# CHEMICAL EXAMINATION OF *ADIANTUM VENUSTUM* Don.

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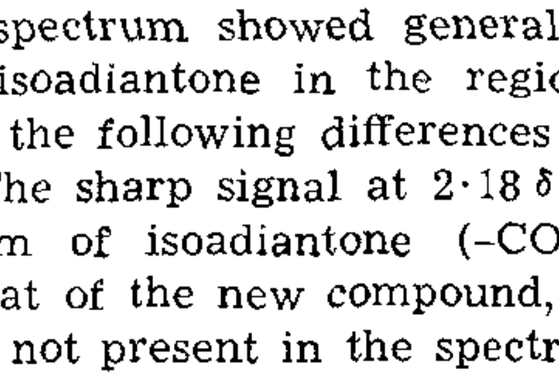
IN recent years increasing attention has been paid to the chemistry of ferns. *Adiantum venustum* is a fern of small size growing in the Himalayan region, regarding which no chemical information is available so far. Our results with this material purchased from a local dealer and identified in the Botany Department of this University are given below.

The material was extracted with petroleum ether, ether and ethyl alcohol in succession. The residue from the petroleum ether extract, a pale yellow solid, was chromatographed on neutral alumina. Petroleum ether eluted a colourless solid, which crystallised from petroleum ether-acetone as glistening plates, m.p. 229–30°. Formula $C_{30}H_{50}$,* $[\alpha]_D$† $+57{\cdot}6°$. Liebermann Burchard reaction : positive (pink); tetranitromethane reaction : positive. The I.R. spectrum showed bands at 1170 cm.$^{-1}$ (isopropyl) and 850 and 790 cm.$^{-1}$ (trisubstituted double bond). The N.M.R. spectrum showed signals at 5·25 $\delta$ (olefinic proton) and 1·64 $\delta$ (methyl group on double bond). Oxidation with $CrO_3$ in acetic acid gave on $\alpha,\beta$-unsaturated ketone (DNP reaction and U.V. absorption at 245 m$\mu$). These led to the conclusion that the hydrocarbon is 3-filicene first isolated from *Adiantum monochlamys* by Ageta *et al.*[1]

In the same chromatography petroleum ether : benzene (7 : 3) eluted a second substance crystallising as glistening needles from benzene-petroleum ether, m.p. 226°, formula $C_{29}H_{48}O$, $[\alpha]_D$ $\pm 0°$. Liebermann-Burchard reaction : positive ; tetranitromethane reaction : negative. It had I.R. absorptions at 1376 and 1364 cm.$^{-1}$ (gem-dimethyl group), 1470 cm.$^{-1}$ (methylene groups) and 1706 cm.$^{-1}$ (carbonyl). The N.M.R. spectrum showed a sharp signal at 2·18 $\delta$ (–CO–$CH_3$ group). It formed a benzylidene derivative, m.p. 268–70°, $[\alpha]_D$ $+49°$, which on ozonolysis gave the nor-acid $C_{28}H_{46}O_2$ (–COOH in place of $-COCH_3$), m.p. 310–12°. This acid was obtained also by the oxidation of the parent ketone with NaOBr (m.p., mixed m.p. and T.L.C.). A search through the literature showed that the parent ketone could be isoadiantone described by Berti *et al.*[2] For further confirmation, it was reduced with $LiAlH_4$ and with $NaBH_4$. With each reagent, a mixture of two isomeric alcohols $C_{29}H_{50}O$, m.p. 189–90° and 197–98° was obtained and these gave acetates, m.p. 197–98° and 205–06° respectively. Oxidation of each alcohol with $CrO_3$ in pyridine gave back the parent ketone.

In the same chromatography mentioned above, petroleum ether-benzene (1 : 3) eluted a third crystalline solid, m.p. 280–300° which, in spite of its large melting range, was homogeneous according to T.L.C. $[\alpha]_D$ $+13°$. Formula $C_{29}H_{48}O_2$, Liebermann-Burchard reaction : positive (pink) ; tetranitromethane reaction : negative. I.R. absorptions at 1380 and 1350 cm.$^{-1}$ (gem-dimethyl) and 1450 cm.$^{-1}$ (methylene) confirmed its triterpenoid nature. The bands at 3492 and 1307 cm.$^{-1}$ showed the presence of hydroxyl group, but it resisted acetylation and may be tertiary. The absorption at 1711 cm.$^{-1}$ showed the presence of a six-membered ring ketone. The compound formed a DNP derivative, m.p. above 315° and gave a positive Zimmermann colour reaction indicating the presence of a $-CH_2-CO-$ group. The iodoform reaction was negative and the compound was recovered unchanged after treatment with NaOBr for 10 hours (absence of $-COCH_3$). Its N.M.R. spectrum showed general similarity to that of isoadiantone in the region 0·74 to 1·06 $\delta$. But the following differences were conspicuous. The sharp signal at 2·18 $\delta$ present in the spectrum of isoadiantone ($-COCH_3$) was absent in that of the new compound, while two new signals not present in the spectrum of isoadiantone were present in that of the new compound. These were (1) a multiplet centred at 2·47 $\delta$ and integrating to *ca* 2 protons which showed the presence of a $-COCH_2-$ group split by neighbouring protons, and (2) a fairly sharp signal at 1·27 $\delta$ integrating to *ca* 3 protons ($CH_3-C-OH$). On the basis of these data, the structure (A) is tentatively suggested for it. Further work to verify this is in progress.




[A]

* All the compounds whose formulæ are given in this communication analysed correctly for C and H.

† All rotations were taken in chloroform solution.

Since according to Berti *et al.*[2] adiantone isomerises to isoadiantone with acids or alkalies or on chromatography over alumina, in another experiment the petroleum ether extract of the fern was chromatographed on silica gel instead of alumina. In this chromatogram the ketone, m.p. 226°, $[\alpha]_D$ 0° was not obtained; instead another substance, m.p. 218°, $C_{29}H_{48}O$, $[\alpha]_D$ + 96° was got. A mixture of the two substances melted at 180–85°. The substance of m.p. 218° underwent isomerisation to the ketone, m.p. 226° (mixed m.p.) on treatment with hot alkali or hot mineral acid. This compound of m.p. 218° should therefore be adiantone.

The ether extract of the plant yielded a gummy residue which was saponified with potash in benzene-alcohol solution. The unsaponifiable matter, a red semi-solid, was chromatographed on neutral alumina. Benzene : chloroform (1 : 1) eluted a reddish-yellow substance which crystallised from benzene-methanol as reddish-yellow plates, m.p. 173–75°. It gave a violet colour with conc. $H_2SO_4$ and a blue colour with $SbCl_3$ in chloroform. It showed absorption in the visible region as below: 497, 467 mμ ($CS_2$), 480, 450 mμ ($C_6H_6$), 478, 449 mμ ($CHCl_3$). These indicate that it may be α-carotene monoepoxide.[3]

The alcoholic extract was concentrated to low bulk and the largely aqueous residue extracted successively with petroleum ether, benzene, ether and ethyl acetate. The ethyl-acetate extract was concentrated and diluted with petroleum ether. The yellow solid that separated was a mixture. It was chromatographed on silica gel and eluted with dry solvents. Benzene : ethyl acetate (3 : 1) eluted a colourless substance, m.p. 275–80° giving a red colour with hot alcoholic HCl (leucoanthocyanidin). Subsequent elution with benzene : ethyl acetate (1 : 3) yielded a bright yellow solid which gave a ferric reaction and a red colour with Mg-HCl (flavonoids).

The leucoanthocyanidin was refluxed with 10% ethanolic HCl and the mixture, after removal of alcohol and replacement by water, was extracted with ether, ethyl acetate and amyl alcohol in succession. The first two extracts yielded nothing. The flavylium salt contained in the amyl alcohol extract was transferred into 0·01% aqueous HCl in the usual manner and utilised for obtaining the pure flavylium salt by means of preparative paper chromatography. The flavylium salt was eluted from the paper chromatogram with 0·01% alcoholic HCl and the rose-red solution used for spectral analysis. It had an absorption maximum at 533 mμ which was unaffected by the addition of $AlCl_3$. These showed that the parent leucoanthocyanidin was leucopelargonidin.

The flavoniod fraction mentioned above was found to be glycosidic in nature (Molisch's test). Thin layer chromatography of the aglycone (obtained by the hydrolysis of the glycoside with 7% $H_2SO_4$) showed the presence of two aglycones. Attempts to separate the glycosidic mixture by column chromatography on silica gel, by preparative T.L.C. and by preparative paper chromatography, all failed. The glycosidic mixture was therefore used as such for further study. Examination of the sugar obtained by the hydrolysis using paper chromatography showed the presence of only one sugar, namely glucose. The aglycones were prepared in sufficient quantity using chromatography on silica gel and identified as kæmpferol and quercetin respectively by spectral examination in the visible and ultra-violet regions, together with shifts in the absorption maxima on the addition of $AlCl_3$, NaOAc, NaOAc + $H_3BO_3$ and NaOEt, and through their $R_f$ values in paper chromatography and T.L.C. in different solvent systems.

To summarise, *Adiantum venustum* contains 3-filicene, adiantone and a new triterpenoid keto-alcohol, a carotenoid which seems to be α-carotene monoepoxide, leucopelargonidin, kæmpferol glucoside and quercetin glucoside. Some new derivatives and reactions of isoadiantone are described and a tentative structure (A) proposed for the new triterpenoid.

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1. Ageta, H., Iwata, K. and Natori, S., *Tetrahedron Letters*, 1964, p. 3413.
2. Berti, G., Bottari, F., Marsili, A., Lehn, J. M., Witz, P. and Ourisson, G., *Ibid.*, 1963, p. 1283.
3. Karrer, P. and Jucker, E., *Carotenoids*, Elsevier Publishing Co., 1950, p. 158.

*Note.*—In the latest issue of *Tetrahedron Letters* we have noticed an article by A. Zaman *et al.* (1966, p. 3943) describing the triterpenoids of *Adiantum venustum*. They too have isolated adiantone and 3-filicene, but by a different method from ours. They have also described a third triterpene for which they have deduced the structure 21-hydroxy-adiantone. With hot alkali or $Ac_2O$ it was found to be transformed into a mixture of isomeric ketols for which they have suggested two tentative structures. It may be pointed out that the first of these two structures is being suggested by us for our third triterpene [*see* structure (A) earlier in this article].