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Structure of Corydaline

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Abstract. 5,8,13,13a-Tetrahydro-2,3,9,10-tetramethoxy-1-methyl-6*H*-dibenzo[*a*,*g*]quinolizine, $C_{22}H_{27}NO_4$, $M_r = 369.46$, monoclinic, $P2_1$, $a = 8.732\ (6)$, $b = 7.639\ (5)$, $c = 14.966\ (10)$ Å, $\beta = 95.85\ (2)°$, $V = 993\ (1)$ Å^3, $Z = 2$, $D_x = 1.235$ g cm,$^{-3}$, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.79$ cm^{-1}, $F(000) = 396$, $T = 293\ (2)$ K, $R = 0.054$ for 1625 reflections with $I > 3.5\sigma(I)$. Ring *B* assumes an almost perfect half-chair conformation while ring *C* has a transitional form between sofa and half-chair. The O(1)—C(18), O(2)—C(19) and O(3)—C(21) bonds are in the planes of their respective phenyl rings, *D* and *A*, as indicated by the corresponding torsion angles, while the O(4)—C(22) bond is perpendicular to the plane of phenyl ring *A*. The mean value of the three C—N—C angles is 111.5 (4)° indicating sp^3 hybridization of the N atom. The C(20)-methyl group is in an axial position. Molecules are held together by van der Waals interactions.

Experimental. In a previous work the crystal and molecular structure of bulbocapnine was solved by Ribár, Mészáros, Gašić, Kanyó & Engel (1991), isolated from the aerial parts of the wild-growing medicinal plants *Corydalis cava* and *C. solida* (L). In a later investigation the minor alkaloid corydaline was isolated from the roots of both species. The isolation of crude alkaloids was carried out according to Preininger, Vesely, Gašić, Šimanek & Dolejš (1975) and Gašić, Popović & Dragutinović (1985). Corydaline was isolated by column chromatography as well as by preparative thin-layer chromatography as described by Gašić, Kanyó, Loukis & Bačić (1991).

Data were collected on a crystal of irregular shape (approximate dimensions 0.33 × 0.33 × 0.33 mm) mounted on a CAD-4 diffractometer (Berne) equipped with a graphite monochromator. Cell constants were refined by least-squares fit for 20 reflections in the range $2.7 < \theta < 9.9°$. Data were collected by ω–2θ scan in the range $\theta < 25°$ with h −10 to 10, k 0 to 9, l 0 to 18. Of 2253 measured reflections, 1625 with $I > 3.5\sigma(I)$ were taken as observed. Only one standard reflection ($\bar{1}2\bar{1}$) was measured every 200 min to control intensity decay and orientation; no intensity variation was recorded. Data were corrected for Lorentz and polarization effects. The structure was solved with *SHELXS86* (Sheldrick, 1986) with all non-H atoms obtained from an *E* map. Full-matrix least-squares refinement with *SHELX76* (Sheldrick, 1976) minimized $\sum w(\Delta F)^2$ for 270 parameters, with $w = [\sigma^2(F_o) + (15.98 \times$

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$10^{-3})F_o^2]^{-1}$. Final $R = 0.054$, $wR = 0.067$, $(\Delta/\sigma)_{\max} = 0.92$. A final difference Fourier map showed excursions of electron density from −0.29 to 0.23 e Å^{-3}. Positions of the H atoms were generated from assumed geometries and their positions were taken into account in structure-factor calculations with refined isotropic temperature factors (riding mode). Scattering factors were taken from the program *SHELX76*. All calculations were performed on a PC-AT computer. The geometrical parameters were computed with *CSU* (Vicković, 1988) and Fig. 1 was drawn with *PLUTO* (Motherwell & Clegg, 1978). The structure is defined in Tables 1 and 2.*

Related literature. Total synthesis of (±)-corydaline was performed by Saa, Guitian, Castedo, Suan & Saa (1986), while its diastereoselective synthesis was performed by Tietze & Brill (1987). The constitutional isomer of corydaline is coralydine (Bruderer, Metzger, Brossi & Daly, 1976). Chiroptical properties of (+)-corydaline were investigated by Snatzke, Hrbek, Hruban, Horeau & Šantavý (1970). The dihedral angle between the least-squares planes for phenyl rings *A* and *D* is 36.7 (1)°, whereas this angle is 33.8 (1)° in isocorypalmine (Ribár, Radivojević, Gašić, Kanyó & Golič, 1992). As shown by the puckering parameters (Cremer & Pople, 1975), the *trans* fused ring *B* [$Q = 0.052$ (7) Å; $\theta = 49.8$ (7), $\varphi = 328.8$ (9)°] assumes an almost perfect half-chair conformation while ring *C* [$Q = 0.512$ (7) Å; $\theta = 54.7$ (8), $\varphi = 133.9$ (9)°] exhibits a transitional state between sofa and half-chair, as similarly found in isocorypalmine. According to Iwasa, Gupta & Cushman (1981), the chiral C atoms C(12) and C(13) possess *S* and *R* configurations, respectively. The title compound shows analgesic and antirheumatic properties (Southon & Buckingham, 1989).

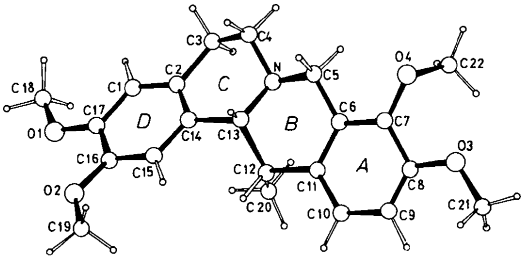

Fig. 1. Perspective view of the molecule with arbitrary numbering.

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

$U_{eq} = (1/3)[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + U_{13}aa^*cc^*\cos\beta]$.

	x	y	z	U_{eq}
C(1)	−6380 (5)	−1679 (10)	−3435 (3)	60 (1)
C(2)	−6788 (5)	−1766 (8)	−2565 (3)	48 (1)
C(3)	−6324 (6)	−3352 (9)	−1987 (3)	58 (1)
C(4)	−7336 (5)	−3507 (9)	−1248 (3)	54 (1)
C(5)	−8042 (5)	−2110 (9)	87 (3)	46 (1)
C(6)	−8019 (4)	−427 (9)	616 (3)	41 (1)
C(7)	−8269 (5)	−486 (9)	1513 (3)	51 (1)
C(8)	−8252 (5)	1053 (10)	2019 (3)	52 (1)
C(9)	−7996 (5)	2627 (9)	1619 (3)	53 (1)
C(10)	−7765 (5)	2660 (9)	715 (3)	48 (1)
C(11)	−7763 (4)	1176 (8)	211 (3)	40 (1)
C(12)	−7486 (4)	1260 (9)	−778 (3)	42 (1)
C(13)	−8027 (4)	−417 (9)	−1269 (2)	40 (1)
C(14)	−7627 (4)	−440 (9)	−2230 (3)	47 (1)
C(15)	−8150 (5)	947 (9)	−2793 (3)	51 (1)
C(16)	−7751 (6)	1031 (10)	−3672 (3)	58 (1)
C(17)	−6845 (6)	−253 (9)	−3999 (3)	60 (1)
C(18)	−5486 (8)	−1286 (15)	−5189 (4)	93 (2)
C(19)	−9157 (10)	3667 (12)	−4007 (4)	96 (2)
C(20)	−5786 (4)	1651 (9)	−869 (3)	52 (1)
C(21)	−8565 (8)	2383 (11)	3433 (3)	76 (1)
C(22)	−7352 (9)	−2684 (10)	2546 (4)	82 (2)
N	−7316 (4)	−1891 (8)	−731 (2)	43 (1)
O(1)	−6501 (5)	−50†	−4857 (3)	81 (1)
O(2)	−8185 (6)	2344 (9)	−4266 (2)	82 (1)
O(3)	−8523 (5)	846 (8)	2904 (2)	72 (1)
O(4)	−8590 (5)	−2073 (8)	1899 (2)	66 (1)

† Coordinate fixed to define origin for structure with non-centrosymmetric space group.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

C(1)—C(2)	1.386 (7)	C(10)—C(11)	1.362 (8)
C(1)—C(17)	1.412 (9)	C(11)—C(12)	1.525 (6)
C(2)—C(3)	1.519 (8)	C(12)—C(13)	1.528 (9)
C(2)—C(14)	1.374 (8)	C(12)—C(20)	1.534 (5)
C(3)—C(4)	1.489 (7)	C(13)—C(14)	1.514 (6)
C(4)—N	1.456 (8)	C(13)—N	1.483 (8)
C(5)—C(6)	1.509 (9)	C(14)—C(15)	1.401 (8)
C(5)—N	1.445 (6)	C(15)—C(16)	1.396 (7)
C(6)—C(7)	1.383 (6)	C(16)—C(17)	1.381 (9)
C(6)—C(11)	1.394 (9)	C(16)—O(2)	1.368 (8)
C(7)—C(8)	1.398 (9)	C(17)—O(1)	1.357 (7)
C(7)—O(4)	1.384 (9)	C(18)—O(1)	1.419 (10)
C(8)—C(9)	1.372 (10)	C(19)—O(2)	1.400 (11)
C(8)—O(3)	1.378 (6)	C(21)—O(3)	1.419 (9)
C(9)—C(10)	1.388 (7)	C(22)—O(4)	1.453 (8)

C(2)—C(1)—C(17)	120.8 (5)	C(11)—C(12)—C(20)	110.2 (4)
C(1)—C(2)—C(3)	119.6 (5)	C(13)—C(12)—C(20)	112.0 (4)
C(1)—C(2)—C(14)	120.3 (5)	C(12)—C(13)—C(14)	112.1 (4)
C(3)—C(2)—C(14)	120.1 (5)	C(12)—C(13)—N	106.5 (4)
C(2)—C(3)—C(4)	110.0 (4)	C(14)—C(13)—N	112.5 (4)
C(3)—C(4)—N	110.6 (4)	C(2)—C(14)—C(13)	122.6 (5)
C(6)—C(5)—N	111.3 (4)	C(2)—C(14)—C(15)	119.4 (5)
C(5)—C(6)—C(7)	119.1 (5)	C(13)—C(14)—C(15)	118.0 (4)
C(5)—C(6)—C(11)	121.0 (5)	C(14)—C(15)—C(16)	120.3 (5)
C(7)—C(6)—C(11)	119.9 (5)	C(15)—C(16)—C(17)	120.6 (5)
C(6)—C(7)—C(8)	120.3 (5)	C(15)—C(16)—O(2)	124.5 (5)
C(6)—C(7)—O(4)	119.5 (5)	C(17)—C(16)—O(2)	114.9 (5)
C(8)—C(7)—O(4)	120.1 (5)	C(1)—C(17)—C(16)	118.5 (5)
C(7)—C(8)—C(9)	119.6 (5)	C(1)—C(17)—O(1)	125.2 (5)
C(7)—C(8)—O(3)	115.5 (5)	C(16)—C(17)—O(1)	116.4 (5)
C(9)—C(8)—O(3)	124.9 (5)	C(4)—N—C(5)	111.7 (4)
C(8)—C(9)—C(10)	119.2 (5)	C(4)—N—C(13)	111.9 (4)
C(9)—C(10)—C(11)	122.2 (5)	C(5)—N—C(13)	110.6 (4)
C(6)—C(11)—C(10)	118.8 (5)	C(17)—O(1)—C(18)	117.5 (5)
C(6)—C(11)—C(12)	120.5 (4)	C(16)—O(2)—C(19)	119.0 (6)
C(10)—C(11)—C(12)	120.8 (4)	C(8)—O(3)—C(21)	117.3 (5)
C(11)—C(12)—C(13)	111.1 (4)	C(7)—O(4)—C(22)	113.0 (5)

C(1)—C(17)—O(1)—C(18)	−5.7 (8)	C(15)—C(16)—O(2)—C(19)	−3.2 (9)
C(7)—C(8)—O(3)—C(21)	−178.0 (5)	C(20)—C(12)—C(13)—N	72.6 (5)
C(8)—C(7)—O(4)—C(22)	−71.4 (7)		

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* 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 55168 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA0018]

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Structure of *cis*,*cis*-4,6-Diphenyl-2-(2-propenyl)-1,3-dioxa-2-phosphorinane 2-Oxide

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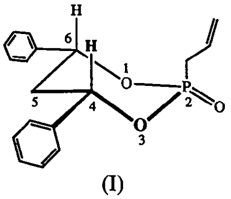
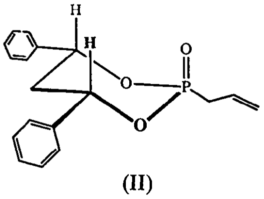
Abstract. $C_{18}H_{19}O_3P$, $M_r = 314.32$, monoclinic, $P2_1/n$, $a = 5.726\,(6)$, $b = 14.234\,(7)$, $c = 20.08\,(1)$ Å, $\beta = 92.54\,(7)°$, $V = 1635\,(4)$ Å^3, $Z = 4$, $D_x = 1.277$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.71$ cm^{-1}, $F(000) = 664$, $T = 296$ K, $R = 0.042$, 1813 unique observed reflections. The X-ray structure determination of the title compound shows that the dioxaphosphorinane ring has a chair conformation in which the phosphoryl O atom (P=O) is equatorial, which explains the absence of substantial NMR deshielding by its P=O group on H(4) and H(6), which are axial.

Experimental. The title compound (I) was prepared from the reaction of *meso*-(*R*,*S*)-1,3-diphenyl-1,3-propanediol with 2-propenylphosphonyl dichloride (Kinnear & Perren, 1952) in the presence of 2.2 equivalents of triethylamine in methylene chloride (52% yield). A mixture of 1.28:1 of (I) and its isomer, *trans*^{2,4},*cis*^{4,6}-4,6-diphenyl-2-(2-propenyl)-1,3-dioxa-2-phosphorinane 2-oxide (II) (NMR indicates this phosphoryl O atom is in the axial position), was formed. Well formed crystals of (I) were obtained from column chromatographic separation (silica gel; ether/hexane 2/1) followed by recrystallization from methylene chloride. Crystal (I) m.p. 461–463 K; isomer (II) m.p. 362–364 K (the crystals were not suitable for X-ray analysis).



(I)



(II)

The chemical shift of the C(4) and C(6) H atoms of (I) [δ 5.52 (*dt*); in $CDCl_3$] is at a higher field than those of (II) [δ 5.81 (*ddd*)] indicating the deshielding effect of the P=O group in (II) on its C(4) and C(6) H atoms.

The crystal used for data collection was 0.43 × 0.35 × 0.22 mm, colorless and equant. Data were

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