The Structure of Vaginatin: a New Sesquiterpene from the Root Extractive of *Selinum vaginatum*

By C. K. MESTA, S. K. PAKNIKAR, and S. C. BHATTACHARYYA*
(*Department of Chemistry, Indian Institute of Technology, Powai, Bombay*-76, *India*)

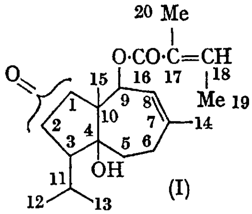
DURING our investigation[1,2] on the chemical composition of the oil obtained from the roots of *Selinum vaginatum* C. B. Clarke, we have isolated a crystalline sesquiterpene, vaginatin, $C_{20}H_{30}O_4$, (M^+ 334), m.p. 77—78°, $[\alpha]_D$ − 266·7°; for which structure (I) is suggested on the basis of chemical degradations and spectral studies: λ_{max} 217 mμ (ϵ, 12,400), ν_{max} (Nujol) 3531 (OH), 1730 (>CO), 1637, 853 (—CH=C<) cm.$^{-1}$ and n.m.r. δ 1·00 (3H, s, C-15), 1·00 (6H, d, *J* 7 c./sec., C-12, 13), 1·82 (9H, m, C-14,19,20), 2·53 (1H, disappeared on D_2O exchange), 5·16 (1H, d, *J* 8 c./sec., C-9), 5·60 (1H, d, *J* 8 c./sec., C-8) and 6·0 (1H, m, C-18). It gave a 2,4-dinitrophenyl hydrazone, m.p. 214°, but no acetate with pyridine and $(Ac)_2O$ (tertiary OH).

Mild alkaline hydrolysis of (I), under N_2 gave angelic acid and dihydroxyvaginatone (II), in poor yields, ν_{max} 3509 (OH), 1742 (cyclopentanone), 1647, 851 (—CH=C<) cm.$^{-1}$. However, excellent yields of α-methylbutyric acid and dihydrodihydroxyvaginatone (III) were obtained from tetrahydrovaginatin (PtO_2–AcOH), when hydrolysed under identical conditions. Vaginatin on hydrogenation with (PtO_2/ethanol) afforded α-methylbutyric acid and dihydrohydroxyvaginatone (IV) due to hydrogenolysis, $C_{15}H_{26}O_2$, ν_{max} (liquid film) 3500 (OH), 1740 (cyclopentanone) and 1410 (CO–CH_2) cm.$^{-1}$, n.m.r. 0·96 (6H, d, *J* 6, C-12,13), 1·02 (3H, s, C-15), 1·04 (3H, d, *J* 7, C-14), 2·2 (2H, q, J_{AB} 19 c./sec., δ_{AB} = 13 c./sec., C-1 or C-2). The allylic nature of the angelyl ester is further supported by n.m.r. spectral data.

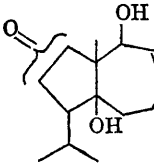
$LiAlH_4$ reduction of (I) gave vaginatriol (V), $C_{15}H_{26}O_3$, m.p. 122°, $[\alpha]_D$ − 80·6°, ν_{max} (Nujol) 3597, 3448, 3390 (OH), 1672, 828 (—CH=C<) cm.$^{-1}$; diacetate, $C_{19}H_{30}O_5$, m.p. 91—92°, n.m.r. consistent with the proposed structure. The other minor product (VI) of the $LiAlH_4$ reduction has the molecular formula, $C_{15}H_{24}O_2$, m.p. 79—80°, ν_{max} 3413 (OH), 1621, 720, 691 (*cis*, -CH=CH-), 1145, 1117, 1087, 1050 (C–O–C) cm.$^{-1}$, n.m.r. δ 0·97 (6H, d, *J* 6, C-12,13), 1·05 (3H, s, C-15), 1·22 (3H, s, C-14), 3·42 (1H, d, J 2·5, C-1 or C-2), 5·87 (2H, q, J_{AB} 9 c./sec., δ_{AB} 7·7 c./sec., C-8,9).

Vaginatriol (V) on Se-dehydrogenation gave daucalene (VII), m.p. 60—61°, trinitrobenzoate, m.p. 132°, picrate, m.p. 90°. Mixed m.p. and spectral comparison with authentic daucalene and its respective derivatives confirmed their identity and suggest that vaginatin may have the same basic skeleton as that of carotol (VIII)[3] and laserpitine (IX),[4] both of which on dehydrogenation give (VII).

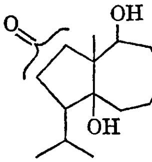
On oxidation with activated MnO_2 in chloroform solution, (V) gave a crystalline compound (X), $C_{15}H_{24}O_3$, m.p. 120°, no strong u.v. absorption, ν_{max} (Nujol) 3575 (OH), 1700 (six-membered ring ketone), 1140, 1120, 1095, 1070, 1045 (C–O–C) cm.$^{-1}$, n.m.r. δ 1·02 (3H, s, C-15), 1·02 (6H, d, J 6 c./sec., C-12,13), 1·26 (3H, s, C-14), 2·25 (1H, disappeared on D_2O exchange), 2·41 (2H, s, C-8), 4·00 (1H, m, C-1 or C-2). Compound (X) must have been formed by initial oxidation to an αβ-unsaturated ketone, followed by ring closure *via* a Michael-type addition of the tertiary hydroxyl to the conjugated system. Similar observations have been made previously in the case of methyl shellolate[5] and several others.[6] Vaginatin (I), therefore, contains a cyclopentanone moiety, a free tertiary hydroxyl group, and it is the angelyl ester of dihydroxyvaginatone. Chemotaxonomically structure (I) of vaginatin is of interest as it forms a link between carotol (VIII) and laserpitine (IX).



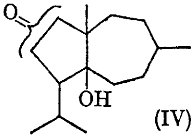
(I)



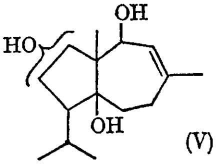
(II)



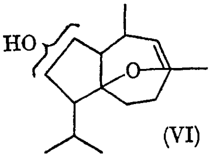
(III)



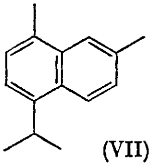
(IV)

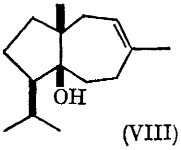


(V)

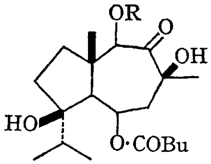


(VI)

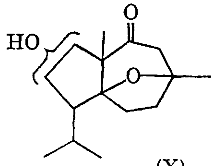

(VII)



(VIII)



(IX)



(X)

We thank Prof. A. K. Bose, of Stevens Institute of Technology, Hoboken, New Jersey, for the mass spectral data, Prof. R. B. Bates, Dept. of Chemistry, University of Arizona, Tucson, for measuring some of the n.m.r. spectra, and Dr. M. Holub of Institute of Organic and Biochemistry, Prague, for supplying the samples of daucalene and its derivatives.

(*Received, March 14th,* 1968; *Com.* 313.)

---

[1] S. N. Shanbhag, C. K. Mesta, M. L. Maheshwari, S. K. Paknikar, and S. C. Bhattacharyya, *Tetrahedron*, 1964, **20**, 2605.

[2] S. N. Shanbhag, C. K. Mesta, M. L. Maheshwari, and S. C. Bhattacharyya, *Tetrahedron*, 1965, **21**, 3591.

[3] V. Herout, M. Holub, L. Novotný, V. Sýkora, and F. Šorm, *Chem. and Ind.*, 1960, 662.

[4] M. Holub, Z. Samek, V. Herout, and F. Šorm, *Coll. Czech. Chem. Comm.*, 1967, **32**, 591.

[5] P. Yates and G. F. Field, *J. Amer. Chem. Soc.*, 1960, **82**, 5754.

[6] R. C. Cookson, N. Lewin, and A. Morrison, *Tetrahedron*, 1962, **18**, 547.