Tetrahedron Letters No. 1, pp. 1-5, 1964. Pergamon Press Ltd.
Printed in Great Britain.

THE STRUCTURE OF ADIANTOXIDE, A TRITERPENOID EPOXIDE WITH A NEW TYPE OF CARBON SKELETON

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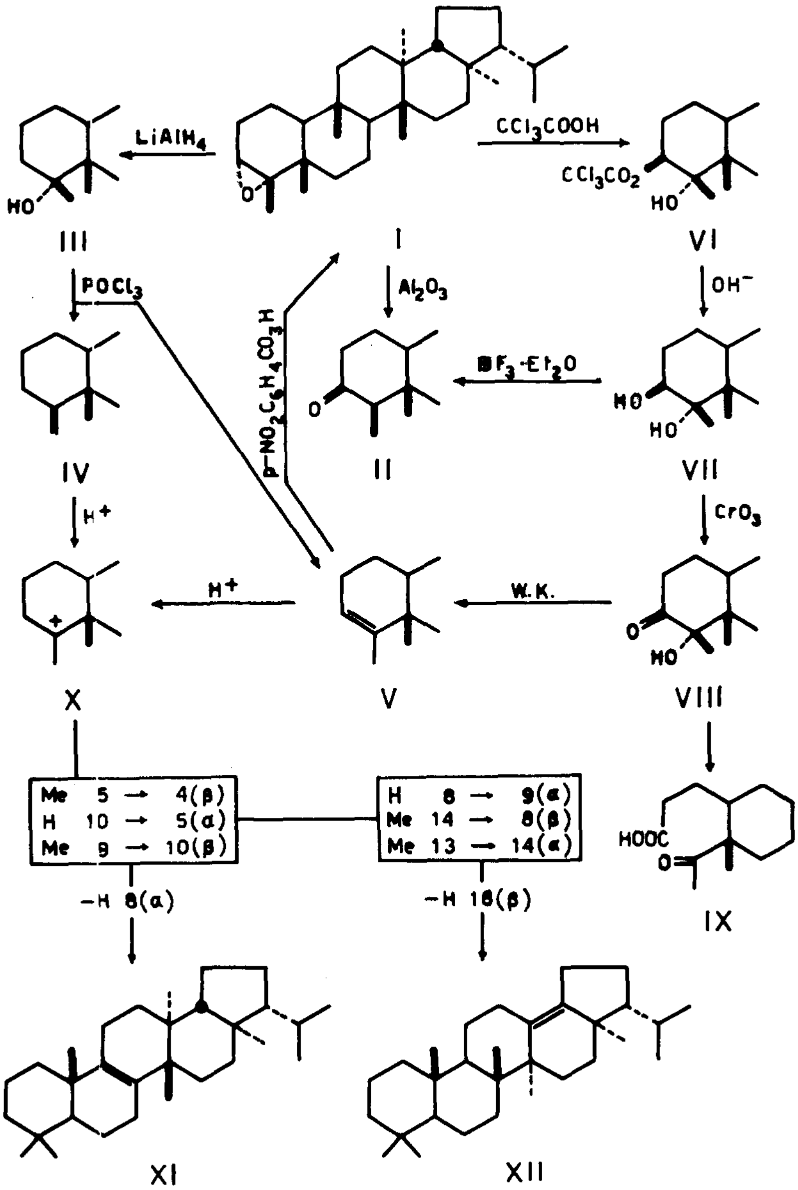
(Received 29 October 1963)

IN a previous paper we had described the isolation from the fern Adiantum capillus Veneris of a compound $C_{30}H_{50}O$ or $C_{29}H_{48}O$, m.p. 229-231°, $[\alpha]_D^{30}$ + 46.8°, which we had called adiantoxide.[1] The preliminary work had shown that the oxygen atom was present as a 1,2-epoxide, linking a secondary carbon atom to a tertiary one, carrying a methyl group, on a terminal six-membered ring. A remarkable similarity in the optical rotations of several derivatives of adiantoxide with those of analogous friedelin derivatives made it very probable that rings A and B of these compounds had the same type of structure and configuration.

Structure I has now been established for adiantoxide, some doubt remaining only about the configuration of the epoxide ring. Determination of molecular weight by mass spectrometry has confirmed the formula $C_{30}H_{50}O$. Circular dichroism curves of the previously described compounds II and IX methyl ester[1] were identical with those of friedelin and methyl friedonate, respectively, a fact which provided further evidence about a friedelane type of structure at least for rings A and B in adiantoxide. Isomerisation of the hydrocarbons IV and V gave interesting results. When V, prepared from the ketol VIII[1] by Wolff-Kishner reduction, or a mixture of IV and V, obtained by dehydration of


LiAlH4
CCl3COOH
HO
O
CCl3CO2
HO
III
I
VI
POCl3
p-NO2C6H4CO3H
Al2O3
OH⁻
BF3·Et2O
O
HO
HO
IV
II
VII
H+
CrO3
H+
W.K.
+
O
HO
X
V
VIII
Me 5 → 4(β)
H 10 → 5(α)
Me 9 → 10(β)
H 8 → 9(α)
Me 14 → 8(β)
Me 13 → 14(α)
HOOC
O
IX
−H 8(α)
−H 18(β)
XI
XII

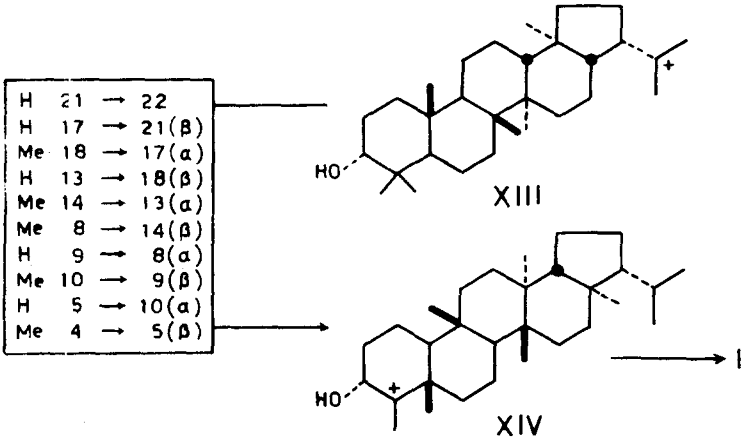
the alcohol III with phosphorus oxychloride[1], was refluxed 6 hrs. with trifluoroacetic acid in benzene, a hydrocarbon (m.p. 183-185°, $[\alpha]_D^{20}$ +14°) was obtained as the main product; a similar isomerisation with hydrochloric acid in boiling acetic acid for 18 hrs. gave smaller amounts of the same compound, and a second hydrocarbon (m.p. 194-196°, $[\alpha]_D^{20}$ +3°). The two olefins were identified respectively as isofernene (XI)[2,3] and hopene-II (XII),[4] by mixed m.p. and comparison of the infra-red spectra with those of authentic samples. The formation of isofernene proved the structures of ring C, D, E, and this completed the elucidation of the adiantoxide ring system.

The transformation of IV and V into XII is comparable with that of friedel-3-ene into olean-13(18)-ene[5] and can be rationalised by a series of 1,2-shifts, starting from the cation X, as shown in the scheme.

The configuration of the epoxide ring has been formulated tentatively as in I, on the basis of the fact that adiantoxide was obtained from V by reaction with p-nitroperoxybenzoic acid: many examples in the steroid field prove that epoxides are formed from olefins preferentially from the less hindered side of the ring system;[6] the 5β-methyl group in V should exert a considerable shielding action on the β-side, and the α-epoxide should form more easily. Work is in progress to subject this point to a more rigorous control.

The carbon skeleton of adiantoxide has not yet been reported for other triterpenoids; we propose for the corresponding hydrocarbon the name of filicane.

The biogenesis of adiantoxide could follow a path similar to that assumed for friedelin,[7] starting from a hopane precursor, such as XIII, and leading through a series of 1,2-shifts, to the hydroxy cation XIV, which could cyclise to the epoxide I, instead of eliminating a proton to give a ketone as in the case



XIII

XIV

of friedelin. A similar type of termination could account for the formation of the 3,5 or 3,10 epoxide ring in campanulin.[8, 9]

It is remarkable that all triterpenoids so far isolated from ferns can fit into a single biogenetic scheme, having a precursor with the skeleton of hopane, which is one of the simplest cyclisation products of squalene in the all-chair conformation: thus, while diplopterol[10] and diploptene[8] present the intact hopane system and adiantone[11] is a 22-norhopanone, fernene[8] and davallic acid[12] can be considered as derived from an intermediate stage in the transformation of the hopane into the filicane ring system.

We wish to thank Prof. G. Ourisson (Strasbourg) for very helpful discussion and for the circular dichroism measurements, Dr. W. Vetter (Gif) for the determination of the molecular mass, Prof. H. Ageta (Tokyo) for the gift of a sample of isofernene, and Consiglio Nazionale delle Ricerche for financial support.

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