

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
O(1)	0.6350 (2)	-0.3605 (2)	0.8980 (2)	4.10 (5)
O(2)	0.4832 (2)	0.0647 (2)	0.7128 (2)	4.23 (6)
O(3)	0.1272 (2)	0.1550 (2)	0.8365 (1)	2.74 (4)
O(4)	0.0337 (2)	0.6269 (2)	0.7431 (2)	4.64 (6)
O(5)	-0.1667 (3)	0.8214 (2)	0.6337 (2)	6.39 (8)
N(1)	-0.0891 (2)	0.6736 (2)	0.6770 (2)	3.80 (6)
C(1)	0.5480 (2)	-0.2948 (2)	0.9744 (2)	2.95 (7)
C(2)	0.5679 (3)	-0.3749 (3)	1.1233 (2)	3.53 (7)
C(3)	0.4229 (3)	-0.0553 (2)	0.7683 (2)	3.01 (7)
C(4)	0.3476 (4)	-0.1297 (3)	0.6925 (2)	4.86 (10)
C(5)	0.4205 (2)	-0.1344 (2)	0.9191 (2)	2.56 (6)
C(6)	0.3175 (2)	-0.0639 (2)	1.0004 (2)	2.72 (6)
C(7)	0.1810 (2)	0.0842 (2)	0.9662 (2)	2.72 (6)
C(8)	0.0908 (3)	0.1765 (3)	1.0404 (2)	3.02 (7)
C(9)	-0.0244 (3)	0.3122 (3)	0.9549 (2)	3.18 (7)
C(10)	0.0011 (2)	0.2954 (2)	0.8332 (2)	2.69 (6)
C(11)	-0.0902 (2)	0.3763 (3)	0.7085 (2)	2.79 (6)
C(12)	-0.1458 (3)	0.5509 (3)	0.6423 (2)	3.16 (6)
C(13)	-0.2463 (3)	0.6169 (3)	0.5327 (2)	4.03 (8)
C(14)	-0.2909 (3)	0.5085 (4)	0.4860 (2)	4.71 (9)
C(15)	-0.2373 (3)	0.3361 (4)	0.5476 (2)	4.47 (9)
C(16)	-0.1374 (3)	0.2711 (3)	0.6574 (2)	3.66 (8)

Table 2. Selected bond distances (\AA) and angles ($^\circ$)

O(1)—C(1)	1.209 (3)	N(1)—C(12)	1.456 (3)
O(2)—C(3)	1.195 (3)	C(1)—C(2)	1.487 (3)
O(3)—C(7)	1.369 (2)	C(1)—C(5)	1.469 (3)
O(3)—C(10)	1.364 (3)	C(3)—C(4)	1.489 (4)
O(4)—N(1)	1.204 (3)	C(3)—C(5)	1.490 (3)
O(5)—N(1)	1.212 (3)	C(10)—C(11)	1.455 (3)
C(7)—O(3)—C(10)	105.7 (1)	O(1)—C(1)—C(2)	120.8 (2)
O(4)—N(1)—O(5)	122.6 (2)	C(2)—C(1)—C(5)	119.7 (2)
O(5)—N(1)—C(12)	117.5 (2)	O(2)—C(3)—C(5)	119.6 (2)
O(4)—N(1)—C(12)	119.8 (2)	O(2)—C(3)—C(4)	122.4 (2)

Data reduction was performed with the program *XP2₁* (Pavelčík, 1987). The structure was solved by direct methods and refinement was by block-diagonal least squares. H atoms were found from difference Fourier maps and their coordinates and displacement parameters were fixed. Calculations were performed with a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973) and *PARST* (Nardelli, 1984).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Enantioselective Synthesis of Isoquinoline Alkaloids from Simple Sugar. II. Structure of 1-(6,7-Dimethoxy-3,4-dihydroisoquinolin-1-yl)-1,2,3,4-butanetetrayl Tetraacetate *N*-Oxide

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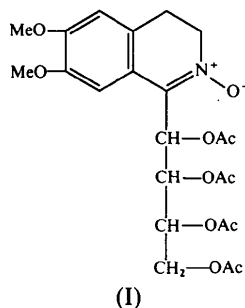
Abstract

The title compound, $\text{C}_{23}\text{H}_{29}\text{NO}_{11}$, is an important intermediate product in the course of the synthesis of some natural products. Among them are two isoquinoline alkaloids: (*R*)-calycotomine and (*S*)-xylopinine. A single-crystal X-ray study of this compound is reported.

Comment

In the course of our work on the development of an efficient enantioselective synthetic strategy for isoquinoline alkaloids, we described a procedure in which the chiral substrate *D*-ribonic acid γ -lactone (1) was used (Czarnocki, 1992*a,b*). In several steps, compound (1) was transformed into 6,7-dimethoxy-3,4-dihydroisoquinolin-1-yl-(1',2',3',4'-tetraacetoxo)butane (2) (Czarnocki, 1992*a,b*, and references therein). Subsequent oxidation of (2) with *m*-chloroperbenzoic acid gave 1-(6,7-dimethoxy-1,2,3,4-tetrahydro-1,2-epoxyisoquinolinyl)-1,2,3,4-butanetetrayl tetraacetate (3)

(Czarnocki & Maurin, 1993) and the title compound (4), from which two isoquinoline alkaloids, (*R*)-(-)-calycotomine and (*S*)-(-)-xylopinine, were prepared. The full reaction scheme has been given by Czarnocki (1992*a,b*).



The molecular geometry and numbering scheme are shown in Fig. 1. The C5–C10 ring is planar. The atoms O2, O3 and C4, which are bonded to the ring, are almost coplanar with it whereas C1 lies 0.075 (5) Å out of the plane of the ring. The O3–C12 methoxy group lies in the plane of the ring whereas the O2–C11 methoxy group is rotated by about 7° around the C6–O2 bond. The conformation of the second ring and the relative configuration on the important chiral atoms C1 and C1' are defined by the series of torsion angles given in Table 2.

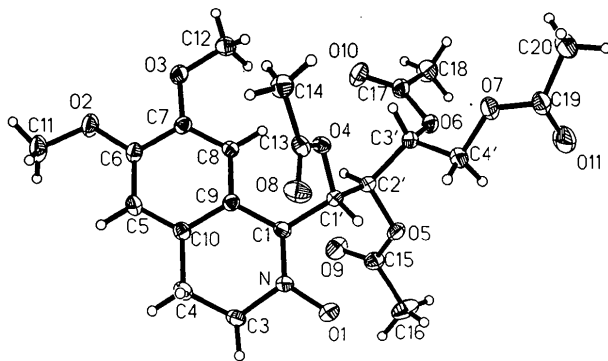


Fig. 1. Molecular geometry and the numbering scheme for the title compound. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Full experimental and spectroscopic data concerning the synthesis of the title compound have been described previously (Czarnocki, 1992*b*). The compound was purified by column chromatography and then crystallized from ethanol and from ethanol/hexane solution. Crystals suitable for X-ray experiments were obtained by slow evaporation of the solvents. The melting point was found to be 413–414 K.

Crystal data

C₂₃H₂₉NO₁₁
M_r = 495.48

Cu Kα radiation
λ = 1.5418 Å

Monoclinic

*P*2₁
a = 12.923 (2) Å
b = 7.5697 (11) Å
c = 13.743 (2) Å
β = 113.749 (12)°
V = 1230.6 (3) Å³
Z = 2
D_x = 1.340 Mg m⁻³

Data collection

KM-4 κ-axis diffractometer
Profile data from ω/θ scans
Absorption correction:
none
2607 measured reflections
2515 independent reflections
2372 observed reflections
[I > 2σ(I)]
R_{int} = 0.029

Refinement

Refinement on F²
R = 0.052
wR(F²) = 0.144
S = 1.043
2515 reflections
346 parameters
Only H-atom U's refined
w = 1/[σ²(F_o²) + (0.1120P)²
+ 0.2155P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.004
Δρ_{max} = 0.31 e Å⁻³
Δρ_{min} = -0.39 e Å⁻³

Cell parameters from 25 reflections
θ = 20–21°
μ = 0.911 mm⁻¹
T = 293 (2) K
Transparent column
0.8 × 0.5 × 0.2 mm
Pale yellow

θ_{max} = 72.04°
h = 0 → 15
k = 0 → 9
l = -16 → 14
2 standard reflections
monitored every 100 reflections
intensity variation: none

Extinction correction:

SHELXL93 (Sheldrick, 1994)

Extinction coefficient:

0.0111 (16)

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)

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

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
O1	-0.0394 (2)	0.4645	0.1570 (2)	0.0769 (9)
O2	0.2970 (2)	0.5298 (8)	0.7598 (2)	0.0708 (8)
O3	0.4292 (2)	0.4359 (7)	0.6689 (2)	0.0588 (7)
O4	0.2244 (2)	0.1612 (6)	0.3345 (2)	0.0424 (4)
O5	0.1825 (2)	0.4889 (6)	0.1319 (2)	0.0530 (6)
O6	0.4144 (2)	0.3637 (7)	0.1905 (2)	0.0539 (6)
O7	0.3345 (3)	0.0159 (7)	0.1034 (2)	0.0701 (7)
O8	0.0613 (2)	0.0336 (7)	0.3133 (3)	0.0747 (8)
O9	0.2005 (3)	0.7434 (7)	0.2196 (2)	0.0816 (9)
O10	0.5053 (2)	0.3780 (8)	0.3669 (2)	0.0767 (9)
O11	0.3378 (4)	0.1037 (9)	-0.0507 (3)	0.1056 (14)
C1	0.1075 (2)	0.4191 (7)	0.3182 (2)	0.0425 (6)
N	0.0091 (2)	0.4862 (7)	0.2586 (2)	0.0523 (7)
C3	-0.0519 (3)	0.5998 (8)	0.3051 (3)	0.0545 (8)
C4	-0.0361 (2)	0.5348 (8)	0.4139 (3)	0.0524 (8)
C5	0.1319 (3)	0.5349 (7)	0.5908 (2)	0.0496 (7)
C6	0.2466 (3)	0.5090 (7)	0.6524 (2)	0.0513 (7)
C7	0.3179 (2)	0.4589 (7)	0.6027 (2)	0.0461 (7)
C8	0.2740 (2)	0.4315 (7)	0.4945 (2)	0.0432 (6)
C9	0.1572 (2)	0.4548 (7)	0.4324 (2)	0.0404 (6)
C10	0.0879 (2)	0.5087 (7)	0.4818 (2)	0.0442 (6)
C11	0.2271 (4)	0.5609 (11)	0.8150 (3)	0.088 (2)
C12	0.5038 (3)	0.3869 (9)	0.6224 (3)	0.0627 (10)
C1'	0.1622 (2)	0.3014 (7)	0.2633 (2)	0.0434 (6)
C2'	0.2475 (2)	0.3968 (7)	0.2286 (2)	0.0441 (7)
C3'	0.3243 (2)	0.2679 (7)	0.2034 (2)	0.0482 (7)

C4'	0.2640 (3)	0.1637 (8)	0.1031 (3)	0.0609 (9)
C13	0.1624 (3)	0.0354 (7)	0.3563 (3)	0.0498 (7)
C14	0.2347 (3)	-0.0878 (8)	0.4376 (3)	0.0627 (9)
C15	0.1617 (3)	0.6619 (7)	0.1388 (3)	0.0550 (8)
C16	0.0844 (4)	0.7310 (9)	0.0334 (4)	0.0874 (15)
C17	0.5048 (3)	0.4028 (8)	0.2816 (3)	0.0574 (8)
C18	0.5996 (3)	0.4797 (10)	0.2590 (4)	0.0775 (13)
C19	0.3693 (3)	0.0051 (9)	0.0249 (3)	0.0655 (10)
C20	0.4488 (5)	-0.1443 (12)	0.0426 (5)	0.105 (2)

[-0.1 (3)] and former experimental evidence indicated that the choice of absolute configuration was correct. Molecular graphics were prepared using *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1162). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected geometric parameters (Å, °)

O1—N	1.290 (3)	C1—C9	1.462 (4)
O2—C6	1.361 (4)	C1—C1'	1.514 (4)
O2—C11	1.413 (5)	N—C3	1.474 (4)
O3—C7	1.369 (3)	C3—C4	1.508 (5)
O3—C12	1.403 (4)	C4—C10	1.507 (4)
O4—C13	1.353 (4)	C5—C10	1.386 (4)
O4—C1'	1.447 (4)	C5—C6	1.394 (4)
O5—C15	1.348 (5)	C6—C7	1.402 (4)
O5—C2'	1.434 (3)	C7—C8	1.377 (4)
O6—C17	1.358 (4)	C8—C9	1.414 (4)
O6—C3'	1.443 (4)	C9—C10	1.386 (4)
O7—C19	1.329 (5)	C1'—C2'	1.545 (4)
O7—C4'	1.441 (5)	C2'—C3'	1.527 (4)
O8—C13	1.198 (4)	C3'—C4'	1.505 (5)
O9—C15	1.190 (5)	C13—C14	1.466 (5)
O10—C17	1.185 (4)	C15—C16	1.484 (5)
O11—C19	1.208 (6)	C17—C18	1.497 (5)
C1—N	1.307 (4)	C19—C20	1.480 (7)
C6—O2—C11	118.1 (3)	C5—C10—C9	120.4 (3)
C7—O3—C12	117.5 (2)	C5—C10—C4	121.5 (3)
C13—O4—C1'	116.7 (2)	C9—C10—C4	118.1 (3)
C15—O5—C2'	117.8 (3)	O4—C1'—C1	109.8 (2)
C17—O6—C3'	115.7 (2)	O4—C1'—C2'	106.3 (2)
C19—O7—C4'	117.7 (4)	C1—C1'—C2'	114.4 (3)
N—C1—C9	119.7 (3)	O5—C2'—C3'	107.0 (2)
N—C1—C1'	116.7 (3)	O5—C2'—C1'	106.8 (2)
C9—C1—C1'	123.6 (2)	C3'—C2'—C1'	112.4 (3)
O1—N—C1	123.7 (3)	O6—C3'—C4'	107.2 (2)
O1—N—C3	115.6 (2)	O6—C3'—C2'	109.7 (3)
C1—N—C3	120.7 (3)	C4'—C3'—C2'	113.5 (3)
N—C3—C4	110.9 (3)	O7—C4'—C3'	108.1 (3)
C10—C4—C3	110.0 (2)	O8—C13—O4	121.6 (3)
C10—C5—C6	120.7 (3)	O8—C13—C14	127.0 (3)
O2—C6—C5	124.7 (3)	O4—C13—C14	111.4 (3)
O2—C6—C7	116.0 (3)	O9—C15—O5	123.2 (3)
C5—C6—C7	119.3 (3)	O9—C15—C16	126.4 (4)
O3—C7—C8	124.4 (3)	O5—C15—C16	110.4 (4)
O3—C7—C6	115.6 (3)	O10—C17—O6	122.5 (3)
C8—C7—C6	120.0 (2)	O10—C17—C18	126.1 (3)
C7—C8—C9	120.6 (3)	O6—C17—C18	111.4 (3)
C10—C9—C8	119.0 (2)	O11—C19—O7	123.6 (4)
C10—C9—C1	119.3 (2)	O11—C19—C20	125.7 (4)
C8—C9—C1	121.7 (2)	O7—C19—C20	110.7 (5)
C9—C1—N—O1	178.4 (3)	C6—C5—C10—C4	179.6 (3)
C1'—C1—N—O1	-3.7 (5)	C1—C9—C10—C5	176.8 (3)
C9—C1—N—C3	0.9 (5)	C8—C9—C10—C4	179.3 (3)
C1'—C1—N—C3	178.9 (3)	C1—C9—C10—C4	-2.3 (5)
O1—N—C3—C4	145.0 (3)	C3—C4—C10—C5	147.9 (3)
C1—N—C3—C4	-37.3 (5)	C3—C4—C10—C9	-33.0 (4)
N—C3—C4—C10	51.2 (4)	N—C1—C1'—O4	-145.3 (3)
C7—C8—C9—C1	-177.3 (3)	C9—C1—C1'—O4	32.5 (4)
N—C1—C9—C10	20.5 (5)	N—C1—C1'—C2'	95.3 (3)
C1'—C1—C9—C10	-157.3 (3)	C9—C1—C1'—C2'	-86.8 (3)
N—C1—C9—C8	-161.1 (3)	C1—C1'—C2'—O5	-79.4 (3)
C1'—C1—C9—C8	21.1 (5)	C1—C1'—C2'—C3'	163.6 (2)

Data collection, cell refinement and data reduction were performed using Kuma diffractometer software. The (*Ok*l) reflections were used for the calculation of R_{int} . The structure was solved using *SHELXS86* (Sheldrick, 1990) and refined using *SHELXL93* (Sheldrick, 1994). The H atoms were positioned according to geometric criteria. The Flack parameter

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Two Heterocyclic 1,2,4,5-Tetrazines

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Abstract

The title compounds, 6-bromo-1,4-dihydro-1,4-di(*o*-tolyl)-1,2,4,5-tetrazin-3(2*H*)-one, $C_{16}H_{15}BrN_4O$, and 3,6-dibromo-1,4-dihydro-1,4-bis(*p*-methoxyphenyl)-1,2,4,5-tetrazine, $C_{16}H_{14}Br_2N_4O_2$, were prepared from 4-bromo-3-(*o*-tolyl)sydnone and 4-bromo-3-(*p*-methoxyphenyl)sydnone, respectively, in thf under ultrasonic irradiation, and identified with IR, 1H NMR, mass spectrum and elemental analyses. The heterocyclic rings of both title compounds appear to lack aromatic character, as judged from the bond lengths.