C4A	0.2512 (2)	0.8193 (2)	0.0600 (4)	0.037
C5	0.2550 (2)	0.5724 (3)	0.0490 (5)	0.040
C6	0.2893 (2)	0.5073 (3)	−0.0439 (5)	0.045
C7	0.3539 (2)	0.5283 (3)	−0.1098 (5)	0.043
C8	0.3852 (2)	0.6152 (3)	−0.0891 (4)	0.035
C8A	0.3511 (2)	0.6800 (2)	0.0015 (4)	0.030
C9	0.3765 (2)	0.7799 (2)	0.0388 (4)	0.030
C9A	0.3155 (2)	0.8430 (2)	−0.0113 (4)	0.035
C10	0.2573 (2)	0.7377 (3)	0.1693 (4)	0.034
C10A	0.2865 (2)	0.6582 (2)	0.0719 (4)	0.031
C11	0.3774 (2)	0.7845 (2)	0.2163 (4)	0.031
C12	0.3159 (2)	0.7603 (2)	0.2841 (4)	0.032
C13	0.4430 (2)	0.8039 (3)	0.3044 (4)	0.036
C14	0.4909 (3)	0.8921 (6)	0.5077 (7)	0.074
C15	0.3098 (2)	0.7451 (3)	0.4543 (4)	0.038
C16	0.2318 (3)	0.7165 (5)	0.6616 (5)	0.058
C17	0.4468 (2)	0.7992 (3)	−0.0386 (5)	0.037
C18	0.5339 (2)	0.9173 (3)	−0.0420 (5)	0.039
C19	0.5558 (2)	1.0122 (3)	0.0139 (5)	0.041
C20	0.5904 (3)	1.0055 (4)	0.1718 (6)	0.060
C21	0.4580 (2)	1.0946 (3)	−0.1027 (5)	0.047
C22	0.4005 (4)	1.1653 (5)	−0.084 (1)	0.082

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.379 (6)	C11—C12	1.347 (5)
C1—C9A	1.389 (5)	C11—C13	1.481 (5)
C2—C3	1.384 (7)	C12—C15	1.488 (5)
C3—C4	1.383 (7)	C18—C19	1.502 (5)
C4—C4A	1.388 (5)	C19—C20	1.514 (6)
C4A—C9A	1.404 (5)	C21—C22	1.496 (7)
C4A—C10	1.507 (5)	C19—N	1.448 (5)
C5—C6	1.391 (6)	C21—N	1.337 (5)
C5—C10A	1.382 (5)	C13—O1	1.330 (5)
C6—C7	1.381 (6)	C13—O2	1.208 (4)
C7—C8	1.392 (5)	C14—O1	1.437 (6)
C8—C8A	1.375 (5)	C15—O3	1.326 (4)
C8A—C9	1.545 (4)	C15—O4	1.199 (4)
C8A—C10A	1.400 (4)	C16—O3	1.453 (5)
C9—C9A	1.529 (5)	C17—O5	1.452 (4)
C9—C11	1.532 (5)	C18—O5	1.347 (4)
C9—C17	1.513 (5)	C18—O6	1.203 (5)
C10—C10A	1.520 (5)	C21—O7	1.219 (5)
C10—C12	1.521 (5)		
C2—C1—C9A	119.5 (4)	C8A—C10A—C10	112.9 (3)
C1—C2—C3	120.8 (4)	C9—C11—C12	114.4 (3)
C2—C3—C4	120.4 (4)	C9—C11—C13	122.0 (3)
C3—C4—C4A	119.5 (4)	C12—C11—C13	123.3 (3)
C4—C4A—C9A	119.9 (3)	C10—C12—C11	113.7 (3)
C4—C4A—C10	126.7 (3)	C10—C12—C15	123.6 (3)
C9A—C4A—C10	113.3 (3)	C11—C12—C15	122.2 (3)
C6—C5—C10A	118.6 (3)	C11—C13—O1	112.0 (3)
C5—C6—C7	120.2 (4)	C11—C13—O2	123.2 (3)
C6—C7—C8	121.3 (4)	O1—C13—O2	124.7 (3)
C7—C8—C8A	118.6 (3)	C12—C15—O3	111.6 (3)
C8—C8A—C9	126.8 (3)	C12—C15—O4	124.6 (4)
C8—C8A—C10A	120.3 (3)	O3—C15—O4	123.6 (3)
C9—C8A—C10A	112.9 (3)	C9—C17—O5	107.6 (3)
C8A—C9—C9A	104.8 (3)	C19—C18—O5	113.1 (3)
C8A—C9—C11	104.6 (3)	C19—C18—O6	123.7 (3)
C8A—C9—C17	110.6 (3)	O5—C18—O6	123.1 (3)
C9A—C9—C11	105.4 (3)	C18—C19—C20	110.5 (4)
C9A—C9—C17	115.5 (3)	C18—C19—N	112.7 (3)
C11—C9—C17	115.0 (3)	C20—C19—N	108.8 (4)
C1—C9A—C4A	119.9 (3)	C22—C21—N	116.4 (5)
C1—C9A—C9	127.3 (3)	C22—C21—O7	122.0 (5)
C4A—C9A—C9	112.7 (3)	N—C21—O7	121.6 (4)
C4A—C10—C10A	105.4 (3)	C19—N—C21	120.1 (4)
C4A—C10—C12	107.3 (3)	C13—O1—C14	115.7 (4)
C10A—C10—C12	104.8 (3)	C15—O3—C16	115.7 (3)
C5—C10A—C8A	120.9 (3)	C17—O5—C18	115.2 (3)
C5—C10A—C10	126.2 (3)		

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and stereo molecular and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71586 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1047]

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Structure of a Mixed Crystal of α- and β-Pipitzol (1:1), $C_{15}H_{20}O_3.C_{15}H_{20}O_3$

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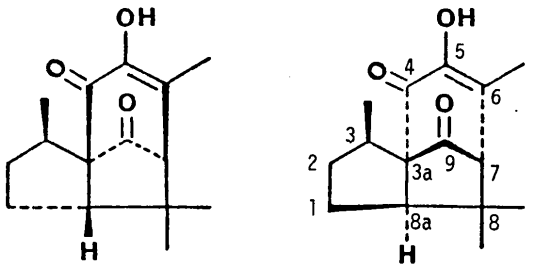
Abstract

The structure of a mixed crystal (1:1, space group *P*1) of α- and β-pipitzol {[3*R*-(3α,3aβ,7β,8aα)]- and [3*R*-(3α,3aα,7α,8aβ)]-1,2,3,7,8,8a-hexahydro-5-hydroxy-3,6,8,8-tetramethyl-4*H*-3a,7-methanoazulene-4,9-dione} is described. The two molecules are enantiomeric at three C centres, but have the same (*R*) configuration at one C atom and are linked into α/β pairs about pseudo centres of symmetry by O—H···O hydrogen bonds.

Comment

Pipitzol is isolated from the roots of *Perezia michoacana* as a mixture of the α and β diastereoisomers. The material is formed from the sesquiterpene quinone, perezone, which has a single chiral centre (Sánchez, Basurto & Joseph-Nathan, 1984). Intramolecular addition of the side-chain double bond of perezone onto the two faces of the quinone gives rise to the pipitzols, while generating three additional chiral centres. Thus α- and β-pipitzol are enantiomeric at three centres, but have the same configuration at C3. Crystal structures have been determined for several derivatives, in particular a mixed crystal (1:1) of the acetates of the α- and β-isomers (see Soriano-

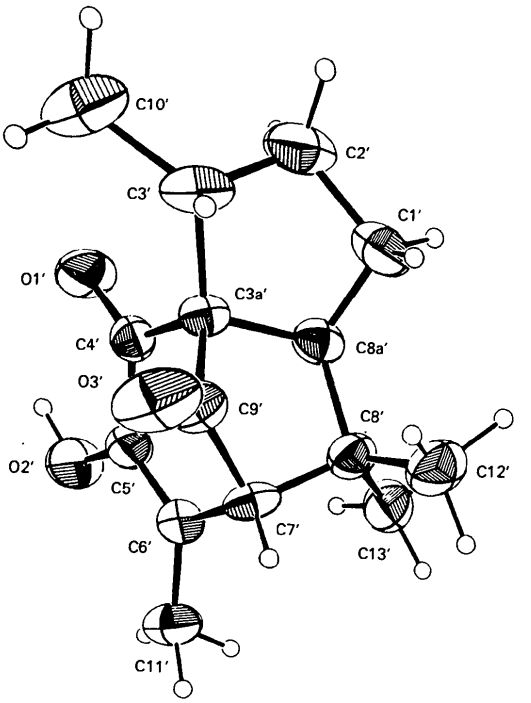
Garciá, Walls, Toscano & López-Celis, 1986, and references therein). We describe here the structure of a mixed crystal (1:1) of α- and β-pipitzols.



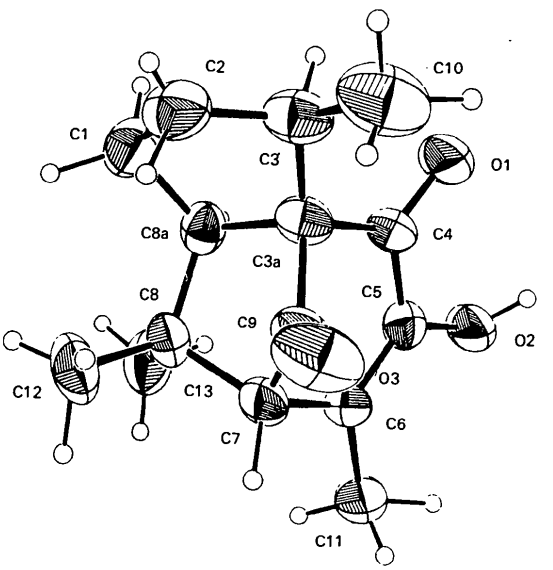
α β

The structure was solved initially in space group $P\bar{1}$; apparent partial occupancy of the C10 site indicated $P1$ as the correct space group. The unit cell contains one molecule each of α- and β-pipitzol, related by a pseudo centre of symmetry; the molecules (Fig. 1) are enantiomeric at atoms C3a, C7 and C8a, but have the same configuration (R) at C3. Refinement proceeded smoothly by full-matrix least-squares methods, but with correlation coefficients as high as 0.89. The general molecular geometry and dimensions (Table 2) are quite similar to those of the acetates (Soriano-Garciá *et al.*, 1986). The five-membered rings containing the C3-methyl substituent have approximate half-chair conformations, but with C1′ and C2′ displaced most from the ring plane in α-pipitzol, and C2 and C3 in β-pipitzol. These conformations are such as to reduce possible intramolecular steric repulsions between the C3-methyl substituents (C10) and the neighbouring O atoms at C4 (O1′) in α-pipitzol, and at C9 (O3) in β-pipitzol.

The molecules are linked into α/β pairs about pseudo centres of symmetry by O—H···O hydrogen bonds: O2—HO2···O1′($x+1, y+1, z-1$), O···O = 2.850 (6), O—H = 0.91, H···O = 2.10 Å, O—H···O = 140°; O2′—HO2′···O1($x+1, y+1, z-1$), O···O = 2.776 (6), O—H = 0.94, H···O = 1.92 Å, O—H···O = 150°. The nonlinearity of the bonds may be due to minor bifurcation involving weak intramolecular hydrogen bonding: HO2···O1 = 2.49 Å, O2—HO2···O1 = 96°, HO2′···O1′ = 2.26 Å, O2′—HO2′···O1′ = 107°.



(*a*)



(*b*)

Fig. 1. Views of the molecules of (*a*) α-pipitzol and (*b*) β-pipitzol with thermal ellipsoids at 50% probability. The third H atom on C10′ is behind the C atom, *i.e. trans* to the H atom on C3′.

Experimental

Crystal data

$C_{15}H_{20}O_3.C_{15}H_{20}O_3$
M_r = 248.32 (per molecule)
Triclinic
$P1$
a = 9.6729 (3) Å
b = 10.5434 (3) Å
c = 7.3228 (2) Å
α = 99.850 (3)°
β = 109.361 (2)°
γ = 98.229 (3)°
V = 677.97 (4) Å^3
Z = 1 (1 α and 1 β)
D_x = 1.216 Mg m^{-3}
D_m = 1.21 Mg m^{-3}
D_m measured by flotation

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 40–49°
μ = 0.64 mm^{-1}
T = 294 K
Block
0.25 × 0.19 × 0.18 mm
Colourless

Crystal source: crystallization from ethanol

Data collection

Enraf–Nonius CAD-4*F* diffractometer
Absorption correction: none
2792 measured reflections
2792 independent reflections
2327 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 75°$
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 0$
$l = -9 \rightarrow 9$
3 standard reflections monitored every 150 reflections
intensity variation: 1%

Refinement

Refinement on *F*
$R = 0.044$
$wR = 0.054$
$S = 2.3$
2327 reflections
323 + 148 H parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: Becker & Coppens (1974)
Extinction coefficient: 0.38×10^4
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

All H-atom parameters refined, except on C10′, where H atoms were placed in calculated positions, since refinement produced unacceptable geometry. Data collection: *CAD*-4 (Enraf–Nonius, 1977). Cell refinement: *CAD*-4. Data reduction: local programs. Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *ORFLS* (Busing, Martin & Levy, 1962). Molecular graphics: *ORTEP*II (Johnson, 1976).

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	U_{eq}
α-Pipitzol				
C1′	0.0532 (6)	0.2463 (6)	0.3987 (7)	0.066
C2′	−0.0926 (8)	0.2474 (7)	0.4331 (11)	0.065
C3′	−0.0435 (8)	0.3138 (7)	0.6552 (11)	0.052
C3a′	0.0991 (7)	0.2604 (7)	0.7524 (10)	0.036
C4′	0.0873 (7)	0.1548 (7)	0.8652 (10)	0.037
C5′	0.2319 (8)	0.1312 (7)	0.9883 (11)	0.041
C6′	0.3642 (7)	0.1999 (7)	1.0024 (11)	0.043
C7′	0.3678 (8)	0.3038 (7)	0.8844 (12)	0.043
C8′	0.3263 (8)	0.2465 (7)	0.6592 (11)	0.046
C8a′	0.1501 (7)	0.2019 (7)	0.5790 (11)	0.042
C9′	0.2371 (7)	0.3675 (7)	0.8824 (11)	0.044
C10′	−0.1681 (8)	0.3027 (8)	0.7375 (13)	0.086
C11′	0.5105 (8)	0.1789 (8)	1.1328 (12)	0.061
C12′	0.3810 (9)	0.3564 (8)	0.5713 (13)	0.069
C13′	0.3979 (8)	0.1304 (8)	0.6165 (12)	0.062
O1′	−0.0295 (7)	0.0879 (7)	0.8543 (10)	0.055
O2′	0.2237 (7)	0.0316 (7)	1.0860 (10)	0.059
O3′	0.2401 (7)	0.4785 (6)	0.9571 (11)	0.071
β-Pipitzol				
C1	0.9019	0.7575	0.6360	0.067
C2	0.9869 (8)	0.6639 (7)	0.5632 (11)	0.070
C3	1.0146 (8)	0.7144 (7)	0.3945 (12)	0.060
C3a	0.8651 (8)	0.7452 (7)	0.2874 (11)	0.047
C4	0.8664 (8)	0.8459 (7)	0.1622 (11)	0.046
C5	0.7213 (8)	0.8651 (7)	0.0351 (11)	0.046
C6	0.5913 (7)	0.7907 (7)	0.0217 (11)	0.045
C7	0.5947 (8)	0.6867 (7)	0.1412 (11)	0.046
C8	0.6287 (8)	0.7416 (7)	0.3697 (11)	0.049
C8a	0.8012 (8)	0.7975 (7)	0.4518 (11)	0.046
C9	0.7298 (7)	0.6314 (7)	0.1509 (11)	0.049
C10	1.0767 (9)	0.6258 (9)	0.2648 (14)	0.092
C11	0.4411 (8)	0.8055 (8)	−0.1100 (12)	0.061
C12	0.5820 (9)	0.6243 (9)	0.4494 (13)	0.072
C13	0.5453 (10)	0.8489 (8)	0.4084 (13)	0.070
O1	0.9846 (7)	0.9098 (7)	0.1686 (10)	0.064
O2	0.7230 (7)	0.9603 (6)	−0.0674 (10)	0.061
O3	0.7357 (8)	0.5206 (7)	0.0835 (11)	0.079

Table 2. *Selected geometric parameters* (Å, °)

	α-Pipitzol	β-Pipitzol
C1—C2	1.514 (7)	1.509 (8)
C1—C8a	1.535 (6)	1.545 (7)
C2—C3	1.538 (7)	1.512 (7)
C3—C3a	1.560 (5)	1.510 (6)
C3—C10	1.515 (7)	1.540 (8)
C3a—C4	1.509 (5)	1.518 (6)
C3a—C8a	1.572 (6)	1.581 (7)
C3a—C9	1.524 (5)	1.557 (5)
C4—C5	1.474 (5)	1.469 (6)
C4—O1	1.214 (4)	1.223 (5)
C5—C6	1.340 (5)	1.347 (5)
C5—O2	1.375 (5)	1.354 (5)
C6—C7	1.510 (6)	1.513 (6)
C6—C11	1.493 (6)	1.501 (6)
C7—C8	1.548 (7)	1.579 (7)
C7—C9	1.511 (5)	1.491 (6)
C8—C8a	1.576 (5)	1.557 (6)
C8—C12	1.530 (7)	1.528 (7)
C8—C13	1.527 (6)	1.521 (7)
C9—O3	1.196 (5)	1.205 (5)
C2—C1—C8a	103.3 (4)	106.9 (4)
C1—C2—C3	104.3 (3)	104.0 (4)
C2—C3—C3a	102.9 (3)	101.9 (4)
C2—C3—C10	114.6 (4)	116.7 (5)
C3a—C3—C10	119.4 (4)	116.0 (5)
C3—C3a—C4	118.8 (3)	116.5 (4)
C3—C3a—C8a	106.6 (3)	106.9 (4)
C3—C3a—C9	114.1 (3)	120.0 (3)
C4—C3a—C8a	106.9 (3)	108.4 (3)
C4—C3a—C9	107.7 (3)	104.0 (3)
C8a—C3a—C9	101.0 (3)	99.4 (3)
C3a—C4—C5	115.0 (3)	117.9 (3)
C3a—C4—O1	124.9 (3)	121.0 (4)
C5—C4—O1	120.1 (3)	121.2 (4)
C4—C5—C6	122.7 (4)	121.0 (4)
C4—C5—O2	116.0 (3)	117.6 (3)
C6—C5—O2	121.4 (3)	121.3 (4)
C5—C6—C7	119.6 (3)	119.5 (4)
C5—C6—C11	122.5 (4)	122.6 (4)
C7—C6—C11	117.9 (4)	117.9 (4)
C6—C7—C8	113.7 (3)	114.8 (3)
C6—C7—C9	106.3 (3)	107.4 (3)
C8—C7—C9	101.1 (3)	100.8 (3)
C7—C8—C8a	103.3 (3)	102.0 (3)
C7—C8—C12	107.8 (4)	106.6 (4)
C7—C8—C13	113.1 (4)	113.1 (4)
C8a—C8—C12	113.1 (4)	113.9 (4)
C8a—C8—C13	111.0 (4)	111.1 (4)
C12—C8—C13	108.5 (4)	110.0 (5)
C1—C8a—C3a	104.2 (3)	102.4 (4)
C1—C8a—C8	120.2 (4)	119.2 (4)
C3a—C8a—C8	106.6 (3)	108.5 (3)
C3a—C9—C7	104.3 (3)	104.7 (3)
C3a—C9—O3	127.3 (3)	126.5 (4)
C7—C9—O3	128.3 (4)	128.6 (4)
C8a—C1—C2—C3	44.2 (5)	34.6 (5)
C1—C2—C3—C3a	−37.2 (4)	−42.7 (5)
C2—C3—C3a—C8a	16.3 (4)	35.1 (4)
C3—C3a—C8a—C1	9.9 (4)	−14.3 (4)
C3a—C8a—C1—C2	−32.7 (5)	−12.3 (5)

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles, together with stereo molecular and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71600 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1061]

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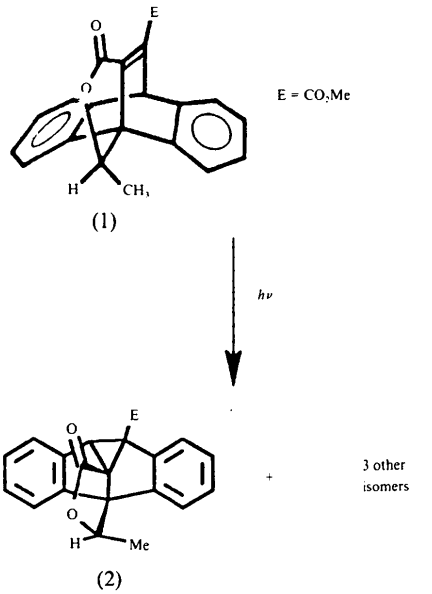

has now been determined by X-ray methods. The general geometry and dimensions of molecule (2) are similar to those of related materials (Pokkuluri, Scheffer & Trotter, 1993, 1994).

Acta Cryst. (1994). C**50**, 281–283

Structure of a Cyclopropapentalene Photolysis Product of a Dibenzobarrelene Ester Lactone

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Abstract

Photolysis of the dibenzobarrelene ester lactone, $C_{21}H_{16}O_4$ (1), can produce several products, the structure of one of which, 8b-methyl 4b-(1-hydroxyethyl)-4b,8b,8c,8d-tetrahydrodibenzo[*a*,*f*]cyclopropa[*cd*]pentalene-8b,8c-dicarboxylate carbolactone (2), has been determined by X-ray methods. The molecule of (2) contains a three-membered ring and has geometry and dimensions similar to those of related materials.

Comment

Photolysis of (1) can give four photoproducts, three of which have been isolated (Chen, Pokkuluri, Scheffer & Trotter, 1992). The structure of one of the products, (2),

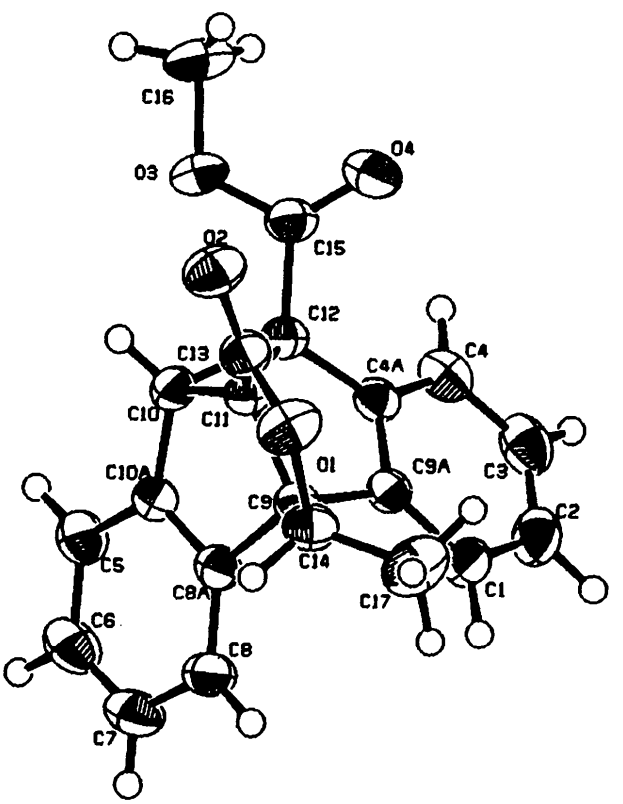

Fig. 1. View of the molecule with 50% probability ellipsoids.