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A typical non-direct process in the application of direct methods: structure determination of a derivative of the natural diterpene jativatriol.

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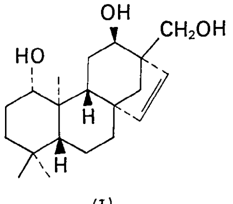
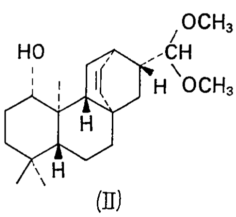
ent-1β-Hydroxy-16*S*-atis-13-en-17-al dimethyl acetal (II) crystallizes in the monoclinic system, space group $P2_1$. There are two molecules of $C_{22}H_{36}O_3$ in a unit cell of dimensions $a = 11{\cdot}923$ (2), $b = 13{\cdot}791$ (3), $c = 6{\cdot}173$ (1) Å and $\beta = 97{\cdot}06$ (3)°. The calculated density, ϱ_x, is 1·110 g cm^{-3}. This diterpene is a minor product in the reaction of jativatriol (I) (Carstenn-Lichterfelde, Panizo, Quesada, Rodriguez, Valverde, Ayer & Ball, *Canad. J. Chem.* (1975), **53**, 1172–1175) with hydrochloric acid and because of the lack of material an X-ray analysis was undertaken.



(I)



(II)

The most important aspect of this work relates to the difficulty encountered in solving the crystal structure by direct methods, and to the strategy used to solve the problem.

Introduction

An approximately cubic crystal of edge ~0·4 mm, cut out of an irregular non-transparent crystalline fragment of material, was used for data collection. All 3059 unique reflexions with $\sin\theta/\lambda < 0{\cdot}705$ were collected with monochromated Mo radiation on a fully automated four-circle diffractometer. The ω–2θ scan mode was used for the intensity measurements. After correction for Lorentz, polarization and background effects, 1782 reflexions were judged as observed. The crystal structure determination was carried out with the tangent formula and anisotropic least-squares refinement. Hydrogen atoms were located in a difference map. The conventional discrepancy indices are 0·067 for the observed reflexions and 0·086 for all reflexions. The X-RAY 70 System (Stewart, Kundell & Baldwin, 1970) was used for

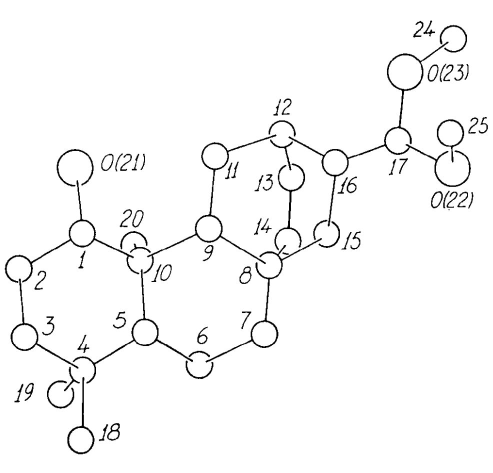


Fig. 1. A computer-generated perspective drawing of the $C_{22}H_{36}O_3$ jativatriol derivative.

Table 1. *Fractional coordinates* (×10^4) *and thermal parameters* (×10^3)

Anisotropic temperature factors are expressed as $\exp(-2\pi^2\sum U_{ij}a_i^*a_j^*h_ih_j)$. Average standard deviations on the last digits are: 5 for x and y, 10 for z and 2 for thermal parameters.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1140	4551	831	37	48	49	−2	−2	−4
C(2)	1141	3446	760	46	51	75	−11	−5	−9
C(3)	2289	3062	296	63	53	61	6	1	−10
C(4)	3267	3398	1979	47	48	55	5	3	−1
C(5)	3195	4521	2201	35	43	48	1	0	5
C(6)	4146	4950	3825	39	56	72	4	−13	2
C(7)	4259	6025	3388	33	53	97	−3	−8	−2
C(8)	3163	6592	3508	34	45	55	−2	−1	2
C(9)	2123	6086	2180	35	41	40	−2	2	4
C(10)	2026	4969	2598	33	44	35	2	3	4
C(11)	1051	6693	2484	35	47	55	1	6	2
C(12)	1378	7629	3790	46	46	57	4	16	1
C(13)	2007	7339	5929	73	57	46	−9	10	−7
C(14)	2902	6793	5815	68	52	48	−10	−13	3
C(15)	3265	7603	2411	41	48	69	−8	9	2
C(16)	2177	8206	2444	43	43	47	−4	5	−2
C(17)	2396	9224	3374	53	47	60	−2	−2	−4
C(18)	4361	3139	1015	58	65	90	15	19	−7
C(19)	3267	2847	4136	67	53	87	7	−2	17
C(20)	1696	4755	4878	54	51	41	−1	12	6
O(21)	30	4868	1177	29	69	81	−1	−4	−11
O(22)	1368	9733	2933	48	49	78	1	11	−4
O(23)	3294	9719	2529	47	53	107	−8	5	−4
C(24)	3165	9891	255	90	68	118	1	53	13
C(25)	1337	10607	4141	81	57	118	−2	39	−21

crystallographic calculations. Final atomic parameters are in Table 1, and Fig. 1 shows the X-ray model.*

Special attention will be paid in this section to the method of structure determination. It is well known that the lower the symmetry present, the slower is the phase-expansion process. This is one reason why structures in space groups such as $P1$ and $P2_1$ are often difficult to solve by direct methods. The present structure raised considerable difficulties. Initial phases were assigned with the multisolution tangent formula approach of Main, Woolfson, Declerq & Germain (1974). Normalization of E's was done with a Wilson plot assuming random atomic distribution. A slight renormalization by parity groups was also performed. Many E maps corresponding to the best sets for the 100, 150, 200 and 300 largest E's were computed. All of them presented the same discouraging shape: a continuous two-dimensional net of hexagons, perpendicular to the short 6·17 Å axis, resembling 'chicken wire'. Too many initial structural fragments were thus indicated. In order to obtain better maps two procedures were carried out simultaneously, attempting (*a*) to optimize the CONVERGE map by changing the starting reflexions and eliminating some reflexions near the bottom of the map which had a reliability value $\alpha_h = 0$; (*b*) to treat the 'chicken wire' effect as though it were produced by the so-called amplitude error (Bürgi & Dunitz, 1971). This error affects some special molecules (those producing a high degree of vector superposition), for which structure factors with amplitudes above a certain limit, *e.g.* the 200 largest E's, do not distribute randomly in reciprocal space, but tend to form a supercell corresponding to those more repetitive interatomic vectors. Consequently the Fourier transform of that E set is modulated by a subcell producing an endless 'chicken wire' effect. The spatial distribution observed for the largest E's of this compound indicated amplitude error. It was partially corrected by eliminating the 50 largest E's (those mostly giving rise to the error) for each E map calculation.

Both procedures gave still too many molecular fragments, although some of them could be eliminated by steric considerations. With E maps from several phase sets, about 15 initial molecular fragments were selected, each containing ~30% of the molecule. Refinement of these fragments by Karle's (1968) procedure using 400 E's failed, as the new E maps were almost identical with the previous ones. Structure factor calculations plus difference maps also gave no new information. Finally a 'hard' least-squares refinement of one fragment moved the model enough to give new atomic information in the next F_{obs} map, and the structure was solved. Only unit-weighted reflexions, with $\sin\theta/\lambda < 0{\cdot}4$, were used for the (hard) overall isotropic least-squares refinement, in which only the positional parameters were varied. Only reflexions with $F_{cal} > 0{\cdot}5\ F_{obs}$ were used for the F_{obs} maps.

The same difficulties in the application of direct methods were also recently encountered in the analysis of a $P1$ terpenoid by Tan, Djerassi, Fayos & Clardy (1975).

Discussion

The results of this crystal structure determination have little further chemical interest because the molecular skeleton found is identical with that reported previously for the natural diterpene isosideritol by Carrascal, Rodriguez, Valverde & Fayos (1975). Both molecules show a bending effect produced by repulsion involving the α-substituents. Representative distances in this compound for these repulsions are 3·30 Å for C(19)–C(20), 3·18 Å for C(20)–C(14) and 3·11 Å for C(13)–C(17), those for isosideritol being 3·33, 3·12 and 3·10 Å, respectively. Standard deviations for both are ~0·01 Å. Only one short intermolecular contact of 2·87 (1) Å is present in this jativatriol derivative, corresponding to the hydrogen bond O(21)–H···O(22).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31509 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.