

Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule showing the atom numbering.

Discussion. Table 1 shows the final atomic parameters.* Fig. 1 (Johnson, 1965) shows the geometry of the structure and the atom labelling. Bond lengths and angles together with their e.s.d.'s are in Table 2.

* Lists of structure factors anisotropic thermal parameters, H-atom parameters and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38854 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1984). **C40**, 146–149

The Structure of Phyllanthocindiol Methyl Ester, $C_{25}H_{32}O_8$ *

BY LUIGI R. NASSIMBENI AND MARGARET L. NIVEN†

Department of Physical Chemistry, University of Cape Town, Rondebosch 7700, South Africa

AND GORDON M. CRAGG AND GEORGE R. PETTIT

Cancer Research Institute and Department of Chemistry, Arizona State University, Tempe, Arizona 85287, USA

(Received 4 July 1983; accepted 12 September 1983)

Abstract. $M_r = 460.52$, monoclinic, $P2_1$, $a = 9.891$ (5), $b = 24.84$ (1), $c = 9.687$ (5) Å, $\beta = 94.82$ (2)°, $V = 2372$ (2) Å³, $Z = 4$, $D_m = 1.21$, $D_x = 1.29$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 0.71$ mm⁻¹, $F(000) = 984$, room temperature. Final $R = 0.072$ for 3692 reflections. The two independent molecules have similarly folded configurations and a network of inter- and intramolecular hydrogen-bonding obtains.

* The present contribution is part 97 of Antineoplastic Agents. For part 96 refer to Pettit, Kamano & Tozawa (1984).

† Author to whom correspondence should be addressed.

0108-2701/84/010146-04\$01.50

The structure analysis confirms that the irradiation of 4-benzoyloxy-3-(*p*-chlorophenyl)-1,1,4-triphenyl-2-aza-1,3-butadiene gives a photoproduct which is derived from the dienol ester through 1,2-acyl migration.

Thanks are due to the staff of the Computing Center of JEN (Madrid) for the facilities provided on the Univac 1100/80 computer.

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Introduction. A detailed chemical investigation of the Central American tree *Phyllanthus acuminatus* Vahl (Euphorbiaceae family) led to isolation and structural elucidation (chemical and spectral methods) of the four most prominent anticancer constituents as amorphous glycosides designated phyllanthostatins 1–3 and phyllanthoside (Pettit, Cragg, Gust, Brown & Schmidt, 1982; Pettit, Cragg, Gust & Brown, 1982). One of these potentially important substances will be selected and evaluated for eventual clinical trial by the US National Cancer Institute. Since configuration of the 7-hydroxyl group in phyllanthostatins 1–3 could not be definitely

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assigned by spectral techniques we have degraded this substance to a crystalline derivative, phyllanthocindiol methyl ester (Pettit, Cragg, Niven & Nassimbeni, 1983). Solution of the phyllanthocindiol methyl ester X-ray crystal structure problem, which is detailed here, completes the structure of phyllanthostatin 3, which entire molecule is illustrated in Fig. 1.

Experimental. Single crystal $0.75 \times 0.50 \times 0.50$ mm suitable for X-ray analysis obtained by recrystallization from an acetone-hexane mixture. Preliminary photography established the space group as $P2_1$. Accurate cell constants by least squares from the settings of 25 high-order reflections measured on a Philips PW 1100 four-circle diffractometer with graphite-monochromated $\text{Cu } K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$); intensities for $8 \leq 2\theta \leq 136^\circ$ ($\pm h, +k, +l$) collected by ω - 2θ scan technique, scan width 1.4° (θ), scan speed 0.047° (θ) s^{-1} ; three reference reflections monitored every 50 measured reflections varied within 0.11%; correction for Lorentz-polarization but not for absorption; 4011 reflections collected, 3692 'observed' ($I_{\text{rel}} > 2\sigma I_{\text{rel}}$).

The structure was solved by direct methods, using the multiresolution tangent-refinement procedures of *SHELX* (Sheldrick, 1978). The best E map obtained gave 36 of the 66 non-hydrogen atoms, which yielded sufficient phase information to locate all the non-hydrogen atoms in subsequent weighted difference syntheses. Methylene and methine hydrogens were placed 1.00 \AA from their parent carbons, their positions being dictated by the geometry of the molecules, while methyl hydrogens were treated as rigid groups. The hydroxyl hydrogens on O(7) and O(14) were not revealed in the final difference maps and could not be placed in calculated positions because of their possible participation in various H-bonding schemes (see *Discussion*); hence they have been omitted from the final model. Owing to the large number of independent atoms, final refinements (on F) were carried out using the blocked-matrix technique. The C and O atoms not involved in ring configurations were treated anisotropically and all other atoms isotropically (program limitations in terms of allowed number of parameters prevented anisotropic treatment of all non-hydrogen atoms).^{*} 408 variables, weighting scheme $w = (\sigma^2 F + 2 \times 10^{-3} F^2)^{-1}$, final $R = 0.072$, $R_w = 0.085$, $U(\text{methyl H}) = 0.10$ (1) \AA^2 , $U(\text{methylene and methine H}) = 0.080$ (5) \AA^2 , final $\Delta\rho$ excursions ≤ 10.3 $e \text{ \AA}^{-3}$.

^{*} Lists of H-atom coordinates, anisotropic temperature factors, all bond distances and angles, and structure factors, and a figure showing endocyclic torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38858 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

An attempt was made to determine the absolute configuration of the molecules by using the coordinates of the other enantiomer. The generalized R factor (Hamilton, 1965) was identical to that obtained previously ($R_G = 0.1068$) and hence we could not infer the correct absolute configuration.

Complex neutral-atom scattering factors from Cromer & Mann (1968) for the C and O atoms, and from Stewart, Davidson & Simpson (1965) for H, with dispersion corrections from Cromer & Liberman (1970). All computations performed at the Computer Centre of the University of Cape Town on a Univac 1100/81 computer.

Discussion. Table 1 lists the final atom parameters. Perspective views of the crystallographically independent molecules (*a*) and (*b*) are shown in Fig. 2 and, in each case, conformational similarities to the previously determined bisabolane phyllanthocin (Kupchan, La Voie, Branfman, Fei, Bright & Bryan, 1977) are immediately apparent: each molecule has a folded configuration in which the principal cinnamate axis runs approximately parallel to the C(6)···C(3) acetate axis while the cinnamate and acetate planes are oriented to each other at about 68° in (*a*) and 61° in (*b*).

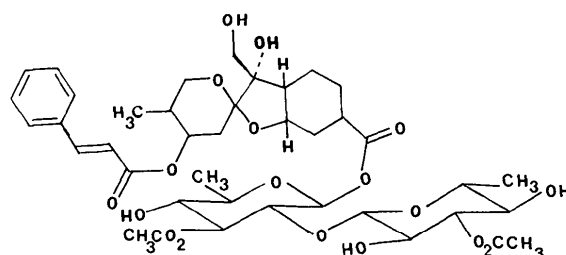


Fig. 1. Diagrammatic representation of phyllanthostatin 3.

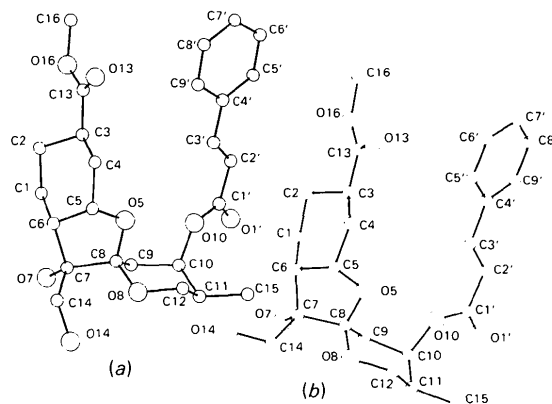


Fig. 2. Perspective views of the crystallographically independent molecules (*a*) and (*b*) of phyllanthocindiol methyl ester.

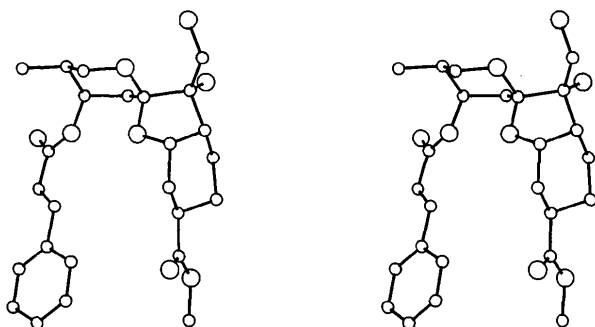


Fig. 3. Stereoview of (a).

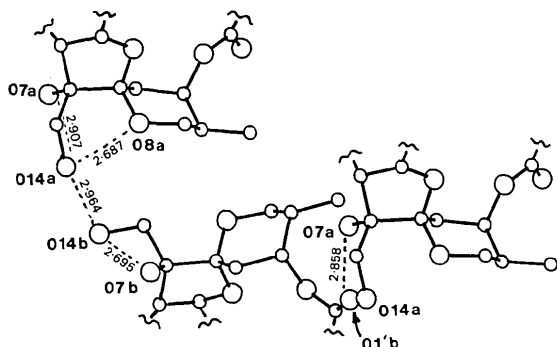


Fig. 4. Molecular fragments showing non-bonded contacts (Å) relevant to hydrogen-bonding schemes. (Standard deviations in range 0.005–0.006 Å.)

There is *cis* fusion of the six- and five-membered rings at C(5)–C(6) and O(7)–H is α (axial) to the five-membered ring as is O(7) in the related epoxide (Kupchan *et al.*, 1977). For each molecule, a conformational analysis of the saturated rings has been carried out in terms of asymmetry parameters (Duax & Norton, 1975) and pucker parameters (Boeyens, 1978). Endocyclic torsion angles have been deposited,* and results of the conformational investigation are shown in Table 2. A stereoview of a single molecule [representative of both (a) and (b)] is shown in Fig. 3 to assist in conformational observations.

All bond lengths and angles have been deposited.* They are of the expected magnitudes with C(7)–C(8) at the spiro junction 1.604 (6) Å in (a) and 1.582 (6) Å in (b), slightly longer than the remaining cyclo C–C bonds in the range 1.424 (6)–1.552 (7) Å.

The most notable difference between (a) and (b) is in the orientation of O(14), as evidenced by the torsion angle O(7)–C(7)–C(14)–O(14) which has the value 61.3 (4)° in (a) and –54.8 (5)° in (b); this is thought to be a consequence of preferential hydrogen-bonding possibilities.

Non-bonded contacts <3.0 Å and involving the O(7) and O(14) hydroxyl groups are relevant in hydrogen-bonding considerations and are shown in Fig. 4. In terms of O–H–O distances and angles more than one H-bonding scheme is feasible; since the hydroxyl

* See deposition footnote.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^3$) for non-hydrogen atoms

	Molecule (a)				Molecule (b)			
	x	y	z	U^*	x	y	z	U^*
C(1)	314 (5)	593	4228 (5)	48 (1)	4846 (5)	7195 (2)	1119 (5)	51 (1)
C(2)	243 (5)	1205 (2)	4281 (6)	52 (1)	5087 (5)	6621 (2)	596 (6)	53 (1)
C(3)	1635 (5)	1442 (2)	4837 (5)	48 (1)	6437 (5)	6594 (2)	–59 (5)	48 (1)
C(4)	2046 (5)	1219 (2)	6278 (5)	47 (1)	6506 (5)	6998 (2)	–1226 (5)	47 (1)
C(5)	1990 (4)	608 (2)	6347 (5)	40 (1)	6014 (5)	7565 (2)	–889 (5)	46 (1)
C(6)	715 (4)	344 (2)	5642 (4)	38 (1)	4753 (5)	7600 (2)	–83 (5)	45 (1)
C(7)	1176 (4)	–248 (2)	5577 (5)	37 (1)	4838 (5)	8196 (2)	381 (5)	45 (1)
C(8)	2773 (4)	–184 (2)	5438 (4)	35 (1)	6412 (4)	8320 (2)	491 (5)	41 (1)
C(9)	3257 (4)	–376 (2)	4075 (5)	40 (1)	7041 (4)	8464 (2)	1939 (5)	43 (1)
C(10)	4808 (5)	–392 (2)	4059 (5)	43 (1)	8482 (5)	8680 (2)	1949 (5)	44 (1)
C(11)	5483 (5)	–675 (2)	5342 (5)	46 (1)	8615 (5)	9104 (2)	855 (5)	46 (1)
C(12)	4935 (5)	–433 (2)	6637 (5)	45 (1)	7990 (5)	8901 (2)	–539 (5)	51 (1)
C(13)	1635 (6)	2047 (2)	4873 (6)	57 (3)†	6738 (5)	6035 (2)	–571 (5)	52 (2)†
C(14)	849 (5)	–546 (2)	6888 (5)	48 (2)†	3986 (5)	8558 (3)	–628 (6)	60 (3)†
C(15)	7046 (5)	–646 (3)	5444 (7)	65 (3)†	10067 (6)	9308 (3)	749 (6)	61 (3)†
C(16)	1225 (11)	2846 (3)	3536 (11)	104 (5)†	6672 (10)	5099 (3)	–92 (7)	85 (5)†
C(1')	6101 (5)	312 (2)	3058 (5)	49 (3)†	10369 (5)	8100 (2)	2659 (6)	52 (3)†
C(2')	6462 (5)	891 (2)	3173 (5)	50 (3)†	10976 (5)	7562 (2)	2416 (6)	54 (3)†
C(3')	5915 (5)	1230 (2)	4018 (5)	48 (2)†	10472 (5)	7216 (2)	1493 (5)	50 (3)†
C(4')	6182 (5)	1817 (2)	4143 (5)	49 (1)	10978 (5)	6661 (2)	1301 (5)	49 (1)
C(5')	7182 (6)	2076 (2)	3470 (6)	60 (1)	10496 (7)	6371 (3)	104 (7)	69 (2)
C(6')	7382 (6)	2631 (3)	3640 (7)	65 (1)	10973 (8)	5860 (3)	–107 (8)	81 (2)
C(7')	6550 (6)	2919 (3)	4482 (7)	66 (2)	11911 (8)	5615 (3)	830 (8)	84 (2)
C(8')	5575 (6)	2669 (3)	5158 (7)	68 (2)	12352 (7)	5894 (3)	2048 (7)	71 (2)
C(9')	5381 (6)	2116 (2)	4993 (7)	59 (1)	11872 (6)	6408 (2)	2249 (6)	59 (1)
O(5)	3046 (3)	376 (1)	5617 (3)	39 (1)	7025 (3)	7844 (1)	12 (3)	42 (1)
O(7)	503 (3)	–507 (1)	4386 (3)	48 (2)†	4343 (4)	8278 (2)	1754 (4)	59 (3)†
O(8)	3482 (3)	–479 (1)	6570 (3)	42 (1)	6596 (3)	8744 (1)	–470 (4)	49 (1)
O(10)	5300 (3)	163 (1)	4046 (3)	48 (3)†	9369 (3)	8218 (1)	1705 (3)	46 (2)†
O(13)	2043 (6)	2321 (2)	5837 (6)	94 (4)†	7217 (7)	5929 (2)	–1638 (5)	96 (4)†
O(14)	1307 (4)	–1098 (2)	6913 (4)	64 (3)†	2586 (5)	8423 (2)	–495 (5)	87 (3)†
O(16)	1136 (6)	2260 (2)	3647 (5)	80 (3)†	6461 (6)	5659 (2)	320 (4)	74 (2)†
O(1')	6480 (6)	18 (2)	2191 (5)	82 (3)†	10796 (5)	8393 (2)	3593 (5)	91 (3)†

* Values without daggers (†) are isotropic temperature factors.

† The value quoted is U_{eq} , calculated according to $U_{eq} = \frac{1}{3}$ (trace of orthogonalized U_{ij} matrix).

Table 2. Conformations of the saturated rings: asymmetry and pucker parameters

The numerical position of a ring atom in the sequences of the first column is used as an identifier in the conformational symbols of the last column.

	Asymmetry parameters*		Pucker parameters†	
	Mol. (a)	Mol. (b)	Mol. (a)	Mol. (b)
C(1)–C(2)–C(3)– C(4)–C(5)–C(6)	$\Delta C_3 C(2) $ 1.4	$\Delta C_3 C(1)–C(2) $ 1.5	$Q(\text{Å})$ 0.536 (5) $\varphi(^{\circ})$ 247 (3) $\theta(^{\circ})$ 168.3 (5) 4C_1	0.535 (5) 213 (2) 165.6 (5) 4C_1
O(5)–C(5)–C(6)– C(7)–C(8)	$\Delta C_3 C(5) $ 6.6	$\Delta C_3 C(5) $ 3.3	$Q(\text{Å})$ 0.435 (4) $\varphi(^{\circ})$ 47.0 (5) $E_2: {}^3H_2$ 1:1	0.436 (4) 43.1 (5) $E_2: {}^3H_2$ 1:1
O(8)–C(8)–C(9)– C(10)–C(11)–C(12)	$\Delta C_3 O(8)–C(12) $ 1.3	$\Delta C_3 O(8)–C(12) $ 1.3	$Q(\text{Å})$ 0.546 (5) $\varphi(^{\circ})$ 132 (5) $\theta(^{\circ})$ 173.1 (6) 4C_1	0.523 (3) 126 (3) 173.5 (3) 4C_1

* In each case, only the parameter of lowest magnitude has been reported. Standard deviations are in the range 0.3–0.7°.

† The total degree of pucker is described by the radial coordinate Q , and the angular coordinates φ and θ (six-membered rings), or φ (five-membered rings) describe the shape of the ring.

hydrogens were not revealed in the final difference maps, we may only postulate their locations in an indication of the H-bonding possibilities.

The ASU–CRI chemists wish to thank the following donors for financial support: Mary Dell Pritzlaff, the Olin Foundation (Spencer T. and Ann W.), the Fannie E. Rippel Foundation, Eleanor W. Libby, the Waddell Foundation (Donald Ware), Jack W. Whiteman, Pearl Spear, Robert B. Dalton and the Upjohn Co. The UCT chemists acknowledge with thanks financial assistance from the University of Cape Town and CSIR, Pretoria.

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Acta Cryst. (1984). **C40**, 149–151

Structure of *N*-(3-Dimethylaminopropyl)dithiocarbamic Acid, $C_6H_{14}N_2S_2$

BY V. SCHRAMM AND S. C. KOKKOU*

FR-17.3 Kristallographie, Universität des Saarlandes, D-6600 Saarbrücken, Federal Republic of Germany

AND P. KARAGIANNIDIS

Laboratory of Inorganic Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

(Received 29 June 1983; accepted 14 September 1983)

Abstract. $M_r = 178.3$, monoclinic, $P2_1/n$ (z -axis unique), $a = 6.9882$ (2), $b = 10.9995$ (5), $c = 12.3087$ (5) Å, $\gamma = 96.830$ (5)°, $V = 939.42$ Å³, $Z = 4$, D_m

$= 1.250$, $D_x = 1.261$ Mg m⁻³, m.p. = 433–434 K, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.576$ mm⁻¹, $F(000) = 384$, $T = 295$ K, $R = 0.048$ for 1444 independent non-zero reflexions. In the planar thioureide group –NCS₂, the C–N bond, 1.338 (5) Å, has strong double-bond character and the two C–S bonds,

* Present address: Applied Physics Laboratory, Aristotle University of Thessaloniki, Thessaloniki, Greece.