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THE STRUCTURE OF ARUNDOIN, THE TRITERPENE METHYL ETHER FROM IMPERATA CYLINDRICA VAR. MEDIA AND ARUNDO CONSPICUA

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IN the previous communication,(1) we have reported on two triterpene methyl ethers from the rhizomes of *Imperata cylindrica* P. Beauv. var. *media* Hubbard(syn. var. *Koenigii* Durand et Schinz.)(Gramineae). The less soluble one, m.p. 269-270°, $(\alpha)_D$ +60°($CHCl_3$), named cylindrin, was proved to be methyl ether(I) of isoarborinol, while the more soluble one, m.p. 242-243°,*1 $(\alpha)_D$ -5.3°($CHCl_3$), was shown to be identical with arundoin, isolated from *Arundo conspicua* (Gramineae) by Eglinton, Hamilton, Martin-Smith, and Subramanian.(2),*2 They proposed the structure(II) for arundoin, since the diene, formed by the acid catalysed cleavage of the epoxide of arundoin, was assumed to be identical with

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*1 Eglinton, et al.(2) reported m.p. 235-237° and 271-273° (dimorphic forms) for arundoin, but we have not so far obtained the higher m.p. form.

*2 The identity has also been confirmed by Dr. Martin-Smith (private communication).

methyl ether of multiflora-7,9(11)-dien-3β-ol(III),[*3] whilst arundoin itself was not identical with methyl ether of multiflorenol(IV). Since we had some incompatible evidences with the structure(II), e.g. the presence of secondary methyl groups was suggested by NMR spectra of arundoin and the derivatives, further studies have been carried out and now reach to a conclusion that arundoin must be expressed by the structure(Va).[*3]

IR absorptions(1103; 815, 790 cm^{-1}), NMR signals(6.66 τ (3H, s); 4.67 τ(1H, m)) and a mass spectrum of arundoin(Va) suggested that Va is a pentacyclic triterpene of a molecular formula, $C_{31}H_{52}O$, having a methoxyl group and a tri-substituted double bond.

As was discussed in the previous communication,(1,3) the $(\alpha)_D$ value of Va suggested the location of the double bond at 7 or 9(11) position, so far as Va has oleanane, ursane, or hopane or their rearranged skelton and the methoxyl group is at 3β-position.(3-6) Although the British workers(2) claimed that arundoin did not isomerise by the acid treatment, Va isomerised to VIa, m.p. 223-224°, $(\alpha)_D$ +28.9°($CHCl_3$). The IR spectrum and the $(\alpha)_D$ value suggested that the double bond had migrated to Δ^8 position.(1,3-8) The action of perbenzoic acid on Va afforded an unstable epoxide(VII), m.p. 271-272°, $C_{31}H_{52}O_2$. Treatment of VII with acid afforded the diene(VIII),

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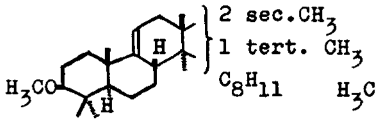
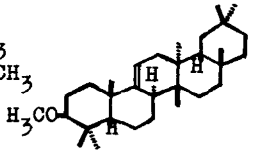
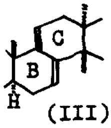
[*3] In a personal communication Dr. Martin-Smith has informed us of the Glasgow group's acceptance of our conclusion. Certain discrepancies between their infrared spectra of the 7,9(11)-diene from arundoin and of the methyl ether of the 7,9(11)-diene derived from multiflorenol (since shown to be impure) were overlooked and the original conclusion of identity has been retracted. The n.m.r. spectrum of arundoin measured on the 40 Mc instrument available to the Glasgow group failed to reveal the splitting of the isopropyl methyl groups which was the important clue to the true identity of arundoin.



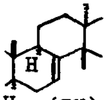
(I)



(II)



(III)



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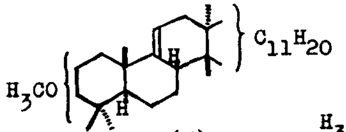
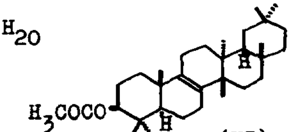
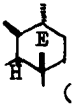


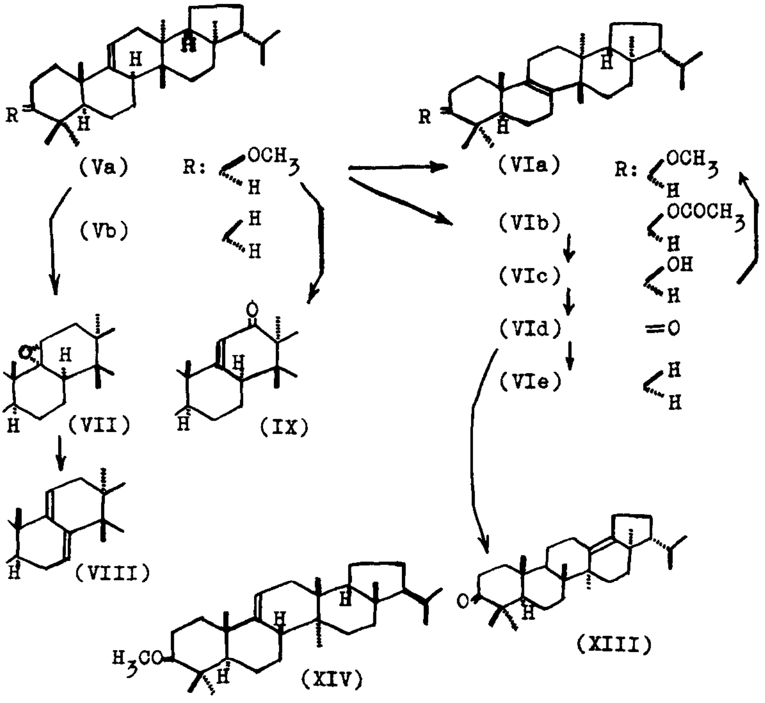
(X)



(XI)



(XII)



m.p. 228-231°, $(\alpha)_D$ -157°($CHCl_3$), $C_{31}H_{50}O$.*3 The UV absorptions(λ_{max}^{hexane} 233, 239, 247 mμ(ε 14700, 16400, 10700)) were characteristic for 7,9(11)-diene with 13α,14β methyl groups(1-8) or 1(10),5-diene,(3,9) in which the latter was ruled out by the $(\alpha)_D$ value. Chromic acid oxidation of Va afforded a conjugated enone(IX), m.p. 282-284°, $(\alpha)_D$ -5.6°($CHCl_3$), $C_{31}H_{50}O_2$, UV λ_{max}^{hexane} 238 mμ(ε 12500), IR 1665, 1610, 1102, 869 cm^{-1}. The ORD curve of the ketone showed a positive Cotton effect curve(peak, $(\Phi)_{368}$ +3540°; trough, $(\Phi)_{314}$ -9260°) and coincided with those of fern-9(11)-en-12-one(6) and methyl 12-ketodavallate.(7) Mass spectrum of Va showed the prominent peaks at 273 and 241 m/e, corresponding to the base peak at M^+-167, diagnostic for $\Delta^{9(11)}$ or Δ^8 compounds.(1,2,6,7,8,10) Very weak signals for b-b and c-c fragments(cf ref. 10) are rather similar to the fragmentation pattern of fernene(Vb)(6) and different from those of multiflorene and bauerene derivatives.(8,10) The mass spectrum of VIa showed the nearly the same fragmentation, which suggested the location of the double bond not at 13(18) but at 8 position.

These observations suggested that Va has the partial formula(X).

Treatment of Va with acetic anhydride-hydrochloric acid in chloroform-phenol(1) afforded an acetate(VIb), m.p. 226-227°, $(\alpha)_D$ +20.3°($CHCl_3$), $C_{32}H_{52}O_2$, IR 1728, 1240 cm^{-1}. Hydrolysis of the acetate afforded a secondary alcohol(VIc), m.p. 195-197°, $C_{30}H_{50}O$. Oxidation of the alcohol(VIc) with chromium trioxide-pyridine afforded a ketone(VId), m.p. 214-216°, $C_{30}H_{48}O$, IR 1706 cm^{-1}. IR and NMR spectra of VIb, VIc, and VId indicated that the double bond has been migrated to a tetra-substituted position. The $(\alpha)_D$ value of VIb and the base peak at 257 m/e of mass spectrum of VId indicated the presence of the double bond at 8 position. ORD curve of the ketone(VId) showed a positive Cotton effect curve(peak, $(\Phi)_{313}$ +2120°, $(\Phi)_{303}$ +2180°, trough, $(\Phi)_{275}$ +380°), which offer a support to the location of the oxygen function at 3 position. NMR spectra of VIb and VIc showed quartets at 5.62 τ and 6.38 τ respectively(VIb, J= 10 and 5 cps.; VIc, J= 13 and 6 cps.) indicating that the acetoxyl and the hydroxyl groups are in equatorial conformation. However, the acetate(VIb) was proved to be not identical either with isomultiflorenyl acetate(XI)(4) or with isobauerenyl acetate(XII).(4) Thus Va must not be oleanane or ursane series of compounds.

Final conclusion of the skelton was obtained by the Wolff-Kishner reduction of the ketone(VId). The hydrocarbon (VIe) thus formed, m.p. 185-186°, $(\alpha)_D$ +20.4°($CHCl_3$), $C_{30}H_{50}$, showed the complete identity with isofernene(fern-8-ene),(3,6) by a mixed fusion, IR spectra, t.l.c., and g.l.c. Treatment of the ketone(VId) with hydrochloric acid-acetic acid afforded the isomer, m.p. 146-148°, which was proved to be identical with hopenone-II(XIII),(11) prepared from hydroxyhopanone, by IR spectra, g.l.c., and t.l.c. The fact offers further confirmation of the nucleus and the location of the oxygen function.

Methylation of the alcohol(VIc) with methyl iodide and potassium afforded the Δ^8 isomer(VIa). Thus the configuration at 3 position has been retained in the derivation of Va to VIc. NMR spectrum of Va showed a quartet at 7.35 τ(J= 12 and 4 cps.), which will be assigned to C_3-axial proton, and suggested that the methoxyl group is also in 3β-position.

From these facts, the structure of arundoin should be expressed by 3β-methoxyfern-9(11)-ene(Va).(6)

Recently, there have been reported the rearranged hopane-zeorinane series of compounds isolated from ferns(3,6,7,12) and our studies offer an example of this class of compounds from higher plants.*4

There has been no decisive evidence on the structure of rings D and E of cylindrin(I), methyl ether of isoarborinol, isolated from the same plant,(1) but it might be possible that I also has the ring system similar to rings D and E of arundoin such as XIV from the biogenetical point of view and from the similarity of the fragmentation pattern of cylindrin and arborinol derivatives with those of fernene derivatives. Further studies on this point are now in progress.

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*4 Quite recently the structures of four triterpenoids from Rhododendron linearifolium have been established as this class of compounds(S. Nakamura, T. Yamada, H. Wada, Y. Inoue, T. Goto and Y. Hirata, Tetrahedron Letters, in the press).

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