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Vaginatin, $C_{20}H_{30}O_4$

BY ROBERT B. BATES* AND ROBERT E. KLENCK

Department of Chemistry, University of Arizona, Tucson, Arizona 85721, *USA*

AND C. K. MESTA AND S. K. PAKNIKAR

Postgraduate Centre, University of Bombay, Susheela, Panaji, Goa 403001, *India*

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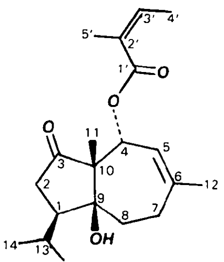
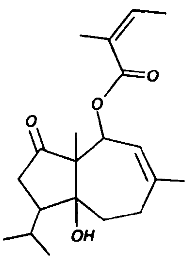
Abstract. $M_r = 334{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 12{\cdot}993\,(7)$, $b = 7{\cdot}979\,(3)$, $c = 18{\cdot}64\,(1)$ Å, $U = 1932\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}15$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}084$ mm^{-1}, $F(000) = 728$, $T = 293$ K. Final $R = 0{\cdot}055$ for 1446 observed reflections. The proposed constitution of this sesquiterpenoid from *Selinum vaginatum* was confirmed, and the relative configurations of the four chiral centers were established. It appears to be a biological oxidation product of carotol.



(I)



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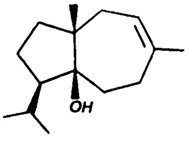

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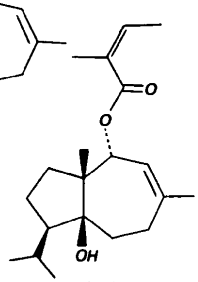

(IV)

Introduction. Vaginatin was isolated from *Selinum vaginatum* (Mesta, Paknikar & Bhattacharyya, 1968) and the partial structure (II) was assigned (Rajendran, Paknikar, Trivedi & Bhattacharyya, 1978). A crystal-structure analysis was performed to check the constitution and to establish the stereochemistry.

Experimental. Crystal dimensions $0{\cdot}3 \times 0{\cdot}3 \times 0{\cdot}3$ mm. Syntex $P2_1$ four-circle diffractometer. Cell constants from 15 reflections with $5 \leq 2\theta \leq 25°$. No absorption correction. $2\theta_{\max} = 50°$. Range of *hkl*: 0–15, 0–9, 0–22. Three check reflections collected after every 100 data points showed no appreciable crystal decay. 1446 of 2014 reflections with $I > 3\sigma(I)$ used in F^2 refinement $R_{\text{int}} = 0{\cdot}055$. Structure solved by *MULTAN*80 (Main *et al.*, 1980) using 150 highest E values; all 24 non-H atoms found in first E map. Refinement of non-H atoms with isotropic temperature factors gave $R = 0{\cdot}125$, refinement with anisotropic temperature factors led to $R = 0{\cdot}091$, final refinement (217 parameters) was of non-H atoms after adding H atoms in calculated positions with isotropic temperature factors; $wR = 0{\cdot}067$, $S = 2{\cdot}6$, weighting scheme of Corfield, Doedens & Ibers (1967), with $p = 0{\cdot}04$. $(\Delta/\sigma)_{\max} = 0{\cdot}11$. $\Delta\rho = -0{\cdot}3$–$0{\cdot}3$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1962). Least-squares refinement program *NUCLS* (Doedens & Ibers, 1967), plotter program *ORTEP* (Johnson, 1965).

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* To whom correspondence should be addressed.

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Discussion. Fig. 1 depicts the final bond lengths and angles for vaginatin (I), Table 1 shows the final atomic positional parameters, and a single molecule and the unit cell are shown in Figs. 2 and 3 respectively.* The proposed constitution is confirmed and the relative configurations are clearly as shown. The absolute configuration shown was not determined crystallographically, but was assigned by analogy with carotol (III) (Bates, Green & Sneath, 1969) and lasidiol angelate (IV) (Wiemer & Ales, 1981). Vaginatin (I) appears from its structure to be formed in nature by the oxidation of (III), probably *via* (IV).

The five-membered ring adopts an envelope conformation (Bucourt, 1974) with C(1) at the flap [torsion angles (e.s.d.'s 0·4–0·7°): C(1)–C(2)–C(3)–C(10) = 27, C(2)–C(3)–C(10)–C(9) = −5, C(3)–C(10)–C(9)–C(1) = −20, C(10)–C(9)–C(1)–C(2) = 36, C(9)–C(1)–C(2)–C(3) = −39°].

The cycloheptene portion of the molecule does not adopt any of the symmetric conformations; the torsion angles are: C(4)–C(5)–C(6)–C(7) = −5, C(5)–C(6)–C(7)–C(8) = −19, C(6)–C(7)–C(8)–C(9) = 75, C(7)–C(8)–C(9)–C(10) = −55, C(8)–C(9)–C(10)–C(4) = −26, C(9)–C(10)–C(4)–C(5) = 75, and C(10)–C(4)–C(5)–C(6) = −39°.

The isopropyl group has a staggered conformation about C(1)–C(13) with C(2) between the isopropyl methyl groups [C(2)–C(1)–C(13)–C(14) = −79, C(2)–C(1)–C(13)–C(15) = 46°]. The long side chain starts with a staggered arrangement about C(4)–O(4) with C(1′) approximately *anti* to C(10) [C(1′)–O(4)–C(4)–C(10) = −158°]. The rest of the side chain is

Table 1. *Final atomic positional parameters* (×10⁴) *and isotropic thermal parameters for the non*-H *atoms of vaginatin* (I) *with e.s.d.'s in parentheses*

Temperature factors are of the form $\exp[-B(\sin^2\theta)/\lambda^2]$.

	x	y	z	B(Å²)
O(3)	9371 (3)	7817 (5)	5803 (2)	5·7 (2)
O(4)	7988 (2)	4410 (4)	6226 (1)	3·4 (1)
O(9)	6292 (3)	8038 (4)	4976 (2)	5·1 (2)
O(1′)	9223 (3)	2457 (5)	6242 (2)	5·1 (2)
C(1)	6735 (3)	7743 (6)	6230 (2)	3·2 (2)
C(2)	7713 (4)	8821 (7)	6177 (3)	4·4 (2)
C(3)	8431 (4)	7745 (6)	5789 (3)	4·2 (2)
C(4)	8226 (3)	4739 (6)	5480 (2)	3·4 (2)
C(5)	7861 (4)	3368 (6)	4982 (2)	3·8 (2)
C(6)	6950 (4)	3191 (7)	4691 (2)	4·1 (2)
C(7)	6011 (4)	4261 (6)	4831 (3)	5·0 (3)
C(8)	6006 (3)	5306 (6)	5513 (3)	3·5 (2)
C(9)	6680 (3)	6879 (6)	5511 (2)	3·5 (2)
C(10)	7841 (3)	6518 (6)	5314 (3)	3·5 (2)
C(11)	8115 (4)	6913 (7)	4534 (2)	4·5 (2)
C(12)	6763 (5)	1815 (7)	4157 (3)	6·1 (3)
C(13)	5778 (4)	8682 (7)	6510 (3)	4·7 (3)
C(14)	5845 (5)	8838 (9)	7337 (3)	6·8 (3)
C(15)	5587 (5)	10396 (8)	6177 (4)	6·5 (3)
C(1′)	8546 (4)	3199 (6)	6555 (3)	3·3 (2)
C(2′)	8215 (4)	2934 (7)	7295 (2)	3·5 (2)
C(3′)	8735 (5)	1922 (8)	7730 (3)	5·3 (3)
C(4′)	9676 (5)	910 (9)	7601 (4)	6·9 (4)
C(5′)	7279 (6)	3877 (10)	7533 (3)	7·6 (4)

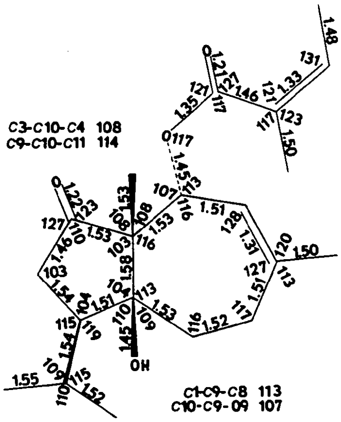

Fig. 1. Bond lengths (Å) and angles (°) for vaginatin (I). E.s.d.'s in bond lengths are 0·005–0·009 Å, and in angles 0·4–0·6°.

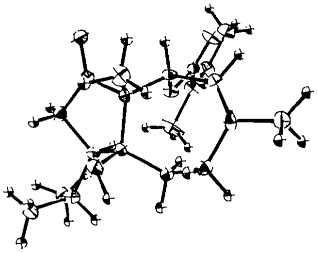

Fig. 2. Perspective view of vaginatin (I), with 50% probability thermal ellipsoids for non-H atoms and spheres for H atoms.

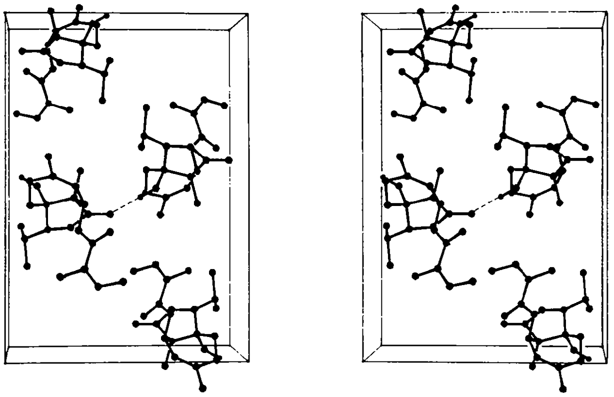

Fig. 3. Stereoscopic illustration of a unit cell of (I), **a** horizontal, **c** vertical. The dotted line indicates an intermolecular hydrogen bond.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38743 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

approximately planar [C(4)—O(4)—C(1′)—C(2′) = −178, O(4)—C(1′)—C(2′)—C(3′) = −173, C(1′)—C(2′)—C(3′)—C(4′) = 0°].

The crystal-packing diagram (Fig. 3) shows the presence of intermolecular hydrogen bonding between the O(9) hydrogen and the O(3) carbonyl oxygen along the *a* axis. The O(3)···O(9) hydrogen-bonding distance is 2·93 Å.

We wish to thank Professor S. C. Bhattacharyya for his active interest in this work, and the University of Arizona Computer Center for computer time.

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L-Arginyl-L-glutamic Acid Dihydrate, $C_{11}H_{21}N_5O_5.2H_2O$

By J. Pandit, T. P. Seshadri and M. A. Viswamitra

Department of Physics and ICMR Centre on Genetics and Cell Biology, Indian Institute of Science, Bangalore 560012, India

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Abstract. $M_r = 339{\cdot}35$, monoclinic, $P2_1$, $a = 11{\cdot}028\,(2)$, $b = 9{\cdot}583\,(2)$, $c = 16{\cdot}010\,(2)$ Å, $\beta = 96{\cdot}57\,(1)°$, $U = 1680{\cdot}85$ Å^3, $Z = 4$, $D_m = 1{\cdot}37$, $D_x = 1{\cdot}34$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 0{\cdot}85$ mm^{-1}, $F(000) = 728$, $T = 300$ K, $R = 0{\cdot}085$ for 2845 diffractometer-measured reflections [$F_o > 3\sigma(F_o)$]. The two molecules in the asymmetric unit have similar conformations except for a static disorder at the C^β and C^γ positions in one of the glutamic-acid side chains. An interesting feature of the crystal structure is a pair of hydrogen bonds between the guanidinium and γ-carboxylate groups of neighbouring molecules. This is the first such specific interaction observed between side chains of arginine and glutamic acid.

Introduction. The arginine side chain is expected to play an important role in the specific recognition process between nucleic acids and proteins. In view of this interest we have initiated a study of arginine-containing peptides and their complexes with nucleotides. We report here the first description of the crystal and molecular structure of an arginine-containing peptide.

Experimental. Thin, needle-like crystal, 0·075 × 0·075 × 0·625 mm, from aqueous solution of the compound (obtained from Bachem Inc.) by diffusion of ethanol; preliminary crystal data from rotation and Weissenberg photographs with Cu $K\alpha$ radiation, cell dimensions from 25 strong reflections, Enraf–Nonius CAD-4 diffractometer; density measurements (flotation in acetone/bromoform) indicated two molecules of the compound and four water molecules in the asymmetric unit, ω–2θ scans up to $\theta = 75°$, h −13–13, k 0–12, l 0–20, $\bar{2}10$ and $\bar{1}22$ monitored periodically, crystal stable to X-rays, correction for Lorentz and polarization but not for absorption; structure solved with *MULTAN* (Germain, Main, & Woolfson, 1971) and refined with *SHELX* (Sheldrick, 1976), block-diagonal least squares, isotropic, $R = 14{\cdot}8\%$. At this stage, other bond distances were normal, but C^α—C^β in the Glu side chain of molecule *B* was 1·84 Å. The difference map exhibited two peaks in the vicinity of C^β and C^γ, suggesting positional disorder. These two atoms were assigned two different positions corresponding to the positions indicated on the difference map [similar situations have been reported in the literature, for example a bond length 0·3 Å greater than expected in the structure of *p*-(*N*-methylbenzylidene)-*p*-methylaniline (Berstein, Bar & Christensen, 1976)]. Four cycles anisotropic refinement on *F* (temperature factor

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