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FERN CONSTITUENT: NATURALLY OCCURRING ADIAN-5-ENE OZONIDE IN THE LEAVES OF ADIANTUM MONOCHLAMYS AND OLEANDRA WALLICHII

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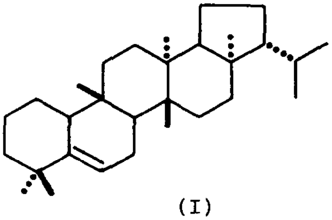
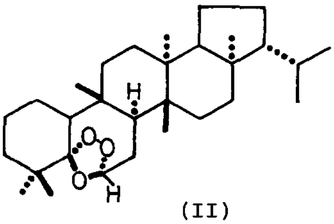
From the methanol extract of the leaves of *Adiantum monochlamys* EATON(Pteridaceae, "Hakoneshida" in Japanese), ten kinds of triterpenoid hydrocarbon including adian-5-ene(I), which belong to hopane and migrated hopane groups, had been isolated in our laboratory.1)2) Hexane extraction of the fresh leaves of the same fern collected in October afforded a triterpenoid, m.p.154-157°, $[\alpha]_D$ +19.4° ($CHCl_3$, c=1.1) as a main constituent(0.12% of the dried leaves estimated), which has been concluded to have the molecular formula, $C_{30}H_{50}O_3$, and to be adian-5-ene ozonide(II) in spectral and chemical evidence described in this communication. The compound was also isolated from the leaves of *Oleandra wallichii* PRESL(Davalliaceae) collected in Formosa.

Neither hydroxyl nor carbonyl absorption was observed in the IR spectrum of II. PMR spectrum of II showed signals of eight methyl groups at δ0.95(C-23), 1.17(C-24), 0.95(C-25), 1.00(C-26), 0.93(C-27), 0.79(C-28) and 0.81d, 0.87d(J=6.5 Hz, C-29,30).3) The chemical shifts of the last five were almost the same with those of I, while those of the first three were remarkably shifted [δ1.00(C-23), 1.06(C-24) and 0.83(C-25) in I]. The molecular peak in MS was found at m/e 458 (altitude 3%) and the base peak at m/e 274(100), which was similar to that of I being formed by loss of A and B rings. Other remarkable peaks were m/e 317(46), 299(25), 287(26), 273(67), 259(65), 231(27), 205(55) and 191(25), the last four of which were again observed in I.

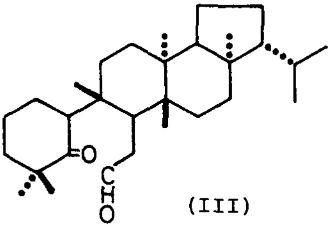
Zinc and acetic acid reduction of II afforded 5,6-secoadianan-5-on-6-al(III), m.p. 152-154°, $[\alpha]_D$ -26.6°($CHCl_3$, c=0.9), in a good yield. IR $\nu_{cm^{-1}}$: 2710, 1722,



(I)



(II)



(III)

and 1710. The methyl signals of C-23, 24 and 25 were observed at reasonably shifted positions of δ1.05, 1.13 and 0.99, respectively. MS peaks were m/e 442 (3%, M^+), 316(15), 273(20), 207(27) and 126(100), among which m/e 316 and 126 must be originated from rings C, D, E and ring A. These facts and the spectral observations of II strongly suggested that II could be a triterpenoid having a 5,6-secoadianane skeleton with three oxygen atoms.

Passing ozone in a hexane solution of I gave a sole crystalline product, which was proved to be identical with naturally occurring compound by IR, PMR and MS comparisons and mixture melting point determination. Hence the structure of the compound has been established to be adian-5-ene ozonide(II).

The stereochemistry of ozonide function can be assigned tentatively by PMR study of II as follows. One proton signal at δ5.65 could be assigned to C-6 position bearing two oxygen atoms. The splitting pattern (triplet, J = 2.5 Hz) showed that C-6 hydrogen and C-7α and β hydrogens had the same coupling constant. Another proton signal at δ2.78 could be assigned to C-8α hydrogen which is remarkably shifted to downfield by the anisotropic effect of the oxygen function at C-6 in diaxial correlation, and its splitting pattern (double doublet, J = 9 and 6.5 Hz) suggested the stereochemical correlation of 8α and 7α, 7β protons; the constants were $J_{6,7\alpha} = J_{6,7\beta} = 2.5$ Hz, $J_{8\alpha,7\alpha} = 6.5$ Hz and $J_{8\alpha,7\beta} = 9$ Hz. These situations can only be satisfied by 5α,6α-epidioxy-5β,6β-epoxy structure(II).

It is very interesting that the triterpene ozonide such as II was found as a fairly stable natural product in the ferns. Further studies on the ozonides of various triterpenoid hydrocarbons are under investigation.

Literature and Note

1) H. Ageta, K. Shiojima(nee Iwata), S. Natori, Tetrahedron Letters, 1964, 3413

2) H. Ageta, K. Shiojima, Y. Arai, Chem. Commun., 1968, 1105

3) The assignments of methyl groups were confirmed by $CDCl_3$-C_6D_6 solvents shift method.