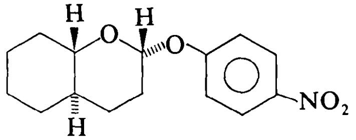

(III)

The extra constraint of the third ring probably has only a minor effect on the bond lengths at the acetal centre; certainly the outer pair of C—O lengths of the C—O—C—O—C system are not significantly different from those in the bicyclic acetals (I) and (III). The low acetal bond angle [O(10)—C(10a)—O(1) = 105·9°] is close to that observed for the two equatorial compounds (I, X = H, NO$_2$) and in the range expected for an acetal adopting the *gauche,trans* conformation (Gorenstein & Kar, 1977).

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Structure of the Hydrogen Bromide Adduct of Spicatine, a Sesquiterpenoid Lactone

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Abstract. C$_{27}$H$_{33}$BrO$_{10}$, $P2_1$, a = 10·415 (5), b = 16·093 (2), c = 8·122 (3) Å, β = 96·96°, Z = 2, V = 1350 Å^3, $\rho_{\text{X-ray}}$ = 1·47 Mg m^{-3}, μ(Cu $K\alpha$) = 2·82 mm^{-1}. The final R value is 0·036 for 2401 independent observed reflexions. The seven-membered ring adopts a twist-chair conformation with the approximate C_2 axis through C(8). The γ-lactone ring has a twist conformation and is *trans*-fused to the cycloheptane ring, while the cyclopentene ring is a *cis*-fused C(1) envelope.

Introduction. Spicatine, C$_{22}$H$_{32}$O$_{10}$, is isolated both from *Liatris spicata* (L.) Kuntze and from *L. pycnostachya* (Michx.) Kuntze (Herz, Poplawski & Sharma, 1975). It is a sesquiterpene lactone of the guainolide type. Studies of this compound by spectroscopic and chemical methods were unsuccessful in determining the complete structure (Karlsson, Pilotti, Wiehager, Wahlberg & Herz, 1975). An X-ray analysis of the hydrogen bromide adduct of spicatine was therefore undertaken.

Three-dimensional data were collected from a parallelepiped crystal, with a volume of approximately 0·002 mm^3, using a computer-controlled Philips PW 1100 diffractometer [graphite monochromator, Cu $K\alpha$ radiation, $\theta/2\theta$ scan and stationary background measurements at ±0·75° (θ) from the peak maxima]. During the period of data collection, three reference reflexions (measured every 90 min) showed a linear intensity decrease with time of approximately 5%. Intensities were measured for all independent reflexions with $2\theta \leq 140°$. Only the 2401 most significant reflexions [$I_{\text{net}} \geq 4\sigma(I_{\text{net}})$] were used in the least-squares refinements.

Lorentz and polarization factors were applied, but no correction for absorption was made. Lattice constants were obtained from the least-squares refinement of the angular coordinates for 25 reflexions.

The structure was solved by a combination of a heavy-atom technique and a direct method. A Patterson map revealed the x and z coordinates of the Br atom. The y coordinate was fixed at 0·25 and was held fixed throughout the computations. Three cycles of

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least-squares refinement gave an R value of 0·37. The Br position was used to calculate structure factors. Phases for 28 reflexions with $|F_{\text{calc}}| \geq 0{\cdot}55|F_{\text{obs}}|$ were used in the starting set together with two reflexions with variable starting phases. These phases were extended and refined by the use of a modified version of the *MULTAN* direct phase-determination procedure (Germain, Main & Woolfson, 1970). The calculated E map unavoidably contained a false mirror plane through the Br atom. Inclusion of 12 peaks belonging to the ring skeleton and to one of the side chains finally suppressed the false symmetry. Repeated Fourier syntheses revealed the remaining non-hydrogen atoms. The structure was refined by a least-squares procedure using the weighting scheme of Hughes (1941). The positions of the 33 H atoms were deduced partly from a difference synthesis (29), and partly from chemical considerations (4). The H atoms were included in the refinement with fixed isotropic parameters (equal to those of their parent atom) and fixed positional coordinates. The final R value was 0·036.[*]

The atomic scattering factors were those listed in *International Tables for X-ray Crystallography* (1962) for C and O, that given by Hanson, Herman, Lea & Skillman (1964) for Br, and that of Stewart, Davidson & Simpson (1965) for H. Table 1 lists the final coordinates for the non-hydrogen atoms. Positional parameters of the H atoms are given in Table 2.

Discussion. The structure established by this analysis is shown in Fig. 1. Bond lengths and bond angles involving the non-hydrogen atoms and the numbering system used are given in Fig. 2. Standard deviations in bond lengths and angles are estimated to be 0·005–0·008 Å and 0·3–0·5° respectively. C–H distances vary in the range 0·73–1·12 Å.

Table 1. *Positional parameters* ($\times 10^4$) *for the non-hydrogen atoms with e.s.d.'s in parentheses*

	x	*y*	*z*
Br	11304 (1)	2500	2648 (1)
C(1)	10490 (4)	3857 (3)	6908 (5)
C(2)	9995 (4)	4689 (3)	6119 (6)
C(3)	9841 (5)	5205 (3)	7604 (7)
C(4)	9797 (5)	4757 (3)	8949 (6)
C(5)	9951 (4)	3833 (3)	8603 (5)
C(6)	8663 (4)	3359 (3)	8550 (5)
C(7)	8831 (4)	2409 (3)	8409 (5)
C(8)	8657 (4)	2081 (3)	6637 (5)
C(9)	9136 (4)	2657 (3)	5340 (5)
C(10)	10451 (4)	3083 (3)	5776 (5)
C(11)	7960 (4)	2073 (3)	9589 (6)
C(12)	7652 (5)	2770 (3)	10661 (6)
O(13)	8120 (4)	3486 (3)	10107 (4)
O(14)	8721 (3)	4541 (2)	5125 (4)
C(15)	8199 (5)	5190 (3)	4244 (6)
O(16)	8741 (5)	5854 (2)	4271 (5)
C(17)	6945 (6)	4963 (4)	3284 (7)
C(18)	9649 (7)	5081 (4)	10664 (8)
O(19)	11370 (3)	2516 (3)	6627 (4)
C(20)	10963 (5)	3391 (3)	4185 (6)
C(21)	7500 (6)	1316 (4)	9786 (8)
O(22)	7076 (4)	2764 (3)	11863 (5)
O(23)	7301 (3)	1976 (2)	6078 (4)
C(24)	6907 (4)	1237 (3)	5431 (6)
C(25)	5567 (4)	1289 (3)	4551 (6)
C(26)	4852 (4)	2088 (3)	4652 (6)
O(27)	4581 (3)	2193 (2)	6366 (5)
C(28)	4459 (6)	2957 (4)	6895 (7)
C(29)	4256 (5)	3005 (4)	8685 (7)
C(30)	4114 (5)	2208 (4)	9608 (7)
O(31)	2856 (4)	1907 (4)	9504 (5)
O(32)	7576 (4)	615 (3)	5573 (8)
C(33)	5136 (5)	620 (3)	3679 (6)
C(34)	3846 (6)	527 (4)	2657 (7)
O(35)	4504 (8)	3558 (3)	6022 (7)
C(36)	4170 (6)	3747 (4)	9347 (7)
C(37)	3910 (8)	3952 (5)	11088 (9)

Table 2. *Positional parameters* ($\times 10^3$) *for the hydrogen atoms*

	x	*y*	*z*
H(C1)	1144	388	718
H(C2)	1058	491	535
H(C3)	983	565	766
H(C5)	1059	355	949
H(C6)	804	353	769
H(C7)	975	238	899
H(C8)	916	154	682
H1(C9)	907	234	425
H2(C9)	845	305	495
H1(C17)	702	449	236
H2(C17)	616	483	402
H3(C17)	667	547	264
H1(C18)	809	480	1111
H2(C18)	1057	492	1142
H3(C18)	951	570	1064
H(O19)	1135	204	595
H1(C20)	1186	362	446
H2(C20)	1038	372	376
H1(C21)	775	87	901
H2(C21)	710	120	90
H1(C26)	547	247	431
H2(C26)	401	211	406
H1(C30)	456	226	1083
H2(C30)	478	185	949
H(O31)	230	206	834
H(C33)	582	19	365
H1(C34)	381	62	346
H2(C34)	407	58	152
H3(C34)	381	−9	269
H1(C36)	417	434	861
H1(C37)	489	391	1152
H2(C37)	324	431	1162
H3(C37)	363	339	1146

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33941 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England

Table 3. *Selected torsion angles* (°)

C(5)–C(1)–C(2)–O(14)	−90	C(2)–C(3)–C(4)–C(18)	180	C(11)–C(7)–C(8)–C(9)	156
C(10)–C(1)–C(2)–C(3)	165	C(3)–C(4)–C(5)–C(6)	−105	C(11)–C(7)–C(8)–O(23)	39
C(10)–C(1)–C(2)–O(14)	48	C(18)–C(4)–C(5)–C(1)	−163	C(6)–C(7)–C(11)–C(21)	165
C(2)–C(1)–C(5)–C(6)	95	C(18)–C(4)–C(5)–C(6)	76	C(8)–C(7)–C(11)–C(12)	−143
C(10)–C(1)–C(5)–C(4)	−162	C(1)–C(5)–C(6)–O(13)	−171	C(8)–C(7)–C(11)–C(21)	38
C(2)–C(1)–C(10)–C(9)	−78	C(4)–C(5)–C(6)–C(7)	−173	O(23)–C(8)–C(9)–C(10)	164
C(2)–C(1)–C(10)–O(19)	159	C(4)–C(5)–C(6)–O(13)	−57	C(8)–C(9)–C(10)–O(19)	41
C(2)–C(1)–C(10)–C(20)	44	C(5)–C(6)–C(7)–C(11)	138	C(8)–C(9)–C(10)–C(20)	162
C(5)–C(1)–C(10)–O(19)	−70	O(13)–C(6)–C(7)–C(8)	148	O(19)–C(10)–C(20)–Br	58
C(5)–C(1)–C(10)–C(20)	175	C(5)–C(6)–O(13)–C(12)	−137	C(7)–C(11)–C(12)–O(22)	−173
O(14)–C(2)–C(3)–C(4)	97	C(6)–C(7)–C(8)–O(23)	−82	C(21)–C(11)–C(12)–O(13)	−174
				C(21)–C(11)–C(12)–O(22)	6

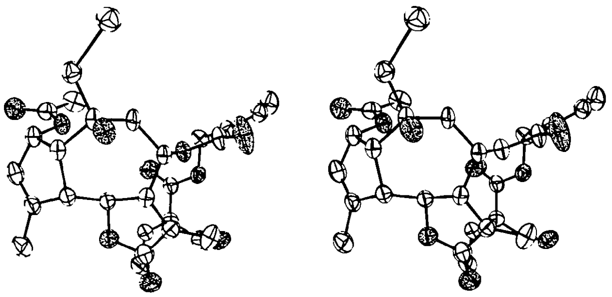

Fig. 1. A stereoscopic view of the molecule. O atoms are shaded.

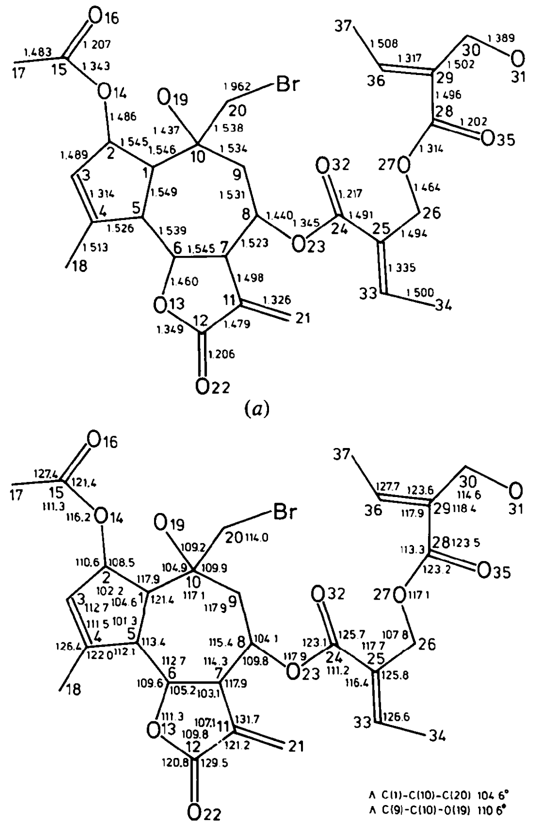

Fig. 2. (*a*) Bond distances (Å) and numbering scheme. (*b*) Bond angles (°).

The endocyclic torsion angles of the title compound are given in Fig. 3; some other torsion angles are listed in Table 3. A comparison of the endocyclic torsion angles measured in the seven-membered ring with the values expected for the boat, twist-boat, chair and twist-chair conformations of cycloheptane (Hendrickson, 1961) reveals that this ring is best described as a twist-chair with the approximate C_2 axis through C(8). The match, however, is not perfect. The approximate twist-chair conformation is also observed in other sesquiterpenoid cycloheptane rings, although the position of the C_2 axis differs. Compounds having the C_2 axis through C(8) are centaurepensin (Hewson, Pettersen & Kennard, 1972) and euparotin bromoacetate (McPhail & Sim, 1973); the same axis through C(5) is observed for 2-bromodihydroisophoto-α-santonic lactone acetate (Asher & Sim, 1965) and solstitialin (Thiessen & Hope, 1970) and, finally, the axis through C(9) for 5α-hydroxy-4α*H*,1,6,11β*H*-guai-2,10(15)-dien-6,12-olide (Ito, Shimizu, Fujimoto & Tatsuno, 1978).

The γ-lactone ring is *trans*-fused, and the cyclopentene ring is *cis*-fused. Puckering parameters for these two rings, calculated according to Cremer & Pople (1975), show that the γ-lactone ring has a twist conformation ($q = 0{\cdot}18$ Å, $\varphi = -86°$) with the C_2 axis through C(12), and the cyclopentene ring is a C(1) envelope ($q = 0{\cdot}28$ Å, $\varphi = -2°$).

The packing arrangement is shown in Fig. 4. The molecules appear to be held in the extended crystal structure by hydrogen bonds of lengths 2·77 Å between

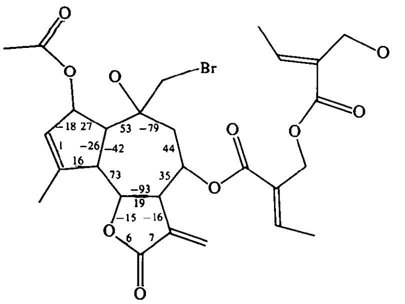

Fig. 3. Endocyclic torsion angles (°).

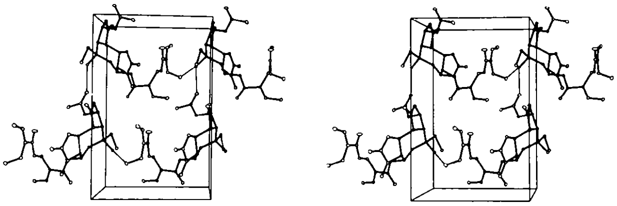

Fig. 4. Packing diagram for the hydrogen bromide adduct of spicatine with **a** horizontal, **b** vertical and **c** upwards, perpendicular to the plane of the paper.

O(19) and O(16)^{i}, and 2·82 Å between O(31) and O(19)^{ii} [(i) $2-x$, $y-\frac{1}{2}$, $1-z$; (ii) $x-1$, y, z]; H(O19)—O(16)^{i} = 1·91 Å, O(19)—H(O19)—O(16)^{i} = 150°, H(O31)—O(19)^{ii} = 1·76 Å and O(31)—H(O31)—O(19)^{ii} = 168°. All intermolecular C—O distances are longer than 3·25 Å; Br—O(31)^{iii} = 3·32 Å [(iii) $x+1$, y, $z-1$]. The intramolecular distance Br—O(19) is 3·22 Å.

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Structure of 1,2-Bis(1,3,7-trimethyl-6-lumazinyl)-*threo*-1,2-butanediol

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Abstract. $C_{22}H_{26}N_8O_6$, M_r = 498·56, monoclinic, $C2/c$, a = 17·840 (8), b = 14·860 (8), c = 18·121 (8) Å, β = 107·98 (1)°, V = 4569·3 Å^3, Z = 8, D_x = 1·45 Mg m^{-3}. The molecule consists of two lumazine derivatives linked together through a butanediol group. The central C—C bond of the butanediol group was found to be much longer than usual C—C bonds; this explains the unusual properties of this compound.

Introduction. During electrochemical studies with various 6- and 7-acyl-1,3-dimethyllumazines it was found that 6-acetyl-1,3,7-trimethyllumazine (I) dimerizes in slightly alkaline solution to the appropriate pinacol in a one-electron reduction process. This reaction resembles those in the literature known as electrohydrodimerizations of aromatic aldehydes and ketones (Fry, 1972) and led to only one stereochemical isomer which was believed, according to analogous findings (Fry, 1972), to be a *threo* form. Furthermore, this molecule, 1,2-bis(1,3,7-trimethyl-6-lumazinyl)-*threo*-1,2-butanediol (II), showed unusual properties due to some steric strain along the C—C glycol bond which is extremely sensitive to chemical modifications. Autoxidation takes place in alcoholic solution back to the starting material (I) and heating above the melting