$C_5H_{11}NO_2.C_9H_{11}NO_2$

have resulted from packing considerations. The fact that the density of the crystals of the DL mixture of a non-polar amino acid is invariably higher than that of the crystals of the corresponding L-isomer, lends support to this conjecture.

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Structure of a Neolignan: $C_{20}H_{28}O_6$

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Abstract. 2-(2*H*-1,3-Benzodioxol-5-yl)-5-ethyl-3a,7a-dimethoxy-3-methyl-2,3,3a,4,5,6,7,7a-octahydro-1-benzofuran-6-ol, $M_r = 336$, monoclinic, $P2_1$, $a = 21\cdot198$ (1), $b = 6\cdot515$ (4), $c = 7\cdot038$ (2) Å, $\beta = 97\cdot0$ (5)°, $V = 964\cdot73$ Å^3, $Z = 2$, $D_x = 1\cdot289$ Mg m^{-3}, $\lambda(Mo K\alpha) = 0\cdot71073$ Å, $\mu = 0\cdot55$ mm^{-1}, $F(000) = 400$, $T = 288$ K, final $R = 0\cdot066$ for 1916 observed reflections. The aims of this crystal structure analysis were to determine the spatial configuration and to resolve the ambiguity of the possible positions of the OCH_3 and OH groups in the chemical structure. The cyclohexane ring formed by C(12), C(13), C(18),

C(17), C(16) and C(15) assumes a half-chair conformation and peripheral atoms C(19), C(20) and O(24) have relatively higher thermal parameters. The hydroxyl group of the compound is involved in a network of hydrogen bonds which stabilize the crystal structure.

Introduction. Lignans are interesting compounds found in plants and also in human and animal urine (Rao, 1978; Setchell, Lawson, Mitchell, Adlercreutz, Kirk & Axelson, 1980). Their biological importance has not yet been fully assessed but the observation of their cyclical excretion in early pregnancy and the known anti-cancer properties of certain plant lignans suggest the possibility of significant physiological roles. Dibenzylbutanes and related structures have been catalogued as lignans and are classified by the National Cancer Institute as being of interest as potential anti-cancer agents (Dombernowski, Nissen & Larsen, 1972). Podophyllotoxin (Kelly & Hartwell, 1954) derived from the roots of the May Apple plant and other synthetic lignans exhibit anti-mitotic activity (McDoneil & Cole, 1972). In these biologically active compounds the substituents about the C2—C3 bond of butane have a *trans* configuration. The structure of the present compound, $C_{20}H_{28}O_6$, a neolignan, 2-(2*H*-1,3-benzodioxol-5-yl)-5-ethyl-3a,7a-dimethoxy-3-methyl-2,3,3a,4,5,6,7,7a-octahydro-1-benzofuran-6-ol (Garg, 1991), has been investigated by X-ray crystallography to determine its three-dimensional structure and to identify the positions of the OCH_3 and OH groups in the structure which were not unequivocally determined by other methods.

Experimental. The neolignan, $C_{20}H_{28}O_6$ (Garg, 1991), crystallizes from a mixture of ethanol and water in the form of transparent needles at room temperature. A crystal with dimensions $0.35 \times 0.20 \times 0.15$ mm was examined. Lattice parameters were obtained from 15 intermediate angle axial reflections in the range $2 < 2\theta < 52°$. 2373 [1720 with $I > 3\sigma(I)$] unique reflections in the range $2\theta \leq 55.36°$ were collected on a CAD-4 diffractometer in the ω–2θ scan mode, using graphite-monochromatized Mo $K\alpha$ radiation. Ranges of h, k and l were -27 to 27, 0 to 8 and 0 to 9 respectively. Data were corrected for Lorentz–polarization effects but not for absorption ($\mu = 0.55$ mm^{-1}). Standard reflections measured every 100 reflections showed no significant variations.

The structure was solved by *SHELXS*86 (Sheldrick, 1986) using 320 E values ($E > 1.2$), which revealed 23 non-hydrogen atoms and the rest were located by successive difference Fourier syntheses. They were refined by least squares (on F) using *SHELX*76 (Sheldrick, 1976). The C(1) y coordinate

Table 1. *Final atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic values of the anisotropic thermal parameters for the non-hydrogen atoms*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
C(1)	0.5680 (3)	0.4091	0.9050 (10)	3.23
O(2)	0.5582 (2)	0.6005 (6)	0.8007 (7)	5.10
C(3)	0.4951 (3)	0.6025 (10)	0.7239 (8)	3.73
C(4)	0.4694 (3)	0.4123 (10)	0.7484 (8)	3.67
O(5)	0.5144 (2)	0.2830 (8)	0.8441 (7)	4.94
C(6)	0.4619 (3)	0.7589 (10)	0.6313 (8)	3.80
C(7)	0.3969 (3)	0.7127 (10)	0.5626 (8)	3.59
C(8)	0.3712 (3)	0.5213 (9)	0.5828 (7)	3.06
C(9)	0.4071 (3)	0.3662 (9)	0.6794 (8)	3.52
C(10)	0.3041 (3)	0.4825 (9)	0.4944 (7)	3.14
C(11)	0.2974 (3)	0.3437 (9)	0.3187 (7)	3.25
C(12)	0.2327 (3)	0.2396 (9)	0.3250 (7)	3.23
C(13)	0.2351 (3)	0.2023 (9)	0.5416 (7)	3.21
O(14)	0.2689 (2)	0.3753 (7)	0.6304 (5)	3.33
C(15)	0.1771 (3)	0.3704 (10)	0.2534 (9)	4.22
C(16)	0.1307 (3)	0.4319 (10)	0.3482 (9)	4.60
C(17)	0.1310 (3)	0.3839 (10)	0.5581 (10)	4.72
C(18)	0.1711 (3)	0.1962 (10)	0.6161 (8)	3.91
C(19)	0.0739 (3)	0.5522 (12)	0.2428 (12)	6.77
C(20)	0.0163 (5)	0.4127 (14)	0.1994 (13)	9.22
C(21)	0.3061 (4)	0.4570 (11)	0.1348 (8)	4.67
O(22)	0.2709 (2)	0.0212 (7)	0.5850 (5)	3.60
O(23)	0.2338 (2)	0.0600 (7)	0.2105 (5)	3.98
O(24)	0.1524 (3)	0.5603 (9)	0.6758 (80)	6.40
C(25)	0.1798 (4)	−0.0670 (11)	0.2021 (90)	5.06
C(26)	0.2766 (4)	−0.0498 (10)	0.7758 (80)	4.69

was held fixed during refinement as required by the space group. The absolute structure was assigned by comparison with the known chirality of similar compounds. All 28 hydrogens were located from a difference Fourier map. Refinement of 26 non-hydrogen atoms with anisotropic thermal parameters and 28 isotropic hydrogen atoms (235 parameters) led to final $R = 0.067$ and $wR = 0.067$, $w = 1/\sigma^2(F_o)$, $\Delta\rho$ peaks 0.35 to -0.3 e Å^{-3}, $(\Delta/\sigma)_{max} = 0.75$. All calculations were carried out on PC/AT(386) and MicroVAXII computers with scattering factors as imbedded in *SHELX*76.

Discussion. Final atomic coordinates for the non-hydrogen atoms are given in Table 1.* The chemical structure with the atom-numbering scheme of the compound is shown in Fig. 1 and the identified positions of the OCH_3 and OH groups, which are anbiguous from other methods, are indicated. Fig. 2 is a *PLUTO* diagram (Motherwell & Clegg, 1978) of the molecule. Table 2 gives bond lengths, bond angles, selected torsion angles and some intermolecular contacts. One interesting feature of this structure

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and intramolecular contacts less than 3·6 Å and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54302 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *bond angles* (°), *selected torsion angles* (°) *and some intermolecular contacts less than* 3·6 Å *with e.s.d.'s in parentheses*

C(1)—O(2)	1·450 (5)	C(12)—C(13)	1·538 (7)
C(1)—O(5)	1·425 (7)	C(12)—C(15)	1·492 (9)
O(2)—C(3)	1·380 (7)	C(12)—O(23)	1·422 (7)
C(3)—C(4)	1·373 (9)	C(13)—O(14)	1·437 (7)
C(3)—C(6)	1·359 (9)	C(13)—C(18)	1·514 (9)
C(4)—O(5)	1·385 (8)	C(13)—O(22)	1·416 (7)
C(4)—C(9)	1·382 (9)	C(15)—C(16)	1·316 (9)
C(6)—C(7)	1·435 (9)	C(16)—C(17)	1·509 (9)
C(7)—C(8)	1·375 (9)	C(16)—C(19)	1·548 (9)
C(8)—C(9)	1·392 (8)	C(17)—C(18)	1·517 (9)
C(8)—C(10)	1·503 (8)	C(17)—O(24)	1·457 (9)
C(10)—C(11)	1·525 (7)	C(19)—C(20)	1·522 (12)
C(10)—O(14)	1·460 (7)	O(22)—C(26)	1·411 (7)
C(11)—C(12)	1·535 (9)	O(23)—C(25)	1·407 (9)
C(11)—C(21)	1·521 (8)		

O(2)—C(1)—O(5)	106·4 (3)	C(11)—C(12)—C(13)	100·1 (4)
C(1)—O(2)—C(3)	106·2 (4)	C(15)—C(12)—O(23)	110·2 (5)
O(2)—C(3)—C(6)	128·0 (6)	C(13)—C(12)—O(23)	115·5 (4)
O(2)—C(3)—C(4)	108·8 (5)	C(13)—C(12)—C(15)	110·8 (5)
C(4)—C(3)—C(6)	123·1 (6)	C(12)—C(13)—O(22)	107·3 (4)
C(3)—C(4)—C(9)	121·9 (6)	C(12)—C(13)—C(18)	115·1 (5)
C(3)—C(4)—O(5)	110·4 (5)	C(12)—C(13)—O(14)	105·2 (4)
O(5)—C(4)—C(9)	127·7 (6)	C(18)—C(13)—O(22)	112·5 (5)
C(1)—O(5)—C(4)	105·9 (4)	O(14)—C(13)—O(22)	109·5 (4)
C(3)—C(6)—C(7)	115·1 (6)	O(14)—C(13)—C(18)	106·9 (4)
C(6)—C(7)—C(8)	122·1 (6)	C(10)—O(14)—C(13)	110·9 (4)
C(7)—C(8)—C(10)	118·5 (5)	C(12)—C(15)—C(16)	127·7 (6)
C(7)—C(8)—C(9)	120·6 (6)	C(15)—C(16)—C(19)	119·7 (6)
C(9)—C(8)—C(10)	121·0 (5)	C(15)—C(16)—C(17)	121·2 (6)
C(4)—C(9)—C(8)	117·1 (6)	C(17)—C(16)—C(19)	119·0 (5)
C(8)—C(10)—O(14)	110·0 (4)	C(16)—C(17)—O(24)	110·9 (5)
C(8)—C(10)—C(11)	115·1 (5)	C(16)—C(17)—C(18)	111·5 (5)
C(11)—C(10)—O(14)	104·1 (4)	C(18)—C(17)—O(24)	110·9 (5)
C(10)—C(11)—C(21)	113·2 (5)	C(13)—C(18)—C(17)	112·5 (5)
C(10)—C(11)—C(12)	103·5 (4)	C(16)—C(19)—C(20)	110·6 (6)
C(12)—C(11)—C(21)	116·2 (5)	C(13)—O(22)—C(26)	117·4 (4)
C(11)—C(12)—O(23)	105·7 (5)	C(12)—O(23)—C(25)	116·0 (5)
C(11)—C(12)—C(15)	114·2 (5)		

C(21)—C(11)—C(12)—O(23)	75·6 (6)	C(18)—C(13)—O(22)—C(26)	−49·0 (7)
C(11)—C(12)—O(23)—C(25)	177·2 (5)	C(8)—C(10)—C(11)—C(12)	150·6 (5)
C(11)—C(12)—C(13)—O(22)	−81·8 (5)	O(14)—C(13)—O(22)—C(26)	69·7 (6)
C(15)—C(12)—O(23)—C(25)	−59·0 (6)	C(8)—C(10)—C(11)—C(21)	−82·8 (6)
C(13)—C(12)—O(23)—C(25)	67·5 (6)	O(22)—C(13)—C(18)—C(17)	−176·1 (5)
O(23)—C(12)—C(13)—O(22)	31·2 (6)	O(14)—C(10)—C(11)—C(21)	156·7 (5)
O(23)—C(12)—C(13)—C(18)	−94·8 (6)	C(12)—C(15)—C(16)—C(19)	−174·7 (6)
O(23)—C(12)—C(13)—O(14)	147·8 (4)	C(15)—C(16)—C(19)—C(20)	120·3 (8)
O(23)—C(12)—C(15)—C(16)	121·7 (7)	C(15)—C(16)—C(17)—C(18)	−23·9 (9)
C(7)—C(8)—C(10)—C(11)	108·4 (6)	C(10)—C(11)—C(12)—O(23)	−159·7 (4)
C(7)—C(8)—C(10)—O(14)	−134·5 (5)	C(15)—C(16)—C(17)—O(24)	100·3 (7)
C(12)—C(13)—O(22)—C(26)	−176·6 (5)	C(17)—C(16)—C(19)—C(20)	−76·6 (8)
C(9)—C(8)—C(10)—C(11)	−70·3 (7)	C(19)—C(16)—C(17)—O(24)	−80·8 (7)
C(9)—C(8)—C(10)—O(14)	46·8 (7)	O(24)—C(17)—C(18)—C(13)	−77·2 (7)
O(22)—C(13)—O(14)—C(10)	97·7 (5)	C(19)—C(16)—C(17)—C(18)	155·0 (6)
C(8)—C(10)—O(14)—C(13)	−131·9 (5)		

O(5)···C(6)(−x + 1, y − ½, −z + 1)	3·446	O(14)···C(21)(x, y, z + 1)	3·581
C(7)···O(22)(x, y + 1, z)	3·361	O(23)···C(26)(x, y, z − 1)	3·372

molecular short contacts. The aromatic heterocyclic ring of the molecule is nearly at right angles to the rest of the structure.

Fig. 3 shows the molecular packing viewed down the *b* axis. It is found that cleavage is possible along the (001) planes parallel to the *ab* planes. Alternate hydrophilic and hydrophobic zones are found in the packing pattern parallel to the *b* axis. It is apparent
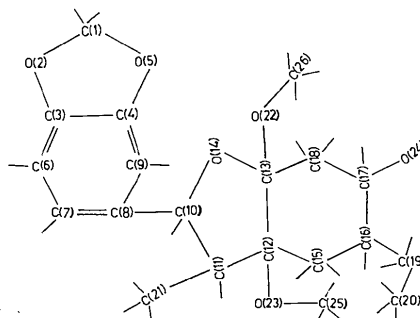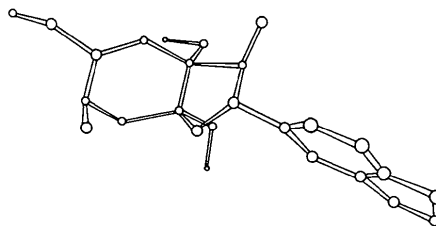

Fig. 1. Chemical diagram of the molecule.
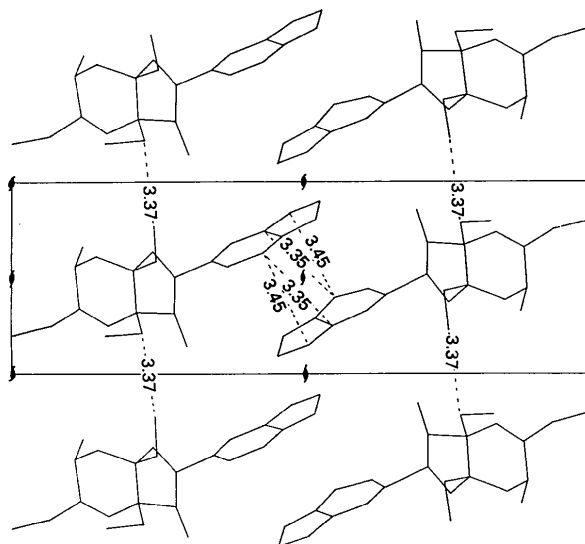

Fig. 2. *PLUTO* diagram of the molecule.

Fig. 3. Packing diagram of the molecule projected down the *b* axis. Distances are given in Å.

is that the cyclohexane ring formed by C(12), C(13), C(18), C(17), C(16) and C(15) assumes a half-chair form with atoms C(15) [−0·062 (7) Å] and C(18) [0·594 (7) Å] being on opposite sides from the least-squares plane formed by the atoms C(12), C(13), C(16) and C(17). It is observed that the thermal parameters (Table 1) of the peripheral atoms C(19), C(20) and O(24) are relatively high whereas those of C(25), O(22), C(26), O(23) and C(21) have normal values because they are mainly stabilized by intra-

that the functional OH group of the compound is involved in an intricate network of hydrogen bonds in the crystal.

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Raspacionin, a New Tetracyclic Triterpenoid from the Sponge Raspaciona aculeata: a Structure Containing Disordered Solvent

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Abstract. 6-[2-(3-Hydroxy-2,2,5a-trimethyl-7-methyl-enedecahydro-1-benzoxepin-6-yl)ethyl]-2,2,5a,7-tetramethyldecahydro-1-benzoxepin-3,7-diyl diacetate, $C_{34}H_{56}O_7$, $M_r = 576.8$, orthorhombic, $P2_12_12_1$, $a = 7.117$ (1), $b = 19.757$ (2), $c = 27.156$ (4) Å, $V = 3819$ (1) Å^3, $Z = 4$, $D_x = 1.003$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, μ(Cu $K\alpha$) = 0.52 mm^{-1}, $F(000) = 1264$, room temperature, final $R = 0.050$ for 2839 reflections with $I \geq 2.5\sigma(I)$ and 371 variables (not including solvent). The structural analysis revealed a new squalene-derived triterpenoid skeleton, characterized by two trans-perhydrobenzoxepine systems linked by an equatorial ethylene bridge. In the crystal, raspacionin molecules are connected by a hydrogen bond between the hydroxyl group and a carbonyl O atom and form channels parallel to a, filled with partially disordered solvent.

Introduction. Marine organisms are a very rich source of substances with interesting pharmacological or biological activities, often correlated to unusual structural features. As part of a program (Cimino, Gavagnin, Sodano, Puliti, Mattia &

Mazzarella, 1988; Mattia, Mazzarella, Puliti, Riccio & Minale, 1988; Cimino, Mattia, Mazzarella, Puliti, Scognamiglio, Spinella & Trivellone 1989; Puliti, De Rosa, Mattia & Mazzarella, 1990) on the structural and biological investigation of marine metabolites, we now present the crystal structure of raspacionin (1), the main metabolite of the Mediterranean sponge Raspaciona aculeata.

(1)
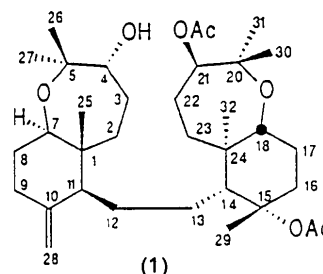
The tetracyclic skeleton of (1), which is structurally related to sipholane and siphonellane metabolites (Carmely & Kashman, 1983; Carmely, Loya & Kashman, 1983), presents a unique feature in nature