the CSD. For Si—O one finds a range of 1·630 to 1·693 Å, and an average of 1·650 Å, while for the Si—O—C bond angle these quantities are 122·5 to 137·9°, with an average of 127·7°.

In this compound, the six ring atoms of the *p*-nitrobenzyl group are coplanar (plane 3). The plane of the NO_2 substituent is tilted about C(20)—N(3) by 17° with respect to plane (3). One may note (Fig. 1) a tendency for the principal axes of the thermal ellipsoids of C(18), C(19), C(21) and C(22) to be normal to plane (3) while C(17) and C(20) are slightly more isotropic. This suggests a slight oscillation of the ring about the C(17)–C(20) axis.

Stereochemistry

As in the case of the penam cyclization (Bedeschi *et al.*, 1986) kinetically controlled intramolecular Michael cyclization of (1) gives the *more* congested bicyclic product (2). While the precise reasons for this behavior are not clear, the outcome can be explained based on butane-type interactions in the transition state leading to (2), particularly since kinetic control was exercized as illustrated in Scheme 1.

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Structures of Two Related Bufadienolides: Gamabufotalin (3β,11α,14-Trihydroxy-5β,14β-bufa-20,22-dienolide) and Arenobufagin (3β,11α,14-Trihydroxy-12-oxo-5β,14β-bufa-20,22-dienolide)

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Abstract. Gamabufotalin, (1), $C_{24}H_{34}O_5$, $M_r = 402{\cdot}54$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}850$ (1), $b = 14{\cdot}766$ (1), $c = 17{\cdot}836$ (1) Å, $V = 2067{\cdot}5$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}293$ Mg m^{-3}, λ(Cu $K\bar{\alpha}$) = 1·54184 Å, $\mu = 0{\cdot}68$ mm^{-1}, $F(000) = 872$, $T = 295$ (1) K, $R = 0{\cdot}037$ for 2284 unique observed reflections. The conformation

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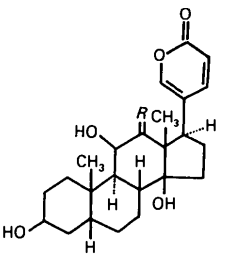
of the 14-isoaethiocholane skeleton of gamabufotalin is almost identical with that of the related bufalin {3β,14-dihydroxy-5β,14β-bufa-20,22-dienolide [Rohrer, Fullerton, Kitatsuji, Nambara & Yoshii (1982). *Acta Cryst.* **B38**, 1865–1868]}. However, the orientation of the planar δ-lactone ring differs by 166° in these two structures. The gamabufotalin molecules are bound together by an infinite chain of OH···O hydrogen bonds along the *a* axis. Two additional but weaker hydrogen bonds in which the oxo group of the lactone ring acts as a bifurcated acceptor cross-bind the molecules along the twofold screw axes in the **b** and **c** directions. Arenobufagin, (2), $C_{24}H_{32}O_6$, $M_r = 416{\cdot}52$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}826$ (1), $b = 14{\cdot}864$ (2), $c = 17{\cdot}841$ (2) Å, $V = 2075{\cdot}3$ (8) Å^3, $Z = 4$, $D_x = 1{\cdot}333$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 0{\cdot}73$ mm^{-1}, $F(000) = 896$, $T = 293$ (2) K, $R = 0{\cdot}031$ for 1997 unique observed reflections. Arenobufagin is a 12-oxo derivative of gamabufotalin. The comparison of their lattice parameters and atomic coordinates reveals that these two related compounds are quasi-isostructural. The additional 12-oxo group hardly has any impact upon the chair conformation of ring *C*.

Introduction. This work started with our report on the structure of digirezigenin (Kálmán, Argay, Ribár, Vladimirov & Živanov-Stakić, 1984), and is part of a systematic study of the cardenolides and bufadienolides isolated from the dried venom of the Chinese toad Ch'an Su. Gamabufotalin (1), which can be regarded as 11α-hydroxybufalin (Rohrer, Fullerton, Kitatsuji, Nambara & Yoshii, 1982), was first described by Meyer (1949). For the present structure analysis it was isolated from Ch'an Su by chromatography in the form of gamabufotalin hydrogensuberate as reported by Höriger, Živanov, Linde & Meyer (1970). After the hydrolysis of this ester the steroid component was recrystallized from a 1:1 mixture of methanol and ethyl acetate. The colourless crystals melt at 538–543 K.



(1): gamabufotalin $R = H_2$
(2): arenobufagin $R = O$

This paper also describes the 12-oxo derivative called arenobufagin (2). The question to be answered is: how does the oxo group influence the conformation and packing of the molecules relative to those of gamabufotalin? Arenobufagin, separated by the same technique as used for gamabufotalin, was recrystallized from a 1:1 mixture of methanol and ethyl acetate. The colourless crystals melt at 450–500 K.

Experimental.

Gamabufotalin (1)

A crystal of 0·23 × 0·27 × 0·30 mm was mounted on a CAD-4 diffractometer equipped with graphite monochromator. Cell constants by least-squares fit for 25 centred reflections with $45 \le \theta \le 50°$. Systematic absences $h00$: $h = 2n + 1$, $0k0$: $k = 2n + 1$, $00l$: $l = 2n + 1$. Scan range $0{\cdot}017 \le \sin\theta/\lambda \le 0{\cdot}626$ Å^{-1}, ω–2θ scan, h: 0 to 9, k: 0 to 18, l: 0 to 22. 2428 unique reflections measured. 2284 taken as observed with $I > 3\sigma(I)$, 144 unobserved reflections. Three standard reflections (531, 374 and 1,2,11), no intensity variations were observed. Structure solved by *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) using 238 $E \ge 1{\cdot}55$. Full-matrix least squares, $\sum w(\Delta F^2)$ minimized, 263 parameters refined. At the end of the isotropic refinement an empirical absorption correction was performed with the program *DIFABS* (Walker & Stuart, 1983); min. and max. absorption corrections 0·815 and 1·125. Final $R = 0{\cdot}037$, $wR = 0{\cdot}052$, $R_{tot} = 0{\cdot}041$, $S = 5{\cdot}41$, $w = 4F_o^2/\sigma^2(F_o^2)$. Max. and min. peak heights in final $\Delta\rho$ map $\pm 0{\cdot}17$ (3) e Å^{-3}. Data were not corrected for extinction. $(\Delta/\sigma)_{max} = 0{\cdot}24$. Positions of H atoms bound to C atoms were generated from assumed geometries, while those linked to O atoms were located in a difference Fourier map; their positions were taken into account without refinement in structure-factor calculations with isotropic temperature factors ($B_{iH} = B_{iX} + 1$ Å^2 where X = C or O).

Arenobufagin (2)

A crystal of 0·12 × 0·20 × 0·60 mm was mounted on the same diffractometer described above. Cell constants by least-squares fit for 25 centred reflections with $45 \le \theta \le 50°$. Systematic absences $h00$: $h = 2n + 1$, $0k0$: $k = 2n + 1$, $00l$: $l = 2n + 1$. Scan range $0{\cdot}017 \le \sin\theta/\lambda \le 0{\cdot}626$ Å^{-1}, ω–2θ scan, h: 0 to 10, k: 0 to 19, l: 0 to 23. 2265 unique reflections measured. 1997 taken as observed with $I > 3\sigma(I)$, 268 unobserved reflections. Three standard reflections (600, 0,0,12, 092), no intensity variations were observed. Structure solved by *MULTAN*82 (Main *et al.*, 1982) using 337 $E \ge 1{\cdot}20$. Full-matrix least squares, $\sum w(\Delta F^2)$ minimized, 399 parameters refined. At the end of the isotropic refinement an empirical absorption correction was also carried out with the program *DIFABS* (Walker & Stuart, 1983); min. and max. absorption corrections 0·637 and 1·261. Final $R = 0{\cdot}031$, $wR = 0{\cdot}032$, $R_{tot} = 0{\cdot}040$, $S = 2{\cdot}93$, $w = 4F_o^2/\sigma^2(F_o^2)$. Max. and min. peak heights in final $\Delta\rho$ map $\pm 0{\cdot}18$ (3) e Å^{-3}. Data were not corrected for extinction. $(\Delta/\sigma)_{max} = 0{\cdot}61$ (for H atoms). Positions of H atoms bound to C atoms

were generated from assumed geometries, while those linked to O atoms were located in a difference Fourier map; their positions were refined in isotropic mode.

Scattering factors for both structure analyses were taken from the Enraf–Nonius (1983) *SDP Plus*. Programs applied: Enraf–Nonius (1983) *SDP Plus* with local modifications adapted to a PDP 11/34 minicomputer (128 K).

Discussion. Atomic coordinates of non-H atoms are in Table 1.* The bond lengths and angles for non-H atoms are listed in Tables 2 and 3. The molecular geometry of gamabufotalin (1) depicted in Fig. 1(*a*) resembles that of bufalin. The best planes of the rings form dihedral angles (see below) which are similar to those observed in bufalin. From this it follows that the conformation of the 14-isoaethiocholane skeleton is almost identical with that of bufalin. In contrast with bufalin and its unsaturated precursors (Ribár, Argay, Kálmán, Vladimirov & Živanov-Stakić, 1983), the conformation of the five-membered ring is no longer an envelope. It assumes a transitional form between E^{14} and ${}_{13}T^{14}$ twist chair [its puckering parameters (Cremer & Pople, 1975) are: $Q = 0{\cdot}377\ (3)$ Å, $\varphi = 26{\cdot}8\ (5)°$]. The δ-lactone ring exhibits an opposite (antiperiplanar) orientation to those found in both bufalin and its precursor 3β,14-dihydroxy-14β-bufa-4,20,22-trienolide (Ribár *et al.*, 1983) about the C(17)–C(20) bond. This arrangement indicates a capability of rotation of *ca* 180° against the large energy barrier calculated by Rohrer *et al.* (1982). The molecules are bound together by an infinite chain of OH···O bonds. (No. 1 in Table 4) along the *a* axis. These chains are cross-linked by two weaker hydrogen bonds along the twofold screw axes in the **b** and **c** directions (Nos. 2 and 3). In these two hydrogen bonds the terminal O(4) atom of the δ-lactone ring acts as a bifurcated acceptor.

The comparison of the lattice parameters and atomic coordinates of arenobufagin (2) with those of gamabufotalin (1) has shown clearly that they are quasi-isostructural. The dihedral angles formed by the best planes of the rings are almost identical:

	A/B	*B/C*	*C/D*	*D/E*
gamabufotalin	66·6 (1)	3·9 (1)	69·3 (1)	81·2 (1)°
arenobufagin	66·3 (1)	3·1 (1)	69·8 (1)	80·2 (1)°

These are corroborated by the perspective views of the molecular structures depicted in Fig. 1. Atom O(6) has no visible effect upon the puckering of ring *C*. Even the rather flexible *D* rings exhibit the same transitional form between E^{14} and ${}_{13}T^{14}$ twist chair. The puckering parameters for (2) are $Q = 0{\cdot}382\ (4)$ Å and $\varphi = 27{\cdot}9\ (6)°$. We can say that the orientations of the δ-lactone rings and the hydrogen bonding of these two quasi-isostructural compounds are the same. A similar phenomenon was also observed by us in the case of digirezigenin (Kálmán, Argay, Ribár, Vladimirov & Živanov-Stakić, 1984) and digitoxigenin reported earlier by Karle & Karle (1969). In addition to the similar intermolecular hydrogen bonds (*cf.* Table 4), there is an intramolecular hydrogen bond formed between the 12-oxo group and the O(5)–H(O5) moiety [O(5)···

Table 1. *Final fractional coordinates for non-*H *atoms, with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}$ trace (*B*.**G**) where **G** is the direct metric tensor.

	x	*y*	*z*	B_{eq}(Å²)
Gamabufotalin				
O(1)	0·7293 (2)	1·2662 (1)	−0·1505 (1)	3·8 (1)
O(2)	1·2403 (1)	0·8725 (1)	0·0515 (1)	3·1 (1)
O(3)	1·2273 (2)	0·6771 (1)	0·3025 (1)	3·4 (1)
O(4)	1·4770 (2)	0·6113 (1)	0·3160 (1)	3·9 (1)
O(5)	0·5531 (1)	0·9769 (1)	0·0606 (1)	3·3 (1)
C(1)	0·6050 (3)	1·0940 (1)	−0·0755 (1)	3·0 (1)
C(2)	0·6423 (3)	1·1855 (1)	−0·0413 (1)	3·4 (1)
C(3)	0·7871 (3)	1·2333 (1)	−0·0790 (1)	3·3 (1)
C(4)	0·9390 (3)	1·1720 (1)	−0·0875 (1)	2·9 (1)
C(5)	0·8970 (2)	1·0816 (1)	−0·1247 (1)	2·7 (1)
C(6)	1·0567 (3)	1·0260 (1)	−0·1361 (1)	3·4 (1)
C(7)	1·1335 (3)	0·9972 (1)	−0·0610 (1)	3·1 (1)
C(8)	1·0071 (2)	0·9489 (1)	−0·0113 (1)	2·3 (1)
C(9)	0·8328 (2)	0·9988 (1)	−0·0024 (1)	2·2 (1)
C(10)	0·7587 (2)	1·0281 (1)	−0·0801 (1)	2·4 (1)
C(11)	0·7179 (2)	0·9382 (1)	0·0457 (1)	2·6 (1)
C(12)	0·8014 (3)	0·9149 (1)	0·1213 (1)	2·9 (1)
C(13)	0·9763 (2)	0·8683 (1)	0·1169 (1)	2·5 (1)
C(14)	1·0901 (2)	0·9261 (1)	0·0648 (1)	2·3 (1)
C(15)	1·1366 (2)	1·0088 (1)	0·1134 (1)	2·8 (1)
C(16)	1·1517 (3)	0·9719 (1)	0·1938 (1)	3·8 (1)
C(17)	1·0609 (3)	0·8792 (1)	0·1957 (1)	2·9 (1)
C(18)	0·9563 (3)	0·7715 (1)	0·0912 (1)	3·6 (1)
C(19)	0·6984 (3)	0·9460 (1)	−0·1244 (1)	3·7 (1)
C(20)	1·1793 (3)	0·8030 (1)	0·2213 (1)	2·8 (1)
C(21)	1·1263 (3)	0·7437 (1)	0·2725 (1)	3·2 (1)
C(22)	1·3526 (3)	0·7926 (1)	0·1972 (1)	3·4 (1)
C(23)	1·4527 (3)	0·7276 (1)	0·2262 (1)	3·4 (1)
C(24)	1·3939 (3)	0·6684 (1)	0·2824 (1)	3·0 (1)
Arenobufagin				
O(1)	0·7199 (2)	1·2652 (1)	−0·1471 (1)	4·0 (1)
O(2)	1·2470 (2)	0·8736 (1)	0·0506 (1)	3·2 (1)
O(3)	1·2362 (3)	0·6759 (1)	0·3008 (1)	3·8 (1)
O(4)	1·4906 (3)	0·6137 (1)	0·3155 (1)	4·2 (1)
O(5)	0·5587 (2)	0·9763 (1)	0·0606 (1)	3·5 (1)
O(6)	0·7331 (3)	0·9288 (1)	0·1766 (1)	4·8 (1)
C(1)	0·6045 (3)	1·0896 (2)	−0·0756 (1)	3·0 (1)
C(2)	0·6367 (4)	1·1802 (2)	−0·0397 (1)	3·5 (1)
C(3)	0·7798 (4)	1·2322 (2)	−0·0764 (1)	3·4 (1)
C(4)	0·9368 (3)	1·1726 (2)	−0·0857 (1)	3·0 (1)
C(5)	0·8994 (3)	1·0827 (1)	−0·1239 (1)	2·7 (1)
C(6)	1·0632 (4)	1·0297 (2)	−0·1351 (1)	3·4 (1)
C(7)	1·1399 (3)	1·0006 (2)	−0·0605 (1)	3·0 (1)
C(8)	1·0130 (3)	0·9492 (1)	−0·0114 (1)	2·3 (1)
C(9)	0·8371 (3)	0·9983 (1)	−0·0032 (1)	2·1 (1)
C(10)	0·7622 (3)	1·0278 (1)	−0·0809 (1)	2·3 (1)
C(11)	0·7208 (3)	0·9373 (1)	0·0445 (1)	2·7 (1)
C(12)	0·8057 (3)	0·9122 (1)	0·1187 (1)	2·7 (1)
C(13)	0·9836 (3)	0·8679 (1)	0·1163 (1)	2·4 (1)
C(14)	1·0944 (3)	0·9257 (1)	0·0643 (1)	2·3 (1)
C(15)	1·1376 (3)	1·0067 (1)	0·1142 (1)	2·9 (1)
C(16)	1·1573 (5)	0·9695 (2)	0·1934 (1)	4·1 (1)
C(17)	1·0681 (4)	0·8767 (2)	0·1953 (1)	2·9 (1)
C(18)	0·9598 (4)	0·7705 (2)	0·0894 (1)	3·5 (1)
C(19)	0·7077 (4)	0·9456 (2)	−0·1265 (1)	3·7 (1)
C(20)	1·1875 (3)	0·8018 (1)	0·2201 (1)	2·8 (1)
C(21)	1·1342 (4)	0·7417 (2)	0·2709 (1)	3·3 (1)
C(22)	1·3619 (4)	0·7937 (2)	0·1981 (1)	3·7 (1)
C(23)	1·4627 (4)	0·7299 (2)	0·2270 (1)	3·7 (1)
C(24)	1·4061 (4)	0·6689 (2)	0·2821 (1)	3·3 (1)

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43612 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

O(6) 2·578 (3), H(O5)···O(6) 2·04 (3) Å and ∠O(5)···O(6) 111 (2)°], which, however, does not alter the molecular packing. A deeper analysis of the molecular packing in these chemically and crystallographically related molecular pairs may perhaps be used to give a better understanding of intermolecular forces.

Table 2. *Bond lengths* (Å) *with their e.s.d.'s*

Gamabufotalin					
O(1)–C(3)	1·438 (3)	C(5)–C(6)	1·513 (4)	C(13)–C(14)	1·546 (3)
O(2)–C(14)	1·440 (3)	C(5)–C(10)	1·561 (3)	C(13)–C(17)	1·562 (3)
O(3)–C(21)	1·371 (3)	C(6)–C(7)	1·530 (3)	C(13)–C(18)	1·510 (3)
O(3)–C(24)	1·362 (3)	C(7)–C(8)	1·509 (3)	C(14)–C(15)	1·541 (3)
O(4)–C(24)	1·223 (3)	C(8)–C(9)	1·563 (3)	C(15)–C(16)	1·539 (3)
O(5)–C(11)	1·439 (3)	C(8)–C(14)	1·544 (3)	C(16)–C(17)	1·544 (4)
C(1)–C(2)	1·510 (4)	C(9)–C(10)	1·564 (3)	C(17)–C(20)	1·529 (3)
C(1)–C(10)	1·553 (3)	C(9)–C(11)	1·532 (3)	C(20)–C(21)	1·332 (3)
C(2)–C(3)	1·497 (4)	C(10)–C(19)	1·523 (3)	C(20)–C(22)	1·435 (3)
C(3)–C(4)	1·505 (3)	C(11)–C(12)	1·539 (3)	C(22)–C(23)	1·343 (4)
C(4)–C(5)	1·526 (3)	C(12)–C(13)	1·538 (3)	C(23)–C(24)	1·409 (3)
Arenobufagin					
O(1)–C(3)	1·432 (4)	C(4)–C(5)	1·529 (4)	C(12)–C(13)	1·541 (4)
O(2)–C(14)	1·445 (3)	C(5)–C(6)	1·518 (4)	C(13)–C(14)	1·533 (4)
O(3)–C(21)	1·370 (4)	C(5)–C(10)	1·551 (4)	C(13)–C(17)	1·563 (4)
O(3)–C(24)	1·375 (4)	C(6)–C(7)	1·522 (4)	C(13)–C(18)	1·537 (4)
O(4)–C(24)	1·211 (4)	C(7)–C(8)	1·528 (4)	C(14)–C(15)	1·535 (4)
O(5)–C(11)	1·424 (4)	C(8)–C(9)	1·565 (4)	C(15)–C(16)	1·527 (4)
O(6)–C(12)	1·204 (4)	C(8)–C(14)	1·534 (4)	C(16)–C(17)	1·546 (5)
C(1)–C(2)	1·512 (4)	C(9)–C(10)	1·568 (4)	C(17)–C(20)	1·519 (4)
C(1)–C(10)	1·541 (4)	C(9)–C(11)	1·541 (4)	C(20)–C(21)	1·339 (4)
C(2)–C(3)	1·511 (5)	C(10)–C(19)	1·529 (4)	C(20)–C(22)	1·425 (5)
C(3)–C(4)	1·523 (4)	C(11)–C(12)	1·528 (4)	C(22)–C(23)	1·337 (5)
				C(23)–C(24)	1·408 (5)

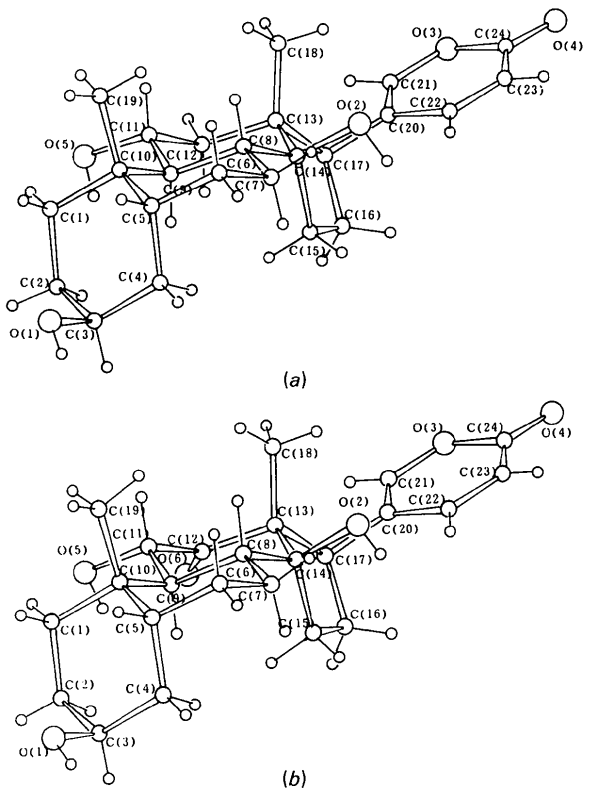


Fig. 1. Perspective views of the molecules [(*a*) gamabufotalin, (*b*) arenobufagin] showing atomic numbering. The H atoms are shown but not labelled.

Table 3. *Bond angles* (°) *with their e.s.d.'s*

Gamabufotalin			
C(21)–O(3)–C(24)	121·4 (3)	C(11)–C(12)–C(13)	115·8 (3)
C(2)–C(1)–C(10)	115·6 (3)	C(12)–C(13)–C(14)	107·4 (3)
C(1)–C(2)–C(3)	112·8 (4)	C(12)–C(13)–C(17)	106·7 (3)
O(1)–C(3)–C(2)	108·5 (3)	C(12)–C(13)–C(18)	110·3 (3)
O(1)–C(3)–C(4)	111·3 (3)	C(14)–C(13)–C(17)	103·7 (3)
C(2)–C(3)–C(4)	111·3 (4)	C(14)–C(13)–C(18)	113·6 (3)
C(3)–C(4)–C(5)	113·5 (3)	C(17)–C(13)–C(18)	114·5 (3)
C(4)–C(5)–C(6)	110·8 (3)	O(2)–C(14)–C(8)	108·7 (3)
C(4)–C(5)–C(10)	111·9 (3)	O(2)–C(14)–C(13)	105·6 (3)
C(6)–C(5)–C(10)	111·7 (3)	O(2)–C(14)–C(15)	109·5 (3)
C(5)–C(6)–C(7)	111·1 (3)	C(8)–C(14)–C(13)	113·9 (3)
C(6)–C(7)–C(8)	112·7 (3)	C(8)–C(14)–C(15)	115·0 (3)
C(7)–C(8)–C(9)	114·4 (3)	C(13)–C(14)–C(15)	103·7 (3)
C(7)–C(8)–C(14)	110·0 (3)	C(14)–C(15)–C(16)	105·1 (3)
C(9)–C(8)–C(14)	112·5 (3)	C(15)–C(16)–C(17)	107·4 (4)
C(8)–C(9)–C(10)	111·4 (3)	C(13)–C(17)–C(16)	105·6 (3)
C(8)–C(9)–C(11)	107·3 (3)	C(13)–C(17)–C(20)	116·9 (3)
C(10)–C(9)–C(11)	116·0 (3)	C(16)–C(17)–C(20)	112·3 (3)
C(1)–C(10)–C(5)	104·5 (3)	C(17)–C(20)–C(21)	120·0 (4)
C(1)–C(10)–C(9)	114·5 (3)	C(17)–C(20)–C(22)	124·4 (4)
C(1)–C(10)–C(19)	106·6 (3)	C(21)–C(20)–C(22)	115·5 (4)
C(5)–C(10)–C(9)	109·5 (3)	O(3)–C(21)–C(20)	123·9 (4)
C(5)–C(10)–C(19)	110·8 (3)	C(20)–C(22)–C(23)	121·1 (4)
C(9)–C(10)–C(19)	110·8 (3)	C(22)–C(23)–C(24)	121·7 (4)
O(5)–C(11)–C(9)	113·6 (3)	O(3)–C(24)–O(4)	116·7 (4)
O(5)–C(11)–C(12)	108·0 (3)	O(3)–C(24)–C(23)	116·3 (4)
C(9)–C(11)–C(12)	111·7 (3)	O(4)–C(24)–C(23)	127·0 (4)
Arenobufagin			
C(21)–O(3)–C(24)	121·5 (4)	O(6)–C(12)–C(13)	122·6 (5)
C(2)–C(1)–C(10)	115·0 (4)	C(11)–C(12)–C(13)	118·2 (4)
C(1)–C(2)–C(3)	113·3 (5)	C(12)–C(13)–C(14)	106·7 (4)
O(1)–C(3)–C(2)	108·3 (4)	C(12)–C(13)–C(17)	108·7 (4)
O(1)–C(3)–C(4)	111·6 (4)	C(12)–C(13)–C(18)	107·6 (4)
C(2)–C(3)–C(4)	110·4 (5)	C(14)–C(13)–C(17)	105·1 (4)
C(3)–C(4)–C(5)	113·7 (4)	C(14)–C(13)–C(18)	114·1 (4)
C(4)–C(5)–C(6)	110·5 (4)	C(17)–C(13)–C(18)	114·3 (4)
C(4)–C(5)–C(10)	111·8 (4)	O(2)–C(14)–C(8)	108·5 (4)
C(6)–C(5)–C(10)	112·2 (4)	O(2)–C(14)–C(13)	105·6 (4)
C(5)–C(6)–C(7)	111·5 (4)	O(2)–C(14)–C(15)	109·7 (4)
C(6)–C(7)–C(8)	112·8 (4)	C(8)–C(14)–C(13)	115·2 (4)
C(7)–C(8)–C(9)	113·1 (4)	C(8)–C(14)–C(15)	115·0 (4)
C(7)–C(8)–C(14)	110·4 (4)	C(13)–C(14)–C(15)	102·3 (4)
C(9)–C(8)–C(14)	112·9 (4)	C(14)–C(15)–C(16)	105·9 (4)
C(8)–C(9)–C(10)	112·1 (4)	C(15)–C(16)–C(17)	107·3 (5)
C(8)–C(9)–C(11)	107·3 (4)	C(13)–C(17)–C(16)	104·2 (4)
C(10)–C(9)–C(11)	115·6 (4)	C(13)–C(17)–C(20)	117·5 (4)
C(1)–C(10)–C(5)	105·8 (4)	C(16)–C(17)–C(20)	112·5 (4)
C(1)–C(10)–C(9)	114·3 (4)	C(17)–C(20)–C(21)	119·6 (5)
C(1)–C(10)–C(19)	106·6 (4)	C(17)–C(20)–C(22)	124·8 (5)
C(5)–C(10)–C(9)	109·0 (4)	C(21)–C(20)–C(22)	115·3 (5)
C(5)–C(10)–C(19)	110·5 (4)	O(3)–C(21)–C(20)	123·9 (5)
C(9)–C(10)–C(19)	110·5 (4)	C(20)–C(22)–C(23)	121·3 (5)
O(5)–C(11)–C(9)	113·4 (4)	C(22)–C(23)–C(24)	122·7 (5)
O(5)–C(11)–C(12)	108·2 (4)	O(3)–C(24)–O(4)	117·4 (5)
C(9)–C(11)–C(12)	111·4 (4)	O(3)–C(24)–C(23)	115·1 (5)
O(6)–C(12)–C(11)	119·2 (5)	O(4)–C(24)–C(23)	127·4 (5)

Table 4. *Intermolecular hydrogen bonds for compounds* (1) *and* (2)

	O···O (Å)	H···O (Å)	∠OH···O (°)
1. O(2)–H(O2)···O(5)($x+1, y, z$)	(1) 2·904 (2)	1·95 (3)	165 (1)
	(2) 2·883 (2)	2·13 (3)	165 (3)
2. O(1)–H(O1)···O(4)($\frac{1}{2}-x, 2-y, -\frac{1}{2}+z$)	(1) 2·991 (2)	2·16 (3)	154 (1)
	(2) 2·970 (2)	2·15 (3)	167 (3)
3. O(5)–H(O5)···O(4)($2-x, \frac{1}{2}+y, \frac{1}{2}-z$)	(1) 2·973 (2)	2·06 (3)	152 (1)
	(2) 3·035 (2)	2·16 (3)	146 (2)

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Structure de l'Acide Diphénylamino-2 Carboxylique

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Abstract. 2-(Phenylamino)benzoic acid, $C_{13}H_{11}NO_2$, $M_r = 213{\cdot}24$, triclinic, $P\bar{1}$, $a = 8{\cdot}0995\ (5)$, $b = 9{\cdot}8268\ (6)$, $c = 14{\cdot}0593\ (11)$ Å, $\alpha = 85{\cdot}96\ (6)$, $\beta = 88{\cdot}62\ (7)$, $\gamma = 73{\cdot}39\ (4)°$, $V = 1069{\cdot}7\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}324$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 6{\cdot}46$ cm^{-1}, $T = 290$ K, $F(000) = 448$, final $R = 0{\cdot}074$ for 2485 observed reflections. Structure solved by direct methods. The two benzene rings are inclined to each other at an angle of 72·7 (2)° in molecule *A* and 53·0 (2)° in molecule *B*. The planes of the carboxylic groups make angles of 2·1 (2) (*A*) and 1·7 (2)° (*B*) with their parent rings. A dimerization occurs through hydrogen bonding of the carboxylic groups.

Introduction. La formation d'urine définitive est sous la dépendance de divers mécanismes de transports ioniques membranaires actifs ou passifs. Le mode d'action de la plupart des diurétiques est explicable par l'effet d'inhibition de ces médicaments vis-à-vis d'un ou de plusieurs de ces systèmes. On a démontré que l'acide diphénylamino-2 carboxylique (DPC) (Fig. 1) bloquait les canaux chlorures de la membrane basolatérale au niveau de la partie ascendante de l'anse de Henle sans affecter le système de co-transport $Na^+2Cl^-K^+$ (Di Stefano, Wittner, Schlatter, Lang, Englert & Greger, 1985). Le dérivé trifluorométhyl-3′ (REFCODE: FPAMCA; McConnell, 1973) présente une activité du même type, mais environ dix fois moindre. Le torasemide (REFCODES: TORSEM et TORSEM01; Dupont, Lamotte, Campsteyn & Vermeire, 1978; Dupont, Campsteyn, Lamotte & Vermeire, 1978), par contre, agit aux deux niveaux alors que certains dérivés voisins sont sans effet sur les canaux chlorures (Wittner, Di Stefano, Wangemann, Delarge, Liégeois & Greger, 1986) par exemple le L 961 (REFCODE: BAGPII; Dupont, Lewinski, Stadnicka & Delarge, 1981) et la triflocine (REFCODE: TRFLOC 10; Dideberg, Campsteyn, Spirlet, Dupont, Lamotte & Vermeire, 1979). Le présent travail s'insère dans notre étude sur le mode d'action des inhibiteurs de transport membranaires.

Partie expérimentale. Cristallisé dans un mélange 50–50% éthanol–acétone. Cristal incolore: 0,6 × 0,6 × 0,4 mm. Paramètres de la maille déterminés à partir de 20 réflexions ($18{,}2 \le \theta \le 21{,}1°$). Diffractomètre Siemens, 2885 réflexions mesurées, $\theta \le 55°$, Cu $K\alpha$ monochromatisée au graphite, balayage ω, 2693 réflexions indépendantes, $-8 \le h \le 8$, $-10 \le k \le 10$,

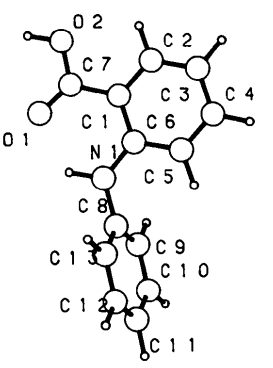

Fig. 1. Vue en perspective de la molécule *A* avec la numérotation des atomes. Les atomes de la molécule *B* sont numérotés en incrémentant de 20 les nombres correspondant de *A*.

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