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Two 2,3-Naphthalenic Schiff Bases

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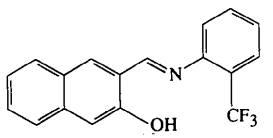
Abstract

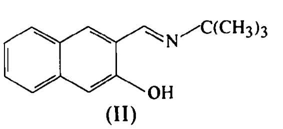
The crystal structures of 2-[2-(trifluoromethyl)phenyliminomethyl]-3-naphthol, (I), $C_{18}H_{12}F_3NO$, and 2-(*tert*-butyliminomethyl)-3-naphthol, (II), $C_{15}H_{17}NO$, have been determined. Both naphthalenic Schiff base molecules crystallize in the enol–imine tautomeric form. It is claimed that in the crystal of compound (I) there are both intra- and intermolecular hydrogen bonds, while in compound (II) there are only intramolecular hydrogen bonds, although a C—H···O interaction is found that may be considered as a weak intermolecular hydrogen bond.

Comment

Despite the considerable number of X-ray studies on the structures of Schiff bases derived from salicylaldehyde (Moustakali-Mavridis, Hadjoudis & Mavridis, 1980; Hadjoudis, Vitorakis & Moustakali-Mavridis, 1986), only a small number of 1,2-naphthalenic Schiff base analogues have been structurally characterized by X-ray crystallography (Acevedo-Arauz, Fernández-G., Rosales-Hoz & Toscano, 1992) and, to our knowledge, there are no reports of single-crystal X-ray diffraction studies on any 2,3-naphthalenic Schiff base analogues. We report here the structures of 2-[2-(trifluoromethyl)phenyliminomethyl]-3-naphthol, (I), and 2-(*tert*-butyliminomethyl)-3-naphthol, (II).



(I)



(II)

In compound (I), the mean C—F bond length is 1.331 (3) Å. Substitution of the trifluoromethyl group at atom C(13) does not cause any perturbation in the geometry and conformation of the benzene ring. The crystals of both compounds, the molecules are in the enol–imine tautomeric form. Examination of the crystal packing reveals that in both structures, the conformation of the side chain at atom C(2) orients the imino N atom in such a way that an intramolecular hydrogen bond is formed from the O(1) hydroxyl group at C(3) to atom N(1). Considering the interactions quoted in Table 3, it appears that in both compounds there is an intramolecular hydrogen bond of the O—H···N type and also intermolecular interactions of the C—H···O type that can be considered as weak hydrogen bonds (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984). In addition, in compound (I) there are intra- and intermolecular attractive interactions of the O—H···F and C—H···F types; the intramolecular ones determine the orientation of the trifluoromethyl group with respect to the phenyl ring, while the intermolecular ones contribute to the packing in the crystal.

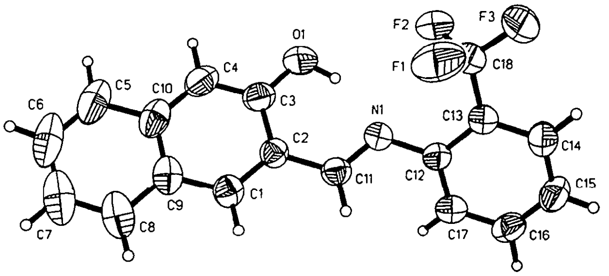


Fig. 1. The molecular structure of compound (I) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

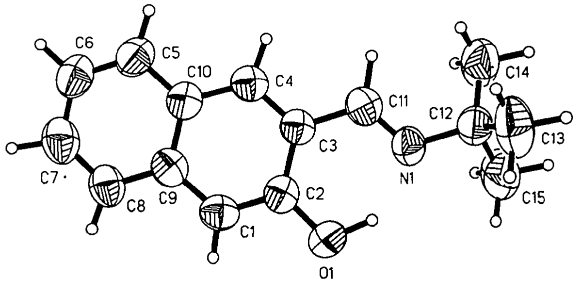


Fig. 2. The molecular structure of compound (II) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

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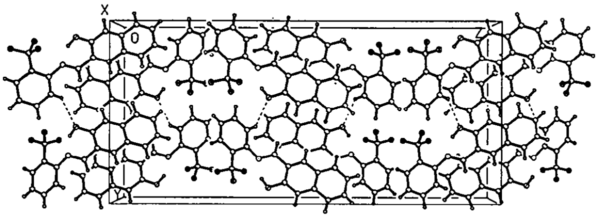

Fig. 3. A perspective drawing of the packing arrangement for compound (I). The dashed lines indicate the intermolecular C—H···O interactions.

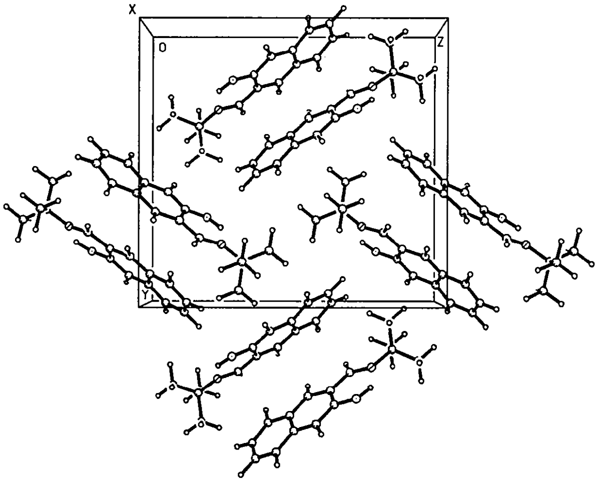

Fig. 4. A perspective drawing of the packing arrangement for compound (II).

Experimental

Compounds (I) and (II) were both recrystallized from CH_2Cl_2/MeOH solution at room temperature.

Compound (I)

Crystal data

$C_{18}H_{12}F_3NO$
$M_r = 315.29$
Orthorhombic
Pbca
$a = 6.988\ (2)$ Å
$b = 14.110\ (3)$ Å
$c = 30.133\ (6)$ Å
$V = 2971.4\ (11)$ Å^3
$Z = 8$
$D_x = 1.410$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 11.8$–$27.2°$
$\mu = 0.968$ mm^{-1}
$T = 293\ (2)$ K
Cubic
0.40 × 0.40 × 0.40 mm
Colourless

Data collection

Nicolet *P*3/*F* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1872 measured reflections
1872 independent reflections
1695 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 55.00°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 32$
3 standard reflections monitored every 100 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0554$
$wR(F^2) = 0.1543$
$S = 1.181$
1872 reflections
256 parameters
All H atoms refined isotropically

$w = 1/[\sigma^2(F_o^2) + (0.0810P)^2 + 0.9158P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.033$
$\Delta\rho_{\max} = 0.285$ e Å^{-3}
$\Delta\rho_{\min} = -0.335$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Compound (II)

Crystal data

$C_{15}H_{17}NO$
$M_r = 227.30$
Orthorhombic
$P2_12_12_1$
$a = 6.076\ (2)$ Å
$b = 14.055\ (6)$ Å
$c = 15.087\ (9)$ Å
$V = 1288.3\ (10)$ Å^3
$Z = 4$
$D_x = 1.172$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 15$–$40°$
$\mu = 0.570$ mm^{-1}
$T = 293\ (2)$ K
Rectangular
0.35 × 0.25 × 0.25 mm
Colourless

Data collection

Nicolet *P*3/*F* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
979 measured reflections
978 independent reflections
921 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.3427$

$\theta_{\max} = 55.07°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 100 reflections
intensity decay: 2.5%

Refinement

Refinement on F^2
$R(F) = 0.0554$
$wR(F^2) = 0.1643$
$S = 1.153$
978 reflections
195 parameters
All H atoms refined isotropically

$w = 1/[\sigma^2(F_o^2) + (0.0580P)^2 + 0.9511P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.004$
$\Delta\rho_{\max} = 0.167$ e Å^{-3}
$\Delta\rho_{\min} = -0.172$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
Compound (I)				
C1	0.4225 (4)	0.2256 (2)	0.50484 (8)	0.0511 (7)
C2	0.3822 (3)	0.2003 (2)	0.54796 (7)	0.0445 (6)
C3	0.2963 (4)	0.1105 (2)	0.55631 (9)	0.0527 (7)
C4	0.2565 (4)	0.0507 (2)	0.52180 (10)	0.0625 (8)
C5	0.2647 (5)	0.0135 (3)	0.44139 (13)	0.0828 (10)
C6	0.3119 (5)	0.0406 (3)	0.39936 (13)	0.0927 (13)

C7	0.3924 (5)	0.1294 (4)	0.39057 (12)	0.0885 (12)
C8	0.4268 (4)	0.1910 (3)	0.42418 (9)	0.0724 (9)
C9	0.3839 (3)	0.1654 (2)	0.46881 (8)	0.0556 (7)
C10	0.3002 (4)	0.0757 (2)	0.47780 (10)	0.0608 (8)
C11	0.4296 (3)	0.2651 (2)	0.58377 (8)	0.0457 (6)
C12	0.4504 (3)	0.3087 (2)	0.65825 (7)	0.0440 (6)
C13	0.5523 (4)	0.2790 (2)	0.69547 (7)	0.0490 (7)
C14	0.5973 (4)	0.3432 (2)	0.72867 (9)	0.0606 (8)
C15	0.5370 (4)	0.4364 (2)	0.72528 (10)	0.0645 (8)
C16	0.4335 (4)	0.4651 (2)	0.68944 (9)	0.0599 (8)
C17	0.3885 (4)	0.4021 (2)	0.65606 (9)	0.0519 (7)
C18	0.6250 (5)	0.1795 (2)	0.69876 (9)	0.0651 (8)
N1	0.4062 (3)	0.24228 (13)	0.62454 (6)	0.0478 (6)
O1	0.2531 (3)	0.08337 (14)	0.59805 (7)	0.0719 (6)
F1	0.7587 (3)	0.16109 (13)	0.66833 (8)	0.0995 (7)
F2	0.4921 (3)	0.11316 (11)	0.69245 (5)	0.0800 (6)
F3	0.7014 (4)	0.16016 (13)	0.73804 (7)	0.1171 (9)
Compound (II)				
C1	0.4125 (10)	0.0979 (4)	0.4223 (4)	0.0601 (13)
C2	0.3319 (9)	0.1613 (3)	0.3624 (3)	0.0550 (13)
C3	0.1145 (9)	0.1993 (3)	0.3736 (3)	0.0534 (12)
C4	−0.0041 (10)	0.1729 (3)	0.4470 (3)	0.0579 (13)
C5	−0.0524 (12)	0.0753 (4)	0.5826 (4)	0.072 (2)
C6	0.0248 (13)	0.0053 (4)	0.6363 (4)	0.079 (2)
C7	0.2340 (13)	−0.0339 (4)	0.6223 (4)	0.082 (2)
C8	0.3634 (12)	−0.0033 (4)	0.5533 (4)	0.067 (2)
C9	0.2891 (9)	0.0670 (3)	0.4956 (3)	0.0598 (14)
C10	0.0740 (9)	0.1074 (3)	0.5100 (3)	0.0568 (13)
C11	0.0137 (10)	0.2602 (4)	0.3056 (4)	0.0626 (14)
C12	0.0166 (10)	0.3400 (4)	0.1639 (4)	0.067 (2)
C13	0.0979 (16)	0.4421 (5)	0.1785 (5)	0.113 (3)
C14	−0.2300 (12)	0.3403 (7)	0.1635 (6)	0.113 (3)
C15	0.1112 (18)	0.3044 (7)	0.0784 (4)	0.124 (3)
N1	0.1176 (8)	0.2820 (3)	0.2354 (3)	0.0637 (12)
O1	0.4545 (6)	0.1879 (3)	0.2921 (3)	0.0712 (11)

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

Compound (I)			
C1—C2	1.377 (3)	C11—N1	1.280 (3)
C1—C9	1.405 (4)	C12—C17	1.388 (3)
C2—C3	1.425 (3)	C12—C13	1.393 (3)
C2—C11	1.453 (3)	C12—N1	1.416 (3)
C3—O1	1.349 (3)	C13—C14	1.386 (4)
C3—C4	1.369 (4)	C13—C18	1.496 (4)
C4—C10	1.405 (4)	C14—C15	1.384 (4)
C5—C6	1.363 (6)	C15—C16	1.361 (4)
C5—C10	1.426 (4)	C16—C17	1.378 (4)
C6—C7	1.398 (6)	C18—F3	1.327 (3)
C7—C8	1.357 (5)	C18—F2	1.332 (3)
C8—C9	1.424 (4)	C18—F1	1.334 (4)
C9—C10	1.421 (4)		
C2—C1—C9	122.2 (3)	N1—C11—C2	121.7 (2)
C1—C2—C3	118.9 (2)	C17—C12—C13	118.9 (2)
C1—C2—C11	119.4 (2)	C17—C12—N1	121.8 (2)
C3—C2—C11	121.6 (2)	C13—C12—N1	119.3 (2)
O1—C3—C4	119.2 (2)	C14—C13—C12	120.0 (2)
O1—C3—C2	120.8 (2)	C14—C13—C18	119.3 (2)
C4—C3—C2	120.0 (3)	C12—C13—C18	120.6 (2)
C3—C4—C10	121.2 (3)	C15—C14—C13	119.9 (3)
C6—C5—C10	120.0 (4)	C16—C15—C14	120.2 (3)
C5—C6—C7	121.6 (3)	C15—C16—C17	120.6 (3)
C8—C7—C6	120.3 (4)	C16—C17—C12	120.4 (2)
C7—C8—C9	120.3 (4)	F3—C18—F2	105.3 (2)
C1—C9—C10	118.1 (2)	F3—C18—F1	106.9 (3)
C1—C9—C8	122.4 (3)	F2—C18—F1	104.7 (2)
C10—C9—C8	119.5 (3)	F3—C18—C13	112.9 (2)
C4—C10—C9	119.5 (2)	F2—C18—C13	114.4 (2)
C4—C10—C5	122.3 (3)	F1—C18—C13	112.0 (2)
C9—C10—C5	118.2 (3)	C11—N1—C12	119.6 (2)
Compound (II)			
C1—C2	1.361 (7)	C6—C7	1.401 (10)
C1—C9	1.405 (7)	C7—C8	1.374 (9)
C2—O1	1.349 (6)	C8—C9	1.392 (7)
C2—C3	1.434 (7)	C9—C10	1.442 (8)
C3—C4	1.371 (7)	C11—N1	1.271 (7)
C3—C11	1.470 (7)	C12—N1	1.485 (7)
C4—C10	1.406 (7)	C12—C15	1.498 (9)
C5—C6	1.358 (9)	C12—C14	1.498 (9)
C5—C10	1.412 (7)	C12—C13	1.534 (9)
C2—C1—C9	122.2 (5)	C8—C9—C10	118.6 (5)
O1—C2—C1	120.3 (5)	C1—C9—C10	118.7 (5)
O1—C2—C3	119.9 (4)	C4—C10—C5	123.4 (5)
C1—C2—C3	119.8 (5)	C4—C10—C9	117.5 (5)
C4—C3—C2	118.6 (5)	C5—C10—C9	118.9 (5)
C4—C3—C11	120.1 (5)	N1—C11—C3	121.0 (5)
C2—C3—C11	121.2 (5)	N1—C12—C15	106.5 (5)
C3—C4—C10	123.1 (5)	N1—C12—C14	114.7 (6)
C6—C5—C10	120.5 (6)	C15—C12—C14	112.4 (7)
C5—C6—C7	120.5 (6)	N1—C12—C13	106.0 (5)
C8—C7—C6	120.7 (6)	C15—C12—C13	108.2 (6)
C7—C8—C9	120.7 (7)	C14—C12—C13	108.6 (7)
C8—C9—C1	122.6 (6)	C11—N1—C12	122.2 (5)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
Compound (I)			
O1—HO1···N1	1.75 (4)	2.609 (3)	153 (3)
C14—H14···F3	2.35 (3)	2.698 (3)	100 (2)
O1—HO1···F2	2.68 (3)	3.325 (3)	127 (3)
C17—H17···O1^{i}	2.56 (3)	3.252 (3)	133 (2)
C6—H6···F1^{ii}	2.66 (4)	3.536 (5)	166 (3)
C15—H15···F2^{iii}	2.66 (3)	3.522 (3)	157 (3)
Compound (II)			
O1—HO1···N1	1.72 (8)	2.583 (6)	138 (6)
C11—H11···O1^{iv}	2.72 (9)	3.552 (7)	133 (6)
C7—H7···O1^{v}	2.68 (6)	3.544 (8)	136 (4)

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

For both compounds, data collection: Nicolet *P*3/*F* diffractometer software; cell refinement: Nicolet *P*3/*F* diffractometer software; data reduction: Nicolet *P*3/*F* diffractometer software; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*93.

We acknowledge MSc Teresa Hernández-Quiroz for technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1150). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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16β-(Acetyloxy)-3β-[(2,6-dideoxy-3-*O*-methyl-L-*arabino*-hexopyranosyl)oxy]-14-hydroxycard-20(22)-enolide Dihydrate

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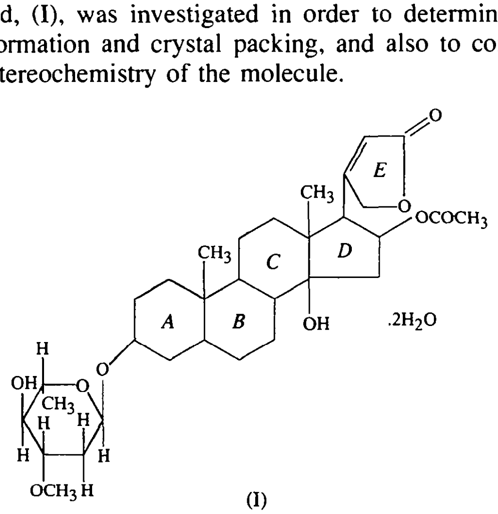
Abstract

In the title compound, $C_{32}H_{48}O_9.2H_2O$, all three six-membered rings of the cardenolide skeleton have chair conformations. The five-membered ring, the γ-lactone ring and the sugar ring adopt envelope, half-chair and envelope conformations, respectively. The crystal structure is stabilized by short C—H···O and O—H···O intramolecular hydrogen bonds. Several intermolecular interactions of the C—H···O type are also present.

Comment

The crystal and molecular structure of the title compound, (I), was investigated in order to determine the conformation and crystal packing, and also to confirm the stereochemistry of the molecule.



(I)

Bond distances and angles are quite similar to those of related compounds. The C(1)—C(2) and C(1)—C(6) bond distances are significantly shorter than the normal value of 1.533 Å for a C—C bond length in *n*-hydrocarbons (Bartell, 1959), but are in agreement with those of a previously reported structure (Soriano-García *et al.*, 1987). The molecules consist of three six-membered rings (*A*, *B* and *C*), one five-membered ring (*D*), a γ-lactone ring (*E*) and a sugar ring (*F*). The *A*/*B* and *C*/*D* ring junctions are *trans*. According to the torsion angle (Table 2) and puckering parameter values (φ_2, θ_2 and Q), the six-membered rings, *A*, *B* and *C*, occur in chair ($^1C_4$), chair ($^1C_4$), chair ($^4C_1$) conformations, respectively, while the *D*, *E* and *F* rings adopt envelope, half-chair and envelope (E_5) conformations, respectively (Boeyens, 1978).

The O—H···O hydrogen-bonding scheme is given in Table 3. The hydroxy groups interact with the water molecules, with O···O distances of 2.821 (5) and 2.741 (5) Å, respectively. One of the water molecules (O*W*1) participates in O—H···O hydrogen bonds with the hydroxy O1 and carbonyl O3 atoms, with O···O distances of 2.825 (5) and 2.847 (5) Å, respectively. The other water molecule (O*W*2) interacts with the O9 and O5 atoms, with O···O distances of 2.793 (5) and 2.837 (5) Å, respectively (Allen, Kennard & Taylor, 1983).

There is a short intramolecular C—H···O hydrogen bond (H17···O5 2.317, C17···O5 2.637 Å, C17—H17···O5 100.6°) which stabilizes the molecule internally. In addition, there are several C—H···O intermolecular interactions with C···O distances in the range 3.323–3.883 Å and C—H···O angles in the range

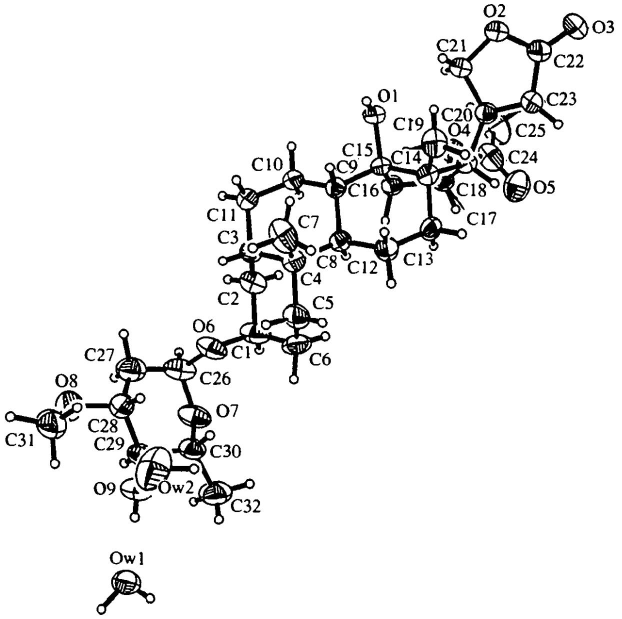


Fig. 1. The molecular structure of the title compound showing the atom-labelling scheme and 50% probability displacement ellipsoids.

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