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Further Characterization of Triterpenoids of Migrated Hopane and Arborane Groups from Gramineae Plants

Arundoin, one of the two major triterpenoids[1] from rhizomes of *Imperata cylindrica* P. BEAUV. var. *media* HUBBARD (チガヤ) (Gramineae), has been proved to be identical[2] with the triterpene from *Arundo conspicua* (Gramineae)[3] and the structure has been revised to 3β-methoxyfern-9(11)-ene (Ia).[2] The other triterpene, named cylindrin, has been characterised[1] as methyl ether (Ⅱ) of isoarborinol.[4] Considerations on biogenesis[5] of migrated hopane, *i.e.* fernane, and arborane derivatives from present knowledges on triterpene chemistry,[6] and the similarity of mass spectral fragmentation,[5] which would be much influenced by the stereochemical relations of the double bond and the rings D and E,[4,7] of fern-9(11)-ene and arbor-9(11)-ene derivatives, lead to our proposal[2] of the most probable structure (Ⅲ) for arbor-9(11)-ene derivatives. This has now been proved to be correct by X-ray analysis of 2α-bromoarborinone (Ⅳ).[8]

Further examinations on the minor constituents of the same plant afforded three triterpenoids of rearranged hopane and arborane groups: simiarenol(adian-5-en-3β-ol) (Va),[9] m.p. 209∼211°, acetate, m.p. 216∼217°, $[\alpha]_D$ +70° (CHCl$_3$); a new triterpene (Ib), m.p. 192∼193°, $[\alpha]_D$ −19° (CHCl$_3$), acetate, m.p. 222∼223°, $[\alpha]_D$ −9° (CHCl$_3$); and isoarborinol (arbor-9(11)-en-3β-ol) (Ⅲb),[4,10] m.p. 295∼300°, acetate, m.p. 296∼298°, in respective yields of 0.001, 0.0005, and 0.0005%. Identification of Va and Ⅲb has been made by the direct comparison with the authentic specimens.[*1]

Although simiarenol (Va) has been correlated with adian-5-ene (Vb),[11] placement of the hydroxyl group at 3β-position has based on ORD and NMR data; thus the acid

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[*1] The authors thanks are due to Miss W.H. Hui, University of Hong Kong, for her kind donation of the authentic specimen of simiarenyl acetate.

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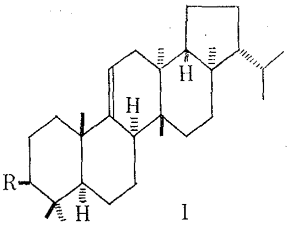
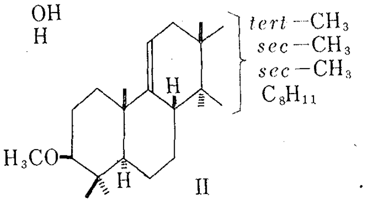
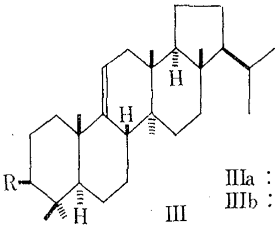

I

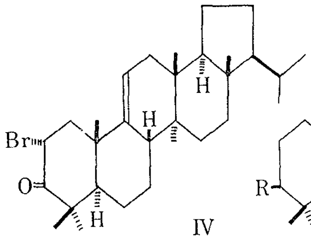
Ia : R=OCH_3
Ib : OH
Ic : H



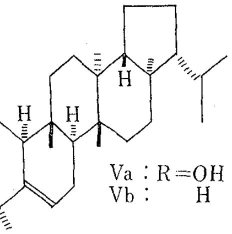
II

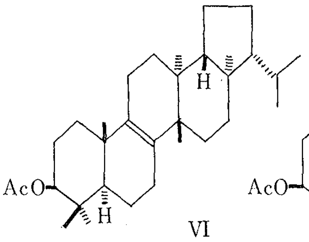

III

IIIa : R=OCH_3
IIIb : OH

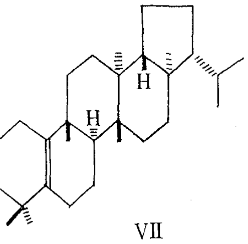


IV


Va : R=OH
Vb : H



VI



VII

catalyzed migration reaction of the acetate of Va has been carried out. From the reaction mixture, 3β-acetoxyfern-8-ene (VI),[2] along with 3β-acetoxyadian-5(10)-ene (VII), m.p. 276~278°, $[\alpha]_D$ −35.8° ($CHCl_3$), and a hydrocarbon, was isolated. Since VI has been further derived[2] to hopenone-II,[12] this offers confirmative evidence for the location of hydroxyl group in simiarenol (Va).

The new triterpene, m.p. 192~193° (Ib), designated fernenol (Ib), $C_{30}H_{50}O$, is a pentacyclic triterpene, having one each of tri-substituted double bond (IR : Ib, 815, 790 cm^{-1}, the acetate, 815, 790 cm^{-1}) and hydroxyl group (IR : Ib, 3530 cm^{-1}, the acetate, 1725, 1250 cm^{-1}). The mass spectrum of Ib (426 (M^+), 259 (M^+-167) (base peak), 241 (M^+-167-H_2O)) suggested the presence of the double bond at 9(11)-position, probably on fernane or arborane nucleus,[5,7] since the fragmentation pattern is quite similar to those compounds and different from Δ^7 compounds[7,13,14] and other groups of triterpenoids.[7] Methylation of Ib with methyl iodide and potassium in benzene afforded arundoin (Ia) and oxidation of Ib with chromium trioxide-pyridine to 3-keto compound, followed by the Wolff-Kischner reduction, afforded fern-9(11)-ene (Ic);[13] thus Ia, Ib, and Ic have been correlated and the structure of the new triterpene has been established as fern-9(11)-en-3β-ol (Ib).

From benzene extract of whole herbs of *Zoysia japonica* Steud. (シバ) (Gramineae), after the treatment by the same method as that for *Imperata cylindrica*,[1] four triterpenoids have been isolated each in 0.001% yield and identified with arundoin (Ia), cylindrin (IIIa), fernenol (Ib), and isoarborinol (IIIb).

The triterpene, isolated from the leaves of *Tripetaleia paniculata* (ホツツジ) (Ericaceae) by Kondo, *et al.*,[*2,15] m.p. 210~211°, has been proved to be identical with simiarenol (Va), which was isolated originally from a Ericaceae plant.[9]

Biogenesis of migrated hopane derivatives (Ia, Ib, Va) and arborane derivatives (IIIa, IIIb) will be explained as shown in Chart 1[5,8,13] and the relationship of hopane-zeorinane group (VIII) and fernane group (I) to arborane group (III) corresponds to those of dammarane group and euphane-tircallane group to lanostane group in tetracyclic triterpenoids, the difference coming from chair and boat conformations of the ring B of all-*trans*-squallene at the initial stage of cation induced cyclization.[6] The occur-

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[*2] The authors thank Prof. T. Takemoto, Tohoku University, for his kind gift of the specimen.

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rence of the pairs of compounds such as Ia and Ⅲa, and Ib and Ⅲb, having the same structure in ring A and enatiomorphic in rings C, D, and E, in the same Gramineae plants might be worth while to note from biogenetical and chemotaxonomical points of view.

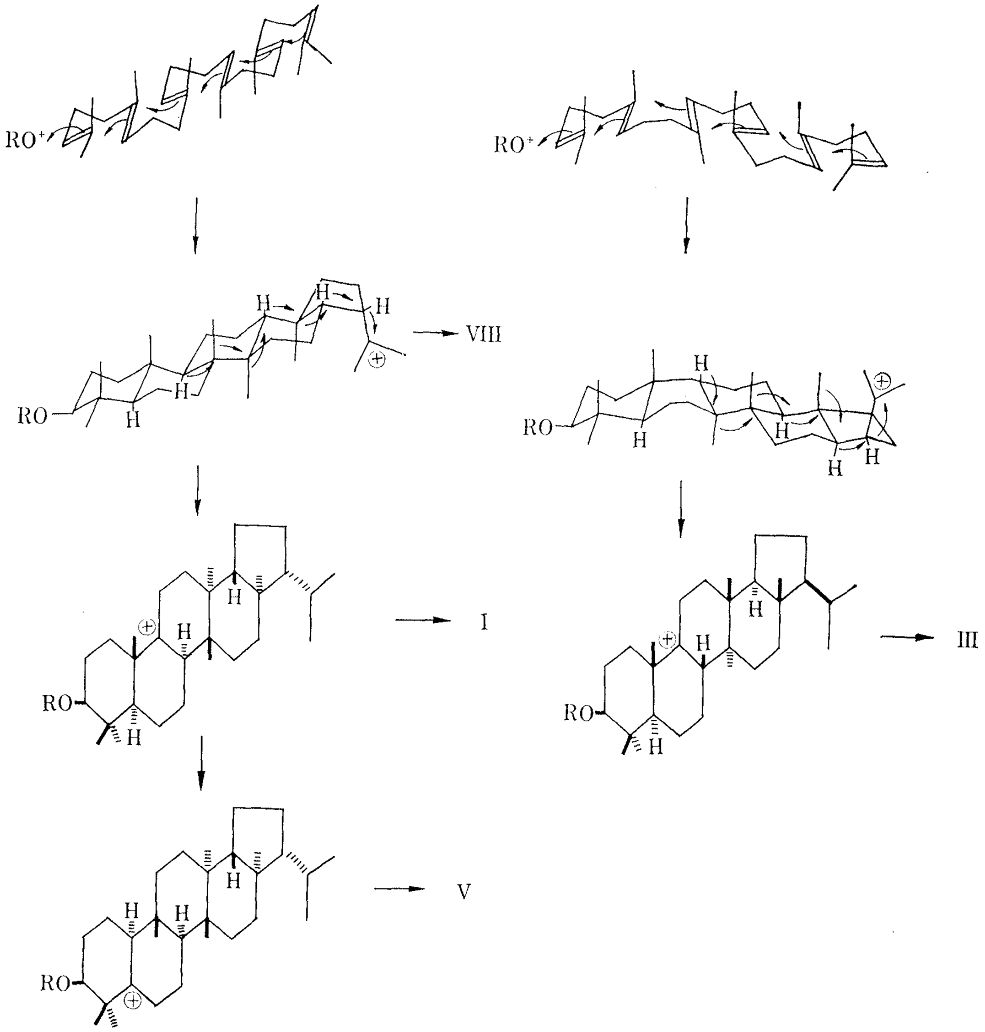

Chart 1. Biogenesis of Migrated Hopane and Arborane Derivatives

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