

Diterpenoid 의 분포

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Distribution of Diterpenoids

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Diterpenoids contain only 20 carbon atoms, and the plants that have been examined for diterpenoids are less numerous. However, a greater variety of the possible cyclization and oxidation patterns has been observed in the diterpenoids. Thus the list of known structures is large. The diterpenoids have often been found in two antipodal forms. Our present state of knowledge does not allow us to draw any conclusions from the distributions of these configurations.

우리의 눈을 자연계에 돌릴때 그 종류와 수에 있어 자연 산물의 어느 group 보다 terpenoid 화합물이 많다는 것에 놀라지 않을 수 없다. 쌍떡잎식물에 있어서만 보더라도 100 과 이상에서 terpenoid 화합물이 발견되었고 최근까지 400 여종의 triterpene 이 증명되었으며 그 중 300 여종에 대하여 그 화학구조가 결정되고 있다.

Diterpenoid 에 있어서는 구성탄소수가 20 개에 불과하고 또한 지금까지 검토된 식물의 종류도 triterpenoid 에 비하면 훨씬 적지만 그러나 cyclization 과 oxidation 의 pattern 이 더욱 다양성을 띤 가능성이 많으므로 그의 분포에 있어서도 거의 triterpene 과 같은 것이 예상되며 따라서 발굴의 여지도 triterpene 에 비하여 훨씬 많을 것이 예측된다.

지금까지 이미 발견된 diterpene 의 수가 200 여종에 달하고 또 앞으로 더 많은 종류가 발견될 것이나 이미 발견된 것을 기초로 하여 그들의 basic skeletal type 를 살펴보면 Fig. 1 과 같다.

또 자연계에 분포되어 있는 diterpene 은 이와같은 basic skeleton 을 기초로 하여 다음과 같이 (4면) 分類되고 있다.

Diterpene 은 geranyl geranyl pyrophosphate 로부터 합성되는 것으로서 이때에 asymmetric carbon 특히 5, 8, 9, 10 및 13 위치에 있는 carbon 이 독특한 configuration 을 형성함으로써 많은 입체이성체를 형성한다. diterpene 은 mono 또는 sesquiterpene 과 같이 때로는 두개의 antipodal form 이 나타나는 경우가 흔히 있다. triterpene 의 경우에서 거의 normal (10 β -methyl) series 로서 존재하

고 있는 것과는 대조를 이루고 있다. 우리들의 오늘날의 지식으로는 이 현상에 대하여 어느 종합적인 결론을 내릴수 없으며 그저 diterpene 의 다양성을 보여주는 일면이라고 해석할 수 밖에 별도리가 없다. 다음 한가지 예를 보더라도 특히 이를 이해할 할 수 있을 것이다.

즉 *Agathis austaris* 하나만 보더라도 이 식물에는 (-)-kaurene(I), agathic acid(II) araucarenolone(III) abietic acid(IV), iso-pimaradiol(V), pimaric acid(VI) 가 함유되고 있으며 이 화합물들은 ring 의 수, A/B ring 의 steric junction, C-13, C-4 에 있어서의 stereo-configuration 또는 oxidation degree 가 모두 달라서 화학적으로 볼때 결코 homogeneous compound 가 아니라는 것을 일견해서 인정할 수 있을 것이다.

Di-와 triterpene 이 동일식물에서 발견되는 경우는 거의 없다. 그 이유로는 그의 precursor 의 synthesis 와 cyclization 에 대하여 요구되는 화학적 및 효소학적 조건의 차이가 이 두 terpene group 의 합성에 있어서 경쟁적 효과를 나타내기 때문이라고 설명하고 있는 것이다. 그러나 이에 대하여도 예외가 점차 나타나고 있다. 즉 coffee oil에서 triterpene 에 속하는 coffesterol²⁰(VII) 과 diterpene 에 속하는 cafestol²¹(VIII) 및 kahweol²²(IX) 이 발견되었으며 화학구조상으로는 ring A 에 있어서 C-4 methyl 가 C-4 ethyl group 으로 전이된 것이라고 볼수있다.

또 diterpenoid 의 분포를 개관하면 taxonomic significance 에 생각이 미칠 것이다. *Erythrophleum*은 적어도

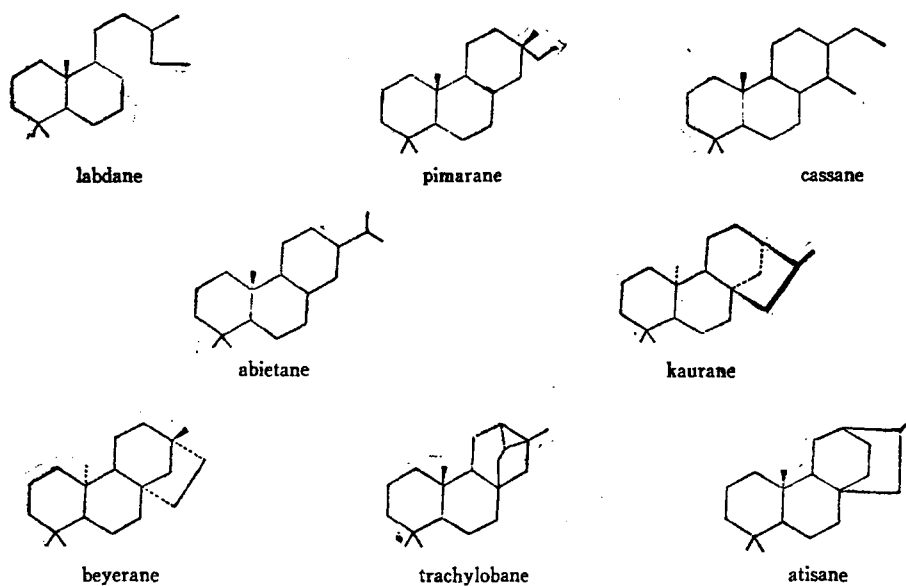
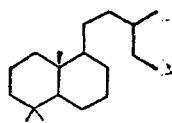
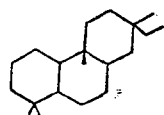


Fig. 1 Basic skeletal types of diterpenoids

Dicyclic diterpenes

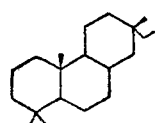


labdane groups
ex. manool

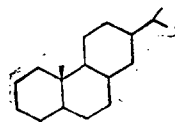


c) rosane groups
ex. rimuene

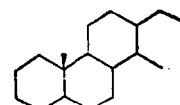
Tricyclic diterpenes



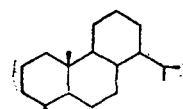
a) pimarane groups
ex. pimaric acid



d) abietane groups
ex. abietic acid

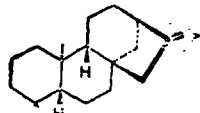


b) cassane groups
ex. cassaidic acid, cassaic acid

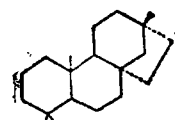


e) rearranged abietane groups
ex. totarol

Tetracyclic diterpenes



a) phyllocladane-kaurane groups
ex. (+)-phyllocladene; (-)-kaurene



b) beyerane groups
ex. hibaene

10종의 alkaloid를 함유하고 있으며 각 종류에서 분리 동정된 alkaloid는 모두 aminoalcohol과 C-7이 산화된 tricyclic diterpene에 속하는 cassamic acid 유도체의 ester이다. 따라서 이 group의 homogeneity가 크기 때문에 taxonomic significance가 있다고 생각된다.

또 *Amherstiae*도 다수의 resin 또는 copal을 함유하

고 있다. 이 resin에는 각종의 bicyclic diterpene이 함유되어 있어 이 방면의 연구자들에게 풍부한 재료를 제공하고 있다. 지금까지 분리된 alcohol, aldehyde 및 acid만해도 15종이상에 달하며 이것들은 모두 소위 antipodal (10 α -methyl) labdane skeleton을 가지고 있는 diterpene이라는 것이 확정되었다. 따라서 이것 역시

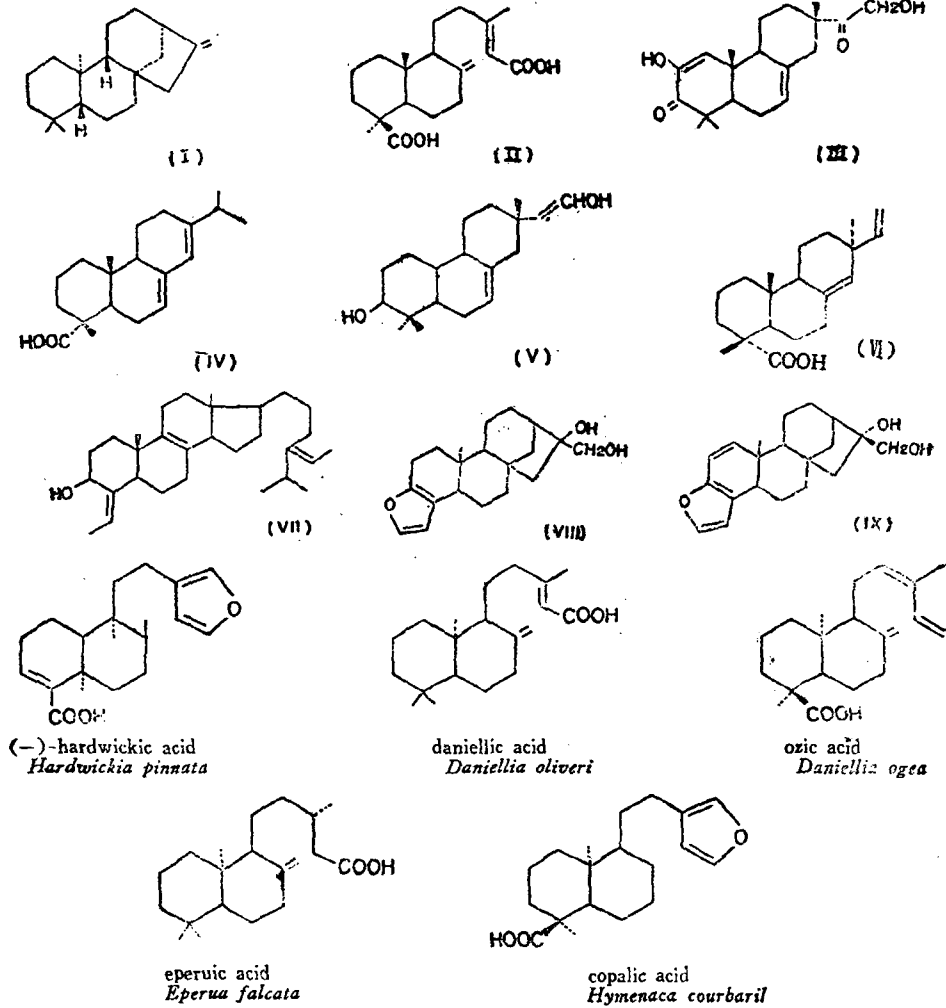


Fig. 2 Some acids of *Amherstiae* (antipodal configuration).

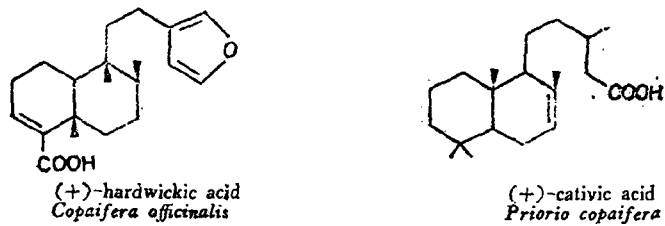


Fig. 3 Acids of *Amherstiae* (normal configuration).

taxonomic significance가 있다고 보겠다. (Fig. 2).

그러나 여기 한가지 큰 문제점은 *Copaifera officinalis*에 있어서 (+)-hardwickic acid (10 β -methyl)가 발견되고 *Prioria copaifera*에서도 (+)-caticic acid (10 β -methyl)가 알려짐으로서 *Prioria*와 *Copaifera*에 대한 taxonomic significance가 없어져버린 사실이다. (Fig.3).

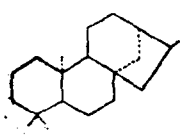
또하나 taxonomy에 있어서의 문제점은 식물 각기판의 정확한 구분이 필요하다는 것이다. *Trachylobium*에

있어서 trunk resin은 bicyclic terpene이 들어있는데 반하여 seedpod resin에는 kaurene과 trachylobane에서 유도되는 tetra와 pentacyclic diterpene이 혼합되어 들어 있다. 따라서 이런 경우에는 식물의 기관 구분에 대하여 세심한 주의가 필요할 것이다.

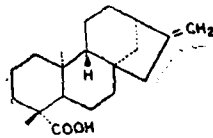
지금까지 발견된 diterpenoid 중에서 가급적 조사된 종류를 식물각과별로 열거한다.⁴⁾

Euphorbiaceae

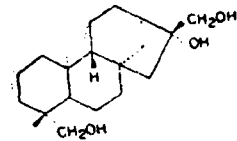
Kaurane derivatives (compounds isolated from a new *Beyeria* species)



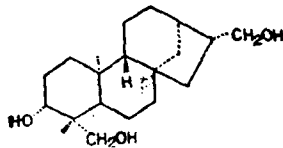
kaurane



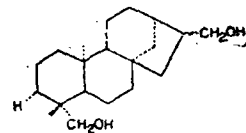
(-)-kaur-16-en-19-oic acid (kaurenic acid)



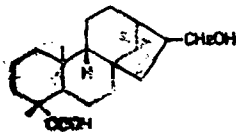
16 β -(-)-kauran-16, 17, 19-triol



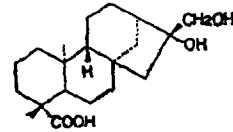
16 α -(-)-kauran-3 α , 17, 19-triol



16-(-)-kauran-17, 19-diol

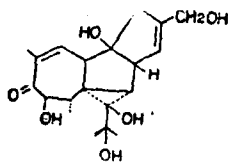


17-hydroxy-16 α -(-)-kauran-19-oic acid

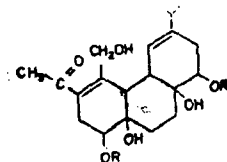


16-17-dihydroxy-16 β -(-)-kauran 19-oic acid

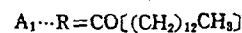
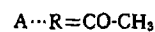
Phorbol derivatives (compounds isolated from croton resin)



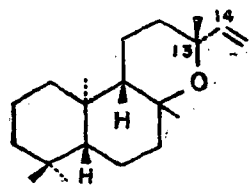
phorbol



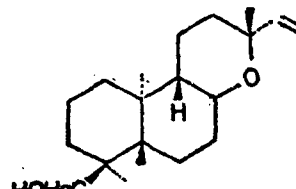
cocarcinogen A



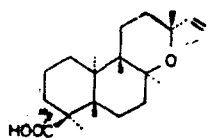
Bicyclic diterpene (compounds isolated from a new *Beyeria* species)



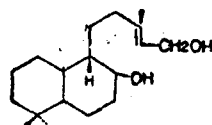
13-epi-(-)-manoyl oxide



18-hydroxy-13-epi-(-)-manoyl oxide



13-epi-(-)-manoyl oxide-18-oic acid



eperu-13-ene-8β, 15-diol

Ricinocarpoideae

TABLE I Tetracyclic diterpenes

species (location)	tetracyclic diterpenes		
	kaurane derivatives	beyerane derivatives	miscellaneous (flavone etc.)
	*2	*1	
<i>Beyeria. lesch</i> (eastern gold fields)	3, 19 17, 19 ^a 17 ^a , 19 3, 16, 17, 3, 17, 19, 12, 17, 19 ^a 3, 16, 17, 19	(1) (2) (2) (3) (2) (2) (3)	5, 4'(OH)-3, 7, 8(OMe) (7)
<i>B. lesch</i> var. <i>drummondii</i> (outer wheatbely of W.A.)		3, 17, 19 (4) 3, 17*, 19 (4) * cinnamate	
<i>B. lesch</i> var. <i>drummondii</i> (east of southern cross)		3 [†] , 17 ^a , 19 ^{AC} (4) 3 [†] , 16 ^{AC} , 17 (4)	seco-beyerene (5)
<i>B. lesch</i> var. <i>drummondii</i> (lake grace-W.A.)		3, 17 (4) 17, 19 (4) 3, 17, 19 (4)	5, 4'(OH)-3, 7, 3'(OMe) (7) 5, 3', 4'(OH)-7(OMe) (7)
<i>B. latifolia</i> (gardinar river south W.A.)	3, 17, 19 (2) 3, 16, 19 (3) 3, 16, 17 (3) 3, 16, 17, 19 (3)	(2) (3) (3) (3)	5, 4'(OH)-7-(O-Me) (7) 5, 7, 4' (OH) (7)
<i>B. brevifolia</i> (south east W.A.)	16, 17, 19 ^a (3)	(3) 3 [†] , 17, 19 (4) 3, 17*, 19 (4)	5, 7, 3'(OH)-3, 8, 4', 5' (OMe) (7) seco acid (8)

TABLE II Tetra- and bicyclic diterpenes

species (location)	tetra- and bicyclic diterpenes		
	kaurane derivatives	eperuane derivatives	miscellaneous (flavone)
<i>B. brevifolia</i> (coolgard-Norseman region)	3 ^{†*} , 17 ^{a*} , 19 (2) 3 [†] , 17 ^a , 19 ^{AC*} (2) 3, 17, 19 (2)		
<i>B. sp.</i> (south west of Norseman)	19 ^a (1) 17, 19 ^a (2) 17, 19 (2) 3, 17, 19 (2) 16, 17, 19 ^a (3)	(1) (2) (2) (2) (3)	8β, 13β-oxidoeperu-14-en-18-ol (6) 5, 4'(OH)-3, 7(O-Me) (7) 8β, 13β-oxidoeperu-14-en-18-oic acid (6) 8β, 13β-oxidoeperu-14-ene. (6) eperu-13-ene-8β, 15-diol (6)

<i>B. viscosa</i>	3, 19	(1)	
(costal region of W.A.)	17, 19	(2)	
	3, 16, 17	(3)	
<i>B. Lepido Petala</i>			eperu-8(20)-ene-15, 18-dioic acid (6)
(170 miles N.E. of Perth)			15-hydroxyeperu-8(20)-ene-18-oic acid (6)
			eperuane-8 β 15, 18-triol (6)
<i>Ricinocarpus stylosus</i>	19 ^a	(1)	polyaltic acid (9) 5(OH)-3, 7, 8, 3', 4'(OMe) (7)
(south west of Norseman)	1, 17 ^a , 19	(2)	5, 3'(OH)-3, 7, 8, 4'(O-Me) (7)
	17 ^a , 19 ^a	(2)	5, 4'(OH)-3, 7, 8(O-Me) (7)
	17 ^a , 19	(2)	5, 3', 5'(OH)-3, 7, 4'(O-Me) (7)
	16, 17, 19 ^a	(3)	
	16, 17, 19	(3)	

TABLE III. Bicyclic diterpenes

species (location)	bicyclic diterpenes	
	eperuane derivatives	miscellaneous(flavone)
<i>R. Muricatus</i> (south west W.A.)	eperuane-8 β , 15-diol	(6) 5, 3', 4'(OH)-3, 7, 8(OMe) (7)
	eperuane-8 β , 15, 18-triol	(6) 5, 7, 3', 4'(OH)-3, 8(OMe) (7)
	15, 16-dihydroxyeperu-8-(20)-en-18-oic acid	(6)
	eperu-8(20)-ene-15, 18-dioic acid	(6)
	15-hydroxyeperu-8(20)-ene-18-oic acid	(6)

* k=ketone, α =acid Ac=acetate. * 1=()内の 숫자는 basic skeletons(Fig. 4)

* 2=OH 또는 어찌글자가 표시하는 radical이 결합되어 있는 C의 번호 (Fig. 4)

*Ricinocarpoideae*에서 발견된 diterpene 을 basic skeleton 에 의하여 분류하면 다음과 같다. (Fig. 4)

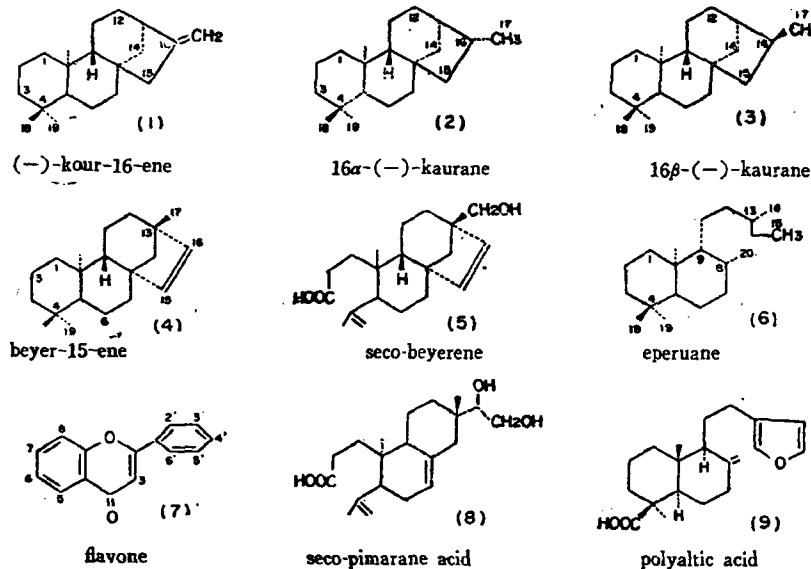
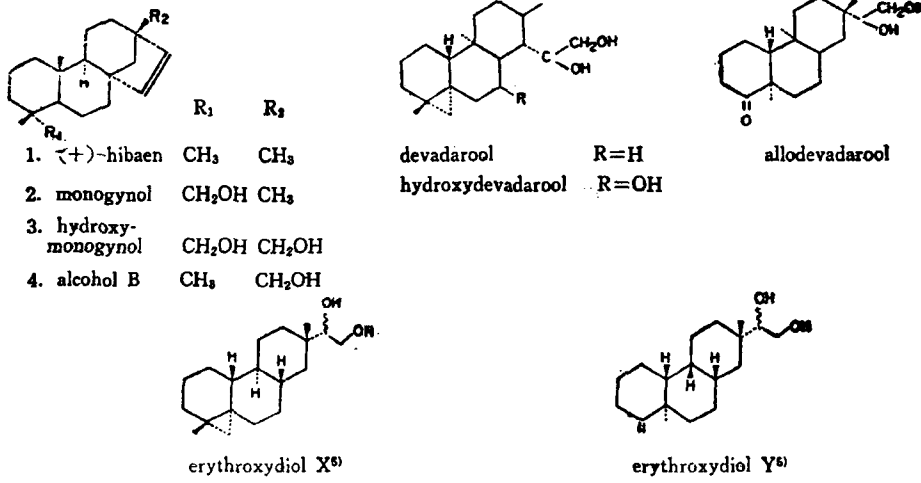


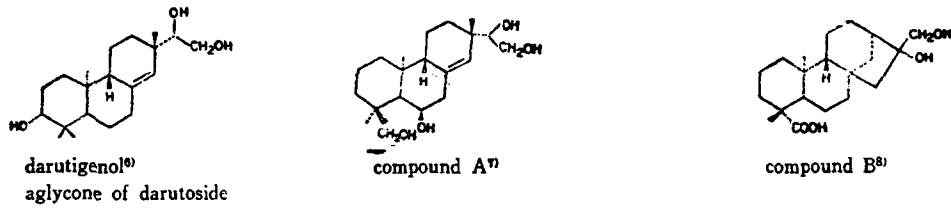
Fig. 4 Basic skeleton of diterpenes in *Ricinocarpoideae*.

Erythroxylaceae (compounds isolated from *Erythroxylum monogynum* "Deva Daru" in india)

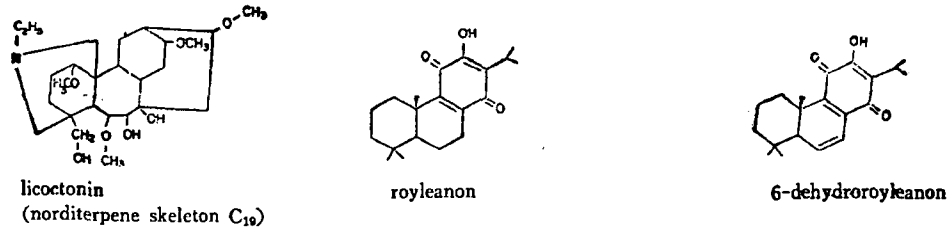


Compositae

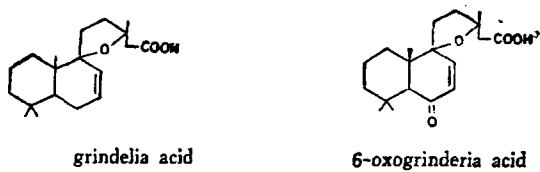
Siegesbeckia sp.



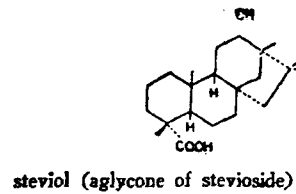
Inula royleana



Grindelia sp.



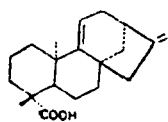
Stevia rebaudiana



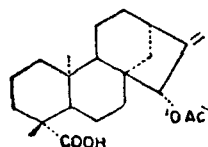
Atractylis gummifera

atractylin (구조미상)

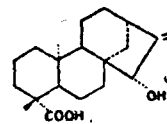
Espeletia schultzii (Wedd)



diterpene carbonic acid S₁⁹⁾

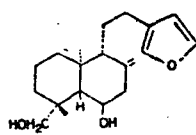


diterpene carbonic acid S₂



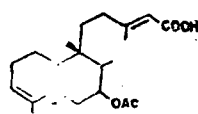
diterpene carbonic acid S₃

Psiadia altissima



Psiadiol¹⁰⁾

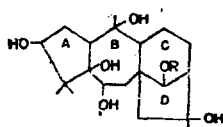
Solidago altissima



solidagonic acid^{11~13)}

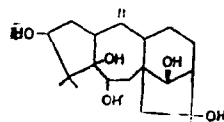
Ericaceae

Leucothoe grayana



andromedotoxin R = -CO-CH₃
grayanotoxin II R = H

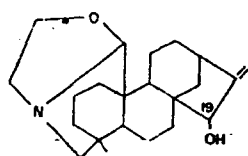
Rhododendrom hymenches



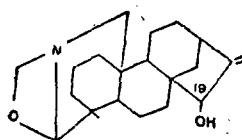
grayanotoxin II

Garryaceae

Garrya sp.



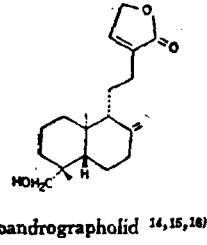
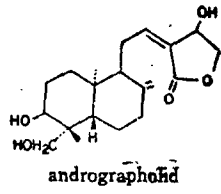
garryfolin (veatchin)
epimer on 19



garryin

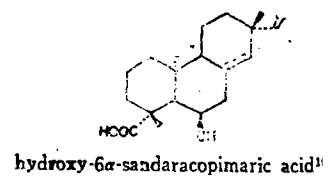
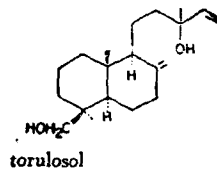
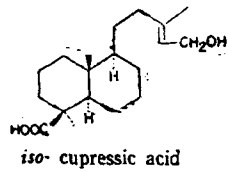
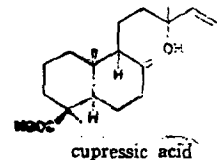
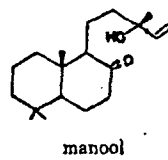
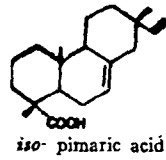
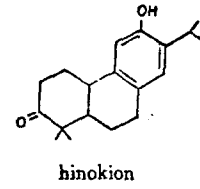
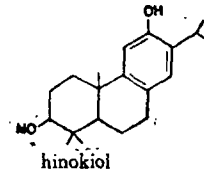
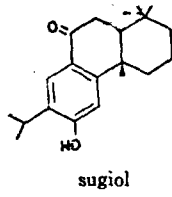
Acanthaceae

Andrographis paniculata

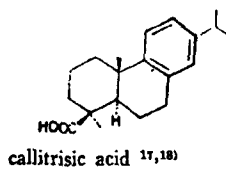


Cupressaceae

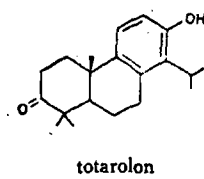
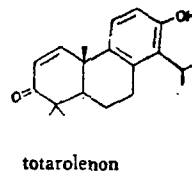
Juniperus sp.



Callitris sp.

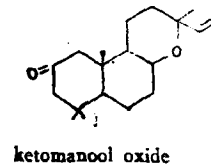
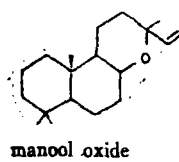
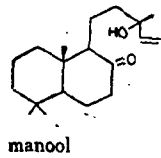


Tetraclinis articulata

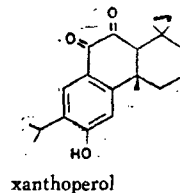
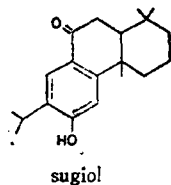
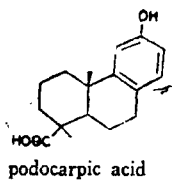
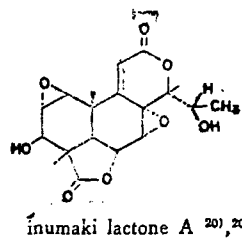
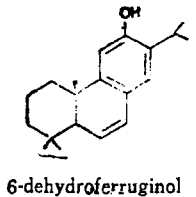
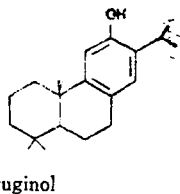
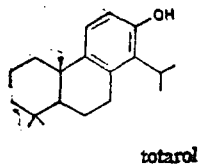
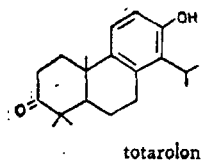
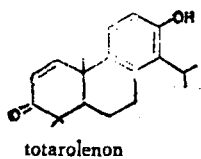


Podocarpaceae

Podocarpium sp.



Podocarpus sp.



Cryptomeriaceae

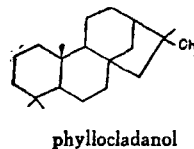
Cryptomeria

xanthoperol

sugiol

cryptopimaric acid $C_{20}H_{30}O_2$

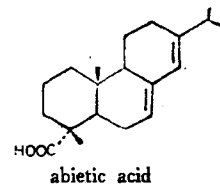
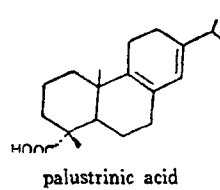
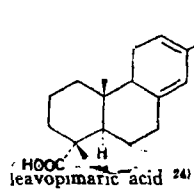
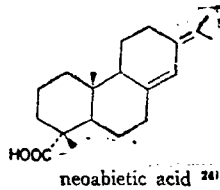
6-ketoferruginol



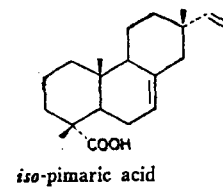
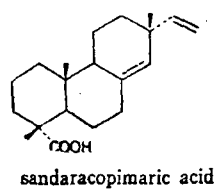
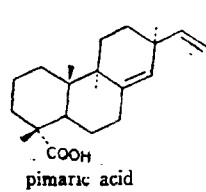
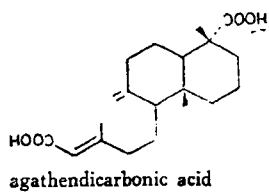
Coniferoidea

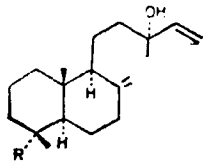
Conifera

a) Abietic acid groups

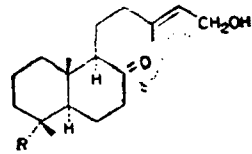


b) Pimaric acid groups ^{22), 23)}

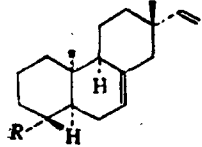




epimanol R=CH₃
hydroxyepimanol R=CH₂OH

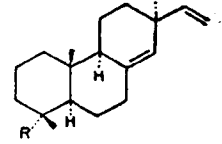


contortol R=CHO
contortadiol R=CH₂OH

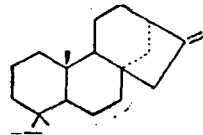


iso-pimaradiene R=CH₃
iso-pimarinol R=CH₂OH
iso-pimarinal R=CHO

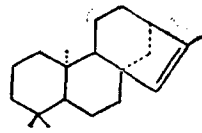
c) Kaurane group



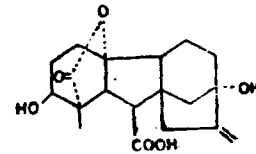
pimaradiene R=CH₃
pimarinol R=CH₂OH
pimarinal R=CHO



phyllocladen



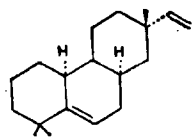
kaurene
mirene (dextrotatory kaurene)



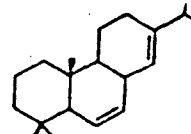
gibberellic acid

d) Rosane group

e) Cupressen group



rimuene 25)

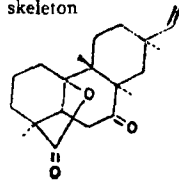


cupressen

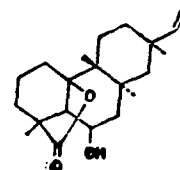
Eumycophyta

Trichothecium roseum, Gibberella Fujikuroi (Fusarium moniliforme)

a) Rosane skeleton

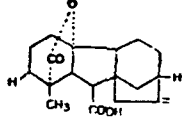


rosenonolactone 26)

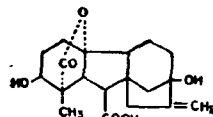


rosinolactone 27)

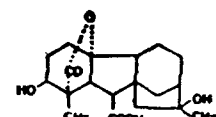
b) gibbane skeleton: 28, 32)



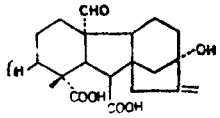
gibberellic acid A₁



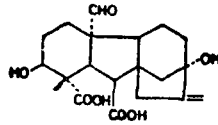
gibberellic acid A₂



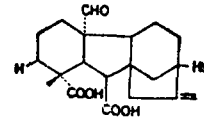
gibberellic acid A₃



gibberellin A₁₉
Bamboo



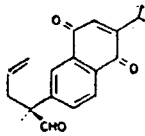
gibberellin A₂₃
Lupinus luteus



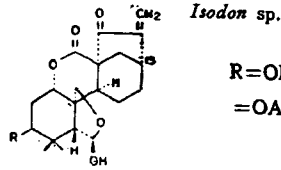
gibberellin A₂₄
Gibberella fujikuroi

Labiatae

Coleus ignarius

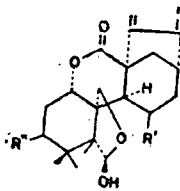


coleon A

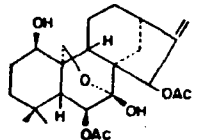


Isodon sp.

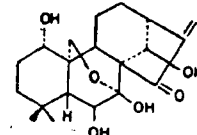
R=OH enmein
=OAc



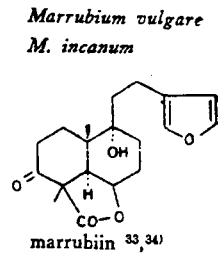
isodon diterpene



trichokaurin



oridonin

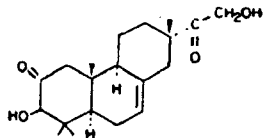


Marrubium vulgare
M. incanum

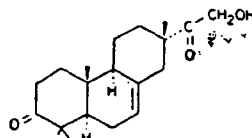
marrubiin ^{33, 34)}

R R' R''
A: CH₂ OH H
B: $\begin{matrix} \text{CH}_2\text{OCH}_2\text{H} \\ \text{H} \end{matrix}$ OH

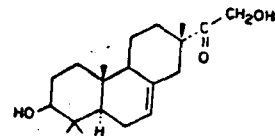
Araucariaceae



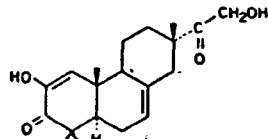
araucarolone



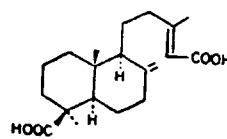
araucaron



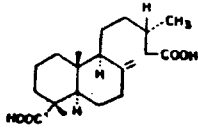
araucarol



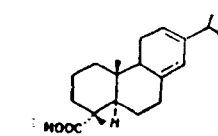
araucarenolone



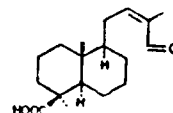
agathic acid



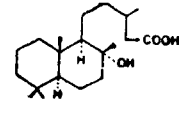
pinifolic acid



laevopimaric acid



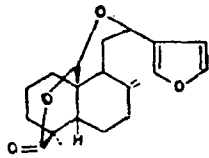
communic acid



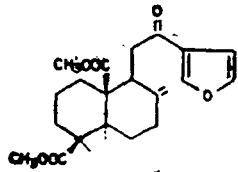
labdanolic acid

Sciadopityaceae

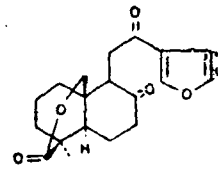
Sciadopitys verticillata 28)



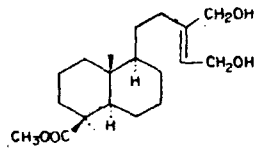
sciadine



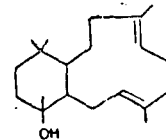
dimethylsciadinonate



sciadinone



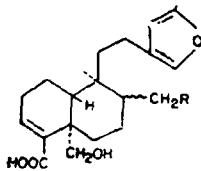
methylsciadonate



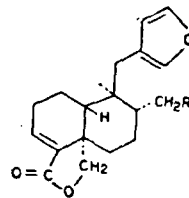
verticillo 28)

Dedonaea sp.

diterpenes of cascarillin group 37)



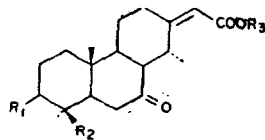
- I R=OAc
- II =OH
- III =H



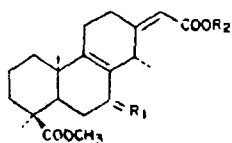
- IV R=OH
- V R=OAc
- VI R=H

Leguminosae 38)

Erythrophleum sp.

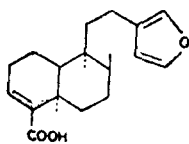


R ₁	R ₂	R ₃
H	COOCH ₃	CH ₂ CH ₂ -N(Me) ₂
OH	COOCH ₃	CH ₂ CH ₂ -N(Me) ₂
OH	CH ₃	CH ₂ CH ₂ -NHMe
OH	CH ₃	aminoalcohol (unknown)
OH	COOCH ₃	// //
OH	COOCH ₃	// //
H	COOCH ₃	// //

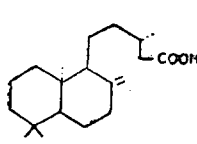


Amherstide

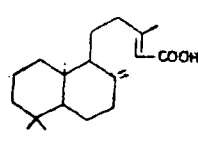
R ₁ =O	R ₂ =aminoalcohol (unknown)
R ₂ $\begin{matrix} \text{OH} \\ \text{H} \end{matrix}$	R ₂ =aminoalcohol //



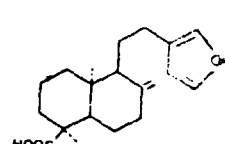
(-) hardwickic acid



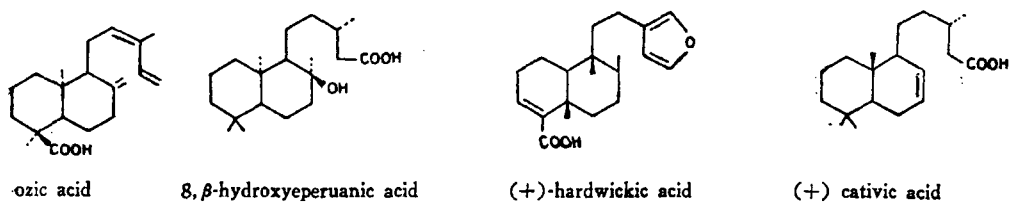
eperuic acid



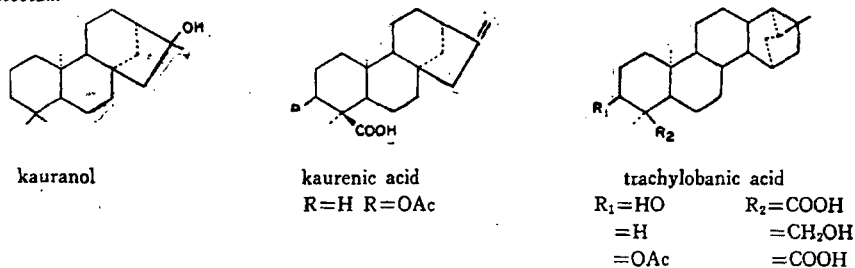
daniellic acid



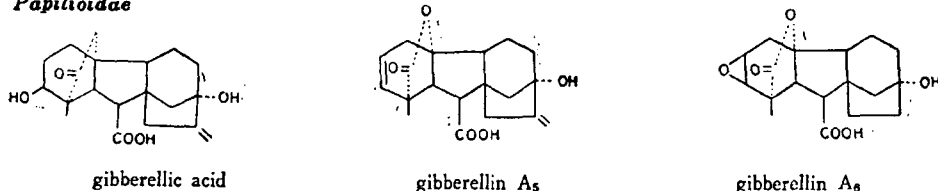
copalic acid



Trachylobium



Papilioidae



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