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The New Pentacyclic Saponine Ecdysantherin [3β-Hydroxy-20-methylpregn-5,14-dien-16-one-(18–20)-lactone] from *Ecdysanthera rosea Hook. et Arn.* (*Apocynaceae*) of Vietnam

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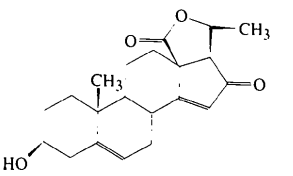
Abstract

Ecdysantherin, 3β-hydroxy-20-methylpregn-5,14-dien-16-one-(18–20)-lactone, $C_{21}H_{26}O_4$, a new pentacyclic saponine, was isolated from the powder of *Ecdysanthera rosea Hook. et Arn.* (*Apocynaceae*) of Vietnam, and its structure was elucidated. It was found that ecdysantherin is a pentacyclic saponine molecule with three six-membered and two five-membered rings. An intermolecular OH···O hydrogen bond generates infinite chains of molecules in the z direction.

Comment

Ecdysanthera rosea Hook. et Arn. is a large climbing shrub scattered in forests of Vietnam, Taiwan and other countries (Ho, 1993; Chuyen, 1975; Ly, 1986; Huang, Sy & Lai, 1990). In Vietnamese folk-medicine, this plant is used as an anti-inflammatory and anti-hepatitic drug (Hsu & Chin, 1980). The fluid extract and the saponine extracted from the powder of the *Ecdysanthera rosea* plant have an anti-inflammatory (inhibiting bacteria) and a diuretic (to treat urinary stones) activity. We have not yet found any toxicity. Only malic acid, tartaric acid together with phytosterols and a new pentacyclic triterpene (Huang, Sy & Lai, 1990) have been isolated previously from this species, and their structures were elucidated on the basis of spectral data. In addition, the new pentacyclic saponine ecdysantherin, (I), has now been isolated from *Ecdysanthera rosea Hook. et Arn.* in Vietnam by column chromatography.



(I)

The sample was recrystallized from chloroform–ethanol, and needle-shaped colourless crystals were obtained. An X-ray analysis was carried out to establish its chemical identity and spatial geometry.

The molecular structure is shown in Fig. 1 along with the atom-numbering scheme. In the molecule, consisting mainly of the pentacyclic ring system *A–E*, two endocyclic double bonds, C5=C6 and C14=C15, were identified, indicated by the short bond lengths of 1.331 (7) and 1.340 (6) Å, respectively.

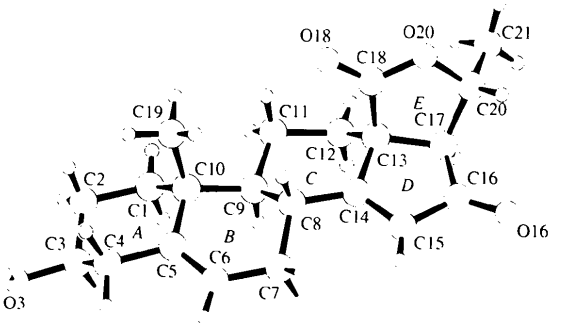


Fig. 1. *SCHAKAL88* (Keller, 1988) drawing of the molecular structure of ecdysantherin showing the numbering scheme.

The ring system is very similar to that of 20-epi-kibataline (Kutschabsky, Pfeiffer, Kretschmer & Adam, 1985; Ngoc, Kutschabsky, Phuong & Adam, 1984), a steroidal alkaloid also isolated from a Vietnamese plant; however, 20-epi-kibataline lacks the C16—O16 keto group and has a C14—C15 single bond. For this compound an *R* configuration was assigned to C20 on the basis of spectroscopic data (Ngoc *et al.*, 1984). It therefore seemed sensible for ecdysantherin, of which the absolute configuration was neither previously known

nor determined by this X-ray analysis, to refine the enantiomer having an *R* configuration at C20.

All bond lengths and angles in the title compound are in the expected ranges and need no further discussion. Table 2 gives a summary of the ring conformations expressed by the Cremer & Pople puckering parameters (Cremer & Pople, 1975; Luger & Bülow, 1983). The six-membered rings *A* and *C* are in normal chair forms, while ring *B* is in a $8\beta,9\alpha$-half chair form as a result of the C5═C6 double bond. The five-membered ring *D* is in a 17α-envelope form but ring *E* has a twist form. In the comparable compound 20-epi-kibataline (Kutschabsky *et al.*, 1985), the six-membered ring conformations were the same; owing to the absence of the C14═C15 double bond, however, the five-membered rings had different conformations, namely 14α-envelope for *D* and 17β-envelope for *E*.

The 3β-OH group is the donor in an intermolecular O3—H30···O16′ hydrogen bond [O3···O16′ 2.831 (6), H30···O16′ 2.03 (2) Å, O3—H30···O16′ = 164 (6)°; symmetry operation for O16′: $\frac{1}{2} - x$, $2 - y$, $z - \frac{1}{2}$] generating infinite molecular chains in the *z* direction (see Fig. 2). Further intermolecular contacts of interest were not seen.

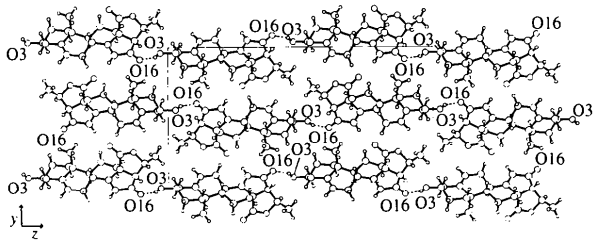


Fig. 2. Packing illustration of the lattice projected onto the *yz* plane.

Experimental

The sample was collected in May 1993 at the Ky Son Forest of Hoa Binh Province, Vietnam. The air-dried material was cut into slices and extracted repeatedly with ethanol at room temperature, and evaporated to remove ethanol. It was then separated with *n*-butanol and hydrolyzed by H_2SO_4 (5%) in C_2H_5OH. Chloroform extracts were concentrated under reduced pressure to afford a syrup residue. This syrup was subjected to column chromatography on silica gel using a solvent system (benzene/ethylacetate 7/3) of increasing polarity, yielding fractions. The fraction IV gave a crystalline compound with colourless needle-shaped crystals. The melting point (513–514 K) was measured by micro melting-point apparatus. The molecular weight (342) was determined by mass spectroscopy and corresponds to the formula $C_{21}H_{26}O_4$. The UV spectrum has an absorption peak maximum at 248 nm and the IR spectrum shows strong absorption at 3420, 2900, 1430 and 1380 cm^{-1}.

Crystal data

$C_{21}H_{26}O_4$
M_r = 342.42
Orthorhombic
$P2_12_12_1$
a = 6.086 (1) Å
b = 11.990 (1) Å
c = 23.831 (2) Å
V = 1739.0 (4) Å^3
Z = 4
D_x = 1.308 Mg m^{-3}
D_m not measured
Cu $K\alpha$ (Ni-filtered) radiation
λ = 1.5418 Å
Cell parameters from 90 reflections
θ = 20–30°
μ = 0.718 mm^{-1}
T = 293 (2) K
Needle
0.43 × 0.10 × 0.04 mm
Colourless

Data collection

Stoe four-circle MicroVAX-controlled diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1525 measured reflections
1525 independent reflections
1121 observed reflections [$F > 2\sigma(F)$]
θ_{max} = 59.99°
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 90 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0436
$wR(F^2)$ = 0.1323
S = 1.052
1520 reflections
230 parameters
H-atom parameters not refined (riding)
$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 1.1728P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.215 e Å^{-3}
$\Delta\rho_{min}$ = −0.194 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0014 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.1 (7) (indeterminate)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
C1	−0.3079 (9)	0.8719 (4)	0.1236 (2)	0.0473 (14)
C2	−0.3544 (10)	0.8600 (5)	0.0605 (2)	0.057 (2)
C3	−0.2607 (10)	0.9585 (5)	0.0297 (2)	0.056 (2)
O3	−0.3186 (7)	0.9574 (5)	−0.02858 (14)	0.0804 (14)
C4	−0.0154 (9)	0.9637 (5)	0.0382 (2)	0.0516 (15)
C5	0.0438 (9)	0.9692 (4)	0.1000 (2)	0.0410 (12)
C6	0.1818 (9)	1.0463 (4)	0.1192 (2)	0.0450 (13)
C7	0.2544 (9)	1.0589 (3)	0.1784 (2)	0.0418 (12)
C8	0.1955 (8)	0.9556 (4)	0.2133 (2)	0.0349 (11)
C9	−0.0441 (8)	0.9237 (4)	0.2010 (2)	0.0380 (12)
C10	−0.0629 (9)	0.8821 (4)	0.1384 (2)	0.0392 (13)
C11	−0.1406 (10)	0.8409 (4)	0.2436 (2)	0.0424 (13)
C12	−0.1032 (8)	0.8811 (4)	0.3045 (2)	0.0422 (13)
C13	0.1406 (8)	0.8947 (4)	0.3174 (2)	0.0363 (11)
C14	0.2405 (8)	0.9747 (4)	0.2744 (2)	0.0358 (11)
C15	0.3638 (9)	1.0537 (4)	0.2988 (2)	0.0430 (12)
C16	0.3650 (9)	1.0385 (4)	0.3595 (2)	0.0458 (13)
O16	0.4794 (8)	1.0886 (3)	0.39348 (14)	0.0667 (13)
C17	0.2012 (9)	0.9470 (4)	0.3743 (2)	0.0404 (12)
C18	0.2679 (9)	0.7858 (4)	0.3180 (2)	0.0441 (12)
O18	0.2905 (7)	0.7213 (3)	0.27969 (14)	0.0572 (10)
C19	0.0528 (10)	0.7691 (4)	0.1293 (2)	0.0509 (14)
C20	0.3012 (11)	0.8527 (4)	0.4094 (2)	0.052 (2)
C21	0.1440 (12)	0.8010 (5)	0.4505 (2)	0.071 (2)
O20	0.3649 (7)	0.7691 (3)	0.36790 (14)	0.0566 (11)

Table 2. *Cremer & Pople* puckering parameters (Å, °) of the rings A–E*

	Size	Q, q_2	Φ, φ_2	θ	Type†
A	6	0.546 (8)	89 (4)	10.9 (8)	*c*
B	6	0.547 (7)	215.2 (9)	50.3 (7)	*h*
C	6	0.520 (7)	171 (3)	14.4 (8)	*c*
D	5	0.111 (7)	144 (3)	—	*e*
E	5	0.189 (7)	52 (2)	—	*t*

* Cremer & Pople (1975); Luger & Bülow (1983). † Type: *c* = chair; *h* = half-chair; *t* = twist; *e* = envelope.

Data collection: Stoe software. Cell refinement: Stoe software. Data reduction: in-house program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SCHAKAL*88 (Keller, 1988). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1101). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-(1-Naphthyloxy)-1,2-benzisothiazole 1,1-Dioxide: Electronic Effects of Conjugation

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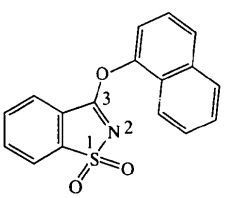
Abstract

The conjugation of oxygen with an aromatic ring, as in 1-naphthol, results in a C—O bond length of 1.35 Å and a C—O—C bond angle of almost 120°, whereas the C—O bond length in an aliphatic ether is about 1.45 Å, with a C—O—C angle of about 110°. The pseudo-saccharyl ether of 1-naphthol, $C_{17}H_{11}NO_3S$, changes the phenolic C—O bond length to 1.422 (7) Å, while maintaining the C—O—C angle. The result implies that the original naphtholic O atom is no longer π-conjugated with the naphthalene ring system, but only with the saccharyl system.

Comment

Derivatives of saccharin are known for their biological activity (Strupczewski *et al.*, 1995). The saccharyl system has also been used as a cheap and effective leaving group in important chemical transformations such as the derivatization of phenols prior to their conversion into arenes by transfer hydrogenolysis (Brigas & Johnstone, 1990) and for cross-coupling C—C bond formation with zinc and tin organometallic reagents (Brigas & Johnstone, 1994). Phenolic saccharyl ethers such as the title compound, 3-(1-naphthyloxy)-1,2-benzisothiazole 1,1-dioxide, (1), are easily prepared in high yield.



(1)

The effect of the saccharyl system on the conjugation of oxygen into an aryl ring has been discussed in a previous paper (Brigas & Johnstone, 1996). Briefly, for a simple benzene compound (the *O*-saccharyl ether of 4-methoxyphenol), it was shown that the original C—O

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