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X-ray Structure of Desacetoxysolaphyllidine, a Steroid Alkaloid from *Solanum hypomalacophyllum* Bitter: (22*R*,23*S*,25*R*)-22,26-Epimino-3β,23-dihydroxy-5α-cholestan-4-one–Ammonium Acetate (1/1), $C_{27}H_{45}NO_3.NH_4^+.C_2H_3O_2^-$

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Abstract. $M_r = 508\cdot75$, orthorhombic, $P2_12_12_1$, $a = 31\cdot862\,(8)$, $b = 12\cdot434\,(4)$, $c = 7\cdot192\,(2)$ Å, $V = 2849$ Å^3, $Z = 4$, $D_m = 1\cdot184\,(5)$, $D_x = 1\cdot186$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot045$ mm^{-1}, $F(000) = 1120$, $T = 295$ K, $R = 0\cdot070$ for 1538 unique reflections with $I > 3\sigma(I)$. The crystalline structure consists of discrete molecules in which rings *A*, *B* and *C* of the androstane moiety and the substituted piperidine ring have chair conformations. The androstane ring *D* has the envelope conformation at C(13), with C(14), C(15), C(16) and C(17) approximately on the same plane. Hydrogen bonds are formed involving the substituted piperidine rings, the ammonium ions and the acetate ions.

Introduction. A study of *Solanum hypomalacophyllum* Bitter, a small tree native to the Venezuelan Andes, has yielded several new 4-keto steroidal alkaloids (Usubillaga, Seelkopf, Karle, Daly & Witkop, 1970; Usubillaga, 1973; Usubillaga, Paredes, Martinod & Hidalgo, 1973; Usubillaga, Zabel & Watson, 1982; Usubillaga, 1984). Solaphyllidine and desacetylsolaphyllidine are the most abundant alkaloids in the green berries of this plant. From the mother liquors of the latter a new alkaloid was obtained which crystallized from ethanol as fine needles, m.p. 477–482 K. The IR spectrum of this compound shows an amide-like band at 1650 cm^{-1}, and its PMR spectrum in $CDCl_3$ solution exhibits a band equivalent to about three protons at δ 2·40. This band shifts to δ 5·75 in pyridine-*d*5 solution. The mass spectrum of this alkaloid showed a molecular ion at *m*/*e* 431, indicative of the molecular formula $C_{27}H_{45}NO_3$, which did not fit with the spectroscopic properties previously described. These features are not modified by recrystallization from MeOH, acetone or acetonitrile, but mild acetylation yielded an O,N-diacetate identical to that obtained from desacetoxysolaphyllidine (Usubillaga, 1984). In order to ascertain the structure of this compound an X-ray analysis was performed.

Experimental. Density determined by flotation in chlorobenzene and bromobenzene. Colourless transparent parallelepiped crystal 0·38 × 0·15 × 0·12 mm. Automated four-circle Philips PW 1100 diffractometer. Lattice parameters determined by least-squares procedure applied to the setting angles of 24 strong reflections in the range $7\cdot0° < \theta < 9\cdot3°$. Intensity data up to $(\sin\theta)/\lambda = 0\cdot605$ Å^{-1} in the range $0 \le h \le 37$, $0 \le k \le 14$ and $0 \le l \le 8$ measured with graphite-monochromated Mo $K\alpha$ radiation. Systematic absences proved the space group to be $P2_12_12_1$. After Lp corrections the initial 2919 reflections were reduced to 1538 unique data with $I > 3\sigma(I)$. Number of unobserved reflections: 1381. No corrections for absorption or extinction. Structure solved by direct methods (*MULTAN*77; Main, Lessinger, Woolfson, Germain & Declercq, 1977) with the geometry of the molecule taken into account. The structure refined by full-matrix least squares with isotropic temperature factors for all non-hydrogen atoms converged to $R = 0\cdot296$. A difference map based on the parameters of this cycle showed additional electron density which was assigned to one included formula unit of ammonium acetate. All the H atoms were placed in geometrically calculated positions and refined as rigid groups with the constraint that all C—H = 1·00 Å, except for H(O2), H(N1) and H(NH_4) which were placed in the positions located from a difference map, and refined restrained to standard values by the method of additional observational equations (Waser, 1963). Individual isotropic temperature factors were assigned to the ammonium H atoms and one overall isotropic temperature factor was used for all other H atoms. All non-hydrogen terminal atoms were refined anisotropically. The final anisotropic–isotropic refinement converged to $R = 0\cdot070$ and $wR = 0\cdot074$, with $(\Delta/\sigma)_{\max} = 0\cdot08$. The absolute configuration could not be determined since another run with two additional cycles having all positional parameters inverted converged to the same final *R*. Max. and min. heights in final difference Fourier synthesis 0·38 and $-0\cdot29$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray*

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Crystallography (1968). The function minimized was $\sum w(|F_o|-|F_c|)^2$ where $w = k/\sigma^2(F)$ and k converged to 1·0000. All calculations performed with the *SHELX*77 system (Sheldrick, 1977) on a Burroughs B 5900 computer at the Universidad de Los Andes.

Discussion. Positional and isotropic thermal parameters and the resulting bond lengths and angles are given in Table 1 and 2, respectively.*

The crystals of the steroidal alkaloid, recrystallized from acetonitrile, have four occluded formula units of ammonium acetate per unit cell. The crystalline structure consists of discrete molecules of $C_{27}H_{45}NO_3$ arranged in such a way that the substituted piperidine rings, related by 2_1 (b), are joined to the ammonium and acetate ions by hydrogen bonds forming infinite layers at $x \sim 0$ and $\frac{1}{2}$. Each substituted piperidine ring is involved in four H bonds, two very strong ones formed with the acetate anion, and two with the ammonium H atoms, see Fig. 1. The acetate and ammonium ions are joined together by a very strong H bond. These five H bridges form a two-dimensional network of 10- and 20-membered rings, which are shown in Fig. 1 as I and II. The three strongest H bonds present in the crystalline structure are probably responsible for the difficulties found in the initial chemical spectroscopic analysis of the alkaloid reported here.

In the molecular structure, rings A, B and C of the substituted androstane moiety and the substituted piperidine ring are all in the chair conformation, Fig. 2. The piperidine moiety is oriented almost perpendicular to the androstane fragment of the molecule. All mean bond lengths and angles are in agreement with those reported (*International Tables for X-ray Crystallography*, 1968), except for the distances N(1)–C(26) and N(1)–C(22) in the substituted piperidine ring which are notably longer: 1·507 (10) and 1·516 (11) Å,

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* Lists of anisotropic thermal parameters, H-atom coordinates refined as rigid groups, isotropic temperature factors, mean-plane calculations and structure factors have been deposited with the British Library Lending Division as Supplementay Publication No. SUP 42169 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* (×10⁴) *and isotropic temperature factors* (Å² ×10³)

	x	y	z	U_{eq} or U_{iso}
C(1)	−7308 (3)	−1723 (9)	−3793 (14)	47 (3)
C(2)	−6857 (3)	−1520 (8)	−3062 (16)	48 (3)
C(3)	−6567 (3)	−2486 (8)	−3363 (14)	41 (3)
O(2)	−6164 (2)	−2157 (6)	−2883 (12)	71*
C(4)	−6614 (3)	−2900 (7)	−5280 (14)	34 (2)
O(1)	−6305 (2)	−3098 (6)	−6244 (10)	55 (2)
C(5)	−7049 (2)	−3113 (7)	−6012 (13)	33 (2)
C(6)	−7065 (3)	−3636 (8)	−7899 (14)	38 (3)
C(7)	−7517 (3)	−3918 (8)	−8392 (15)	44 (3)
C(8)	−7799 (2)	−2924 (7)	−8338 (13)	31 (2)
C(9)	−7776 (2)	−2355 (7)	−6453 (13)	33 (2)
C(10)	−7320 (3)	−2084 (7)	−5848 (12)	29 (2)
C(11)	−8071 (3)	−1366 (7)	−6442 (15)	42 (3)
C(12)	−8524 (3)	−1636 (8)	−7018 (13)	40 (3)
C(13)	−8548 (2)	−2231 (7)	−8888 (12)	26 (2)
C(14)	−8257 (2)	−3202 (7)	−8719 (14)	34 (2)
C(15)	−8363 (3)	−3899 (8)	−10411 (14)	47 (3)
C(16)	−8841 (3)	−3732 (8)	−10646 (15)	40 (3)
C(17)	−8970 (2)	−2785 (7)	−9364 (13)	29 (2)
C(18)	−8418 (3)	−1482 (7)	−10516 (15)	43*
C(19)	−7131 (3)	−1192 (7)	−7071 (16)	45*
C(20)	−9328 (2)	−2122 (7)	−10217 (13)	32 (2)
C(21)	−9456 (3)	−1162 (7)	−8973 (16)	46*
C(22)	−9707 (2)	−2855 (7)	−10735 (12)	31 (2)
C(23)	−10018 (3)	−2338 (7)	−12082 (13)	34 (2)
O(23)	−9817 (2)	−1941 (5)	−13719 (9)	44*
C(24)	−10363 (3)	−3127 (8)	−12575 (13)	37 (2)
C(25)	−10594 (3)	−3533 (7)	−10864 (13)	34 (2)
C(26)	−10289 (3)	−3990 (7)	−9460 (13)	37 (2)
N(1)	−9947 (2)	−3194 (6)	−9013 (10)	33 (2)
C(27)	−10922 (3)	−4374 (8)	−11342 (17)	57*
C(28)	−9319 (3)	−4444 (8)	−5578 (15)	41 (3)
O(28)1	−9325 (2)	−3560 (6)	−4814 (10)	64*
O(28)2	−9551 (2)	−4700 (5)	−6917 (10)	55 (2)
C(29)	−9000 (3)	−5256 (10)	−4994 (18)	79 (4)
N(2)	−9607 (2)	−6710 (7)	−8234 (10)	22*
H(O2)	−5988 (22)	−2671 (54)	−3487 (114)	38 (4)
H(N1)	−9752 (20)	−3641 (55)	−8179 (98)	38 (4)
H(N2)1	−9588 (36)	−5944 (42)	−7957 (167)	88 (42)
H(N2)2	−9562 (30)	−6526 (73)	−9439 (76)	42 (30)
H(N2)3	−9788 (42)	−7218 (102)	−7447 (206)	173 (73)
H(N2)4	−9841 (25)	−6766 (86)	−9033 (135)	73 (35)

* Anisotropic temperature factors. $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)–C(2)	1·551 (13)	C(13)–C(17)	1·551 (11)
C(1)–C(10)	1·545 (13)	C(13)–C(18)	1·552 (12)
C(2)–C(3)	1·529 (13)	C(14)–C(15)	1·531 (13)
C(3)–C(4)	1·479 (14)	C(15)–C(16)	1·546 (11)
C(3)–O(2)	1·393 (11)	C(16)–C(17)	1·552 (12)
C(4)–C(5)	1·507 (11)	C(17)–C(20)	1·534 (11)
C(4)–O(1)	1·230 (10)	C(20)–C(21)	1·547 (12)
C(5)–C(6)	1·506 (13)	C(20)–C(22)	1·556 (11)
C(5)–C(10)	1·546 (12)	C(22)–C(23)	1·528 (12)
C(6)–C(7)	1·522 (11)	C(22)–N(1)	1·516 (11)
C(7)–C(8)	1·528 (12)	C(23)–O(23)	1·428 (11)
C(8)–C(9)	1·531 (12)	C(23)–C(24)	1·518 (12)
C(8)–C(14)	1·524 (11)	C(24)–C(25)	1·519 (13)
C(9)–C(11)	1·549 (11)	C(25)–C(27)	1·518 (12)
C(9)–C(10)	1·554 (11)	C(25)–C(26)	1·512 (12)
C(10)–C(19)	1·538 (12)	C(26)–N(1)	1·507 (10)
C(11)–C(12)	1·540 (12)	C(28)–C(29)	1·492 (13)
C(12)–C(13)	1·537 (12)	C(28)–O(28)1	1·229 (11)
C(13)–C(14)	1·527 (11)	C(28)–O(28)2	1·255 (11)
C(2)–C(1)–C(10)	113·2 (8)	C(14)–C(13)–C(17)	101·2 (6)
C(1)–C(2)–C(3)	112·5 (8)	C(14)–C(13)–C(18)	111·8 (7)
C(2)–C(3)–C(4)	110·1 (8)	C(17)–C(13)–C(18)	109·4 (7)
C(2)–C(3)–O(2)	106·9 (8)	C(8)–C(14)–C(13)	114·6 (7)
C(4)–C(3)–O(2)	115·2 (9)	C(8)–C(14)–C(15)	118·8 (8)
C(3)–C(4)–C(5)	118·6 (8)	C(13)–C(14)–C(15)	104·5 (7)
O(1)–C(4)–C(3)	121·0 (8)	C(14)–C(15)–C(16)	103·2 (8)
O(1)–C(4)–C(5)	120·4 (8)	C(15)–C(16)–C(17)	107·4 (8)
C(4)–C(5)–C(10)	109·9 (7)	C(13)–C(17)–C(16)	103·7 (7)
C(6)–C(5)–C(10)	114·1 (8)	C(13)–C(17)–C(20)	119·6 (7)
C(4)–C(5)–C(6)	115·0 (8)	C(16)–C(17)–C(20)	111·6 (7)
C(5)–C(6)–C(7)	109·9 (8)	C(17)–C(20)–C(22)	110·9 (6)
C(6)–C(7)–C(8)	111·4 (8)	C(17)–C(20)–C(21)	112·3 (7)
C(7)–C(8)–C(9)	111·6 (8)	C(21)–C(20)–C(22)	112·7 (7)
C(7)–C(8)–C(14)	112·1 (7)	C(20) C(22)–N(1)	111·0 (7)
C(9)–C(8)–C(14)	108·1 (7)	C(20)–C(22)–C(23)	114·1 (7)
C(8)–C(9)–C(10)	113·2 (7)	N(1)–C(22)–C(23)	107·9 (6)
C(10)–C(9)–C(11)	113·2 (7)	C(22)–C(23)–O(23)	112·2 (7)
C(8)–C(9)–C(11)	110·0 (7)	C(24)–C(23)–O(23)	110·9 (7)
C(1)–C(10)–C(5)	107·5 (8)	C(22)–C(23)–C(24)	110·3 (7)
C(1)–C(10)–C(9)	110·7 (7)	C(23)–C(24)–C(25)	112·1 (7)
C(5)–C(10)–C(9)	108·6 (7)	C(24)–C(25)–C(26)	110·8 (7)
C(1)–C(10)–C(19)	109·1 (8)	C(24)–C(25)–C(27)	112·2 (8)
C(5)–C(10)–C(19)	109·6 (7)	C(26)–C(25)–C(27)	109·6 (7)
C(9)–C(10)–C(19)	111·2 (7)	C(25)–C(26)–N(1)	111·1 (7)
C(9)–C(11)–C(12)	113·3 (8)	C(26)–N(1)–C(22)	111·9 (7)
C(11)–C(12)–C(13)	112·7 (8)	O(28)1–C(28)–O(28)2	124·1 (9)
C(12)–C(13)–C(14)	106·4 (7)	C(29)–C(28)–O(28)1	119·4 (10)
C(12)–C(13)–C(17)	116·7 (7)	C(29)–C(28)–O(28)2	116·4 (10)
C(12)–C(13)–C(18)	111·0 (7)		

respectively, *vs* the expected 1·479 (5) Å. The observed lengthening of these C—N bonds could be a consequence of the H bonds present in the crystalline structure involving N(1) and the H attached to it, H(N1).

A comparison between the structure reported here and that of solamalidine, an alkaloid with a similar substituted androstane skeleton (Usubillaga, Zabel & Watson, 1982), shows that the bond distances and angles of the androstane moieties are similar within standard deviations.

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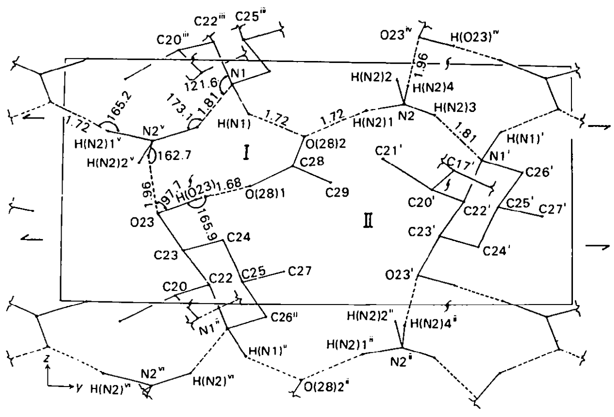

Fig. 1. (100) projection of the layer content of one unit cell at $x = 0$, showing the symmetry elements that are on the plane *yz* and the H-bond distances (Å) and angles (°). The numbered atoms are those which belong to the 10- and 20-membered rings, shown as I and II, respectively. Superscripts refer to the following symmetry operations: (i) $-x$, $0{\cdot}5+y$, $0{\cdot}5-z$; (ii) x, y, $z-1$; (iii) x, y, $1+z$; (iv) $-x$, $0{\cdot}5+y$, $1{\cdot}5-z$; (v) $-x$, $y-0{\cdot}5$, $1{\cdot}5-z$; (vi) $-x$, $y-0{\cdot}5$, $0{\cdot}5-z$. E.s.d.'s for distances 0·5 Å, for angles 8·0°.

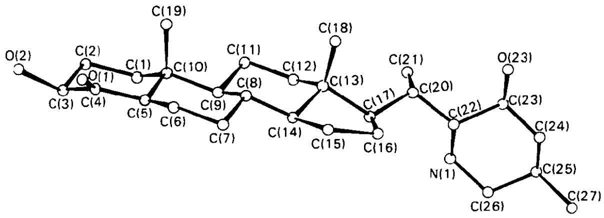

Fig. 2. A perspective view of the molecule showing the labeling of the atoms.

References

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Sheldrick, G. M. (1977). Program for crystal structure determination. Univ. of Cambridge, England.

Usubillaga, A. (1973). *Rev. Latinoam. Quím.* **4**(1), 32–34.

Usubillaga, A. (1984). *J. Nat. Prod.* **47**(1), 52–54.

Usubillaga, A., Paredes, A., Martinod, P. & Hidalgo, J. (1973). *Planta Med.* **23**(3), 286–289.

Usubillaga, A., Seelkopf, C., Karle, J. L., Daly, J. W. & Witkop, B. (1970). *J. Am. Chem. Soc.* **92**, 700–701.

Usubillaga, A., Zabel, V. & Watson, W. (1982). *Acta Cryst.* B**38**, 966–969.

Waser, J. (1963). *Acta Cryst.* **16**, 1091–1094.

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Structure of 6-Azidotetrazolo[5,1-*a*]phthalazine, $C_8H_4N_8$, Isolated from the Toxic Dinoflaggelate *Gymnodinium breve*

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Abstract. $M_r = 212$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}458\,(3)$, $b = 14{\cdot}669\,(4)$, $c = 4{\cdot}980\,(1)$ Å, $V = 910{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}547$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}7$ cm^{-1}, $F(000) = 432$, $T = 293$ K, final $R = 0{\cdot}035$ for 892 observed reflections. The three-fused-ring system is perfectly planar; the r.m.s. deviation of individual atoms from the mean plane is 0·020 Å, with the azido group slightly bent (9·1°) out

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