CHEMISTRY OF PIMARANES

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DITERPENES, are a group of isoprenoid compounds which contain twenty carbon atoms. They are classified as acylic, monocyclic, bicyclic, tricyclic, tetracyclic and pentacyclic diterpenes. The naturally occurring tricyclic diterpenes fall into six groups, *viz.*, pimaranes, cassanes, rosanes, abietanes and ring C-aromatic compounds like ferrugenol and totarol. With the help of modern experimental techniques a large number of compounds of the pimarane group have been isolated and characterised. There is therefore need to survey the chemistry of pimaranes.

The pimaranes are divided[1] into two subgroups (*i*) pimaranes (I) and (*ii*) isopimaranes (II), depending on the orientation of C-13 methyl group. In the former it is alpha and in the latter it is beta. They are usually found as dienes with a vinyl group at C-13 and a trisubstituted double bond either at 8, 14 or at 7, 8 positions. The naturally occurring compounds are summed up in Table I.

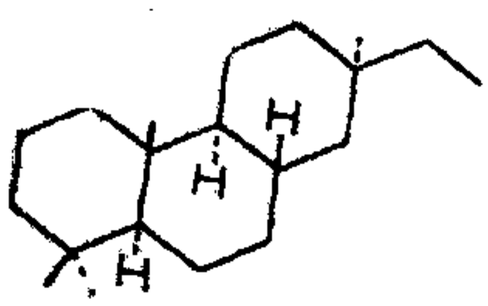
TABLE I
Naturally occurring compounds of pimaranes

No.	Diterpenoid	Molecular formula	Formula No.	Source	M.P., °C	$[\alpha]_D^\circ$ (Solvent)	Ref.
			a. Pimaradiene skeleton				
	A. PIMARANE TYPE						
1	Pimaradiene ..	$C_{20}H_{32}$	III*a*	*Pinus silvestris*	n_D^{20} 1·5270	+92 ($CHCl_3$)	2
2	Pimarinol ..	$C_{20}H_{32}O$	III*b*	,,	85–6	+83 ($CHCl_3$)	2
3	Pimarinal ..	$C_{20}H_{30}O$	III*c*	,,	51–2	+87 ($CHCl_3$)	2
4	Pimaric acid ..	$C_{20}H_{30}O_2$	III*d*	*Pinus* Spp.	211–212	+60 (EtOH)	3
			b. *ent* Pimaradiene skeleton				
5	*ent* pimaradiene ..	$C_{20}H_{32}$	IV*a*	*Erythroxylum monogynum*	..		4
6	*ent* pimarinol ..	$C_{20}H_{32}O$	IV*b*	*Aralia cordata*	109-110	−96·0 ($CHCl_3$)	5
7	*ent* pimaric acid ..	$C_{20}H_{30}O_2$	IV*c*	,,	163–4	−120·6 ($CHCl_3$)	6
8	*ent* hydroxy pimaric acid (7α)	$C_{20}H_{30}O_3$	IV*d*	*Aralia* Spp.	292–94	−70·4 (C_5H_5N)	5
9	*ent* hydroxy pimaric acid (7β)	$C_{20}H_{30}O_3$	IV*e*	,,	218	−62·8 (C_5H_5N)	5
10	*ent* keto pimaric acid ..	$C_{20}H_{28}O_3$	IV*f*	,,	241–45	−54·2 (C_5H_5N)	5
11	Macrangenol ..	$C_{20}H_{30}O_2$	IV*g*	*Macranga tanarius*	210–11	−142 ($CHCl_3$)	7
12	Darutigenol ..	$C_{20}H_{34}O_3$	IV-A-*h*	*Siegesbeckia orientalis*	169–70	−11 (EtOH)	8
13	Tetrahydroxy darutigenol	$C_{20}H_{34}O_4$	IV-A-*i*	*Siegesbeckia pubescens*	192–93	−22 (Dioxane)	9
	B. ISOPIMARANE TYPE						
			c. Isopimara-8 (14), 15 diene skeleton (sandaracopimaradiene)				
14	Sandaracopimardiene ..	$C_{20}H_{32}$	V*a*	*Xylia dolabriformia* *Dacrydium colensoi*	39–39·5	−12·4 ($CHCl_3$)	10
15	Sandaracopimaradien-3-ol	$C_{20}H_{32}O$	V*b*	*Xylia dolabriformia*	127–28	−20 ($CHCl_3$)	10
16	Sandaracopimaradien-18-ol	$C_{20}H_{32}O$	V*c*	*Dacrydium colensoi*	108–9	..	12
17	Sandaracopimaradien-19-ol	$C_{20}H_{32}O$	V*d*	*Thuja plicata*	43-45	..	13
18	Sandaracopimaradien-3, 18-diol	$C_{20}H_{32}O_2$	V*e*	*Xylia dolabriformia* *Dacrydium colensoi*	152–53 170-72	−19 ($CHCl_3$)	10, 14
19	Sandaracopimaradien-2, 18, 19-triol	$C_{20}H_{32}O_3$	V*f*	*Dacrydium colensoi*	224–27	..	15
20	Sandaracopimaradien-3, 18, 19-triol	$C_{20}H_{32}O_3$	V*g*	,,	163–66	..	15
21	Sandaracopimaradien-2 3, 18, 19-tetrol	$C_{20}H_{32}O_4$	V*h*	,,	210–14	..	15
22	Sandaracopimaradien-3-one	$C_{20}H_{30}O$	V*i*	*Xylia dolabriformia*	59–60	−56 ($CHCl_3$)	10
23	Sandaracopimaric acid ..	$C_{20}H_{30}O_2$	V*j*	*Cryptomeria japonica* *Tetraclinus articulata* *Callitris quadrivalvis* *Callitris columellaris* *Juniperus phoenicea*	169°	−20 (EtCH)	16, 17, 18, 19

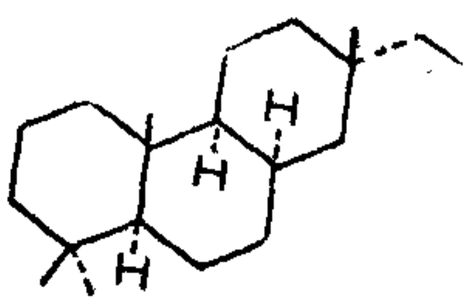
TABLE *I*—*Contd.*

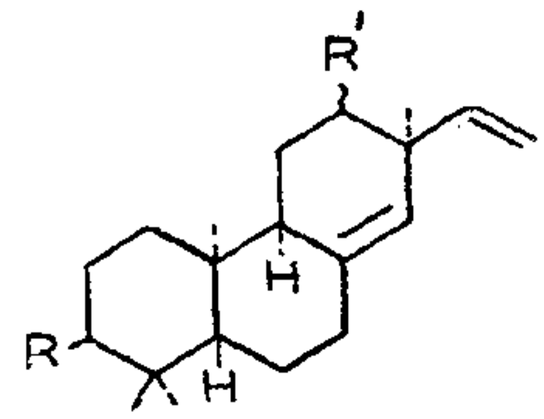
No.	Diterpenoid	Molecular formula	Formula No.	Source	M P °C	$[\alpha]_D°$ (Solvent)	Ref.
24	Hydroxy sandaracopimaric acid (6 α)	$C_{20}H_{30}O_3$	V*k*	*Juniperus phoenicea*	265-70	..	19
25	Hydroxy sandaracopimaric acid (12 β)	$C_{20}H_{30}O_3$	V*l*	*Callitris quadrivalvis*	269–70	−11 ($CHCl_3$)	20
26	Sandaracopimara-8β-hydroxy-15-ene	$C_{20}H_{34}O$	V*m*	*Dacrydium colensoi*	40–41	−6·8 ($FHCl_3$)	11
	d. ent Isopimara-8 (14), 15-diene skeleton						
27	*ent* isopimaradien-3-ol ..	$C_{20}H_{32}O$	VI*a*	*Cleistanthus schlechkeri*	126–27	+25 ($CHCl_3$)	21
28	*ent* isopimara dien-3, 12-diol	$C_{20}H_{32}O_2$	VI*b*	,,	161–62	+28 ($CHCl_3$)	21
29	*ent* isopimaradien-12-one	$C_{20}H_{30}O$	VI*c*	,,	157–58	+29 ($CHCl_3$)	21
	e. Isopimara-7, 15-diene skeleton						
30	Isopimaradiene ..	$C_{20}H_{32}$	VII*a*	*Dacrydium bidwilli*	..	..	22
31	Isopimaradienol ..	$C_{20}H_{32}O$	VII*b*	,,	81–2	−17 ($CHCl_3$)	22
32	Virescenol-A ..	$C_{20}H_{32}O_3$	VII*c*	*Oostora virescens*	149–50	−44 ($CHCl_3$)	23
33	Virescenol-B ..	$C_{20}H_{32}O_2$	VII*d*	,,	146–47	−25 ($CHCl_3$)	23
34	Isopimarinal ..	$C_{20}H_{30}O$	VII*e*	*Dacrydium bidwilli*	..	..	22
				Pinus silvestris	n_D^{20} 1·52·3	−12·2 ($CHCl_3$)	2
35	Isopimaric acid ..	$C_{20}H_{30}O_2$	VII*f*	*Pinus* spp.	162–64	±0 ($CHCl_3$)	3, 18, 22
				Callitris columellaria			
				Dacrydium bidwilli			
36	Araucarol ..	$C_{20}H_{32}O_3$	VII*A-g*	*Agarhis australis*	124–25	−24 ($CHCl_3$)	24
37	Araucarolone ..	$C_{20}H_{30}O_4$	VII-*A-h*	,,	157–9	−42 ($CHCl_3$)	24
38	Araucarone ..	$C_{20}H_{30}O_3$	VII *A-i*	,,	115–16	−52 ($CHCl_3$)	24
	f. *ent* Isopimara-7, 15-dione skeleton						
39	*ent* isopimaradiene ..	$C_{20}H_{32}$	VIII*a*	*Croton oblongifolius*	.	+23·2 ($CHCl_3$)	25
40	*ent* isopimaradien-3-ol ..	$C_{20}H_{32}O$	VIII*b*	,,	143-4	+37·5 ($CHCl_3$)	25
41	*ent* isopimaradien-19-ol ..	$C_{20}H_{32}O$	VIII*c*	,,	82-3	+28·3 ($CHCl_3$)	25
42	*ent* isopimaradien-3 19-diol (oblongifoliol)	$C_{20}H_{32}O_2$	VIII*d*	,,	147–8	+27·4 ($CHCl_3$)	26
43	*ent* isopimaradien-19-al ..	$C_{20}H_{30}O$	VIII*e*	,,	..	..	25
44	*ent* isopim radien-19-oic acid (Oblongifolic acid)	$C_{20}H_{30}O_2$	VIII*f*	,,	151-2	+11·0 ($CHCl_3$)	27
	g. Nor compounds						
45	19-nor-pimara dien-3-one	$C_{19}H_{28}O$	ix	*Pinus silvestris*	85-86°	..	28
46	19-nor-isopimara-8 (14), 15-diene-3-one	$C_{19}H_{28}O$	x	,,	..	..	28
47	19-nor-isopimara-7, 15-dien-3-one	$C_{19}H_{28}O$	xi	,,	..	..	28
48	Nor-isopimaratriene	$C_{19}H_{28}$	xii	*Dacrydium biforme*	62·5-63	+53 ($CHCl_3$)	29
49	4α-hydroxy nor-isopimara-8 (14), 15-diene	$C_{19}H_{30}O$	xiii	*Tkuja plicata*	100–101	..	13
50	4β-hydroxy nor-isopimara-8 (14), 15-diene	$C_{19}H_{30}O$	xiv	,,	82–84	..	13
51	Nor-isopimara-7, 15-dien-4-ol	$C_{19}H_{30}O$	xv	*Dacrydium bidwilli*	117–18	−38 ($CHCl_3$)	22

Pimaric acid (III *d*) sandaracopimaric acid (V *j*) and isopimaric acid (VII *f*) are the well known resin acids in this group which could be chosen for discussing the important features of the chemistry of the group. Pimaric acid (III *d*) has the pimarane skeleton while sandaracopimaric acid (V *j*) and isopimaric acid (VII *f*) have the isopimarane skeleton. Sandaracopimaric acid (V *j*) occupies a midway position since in it the double bonds are in the same position as in pimaric acid and only the stereochemistry of C-13 is different. In isopimaric acid (VII *f*) both these differ from pimaric acid (VII *d*). The epimeric nature of pimaric and sandaracopimaric acids (III *d* and V *j*) has been shown[17] by converting the two acids into a common nor acid (XVI) by the vinyl group being changed into methyl. This was effected by selective osmylation of the vinylidene group, periodate cleavage of the resulting diol followed by Wolff-Kishner reduction of the aldehyde to a methyl group. Sandaracopimaric acid (V *j*) is the double bond isomer of isopimaric acid (VII *f*). This has been shown by first reducing the exocyclic double bond; the two 15, 16-dihydro acids in chloroform gave the same Δ 8(9) isomer (XVII) by treatment with dry hydrogen chloride gas[17].



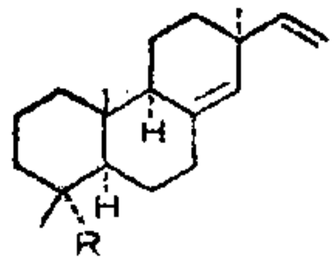
II





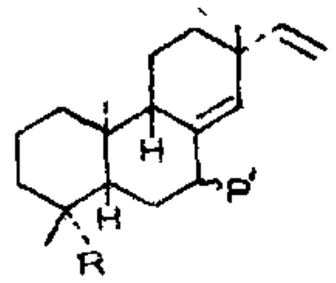
VI

	R	R'
a.	OH	H
b.	OH	OH
c.	H	=O



III

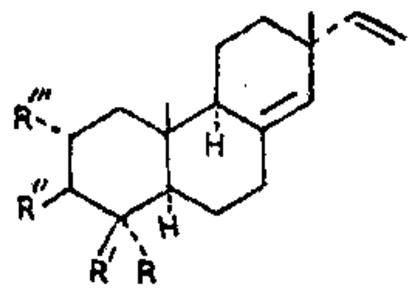
	R
a.	CH_3
b.	CH_2OH
c.	CHO
d.	CO_2H



IV

	R	R'
a.	CH_3	H
b.	CH_2OH	H
c.	CO_2H	H
d.	CO_2H	—OH
e.	CO_2H	—OH
f.	CO_2H	=O
g.	CH_3	H

=O at C-2 & OH at C-12



V

	R	R'	R''	R'''
a.	CH_3	CH_3	H	H
b.	CH_3	CH_3	OH	H
c.	CH_2OH	CH_3	H	H
d.	CH_3	CH_2OH	H	H
e.	CH_3	CH_2OH	OH	H
f.	CH_2OH	CH_2OH	H	OH
g.	CH_2OH	CH_2OH	OH	H
h.	CH_2OH	CH_2OH	OH	OH
i	CH_3	CH_3	=O	H
j.	CO_2H	CH_3	H	H
k.	CO_2H	CH_3	H	H

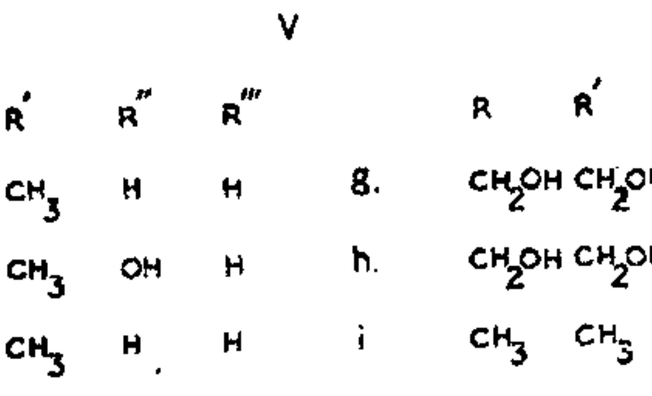
—OH at C-6

l.	CO_2H	CH_3	H	h.

OH at C-12

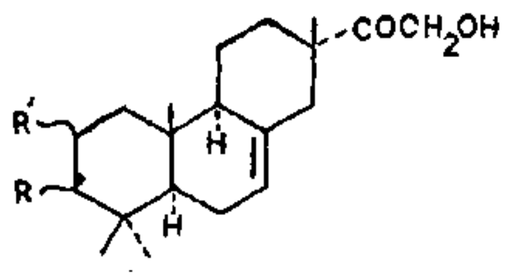
m.	CH_3	CH_3	H	H

OH at C-8



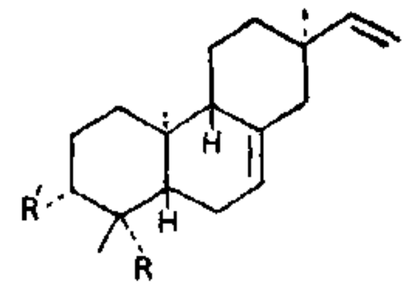
IV-A

	R	R'	R''
n.	CH_3	OH	H
l.	CH_2OH	OH	OH



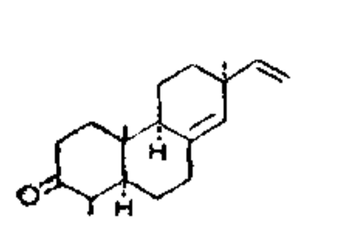
VII-A

	R	R
g.	OH	=O
h.	=O	H
i	OH	H



VIII

	R	R'		R	R'
a.	CH_3	H	d.	CH_2OH	OH
b.	CH_3	OH	e.	CHO	H
c.	CH_2OH	H	f.	CO_2H	H



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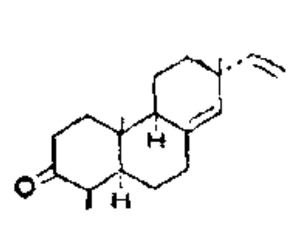
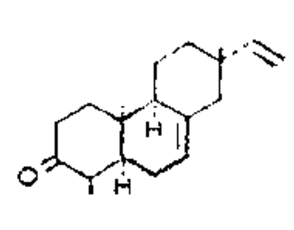
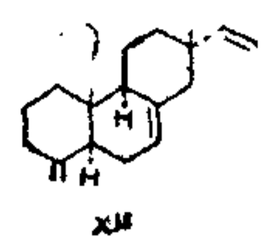


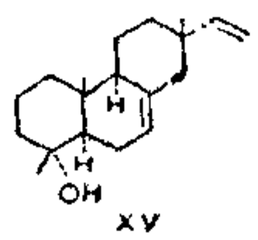
X



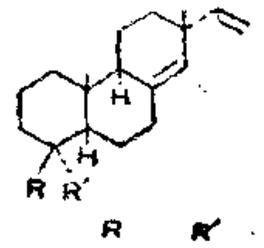
XI



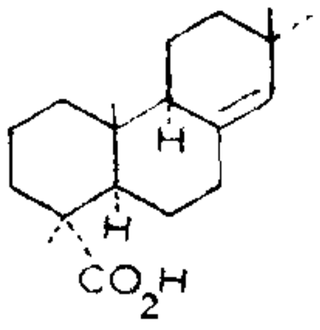
XII



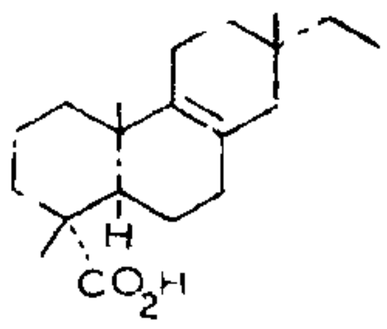
XV



	R	R'
XIII	CH_3	OH
XIV	OH	CH_3



XVI

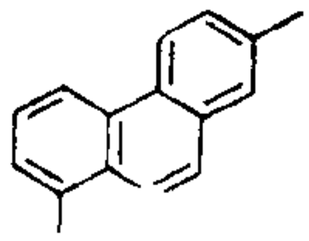


XVII

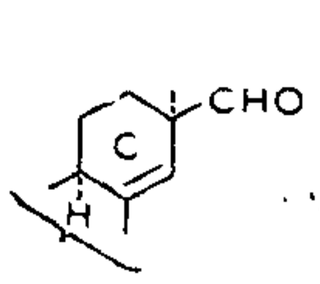
I. Degradative and Synthetic Studies

(*a*) *Skeleton.*—The parent skeleton is determined by the well-known selenium or sulphur dehydrogenation. Pimaranes on such dehydrogenation yield 1,7-dimethyl phenanthrene (XVIII)[30].

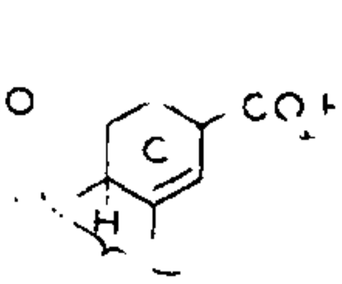
(*b*) *Vinyl group.*—The position of the vinyl group has been shown[31] to be at C-13 in all the compounds of the pimarane group. Its presence can be determined by ozonolysis of the compound followed by decomposition to give formaldehyde as one of the products. The vinyl group can be reduced by catalytic hydrogenation and can be oxidised to an aldehyde[17] (XIX) with OsO_4/HIO_4 and to an acid[32] (XX) with $KMnO_4/HIO_4$.



XVIII



XIX

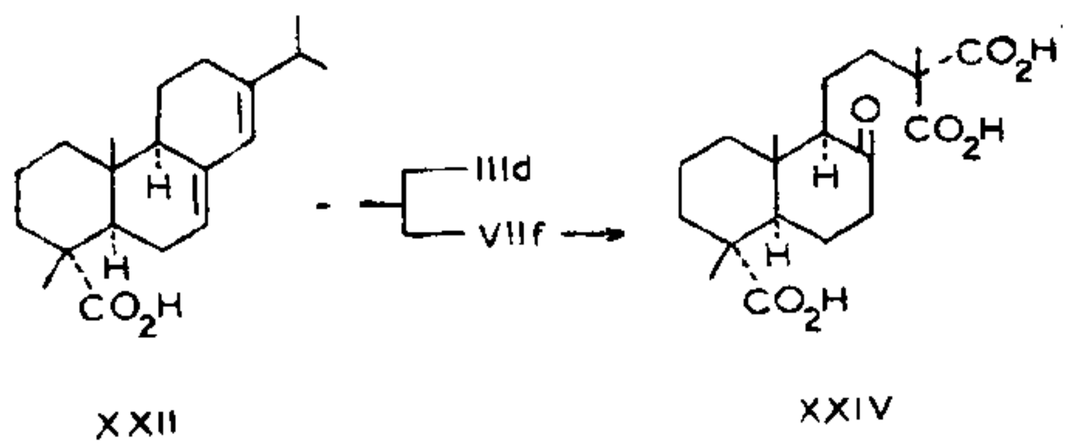


XX

A number of chemical, spectral and synthetic methods have been employed[32-34] to assign the stereochemistry of the vinyl group in resin acids. As a result the vinyl group of pimaric acid (III *d*) is considered to be quasi axial and of sandaracopimaric and isopimaric acids (V *j*) and VII *f*) quasi-equatorial.

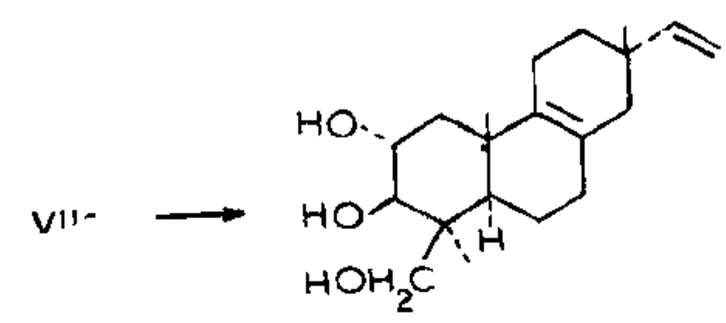
(*c*) *Trisubstituted double bond.*—This double bond requires vigorous conditions for catalytic hydrogenation. Its position could be fixed by a special procedure. For this purpose the readily prepared dihydro pimarane derivatives are used; in them the exocyclic double bond had been reduced. By hydroboration followed by oxidation a ketone (XXI *a* or XXI *b*) is obtained. From the NMR and mass spectra[35,36] of the derived ketone the position of the trisubstituted double bond can be easily fixed.

(*d*) *Migration of double bonds.*—The two double bonds undergo easy migration on treatment with mineral acids and ozonolysis. For example, pimaric acid (III *d*) and isopimaric acid (VII *f*) undergo change in the presence of a little conc. sulphuric acid at low temperature into abietic acid[37] (XXII) in which the two double bonds form a stable conjugated system. The migration of trisubstituted double bond to the stable 8(9) position without affecting the vinyl group can be effected by dry hydrogen chloride gas. This has been carried out[23] for the conversion of virescenol-A (VII *c*) into isovirescenol-A (XXIII). The trisubstituted double bond in isopimaric acid (VII *f*) migrates to Δ 8(14) position during ozonolysis of the compound and gives the oxo-tricarboxylic acid (XXIV)[38].



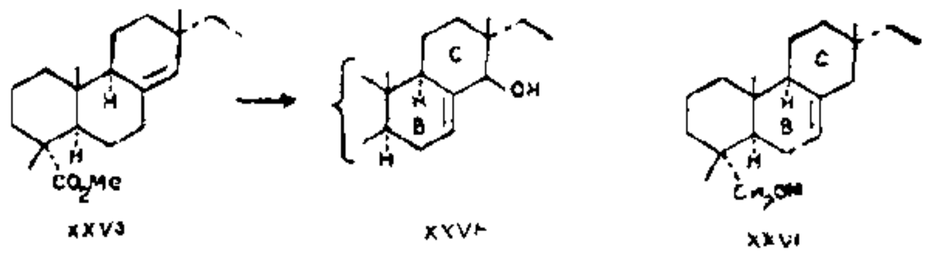
XXII

XXIV



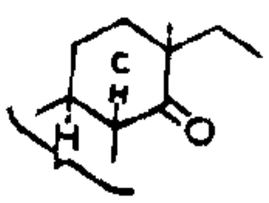
XXIII

(*e*) *Interconversions.*—A number of attempts have been made for the interconversion of one type into another among the pimarane group. These are useful for the determination of structure by correlation.

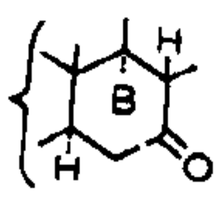


XXV *a* XXV *b* XXVI

(*i*) ApSimon[39] showed that the Δ (14) type of compounds could be converted into the Δ 7 compounds by a simple procedure. For example, dihydro methyl sandaracopimarate (XXV *a*) on epoxidation gave an epoxide and an allylic alcohol (XXV *b*). When the alcohol



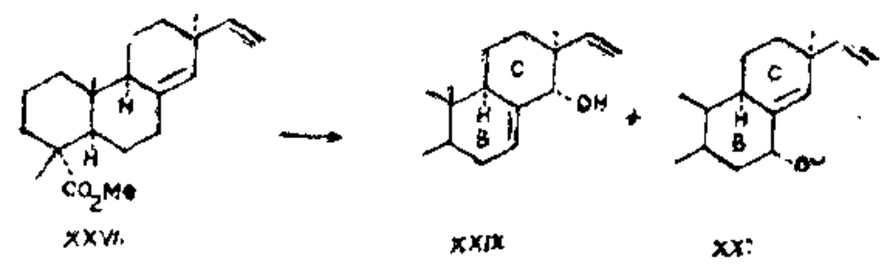
XXI *a*



XXI *b*

was acetylated followed by lithium-ethyl amine treatment it gave isopimara-7-ene-18-ol (XXVI).

(*ii*) Another method[40] of converting the Δ 8(14) compounds into the Δ 7 compounds or *vice versa* is by the allylic photosensitized oxidation. This has been carried out in the case of methyl pimarate (XXVII) and methyl isopimarate (XXVIII). The former yielded 14-α-hydroxy-7, 15-dien methyl ester (XXIX), and 7 α-hydroxy methyl pimarate (XXX). The latter yielded methyl 7 α-hydroxy sandaracopimarate (XXXI).

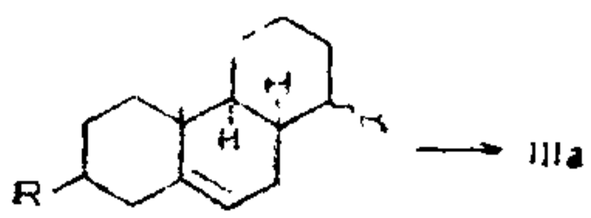


XXVII XXIX XX

XXVIII XXXI

(*f*) *Synthesis.*—The structure and absolute configuration of the main dienes have been confirmed by stereospecific synthesis also.

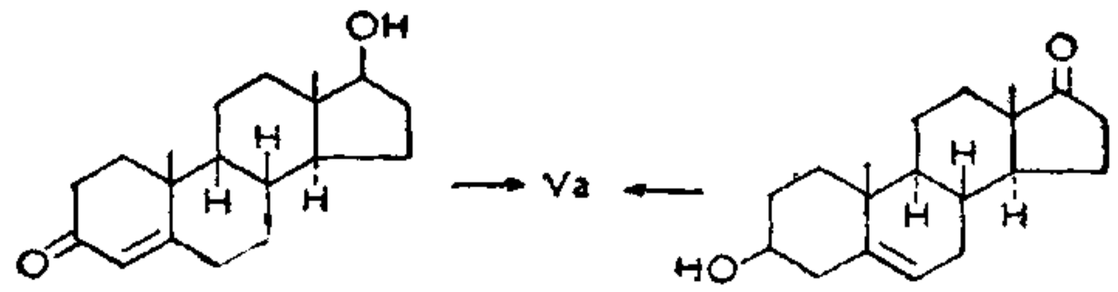
(*i*) Milne and Smith[41] transformed a steroidal ketone acetate (XXXII), obtained from cholesteryl acetate into pimaradiene (III *a*).



XXXII

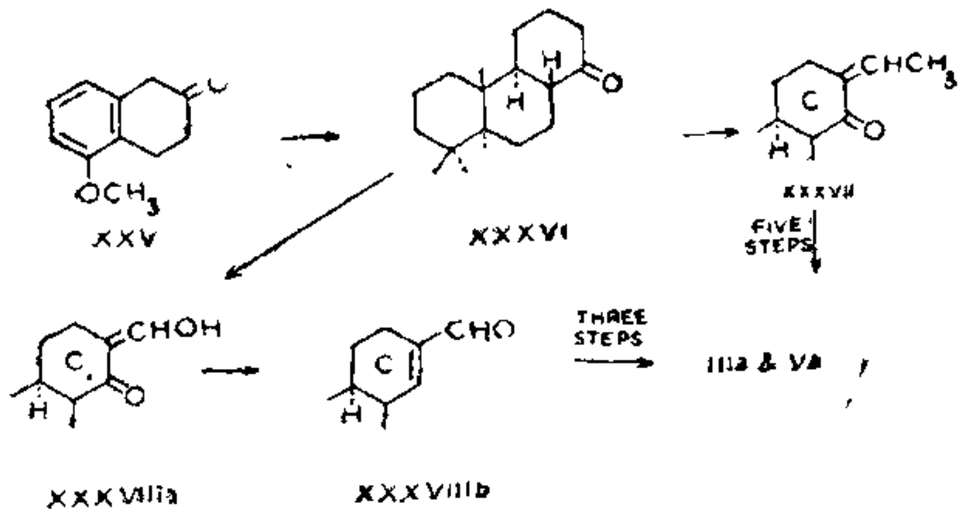
R =OAc ; R' =O

Sandaracopimaradiene (V *a*) has been synthesised from testosterone (XXXIII) by Bose and Harrison[42] and 3 β-hydroxy androst-5-en-17-one (XXXIV) by Fetizon and Golfier[43]. Finally, Johnston *et al.*[44] synthesised the diene (V *a*) from these two steriods by a different route. In this process 4, 4-dimethyl-5 α-androst-14-ene and its 17-hydroxy derivative were prepared by acid-catalysed isomerisation of the related 5, 7-dienes, hydrogenation and further isomerisations of the resulting 8(14) olefines. Cleavage of ring D by reduction of the ozonide and selective oxidation of the seco-triol with manganese dioxide yielded ring D homolactones which were converted by way of the β-keto lactone into sandaracopimaradiene (V *a*).



XXXIII XXXI

Finally, synthetic work of Church and Ireland[45] confirmed the structure of these two dienes. They started with 5-methoxy-2-tetralone (XXXV) and converted it into (±) 14 podocarpanone (XXXVI). Two sequences were then followed for the construction of the ring C substitution pattern of the dienes: (*i*) methylation of (±)13-ethylidene-14- carpanone (XXXVII) followed by the removal of carbonyl group; (*ii*) methylation of (±) podocarpen-13-carboyldehyde (XXXVIII b).



XXV XXXVI XXXVII

XXXVIIIa XXXVIIIb

Spectral Methods

Spectral methods have vastly increased our capacity to understand molecular structures and they have come into common use with the development of instrumentation. The important spectral methods that have found application in the structural elucidation of the pimarane group are discussed below.

(*a*) *Infrared Spectroscopy.*—In addition to the information about the presence of various functional groups, certain generalizations have been reached from the IR spectra, regarding the precise determination of configuration of certain groups. One such application relates to the vinyl group[45]. Compounds having an equatorial vinyl group show a strong peak at ~ 911 cm^{-1} whereas compounds having an axial vinyl group show a peak at ~ 919 cm^{-1}.

Bory and Fetizon[46] in their study of the infrared spectra of the methyl esters of C-4 diterpene carboxylic acids observed that the

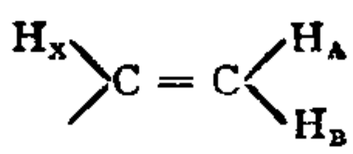
compounds having equatorial methyl ester groups show a strong peak at *ca.* 1245 cm^{-1} whereas compounds having axial methyl ester group show bands at *ca.* 1230 (W), 1190 (*m*) and 1155 (s) cm^{-1}.

(b) *NMR spectroscopy.*—The NMR spectra of the pimarane group were systematically studied by Wenkert *et al.*[47,48]; subsequently important observations were made for the di- and tetra-hydro derivatives by ApSimon *et al.*[49]. A comparative study of the chemical shift of the methyls, the allylic protons and the olefinic protons of the main dienes and their derivatives have led to the following conclusions.

(*i*) *C-methyl group.*—Of the C-4, C-10 and C-13 methyl signals the C-10 methyl signal is most shielded in all the cases and appears at $\sim \delta$ 0·80. The C-13 methyl signal usually appears at $\sim \delta$ 1·00. The C-4 methyl signal is most deshielded ($\sim \delta$ 1·00) and its chemical shift depends on the other substituent at C-4.

(*ii*) *Allylic Protons.*—The allylic proton signals indicate the position of the trisubstituted double bond in the compound. In the isopimaradiene type (VII) the secondary allylic protons at C-14 appear as singlet at $\sim \delta$ 1·96 and the allylic protons situated at C-6 appear at $\sim \delta$ 1·70 as a multiplet. In pimaradiene and sandaracopimaradiene types (III and V) the secondary allylic protons present at C-7 appear as a multiplet at $\sim \delta$ 1·70. The allylic methine proton (C-9) signal in isopimaradiene type (VII) is masked by the secondary allylic proton signal but in other two types it appears at $\sim \delta$ 2·20.

Vinyl Protons



The signals for the protons on the vinylic group form an ABX system. The related isopimaradiene and sandaracopimaradiene types (VII and V) exhibit twelve lines with a quartet for the H_X while the pimaradiene type (III) shows fourteen lines with a sextet for the H_X. The difference in the number of lines could be attributed to the difference in the configuration of vinyl group. In the isopimaradiene and sandaracopimaradiene types (VII and V) the vinyl group has quasi-equatorial configuration whereas in pimaradiene (III) type it has a quasi-axial configuration. The coupling constants $J_{AX} \sim 1{\cdot}8$ Hz, $J_{AX} \sim 10$ Hz and $J_{BX} \sim 18$ Hz are characteristic of ABX system.

Proton of the Trisubstituted Double Bond

This proton signal appears in isopimaradiene (VII) type at $\sim \delta$ 5·33 as a triplet or an unresolved triplet with $W_{\frac{1}{2}} \sim 9$ Hz while in sandaracopimaradiene (V) type it is at $\sim \delta$ 5·23 as a broad singlet with $W_{\frac{1}{2}} \sim 3{\cdot}5$ Hz and in pimaradiene (III) type at $\sim \delta$ 5·15 as a singlet.

Apart from the above-mentioned information, NMR is being widely used to assign the configuration of the hydroxyl, aldehyde, carboxyl and other functional groups.

(*i*) If the proton on the carbon carrying secondary acetoxyl group is axial it is recorded between δ 4·00 to 4·75 and if it is equatorial proton the position is between δ 5·00 to 5·48[50]. Gaudemer *et al.*[51] made a study of a number of diterpene alcohols and their corresponding acetates having an axial or an equatorial group at C-4 and found that the hydroxy or acetoxy methyl protons appear either as a singlet or as a quartet. The quartet will be of AB type with a coupling constant of 10·5 Hz and 12 Hz respectively. The signals due to axially oriented $-CH_2OH$ and $-CH_2OAc$ appear (δ 3·70 and 4·20 respectively) downfield as compared to the equatorially oriented $-CH_2OH$ and $-CH_2OAc$ (δ 3·30 and 3·80 respectively).

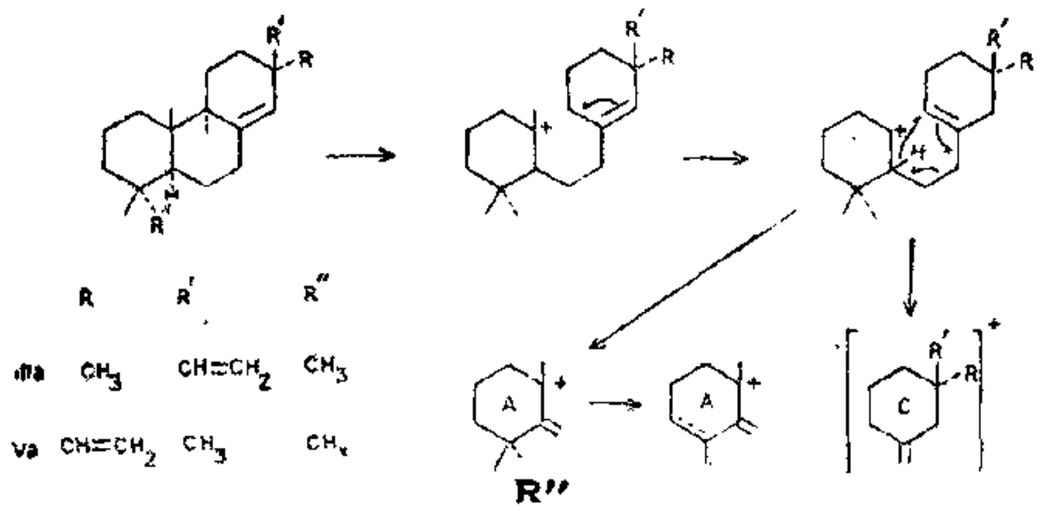
(*ii*) In the study[52] of the spectra of diterpenes having an aldehyde group at C-4 and an axial proton at C–3, the equatorial aldehydic proton appears at δ 8·9–9·30 as singlet, while axial aldehydic proton records at δ 9·70–9·90 as doublet ($J > 3$ Hz).

Narayanan *et al.*[53] have shown that NMR spectroscopy is a convenient method to determine the configuration of the carboxyl group and also to find whether carbon having a carboxyl group also carries a methyl group. They observed from a study of the spectra of a number of diterpenes having carboxyl group at C-4 and the corresponding methyl esters recorded in deuterated pyridine that the C-10 methyl which has a 1, 3 diaxial relation with the C-4 carboxyl group suffers a deshielding effect of $\sim$ 17 Hz when the ester is changed to the acid anion. Under the same conditions, the equatorial acids which have no such relation show only a deshielding effect of $\sim$ 4 Hz. They also noted that the C-4 methyl group undergoes a uniform downfield shift of $\sim$ 10 Hz when either axial or equatorial methyl esters change into the acid anion.

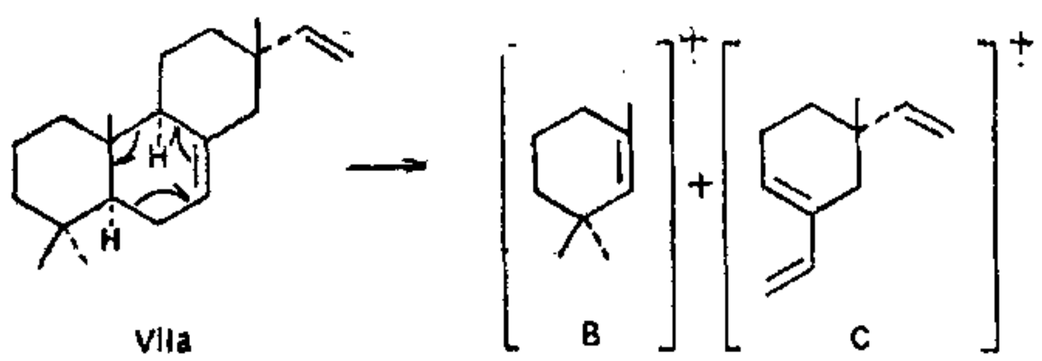
Mass Spectrometry

Mass spectrometry has found extensive application in sorting out the type of com-

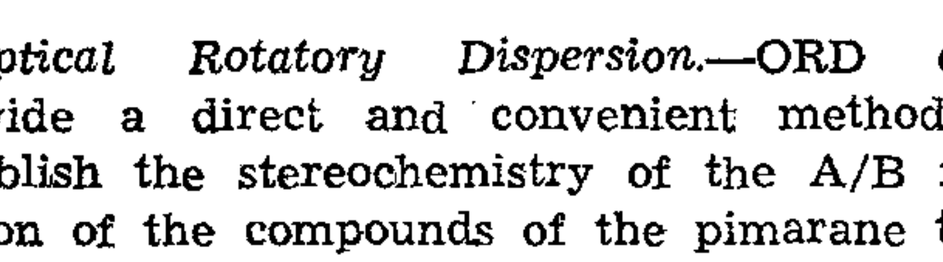
pounds in the pimarane group, apart from the determination of the correct molecular weight and subsequently the correct molecular formula. The mass spectra of the pimaradiene and sandaracopimaradiene (III and V) types[54] undergo cleavage of the allylic bonds, C(6)-C(7) and C(9)-C(10) with the formation of fragments as indicated below.



Compounds of the isopimaradiene (VII) type[55] undergo a facile retro-Diels Alder fission involving a double bond at 7, 8 to yield fragments B and C.



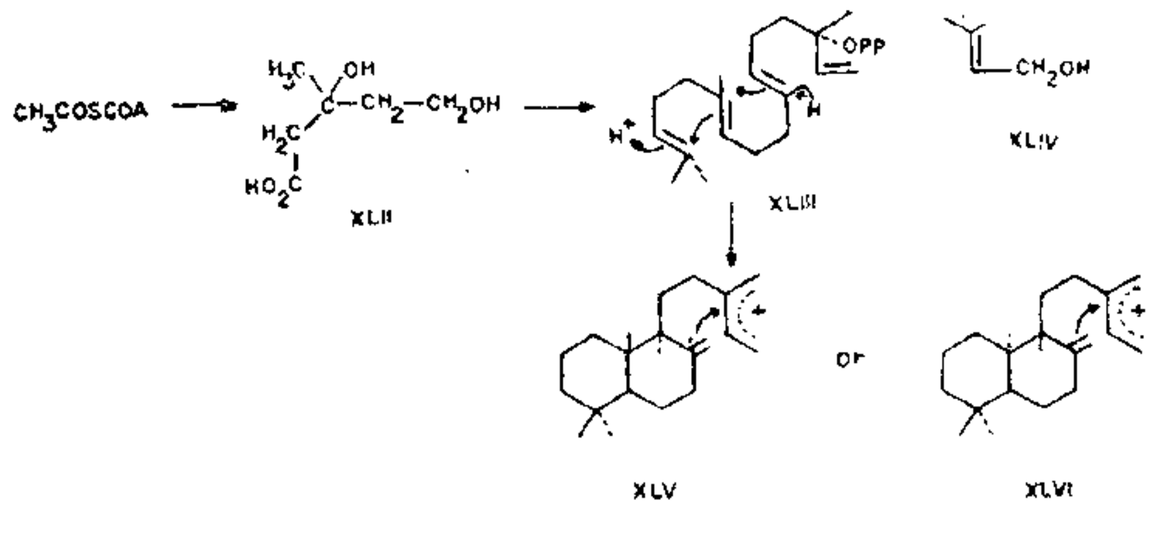
Optical Rotatory Dispersion.—ORD data provide a direct and convenient method to establish the stereochemistry of the A/B ring fusion of the compounds of the pimarane type having 3-keto group. For example, 3-keto sandaracopimaradiene (XXXIX) having normal fusion (10 β, 5 α) showed the negative cotton effect curve whereas *ent* 3-keto sandaracopimaradiene (XL) having antipodal fusion (10 α, 5 β) showed the positive cotton effect curve[21].



XXXIX XL

Enzell *et al.*[56], from a study of different 15, 16-dihydro derivatives of pimara, sasdaracopimara and isopimara dienes, found that the first two showed a plain positive curve whereas the last showed a negative plain curve with molecular rotation at $\sim 225\,m\mu$ of the order of -4000 to $-7000°$. They also observed that the Δ 7, 15 compounds gave a negative plain curve but the sign of the ORD curves of the 8(14), 15 diene compounds depends on the configuration at C-13-vinyl group. Sandaracopimaradiene (V a) had a negative plain curve and pimaradiene (III a) a positive plain curve.

Biogenesis.—Mevalonic acid (MVA) (XLII) has been found to be the precursor of diterpenes in plants and is itself formed from acetyl coenzyme-A (XLI). It is then transformed into geranyl-geranyl pyrophosphate or its C-13 allylic isomer, geranyl-linalyl (XLIII and XLIV) pyrophosphate[57]. The cyclic diterpenes are derived from one of these pyrophosphates by cyclization initiated by protonation. The cyclization stops at the stage of bicyclic cation (XLV) and both normal and antipodal series are formed. Further cyclisation leads to the tricyclic pimarane skeleton as indicated below.



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