Tetrahedron Letters No.46, pp. 3413-3418, 1964. Pergamon Press Ltd.
Printed in Great Britain.

FERN CONSTITUENTS: ADIANENE, FILICENE, 7-FERNENE, ISOFERNENE AND DIPLOPTENE. TRITERPENOID HYDROCARBONS ISOLATED FROM ADIANTUM MONOCHLAMYS

H. Ageta, K. Iwata and S. Natori
Shōwa College of Pharmacy, Setagayaku, Tokyo, Japan

(Received 21 August 1964; in revised form 16 September 1964)

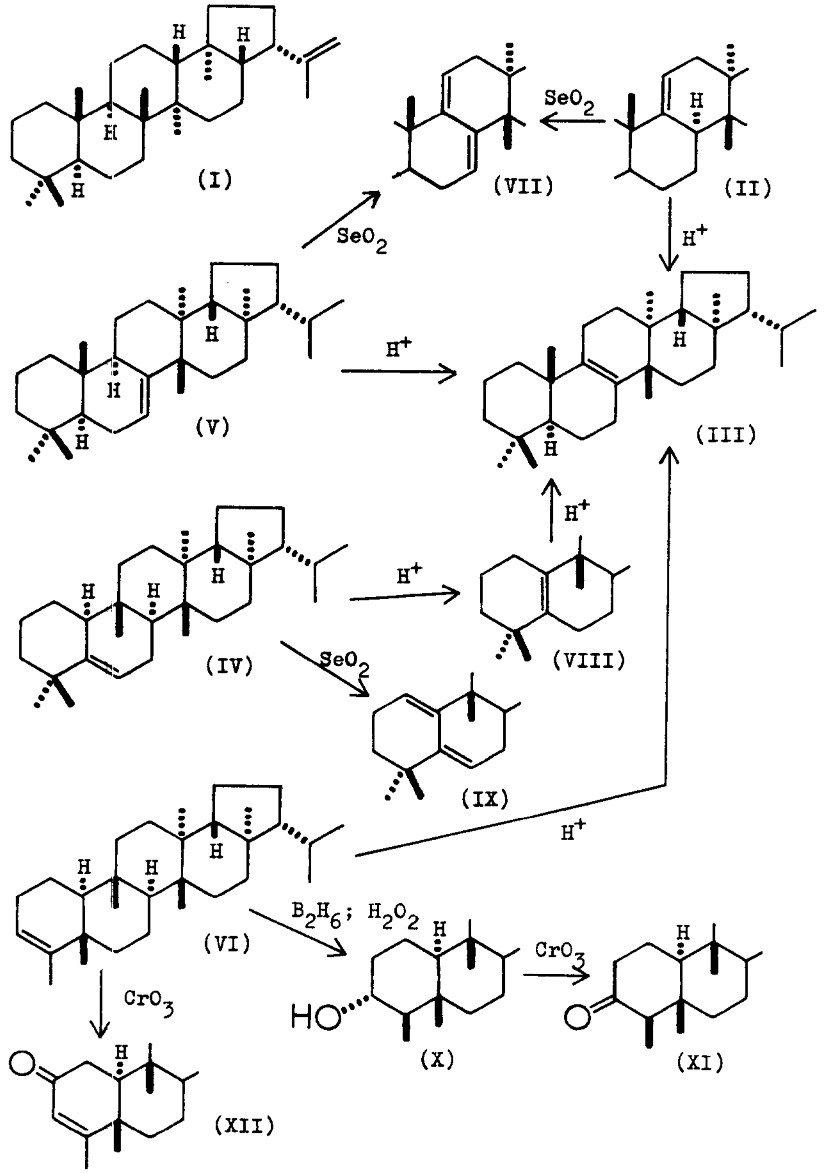
WE had already reported the studies on two fern triterpenoid hydrocarbons, diploptene (I) and fernene (II),(1)(2) isolated from *Dryopteris crassirhizoma*. In this communication, the isolation and structural studies on triterpenoids isolated from a japanese fern, *Adiantum monochlamys* EATON (Adiantaceae) are presented.

Methanolic extraction of the dried leaves, followed by careful separation by chromatography, afforded five hydrocarbons together with one ketone and one alcohol. The hydrocarbons are shown in Table I according to the order of elution with hexane.

Table I

isofernene (fern-8-ene)(III)	m.p. 189-190°	$[\alpha]_D$+18°(3)
adianene (adian-5-ene)(IV)	190,5-191.5°	+51°
7-fernene (fern-7-ene)(V)	208.5-209.5°	-27°
filicene (filic-3-ene)(VI)	228.5-229.5°	+50°
diploptene (hopene-b)(I)	210-211°	+61°

The first and the fifth hydrocarbon, isofernene (III) and diploptene (I) were identified by direct comparison with the


(I)
(VII)
SeO_2
(II)
SeO_2
H^+
(V)
H^+
(III)
H^+
(IV)
H^+
(VIII)
SeO_2
(IX)
H^+
(VI)
B_2H_6; H_2O_2
CrO_3
(X)
(XI)
CrO_3
(XII)
HO
O
H

samples from previous studies.(1) The second hydrocarbon (IV), named adianene, $C_{30}H_{50}$, has one trisubstituted double bond (ν_{max}^{KBr} 822, 790 cm^{-1}; τ4.50). Treatment of the hydrocarbon with 6 v/v % sulphuric acid in benzene-acetic acid afforded a mixture of two hydrocarbons, isofernene (III), m.p. 189-190°, and a new compound, isoadianene, m.p. 193.5-195°, $[\alpha]_D$ -108°. A milder condition of acid-induced migration (HCl gas in chloroform solution at 0°C) gave a mixture of starting material and isoadianene as indicated by gas chromatography on an N.G.S. column. Selenium dioxide oxidation of adianene afforded a heteroannular diene, $C_{30}H_{48}$, m.p. 203.5-204.5°, $[\alpha]_D$ +105°, ν_{max}^{KBr} 821, 815 cm^{-1}, λ_{max}^{EtOH} 232, 240, 248 mμ (ε 14,800, 16,000, 11,000), which was clearly different from ferna-7,9(11)-diene (VII).(2)(4) Since the formation of isofernene shows adianene is a hydrocarbon of the migrated hopene type having a double bond on ring A or B, the only biogenetically possible structure for adianene is IV, which represents a new triterpenoid skelton. It follows that isoadianene and heteroannular diene must be adian-5(10)-ene (VIII) and adiana-1(10),5-diene (IX), respectively. The $[\phi]_D$ values (Table II) of adianene, adian-5(10)-ene and adiana-1(10),5-diene are in good agreement with the values observed in the alnusane series. We would like to propose the name, adianane, for the saturated hydrocarbon corresponding to adianene; the former occupies a position parallel to alnusane in the migratory oleanane series.

The structure of the third hydrocarbon (V), $C_{30}H_{50}$, was elucidated as follows. The presence of a trisubstituted double bond was revealed by I.R. (ν_{max}^{KBr} 828, 819 cm^{-1}) and p.m.r. (τ4.65). Treatment of the hydrocarbon with hydrochloric acid in acetic acid solution for a short time gave isofernene (III) in good yield.

Selenium dioxide dehydration of V afforded ferna-7,9(11)-diene (VII), m.p. 199.5-200.5°, λ_{max}^{EtOH} 232, 240, 248 mμ (ε 13,600, 14,800, 9,700), also in good yield.(2)(4) Since the structure of III and VII has been established, V is clearly different from fernene (II), and V gives III more readily than II, the hydrocarbon should be fern-7-ene (V). $[\phi]_D$ values (Table II) of fern-7-ene and isofernene are similar to those of Δ^7, Δ^8 compounds of migratory oleanane.

The fourth hydrocarbon, *filicene* (VI), $C_{30}H_{50}$, also has a trisubstituted double bond (ν_{max}^{KBr} 798, 780 cm^{-1}; τ 4.92). The p.m.r. spectrum of this hydrocarbon showed the presence of seven methyl groups at higher field than τ 9.00 and one methyl group attached to an olefinic carbon atom at τ 8.44. Acid treatment of filicene gave, again, isofernene (III), showing the presence of the double bond in ring A or B of a rearranged hopane nucleus. From the p.m.r. data and biogenetic consideration, a friedel-3-ene type structure became quite probable. Hydroboration of VI followed by alkaline hydrogen peroxide oxidation gave a saturated secondary alcohol, filican-3α-ol (X), m.p. 281.5-282.5°, $[\alpha]_D$ +13°, ν_{max}^{KBr} 3450, 1034 cm^{-1}. Oxidation of X with chromic acid afforded a saturated ketone, filican-3-one (XI), m.p. 247.5-249°, $[\alpha]_D$ -27°, ν_{max}^{KBr} 1715 cm^{-1}. The O.R.D. curve of XI (molecular amplitude (a) -12,450) was found to be superimposable with that of friedelin, comfirming the assignment. Chromic acid oxidation of filicene afforded filic-3-en-2-one (XII), m.p. 265.5-267.5°, $[\alpha]_D$ +45°, ν_{max}^{KBr} 1656, 1614 cm^{-1}, λ_{max}^{EtOH} 237 mμ (ε 12,900). The $[\phi]_D$ values(Table II) of filicene, filican-3α-ol and filican-3-one are very similar to the values observed in the friedelane derivatives. When we reached this conclusion, the structure of

Table II Comparison of $[\phi]_D$ values

fern-7-ene	-111	multiflor-7-ene	-82(5)
fern-8-ene	+74	multiflor-8-ene	+102*
fern-9(11)-ene	-68	-----	
ferna-7,9(11)-diene	-694	multiflora-7,9(11)-diene	-616(5)
adian-5(10)-ene	-443	alnus-5(10)-ene	-172(6)
adian-5-ene	+209	alnus-5-ene	+230(7)
adiana-1(10),5-diene	+428	alnus-1(10),5-diene	+396**
filic-3-ene	+205	friedel-3-ene	+217(8)
filican-3α-ol	+57	friedelinol	+73(8)
filican-3-one	-115	friedelin	-123(8)

*culculated value from multiflor-8-en-3β-ol(5)

**culculated value from alnus-1(10),5-dien-3β-yl acetate(9)

adiantoxide from *Adiantum capillus-veneris* had been established by Prof. G. Berti and co-workers.(10) Direct comparison of filican-3-one (XI) with the authentic specimen derived from adiantoxide confirmed the identity of the two samples. The names, filicene and those of its derivatives shown above are based on Prof. Berti's proposal.

It should be mentioned that *Adiantum monochlamys* contains various triterpenoid hydrocarbons in a single biogenetic sheme. Squalene in the all chair conformation could be a precursor of diploptene (I). Concerted 1,2-shifts of 21 carbanion derived from I lead to fern-7-ene (V) and isofernene (III) having the fernane skeleton, further to adianene (IV) having the adianane skeleton, and finally to filicene (IX) having the filicane skeleton.

Acknowledgements. We wish to thank Prof. G. Berti for the gift of a sample of filican-3-one. P.m.r. spectra and O.R.D. curves of the compounds were kindly run at Takeda Pharmaceutical Laboratories, University of Tokyo and Japan Spectroscopic Co.

References.

(1) H. Ageta, K. Iwata, K. Yonezawa: Chem. Pharm. Bull. (Tokyo), 11, 408 (1963).

(2) H. Ageta, K. Iwata, S. Natori: Tetrahedron Letters, 1963, 1447.

(3) All melting points were corrected. Optical rotations were measured in chroloform solution.

(4) ε value of this compound in previous paper(2) was slightly lower.

(5) P. Sengupta, H.N. Khastgir: Tetrahedron, 19, 123 (1963).

(6) J.L.Courtney, R.M. Gascoigne, A.Z. Szumer: Chem. & Ind., 1956, 1479.

(7) J.M. Beaton, F.S. Spring, R. Stevenson: Chem. & Ind. 1956, 1056.

(8) G. Brownlie, F.S. Spring, R. Stevenson, W.S. Strachan: J. Chem. Soc. 1956, 2419.

(9) F.S. Spring, J.M. Beaton, R. Stevenson, J.L. Stewart: Chem. & Ind. 1956, 1055.

(10) G. Berti, F. Bottari, A. Marsili: Tetrahedron Letters, 1964, 1.