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THE STRUCTURES OF ARUNDOIN, CYLINDRIN AND FERNENOL

TRITERPENOIDS OF FERNANE AND ARBORANE GROUPS OF *IMPERATA CYLINDRICA* VAR. *KOENIGII**

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Abstract—Five triterpenoids, arundoin (Ia), cylindrin (IIa), fernenol (Ib), isoarborinol (IIb) and simiarenol (IVa), have been isolated and the structures of Ia, IIa and Ib determined.

The biogenetical relationship of these compounds, based on the established structures is discussed.

THE rhizomes of *Imperata cylindrica* Beauv. var. *koenigii* Durand et Schinz‡ (Japanese name: Chigaya) (Gramineae) have been used in Chinese medicine as diuretic and anti-inflammatory agents. Although analyses of sugars,[4,5] organic acids,[4] and potassium content[5] of the drug are known, only a preliminary paper[4] concerning the constituents of the plant and the presence of two triterpenoids in the rhizomes has been reported.[6]

The hexane or benzene extracts of the rhizomes reveal the presence of five triterpenoids of migrated hopane and arborane groups including three new compounds. This paper gives a full account of the isolation and structure elucidation of these compounds.* The biogenetic relationship of the constituents and other observations obtained in the course of the study will also be discussed.

Isolation of the triterpenoid compounds. The hexane or benzene extracts of the rhizomes were separated into hexane, benzene, and ethyl acetate fractions by chromatography. Rechromatography of the hexane fraction afforded two triterpenoids, Ia, m.p. 242–243°, $[\alpha]_D$ −5·3° ($CHCl_3$); and IIa, m.p. 269–270°, $[\alpha]_D$ +60° ($CHCl_3$), both in 0·01% yield. They were proved to be identical with the compounds reported by Ohno *et al.*[4] While the present work was in progress, Eglinton *et al.*[7] reported the isolation of arundoin, from *Arundo conspicua* (Gramineae). Since Ia is identical with arundoin by direct comparison, this name was adopted, though the structure III proposed[7] proved to be wrong.[2] The triterpene IIa is a new compound and designated cylindrin.[1]

From the benzene fraction three triterpenoids were isolated: Ib, m.p. 192–193°,

* Preliminary communications of this work have been published.[1–3]

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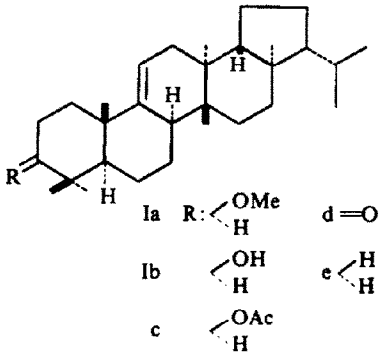
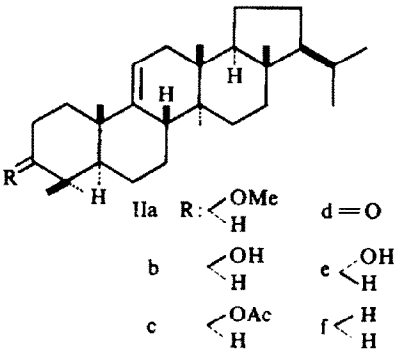
‡ In the preliminary communications,[1–3] we have erroneously adopted the name *Imperata cylindrica* P. Beauv. var. *media* Hubbard for the plant.

$[\alpha]_D$ −19·4° ($CHCl_3$); IVa, m.p. 209–211°; and IIb, m.p. 295–300° in yields of 0·0005, 0·001 and 0·0005%, respectively. Ib is a new compound and the name fernenol is based on the established structure;[3] IVa and IIb are identical with simiarenol[8] and isoarborinol[9] respectively.

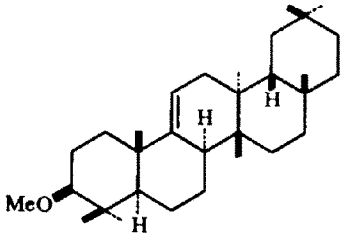
The ethyl acetate fraction consisted chiefly of mixture of phytosterols.



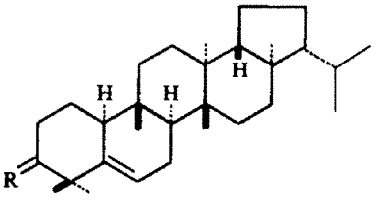
Ia R: OMe H d =O
Ib OH H e H H
c OAc H



IIa R: OMe H d =O
b OH H e OH H
c OAc H f H H



III



IVa R: OH H
b =O
c H H
d OAc H

The structure of arundoin (Ia). The elemental analysis and the mass spectrum of Ia suggest the molecular formula, $C_{31}H_{52}O$. The IR absorption (1103, 815, 790 cm^{-1}), the NMR signals (6·66 τ (3H, s); 4·67 τ (1H, m)), and the mass spectrum peaks (—MeOH peaks) (Fig. 1A, Table 1) suggest that Ia is a pentacyclic triterpene having a MeO group and a tri-substituted double bond. The NMR spectrum of Ia (Fig. 2A) shows the presence of at least two secondary Me groups, which excludes the possibility that Ia is an oleanane or migrated oleanane derivative.[10]

As shown in Table 2, the optical rotation value suggests that Ia may be a D:C or E:C-friedo type[11] compound having the trisubstituted double bond in the 7 or 9(11) position.[12–18] The mass spectrum of Ia shows prominent peaks at *m/e* 273 and 241 (273—MeOH) (Fig. 1A and Table 1), corresponding to the base peak at $M^+ - 167$ diagnostic for $\Delta^{9(11)}$ or Δ^8 compounds.[7,9,12,16,17] The fragmentation patterns, especially the very weak signals for b–b and c–c fragments (cf. Chart 1), are similar

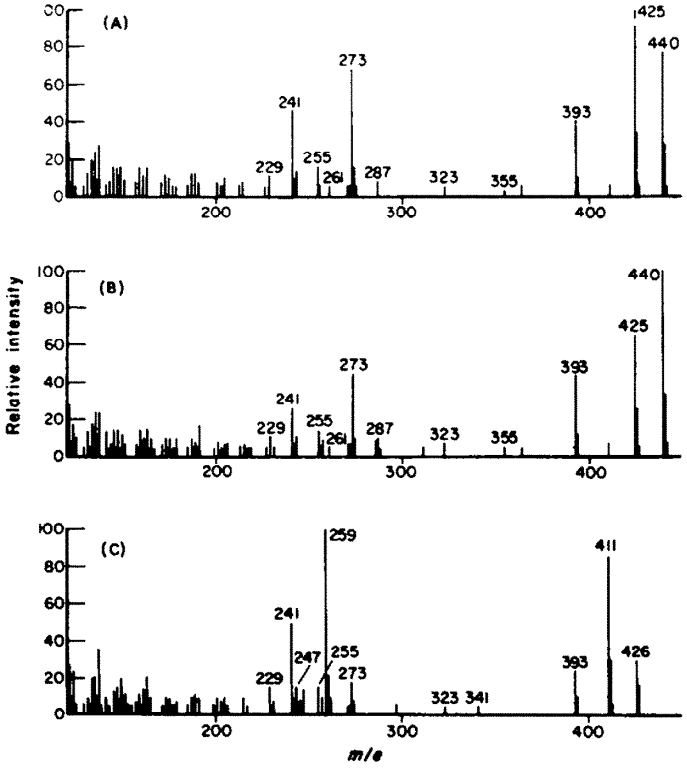

(A)
(B)
(C)
Relative intensity
m/e
425
440
273
241
393
229
255
261
287
323
355
411
259
247
426
341

FIG. 1.

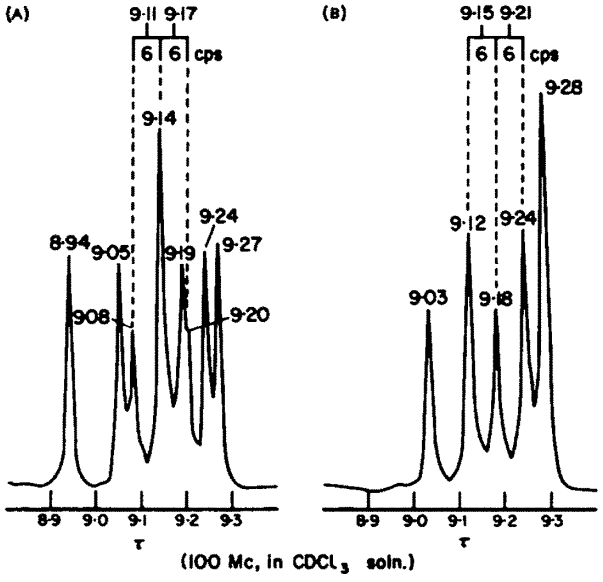

(A)
(B)
9·11 9·17
9·15 9·21
6 6 cps
9·14
9·28
9·24
9·12
8·94
9·05
9·19
9·27
9·03
9·18
9·08
9·20
8·9 9·0 9·1 9·2 9·3
τ
(100 Mc, in CDCl3 soln.)

FIG. 2

TABLE 1. COMPARISON OF THE MASS SPECTRA OF D:C- AND E:C-FRIEDO-TRITERPENOIDS

	b–b	c–c	d–d	e–e	f–f	g–g	$M^+ - 15$	M^+	Ref.
Multiflor-7-ene	205 (60)	204 (100)	231 (66)	243 (58)	257 (12)		395 (16)	410 (8)	9
Multiflor-7-en-3-one	205 (55)	218 (100)	245 (38)	257 (34)	271 (8)		409 (10)	428 (8)	17
Multiflor-8-en-3-one	205 (100)	218 (12)	245 (45)	257 (62)			409 (10)	424 (8)	17
Bauer-7-ene	205 (8)	204 (20)	231 (100)	243 (20)	257 (8)		395 (18)	410 (10)	9
Bauer-7-en-3-one	205 (22)	218 (10)	245 (100)	257 (20)	271 (15)		409 (14)	424 (16)	17
Fern-9(11)-ene (Ie)			231 (17)	243 (100)	257 (20)		395 (40)	410 (11)	12
Arundoin (Ia)*	205 (10)		261 (6) 229 (13)	273 (68) 241 (47)	287 (8) 255 (16)	355 (3) 323 (5)	425 (100) 393 (40)	440 (78)	
Fernenol (Ib)*	205 (10)		247 (15) 229 (17)	259 (100) 241 (50)	273 (18) 255 (17)	341 (5) 323 (5)	411 (87) 393 (25)	426 (30)	
Fern-8-ene (Vd)			231 (14)	243 (100)	257 (16)		395 (32)	410 (17)	12
Fern-8-en-3-one (Vc)	205 (7)		245 (14)	257 (100)	271 (10)		409 (71)	424 (42)	
3β-Methoxyfern-8-ene (Ve)*	205 (10)		261 (10) 229 (15)	273 (78) 241 (60)	287 (10) 255 (18)		425 (100) 393 (40)	440 (75)	
Arbor-9(11)-ene (IIf)			231 (18)	243 (100)	257 (28)	325 (10)	395 (66)	410 (38)	9
Arborenone (IId)			245 (25)	257 (100)	271 (38)	339 (30)	409 (98)	424 (62)	17
Cylindrin (IIa)*			261 (5) 229 (10)	273 (45) 241 (26)	287 (10) 255 (14)	355 (5) 323 (7)	425 (76) 393 (34)	440 (100)	

* Figures shown in the lower line indicate those corresponding to the peak shown in the upper line—MeOH or H_2O.

to those of fern-9(11)-ene[12] but differ from those of multiflorene and baurene derivatives (*vide infra*).[9, 17]

CHART 1. Fragmentations of D:C- or E:C-friedo triterpenoids

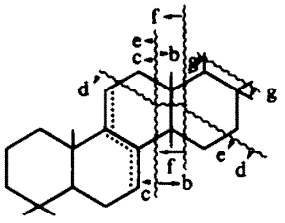


TABLE 2. COMPARISON OF MOLECULAR ROTATIONS OF TRITERPENES: HYDROCARBONS, 3β-HYDROXY- AND 3β-METHOXY DERIVATIVES

Nucleus	Postion of the double bond	Hydrocarbon	$[\phi]_D$ in $CHCl_3$ 3β-Ol	$[\phi]_D$ in $CHCl_3$ 3β-O-Methyl ether
O	18	olean-18-ene (+25°)	germanicol (+24°)	miliacin[27] (+35°)
O	14	taraxerene (+13°)	taraxerol (+13°)	sawamilletin[28] (+36°)
O	13(18)	olean-13(18)-ene (−147°)	∂-amyrin (−222°)	3β-methoxy-olean-13(18)-ene[27] (−101°)
O	12	olean-12-ene (+385°)	β-amyrin (+375°)	isosawamilletin[7, 28] (+406°)
U	12	urs-12-ene (+398°)	α-amyrin (+357°)	α-amyrin methyl ether[2] (+403°)
H	9(11)	fern-9(11)-ene (Ie) (−70°)	fernenol (Ib) (−81°)	arundoin (Ia) (−40°)
A	9(11)	arbor-9(11)-ene (IIf) (+215°)	isoarborinol (IIb) (+200°)	cylindrin (IIa) (+264°)
H	8	fern-8-ene (Vd) (+74°)	fern-8-en-3β-ol (Vb) (+104°)	3β-methoxyfern-8-ene (Ve) (+128°)
O	7	multiflor-7-ene (−82°)	multiflorenol (−119°)	multiflorenol methyl ether[7] (−141°)
U	7	—	bauerenol (−128°)	bauerenol methyl ether[7] (−141°)

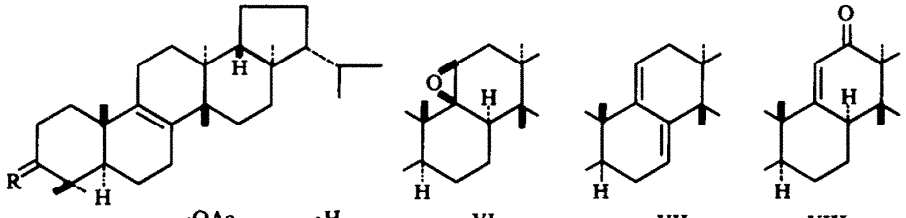
O: oleanane U: ursane H: hopane A: arborane.

Treatment of Ia with hydrobromic acid–acetic anhydride in chloroform–phenol afforded an acetate Va, m.p. 226–227°, $[\alpha]_D$ +20·3° ($CHCl_3$).* Hydrolysis of the acetate afforded a secondary alcohol Vb, m.p. 199–200°, $[\alpha]_D$ +24·5° ($CHCl_3$). Oxidation of the alcohol with chromium trioxide–pyridine gave a ketone Vc, m.p.

* The compound should be identical with isomultiflorenyl acetate, if arundoin has the structure III. Actually, Va is not identical with isomultiflorenyl acetate or isobauerenyl acetate by direct comparison.

214–216°.* The IR and NMR spectra of Va, Vb and Vc indicate that the tri-substituted double bond in Ia has migrated to a tetra-substituted position. The $[\alpha]_D$ values of Va and Vb and the base peak at 257 *m/e* of the mass spectrum of Vc (Table 1) agree with those of compounds having the double bond in the 8 position. The Wolff–Kischner reduction of the ketone gave a hydrocarbon, m.p. 185–186°, $[\alpha]_D$ +20·4° ($CHCl_3$), which is identical with fern-8-ene (Vd)[12, 13] by a mixed fusion, IR, TLC and GLC. Thus Ia must be a migrated hopane derivative.

Since the above reaction involves migration of the double bond, the position of the double bond in Ia has been confirmed by the following reactions: This bond is inert to catalytic hydrogenation. Selenium dioxide oxidation of Ia was also unsuccessful. The action of perbenzoic acid on Ia afforded an unstable epoxide VI, treatment of which with acid easily formed the diene VII, m.p. 228–231°, $[\alpha]_D$ −157°.† The UV absorptions of VII, λ_{max}^{hexane} 233, 239, 247 mμ (ε 14,700, 16,400, 10,700) were characteristic for 7,9(11)-diene with 13α, 14β-Me groups[12–16] and 1(10),5-diene,[13, 19] in which the latter has been ruled out from the $[\alpha]_D$ value.[13] Chromic acid oxidation of Ia afforded a conjugated enone VIIIa, m.p. 297–298°, $[\alpha]_D$ −5·6°, UV λ_{max}^{hexane} 238 mμ (ε 12,500), IR 1665, 1610, 869 cm^{-1}. The ORD curve of the ketone VIIIa shows a positive cotton effect (Fig. 3) and is similar to those of fern-9(11)-en-3-one (VIIIb)[12] and methyl 12-ketodavallate.[16] This fact, together with the mass spectra of Ia and the derivatives, suggests location of the double bond at the 9(11)-position. After isolation of fernenol (Ib), arundoin (Ia) has been directly correlated with fern-9(11)-ene (Ie);[12] hence unequivocal proof for the location of the double bond has now been provided (*vide infra*).



Finally, the position of the OMe group has been proved as follows: Acid-induced migration of the ketone Vc afforded its isomer, m.p. 152–153°, which is identical with hopenone-II (X),[20] prepared from hydroxyhopanone.[20] This offers further confirmation of the nucleus and the location of the oxygen function at the 3-position.

* After our preliminary communication,[2] a ketone assumed to be identical with Vc has been obtained as one of the acid-catalysed migration product of simiarenone (IVb)[8] and motienone.[18]

† Eglinton, *et al.*[7] claimed that the diene formed from arundoin is identical with 3β-methoxymultiflora-7,9(11)-diene (IX) prepared from multiflorenol, this fact being the only evidence for their assignment of the structure III for arundoin as a multiflorene derivative. Dr. Martin-Smith informed us of certain discrepancies between their spectra of both compounds (private communication; cf. footnote 3 in Ref. 2).

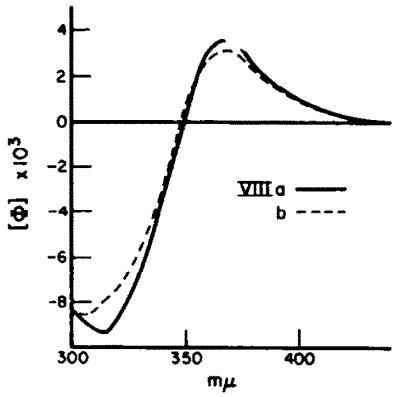
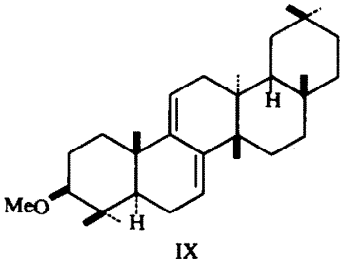
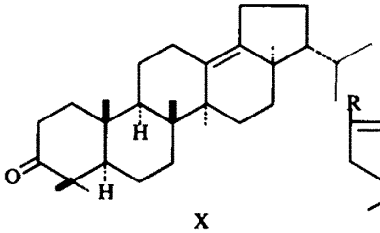


FIG. 3

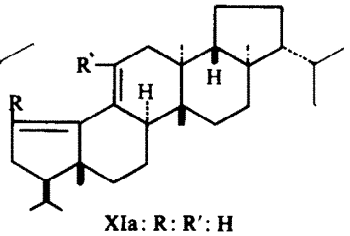
The acid treatment of arundoin (Ia) afforded its isomer Ve, m.p. 223–224°, $[\alpha]_D$ +28·9°. The same compound was obtained by the methylation[21] of the alcohol Vb, confirming the retention of the configuration at the 3-position in the course of reactions changing Ia to Vb. In the NMR spectra of Ia, Va and Vb the hydrogen attached to the carbon bearing oxygen function appears in quartets at 7·35, 5·62, and 6·38 τ respectively, coupling constants being 12 and 4, 10 and 5, and 13 and 6 c/s. This indicates the axial hydrogen atom at the 3-position. From this evidence the structure of arundoin must be expressed as 3β-methoxyfern-9(11)-ene (Ia).



IX



X



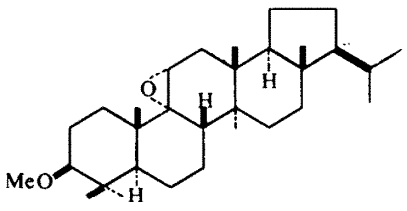
XIa: R: R': H
XIb: R or R': Ac

The treatment of Ia with *p*-toluenesulphonic acid in acetic anhydride to obtain a demethylated product, resulted in a complex mixture from which two compounds, m.p. 209–211° (XIa) and m.p. 188–190° (XIb), were isolated in minute amounts. Spectroscopic properties of the former (M^+ 408, IR 1632, 815, 803, 783 cm^{-1}, UV λ_{max} 243 mμ (ε 9400)*) suggest that the compound may be a cisoid heteroannular diene such as XIa. The formation of a conjugated diene by elimination reaction and accompanied migration reaction has been reported.[23] The compound XIb is assumed to be a methyl ketone conjugated with heteroannular diene from the spectroscopic data (M^+ 450, IR 1648 (s, conj. ketone), 1608, 835 cm^{-1}, UV λ_{max}^{hexane} 273 mμ (ε 7900), NMR 7·92 τ (3H, s, MeCO), 4·45 τ (1H, m)) and the structure XIb is tentatively proposed for this compound.

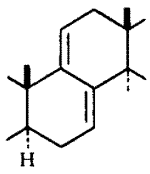
* 7,14-Cholestadien-3-one, λ_{max} 242 mμ (ε 9700).

The structure of cylindrin (IIa). Cylindrin has a molecular formula, $C_{31}H_{52}O$ (elemental analysis and M^+ 440). The presence of a tri-substituted double bond and a MeO group is suggested by IR (1105; 805 cm^{-1}), NMR (6·63 τ (3H, s), 4·74 τ (1H, m)), and the mass spectrum (—MeOH peaks) (Fig. 1B, Table 1). The NMR spectrum of IIa (Fig. 2B) indicates the presence of two secondary Me groups. The mass spectrum of IIa shows nearly the same fragmentation pattern as Ia, prominent peaks at *m/e* 273 and 241 (273 —MeOH) suggesting the presence of the double bond at the 9(11)-position.[7,9,12,16,17] However, the resistance to the acid-catalysed migration reaction and the $[\alpha]_D$ value of IIa (cf. Table 2) do not agree with the properties of bauerene, multiflorene and fernene derivatives.

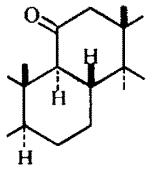
Compound IIa is inert to catalytic hydrogenation and selenium dioxide dehydrogenation; treatment with peracid afforded a stable epoxide XII. Acid-catalysed cleavage of XII afforded a conjugated diene XIII, m.p. 246–247°, $[\alpha]_D$ +90·4° ($CHCl_3$), and a saturated ketone XIV, m.p. 284–285°. The UV absorptions of XIII (λ_{max}^{hexane} 237, 244, 252 mμ (ε 17,500, 20,700, 14,200)) coincide with the value reported for 7,9(11)-diene with 13β, 14α-methyl group.[9] The ketone XIV shows a positive Cotton effect curve (peak: $[\phi]_{328}^{dioxan}$ +2190°; trough: $[\phi]_{267}^{dioxan}$ −3280°), indicating the presence of the carbonyl group at the 11-position.[9] All these facts show that IIa may be a arbor-9(11)-ene derivative.



XII



XIII



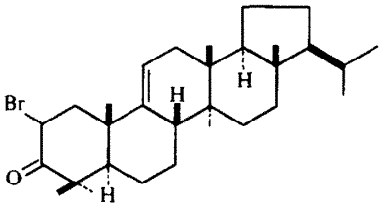
XIV

Treatment of IIa with hydrobromic acid-acetic anhydride afforded an acetate, m.p. 288°, which was identified as isoarborinyl acetate (IIc)[9] by a mixed fusion, IR, TLC and GLC. Hydrolysis of IIc gave isoarborinol[9] (IIb) and the oxidation of IIb gave arborinone (IId);[9] both being identical with authentic samples.

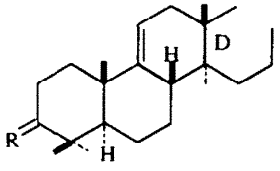
Finally, methylation of IIb with potassium and methyl iodide afforded the original compound, cylindrin. Thus cylindrin is isoarborinol methyl ether (3β-methoxyarbor-9(11)-ene) (IIa).

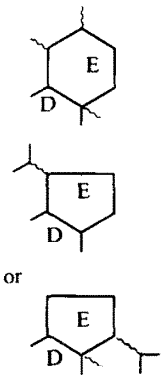
The structure of arborane derivatives has now been established by the X-ray analysis of 2α-bromoarborinone (XV) by Kennard *et al.*[24] However, at the time of this work,[1–3] the exact nature of rings D and E of arborane derivatives was not known and, from the presence of two secondary Me groups, the partial structure XVI had been proposed by Vorbrüggen *et al.*[9] From a comparison of the mass spectra of cylindrin (IIa) and the derivatives with those of D:C- or E:C-friedo type compounds so far reported[1,2,9,12,16,17] (Table 1 and Chart 1) and from the considerations on biogenesis of these compounds (*vide infra*), we put forward the structure IIa as the most probable structure of cylindrin.[2,25] As clearly shown in Table 1, the fragmentation of fernane derivatives and arborane derivatives are similar, but

they differ from those of migrated oleanane (multiflorane) and ursane (bauerane) derivatives; i.e. in fernane and arborane derivatives, e–e fragments are quite strong, while b–b and d–d are weak and c–c are not observed. Such a similarity between fernane and arborane derivatives suggests that they may be diastereoisomers and,



XV





XVI

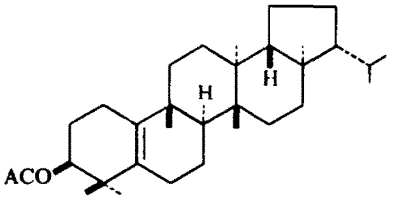
in view of the instability of the *trans*-fused 5-membered ring E in fernane to fragmentation, it is very probable that the rings C, D and E of arborane are "antipodal" to those of fernane. This assumption has now been proved to be the case.

The structure of fernenol (Ib) *and some reactions of simiarenol* (IVa). After completion of the structural studies on Ia and IIa,[1,2] accumulation of the more polar fraction enabled us to work on the minor components in the rhizomes. Two of the three triterpenoids from the fraction were identified as simiarenol[8] (IVa) and isoarborinol[9] (IIa). The other, Ib, named fernenol, $C_{30}H_{50}O$ (M^+ 426), is a pentacyclic triterpene with one OH group (IR 3530 cm^{-1}) and a tri-substituted double bond (IR 815, 790 cm^{-1}). Ib readily forms an acetate Ic.

Close similarity of the δ_{C-H} region in the IR spectra of Ib, Ic and arundoin (Ia) and the fragmentation patterns of mass spectra of Ib and Ia (Fig. 1A, 1C and Table 1) suggests that Ib belongs to the fern-9(11)-ene group. This has been proved by chromium trioxide oxidation of Ib to the ketone Id, m.p. 198–199°, followed by the Wolff–Kischner reduction to the hydrocarbon, fern-9(11)-ene (Ie),[12] m.p. 160–161°. On the other hand, methylation of Ib with methyl iodide and potassium afforded arundoin (Ia). These correlations established the structure of fernenol as 3β-hydroxyfern-9(11)-ene and, at the same time, confirmed the location of the double bond in arundoin (Ia). After the completion of this work,[3] Rao *et al.* isolated the same compound from *Artemisia vulgaris* (Compositae) and were arriving at the same conclusion regarding structure. After identification with our specimen, they reported the results adopting our designation "fernenol".[26]

The structure of simiarenol, originally isolated from *Rhododendron simiarum*,[8] has been established by Aplin *et al.*[8] as adian-5-en-3β-ol (IVa) by the correlation with adian-5-ene (IVc),[13] spectroscopic evidences and migration reactions. Although the migration reactions of simiarenol derivatives were extensively studied,[8] none of the products has been identified with the known compound to establish the 3β-position of the OH group. Thus the acid-catalysed migration reaction of simiarenyl acetate

(IVd) has been examined. Under mild conditions an acetate, m.p. 276–278°, $[\alpha]_D$ −35·8°, assumed to be 5(10)-ene derivative (XVII),* was the main product, while, under more vigorous conditions another migration product, m.p. 220–222°, was the major product and was identical with 3β-acetoxyfern-8-ene (Va), obtained from arundoin. Under similar conditions, XVII also afforded Va. Since Va has been correlated with hopenone-II (X), the 3β-position of the OH group in simiarenol (IVa) is unequivocally established.



XVII

Biogenesis and chemotaxonomy. Triterpenoid constituents in *Imperata cylindrica* var. *koenigii* have now been clarified as arundoin (Ia) and cylindrin (IIa) as the major constituents and fernenol (Ib), simiarenol (IVa) and isoarborinol (IIb) as the minor products, in which Ia, Ib and IVa belong to the migrated hopane group and IIa and IIb to the arborane group.

Triterpene methyl ethers such as Ia and IIa are rare compounds; miliacin,[27] crusgallin (sawamilletin),[28] and β-amyrin methyl ether[7] from Gramineae plants and abieslactone[29] and two serratenediol derivatives[30] from Pinaceae plants are the known examples.

The migrated hopane derivatives were first isolated from ferns[12,13,16,31,32] but, while this work was in progress, the isolation and the structural elucidation of simiarenol (IVa) from *Rhododendron simiarum* (Ericaceae),[8]† adianenediol, motiol, motidiol, fernenediol, and neomotiol from *R. linearifolium* (Ericaceae),[18,34] and fernenol (Ib) from *Artemisia vulgaris* (Compositae),[26] have been reported with some correlation with our work. While about thirty hopane and migrated hopane derivatives hitherto characterised from ferns, lichens and a mould have no oxygen function at the 3-position except in the case of pixinic acid,[35] those from higher plants have an oxygen function at the 3-position as in the case of most of other hitherto known triterpenoids.

The arborane group of triterpenoids, to which IIa and IIb belong, is a new group and the isolation of arborinol (IIe) and isoarborinol (IIb) from *Glycosmis arborea* (Rutaceae)[9] and IIb and arborinone (IId) from *Hedyotis acutangula* (Rubiaceae)[36] are the known examples of this group. Thus cylindrin is the fourth compound of this group.

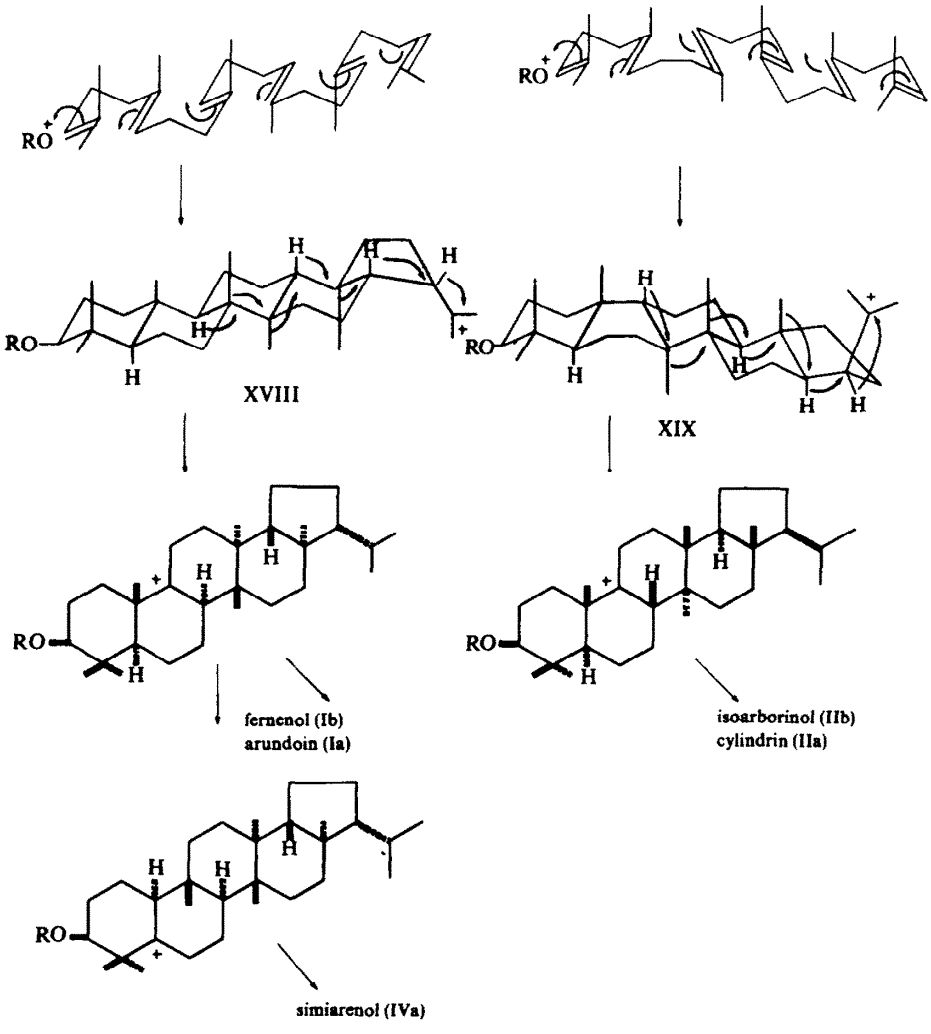
Our proposal for the structure of cylindrin,[2,25] was partly based on the consideration of the biogenesis of these compounds. This will be summarised as follows (Chart 2): Fernane derivatives (I) and arborane derivatives (II) have the same configuration at 3-, 5-, and 10-positions and are enantiomeric at 8-, 13-, 14-, 17-, 18- and 21-positions. This relationship will be assumed as the same as that of tirucallane

* The compound assumed to be identical with XVII has been obtained by Aplin *et al.*[8]

† The triterpene from the leaves of *Tripetaleia paniculata* (Ericaceae), m.p. 210–211°, isolated by Kondo *et al.*[33] has been identified with simiarenol (IVa).

and lanostane in tetracyclic triterpenoids, the difference arising from chair and boat conformation of the ring B at the initial stage of cation-induced cyclization.[37,38] In the hopane series the initial cyclization product XVIII is stable, so that unmigrated hopane derivatives exist widely in nature. Further migrations afford migrated hopane derivatives; neohopene derivatives,[18,39] fernene derivatives[12] such as Ia and Ib, adianene derivatives[13] such as IVa, and filicene derivatives.[13,31] On the contrary the intermediate XIX from the boat form of ring B is unstable due to the syn-configuration of C_9 and C_{10}, which facilitates the migration to arborane derivatives. This relationship between hopane (XVIII), fernane (I) and arborane (II) corresponds to that of dammarane, tirucallane and lanostane in tetracyclic triterpenoids.

CHART 2. Biogenesis of migrated hopane and arborane derivatives.



Co-existence of the diastereomeric pairs of compounds in the same plant is interesting from a biogenetic point of view. Rather wide distribution and co-existence of Ia, Ib, IIa and IIb have recently been proved for several Gramineae plants[40,*] and the work on this line is now in progress in the laboratory by one of us (T. O.).

EXPERIMENTAL

M.ps were determined in a Yanagimoto m.p. apparatus and are uncorrected; the rotations were determined in $CHCl_3$ soln at 23–24°; the UV spectra were taken in hexane solns on a Hitachi EPU-2A spectrophotometer; the IR spectra were measured on a Nihon Bunko DS-301 spectrophotometer in KBr discs; the NMR spectra were run in $CDCl_3$ solns on a Varian Associates A-60 (60 Mc) or HR-100 (100 MC) and recorded in τ values with TMS as internal reference; the mass spectra were determined on a Hitachi RMU-6D mass spectrometer with direct inlet system operating at the ionization potential (80 eV) and the ionization temp (250°); the ORD curves were measured in 0·1% dioxan soln on a Nihon Bunko ORD-UV 5 machine.

For the column chromatography alumina (Brockmann standard) or silica gel (Mallinckrodt) was employed unless otherwise specified.

At each stage of the separation and purification, TLC and GLC were adopted for monitoring the purity of the specimen. For TLC silica-gel G or alumina G impregnated with $AgNO_3$ was used. Gas chromatography was carried out on 1·5% SE-30 or 1% NGS column at 250° in a Shimadzu GC-1B or a Hitachi F6-D gas chromatograph.

Isolation of arundoin (Ia), *cylindrin* (IIa), *fernenol* (Ib), *simiarenol* (IVa) *and isoarborinol* (IIb)

The rhizomes (10 kg) were extracted 3 times with boiling hexane for 2 hr. The combined extracts (45 g) were chromatographed on a column of alumina (500 g) and eluted successively with hexane (3 l.), benzene (3 l.) and AcOEt (3 l.). The hexane fraction gave rise to a crystalline residue (ca. 3 g), the benzene fraction an oily residue (ca. 17 g), and the AcOEt a crystalline residue (ca. 10 g).

The hexane fraction was introduced onto a column of alumina (Wako, basic, 500 g) and eluted with hexane (6 l.), Ia being eluted faster than IIa. Each fraction was examined by TLC and GLC and the fractions containing only Ia or IIa were combined respectively and the fractions containing both were rechromatographed under similar conditions for further separation. *Arundoin* (Ia) recrystallized from hexane as colourless needles, m.p. 242–243°,† $[\alpha]_D$ −5·3° (c, 0·79), yield, 0·01%; ν_{max} 2930 (s), 1630, 1450, 1380, 1260, 1182, 1103 (s), 1013, 993, 972, 943, 872, 865, 815, 790 cm^{-1}; NMR (100 Mc) τ 9·27 (3H), 9·24 (3H), 9·20 (1·5H), 9·19 (3H), 9·14 (6H), 9·08 (1·5H), 9·05 (3H), 8·94 (3H), 7·35 (1H, q, J = 12, 4 c/s), 6·66 (3H, s), 4·67 (1H, m); mass spectrum (Fig. 1A and Table 1). (Found: C, 84·39; H, 11·82. $C_{31}H_{52}O$ requires: C, 84·48; H, 11·89%.) The identity with the compound from *Arundo conspicua* has been confirmed by a mixed fusion, IR, TLC and GLC by us and also by the Glasgow group.

Cylindrin (IIa) recrystallized from hexane as colourless needles, m.p. 269–270°, $[\alpha]_D$ +60·0° (*c*, 1·15), yield, 0·01%; ν_{max} 2930 (s), 1630, 1450, 1380, 1370, 1190, 1105 (s), 1013, 983, 943, 900, 862, 805 cm^{-1}; NMR (100 Mc) τ 9·28 (9H), 9·24 (4·5H), 9·18 (3H), 9·12 (4·5H), 9·03 (3H), 7·50 (1H, q, J = 12, 4 c/s), 6·63 (3H, s), 4·75 (1H, m); mass spectrum (Fig. 1B and Table 1). (Found: C, 84·80; H, 11·61. $C_{31}H_{52}O$ requires: C, 84·48; H, 11·89%.)

The benzene fraction was rechromatographed on a column of alumina (600 g) and eluted successively with benzene (1·8 l.) and benzene–ether (10:1; 7 l.). Each fraction was examined by TLC and GLC the fractions eluted with benzene–ether containing IVa and IIb were combined and the residue was dissolved in a small amount of acetone to deposit colourless plates, which were further purified from acetone to give *simiarenol* (IVa), m.p. 209–211° (lit.[8] m.p. 209–210°), yield, 0·001%. IVa formed *the acetate* (IVd), colourless plates, m.p. 216–217°, $[\alpha]_D$ +70·4° (c, 0·42) (lit.[8] m.p. 209°, $[\alpha]_D$ +73·9°). The identity with an authentic sample has been confirmed by a mixed fusion, IR, TLC and GLC. The acetone mother liquor of IVa was evaporated and the oily residue was treated with EtOH to deposit colourless needles, which were further recrystallized from EtOH–benzene to afford *isoarborinol* (IIb), m.p. 295–300° (lit.[9] m.p. 294–294·5°), yield of IIb was 0·0005%. *The acetate* (IIc), colourless needles, m.p. 296–298° (lit.[9] m.p.

* The rhizomes of *Imperata cylindrica* (Japanese name: Fushikechigaya), original species of the variety used in this study, collected at Thailand, also contain Ia and IIa.

† According to Eglinton *et al.*[7] arundoin shows dimorphic forms, m.p. 235–237°/271–273°. We have not so far obtained the higher melting form.

287–288°), was prepared by the conventional method. The identification with the authentic specimen has been carried out by the ordinary methods.

The fraction eluted after that containing IVa and IIb left a yellow oily residue containing another triterpenoid, which was acetylated with Ac_2O and pyridine. The crude acetate was passed through a column of silica gel (20 g) and eluted with hexane (1 l.) and then with hexane–benzene (97·5:2·5) (1 l.). The latter fraction afforded a waxy substance, which turned crystalline on treatment with EtOH. Crystallization from acetone afforded *fernenol acetate* (Ic), colourless needles, m.p. 222–223°, $[\alpha]_D$ −8·9° (*c*, 0·96) (lit.[34] m.p. 221°, $[\alpha]_D$ −10°; lit.[26] m.p. 215–216°, $[\alpha]_D$ −10°); ν_{max} 2930 (s), 1725 (s), 1640, 1440, 1378, 1245, 1075, 1028, 1013, 990, 978, 955, 905, 865, 815, 790 cm^{-1}. (Found: C, 82·47; H, 10·86. $C_{32}H_{52}O_2$ requires: C, 81·99; H, 11·18%.) Hydrolysis of the acetate afforded *fernenol* (Ib), colourless needles, m.p. 192–193°, $[\alpha]_D$ −19·4° (*c*, 0·82) (lit.[34] m.p. 188°, $[\alpha]_D$ −17°; lit.[26] m.p. 194°, $[\alpha]_D$ −24°), from MeOH, yield, 0·0005%; ν_{max} 3520, 2930 (s), 1630, 1440, 1378, 1175, 1080, 1018, 977, 950, 865, 815, 790 cm^{-1}; mass spectrum (Fig. 1C and Table 1).

The AcOEt fraction of the first chromatography afforded a mixture of phytosterols (5 g) after the recrystallization from AcOEt. Gas chromatography showed that the mixture was composed of stigmasterol, β-sitosterol and campesterol.

Reaction of arundoin (Ia) *with hydrobromic acid–acetic anhydride*

Formation of 3β-*acetoxyfern*-8-*ene* (Va). Ia (200 mg) was dissolved in $CHCl_3$ (25 ml), phenol (20 ml), and Ac_2O (25 ml) and, after the addition of HBr (47%, 6 ml), was refluxed under N_2 stream for 3 hr. A further amount of HBr (47%, 2 ml) was added and the heating was continued for 3 hr. The reaction mixture was evaporated under N_2 stream and the residue was washed with water and dried. After repeating this procedure 3 times, the combined reaction products (ca. 600 mg) were introduced onto a column of silica gel (120 g) and eluted with hexane. After the elution of the starting material, the main product was recrystallized from acetone as colourless needles (250 mg) of 3β-*acetoxyfern*-8-*ene* (Va), m.p. 226–227°, $[\alpha]_D$ +20·3° (*c*, 0·92); ν_{max} 2930 (s), 1725 (s), 1630, 1450, 1240 (s), 1165, 1080, 1038, 1010, 980, 940, 900 cm^{-1}; NMR τ 9·26–9·03 (24H), 8·03 (3H, s), 5·62 (1H, q, J = 5, 10 c/s). (Found: C, 81·98; H, 11·00. $C_{32}H_{52}O_2$ requires: C, 81·99; H, 11·18%.) Further elution of the column with hexane and then with benzene afforded a mixture of Va and another product. Rechromatography and recrystallization afforded colourless needles (30 mg), m.p. 272–273°, $[\alpha]_D$ −74·7° (*c*, 0·72); ν_{max} 2920 (s), 1725 (s), 1630, 1440, 1375, 1250 (s), 1150, 1083, 1060, 1032, 988, 902 cm^{-1}. (Found: C, 81·77; H, 11·25. $C_{32}H_{52}O_2$ requires: C, 81·99; H, 11·18%.)*

Hydrolysis of 3β-*acetoxyfern*-8-*ene* (Va) *to fern*-8-*en*-3β-*ol* (Vb)

Compound Va (120 mg) was refluxed with ethanolic KOH (2%, 50 ml) for 30 min. Evaporation under a reduced press and addition of water afforded a ppt (110 mg), which was crystallized from EtOH as colourless needles, m.p. 199–200°, $[\alpha]_D$ +24·5° (*c*, 0·74), ν_{max} 3510, 2930 (s), 1630, 1450, 1378, 1168, 1085, 1010, 940 cm^{-1}; NMR τ 9·25–9·04 (24H), 6·38 (1H, q, J = 6, 13 c/s). (Found: C, 83·89; H, 11·84. $C_{30}H_{50}O$ requires: C, 84·44; H, 11·81%.)

Oxidation of fern-8-*en*-3β-*ol* (Vb) *to fern*-8-*en*-3-*one* (Vc)

Compound Vb (100 mg) was dissolved in pyridine (1 ml) and allowed to stand with CrO_3–pyridine (100 mg in 1 ml) overnight. The reaction product was extracted with hexane and chromatographed through a silica gel column (10 g). The elution with hexane and then with a mixture of hexane and benzene, followed by recrystallization from EtOH, afforded colourless needles (80 mg), m.p. 214–216° (lit.[8] m.p. 200–202°, $[\alpha]_D$ +54·5°; lit.[18] m.p. 209°); ORD peak $[\phi]_{313}$ +2120°, $[\phi]_{303}$ +2180°, trough $[\phi]_{275}$ +380°, ν_{max} 2930 (s), 1705 (s), 1630, 1468, 1445, 1385, 1245, 1197, 1168, 1115, 1013, 963 cm^{-1}; mass spectrum (Table 1). (Found: C, 85·03; H, 10·92. $C_{30}H_{48}O$ requires: C, 84·84; H, 11·39%).

Reduction of fern-8-*en*-3-*one* (Vc) *to fern*-8-*ene* (Vd)

Compound Vc (65 mg) was dissolved in benzene (3 ml) and heated with diethylene glycol (10 ml), hydrazine hydrate (85%, 0·3 ml) and Na (0·1 g) at 100–110° for 2 hr. The mixture was heated gradually

* This compound is assumed to be 3β-acetoxyneohop-13(18)-ene but the compound assigned this structure has been obtained from neomotiol (isoneomotiol acetate) and reported to be m.p. 223°, $[\alpha]_D$ −136°.[18]

to 200° while distilling off and then heated at 200–210° for 5 hr. After cooling, the separated crystalline substance was collected, washed and dried. Recrystallization from acetone afforded colourless needles (63 mg), m.p. 185–186°, $[\alpha]_D$ +20·4° (*c*, 0·54) (lit.[12,13] m.p. 189–190°, $[\alpha]_D$ +18°), ν_{max} 2930 (s), 1630, 1470, 1455, 1388, 1375, 1237, 1168, 1132, 1010, 970, 945 cm^{-1}. (Found: C, 88·06; H, 11·75. $C_{30}H_{50}$ requires: C, 87·72; H, 12·27%.) The identity with an authentic sample has been established by a mixed fusion, IR, TLC and GLC.

Epoxidation of arundoin (Ia)

Compound Ia (200 mg) in $CHCl_3$ (50 ml) was treated with perbenzoic acid in $CHCl_3$ (6 ml, 1 ml = 0·1N $Na_2S_2O_3$ 8·1 ml) for 4 days at a room temp. The reaction product (213 mg) was recrystallized from acetone–hexane and then from acetonitrile as colourless needles (VI), m.p. 271–272°; ν_{max} 2930 (s), 1450, 1383, 1182, 1103 (s), 1015, 988, 963, 921, 857, 798, 772 cm^{-1}. (Found: C, 81·58; H, 11·43. $C_{31}H_{52}O_2$ requires: C, 81·52; H, 11·48%.)

Acid-catalysed cleavage of the epoxide (VI)

Formation of 3β-*methoxyferna*-7,9(11)-*diene* (VII). The epoxide VI (60 mg) was refluxed with AcOH (30 ml) and conc. HCl (0·3 ml) for 3 hr. After evaporation, water was added and the ppt thus formed was separated and chromatographed through alumina (30 g) with hexane. Recrystallization from acetone–benzene gave colourless needles (30 mg), m.p. 228–230°, $[\alpha]_D$ −157·3° (*c*, 0·48); λ_{max} mμ (ε) 233, 239, 247 (14,700, 16,400, 10,700); ν_{max} 3030, 2930 (s), 1620, 1440, 1365, 1178, 1100 (s), 1010, 970, 858, 811, 793 cm^{-1}. (Found: C, 84·59; H, 11·47. $C_{31}H_{50}O$ requires: C, 84·86; H, 11·49%.)

The chromium trioxide oxidation of arundoin (Ia)

The formation of 3β-*methoxyfern*-9(11)-*en*-12-*one* (VIIIa). To Ia (100 mg) in AcOH (50 ml) CrO_3 (100 mg) in AcOH (50 ml) was added and heated at 130–140° for 5 hr. The reaction mixture was dissolved in benzene and chromatographed on a column of silica gel (5 g). The elution with hexane–benzene (9:1) afforded the starting material and then VIIIa, which was purified from EtOH–benzene as colourless needles (30 mg), m.p. 297–298°, $[\alpha]_D$ −5·6° (*c*, 0·54); ORD peak $[\phi]_{368}$ +3540°, trough $[\phi]_{314}$ −9260; ν_{max} 2950, 1665, 1610, 1440, 1380, 1365, 1294, 1258, 1180, 1153, 1103, 1014, 970, 869 cm^{-1}. (Found: C, 82·05; H, 11·02. $C_{31}H_{50}O_2$ requires: C, 81·88; H, 11·08%.)

Acid-catalysed migration of arundoin (Ia) *to* 3β-*methoxyfern*-8-*ene* (Ve)

Compound Ia (200 mg) in AcOH (80 ml) and conc HCl (3 ml) was refluxed for 4 hr and the residue obtained by the evaporation was washed, dried and chromatographed on a column of alumina (Wako, basic, 120 g). Each fraction eluted by hexane was examined by GLC and the fractions not contaminated with the starting material were combined and crystallized from hexane as colourless needles (50 mg), m.p. 223–224°, $[\alpha]_D$ +28·9° (*c*, 0·74); mass spectrum (Table 1), ν_{max} 2920 (s), 1620, 1445, 1375, 1193, 1172, 1105, 1010, 973, 860, 840 cm^{-1}. (Found: C, 84·45; H, 11·55. $C_{31}H_{52}O$ requires C, 84·48; H, 11·89%.)

Acid-catalysed migration of fern-8-*en*-3-*one* (Vc) *to hopenone*-II(X)

Compound Vc (70 mg) in AcOH (40 ml) and conc HCl (7 ml) was refluxed for 25 hr. The reaction products were chromatographed on a column of silica-gel (5 g) and eluted with hexane–benzene (19:1–4:1). Each fraction was examined by TLC and GLC and the fractions containing the main reaction product were collected and recrystallized from MeOH as colourless prisms, m.p. 152–154°; ν_{max} 2930 (s), 1702 (s), 1635, 1450, 1384, 1373, 1258, 1245, 1198, 1140, 1120, 1115, 1085, 1014, 1002, 977, 964, 844 cm^{-1}. It was identical in every respect with hopenone-II (X) prepared from hydroxyhopanone.

Preparation of hopenone-II (X)[20]

Hydroxyhopanone (100 mg), separated from Dammar resin,[20] was dissolved in benzene (7 ml) and, after the addition of AcOH (23 ml) and conc H_2SO_4 (3·2 ml), the mixture was allowed to stand at a room temp for 3 days. The mixture was poured onto ice-water, extracted with benzene, washed thoroughly and evaporated. The residue was chromatographed through a column of silica gel (5 g) and eluted with hexane–benzene (19:1–4:1). Each fraction was examined by TLC and GLC and the objective compound was recrystallized from MeOH as colourless prisms (X), m.p. 152–154°. The mother liquor gave rise to colourless needles, m.p. 168–169°, which showed two peaks in GLC, one of them being identical with that of X.

Methylation of fern-8-en-3β-ol (Vb)

Compound Vb (20 mg) and K (50 mg) in benzene (10 ml) were heated under reflux for 2 hr under N_2 stream. MeI (1 ml) in benzene (10 ml) was added dropwise and refluxed for 4 hr. The excess K was decomposed with MeOH and the reaction mixture was washed with water. The residue from the benzene layer was dissolved in hexane and chromatographed through a column of silica gel (3 g). Recrystallization from hexane afforded colourless needles (5 mg) of 3β-*methoxyfern-8-ene* (Ve), m.p. 224–225°. The identity with the compound obtained by the acid-treatment of arundoin (Ia) was confirmed.

Reaction of arundoin (Ia) *with p-toluenesulfonic acid and acetic anhydride*

Compound Ia (130 mg) in AcOH (10 ml), Ac_2O (10 ml) and *p*-toluenesulphonic acid (50 mg) was heated at 100–120° for 15 min under N_2 stream. The reaction mixture was poured onto water, extracted with $CHCl_3$ and the layer washed with 2% Na_2CO_3 aq and then with water. The residue from the $CHCl_3$ layer, showing 3 peaks in GLC, was introduced onto a column of alumina (50 g) and eluted successively with hexane (250 ml), benzene (150 ml) and $CHCl_3$ (150 ml). The hexane fraction was re-chromatographed and the eluate was recrystallized from acetone and then from benzene as colourless needles (XIa; 10 mg), m.p. 210–211°; λ_{max} 243 mμ (ε 9400). ν_{max} 2900 (s), 1632, 1447, 1382, 1170, 1003, 947, 890, 815, 803, 783 cm^{-1}; mass spectrum: M^+ ($C_{30}H_{48}$) *m/e* 408 (100%), M^+ —Me 393 (53), M^+ —C_3H_7 365 (15), 255 (32), 241 (33), 229 (20), 219 (32). From the $CHCl_3$ fraction a crystalline substance was obtained, which was recrystallized from EtOH as colourless prisms (XIb; 22 mg), m.p. 188–190°; λ_{max} 273 mμ (ε 7900); ν_{max} 2900 (s), 1648 (s), 1608, 1443, 1375, 1355, 1315, 1275, 1242, 1174, 1004, 992, 943, 917, 893, 835 cm^{-1}; NMR τ 7·92 (3H, s), 4·3–4·6 (1H, m); mass spectrum: M^+ 450 *m/e* (100%), 244 (39), 231 (14), 205 (12).

Epoxidation of cylindrin (IIa)

The reaction of IIa (238 mg) was carried out as for Ia. The product was recrystallized from benzene as colourless needles (200 mg; XII), m.p. 263°; ν_{max} 2930, 1440, 1380, 1362, 1170, 1095, 930, 885 cm^{-1}; NMR τ 9·3–9·0 (21H), 8·81 (3H, s), 7·45 (1H, m), 6·88 (1H, m), 6·67 (s, 3H). (Found: C, 81·60; H, 11·19. $C_{31}H_{52}O_2$ requires: C, 81·52; H, 11·48%.)

Acid-catalysed cleavage of the epoxide (XII)

(a) Compound XII (17 mg) was refluxed with AcOH (10 ml) for 20 hr, AcOH was evaporated, and the residue was introduced onto a column of silica gel (1·5 g). The fraction eluted by hexane–benzene (9:1) was recrystallized from benzene as colourless plates (9 mg) of the 7,9(11)-*diene* (XIII), m.p. 246–247°, $[\alpha]_D$ +90·4° (*c*, 0·42); λ_{max} (ε) 237, 244·5, 252 mμ (17,480, 20,790, 14,190). ν_{max} 2920 (s), 1620, 1440, 1370, 1196, 1180, 1103 (s), 1020, 978, 960, 906, 860, 798 cm^{-1}. (Found: C, 84·81; H, 11·52. $C_{31}H_{50}O$ requires: C, 84·86; H, 11·49%). The fraction eluted by hexane–benzene (1:1) was recrystallized from AcOEt as colourless needles (4 mg) of 3β-*methoxyarbor-11-one* (XIV), m.p. 284–285°; ν_{max} 2920 (s), 1678, 1440, 1368, 1182, 1096 (s), 1010, 965 cm^{-1}. (Found: C, 81·36; H, 11·12. $C_{31}H_{52}O_2$ requires: C, 81·52; H, 11·48%.)

(b) Dry HCl gas was passed through XII (163 mg) in $CHCl_3$ (35 ml) for 1·5 hr. The reaction mixture was kept at 34° for 5 days, washed with 5% $NaHCO_3$ aq and water and then evaporated. The residue (147 mg) was recrystallized from benzene and then from benzene–acetone as colourless needles of XIV, m.p. 284–285°.

Reaction of cylindrin (IIa) *with hydrobromic acid and acetic anhydride*

Formation of isoarborinol acetate (IIc). IIa (100 mg) in $CHCl_3$ (10 ml) was refluxed with phenol (100 mg), HBr (48%, 10 ml) and Ac_2O (12 ml) for 3 hr under N_2 stream. The reaction mixture was concentrated and poured into ice-water. The ppt was collected and chromatographed through silica gel (5 g). The hexane–benzene (9:1) fraction was recrystallized from benzene as colourless needles (68 mg), m.p. 288°. The identity with isoarborinol acetate (IIc)[9] was established.

Hydrolysis of IIc afforded *isoarborinol*[9] (IIb), m.p. 299–300°. The oxidation of IIb by CrO_3 in AcOH gave *arborinone* (IId), m.p. 216–217° (lit.[9] m.p. 214–215°). Both compounds were also compared with the authentic samples for identification.

Methylation of isoarborinol (IIb)

Compound IIb (28 mg) was methylated by the same method used for Vb. The product was purified by chromatography through a column of silica gel (5 g) and the fraction eluted by hexane–benzene (9:1)

was recrystallized from benzene as colourless prisms (23 mg), m.p. 255–257°, which proved to be identical with *cylindrin* (IIa).

Reaction of cylindrin (IIa) *with boron trifluoride*

Ether (10 ml) and Ac_2O (2 ml) were added to IIa (200 mg) in CS_2 (5 ml) and cooled to 0°. BF_3–etherate (0·3 ml) was added and kept at 0° for 14 hr. The reaction mixture was washed with 5% $NaHCO_3$ aq and then water. The chromatography of the residue revealed that the products were the mixture of hydrocarbons.[9]

*Isoarborinol bromoacetate and iodoacetate**

These compounds were prepared by the conventional methods—bromoacetate, m.p. 237°. (Found: C, 69·88; H, 9·15. $C_{32}H_{51}O_2Br$ requires: C, 70·18; H, 9·15%.) Iodoacetate, m.p. 227°. (Found: C, 65·56; H, 8·60. $C_{32}H_{51}O_2I$ requires: C, 64·63; H, 8·65%.)

Chromium trioxide oxidation of fernenol (Ib)

To a pyridine soln (1 ml) of Ib (60 mg) CrO_3–pyridine (100 mg in 1 ml) was added and, after being kept at a room temp for 20 hr, the reaction mixture was treated by the conventional method. The hexane-soluble portion of the products was chromatographed on a column of alumina (8 g), eluted with hexane–benzene (19:1) and the residue from the eluate was recrystallized from MeOH as colourless needles (40 mg) of *fern*-9(11)-*en*-3-*one* (Id), m.p. 198–199°, $[\alpha]_D$ −41·2° (*c*, 0·39) (lit.[34] m.p. 196°, $[\alpha]_D$ −60°); ν_{max} 2920 (s), 1700 (s), 1635, 1468, 1440, 1378, 1114, 1005, 980, 960, 940, 863, 810, 790 cm^{-1}. (Found: C, 84·82; H, 11·28. $C_{30}H_{48}O$ requires: C, 84·84; H, 11·39%.)

Reduction of fern-9(11)-*en*-3-*one* (Id)

To Id (15 mg) in benzene (1 ml) was added diethylene glycol (5 ml), KOH (0·5 g) and hydrazine hydrate (85%, 0·1 ml) and the mixture was heated at 100–110° for 1·5 hr and the temp then raised to 200–210° gradually under distillation. After heating at that temp for 1 hr, the reaction product was treated by the conventional methods. The product was recrystallized from acetone as colourless needles (5 mg), m.p. 160–161°. The identity with *fern*-9(11)-*ene* (Ie) was confirmed by a mixed fusion, IR, TLC and GLC.

Methylation of fernenol (Ib)

Compound Ib (20 mg) in benzene was methylated with K (50 mg) and MeI (2 ml) by the method for the methylation of IIb and Vb (loc. cit.). The reaction product was purified by the chromatography through a column of alumina (3 g) and the hexane fraction was recrystallized from hexane–acetone as colourless needles (5 mg), m.p. 237–239°. The compound was proved to be *arundoin* (Ia) by every means of identification.

Acid-catalysed migration reaction of simiarenyl acetate (IVd)

(a) Compound IVd (30 mg) was refluxed with AcOH (20 ml) and conc HCl (2 ml) for 7 hr. After evaporation the residue was introduced onto a column of silica gel (5 g) and eluted with hexane (350 ml) and then hexane–benzene (9:1; 250 ml). The latter fraction was recrystallized from acetone as colourless needles (10 mg), m.p. 220–222°. This compound is identical with 3β-*acetoxyfern*-8-*ene* (Va) by a mixed fusion, IR, GLC and TLC.

(b) Dry HCl was introduced into IVd (78 mg) in $CHCl_3$ (20 ml) for 20 min. After standing at a room temp for 20 hr, the reaction mixture was treated by the usual method and recrystallized from EtOH–benzene to afford colourless leaflets (30 mg), m.p. 276–278°, $[\alpha]_D$ −35·8° (*c*, 0·64); ν_{max} 2920 (s), 1720 (s), 1635, 1460, 1370, 1248 (s), 1168, 1020, 972, 918, 905 cm^{-1}. This compound was assumed to be 3β-*acetoxy-adian*-5(10)-*ene* (XVII) (lit.[8] m.p. 268–270°, $[\alpha]_D$ −35·0°). The examination of the course of the reactions under the conditions of (a) and (b) by TLC and GLC revealed that IVd changed first into XVII and then to Va.

* These compounds and 2α-bromoarborinone (XV)[9] had been prepared for X-ray analysis. While our analysis was at the preliminary stage, we learned that the analysis of XV had been completed (H. Vorbrüggen, private communication; cf. Ref. 24), thus we abandoned further work. We would like to acknowledge the late Professor Y. Tomiie, Kansei Gakuin University, and his associates for their kind cooperation all the same.

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Note Added in Proof. Recently the full characterization of the triterpene methyl ethers from the grass originally designated *Arundo conspicua* Forst. f.[7] but now identified as *Cortaderia toetoe* Zotov has been published (T. A. Bryce, G. Eglinton, R. J. Hamilton, M. Martin-Smith and G. Subramanian, *Phytochem.* **6**, 727 (1967)). In this paper our structure for arundoin (Ia) has been approved and the discrepancies in the results eliminated. The presence of α-amyrin methyl ether and β-amyrin methyl ether in the grass has been reported in the paper. Arundoin has also been isolated from other two *Cortaderia* spp. (M. Martin-Smith, G. Subramanian and H. E. Connor, *Phytochem.* **6**, 559 (1967)) and from *Saccharum officinarum* L. (T. A. Bryce, M. Martin-Smith, G. Osske, K. Schreiber and G. Subramanian, *Tetrahedron* **23**, 1283 (1967)).

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