**Tetrahedron Letters No.33, pp. 3943-3947, 1966. Pergamon Press Ltd.
Printed in Great Britain.**

A NEW NORTRITERPENOID KETOL FROM TWO ADIANTUM SPECIES

A. Zaman and A. Prakash
Department of Research in Unani Medicine, Tibbiya College,
A. M. U. Aligarh, India
G. Berti, F. Bottari, B. Macchia, A. Marsili and I. Morelli
Institutes of Organic Chemistry and Pharmaceutical Chemistry
of the University of Pisa, Italy

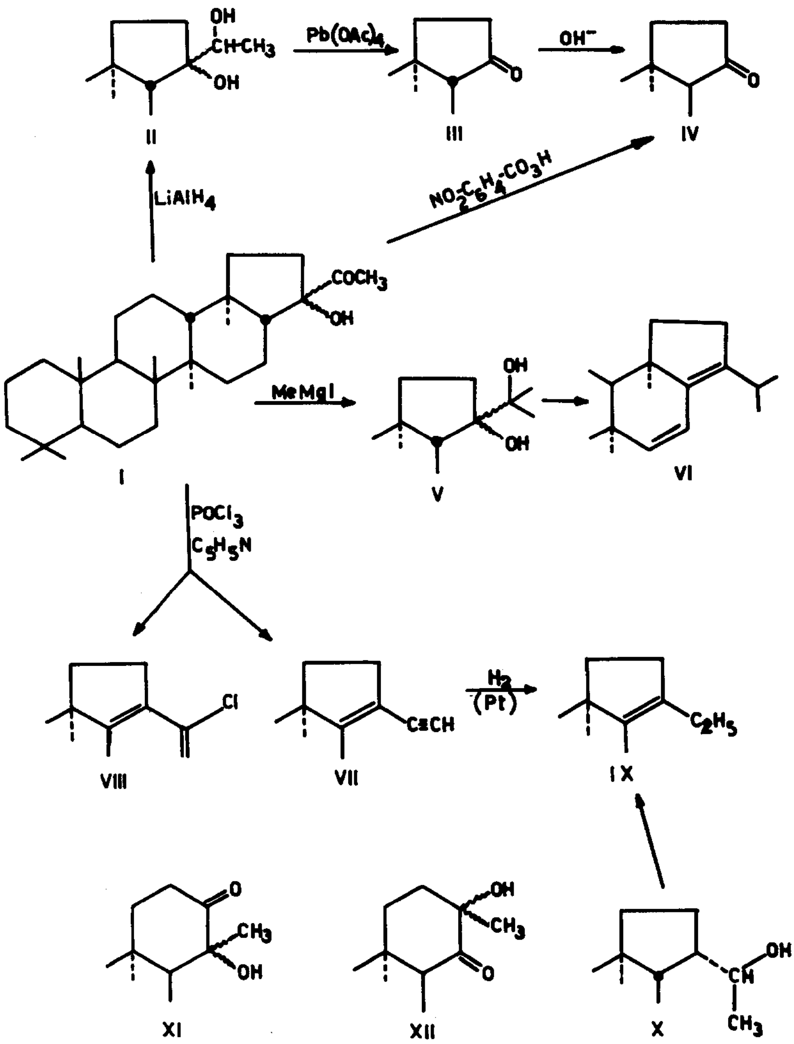
(Received 14 June 1966)

During a study of constituents of the fern Adiantum venustum Don conducted at Aligarh it was found that the plant contains a new triterpenoid compound. The same compound had been obtained in Pisa from Adiantum capillus-Veneris L., but had not been investigated because of the very small amount that was available. On isolation of somewhat larger amounts in Aligarh a joint study led to the identification of the compound as 21-hydroxy-30-norhopan-22-one (21-hydroxyadiantone, I).

The compound was isolated from the petroleum ether extract of Adiantum venustum, which also contains a large excess od adiantone (1) and traces of 3-filicene (2,3). It crystallizes out from the extract, on concentration and cooling, along with adiantone, and is freed from the latter by taking advantage of its sparing solubility in benzene. It was further purified by repeated crystallization from benzene-chloroform and finally recrystallized from pyridine-dioxane. It has m.p. 281-284° (dec.) and gives a positive Cotton effect curve, a = +18°, $[\phi]_{303}$ +1490°, $[\phi]_{265}$ -280° (dioxane). Elemental analysis pointed to the formula $C_{29}H_{48}O_2$, which was confirmed by mass spectroscopy: molecular peak at m/e 428; strong base peak at m/e 191, due to the $C_{14}H_{23}^+$ fragment usually found in pentacyclic triterpenoids having no oxigen or double bonds in rings A, B and C (4). IR bands at 2.93 and 5.90 µ showed that the two oxygen atoms are present as a hydroxyl and a carbonyl group. The fact that the compound was not oxidized by Jones' reagent pointed to a tertiary hydroxyl group. Reduction of I with $LiAlH_4$ gave a diol (II), m.p. 260-264°, $[\alpha]_D^{21}$ +33° ($CHCl_3$), which reacted with lead tetraacetate at room temperature to form a ketone, m.p. 170-175°, $[\alpha]_D^{21}$ -21° ($CHCl_3$); this was transformed by KOH in ethanol into an isomeric ketone, m.p. 238-240°, $[\alpha]_D^{27}$ +145° ($CHCl_3$). The two ketones were identified as the 17βH- and 17αH-bisnorketones III and IV (1,5) by comparison of the IR spectra with those of authentic samples. The ketone IV was also obtained as the product of a Baeyer--Villiger oxidation of I with p-nitroperoxybenzoic acid and trifluoroacetic acid in chloroform.

The reaction of I with methylmagnesium iodide led to the diol V, m.p. 268-273°, $[\alpha]_D^{20}$ +21° ($CHCl_3$). V was dehydrated by $POCl_3$ in pyridine to a mixture of conjugated dienes, which was isomerized by HCl in ethanol to a different mixture, in which 15,17(21)-hopadiene (VI) (6) was the major component, as shown by GLC and IR spectrum.

The reaction of I with $POCl_3$ in pyridine took an unusual course: it gave, beside other products, about 30% of the enyne VII, m.p. 230-235°, $[\alpha]_D^{27}$ +117° ($CHCl_3$), λ_{max} (cyclohexane) 237 mµ (ε = 13,000); the acetylenic group was clearly evidenced by sharp bands at 3.04 and 4.80 µ in the IR and a one-proton singlet at 3.02 δ in the NMR spectrum; no ethylenic proton peaks appeared in the NMR spectrum. The


OH
CH-CH$_3$
OH
II
Pb(OAc)$_4$
O
III
OH$^-$
O
IV
LiAlH$_4$
NO$_2$-C$_6$H$_4$-CO$_3$H
COCH$_3$
OH
I
MeMgI
OH
OH
V
VI
POCl$_3$
C$_5$H$_5$N
Cl
VIII
C≡CH
VII
H$_2$
(Pt)
C$_2$H$_5$
IX
O
CH$_3$
OH
XI
OH
CH$_3$
O
XII
OH
CH
CH$_3$
X

reaction probably involves a dehydration, formation of the chlorodiene VIII, followed by dehydrochlorination to give VII. This hypothesis was confirmed by the isolation in about 10% yield from the reaction mixture of I with $POCl_3$ of compound VIII, m.p. 192-195°, $[\alpha]_D^{20}$ +46° ($CHCl_3$), λ_{max} 246 mμ (ε = = 11,000), strong band at 11.2 μ ($>C=CH_2$). Catalytic reduction of VII over Adams Pt in cyclohexane-acetic acid, gave the olefin IX, m.p. 166-169°, which was also prepared by refluxing adiantol (X) (7) with benzoyl chloride.

The ketol I is transformed by reflux with KOH in ethanol, or with acetic anhydride, into a mixture of isomeric ketols, m.p. 280-290°, which does not show the CH_3CO peak in the NMR spectrum. Although this reaction has not yet been investigated further, because of lack of starting material, it very probably involves a ring enlargement reaction to XI or XII, similar to those which lead from 17-hydroxypregnane-20-ones to D-homosteroids (8).

The peculiar degradation of the hopane to the 30--norhopane skeleton appears to be characteristic of ferns of the Adiantum genus: beside the isolation of I from A. Venustum and A. capillus-Veneris, adiantone has been found in the same two species, and also in A. pedatum and A. monochlamys (9), but so far in no species of any other genus.

We thank Professor Ludwig Bauer (Chicago) for the mass spectrum of I and Dr. G. Ceccarelli (Pisa) for the NMR spectra. The work of the Italian group was supported by the Consiglio Nazionale delle Ricerche.

REFERENCES

1. G. Berti, F. Bottari, A. Marsili, J. M. Lehn, P. Witz and G. Ourisson, Tetrahedron Letters, 1283 (1963).
2. G. Berti, F. Bottari and A. Marsili, Il Farmaco (Pavia), Ed. Sci., **18**, 441 (1963); Tetrahedron Letters, 1 (1964).
3. H. Ageta, K. Iwata, and S. Natori, Tetrahedron letters, 3413 (1964).
4. H. Budzikiewicz, J. M. Wilson and C. Djerassi, J. Amer. Chem. Soc., **85**, 3688 (1963).
5. G. V. Baddeley, T. G. Halsall and E. R. H. Jones, J. Chem. Soc., 1715 (1960).
6. Y. Tsuda and K. Isobe, Tetrahedron Letters, 3337 (1965); G. Berti, F. Bottari, A. Marsili and I. Morelli, ibid., 979 (1966).
7. G. Berti, F. Bottari, A. Marsili and L. Mazzanti, Il Farmaco (Pavia), Ed. Sci., **18**, 424 (1963).
8. L. F. Fieser and M. Fieser, Steroids, p. 578. Reinhold Publishing Corporation, New York (1959).
9. H. Ageta, K. Iwata, Y. Otake and S. Natori, Paper presented at the IUPAC Symposium on Natural Products, Kyoto, April 1964.