Acta Cryst. (1980). B36, 2802–2804

The Structure of Onychiol B, [1a*S*,3a*S*-(1β,1aα,3aβ,5α,5aα,6α,10aβ)]-1-[1-(Hydroxymethyl)vinyl]-3a,5a,8-trimethyl-2,3,3a,4,5,5a,9,10,10a,10b-decahydro-1*H*,6*H*-cyclohept[*e*]indene-5,6-diol: A Diterpene Alcohol from *Onychium japonicum* (Thunb.) Kunze

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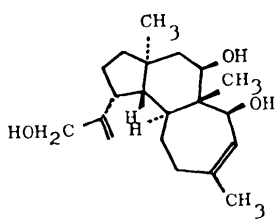
(*Received* 12 *February* 1980; *accepted* 21 *May* 1980)

Abstract. $C_{20}H_{32}O_3$, $M_r = 320{\cdot}47$, orthorhombic, space group $P2_12_12_1$; $a = 7{\cdot}169\ (3)$, $b = 15{\cdot}260\ (3)$, $c = 16{\cdot}647\ (5)$ Å; $Z = 4$, $D_c = 1{\cdot}17$, $D_m = 1{\cdot}17$ Mg m^{-3}. The structure was solved by direct methods and refined by full-matrix anisotropic least squares to a final R of 0·063 for 1449 reflections. The carbon skeleton of the compound resembles the antibiotic substances cyathins, produced by the bird's-nest fungus *Cyathus helenae* Brodie. Both the five- and seven-membered rings are *trans*-fused to the central six-membered ring. The cyclopentane moiety has the 'envelope' conformation and both the cyclohexane and cycloheptene rings are in the 'chair' form.

Introduction. Onychiol B(I) was extracted from the rhizome and frond of *Onychium japonicum* (Thunb.) Kunze (Hsu, 1979). It was recrystallized from chloroform–ethyl acetate (3:1). A transparent single crystal with dimensions 0·5 × 0·6 × 0·2 mm was selected for the structure analysis. The cell parameters were determined from setting angles of 25 reflections measured on a Nonius CAD-4F automatic diffractometer.



(I)

Intensity data were collected at room temperature using a θ–2θ scan technique. During the data collection, the intensities of the three standard reflections were remeasured periodically and the orientation was checked every 300 reflections. No time-decay correction was made since these standard intensities showed only random fluctuation (<2·5%). Of 1742 independent reflections collected ($2\theta \geq 130°$) with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å), 1449 had $I > 3\sigma(I)$. The intensity data were corrected for Lorentz and polarization effects but not for absorption ($\mu = 0{\cdot}609$ mm^{-1}).

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). All non-hydrogen atoms were located from an E map. Full-matrix least-squares refinement with isotropic thermal parameters for these atoms led to an R of 0·147 and R_w of 0·154, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme given by Stout & Jensen (1968). After three cycles of least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms, a difference Fourier synthesis located all H atoms. The final

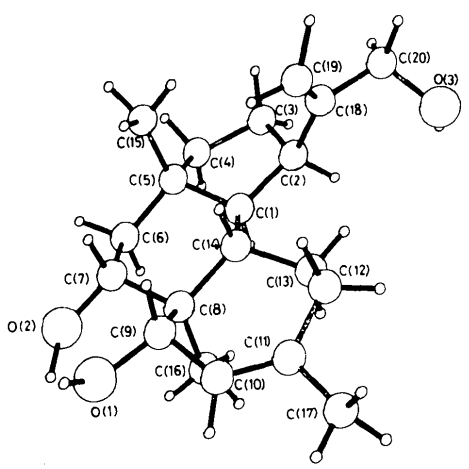


Fig. 1. A perspective drawing and numbering scheme of onychiol B.

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Table 1. *Fractional atomic coordinates and thermal parameters* ($\times 10^4$, $\times 10^3$ *for* H) *with their estimated standard deviations in parentheses*

The equivalent thermal parameters are of the form

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

All hydrogen atoms were kept fixed during the refinement and were assigned the same isotropic temperature factors as their attached heavy atoms.

	x	y	z	U_{eq}/U_{iso} (Å^2)
C(1)	1202 (7)	6681 (3)	7033 (3)	358 (12)
C(2)	744 (7)	5957 (3)	6404 (3)	425 (14)
C(3)	−945 (9)	6358 (4)	5935 (4)	610 (15)
C(4)	−1323 (9)	7266 (4)	6318 (4)	636 (14)
C(5)	551 (8)	7550 (3)	6671 (3)	462 (11)
C(6)	416 (8)	8211 (3)	7352 (3)	482 (11)
C(7)	2266 (8)	8309 (3)	7779 (3)	439 (15)
C(8)	3078 (7)	7444 (3)	8143 (3)	360 (16)
C(9)	5151 (7)	7642 (3)	8374 (3)	415 (13)
C(10)	6221 (8)	6956 (4)	8820 (3)	505 (13)
C(11)	6578 (8)	6123 (4)	8616 (3)	505 (12)
C(12)	5791 (9)	5677 (4)	7895 (4)	627 (11)
C(13)	3719 (9)	5804 (3)	7742 (3)	498 (13)
C(14)	3115 (7)	6728 (3)	7458 (3)	352 (13)
C(15)	1788 (10)	7897 (4)	5995 (3)	607 (18)
C(16)	1978 (8)	7169 (4)	8879 (3)	478 (13)
C(17)	7911 (9)	5571 (4)	9103 (4)	668 (15)
C(18)	2179 (8)	5612 (3)	5809 (3)	410 (12)
C(19)	3861 (9)	5934 (4)	5632 (3)	560 (15)
C(20)	1555 (9)	4801 (3)	5364 (3)	505 (15)
O(1)	5140 (6)	8416 (3)	8866 (3)	688 (9)
O(2)	1980 (6)	8969 (2)	8387 (2)	492 (10)
O(3)	1429 (6)	4059 (2)	5883 (3)	633 (9)
H(011)	24	655	747	32
H(031)	−208	598	596	57
H(041)	−235	722	672	60
H(061)	3	881	715	47
H(071)	316	855	736	37
H(101)	681	705	938	44
H(122)	616	505	792	54
H(132)	298	568	825	42
H(151)	214	751	560	48
H(153)	129	833	557	48
H(162)	88	684	878	47
H(171)	915	538	887	62
H(173)	743	506	943	62
H(192)	425	577	500	51
H(202)	34	488	508	46
H(221)	292	907	891	45
H(021)	35	540	667	38
H(032)	−63	644	533	57
H(042)	−177	770	588	60
H(062)	-53	803	777	47
H(091)	584	776	785	37
H(121)	655	595	742	54
H(131)	324	538	731	42
H(141)	400	692	705	28
H(152)	314	807	609	48
H(161)	129	763	922	47
H(163)	251	672	927	47
H(172)	842	586	954	62
H(191)	446	650	589	51
H(201)	252	462	493	46
H(211)	630	872	884	59
H(231)	28	400	608	53

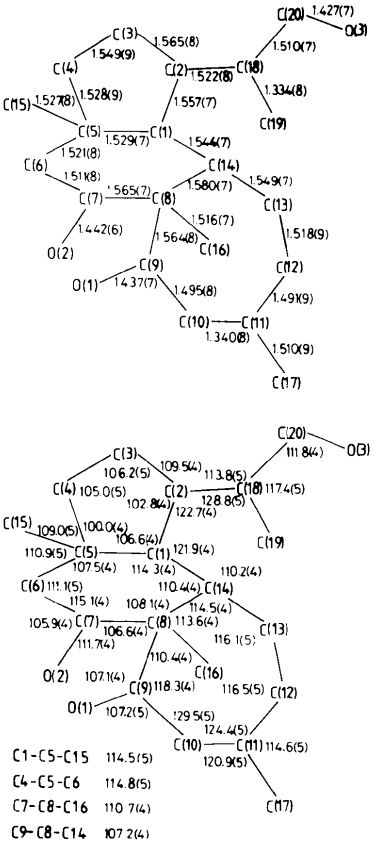


Fig. 2. Selected bond lengths (Å) and angles (°) in onychiol B.

refinement with anisotropic thermal parameters for non-hydrogen atoms and with H atoms added led to values of R and R_w of 0·063 and 0·059, respectively.* The scattering factors were all taken from *International Tables for X-ray Crystallography* (1962).

The final atomic coordinates are listed in Table 1. A perspective view of the molecule is given in Fig. 1. Selected bond distances and angles are presented in Fig. 2.*

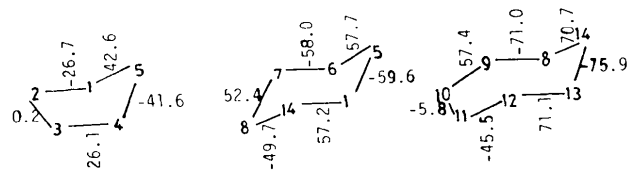
Discussion. *Onychium japonicum* (Pteridaceae) is a common fern growing in Taiwan, Japan, Korea and other Asiatic countries. Its rhizome and frond taste rather bitter and have been used locally as an ingredient in making bitter tea. While onychiol B tastes slightly bitter, its glucoside, onychioside B, is one of the bitter principles of the fern (Hsu, 1979). Interestingly, the carbon skeleton of onychiol B resembles the cyathins, metabolites of the bird's-nest fungus *Cyathus helenae* Brodie (Ayer & Taube, 1972). They differ in the number of chiral centers in the skeleton.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35369 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The absolute configuration of onychiol B was not determined. The seven chiral centers have the 1*S*,2*R*,5*S*,7*R*,8*S*,9*S*,14*S* configuration from the structure shown in Fig. 1. Both the five- and seven-membered rings are *trans*-fused to the central six-membered ring. Because of these *trans* junctions, the conformations of these rings are those commonly observed: envelope form for the cyclopentane, and chair form for both the cyclohexane and cycloheptene moieties. Their endocyclic torsion angles and Cremer & Pople (1975) puckering parameters are given in Table 2.

Table 2. *Ring-puckering parameters (Cremer & Pople, 1975) and endocyclic torsion angles for onychiol B*

The estimated standard deviations are in the range 0·5–1·0°.



Five-membered	Six-membered	Seven-membered
$q_2 = 0{\cdot}431$ Å	$q_2 = 0{\cdot}043$ Å	$q_2 = 0{\cdot}169$ Å
$\varphi_2 = -35{\cdot}4°$	$q_3 = 0{\cdot}575$ Å	$q_3 = 0{\cdot}659$ Å
	$\varphi_2 = 54{\cdot}6°$	$\varphi_2 = -2{\cdot}6°$
	$Q = 0{\cdot}576$ Å	$\varphi_3 = 182{\cdot}5°$
	$\theta = 4{\cdot}2°$	$Q = 0{\cdot}682$ Å

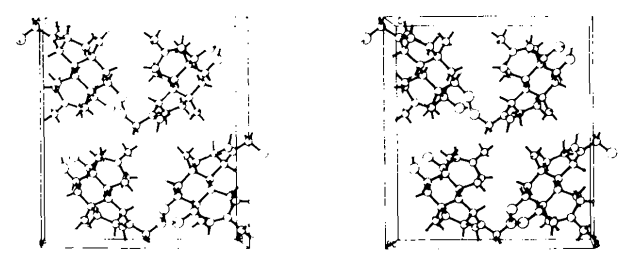


Fig. 3. A stereoview of the crystal packing of onychiol B.

The general shape of the molecule is flat disk-like, with all hydroxyl groups located on the outer rim. Two (7α,9α) hydroxyl groups are situated in close proximity on one side of the rim and the propenolic –OH group is on the opposite side. A stereoview of the crystal packing of the molecules is shown in Fig. 3. The molecules related by twofold screw symmetry along **b** are linked together by a repeating sequence of three hydrogen bonds. Each of the three hydroxyl groups act as a donor and acceptor. These hydrogen bonds are in the donor–acceptor sequence ›O(3)→O(2)→O(1)→O(3)→, running in a helical form along **a**. The O···O distances are O(1)···O(2) 2·55 (1), O(2)···O(3) 2·73 (1), and O(1)···O(3) 2·68 (1) Å, with the intramolecular O(1)···O(2) distance the shortest. Along **c**, the hydrogen-bonded molecules, parallel to the *ab* plane, are held together by van der Waals interactions. The packing thus appears to be governed by hydrogen-bonding in one direction and van der Waals interactions in the other.

We thank Professor C. M. Chen for providing the crystals for the study.

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