Fig. 2. Projection de la structure sur le plan (001).

homologue entraînent une dimérisation de la molécule. La cohésion cristalline est assurée en outre par des forces de van der Waals (Tableau 6).

Bien que cette molécule possède un enchaînement de type aryloxypropanolamine (AOPA), sa comparaison à des molécules à propriétés β-bloquantes (Léger, Gadret & Carpy, 1980) montre une conformation tout à fait différente. En particulier l'angle dièdre C(8)–C(9)–C(13)–N(12) vaut ici 244 (1)° alors que dans les composés évoqués il est toujours voisin de 180°. Les premiers résultats de l'étude pharmacologique confirment que la molécule ne possède pas de propriétés β-sympatholytiques, mais qu'elle est par contre douée d'une activité anorexigène de type amphétamine.

Tableau 6. *Principaux contacts intermoléculaires*

Code de symétrie: (i) x,y,z; (ii) $2 - x, -1 - y, -z$; (iii) $1 + x, y, z$; (iv) $1 - x, -y, 1 - z$.

N(12^i)···N(14^{ii})	2,97 (1) Å	N(12^i)···H(141^{ii})	1,95 (4) Å
N(12^i)···H(141^{ii})–N(14^{ii})		168 (4)°	
C(13^i)···O(10^{iii})	3,31 (1) Å	H(131^i)···O(10^{iii})	2,41 (5) Å
C(13^i)–H(131^i)···O(10^{iii})		147 (4)°	
C(8^i)···C(6^{iii})	3,59 (2) Å	H(81^i)···C(6^{iii})	2,74 (4) Å
O(7^i)···C(16^{iv})	3,56 (1)	O(7^i)···H(160^{iv})	2,57 (4)
O(10^i)···C(16^{iv})	3,28 (1)	O(10^i)···H(160^{iv})	2,89 (4)
C(16^i)···O(15^{iv})	3,36 (2)	H(160^i)···O(15^{iv})	2,54 (4)

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The Revised Structure of Solamaladine, 3β-Hydroxy-22-(4-methyl-1-pyrrolin-2-yl)-23,24-dinor-5α-cholane-4,22-dione

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Abstract. $C_{27}H_{41}NO_3$, $M_r = 427 \cdot 63$, orthorhombic, $P2_12_12_1$, $a = 14 \cdot 978$ (3), $b = 21 \cdot 486$ (5), $c = 7 \cdot 478$ (1) Å, $V = 2406 \cdot 6$ (6) Å³, $Z = 4$, $d_c = 1 \cdot 180$ Mg m⁻³, λ(Cu $K\alpha$) $= 1 \cdot 54178$ Å, $\mu = 0 \cdot 505$ mm⁻¹. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1988 reflexions led to a final R of 0·064. The steroidal alkaloid exists in a fully extended conformation with all ring junctures *trans*-fused. The C(17) β-side chain contains a 4-methyl-1-pyrroline moiety rather than the six-membered heterocyclic ketone proposed originally.

Introduction. Solamaladine is one of the minor alkaloids present in the green berries of *Solanum hypomalacophyllum* Bitter. It was obtained by column chromatography on silica gel of a crude extract, the least polar fractions being eluted with chloroform to yield solamaladine, m.p. 451–453 K. Based on spectroscopic and chemical evidence, a 4-keto-tomatillidine structure (I) was suggested for solamaladine (Usubil-

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Table 1. Positional parameters ($\times 10^4$, for H $\times 10^3$)

For nonhydrogen atoms $U_{eq} = (U_{11} U_{22} U_{33})^{1/3}$ (standard deviations 0·2–0·4 Å² $\times 10^2$).

|	x	y	z	U_{eq}/U (Å² $\times 10^2$)
C(1)	4522 (3)	862 (3)	2559 (5)	6·0
C(2)	3507 (3)	902 (3)	2297 (7)	7·1
C(3)	2987 (3)	507 (2)	3608 (7)	7·1
O(3)	2063 (2)	641 (2)	3448 (5)	8·6
C(4)	3332 (3)	626 (2)	5478 (6)	6·2
O(4)	2822 (2)	795 (2)	6653 (5)	8·4
C(5)	4315 (2)	544 (2)	5746 (5)	5·2
C(6)	4591 (3)	594 (3)	7698 (6)	6·5
C(7)	5594 (3)	493 (2)	7880 (5)	6·2
C(8)	6123 (2)	949 (2)	6701 (4)	4·4
C(9)	5832 (2)	875 (2)	4733 (4)	4·3
C(10)	4810 (2)	1008 (2)	4487 (4)	4·7
C(11)	6427 (2)	1250 (2)	3451 (4)	4·9
C(12)	7430 (2)	1144 (2)	3751 (4)	4·8
C(13)	7692 (2)	1275 (2)	5679 (4)	4·4
C(14)	7123 (2)	845 (2)	6871 (4)	4·6
C(15)	7541 (3)	898 (2)	8729 (4)	5·5
C(16)	8542 (3)	1007 (2)	8355 (5)	6·0
C(17)	8636 (2)	1069 (2)	6289 (4)	5·0
C(18)	7554 (3)	1963 (2)	6096 (5)	5·7
C(19)	4583 (3)	1675 (2)	4955 (7)	6·3
C(20)	9439 (2)	1478 (2)	5780 (6)	6·0
C(21)	10245 (3)	1224 (2)	6799 (6)	6·1
C(22)	10649 (3)	1619 (2)	8223 (6)	6·0
C(23)	11362 (3)	1375 (2)	9476 (6)	6·6
C(24)	11732 (3)	1978 (2)	10196 (6)	6·6
C(25)	10939 (4)	2426 (2)	9972 (7)	7·0
N(26)	10399 (3)	2177 (2)	8477 (5)	6·7
O(27)	10573 (2)	725 (1)	6464 (6)	8·2
C(28)	12550 (5)	2194 (4)	9167 (9)	9·0
C(29)	9656 (4)	1466 (4)	3773 (7)	8·4
H(1a)	482 (3)	117 (3)	179 (6)	9·1 (8)
H(1b)	412 (2)	44 (2)	230 (5)	4·5 (7)
H(2a)	335 (2)	75 (3)	110 (7)	8·8 (8)
H(2b)	331 (3)	133 (2)	249 (5)	5·9 (8)
H(3)	307 (3)	5 (2)	334 (7)	6·6 (8)
H(5)	449 (3)	11 (2)	541 (6)	6·7 (9)
H(6a)	428 (3)	27 (2)	840 (6)	7·7 (8)
H(6b)	445 (3)	102 (2)	814 (5)	6·6 (8)
H(7a)	575 (3)	7 (2)	747 (6)	5·2 (8)
H(7b)	578 (3)	57 (2)	913 (6)	6·4 (8)
H(8)	600 (2)	137 (2)	708 (5)	6·8 (8)
H(9)	592 (3)	43 (2)	440 (5)	6·1 (9)
H(11a)	654 (2)	170 (2)	356 (5)	3·7 (6)
H(11b)	651 (3)	110 (2)	222 (5)	7·5 (7)
H(12a)	777 (3)	143 (2)	299 (5)	5·9 (8)
H(12b)	758 (3)	70 (2)	351 (6)	4·7 (9)
H(14)	714 (2)	40 (2)	649 (4)	2·9 (7)
H(15a)	745 (4)	50 (3)	938 (9)	8·4 (7)
H(15b)	728 (3)	126 (2)	937 (7)	8·0 (9)
H(16a)	889 (3)	64 (3)	877 (8)	8·8 (8)
H(16b)	873 (3)	140 (2)	893 (7)	8·3 (9)
H(17)*	880 (2)	68 (2)	563 (4)	4·5 (8)
H(18a)	772 (3)	208 (2)	746 (8)	7·4 (2)
H(18b)	696 (3)	210 (2)	586 (7)	6·1 (10)
H(18c)	799 (3)	223 (2)	526 (6)	6·1 (10)
H(19a)	470 (9)	189 (6)	387 (25)	21·9 (49)
H(19b)	474 (6)	183 (4)	597 (14)	13·4 (27)
H(19c)	395 (5)	170 (3)	510 (10)	11·2 (20)
H(20)	929 (2)	192 (2)	609 (6)	5·4 (9)
H(23a)*	1181 (4)	114 (2)	879 (8)	8·1 (9)
H(23b)	1108 (4)	112 (2)	1042 (6)	5·6 (10)

Table 1 (cont.)

	x	y	z	U (Å² $\times 10^2$)
H(24)*	1195 (4)	195 (3)	1146 (7)	9·8 (9)
H(25a)*	1046 (3)	288 (3)	1005 (6)	8·0 (9)
H(25b)*	1128 (5)	226 (3)	1090 (6)	9·2 (9)
H(28a)	1286 (5)	250 (4)	946 (10)	11·2 (21)
H(28b)	1301 (4)	194 (3)	934 (10)	9·2 (19)
H(28c)	1238 (5)	219 (3)	809 (11)	9·7 (19)
H(29a)	970 (4)	99 (3)	345 (9)	9·5 (17)
H(29b)	1013 (4)	170 (3)	364 (9)	9·0 (14)
H(29c)	927 (4)	171 (2)	313 (9)	8·5 (15)

* Hydrogen positions initially calculated.

laga, 1973); however, a revised structure was proposed for tomatillidine (II) by Kusano, Takemoto, Sato & Johnson (1976). They demonstrated by synthesis that the side chain of tomatillidine contained a 4-methyl-1-pyrroline moiety rather than 5-methyl-3,4,5,6-tetra-hydro-4-pyridinone. The revision suggests the structure of solamaladine should be modified to (III); however, an X-ray structure of solaphyllidine obtained from the same plant showed the side chain to contain the six-membered heterocyclic ring proposed originally for structure (I) (Usubillaga, Seelkopf, Karle, Daly & Witkop, 1970). The 4-keto function in solamaladine made it difficult to synthesize from available starting materials, and an X-ray analysis was initiated to confirm the structure of solamaladine and the related tomatillidine alkaloids.

(I)   (II)   (III)
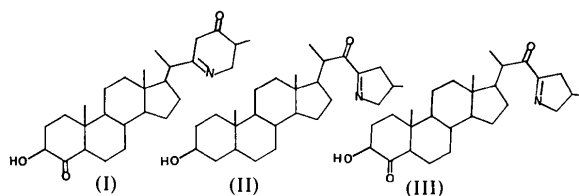
A crystal of dimensions 0·15 × 0·10 × 0·60 mm was selected for X-ray analysis. All data were collected on a Syntex $P2_1$ diffractometer by the $\theta:2\theta$ scanning technique using a variable scan speed and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure using 15 reflexions whose angles were measured by a centering routine associated with the diffractometer. Systematic absences were consistent with space group $P2_12_12_1$. A periodically monitored reflexion showed no significant change in intensity. Of the 2416 independent reflexions measured ($2\theta < 140°$), 1988 had intensities greater than $2\sigma(I)$. Lorentz and polarization corrections were applied but no absorption corrections were made.

The direct-methods program MULTAN78 (Main, Lessinger, Woolfson, Germain & Declercq, 1978) was used to calculate phases for the 308 $|E|$ values greater than 1·40. The phase set with the highest combined figure of merit was selected, and the E map calculated

with these phases revealed the positions of 30 non-hydrogen atoms. Alternate least-squares and difference Fourier calculations yielded the coordinates of the missing heavy atom and most of the H atoms. Additional H-atom positions were calculated. Three reflexions showing significant secondary extinction were omitted from the refinement. Full-matrix least-squares refinements converged to an R of 0·064 where $R = \sum||F_o| - |F_c||/\sum|F_o|$. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(I)$ was determined from counting statistics.

A final difference map showed no peak larger than 0·35 e Å^{-3} and the average shift/error during the final cycle of refinement was 0·17. Atomic scattering factors and the real and imaginary contributions to the anomalous dispersion were calculated by the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic positional parameters are given in Table 1 while interatomic distances, valence angles and torsion angles are given in Tables 2, 3 and 4.*

Table 2. Interatomic distances (Å)

C(1)–C(2)	1·535 (6)	C(12)–C(13)	1·521 (4)
C(2)–C(3)	1·512 (7)	C(13)–C(14)	1·541 (5)
C(3)–C(4)	1·512 (7)	C(13)–C(17)	1·550 (5)
C(3)–O(3)	1·419 (5)	C(14)–C(15)	1·528 (5)
C(4)–C(5)	1·498 (5)	C(15)–C(16)	1·543 (6)
C(4)–O(4)	1·220 (5)	C(16)–C(17)	1·557 (5)
C(5)–C(6)	1·521 (6)	C(17)–C(20)	1·539 (5)
C(5)–C(10)	1·558 (5)	C(20)–C(21)	1·528 (6)
C(6)–C(7)	1·523 (6)	C(20)–C(29)	1·535 (7)
C(7)–C(8)	1·538 (5)	C(21)–C(22)	1·490 (6)
C(8)–C(9)	1·543 (4)	C(21)–O(27)	1·206 (5)
C(8)–C(14)	1·520 (5)	C(22)–C(23)	1·514 (6)
C(9)–C(10)	1·568 (5)	C(23)–C(24)	1·508 (6)
C(9)–C(11)	1·538 (5)	C(24)–C(25)	1·539 (7)
C(10)–C(1)	1·537 (5)	C(25)–N(26)	1·480 (6)
C(10)–C(19)	1·515 (5)	C(22)–N(26)	1·271 (5)
C(11)–C(12)	1·536 (5)	C(24)–C(28)	1·519 (9)
C(13)–C(18)	1·524 (5)		

Table 3. Valence angles (°)

C(2)C(1)C(10)	112·7 (3)	C(12)C(13)C(14)	107·1 (3)
C(1)C(2)C(3)	113·3 (4)	C(8)C(14)C(13)	114·1 (2)
C(2)C(3)C(4)	109·2 (4)	C(13)C(14)C(15)	104·7 (3)
C(2)C(3)O(3)	109·5 (4)	C(14)C(15)C(16)	104·2 (3)
C(4)C(3)O(3)	112·1 (4)	C(15)C(16)C(17)	106·3 (3)
C(3)C(4)C(5)	116·1 (3)	C(16)C(17)C(13)	103·6 (3)
C(3)C(4)O(4)	120·2 (4)	C(17)C(13)C(14)	99·4 (2)
C(5)C(4)O(4)	123·7 (4)	C(12)C(13)C(17)	117·4 (3)
C(4)C(5)C(6)	112·8 (3)	C(12)C(13)C(18)	109·8 (3)
C(4)C(5)C(10)	108·2 (3)	C(14)C(13)C(18)	112·8 (3)
C(6)C(5)C(10)	114·0 (3)	C(17)C(13)C(18)	109·8 (3)
C(5)C(6)C(7)	110·1 (3)	C(13)C(17)C(20)	118·5 (3)
C(5)C(10)C(1)	107·6 (3)	C(16)C(17)C(20)	111·4 (3)
C(6)C(7)C(8)	111·5 (8)	C(17)C(20)C(21)	106·8 (3)
C(7)C(8)C(9)	109·6 (3)	C(17)C(20)C(29)	113·4 (4)
C(7)C(8)C(14)	111·5 (3)	C(21)C(20)C(29)	108·4 (3)
C(9)C(8)C(14)	110·0 (2)	C(20)C(21)C(22)	118·3 (3)
C(8)C(9)C(10)	111·7 (2)	C(20)C(21)O(27)	122·4 (3)
C(10)C(9)C(11)	113·4 (2)	C(22)C(21)O(27)	119·2 (3)
C(9)C(10)C(5)	106·1 (3)	C(21)C(22)C(23)	122·2 (3)
C(1)C(10)C(9)	110·3 (3)	C(21)C(22)N(26)	121·6 (3)
C(1)C(10)C(19)	110·3 (3)	C(22)C(23)C(24)	100·6 (3)
C(5)C(10)C(19)	111·0 (3)	C(23)C(24)C(25)	102·4 (4)
C(9)C(10)C(19)	111·3 (7)	C(24)C(25)N(26)	106·1 (3)
C(8)C(9)C(11)	112·1 (3)	C(25)N(26)C(22)	107·0 (3)
C(9)C(11)C(12)	113·5 (3)	C(23)C(22)N(26)	116·2 (3)
C(11)C(12)C(13)	111·3 (3)	C(23)C(24)C(28)	112·2 (4)
C(8)C(14)C(15)	118·0 (3)	C(25)C(24)C(28)	112·2 (4)

Table 4. Torsion angles (°)

|			
1–2–3–4	48·3 (6)	5–6–7–8	55·8 (5)
2–3–4–5	−54·0 (5)	6–7–8–9	57·4 (4)
3–4–5–10	60·1 (4)	7–8–9–10	59·6 (4)
4–5–10–1	−58·6 (4)	8–9–10–5	−57·6 (3)
5–10–1–2	57·3 (5)	9–10–5–6	57·1 (4)
10–1–2–3	−53·7 (6)	10–5–6–7	−57·3 (5)
8–9–11–12	49·7 (4)	13–14–15–16	−32·0 (4)
9–11–12–13	−55·1 (4)	14–15–16–17	4·8 (4)
11–12–13–14	57·4 (4)	15–16–17–13	23·7 (4)
12–13–14–8	−60·7 (3)	16–17–13–14	−42·0 (3)
13–14–8–9	56·5 (3)	17–13–14–15	46·1 (3)
14–8–9–11	−48·9 (4)		
O(3)–3–4–O(4)	2·5 (5)	22–23–24–25	25·4 (4)
29–20–21–O(27)	−53·9 (5)	23–24–25–N(26)	26·4 (4)
17–20–21–O(27)	68·7 (5)	24–25–N(26)–22	15·8 (5)
29–20–21–22	124·5 (5)	25–N(26)–22–23	1·7 (5)
17–20–21–22	−113·0 (5)	N(26)–22–23–24	−18·5 (5)
O(27)–21–22–23	10·3 (5)		
O(27)–21–22–N(26)	171·2 (5)		
20–21–22–23	171·3 (5)		
20–21–22–N(26)	−7·2 (5)		
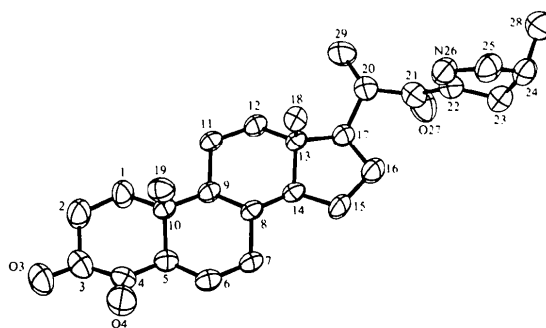
Fig. 1. *ORTEP* drawing of solamaladine with anisotropic thermal parameters at the 35% probability level.
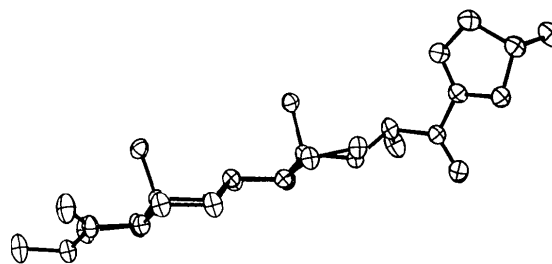

Fig. 2. Side view of solamaladine showing the extended conformation and the shape of the steroid backbone.

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1971) of solamaladine while Fig. 2 presents a side view of the molecule showing the extended conformation and indicates little bending of the steroid skeleton. All rings are *trans*-fused with the six-membered rings exhibiting chair conformations and the five-membered rings envelope conformations as indicated by the torsion angles. An $O(3)\cdots O(27)(x-1,y,z)$ distance of 3·178 (5) Å may indicate a weak hydrogen bond; however, the hydroxyl H atom could not be located in a difference Fourier map. All interatomic distances and valence angles are consistent with the structures of other steroids. The present analysis confirms the side-chain structure in solamaladine as being identical to that in the revised structure of tomatillidine and its derivatives.

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The Structure of 2-Chloro-8,9,10,11-tetrahydro-6H,11aH-pyridazino[1,2-a]cinnoline-1,4-dione

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Abstract. $C_{12}H_{13}ClN_2O_2$, $M_r = 252·70$, monoclinic, $P2_1/a$, $a = 13·340$ (2), $b = 18·769$ (4), $c = 4·7181$ (5) Å, $\beta = 99·53$ (2)°, $U = 1165·0$ (3) Å^3, $Z = 4$, $D_c = 1·44$ Mg m^{-3}, $F(000) = 528$. The final $R = 0·072$ for 1529 reflexions. The molecules are held together by van der Waals forces. The dihydropyridazine ring has a half-chair conformation with a maximum torsion angle of 37·4 (6)° at the N—N bond. The diazaquinone ring has an envelope conformation.

Introduction. A study is being carried out in the Departamento de Química Orgánica of the Universidad Complutense in Madrid to obtain diazapolycyclic compounds with quinone structure, which could have biological activity, by introduction of substituents in the diazaquinonic ring (Lora-Tamayo, Pardo, Soto, Verde & Gonzalez, 1980), leading to the synthesis of antibacterial compounds (Gomez-Contreras, Lora-Tamayo & Navarro, 1977; Gomez-Contreras & Lora-Tamayo, 1979). As part of the study, the structure of the title compound (I) has been determined.

(I)
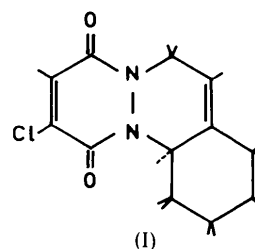
A crystal of dimensions $0·3 \times 0·2 \times 0·35$ mm was used to collect the data on a PW 1100 four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å). 3454 reflexions were measured in the $\omega/2\theta$ scan mode. The intensities were not corrected for absorption. By the criterion $I < 2\sigma(I)$,