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STRUCTURE OF HYPACRONE, A NOVEL SECO-ILLUDOID, POSSIBLE BIOLOGICAL PRECURSOR OF PTEROSINS IN HYPOLEPIS PUNCTATA METT.

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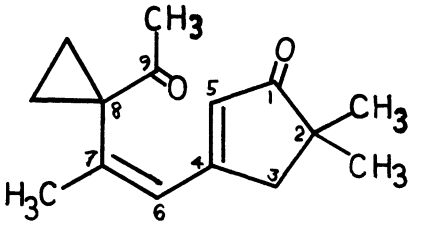
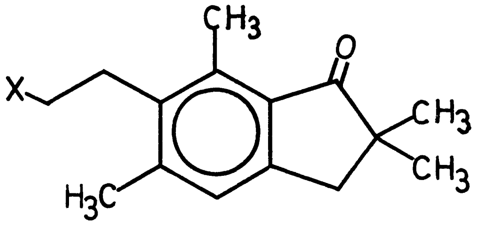
Further investigation of Hypolepis punctata results in the isolation of a novel seco-illudane sesquiterpenoid, hypacrone, as an acrid principle of the plant. This compound is also shown to be a biological precursor of pterosins.

In a previous paper$^{1)}$, the structures and the syntheses of three sesquiterpenoid indanone derivatives, pterosin H (2), I (3) and Z (4), (tentative names : hypolepins), isolated from a fern, Hypolepis punctata Mett., have been reported. Pterosins have been considered to be formed in an analogous biogenetic pathway to that for known non-aromatic illudoids, such as illudins$^{2)}$, illudol$^{3)}$ or marasmic acid$^{4)}$, which have been discovered from fungal plants. This communication deals with the isolation and the structure determination of a principle, designated as hypacrone, of acrid taste which is characteristic of this fern. It is remarkable to note that hypacrone has a novel seco-illudane skeleton$^{5)}$ and is regarded as a possible biological precursor of pterosins, since its chemical transformation into the latter compounds is readily carried out.

Hypacrone (1), a colorless liquid, bp. 90°/0.02 mm Hg, $C_{15}H_{20}O_2$, ν_{max}^{neat} 1695, 1625, 1590 cm^{-1}, λ_{max}^{EtOH} 285 nm (log ε : 4.26), m/e 232.1476 (M^+: calcd. 232.1463), 217.1237 ($M^+ - CH_3$: calcd. 217.1228), 203.1122 ($M^+ - C_2H_5$: calcd. 203.1072), 189.1298 ($M^+ - CH_3CO$: calcd. 189.1279), was isolated in ca 0.003 % yield from fresh shoots by quick extraction with hot water, followed by careful fractionation (charcoal-ethanol, then polyamide-water) and finally by preparative layer chromatography (SiO_2-$CHCl_3$-ether). The ir and uv spectra suggested the presence of a substituted α,β-γ,δ-unsaturated carbonyl system.



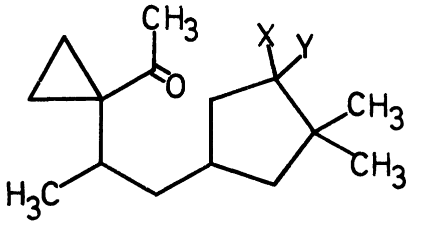
(1)



(2) X : Cl

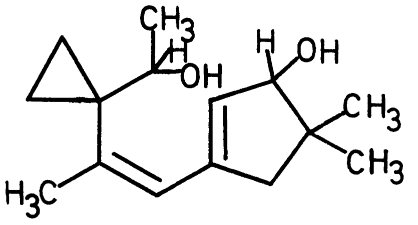
(3) X : OCH_3

(4) X : OH



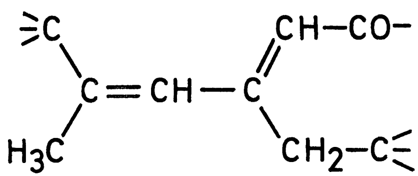
(6) X, Y : =O

(7) X : OH, Y : H

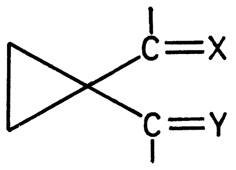


(8)

The nmr spectrum showed signals for four methyl groups, a sharp six-proton singlet at 1.04 ppm (gem-dimethyl group), a doublet (J=1.3 Hz) at 2.06 ppm (methyl group at C_7) coupled with one olefinic proton, H_6, at 6.22 ppm, and a sharp singlet at 2.11 ppm (methyl ketone group), respectively. Another olefinic proton, H_5, at 5.82 ppm interacted (J=1.5 Hz) with a two-proton doublet at 2.49 ppm (C_3-methylene group) with which H_6 was also coupled slightly. Little interaction was observed between two olefinic protons. Additional four-proton signals at 0.94 (2H) and 1.50 (2H) ppm appeared in a symmetrical pair of quartets (A_2B_2 type) which were assigned to two methylene groups of cyclopropane ring conjugated with other unsaturated function (or functions), because the corresponding signals occurred at 0.73 and 1.11 ppm in a tetrahydro derivative (6). From these spectral informations, two partial structures, (A) and (B), resulted. Rather simple pattern of the nmr signals except for some long-range interactions further suggested a symmetrical property of the molecule.

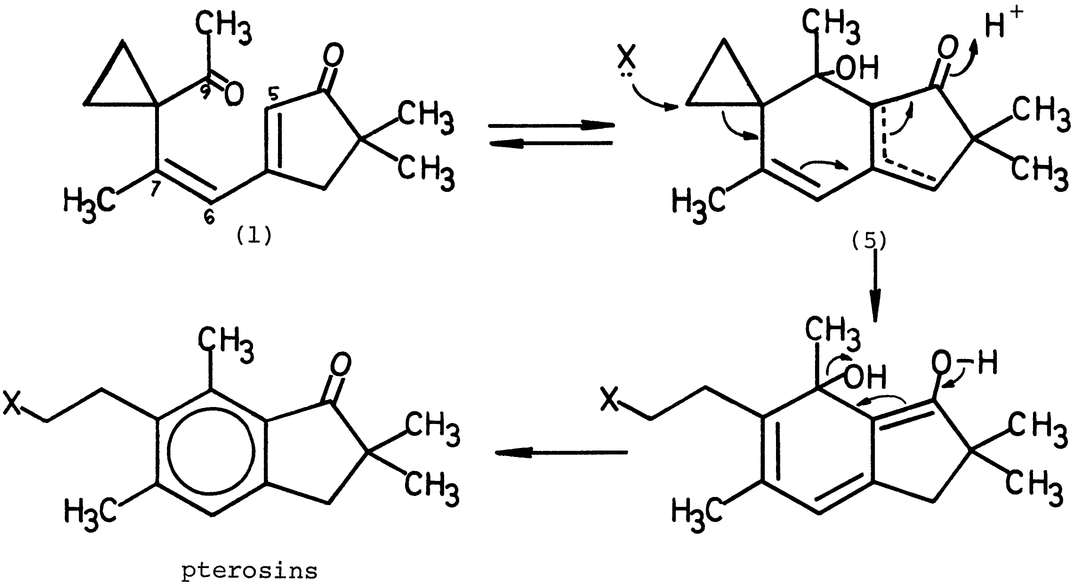


(A)



(B)

The transformation of hypacrone by acid treatment (refluxing for 4hrs) into pterosins, pterosin Z with 2N-sulfuric acid and pterosin H and Z with 2N-hydrochloric acid, established the gross structure (1) of hypacrone. The configuration of the 6,7-double bond must be in cis, as shown, because of the facile bond formation between C_5 and C_9. A plausible mechanism of the above conversion is depicted as follows. Possibly, two structures, (1) and (5), would be in equilibrium under the condition.



Catalytic hydrogenation of hypacrone (PtO_2 in EtOAc) afforded a diketone (6), $C_{15}H_{24}O_2$, m/e 236, ν_{max} 1730, 1685 cm^{-1}, and a hydroxy ketone (7), $C_{15}H_{26}O_2$, m/e 238, ν_{max} 3300, 1685 cm^{-1}, and $NaBH_4$ reduction gave an olefinic diol (8), $C_{15}H_{24}O_2$, m/e 236, ν_{max} 3350, 3060 cm^{-1}. These products also supported the diketonic seco-illudane structure (1) for the natural compound.

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