Structures of Stachysterones C and D

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Summary Structures (I) and (II) have been derived for stachysterones C and D, respectively.

THE screening of plants for phytoecdysones has disclosed many new and promising sources,[1] one being the bark of *Stachyurus praecox* Sieb. et Zucc. ('kibushi' in Japanese) which contains β-ecdysone (0·06% yield) and four new compounds, stachysterones A, B, C, and D. This communication deals with the structures of stachysterones C and D, both isolated in yields of 0·002%, respectively.

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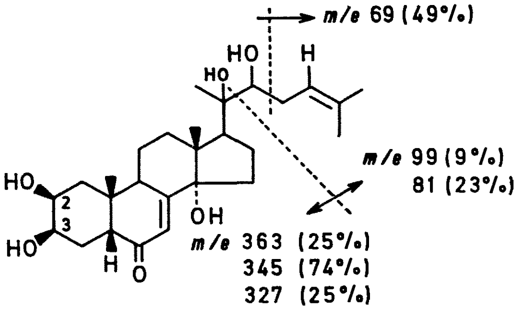
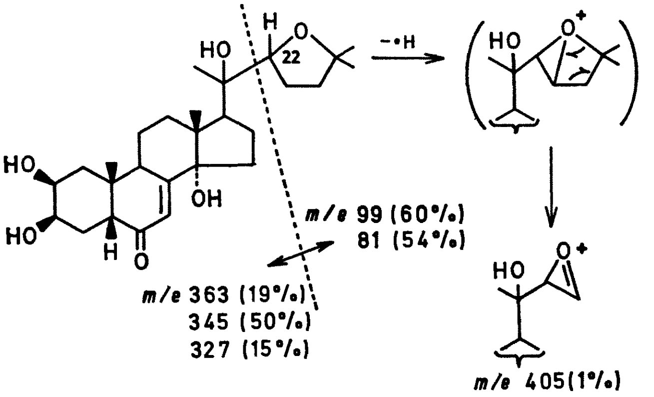
Stachysterone C and its triacetate possess the following physical properties. *Stachysterone C* (I), m.p. 235—240° (decomp.); $C_{27}H_{42}O_6$ (M^+ at *m/e* 462), $M - 18$ peak at *m/e* 444·2863 (calc. for $C_{27}H_{40}O_5$ 444·2874);‡ i.r. (KBr) 3400 and 1640 cm^{-1}; u.v. (MeOH) 242 nm (ϵ 10,500); o.r.d. (dioxan) a +43 ($n \rightarrow \pi^*$). *Stachysterone C* 2,3,22-*triacetate*, m.p. 138—142°, $M - 18$ peak at *m/e* 588. Stachysterone C contains the 2β,3β,14α,20-tetrahydroxy-5β-7-en-6-one partial structure commonly present in the ecdysones as indicated by the chemical shifts and coupling constants of n.m.r. signals due to 2α-, 3α, 7-, 18-, 19-, and 21-protons,[2] m.s. fragmentation patterns,[3] and the spectral data given above, all of which were typical. Presence of the 24-ene is demonstrated by: (i) n.m.r. signals (in deuteriopyridine) assignable to two olefinic methyls (1·60 and 1·66 p.p.m.) and an olefinic proton (5·51 p.p.m., dd 7, 7 Hz) which has an adjacent methylene group; (ii) the intense m.s. peak at *m/e* 69 which is absent in other ecdysones (see I); and (iii) the fact that the *m/e* 99 and 81 peaks (C-20/C-22 fission) are two mass-units lower than corresponding peaks encountered in the spectra of ecdysones with the saturated 20,22-dihydroxy-cholestane side-chain.

The physical data for *stachysterone D* (II) are as follows: m.p. 245—250° (decomp.), $C_{27}H_{42}O_6$ (M^+ at *m/e* 462), $M - 36$ peak at *m/e* 426·2723 (calc. for $C_{27}H_{38}O_4$ 426·2769); i.r. (KBr) 3400 and 1650 cm^{-1}; u.v. (MeOH) 243 nm (ϵ 10,950); o.r.d. (dioxan) a +65 ($n \rightarrow \pi^*$). *Stachysterone D* 2,3-*diacetate*, m.p. 233—235° (decomp.), $M - 18$ peak at *m/e* 546. Here again the spectral data were typical for the 2β,3β,14α,20-tetrahydroxy-5β-7-en-6-one partial structure. As in the case of stachysterone C, the C-20/C-22 fission peaks at *m/e* 99 and 81 were also two mass-units lower, thus showing that the side-chain was cyclic (or unsaturated); the characteristic peak at *m/e* 405 can be accounted for by the oxonium ion illustrated.[4] The cyclic ether structure is corroborated by the chemical shift and half-band-width of 22-H, *i.e.*, at 3·95 p.p.m. (in deuteriopyridine) for (II), and 3·85 p.p.m. (in deuteriochloroform, $W_{\frac{1}{2}}$ 12 Hz) for (II)-diacetate; the 21-H signal, usually at *ca.* 1·54 p.p.m. (for free ecdysone in deuteriopyridine), has now been shifted and cannot be distinguished from the 26- and 27-H signals, these three methyl groups appearing at 1·06, 1·20, and 1·37 p.p.m.

The insect moulting hormone activity of stachysterone C, as measured by the *Chilo* dipping test,[5] is comparable to other phytoecdysones but that of stachysterone D is extremely weak or occasionally non-observable.



(I) chemical shifts (in C_5D_5N): 18-H, 1·05; 19-H, 1·17; 21-H, 1·55 p.p.m.



(II) chemical shifts (in C_5D_5N): 18-H, 1·06; 19-H, 1·20 p.p.m.

% *in parentheses denote intensities of m.s. peaks relative to base peak at* m/e 43.

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[1] S. Imai, T. Toyosato, M. Sakai, Y. Sato, S. Fujioka, E. Murata, and M. Goto, *Chem. and Pharm. Bull.* (*Japan*), 1969, **17**, 335.

[2] See for example: S. Imai, E. Murata, S. Fujioka, M. Koreeda, and K. Nakanishi, *Chem. Comm.*, 1969, 546.

[3] (a) M. Koreeda, K. Nakanishi, K. Morita, S. Imai, T. Tsuchiya, and N. Wasada, 4th Mass Spectrometry Symposium (Japan), Nagoya, Nov. 1968, Abstracts p. 5; (b) M. Koreeda, K. Nakanishi, S. Imai, T. Tsuchiya, and N. Wasada, *Shitsuryo Bunseki*, 1969, **17**, 669 (in English).

[4] For loss of β-hydrogen in five-membered ethers upon electron impact, see: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," 1967, Holden-Day, San Francisco, pp. 251—258.

[5] Y. Sato, M. Sakai, S. Imai, and S. Fujioka, *Appl. Entomol. Zool.* (*Japan*), 1968, **3**, 49.