqueous ammonia (50 ml) for 1.5 h at room temperature. The reaction mixture was adjusted with aqueous HCl to pH 6 and stirred for 1 h at 318 K, giving a white precipitate. The precipitate was separated by filtration, washed twice with water and dried under reduced pressure to obtain the title compound, (I). Recrystallization of (I) from an aqueous solution gave well shaped single crystals. C, H and N were analysed using a Carlo–Erba 1160 instrument. Analysis calculated for $C_{10}H_{17}NO_3$: C 60.30, H 8.54, N 7.04%; found: C 59.78, H 8.64, N 7.10%. The ^{1}H NMR spectrum of (I) was recorded on an Avance DMX500 spectrometer in $CDCl_3$; δ, p.p.m.: 0.95 (3H), 1.24–1.34 (6H), 1.57–2.39 (4H), 2.86 (1H), 5.62–5.93 (2H). The specific optical rotation of the sample was determined using a WZZ-1S instrument at 293 K.

Crystal data

$C_{10}H_{17}NO_3$
M_r = 199.25
Orthorhombic, $P2_12_12_1$
a = 7.2389 (14) Å
b = 11.2125 (14) Å
c = 12.7427 (15) Å
V = 1034.3 (2) Å^3
Z = 4
D_x = 1.280 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
θ = 8.6–12.5°
μ = 0.09 mm^{-1}
T = 298 (2) K
Prism, colourless
0.54 × 0.48 × 0.36 mm

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
1073 measured reflections
1073 independent reflections
941 reflections with $I > 2\sigma(I)$
θ_{max} = 25°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections
every 100 reflections
intensity decay: 0.3%

Refinement

Refinement on F^2
$R(F)$ = 0.040
$wR(F^2)$ = 0.111
S = 1.04
1073 reflections
127 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0701P)^2 + 0.2891P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

H atoms were located from a difference Fourier map. Methyl H atoms were placed in calculated positions, with C—H distances of 0.96 Å. All H atoms were included in the final cycles of the least-squares refinement with fixed coordinates and with U_{iso} = 0.08 Å^2.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*); program(s) used to solve structure: *SHELXS*93 (Sheldrick, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994).

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.204 (4)	C1—C2	1.568 (4)
O2—C7	1.324 (4)	C2—C3	1.574 (4)
O3—C10	1.236 (3)	C3—C4	1.538 (4)
N1—C10	1.326 (4)	C4—C5	1.513 (4)
C1—C5	1.541 (4)		
C5—C1—C2	102.0 (2)	O1—C7—C1	125.2 (3)
C1—C2—C3	100.9 (2)	O2—C7—C1	112.7 (3)
C4—C3—C2	106.1 (2)	O3—C10—N1	122.1 (3)
C5—C4—C3	106.7 (2)	O3—C10—C3	123.2 (2)
O1—C7—O2	122.0 (3)	N1—C10—C3	114.8 (2)
C5—C1—C2—C3	42.3 (3)	C3—C4—C5—C1	20.5 (3)
C1—C2—C3—C4	−30.4 (2)	C2—C1—C5—C4	−39.7 (3)
C2—C3—C4—C5	6.7 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^{i}	0.90	2.40	3.238 (4)	156
N1—H1B···O1^{ii}	1.01	2.20	3.193 (4)	165
O2—H2···O3^{iii}	0.87	1.85	2.698 (4)	163

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1358). Services for accessing these data are described at the back of the journal.

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