

and O(6) to H(2)C(12) on a neighboring molecule at $x, -y-0.5, z-0.5$ are 2.697 (2) and 2.827 (2) Å, respectively. Investigations of several other analogues of L-652,731 are now in progress in our laboratory to ascertain the possible biological significance of these intermolecular interactions and their relevance in the design of more potent and specific antagonists.

This work was supported in part by the American Cancer Society, Illinois Division, Inc. (JRP, grant No. 87-53), the Elsa U. Pardee Foundation (JRP), and by the Donors of the Petroleum Research fund (JRP and RDR), administered by the American Chemical Society. JRP acknowledges support by the Northern Illinois University Graduate School and Biomedical Research Support Group. The US National Science Foundation's Chemical Instrumentation Program provided funding to purchase the diffractometer.

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Acta Cryst. (1989). **C45**, 300-303

Structure of Columbin, a Diterpenoid Furanolactone from *Tinospora cordifolia* Miers

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(Received 4 July 1988; accepted 26 August 1988)

Abstract. (1*S*,4*R*,5*R*,8*S*,10*R*,12*S*)-4-Hydroxy-15,16-epoxycyleroda-2,13(16),14-trieno-17,12:18,1-biscarbolactone, C₂₀H₂₂O₆, $M_r = 358.2$, m.p. = 453-454 K, orthorhombic, $P2_12_12_1$, $a = 7.3869$ (6), $b = 11.986$ (1), $c = 19.896$ (2) Å, $V = 1761.65$ Å³, $Z = 4$, $D_x = 1.351$, D_m (by flotation) = 1.349 g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 8.36$ cm⁻¹, $F(000) = 760$, $T = 295$ K, $R = 0.0432$ for 1662 observed reflections. Two terpene rings, two δ -lactones, two methyl groups, a tertiary hydroxyl group and a β -substituted furan ring are present in the structure. The H atoms at C(12) and C(8) are α - and β -oriented. The terpene ring *A* is locked

into a boat conformation by the C(1)-C(4) lactone bridge. The furan ring is attached equatorially at atom C(12). The hydroxyl group is involved in intramolecular hydrogen bonding.

Introduction. The medicinal properties of the plant *Tinospora cordifolia* have been studied extensively and many compounds have been isolated from this plant. The structural investigation of the title compound was undertaken to determine the stereochemistry.

Experimental. Dried and finely powdered stems of the plant were used for extraction with chloroform in a Soxhlet apparatus. Repeated column chromatography

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Table 1. Positional parameters ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for non-H atoms with e.s.d.'s in parentheses
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
C(1)	5147 (5)	2241 (3)	2638 (2)	44 (3)
C(2)	5165 (6)	2777 (3)	1957 (2)	58 (4)
C(3)	6418 (6)	2346 (3)	1560 (2)	57 (4)
C(4)	7508 (5)	1433 (3)	1878 (2)	50 (3)
C(5)	8496 (4)	1889 (3)	2528 (2)	42 (3)
C(6)	9437 (5)	936 (3)	2890 (2)	55 (3)
C(7)	10235 (5)	1269 (3)	3572 (2)	65 (4)
C(8)	9061 (4)	2085 (3)	3973 (2)	46 (3)
C(9)	7073 (4)	2169 (3)	3735 (1)	37 (3)
C(10)	6999 (4)	2435 (2)	2970 (1)	36 (2)
C(11)	6190 (4)	3124 (3)	4132 (2)	42 (3)
O(2)	9073 (3)	4117 (2)	4213 (1)	62 (3)
O(3)	11633 (3)	3259 (3)	4131 (2)	82 (4)
O(4)	8749 (4)	944 (2)	1422 (1)	79 (3)
O(5)	6139 (4)	-390 (2)	1979 (1)	71 (3)
O(6)	4916 (3)	1021 (2)	2540 (1)	51 (2)
C(17)	9991 (5)	3185 (3)	4091 (2)	54 (4)
C(18)	6144 (5)	591 (3)	2128 (2)	52 (3)
C(19)	9913 (5)	2751 (3)	2301 (2)	60 (4)
C(20)	6077 (5)	1089 (3)	3937 (2)	48 (3)
C(12)	7145 (4)	4216 (3)	4063 (2)	47 (3)
C(13)	6433 (6)	5105 (3)	4520 (2)	63 (4)
C(14)	7355 (8)	6024 (6)	4766 (4)	149 (10)
C(15)	6294 (9)	6615 (5)	5159 (4)	146 (9)
C(16)	4696 (7)	5254 (3)	4737 (2)	63 (4)
O(1)	4566 (7)	6218 (3)	5106 (2)	121 (5)

over silica gel with 3% methanol-chloroform and recrystallization from methanol (Hanuman, Bhatt & Sabata, 1986) yielded transparent crystals. Intensity data (crystal dimensions $0.35 \times 0.35 \times 0.07$ mm) were collected on an Enraf-Nonius CAD-4 diffractometer, Ni-filtered Cu $K\alpha$ radiation, ω - 2θ scan. Lattice parameters obtained from photographs were refined by least-squares analysis using 25 reflections, $4 < \theta < 43^\circ$. Intensities of two standard reflections recorded for every 30 min of data collection showed no significant changes. Data were collected in the range $0 < \theta < 70^\circ$ (resolution $d = 0.82$ \AA, $h_{max} = 9$, $k_{max} = 14$, $l_{max} = 24$). Of 1983 unique reflections 1769 reflections had $|F_o| > 3\sigma(|F_o|)$. Lp corrections, empirical absorption correction based on ψ scans of six strong reflections (North, Phillips & Mathews, 1968). Minimum and maximum transmission factors for F are 0.8848 and 0.9994. Structure was solved by direct methods, MULTAN11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982; SDP, Enraf-Nonius, 1982) with molecular scattering factors for the terpene rings (Ramakumar, 1976). H atoms were located from difference Fourier maps. Structure refinement by SHELX76 (Sheldrick, 1976) using least-squares method based on F values, with anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. In the final calculation reflections with $|F_o| < 5\sigma(|F_o|)$ and those for which $F_o < F_c$ with $\Delta F/\sigma(|F_o|) > 4.0$ were omitted. For 1662 reflections $R = 0.0432$, unit weights, $(\Delta/\sigma)_{max}$

Table 2. Important bond lengths (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$) with e.s.d.'s in parentheses

C(2)-C(1)	1.500 (5)	C(10)-C(9)	1.555 (4)
C(10)-C(1)	1.537 (4)	C(11)-C(9)	1.536 (4)
O(6)-C(1)	1.485 (4)	C(20)-C(9)	1.543 (4)
C(3)-C(2)	1.322 (5)	C(12)-C(11)	1.493 (5)
C(4)-C(3)	1.500 (5)	C(17)-O(2)	1.329 (5)
C(5)-C(4)	1.583 (4)	C(12)-O(2)	1.460 (4)
O(4)-C(4)	1.416 (4)	C(17)-O(3)	1.219 (4)
C(18)-C(4)	1.511 (5)	C(18)-O(5)	1.213 (4)
C(6)-C(5)	1.520 (5)	C(18)-O(6)	1.327 (4)
C(10)-C(5)	1.558 (4)	C(13)-C(12)	1.497 (5)
C(19)-C(5)	1.539 (5)	C(14)-C(13)	1.385 (8)
C(7)-C(6)	1.532 (5)	C(16)-C(13)	1.366 (6)
C(8)-C(7)	1.532 (5)	C(15)-C(14)	1.314 (10)
C(9)-C(8)	1.547 (4)	O(1)-C(15)	1.366 (8)
C(17)-C(8)	1.506 (5)	O(1)-C(16)	1.372 (5)
C(10)-C(1)-C(2)	108.4 (3)	C(20)-C(9)-C(8)	108.5 (2)
O(6)-C(1)-C(2)	107.7 (3)	C(20)-C(9)-C(10)	114.2 (2)
O(6)-C(1)-C(10)	107.9 (2)	C(20)-C(9)-C(11)	106.8 (2)
C(3)-C(2)-C(1)	112.3 (3)	C(5)-C(10)-C(1)	109.0 (2)
C(4)-C(3)-C(2)	114.1 (3)	C(9)-C(10)-C(1)	114.9 (2)
C(5)-C(4)-C(3)	109.9 (3)	C(9)-C(10)-C(5)	116.2 (2)
O(4)-C(4)-C(3)	112.3 (3)	C(12)-C(11)-C(9)	113.9 (3)
O(4)-C(4)-C(5)	111.6 (3)	C(12)-O(2)-C(17)	121.9 (3)
C(18)-C(4)-C(3)	105.6 (3)	C(18)-O(6)-C(1)	112.7 (3)
C(18)-C(4)-C(5)	105.7 (2)	O(2)-C(17)-C(8)	122.2 (3)
C(18)-C(4)-O(4)	111.5 (3)	O(3)-C(17)-C(8)	121.9 (4)
C(6)-C(5)-C(4)	109.8 (3)	O(3)-C(17)-O(2)	115.8 (4)
C(10)-C(5)-C(4)	106.2 (2)	O(5)-C(18)-C(4)	124.7 (3)
C(10)-C(5)-C(6)	111.9 (3)	O(6)-C(18)-C(4)	113.6 (3)
C(19)-C(5)-C(4)	107.8 (3)	O(6)-C(18)-O(5)	121.7 (3)
C(19)-C(5)-C(6)	109.5 (3)	O(2)-C(12)-C(11)	111.8 (3)
C(19)-C(5)-C(10)	111.5 (3)	C(13)-C(12)-C(11)	113.7 (3)
C(7)-C(6)-C(5)	113.6 (3)	C(13)-C(12)-O(2)	106.1 (3)
C(8)-C(7)-C(6)	114.2 (3)	C(14)-C(13)-C(12)	127.5 (4)
C(9)-C(8)-C(7)	114.8 (3)	C(16)-C(13)-C(12)	128.0 (4)
C(17)-C(8)-C(7)	112.5 (3)	C(16)-C(13)-C(14)	104.3 (4)
C(17)-C(8)-C(9)	115.1 (3)	C(15)-C(14)-C(13)	110.2 (5)
C(10)-C(9)-C(8)	110.3 (2)	O(1)-C(15)-C(14)	108.9 (6)
C(11)-C(9)-C(8)	107.1 (2)	O(1)-C(16)-C(13)	110.2 (4)
C(11)-C(9)-C(10)	109.6 (2)	C(16)-O(1)-C(15)	105.6 (5)
C(10)-C(1)-C(2)-C(3)	60.9 (4)	C(6)-C(7)-C(8)-C(17)	-117.2 (3)
C(2)-C(1)-C(10)-C(5)	-60.7 (3)	C(7)-C(8)-C(17)-O(2)	156.4 (3)
C(2)-C(3)-C(4)-C(5)	-59.2 (4)	C(11)-C(9)-C(10)-C(5)	153.6 (3)
C(3)-C(4)-C(5)-C(6)	174.0 (3)	C(10)-C(9)-C(11)-C(12)	-63.2 (3)
C(4)-C(5)-C(6)-C(7)	-172.9 (3)	C(9)-C(11)-C(12)-C(13)	-172.3 (3)
C(6)-C(5)-C(10)-C(1)	-115.4 (3)	C(11)-C(12)-C(13)-C(14)	154.0 (5)
C(4)-C(5)-C(10)-C(9)	136.2 (3)	O(2)-C(12)-C(13)-C(14)	30.7 (6)

$= 0.128$, $\Delta\rho$ in the final difference Fourier map -0.20 to 0.23 e \AA^{-3} , number of parameters refined: 315, including all but two H atoms. C-H distances in the range $0.91(3)$ - $1.17(4)$ \AA and O-H distance $0.79(4)$ \AA. Computers PDP 11/44 for structure solution and CYBER-180 for refinement. Atomic scattering factors those of SHELX76.

Discussion. The positional parameters and equivalent isotropic temperature factors for non-H atoms are given in Table 1.* Important bond lengths, bond angles and

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares-planes details and hydrogen-bond data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51398 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

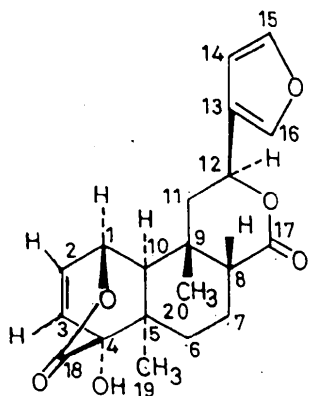


Fig. 1. Structural formula.

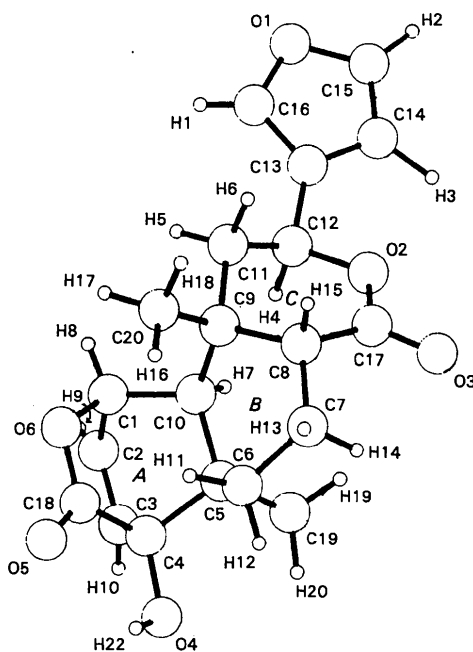


Fig. 2. General view of the molecule.

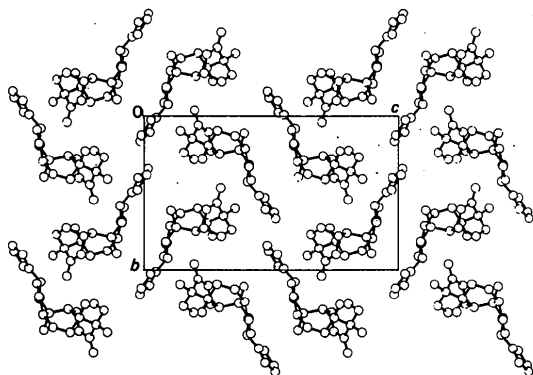


Fig. 3. Unit-cell packing diagram.

torsion angles are given in Table 2. Fig. 1 gives the structural formula of the compound. Fig. 2 is the *PLUTO78* drawing (Motherwell & Clegg, 1978) of the general view of the molecule and Fig. 3 is the packing diagram.

The crystal structure of the 1-(*p*-iodophenyl)-3-phenylpyrazoline adduct of isocolumbin has been reported (Cheung, Melvilla, Overton, Robertson & Sim, 1966). The present structure resembles those of similar compounds (Swaminathan, Sinha, Bhatt & Sabata, 1988; Swaminathan, Sinha, Bhatt, Sabata & Tavale, 1989). For comparison some of the corresponding parameters of these two compounds are given in square brackets, where the second value is the average of the values of two molecules. The chirality was assigned on the basis of detailed NMR and irradiation studies. The terpene ring *A* is locked into a boat conformation by the C(1)–C(4) lactone bridge. The absence of the epoxy oxygen O(7) which is present in the other two compounds makes the C(2)=C(3) distance 1.322 (5) Å [1.440 (4), 1.450 (5) Å] and hence the atoms H(9) and H(10) are coplanar with the mean plane of atoms C(1), C(2), C(3) and C(4). Atom O(4) of the hydroxyl group is coplanar with the mean plane of the lactone function. O(4)–H(22) is 0.79 (4) Å [0.86 (4), 0.89 (5) Å]. The furan ring is effectively planar with maximum deviation of 0.0050 (5) Å and attached equatorially to the ring *C* at atom C(12). Atom H(4) is α -oriented at site C(12) and atom H(15) is β -oriented at atom C(8). The α and β orientations of atoms H(7) at C(10) and O(6) of the lactone function at C(1) indicate the *trans*-diaxial relationship. Atom O(4) of the hydroxyl group is involved in intramolecular hydrogen bonding with atom O(5), with bond distance 2.739 (8) Å.

The authors thank Professor M. A. Viswamitra, Department of Physics, IISc, Bangalore, for his kind permission to use the CAD-4 diffractometer for data collection.

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Acta Cryst. (1989). C45, 303–306

1:1 and 1:2 Complexes Between Diaza-18-crown-6 and 2,7-Dihydroxynaphthalene

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(Received 31 March 1988; accepted 21 September 1988)

Abstract. 1:1 Complex, $C_{12}H_{26}N_2O_4 \cdot C_{10}H_8O_2$, $M_r = 422.53$, monoclinic, $P2_1/c$, $a = 17.813$ (3), $b = 7.563$ (2), $c = 18.297$ (2) Å, $\beta = 97.80$ (1)°, $V = 2442.3$ (6) Å³, $Z = 4$, $D_x = 1.149$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.78$ cm⁻¹, $F(000) = 912$, $T = 295$ K, $R = 0.0687$ for 1964 observed reflections. 1:2 Complex, $C_{12}H_{26}N_2O_4 \cdot 2C_{10}H_8O_2$, $M_r = 582.70$, monoclinic, $P2_1/n$, $a = 11.957$ (2), $b = 7.551$ (1), $c = 18.474$ (2) Å, $\beta = 105.85$ (1)°, $V = 1604.4$ (3) Å³, $Z = 2$, $D_x = 1.206$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.81$ cm⁻¹, $F(000) = 624$, $T = 295$ K, $R = 0.0424$ for 1745 observed reflections. The conformations of the diaza-18-crown-6 molecules are analogous to the D_{3d} conformation of 18-crown-6. In the 1:1 complex the dihydroxynaphthalene bridges two independent diaza-18-crown-6 molecules by hydrogen bonding to the diaza N atoms. In the 1:2 complex one hydroxyl O(7) hydrogen bonds to the diaza N atom while the other hydroxyl O(2) hydrogen bonds to O(7) of an adjacent molecule.

Introduction. Diaza-18-crown-6 (IUPAC name: 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) forms stable complexes with neutral organic molecules containing proton donors (Watson, Galloy, Grossie, Vögtle & Müller, 1984; Vögtle, Müller & Watson, 1984). The hydrogen bonds always involve the diaza N atoms. If the guest donor is sufficiently acidic, proton transfer occurs yielding a diaza-18-crown-6 dication (Watson, Vögtle & Müller, 1988a). In a recent investigation (Watson, Vögtle & Müller, 1988b), it was found that diaza-18-crown-6 could be used to selectively precipitate some polyhydroxy guests from mixtures of oligohydroxy phenols. Chemical analysis of a complex formed with 2,7-dihydroxynaphthalene indicated a host:guest ratio

of 2:3. Since this is a rather unusual ratio for guests of this type, we believed the structure would be of interest. Upon careful control of the guest: host stoichiometries we isolated 1:1 and 1:2 complexes but no trace of a 2:3 complex. An initial 2:3 host:guest ratio leads to an approximate equimolar mixture of 1:2 and 1:1 complexes giving a 2:3 chemical analysis.

Experimental. Data were collected on a Nicolet R3m/μ update of a P2₁ diffractometer ($3 \leq 2\theta \leq 45^\circ$) in the Wyckoff mode (2θ fixed, ω varied) using a variable scan rate (4 to 29.3° min⁻¹) and graphite-monochromated Mo Kα radiation. Lorentz–polarization corrections and a ψ -scan-based empirical absorption correction were applied; structure solved by direct methods and refined by block-cascade least-squares techniques. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. Computer programs for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986); scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

1:1 Complex: Obtained by refluxing a 1:1 molar ratio of the two components in a minimum quantity of ethyl acetate, colorless crystals 0.15 × 0.38 × 0.52 mm, 25 reflections ($32.03 \leq 2\theta \leq 40.93^\circ$) used to determine unit-cell dimensions; systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) and Laue symmetry $2/m$ consistent with space group $P2_1/c$; 3189 independent reflections ($-19 \leq h \leq 19$, $0 \leq k \leq 8$, $0 \leq l \leq 19$), $1964 \geq 3\sigma(I)$; transmission factors 0.920 to 0.966; all H atoms located in a difference map, OH and NH H atoms refined isotropically, all other H atoms allowed to ride on attached atom, one isotropic thermal parameter refined for naphthalene H atoms and another for H atoms of one crown, H atoms of crown with large thermal parameters assigned isotropic value of attached atom; $R = 0.0687$, $wR = 0.0534$ for 286 parameters

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