Tetrahedron Letters No. 22, pp. 1447-1450, 1963. Pergamon Press Ltd.
Printed in Great Britain.

A FERN CONSTITUENT, FERNENE
A TRITERPENOID HYDROCARBON OF A NEW TYPE

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(Received 3 July 1963)

IN a previous communication$^{(1)}$ we had reported the isolation of two triterpenoid hydrocarbons, fernene, $C_{30}H_{50}$, m.p. 170-171°, $[\alpha]_D^{16}$ -16.5 (c= 0.79, $CHCl_3$), one olefinic proton at δ^{CCl_4} 5.28 ppm., and diploptene (hopene-b, II) from the leaflets of a fern, <u>Dryopteris crassirhizoma</u> NAKAI (Aspidiaceae). Now it has been shown that fernene has structure I.

Oxidation of fernene with selenium dioxide in a solution of acetic acid gave ferna-7,9(11)-diene (III)*, $C_{30}H_{48}$, m.p. 198-199°, $[\alpha]_D^{20}$ -157.3°(c= 0.50, $CHCl_3$), having λ_{max}^{EtOH} 232, 240, 248 mμ(ε 10,200, 10,800, 6,600), characteristic of a conjugated heteroannular diene. Chromic acid oxidation of fernene in

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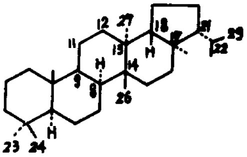
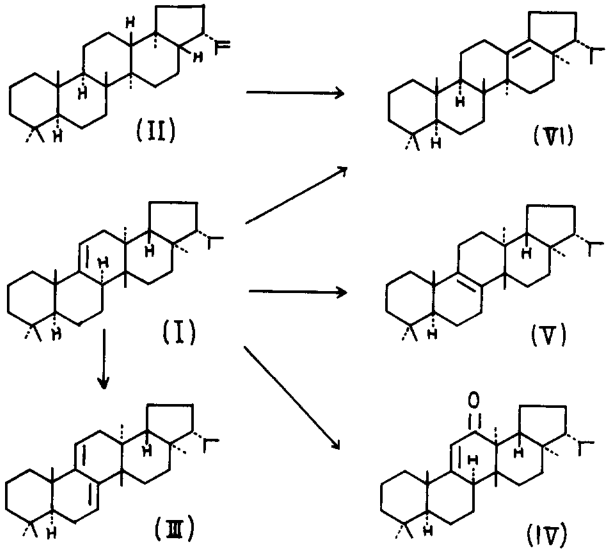
*The name, fernane is proposed for the following saturated hydrocarbon corresponding to fernene.



acetic acid afforded 12-keto-fern-9(11)-ene (IV), $C_{30}H_{48}O$, m.p. 221.5-223°, $[\alpha]_D^{17}$ -28.0 (c= 1.00, $CHCl_3$), λ_{max}^{EtOH} 246 mμ (e 9,000), ν_{max}^{KBr} 1672,1611 cm^{-1}, which showed a positive Cotton effect of molecular amplitude (a) +12,000 in the optical rotatory dispersion curve$^{(3)}$.



The mass spectra of fernene, isofernene (V)$^{(1)}$, m.p. 184-185°, $[\alpha]_D^{16}$ +15.2°($CHCl_3$), and ferna-7,9(11)-diene (III) showed characteristic base peaks at m/e 243,243 and 255, respectively. Placement of methyl groups at C-13 and C-14, and double bonds at 9(11)(in fernene) and 7,9(11)(in fernadiene) follows from the fact that the same base peaks at m/e 243 and 255 were observed in arborene ($\Delta^{9(11)}$) and arboradiene ($\Delta^{7,9(11)}$)$^{(2)}$, and the identity of fernene with davallene$^{(3, 4)}$. The configurations of the two methyl groups were concluded to be 13α and 14β on the basis of similarities of the UV spectrum of ferna-7,9(11)-diene with those of corresponding dienes from euphol(5), multiflorenol(6) and bauerenol(7). This was also confirmed by the highly negative change of $[\alpha]_D$ values from isofernene (V) to the diene III, and the O.R.D. curve(2, 3) of 12-keto-fern-9(11)-ene (IV).

Treatment of fernene with 6% hydrochloric acid in boiling acetic acid for 20 hours yielded a hydrocarbon (m.p. 196.5-198°) in addition to isofernene. It was found that this hydrocarbon (VI) was identical with hopene-II(8,9) by mixed melting point, infrared spectra, and gas chromatography retention time using SE-30 and QF-1 columns.

Biogenetically, fernene is assumed to be formed from diploptene by the migration of hydrogen and methyl groups (21βH→22, 17βH→21β, $18\alpha CH_3 \rightarrow 17\alpha$, 13βH→18β, $14\alpha CH_3 \rightarrow 13\alpha$, $8\beta CH_3 \rightarrow 14\beta$, and 9αH→8α), followed by formation of the 9(11)-double bond. The configuration at carbons 17 and 21 in fernenes and hopene-II were assigned on the same basis.

Isolation of the onocerane(10, 11) and zeorinane (hopane) series(1,9) have already been reported, and thus fernane is the third triterpene skeleton from fern plants.

We wish to thank Prof. K. Nakanishi, Tohoku University, for his kind encouragements and helpful discussion, and also to thank Prof. C. Djerassi and Dr. H. Vorbrüggen, Stanford Univ., for determinations of mass spectra of fernenes and related compounds, and for a manuscript of their paper on arborinol before publication. Thanks are due to Dr. N. Ikekawa, Institute for physical and Chemical Research, for gas chromatography, and to the Takeda Research Laboratory

for n.m.r. spectra determination.

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