

The Isolation of Serratene from *Polypodium vulgare*

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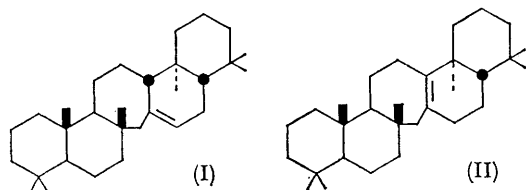
ONE characteristic aspect of the triterpenoids isolated from ferns is the very frequent occurrence of triterpene hydrocarbons,¹ a class of compounds that has not been found in any species of other families, with the only exception of taraxerene, which was isolated from a lichen.²

The rhizomes of *Polypodium vulgare* contain about 0.4% of a mixture of triterpene hydrocarbons; gas-liquid chromatographic analysis (on neopentylglycol succinate) showed that it consisted of three components, two of which had been identified before as 9(11)-fernene and 22(29)-hopene.³ The third component, which had a retention time that was intermediate between those of 9(11)-fernene and 22(29)-hopene, was isolated in a pure state by column chromatography over silica gel impregnated with silver nitrate. Elemental analysis and mass spectrometry indicated that the new compound, m.p. 237—239°, $[\alpha]_D -13.4^\circ$ (CHCl₃), corresponded to the formula C₃₀H₅₀. The mass spectrum showed a peak at m/e 286 ($M^+ - C_9H_{16}$), which could be

attributed to a retro-Diels-Alder cleavage of a Δ^{14} -triterpene,⁴ and a base peak at m/e 191 (C₁₄H₂₃⁺) which is characteristic for triterpenes with saturated and non-oxygenated rings A and B.⁵ The n.m.r. spectrum (60 Mc./sec.) showed seven non-coupled methyl groups at τ 9.26 (1), 9.13 (2), and 9.09 (4) and a non-resolved vinylic proton multiplet (one proton) at τ 4.66. Treatment with hydrogen chloride in chloroform led to an isomeric hydrocarbon, m.p. 184—188°, $[\alpha]_D +84.8^\circ$, with a tetrasubstituted double bond. The evidence outlined above made it very probable that the hydrocarbon from *P. vulgare* was serratene (I)^{6,7} and its isomer isoserratene (II).^{7,8} This was proven by direct comparison with samples of (I) and (II), kindly provided by Dr. Rowe and Prof. Inubushi. Serratene had never been obtained from a natural source, but had been prepared by transformation of the naturally occurring triterpenoid serratenediol.

Serratene is the first triterpene hydrocarbon from

a fern that does not contain a hopane or rearranged hopane skeleton, and its finding is interesting because most of the other pentacyclic triterpenes lacking oxygen at the 3-position are biogenetically derivable from a hopane precursor. Serratene is almost certainly originated from an onoceradiene



type of precursor, formed by a cyclization of squalene starting from both ends of the molecule. The finding of an increasing number of triterpenoids without oxygen in the 3-position, provides strong support for a squalene cyclization mechanism which involves initiation by H^+ , rather than by OH^+ , or an equivalent species, as usually assumed.⁹ The recent results by Barton and Moss¹⁰ on the enzymic oxygenation of lanosta-8,24-diene to lanosterol have offered experimental evidence for the possibility of an H^+ -initiated cyclization.

(Received, November 28th, 1966; Com. 936.)

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