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Structure of (–)-Canadinium (+)-10-Camphorsulfonate

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Abstract. $C_{20}H_{22}NO_4^+ \cdot C_{10}H_{15}O_4S^-$, $M_r = 571.69$, orthorhombic, $P2_12_12_1$, $a = 11.231$ (2), $b = 32.025$ (5), $c = 7.584$ (1) Å, $V = 2727.8$ (10) Å³, $Z = 4$, $D_x = 1.392$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 0.1764$ mm⁻¹, $F(000) = 1216$, room temperature. Final $R = 0.055$ for 1440 unique observed reflections. The absolute configuration of (–)-canadine was obtained in relation to that of (+)-10-camphorsulfonic acid and also by use of the anomalous-dispersion effects of the S and the O atoms. In the crystal of the title compound, (–)-canadine, (–)-(13a*S*)-5,6,13,13a-tetrahydro-9,10-dimethoxy-2,3-methylenedioxy-8*H*-dibenzo[*a,g*]quinolizine, takes a *trans* configuration in the quinolizidine ring. The distance between the N atom of the canadinium ion and one O atom in the sulfonate group of the camphorsulfonate ion, 2.683 Å, indicates that these two are connected by a hydrogen bond.

Introduction. (–)-Canadine, which belongs to the protoberberine-type alkaloids, was isolated from several *Corydalis* plants (Papaveraceae), *i.e.* *Corydalis cheilanthifolia*, *C. ophiocarpa* and *C. ternata*, and its structure was determined to be that of tetrahydroberberine (Manske & Holmes, 1954; Boit, 1961). Studies on the crystal-structure analysis of proto-

berberine-type alkaloids showed that there are a few alkaloid salts which have the *B/C-cis* ring-juncture configuration (Shimanouchi, Sasada, Ihara & Kametani, 1969; Shimanouchi, Sasada, Kametani & Ihara, 1970). However, there have been no detailed studies on these salts with the *B/C-trans* juncture configuration. (–)-Canadinium (+)-10-camphorsulfonate should be obtainable in the process of optical resolution of racemic (±)-canadine as a diastereomeric salt. We prepared this compound, which was, by spectroscopic studies, to have the *trans* juncture configuration, and used this to determine the crystal structure. If the crystal structure is determined, the absolute configuration of (–)-canadine could be obtained in relation to that of (+)-10-camphorsulfonic acid. Until now we have a report suggesting the absolute configuration of (–)-canadine by circular dichroism (Snatzke, Hrubek, Hruban, Horeau & Šantavý, 1970).

Experimental. Compound prepared by reaction of stoichiometric quantities of constituent molecules in acetic acid. Crystal specimens obtained from dimethyl sulfone solutions. Crystal 0.1 × 0.3 × 0.5 mm, thin rectangular plate. Rigaku AFC-5 four-circle diffrac-

Table 1. Comparison of observed and calculated structure factors of reflections which show large differences in the Bijvoet-pair values by the anomalous-dispersion effect

<i>h</i>	<i>k</i>	<i>l</i>	$I_o(hkl)$	$I_o(-hkl)$	$ F_c(hkl) $	$ F_c(-hkl) $
3	3	1	<	>	25.7	28.1
5	8	1	>	<	21.9	19.7
1	10	3	<	>	17.4	20.4
3	10	3	<	>	22.6	25.3
2	14	3	<	>	14.9	17.0
1	8	4	>	<	20.9	18.9

tometer, graphite-monochromated Mo $K\alpha$, Laue group *mmm*. Cell parameters refined by least-squares methods on the basis of 25 2θ values ($33 < 2\theta < 37^\circ$). Intensity measurement performed to $2\theta = 50^\circ$, $\omega-2\theta$ scan technique, scan speed $2^\circ \text{ min}^{-1}(\theta)$. Three reference reflections showed no significant variation, $0.984 < |F_o|/|F_o|_{\text{initial}} < 1.020$. Space group $P2_12_12_1$ determined from systematic absences ($h00, h \text{ odd}; 0k0, k \text{ odd}; 00l, l \text{ odd}$), 3145 reflections measured, $0 \leq h \leq 12, 0 \leq k \leq 38, 0 \leq l \leq 8$, 718 weak reflections classified as unobserved [$|F_o| \leq 3\sigma(|F_o|)$], 987 zero and 1440 observed unique reflections. Lorentz-polarization correction, no absorption correction. Structure solved by direct methods with *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). 20 out of 25 non-H atoms in cation and SO_3 in anion determined from *E* map and the others from Fourier syntheses; full-matrix least-squares refinement on *F* with anisotropic thermal parameters using *UNICSII* (1967) computing programs. H atoms found from difference syntheses and refined with isotropic thermal parameters. Unit weights on all reflections. Final $R = 0.055, wR = 0.067, S = 2.3, \Delta/\sigma < 0.35$ for non-H atoms and < 1.1 for H atoms. Max. and min. height in final difference synthesis $0.2 e \text{ \AA}^{-3}$. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).

The absolute configuration of (–)-canadine was obtained in relation to that of (+)-10-camphorsulfonic acid, which is synthesized from (+)-camphor [C(1)*R* and C(4)*R*], the starting material for (+)-3- and (+)-8-bromocamphor (Klyne & Buckingham, 1978). The result was confirmed by the intensity measurements of the Bijvoet pairs by Cu $K\alpha$ radiation. Reflections used are listed in Table 1.

The atomic coordinates of the non-H atoms are given in Table 2.* A perspective drawing (Johnson, 1965) with the numbering schemes of both ions is shown in Fig. 1. The number of reflections used for the

least-squares refinement is 46% of that of reflections measured. Only a relatively small number of unique reflections caused the large e.s.d. values in Table 2. This is especially notable in the *z* coordinate due also to the smaller cell parameter *c*.

Table 2. Final fractional coordinates for non-H atoms

E.s.d.'s in parentheses are in the units of the least-significant digit.

$$B_{eq} = \frac{1}{3} \sum_i \sum_j b_{ij}(\mathbf{a}_i, \mathbf{a}_j).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq} (\text{\AA}^2)$
Canadinium				
O1	0.5349 (7)	0.0933 (2)	0.2709 (13)	4.42 (26)
O2	0.3396 (7)	0.1033 (2)	0.3297 (11)	3.54 (24)
O3	0.7916 (7)	0.3872 (2)	0.1052 (10)	3.38 (22)
O4	1.0309 (8)	0.3843 (2)	0.1943 (11)	4.00 (26)
C1	0.5892 (10)	0.1675 (3)	0.2202 (18)	3.59 (37)
C2	0.5122 (9)	0.1350 (3)	0.2610 (19)	3.53 (38)
C3	0.3918 (10)	0.1412 (3)	0.2927 (13)	2.76 (34)
C4	0.3428 (10)	0.1805 (3)	0.2872 (15)	2.96 (34)
C5	0.3634 (9)	0.2577 (3)	0.2326 (14)	2.84 (31)
C6	0.4415 (10)	0.2881 (4)	0.1315 (17)	3.81 (39)
N7	0.5652 (7)	0.2859 (2)	0.2113 (11)	2.46 (25)
C8	0.6388 (11)	0.3195 (3)	0.1349 (16)	3.71 (38)
C9	0.8439 (18)	0.3512 (3)	0.1738 (14)	2.82 (59)
C10	0.9632 (13)	0.3483 (4)	0.2136 (15)	2.57 (37)
C11	1.0081 (10)	0.3112 (3)	0.2815 (18)	4.18 (40)
C12	0.9340 (9)	0.2766 (3)	0.2980 (18)	3.35 (36)
C13	0.7367 (9)	0.2419 (3)	0.2803 (16)	2.97 (35)
C14	0.6226 (10)	0.2436 (2)	0.1719 (14)	2.88 (31)
C15	0.5385 (10)	0.2083 (3)	0.2149 (17)	3.45 (37)
C16	0.4183 (10)	0.2142 (3)	0.2470 (14)	2.57 (31)
C17	0.7672 (7)	0.3162 (2)	0.1904 (12)	2.56 (23)
C18	0.8147 (10)	0.2790 (3)	0.2513 (16)	3.33 (34)
C19	0.4258 (13)	0.0738 (3)	0.2984 (22)	5.81 (50)
C20	0.7788 (12)	0.4196 (2)	0.2352 (16)	4.06 (38)
C21	1.1492 (10)	0.3835 (4)	0.2393 (20)	5.02 (44)
Camphorsulfonate				
S	0.4652 (3)	0.3458 (1)	0.5921 (4)	2.90 (7)
O(1)	0.3698 (8)	0.3459 (2)	0.4690 (11)	4.96 (27)
O(2)	0.4242 (8)	0.3388 (2)	0.7675 (11)	5.40 (28)
O(3)	0.5627 (6)	0.3170 (2)	0.5398 (9)	3.39 (21)
O(4)	0.5402 (10)	0.4720 (2)	0.3811 (13)	6.65 (37)
C(1)	0.4617 (11)	0.4348 (3)	0.6360 (14)	3.18 (33)
C(2)	0.4933 (13)	0.4718 (3)	0.5171 (17)	4.30 (43)
C(3)	0.4493 (12)	0.5106 (3)	0.6222 (18)	5.08 (42)
C(4)	0.3995 (11)	0.4908 (3)	0.7827 (17)	4.05 (40)
C(5)	0.2808 (13)	0.4714 (4)	0.7276 (20)	6.64 (50)
C(6)	0.3227 (10)	0.4341 (3)	0.6226 (18)	4.89 (41)
C(7)	0.4842 (12)	0.4531 (3)	0.8201 (15)	4.08 (38)
C(8)	0.6136 (11)	0.4639 (4)	0.8550 (23)	6.28 (53)
C(9)	0.4406 (15)	0.4268 (4)	0.9710 (16)	6.02 (52)
C(10)	0.5301 (9)	0.3958 (2)	0.5777 (13)	3.01 (26)

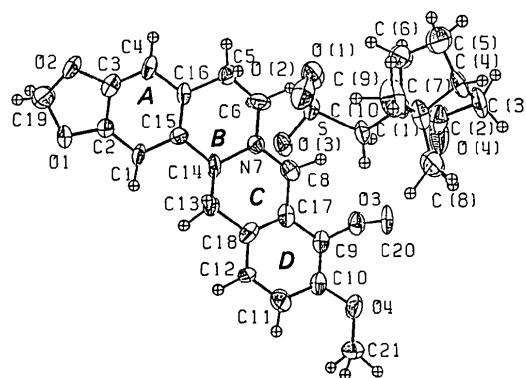


Fig. 1. Perspective drawing showing the numbering schemes of both ions.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-planes' data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43272 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

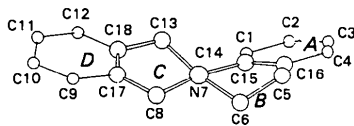


Fig. 2. Rings *B* and *C* of the (-)-canadine molecule with their neighbours viewed along the N7–C14 juncture axis.

Table 3. Intramolecular bond distances (Å) with e.s.d.'s in parentheses

Canadinium			
O1–C2	1.362 (12)	C6–N7	1.517 (14)
O1–C19	1.391 (16)	N7–C8	1.475 (13)
O2–C3	1.377 (12)	N7–C14	1.530 (10)
O2–C19	1.373 (14)	C8–C17	1.506 (15)
O3–C9	1.395 (14)	C9–C17	1.419 (16)
O3–C20	1.439 (12)	C9–C10	1.377 (25)
O4–C10	1.389 (15)	C10–C11	1.390 (17)
O4–C21	1.372 (15)	C11–C12	1.391 (14)
C1–C2	1.388 (15)	C12–C18	1.388 (15)
C2–C3	1.388 (15)	C13–C18	1.492 (14)
C3–C4	1.374 (14)	C13–C14	1.523 (15)
C4–C16	1.406 (15)	C14–C15	1.509 (14)
C5–C16	1.527 (14)	C15–C16	1.385 (16)
C5–C6	1.518 (16)	C15–C1	1.426 (14)
		C17–C18	1.385 (12)
Camphorsulfonate			
S–O(1)	1.421 (9)	C(1)–C(10)	1.532 (13)
S–O(2)	1.425 (9)	C(2)–C(3)	1.557 (16)
S–O(3)	1.486 (7)	C(3)–C(4)	1.482 (18)
S–C(10)	1.763 (8)	C(4)–C(5)	1.529 (19)
O(4)–C(2)	1.158 (17)	C(5)–C(6)	1.511 (18)
C(1)–C(2)	1.531 (15)	C(4)–C(7)	1.563 (16)
C(1)–C(6)	1.565 (17)	C(7)–C(8)	1.517 (18)
C(1)–C(7)	1.535 (15)	C(7)–C(9)	1.503 (17)

Table 4. Intramolecular bond angles (°) with e.s.d.'s in parentheses

Canadinium			
C2–O1–C19	106.5 (8)	O4–C10–C9	117.0 (11)
C3–O2–C19	105.7 (9)	O4–C10–C11	123.4 (12)
C9–O3–C20	112.5 (8)	C9–C10–C11	119.5 (11)
C10–O4–C21	119.2 (9)	C10–C11–C12	119.8 (11)
C8–N7–C14	109.5 (8)	C11–C12–C18	120.7 (10)
C8–N7–C6	108.8 (8)	C14–C13–C18	112.7 (9)
C14–N7–C6	110.4 (8)	C13–C14–C15	112.5 (8)
		C15–C14–N7	110.9 (8)
C15–C1–C2	116.4 (10)	C13–C14–N7	106.3 (7)
C1–C2–C3	122.6 (9)	C14–C15–C1	116.3 (9)
C1–C2–O1	129.1 (10)	C14–C15–C16	123.1 (9)
C3–C2–O1	108.3 (9)	C16–C15–C1	121.2 (8)
C2–C3–C4	121.1 (10)	C4–C16–C5	118.2 (9)
C2–C3–O2	108.9 (8)	C4–C16–C15	118.2 (9)
C4–C3–O2	130.0 (10)	C5–C16–C15	120.4 (9)
C3–C4–C16	117.9 (10)	C8–C17–C18	121.5 (8)
C16–C5–C6	112.8 (9)	C9–C17–C18	118.4 (10)
C5–C6–N7	107.3 (9)	C8–C17–C9	120.1 (9)
N7–C8–C17	112.1 (8)	C17–C18–C12	120.3 (9)
C17–C9–C10	121.2 (10)	C17–C18–C13	120.5 (9)
C17–C9–O3	115.5 (14)	C12–C18–C13	119.0 (9)
C10–C9–O3	123.2 (12)	O1–C19–O2	109.8 (8)
Camphorsulfonate			
O(1)–S–O(2)	111.7 (5)	C(1)–C(2)–C(3)	104.0 (10)
O(2)–S–O(3)	112.9 (5)	C(2)–C(3)–C(4)	101.5 (8)
O(1)–S–O(3)	112.4 (5)	C(3)–C(4)–C(5)	106.2 (11)
O(1)–S–C(10)	105.6 (5)	C(3)–C(4)–C(7)	104.5 (10)
O(2)–S–C(10)	109.5 (5)	C(5)–C(4)–C(7)	105.4 (9)
O(3)–S–C(10)	104.0 (4)	C(4)–C(5)–C(6)	101.2 (10)
C(2)–C(1)–C(6)	101.8 (9)	C(1)–C(6)–C(5)	105.4 (9)
C(2)–C(1)–C(7)	101.7 (8)	C(1)–C(7)–C(4)	91.7 (9)
C(2)–C(1)–C(10)	110.2 (9)	C(1)–C(7)–C(8)	113.8 (11)
C(6)–C(1)–C(7)	103.2 (10)	C(1)–C(7)–C(9)	115.1 (9)
C(6)–C(1)–C(10)	118.0 (8)	C(4)–C(7)–C(8)	116.0 (9)
C(7)–C(1)–C(10)	119.4 (9)	C(4)–C(7)–C(9)	111.9 (11)
O(4)–C(2)–C(1)	129.4 (10)	C(8)–C(7)–C(9)	107.9 (11)
O(4)–C(2)–C(3)	126.6 (10)	C(1)–C(10)–S	121.0 (8)

Discussion. The (-)-canadine molecule consists of four fused rings (*A–D*). The 4,5-methylenedioxyphenylene nucleus (ring *A*) and the 3,4-dimethoxyphenylene nucleus (ring *D*) are planar while the six-membered rings *B* and *C* have a half-chair conformation. Rings *B* and *C* and their neighbours viewed along the juncture axis (N7–C14) are shown in Fig. 2. The juncture has a *trans* configuration. Bond lengths and angles are listed in Tables 3 and 4 with their e.s.d.'s. The three C–N–C bond angles are 109.5 (8), 108.8 (8) and 110.4 (8)°, indicating that the N atom is tetrahedrally hybridized. The torsion angles C2–C1–C15–C14 and C1–C15–C14–N7, which show the puckering direction of the N-atom position in relation to plane *A*, are 179.5 (9) and –167.0 (10)°. The torsion angles C10–C9–C17–C8 and C9–C17–C8–N7, which show the puckering direction of the N-atom position in relation to plane *D*, are –176.1 (10) and 162.0 (8)°. The dihedral angle between the two aromatic planes *A* and *D* is 25.72 (5)°. All H atoms are obtained at the expected positions except those of one methyl, C20, which is deviated far from plane *D* and is oriented towards atom C(8) of the camphorsulfonate ion. The B_{eq} of atom C20 is not very large in comparison with those of the other methyls C21, C(8) and C(9) so that the three H atoms in C20 are likely to be in the disordered state.

The norbornane skeleton of the (+)-10-camphorsulfonate ion is similar to those of (+)-3-bromocamphor (Allen & Rogers, 1966) and (+)-8-bromocamphor (Beer & Trotter, 1975). The dihedral angles of the bridge three-atom plane (I), C(1)–C(7)–C(4), to the four-atom planes (II), C(1)–C(2)–C(3)–C(4), and (III), C(1)–C(6)–C(5)–C(4), are 124.46 (2) and 127.55 (3)°, respectively. The thermal parameters for the atoms of the norbornane skeleton are only a little larger than those of the cation. High values are observed in atoms O(4), C(5), C(8) and C(9). The bond lengths between the S and O atoms are 1.423 Å (mean)

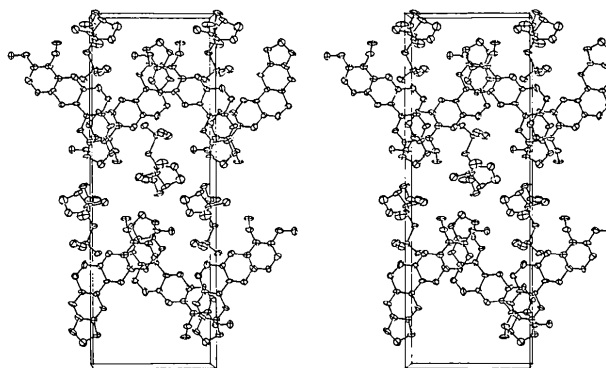


Fig. 3. Stereoview of the molecular packing.

for the two double bonds and 1.486 Å for the single bond.

Geometry of the molecule. The packing scheme of canadinium camphorsulfonate is shown in Fig. 3. The canadinium ion has a nearly flat shape. It extends in the y direction and is placed normal to the c axis. The ions are so arranged that they stack in the x direction forming a ribbon. Ring A of one ion in a ribbon at about $z = \frac{1}{4}$ is faced parallel to two D rings at $z = \frac{3}{4}$ and $-\frac{1}{4}$. These ions, each having the central part (rings B and C) at around $y = \frac{1}{2}$ thus make a layer perpendicular to the y axis. The shortest distance between canadinium and camphorsulfonate ions, 2.683 (11) Å, is found from atom N7 of the former to atom O(3) of the sulfonate group. The N atom is protonated as would be expected in an organic sulfonate salt and is the donor to the sulfonate group. The bulky negatively charged camphorsulfonate ions are tied to the planar ions by the hydrogen bonds and seem to toss about in the vacant trenches surrounded by the positive-ion layers.

Calculations were carried out on a FACOM-M380 computer at the Data Processing Center, Kyoto University. The values for the molecular geometry were calculated using a part of the program package *KPPXRAY* (Taga, Higashi & Iizuka, 1985).

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4-Methylene-1,2,3,5-tetraphenylbicyclo[3.1.0]hex-2-ene (Tetraphenylhomofulvene)

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Abstract. $C_{31}H_{24}$, $M_r = 396.5$, monoclinic, $P2_1/c$, $a = 20.130$ (5), $b = 9.303$ (4), $c = 12.102$ (4) Å, $\beta = 93.60$ (4)°, $V = 2261.9$ (6) Å³, $Z = 4$, $D_x = 1.163$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.33$ cm⁻¹, $F(000) = 840$, $T = 295$ K, $R = 0.074$ for 2350 observed reflexions. Only one of the four phenyl rings is slightly conjugated with the five-membered ring, the three others are nearly perpendicular. The distances in the cyclopropane part of the title compound are longer than those found in the 'normal' cyclopropane ring and consequently weaker. This probably explains why in homofulvenes the opening of the three-membered ring is preferred.

0108-2701/87/010101-03\$01.50

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Introduction. In previous work the photochemical behaviour of the 4-methylenebicyclo[3.1.0]hex-2-ene system ['homofulvene' system (Rey, Huber & Dreiding, 1968)] with respect to singlet (Hüther & Brune, 1968; Jobst & Brune, 1979; Brune, Jobst & Lach, 1980; Brune, Lach & Schmidtberg, 1984; Brune, Lach & Schmidtberg, 1985*a, b, c*) and triplet (Jobst & Brune, 1979; Lach, 1984; Hofmann, 1984) excitation was studied. An unexpectedly strong influence of the substituents on the photo-stationary equilibrium and especially on the mechanisms of the photoreaction processes and their products was observed. To understand this influence, reliable information about the

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