Fern Constituents: Neohopene, Hopene-II, Neohopadiene, and Fernadiene isolated from *Adiantum* Species

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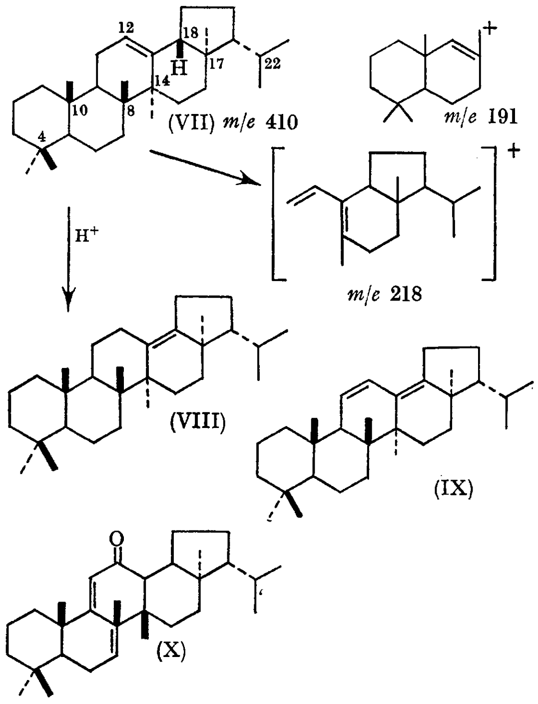
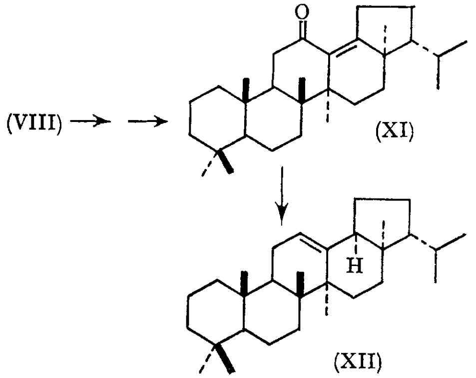
WE have already reported the isolation of the triterpenoid hydrocarbons, isofernene (I), adianene (II), 7-fernene (III), diploptene (IV), and filicene (V) from *Adiantum monochlamys* Eaton (Japanese name: Hakoneshida),[1] and (I), fernene (VI), (II), (III), and (V) from *A. pedatum* Linn. (Kujakushida),[2] both of Japanese origin. Further investigations on the minor hydrocarbons of the two ferns have afforded four additional compounds (yields less than 2% each of the total triterpenoid hydrocarbons), neohopene (VII), neohop-13(18)-ene (hopene-II) (VIII), neohopa-11,13(18)-diene (IX), and ferna-7,9(11)-diene (X), as well as (VI). The known compounds (VIII),[3] (IX),[4] and (X)[5] were identified by direct comparison with authentic samples.

The mass spectrum of neohopene (VII), m.p. 210—211°, $[\alpha]_D + 41{\cdot}6°$ (*c* 0·4, $CHCl_3$), $C_{30}H_{50}$ (M^+ *m/e* 410, 7% of the base peak) showed clearly the presence of the 12,13-double bond by giving the base peak at *m/e* 218, accompanied by peaks at *m/e* 203 (32; $218 - CH_3$, m^* 189·0), 175 (48; $218 - C_3H_7$, 140·5), 191 (28), and 177 (11; $191 - CH_2$, 164·0).

Mild acid treatment of (VII) afforded (VIII), illustrating the structure of the remaining part of the molecule, and thus the structure of neohopene must be formulated as (VII) except for the configuration at C-18. The formula (VII) has already been assigned to neomotiene, the corresponding hydrocarbon derived from neomotiol,[6] but the physical constants (m.p., $[\alpha]_D$, and i.r. spectrum) given for neomotiene were different from those of neohopene. This ambiguity has been resolved by Prof. Hirata as the compound, when re-investigated, gave the same melting point, $[\alpha]_D$, i.r. spectrum, and v.p.c. characteristics as neohopene. Hence, the establishment of the structure of neohopene gives chemical proof of the configuration at C-18 in neomotiol.

The proof of the stereochemistry at C-18 of (VII) was obtained by the synthesis of the C-18 isomer having the more stable D : E-*cis*-structure in the following way. Neohop-13(18)-en-12-one (XI), m.p. 212—216°, ν_{max} (KBr) 1672 and 1612 cm.$^{-1}$, derived from (VIII),[3,7] was reduced by a forced Wolff–Kishner method to give the hydrocarbon, $18\alpha H$-neohop-12-ene (XII),† m.p. 134—137°, $[\alpha]_D$ $+18{\cdot}4$ (c 0·7, $CHCl_3$), the mass spectrum of which [m/e: 410 (M^+; 10), 218 (100), 203 (25), 191 (35), and 175 (200)] was very similar to that of (VII). Acid treatment of (XII) readily gave (VIII) as expected.





Comparison of the n.m.r. spectrum of (VII) with those of (VIII) and (XII), and also with that of olean-12-ene[9] (Table), confirms the 17α,18β-structure for (VII) and the 17α,18α-structure for (XII). The only conformation given by the Dreiding model for formula (VII) is quasi-boat (ring C) and boat (ring D), and the methyl group attached to C-8 comes on the upper side of the 12,13-double bond. The interaction between the two methyl groups attached to C-14 and C-17 will displace the C-8 methyl group towards the C-12 double bond, thereby causing shielding; hence the chemical shift of the methyl group at C-8 in (VII) is τ 9·25. The other high value for the methyl group attached to C-17 is reasonable because signals of methyl groups attached to the C : D-*trans*-ring juncture in most of the hopanes and the rearranged hopanes appear at τ 9·30—9·40. On the other hand, the compound (XII) has quasi-chair (ring C) and chair (ring D)

Chemical shifts of the methyl and olefinic protons

(Varian A-60, τ values in CCl_4 solution)

	Location of methyl							Proton at
Compound	4α	4β	10	8	14	17	22 or 20	C-12
(VII)	9·12	9·18	9·12	9·25	8·88	9·28	9·07d, 9·14d (J 6·5 c./sec.)	4·98m
(VIII)	9·15	9·20	9·20	9·15	8·90	9·15	9·06d, 9·11d (J 6·5 c./sec.)	—
(XII)	9·10	9·17	9·10	9·05	8·94	9·11	9·08d, 9·11d (J 6·5 c./sec.)	4·70m
Olean-12-ene	9·12	9·16	9·06	9·02	8·85	9·16	9·12, 9·12	

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† The same compound was obtained by Prof. Berti.[8]

conformation like olean-12-ene, and the chemical shifts of the five methyl groups attached to 4α, 4β, 10, 8, and 14 in (XII) are very similar to those of olean-12-ene.

The isolation of hopene-II and neohopadiene is recently reported from an Indian fern, *Oleandra wallichi*.[10] It is somewhat doubtful whether (VIII), (IX), and (X) are genuine natural products. Compound (VII) changes partly into (VIII) during chromatography, and some oxygenated precursors of (IX) and (X) might originate in the plants.

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