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PART II

CHEMICAL INVESTIGATION ON GYNOCARDIA ODORATA (R BR)

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CHAPTER 1

REVIEW OF PENTACYCLIC TRITERPENOIDS IN BRIEF

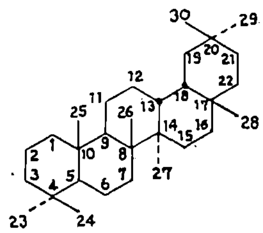
Triterpenoids constitute by far the largest terpenoid class. They have been known and investigated for over hundred years. This class of compounds holds a position of pre-eminence by virtue of the diversity in structures, the fascinating variety of reactions they undergo and their widespread occurence in nature, mainly in plant kingdom. Many of these natural compounds exhibit important physiological and pharmacodynamic properties. Though some of these natural products have been synthesized, yet from the stand point of economy and availability, these synthetic compounds have failed to a great extent to replace the natural products in medicine. Evidently, these natural products will not lose their importance for years to come.

The term triterpenoid refers to a group of natural products containing thirty carbon atoms based on six isoprene (2-methyl-1, 3-butadiene) units. This definition, though generally acceptable, is by no means rigid, since several substances which contain carbon atoms more or less than thirty, and also those which do not strictly follow isoprene rule have been isolated and characterized as triterpenoids.

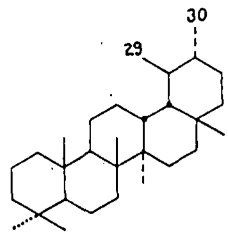
The triterpenoids may be classified[1] into three groups as follows : a) ambrein and squalene, b) the tetracyclic triterpenoids and c) the pentacyclic triterpenoids. All the pentacyclic triterpenoids with thirty carbon atoms may well be categorized according to twenty five different skeletons as shown in Chart 1. Pentacyclic triterpenoids (C_{30}) isolated upto 1970 have been grouped to belong to first nineteen (1-19) carbon skeletons[5,6], and the additional skeleton of six different types (20-25) have been added to make it up-to-date.

The invention of highly sophisticated physicochemical techniques in recent years has accelerated the isolation and characterization of a huge number of different triterpenoids which have been reviewed from time to time[2-9]. Reviews on specific aspects of triterpenoids, viz, MS[10,11], GLC[12], biosynthesis[13,14], friedelin derivatives[15], seco-compounds[16] and sapogenins[17-20] have also been published. The aim of this present review is not to cover all the aspects of pentacyclic triterpenoids but is mainly focused to record a list (Chart 2) of naturally occuring pentacyclic triterpenoid lactone derivatives belonging to various carbon skeletons (C_{30}) of those compounds which have reported upto 1988.

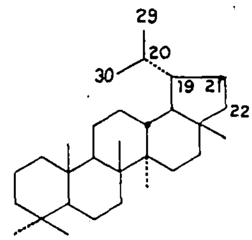
Chart 1. Carbon skeletons of pentacyclic triterpenoids (C_{30})*



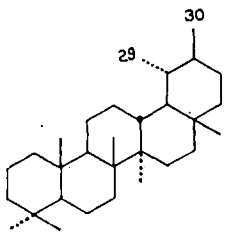
1
Oleanane



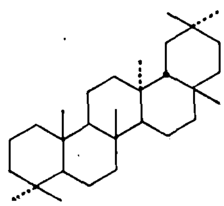
2
Ursane

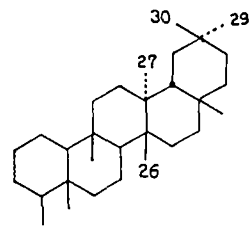


3
Lupane

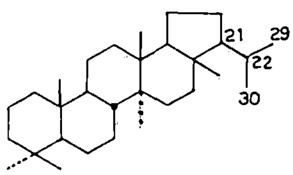


4
Taraxastane

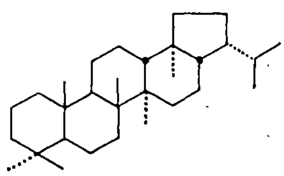

5
Taraxerane
= D-Friedooleanane

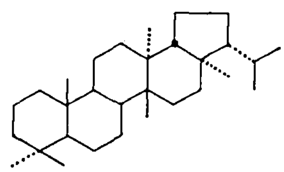


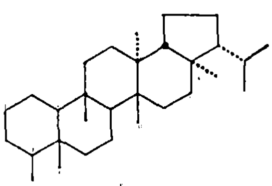
6
Friedelane
= D:A-Friedooleanane

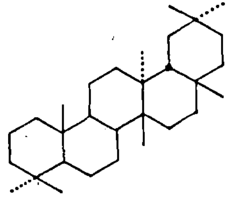


7
Arborane


8
Hopane


9
Fernane
= E:C-Friedohopane


10
Filicane
= E:A-Friedohopane


11
Multiflorane
= D:C-Friedooleanane

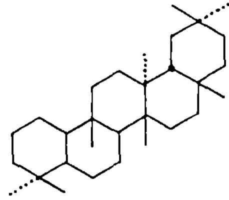
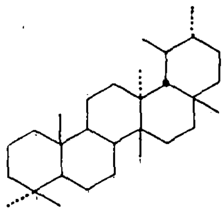
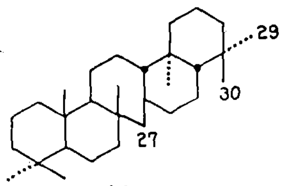

12
Glutane
= D:B-Friedooleanane

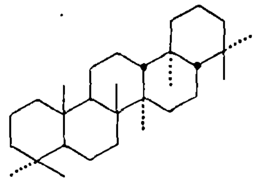
Chart 1 (contd.)



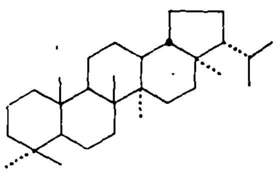
13
Baurane
= D:C-Friedoursane



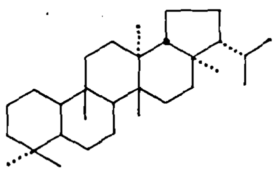
14
Serratane



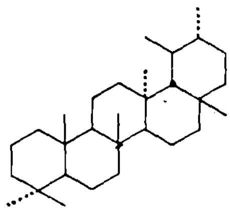
15
Gammacerane



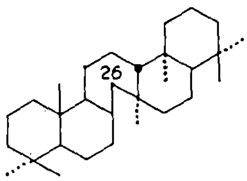
16
Neohopane
= E-Friedohopane



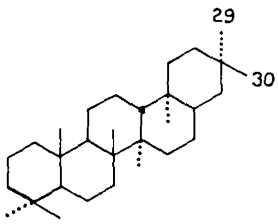
17
Simiarane
= E:B-Friedohopane



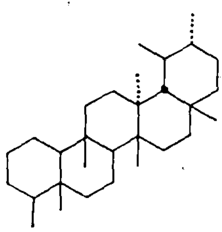
18
Isoursane
= D-Friedoursane



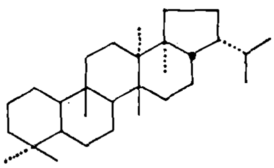
19
Onocerane



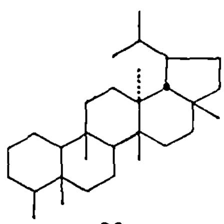
20
Stictane[7,21]



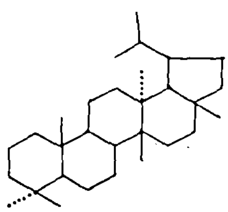
21
Eupacane[22]
= E:A-Friedoursane



22
D:B-Friedohopane[8,23]

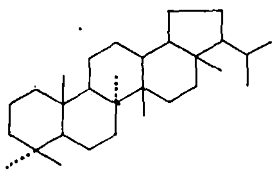


23
D:A-Friedolupane[8,24]
(18β,19α-H-form)



24
D:C-Friedolupane[25]
(19α-H-form)

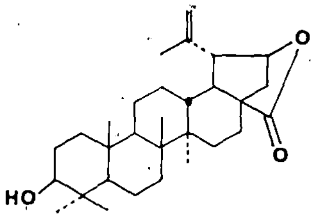
Chart 1 (contd.)

 25 Boehmarane[26]		

*Carbon atoms are numbered according to Dictionary of Organic Compounds, 5th edn (Chapman and Hall, London) 1982.

Chart 2. Naturally occuring pentacyclic triterpenoid lactones (with C_{30} skeletons)

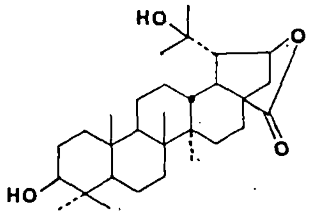
Therberogenin



$C_{30}H_{46}O_3$
Mp 283-5°
$[\alpha]_D$ +11°

Djerassi C et al, JACS, 77(1955)5330
Mark M et al, J Org Chem, 32(1967)3150

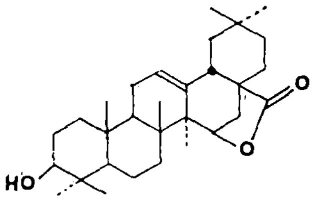
Stellatogenin



$C_{30}H_{48}O_4$
Mp 317-9°
$[\alpha]_D$ +36°

Djerassi C et al, JACS, 77(1955)5330
Mark M et al, J Org Chem, 32(1967)3150

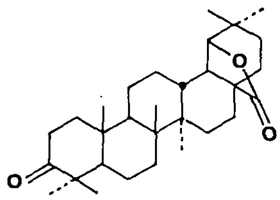
Dumortierigenin



$C_{30}H_{46}O_3$
Mp 292-5°
$[\alpha]_D$ -19°

Djerassi C et al, JACS, 78(1956)5685

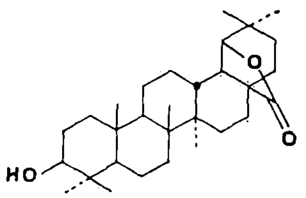
Oxyallobetulone



$C_{30}H_{46}O_3$
Mp 331-2°
$[\alpha]_D$ +84°

Jarolim V et al, Chem & Indus, (1958) 1142
Ikan R et al, J Chem Soc, (1960)893

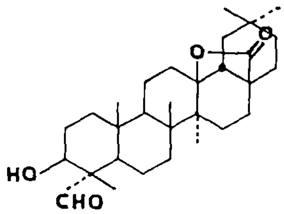
Oxybetulin



$C_{30}H_{48}O_3$
Mp 345-6°
$[\alpha]_D$ +47 °

Jarolin V et al, Chem & Indus, (1958)1142
Ikan R et al, J Chem Soc, (1960)893

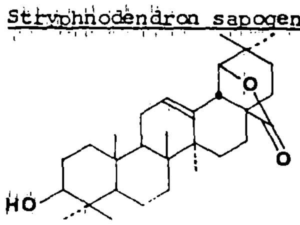
Gypsogenin lactone



$C_{30}H_{46}O_4$
Mp 330-1°
$[\alpha]_D$ +30°

Khorlin A Ya et al, Zhurn Obschei Khimii, 32(1962)782

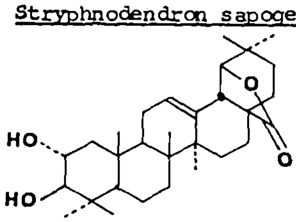
Stryphnodendron sapogenin B



$C_{30}H_{46}O_3$
Mp 240-3°
$[\alpha]_D$ -16°

Tursch B et al, J Org Chem, 28(1963)2390

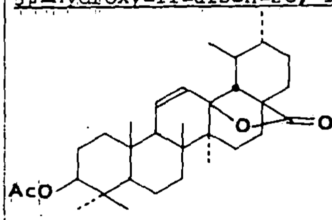
Stryphnodendron sapogenin F



$C_{30}H_{46}O_4$
Mp 265-7°
$[\alpha]_D$ +5°

Tursch B et al, J Org Chem, 28(1963) 2390

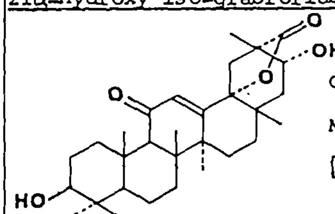
3β-Hydroxy-11-ursen-28, 13β-olide



$C_{32}H_{48}O_4$
Mp 252°
$[\alpha]_D$ +46°

Horn D H S et al, Anst J Chem, 17(1964) 477

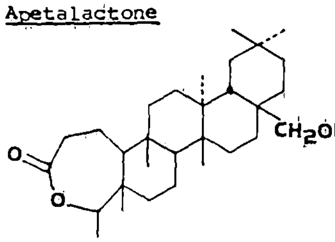
21α-Hydroxy iso-glabrolide



$C_{30}H_{44}O_5$
Mp 304°(d)
$[\alpha]_D$ -11°(Py)

Canonica et al, Gazz Chim Ital, 97(1967) 1347

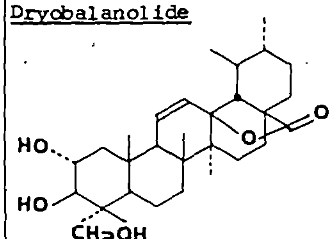
Apetalactone



$C_{30}H_{50}O_2$
Mp 335°(d)
$[\alpha]_D$ +37.5°

Govindachari T R et al, J Chem Soc (C), (1968)1323

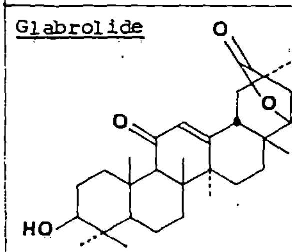
Dryobalanolide



$C_{30}H_{46}O_5$
Mp 278°
(acetonide drv)

Chung H T et al, Tet Lett, (1968)4363

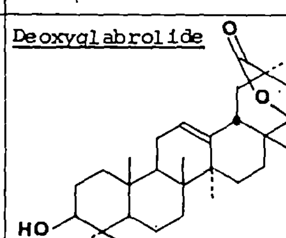
Glabrolide



$C_{30}H_{44}O_4$
Mp 360-5°
$[\alpha]_D$ +80°

Russo G et al, Corsi Semin Chim, 11 (1968)20

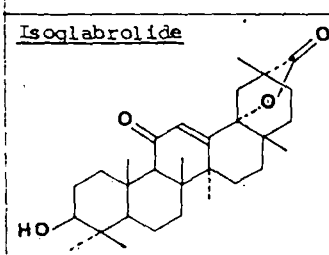
Deoxyglabrolide



$C_{30}H_{46}O_3$

Russo G et al, Corsi Semin Chim, 11 (1968)20

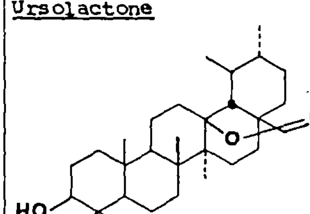
Isoglabrolide



$C_{30}H_{44}O_4$
Mp 318-25°
$[\alpha]_D$ + 46°

Russo G et al, Corsi Semin Chim, 11 (1968)20

Ursolactone



$C_{30}H_{48}O_3$
Mp 252°(ac drv)
$[\alpha]_D$ +12°(ac drv)

Orzalesi G et al, Boll Chim Farm, 108 (1969) 540

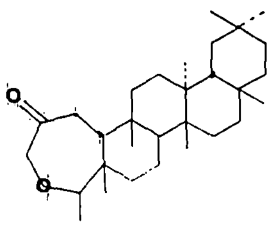
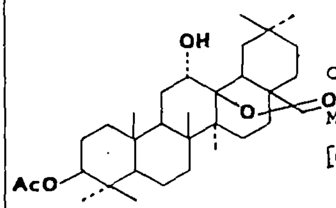
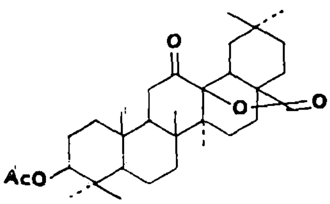
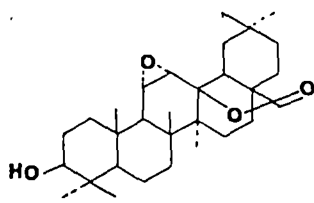
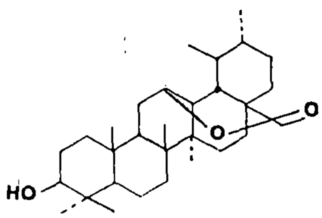
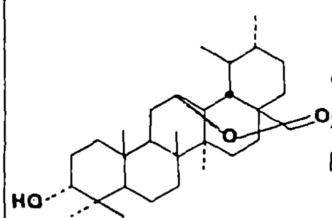
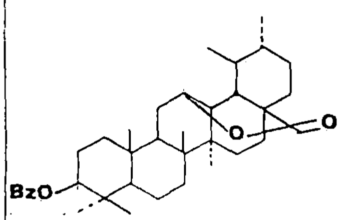
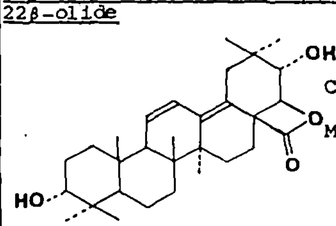
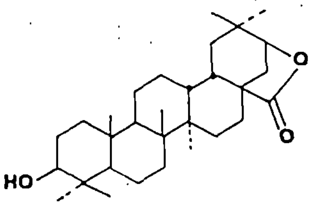
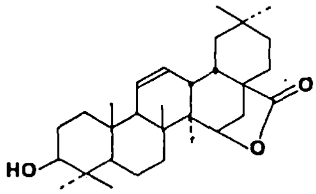
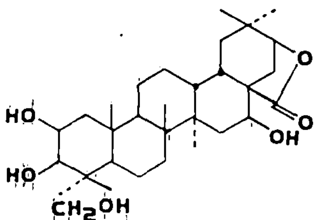
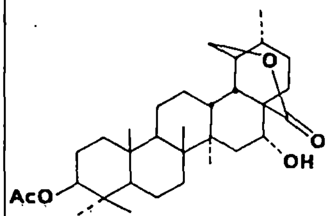
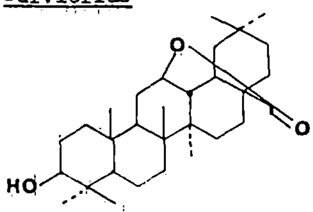
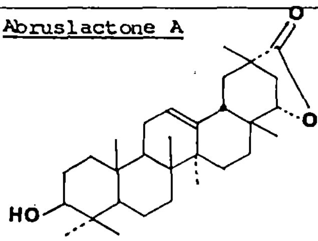
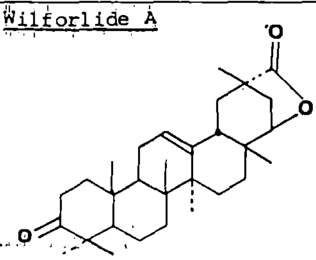
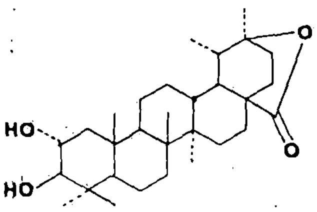
Lithocarpic lactone  $C_{30}H_{50}O_2$ Mp 319-20° $[\alpha]_D$ +54° Hui W H et al, JCS, Perkin I, (1975)617	3β-Acetoxy-12α-hydroxy-28, 13β-oleanolide  $C_{32}H_{50}O_5$ Mp 284-6° $[\alpha]_D$ +39.7° Hui W H et al, Phytochemistry, 15(1976) 1741
3β-Acetoxy-12-oxo-28, 13β-oleananolide  $C_{32}H_{48}O_5$ Mp 287-9° $[\alpha]_D$ +38° Hui W H et al, Phytochemistry, 15(1976) 1741	11α, 12α-Epoxy-3β-hydroxy-28, 13β-oleananolide  $C_{30}H_{48}O_4$ Mp 329-31° $[\alpha]_D$ +45.3° Hui W H et al, Phytochemistry, 15(1977) 1741
3β-Hydroxy-13α-H-28, 12β-ursanolide  $C_{30}H_{48}O_3$ Mp 385-6° $[\alpha]_D$ +17° Hui W H et al, Phytochemistry, 16(1977) 113	3α-Hydroxy-13α-H-28, 12β-ursanolide  $C_{30}H_{48}O_3$ Mp 319-21° $[\alpha]_D$ +9° Hui W H et al, Phytochemistry, 16(1977) 113
3β-Benzoyl-13α-H-28, 12β-ursanolide  Mp 340-2° $[\alpha]_D$ +32° Hui W H et al, Phytochemistry, 16(1977) 113	3α, 21α-Dihydroxy-11, 13(18)-oleanen-28, 22β-olide  $C_{30}H_{44}O_4$ Mp 188-9° Ogihara Y et al, Chem Commun, (1978)364

Chart 2 (contd.)

Dihydromachaerinic acid lactone  $C_{30}H_{48}O_3$ Tomová M et al, Farmatsiya, 28(1978)31	3β-Hydroxy-11-oleanen-28, 15β-olide  $C_{30}H_{46}O_3$ Woitke H D et al, Pharmazie, 33(1978)541
2β, 23-Dihydroxyacacic acid lactone  $C_{30}H_{48}O_6$ Mp 189-92° $[\alpha]_D$ +16.2° Parkhurst R M et al, Phytochemistry, 19 (1980) 273	3β-Acetoxy-16α-hydroxy-28, 29-ursanolide  $C_{32}H_{50}O_5$ Mp 262-3° Katai M et al, Chem Pharm Bull, 29(1981) 261
Salviolide  $C_{30}H_{48}O_3$ Katai M et al, Chem Pharm Bull, 29(1981) 261	Abruslactone A  $C_{30}H_{46}O_3$ Mp 329-30° Chang H M et al, Chem Commun, (1982)1197
Wilforlide A  $C_{30}H_{44}O_3$ Qin G et al, Huaxue Xuebao, 40(1982)637	Wilforlide B $C_{30}H_{46}O_3$ Structurally similar to ABRUSLACTONE A Qin G et al, Huaxue Xuebao, 40(1982)637

Careyagenolide

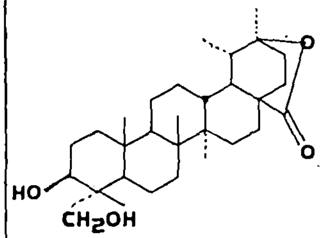


$C_{30}H_{48}O_4$

Mp 299°(d)

Das M C et al, Phytochemistry, 21(1982) 2069

Nahagenin

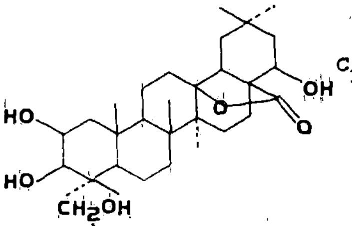


$C_{30}H_{48}O_4$

Mp 290°

Atta-ur-Rahaman et al, Heterocycles, 19 (1982)217

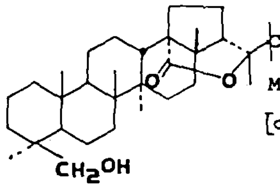
Atroxigenic acid lactone



$C_{30}H_{48}O_6$

Bababy-Bila et al, Bull Soc Chim, 91 (1982)321

17 , 24-Dihydroxyhopan-28, 22 -olide



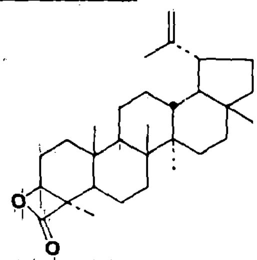
$C_{30}H_{48}O_4$

Mp 258-65°

$[\alpha]_D$ 48.5°(py)

Tanaka N et al, Chem Pharm Bull, 30 (1982)3632

Lupeolactone

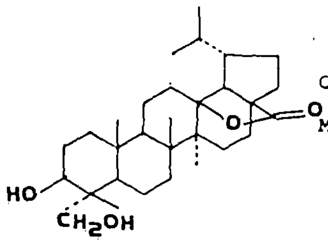


$C_{30}H_{46}O_2$

Mp 186-91°

Kikuchi H et al, Chem Lett, (1983)603

Palustrolide

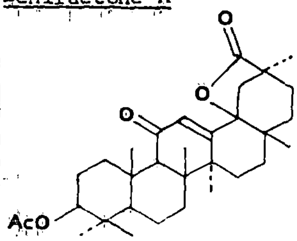


$C_{30}H_{48}O_4$

Mp 310°(d)

Bhandari P et al, Phytochemistry, 23 (1984)2082

Echilactone A

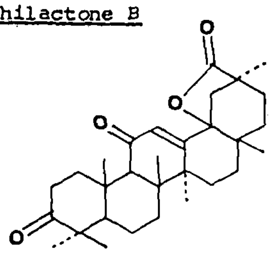


$C_{32}H_{46}O_5$

Mp 245°

Sandiya R, Chem Commun, (1984)1091

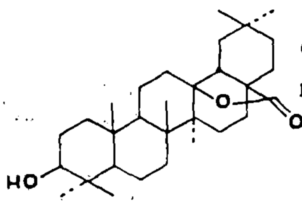
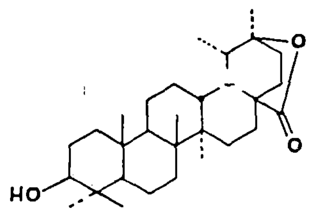
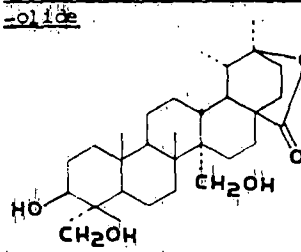
Echilactone B



$C_{30}H_{42}O_4$

Mp 295°

Sandiya R et al, Chem Commun, (1984)1091

3β-Hydroxyoleanan-28,13β-olide  $C_{30}H_{48}O_3$ Mp 282° Al-Hazimi H M G et al, Phytochemistry, 26 (1987) 1091	3β-Hydroxytaraxastan-28,20β-olide  $C_{30}H_{48}O_3$ Mp 294-7° Errington S G et al, Phytochemistry, 27 (1988) 543
3β,23,27-Trihydroxytaraxastan-28,20β-olide  $C_{30}H_{48}O_5$ Mp 330-2° Errington S G et al, Phytochemistry, 27 (1988) 543	