CHAPTER I

Introduction

Terpenoid Constituents of Umbelliferae

TERPENOID CONSTITUENTS OF UMBELLIFERAE*

In the systematic botanical classification Umbelliferae* family belongs to the order Umbellales[1] as shown below

Division	..	Spermatophyta
Class	..	Angiospermae
Sub-class	..	Dicotyledoneae
Order	..	Umbellales
Family	..	UMBELLIFERAE

Umbelliferae has plants, mostly biennial or perennial herbs and rarely shrubs. It has been considered to be an advanced family[2] in the order, because of its fruits and prevalently herbaceous habit. Economically, members of this family are important as foods, condiments, drugs and ornaments. Some members possess resins or alkaloids in lethally poisonous quantities.

From the chemotaxonomic point of view, the umbelliferae is difficult to survey exhaustively, since it is a large family with 240-300 genera and over 3000 species. It is normally arranged in three sub-families, Hydrocotyloideae, Saniculoideae and Apioideae[4]. The plants of this family are distributed over Europe, West, Central and North Asia and a few are found in North America as well as tropical and southern hemisphere. They are relatively rich in

*Some authors, as allowed by Art. 23 of Rules(Ed.3) reject the name umbelliferae for this family and substitute for it an alternative name, Apiaceae[3] Lindl(1836) or Ammiaceae Prese ex Britton and Brown(1913)

secondary metabolites and much chemical work has been carried out[4], especially on flavonoids, furanocoumarins, terpenoids and polyacetylenes occuring in these plants.

As mentioned earlier, the family is too large to study all the genera in the world, we therefore confine our study to the sub-family Apioideae of Europe[5] and India[6] with special reference to terpenic constituents.

The sub-family Apioideae is further divided into eight tribes as shown below:

1) Echinophoreae
2) Scandiceae
3) Coriandreae
4) Smyrniae
5) Apieae
6) Peucedaneae
7) Laserpiteae
8) Dauceae

Tribe 1 : Echinophoreae

No terpenic constituent appears to have been reported from any genus of this tribe.

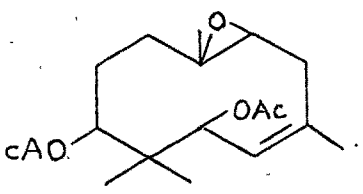
Tribe 2: Scandiceae

The tribe is further divided into two sub-tribes, scandicineae and caucalineae.

Scandicineae: The sub-tribe consists of eight genera and no terpenic constituents have been reported.

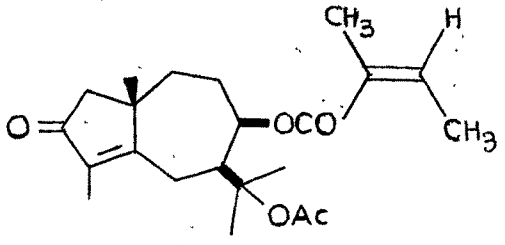
Caucalineae: Terpenic constituents have been reported in this sub-tribe and will be discussed here

Caucalis Makino.: Sasaki et al.[7,8] have reported the isolation of caucalol diacetate (1) from the fluffy seeds of Caucalis scarba Makino.



(1)

Torilis DC.: From the ethanolic extract of the seeds of Torillis japonica DC Nakazaki et al.[9,10] have isolated a new sesquiterpene ester torilin, which has been assigned the following structure(2)



(2)

Tribe 3: Coriandreae

This is a minor tribe of Apiodeae and Coriandrum is the only genus to be studied from this tribe.

Coriandrum L.: Coriander is an annual herb originating in the Mediterranean countries, and is now-a-days mostly grown in Italy, Morocco, India and Eastern Europe. Two types of coriander are distinguished according to the size of the fruit, Coriandrum sativum L (fruit diameter 3-5 mm) and Coriandrum vulgare L(fruit dia. 1.5 - 3 mm). Steam distillation of the fruits yeilds volatile oil which is used in food industry, perfumery and pharmacy.

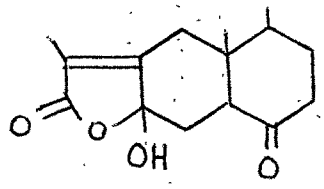
Schratz et al.[11] have studied the essential oil composition of Coriandrum sativum L, during ontogenesis (stage of plant development). The authors have reported the isolation of borneol, trans-2-tridecane-1-al,decanal, linalool and geraniol.

Taskinen and Nykanen[12] have extended this study and have identified thirty components of the essential oil, the major one being linalool.

Tribe 4: Smyrniae

The tribe consists of about fifteen genera and only very recently a sesquiterpene has been isolated from the genus Smyrnium.

Smyrnium L.: Holub et al[13] have isolated a new sesquiterpene lactone istanbulin A (3) from the roots of Smyrnium olusatrum L.



(3)

Smyrnium rotundifolium Mill.: Ulubelen[14] has reported the isolation of a triterpene of molecular formula $C_{34}H_{56}O_7$ from the roots of Smyrnium rotundifolium Mill.

Tribe 5: Apieae

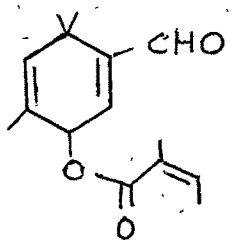
This tribe comprises of thirty nine genera and is the largest in Apioideae. Apart from sesquiterpenes a number of triterpenes and saponins have been isolated.

Apium L.: Apium is the genus, cosmopolitan in distribution. Apium graveoleus Celery is cultivated for edible petioles and the seeds are used for flavouring. Sutherland et al[15] have reported the occurence of the following monoterpenes. Thymol, carvacrol, γ-terpentine, p-cymene, β-pinene, α-pinene, myrcene, α-thujene, limonene, saninene, cis and trans ocimene and β-phellandrene.

Bupleurum L.: The roots of Bupleurum falcatum L have been subjected to extensive study by two groups of Japanese workers. In addition to α-spinasterol[16](4) and Δ^7-stigmasterol(5), Shibata et al.[17-21] and Kubota et al.[22-26] have reported seven new triterpenes which have been named as saikogenin A, B, C, D, E, F and G

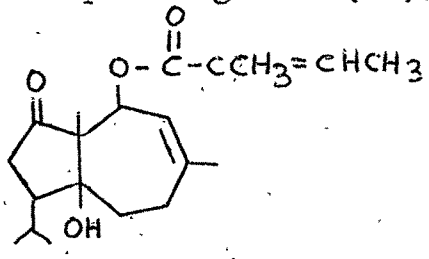
(6-12)(Fig. I). Further Kubota et al.[27] have isolated longispirogen (13) and saponins C, a and d. The structures of these compounds are shown in Fig. II.

From the roots of Bupleurum gibraltaricum Lam, Bohlmann et al.[28] have isolated a terpene aldehyde ester (17)



(17)

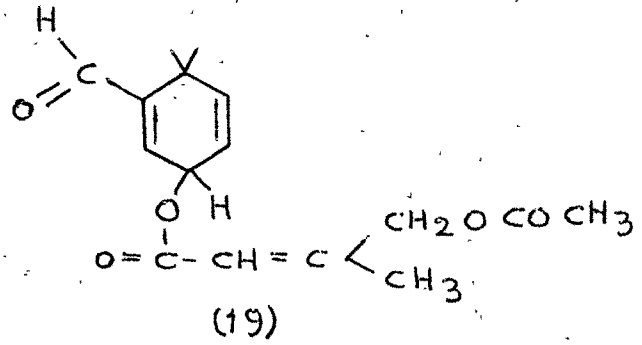
Selinum Clarke.: Bhattacharya et al.[29] have examined the roots of Selinum vaginatum Clarke and have reported the isolation of a new sesquiterpene vaginatin(18).



(18)

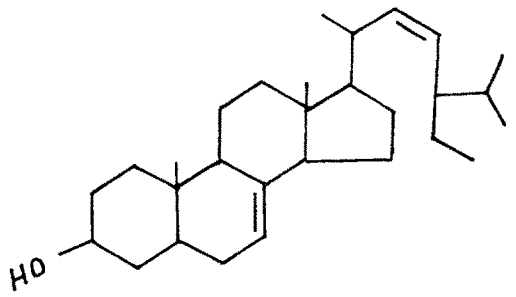
The compound has a daucane skeleton and chemotaxonomically forms a link between carotol (82) and laserpitine (70).

From the roots of Selinum carvifolia L, Bohlmann et al.[30] have isolated a terpene derivative (19).

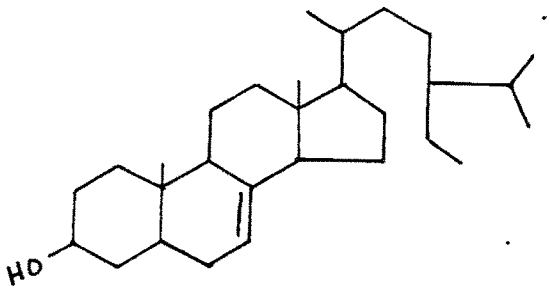


(19)

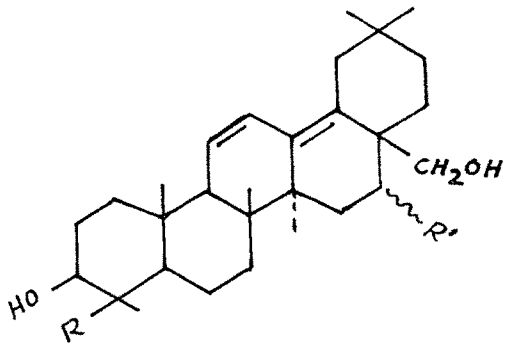
STEROLS AND SAPOGENINS OF BUPLEURUM FALCATUM L

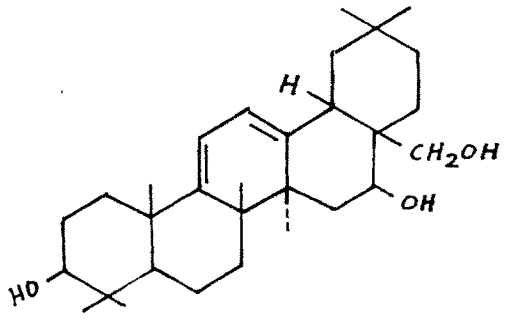


(4)



(5)

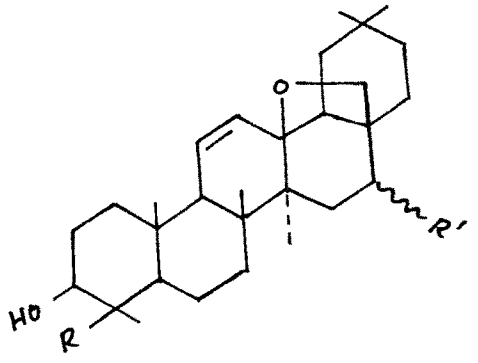




(6) SAIKOGENIN A, $R = CH_2OH$, $R' = \beta\text{-}OH$ (7) SAIKOGENIN B

(8) SAIKOGENIN C, $R = CH_3$, $R' = \beta\text{-}OH$

(9) SAIKOGENIN D, $R = CH_2OH$, $R' = \alpha\text{-}OH$

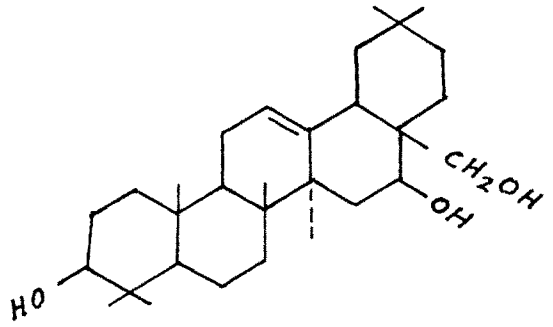


(10) SAIKOGENIN E, $R = CH_3$, $R' = \beta\text{-}OH$

(11) SAIKOGENIN F, $R = CH_2OH$, $R' = \beta\text{-}OH$

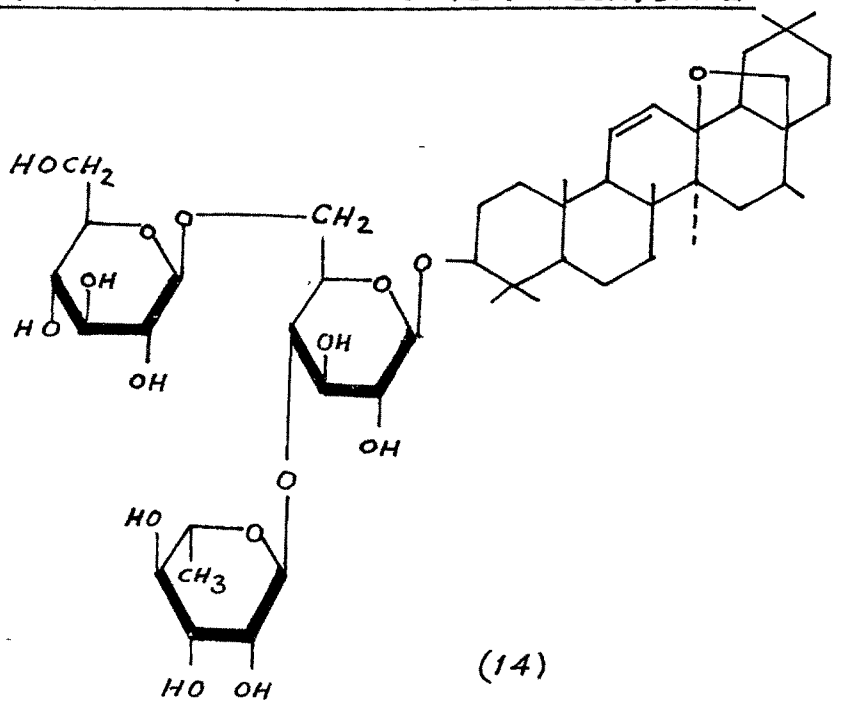
(12) SAIKOGENIN G, $R = CH_2OH$, $R' = \alpha\text{-}OH$

FIG. I



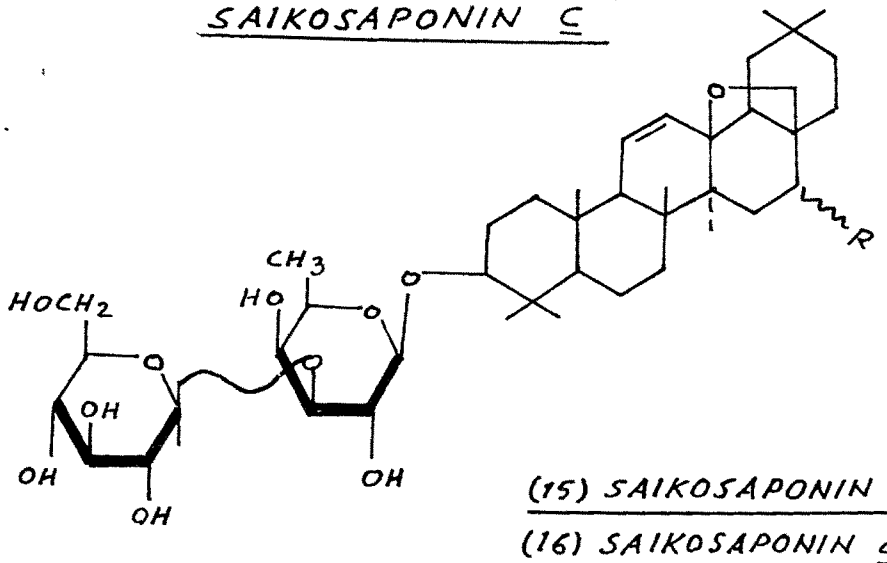
(13)

SAPONINS FROM BUPLEURUM FALCATUM L



(14)

SAIKOSAPONIN c

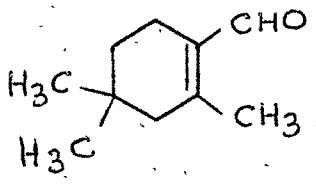


(15) SAIKOSAPONIN a, R = β.OH

(16) SAIKOSAPONIN d, R = α.OH

FIG. II

Seseli Wight and Arnold.: Seseli is a genus of north temperate zone. From the essential oil of the seeds of Seseli indicum Wight and Arnold, Sukh Dev et al.[31] have isolated a new monoterpene aldehyde β-cyclo-lavandulal(20)

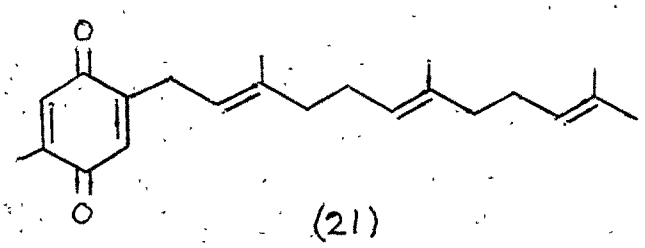


(20)

Rao et al.[32] have also examined the essential oil from the seed of Seseli indicum and have reported the presence of (+)-limonene (major component), (-)β-selinene and β-cyclolavandulic acid.

Kapoor et al.[33] have isolated a fenchyl ester of p-hydrocy cinnamicacid from the petrol ether extracts of the roots of the Seseli sibiricum Benth. Sklyar et al.[34] have reported the isolation of borneol trans-p-hydroxy cinnamate from Seseli mucronatum and Seseli asperulum.

Bohlmann et al.[35] have investigated three Seseli species namely Seseli elatum L, Seseli leucospermum Waldst and Kit and Seseli annuum L and have reported the isolation of a new sesquiterpene quinone(21) from them.

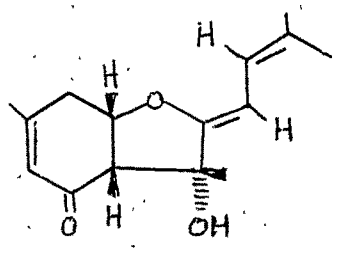


(21)

Tribe 6: Peucedaneae

The tribe consists of fourteen genera from which a number of sesquiterpenes have been isolated.

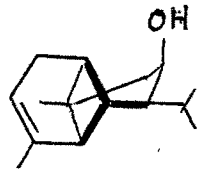
Angelica L.: Angelica is a genus of north temperate region and New Zealand. Sorm et al.[36] have reported the isolation of a new sesquiterpene bisabolangelone(22) from the seeds of Angelica silvestris L.



(22)

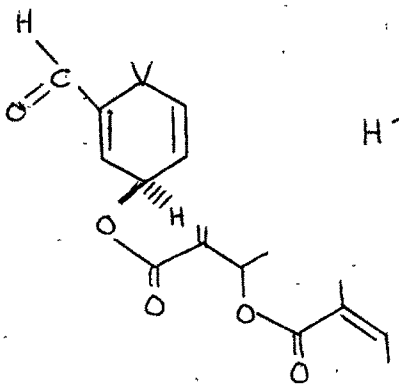
From the ether extract of the roots of Angelica koreana Max, Hata et al.[37] have reported the same compound(22) under the name angelikoreanol.

From the essential oil of the roots of Angelica archangelica L, Taskinen[38] has isolated a new sesquiterpene alcohol, cis- α -copaene-8-ol(23)

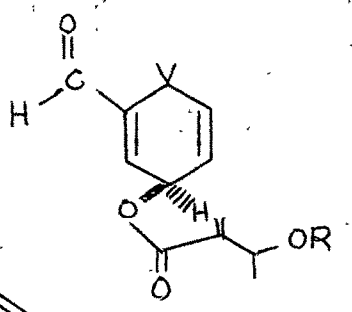


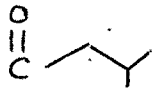
(23)

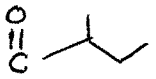
Peucedanum: Bohlmann and Grenz[39] have examined the roots of Peucedanum luxurians Tamamsch and have reported the isolation of five new terpene aldehyde esters(24-28)

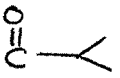


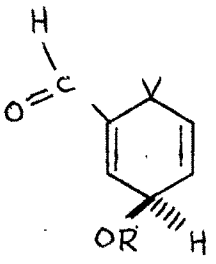
(24)



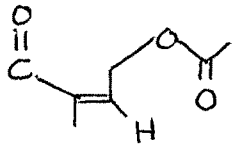
(25) R = 

(26) R = 

(27) R = 

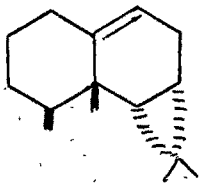


(28)

R = 

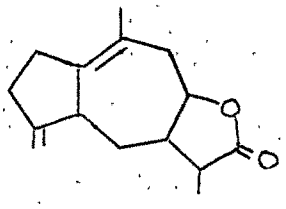
Ferula: The genus Ferula occurs from Mediterranean to Central Asia and Abyssinia. Ferula asafoetida yields asafoetida, a very ill-scented drug which is used as a condiment and stimulant.

The neutral fraction of the latex of Ferula communis L on steam distillation gave a mixture of sesquiterpene hydrocarbons from which Carboni et al.[40] have isolated a major constituent α-ferulene(29).



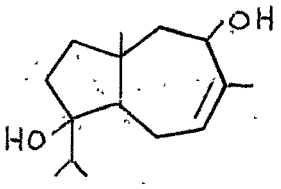
(29)

Kiryalov[41] has reported the isolation of a new guaianolide, grilactone(30) from the roots of Ferula grigoriewii.

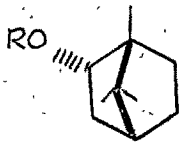


(30)

Kiryalov[42] has also studied the roots of Ferula tschimganica and has reported the occurence of chimgandiol(31), a new daucane-based sesquiterpene alcohol.



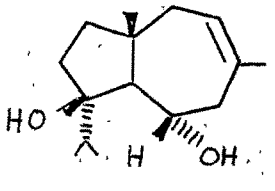
From the same species Nikonov and Kadyrov[43] have isolated two monoterpenoid esters, tschimganin(32)and tschimgin(33)



(32), R = 3,4-MeO(OH)$C_6H_3CO_2$

(33), R = p-$OHC_6H_4CO_2$

From the roots of Ferula jaeshkeana Vatke, Sukh Dev et al.[44] have isolated jaeshkeanadiol(34).



(34)

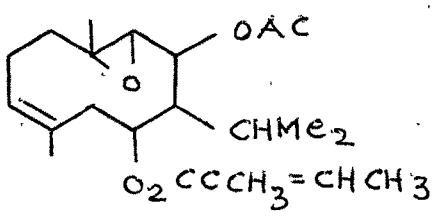
Ferula oopoda has been extensively studied by Kiryalov and Serkerov.[45-48] From its roots they have isolated badkhyzin(35), oopodin(36), dehydrooopodin (37), ferulin(38) and badkhysinin(39). The structures 35-39 are shown in the Fig.III.

In addition to this Serkerov[49-50] has isolated three more sesquiterpene lactones, feropodin(40), semopodine(41) and hydroxy lactone (42).

Saidkhodzhaev et al.[51] have reported the isolation of sesquiterpene lactone (43) from the roots of Ferula diversivittata.

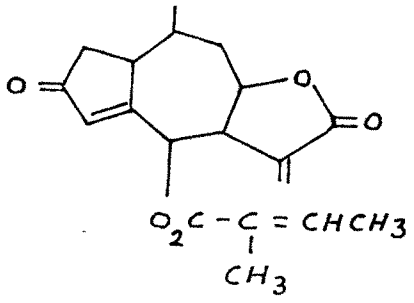
Investigation of the roots of Ferula olgae by Rybalko et al.[52,53] resulted in the isolation of six new sesquiterpene lactones, olgoferin (44), oferin(45),talasin A(46), talasin B(47), laferin(48) and olgin(49). The structures 40-49 are shown in Fig. IV.

The isolation of a new ester fecorine (50) from the roots of Ferula korshinskyi has been reported by Saidkhodzhaev et al.[54]



(50)

SESQUITERPENES OF FERULA OOPODA



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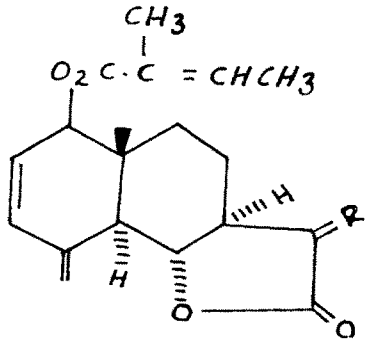
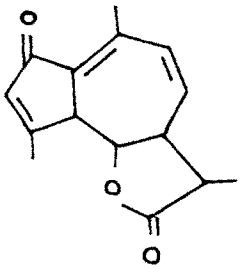
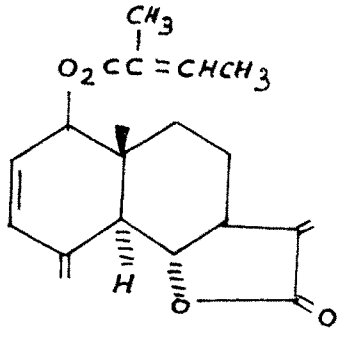


(36) $R = H, CH_3$

(37) $R = CH_2$

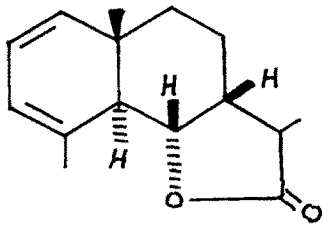


(38)



(39)

FIG. III



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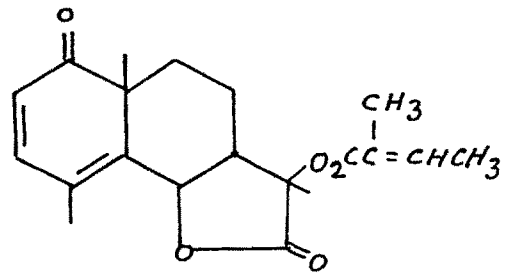
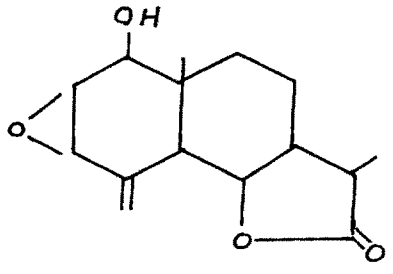
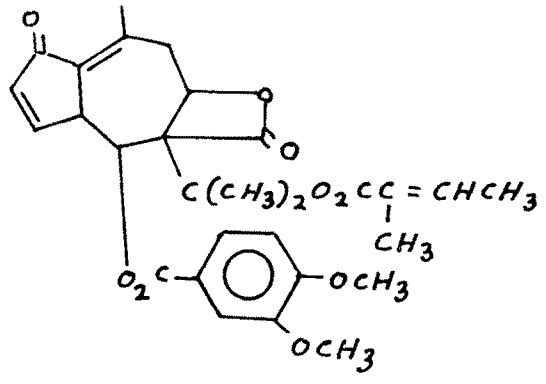


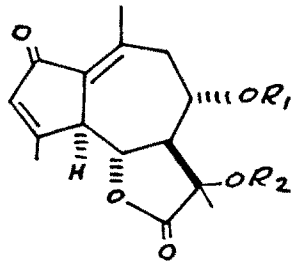
(41)

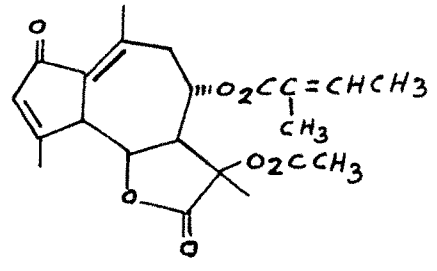


(42)



(43)





(49)

(44) $R_1, R_2 = CH_2 = CCH_3CO$

(45) $R_1 = CH_2 = CCH_3CO$, $R_2 = (CH_3)_2CHCO$

(46) $R_1, R_2 = CH_3CH = CCH_3CO$

(47) $R_1 = CH_3CH = CCH_3CO$, $R_2 = (CH_3)_2CHCO$

(48) $R_1 = CH_3CH = CCH_3CO$, $R_2 = COCH_3$

FIG. IV

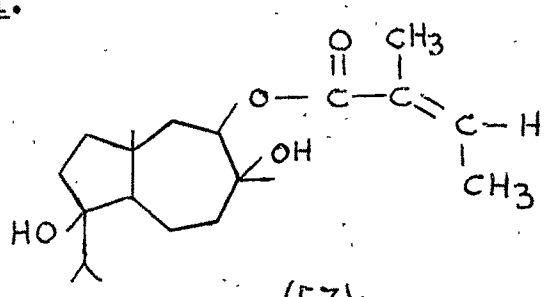
The same Russian group[55-57] has investigated different species of genus Ferula. From the roots of Ferula kuhistanica, they have reported isolation of sesquiterpene alcohol ester ferutidin(51).

From the roots of Ferula tenuisecta, they have isolated another ester teferidine(52). The isolation of akierin(53) has been reported from Ferula akitschkensis

Sukh Dev et al. have also isolated three sesquiterpene alcohol esters(54-56)(Chapter IV) from acetone extracts of the roots of Ferula jaeshkeana Vatke.

The structures 51-56 are shown in Fig. V.

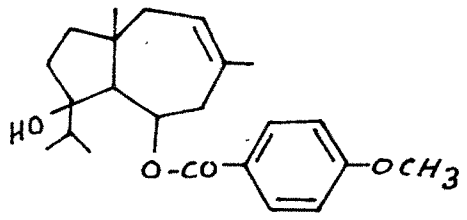
Recently Gonzalez et al.[58] have reported the isolation of linkiol(57), a sesquiterpene alcohol ester from the roots of Ferula linkii.



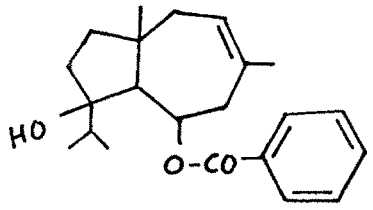
(57)

A number of sesquiterpenes and coumarins have been isolated from the genus Ferula. It is interesting to note that some sesquiterpenes occur as the ether derivatives of coumarins. About nineteen such compounds have been reported in literature, but the mention of only nine coumarin derivatives has been made in this section.

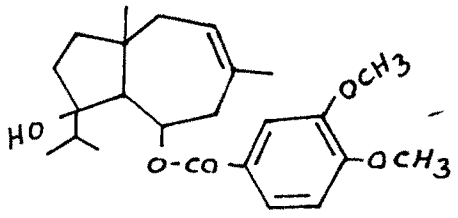
SESQUITERPENE ESTERS OF GENUS FERULA



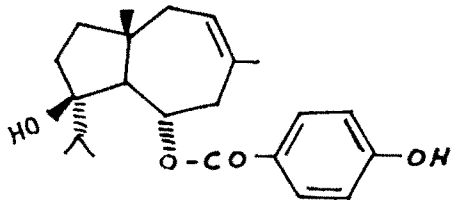
(51)



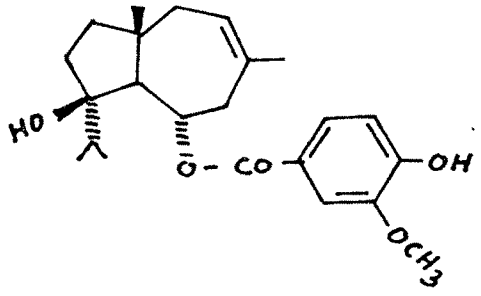
(52)



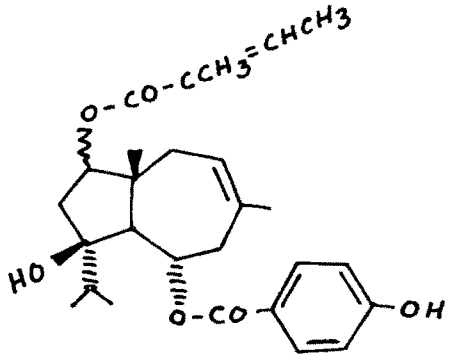
(53)



(54)



(55)



(56)

FIG. V

Skylar et al.[59] have reported occurence of conferidone(58) and conferin(59) from the roots of Ferula conocaula.

Ferukrin(60) has been isolated by the same group[60] from the roots of Ferula krylovii.

Saidkhodzhodzhaev et al.[61] have reported the isolation of polyanthin(61) and polyanthinin(62) from Ferula polyantha roots.

Isolation of kopetdaghin(63) has been reported by Nikonov and Kamilov[62] from the roots of Ferula copetdaghensis.

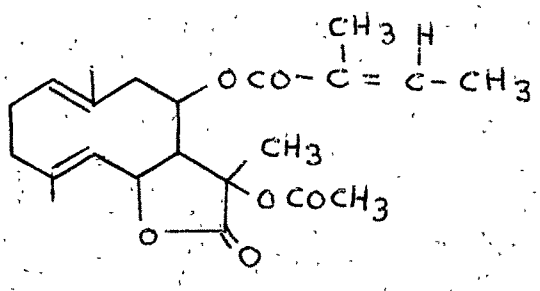
Arigoni et al.[63] have reported the isolation of farnesiferol A(64), B(65) and C(66) from the neutral fraction of the resin of Ferula asafoetida.

All these compounds occur as ether derivatives of umbelliferone. The structures of compounds(58-66) are shown in Figs. VI

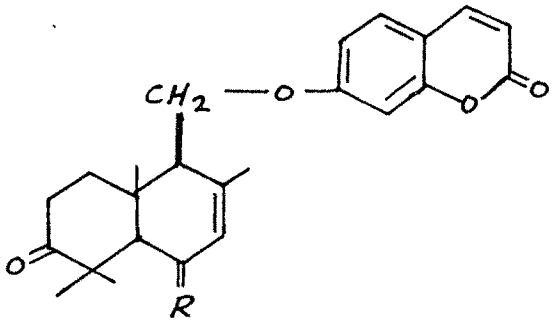
Tribe 7: Laserpiteae

Laserpiteae is a small tribe consisting of only four genera. A number of sesquiterpenes have been isolated from them.

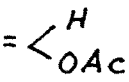
Laser Borkh.: The isolation of laserolide(67) from Laser trilobum Borkh has been reported by Sorm et al.[64]

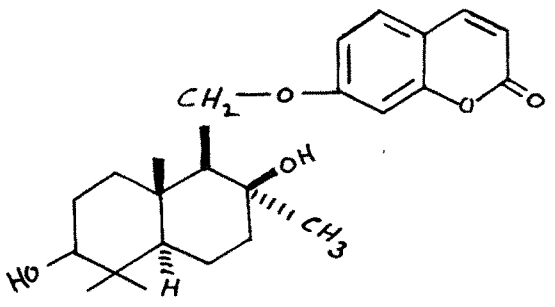


(67)

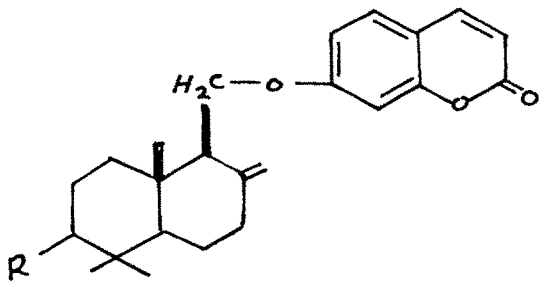


(58) R = O

(59) R = 

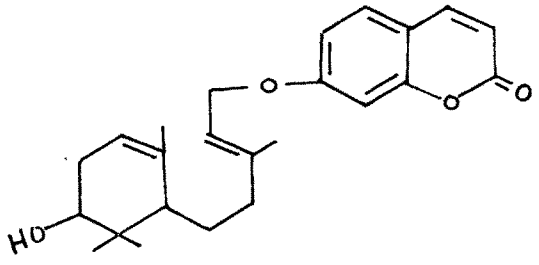


(60)



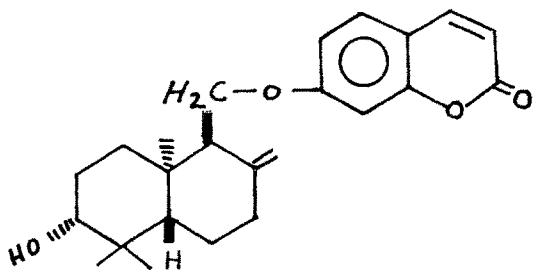
(61) R = β-OAc

(62) R = α-OAc

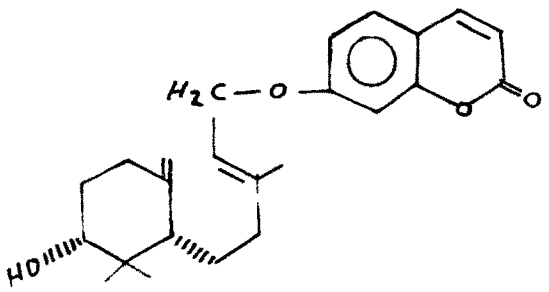


(63)

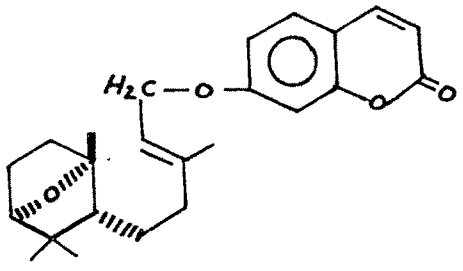
FIG. VI



(64)



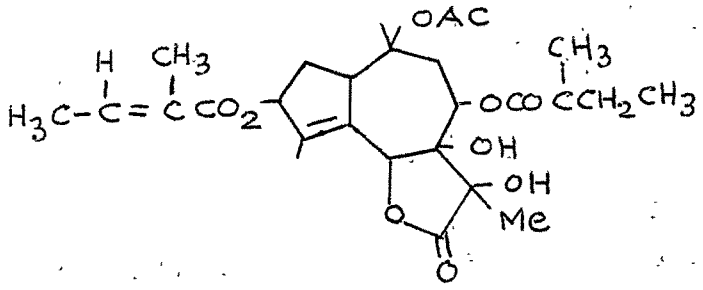
(65)



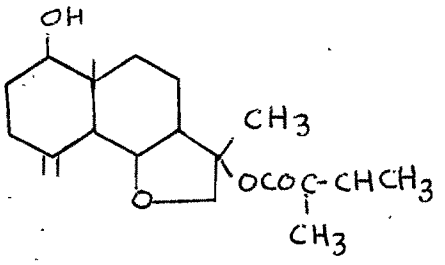
(66)

FIG. VI

Holub et al.[65,66] have isolated a sesquiterpene triester lactone trilobolide(68) and lasolide(69)from the same species.



(68)



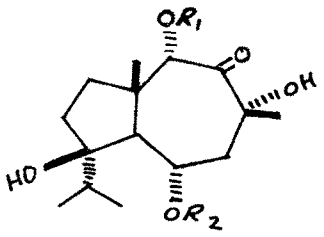
(69)

Laserpitium L.: From the roots of Laserpitium latifolium L Sorm et al.[67] have isolated five closely related sesquiterpenes, laserpitine(70), monoangelic ester laserol(71),laserpitinol(72), isolaserpitine(73) and deoxodehydrolaserpitine(74).

The above authors[68,69] have also examined the roots of Laserpitium siler L and have isolated new sesquiterpene lactones, montanolide(75), isomontanolide(76) and acetyl isomontanolide(77).

The structures of these compounds (70-77) are shown in Fig. VII

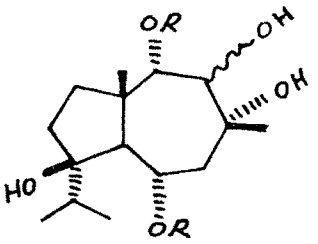
Bohlmann and Zdero[70] have examined the roots of Laserpitium prutenicum L and have reported the isolation of four new closely related sesquiterpene lactone(78-81). Their structures are depicted in Fig. VIII



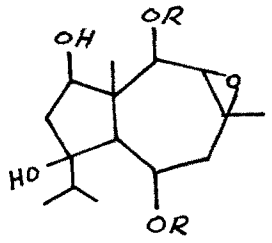
(70) R_1, R_2 = CO · C(CH3) = CH · CH3

(71) R_1 = CO · C(CH3) = CH · CH3

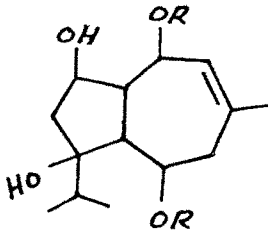
R_2 = H



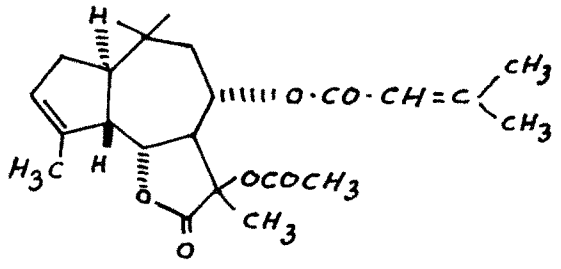
(72) R = CO · C(CH3) = CH · CH3



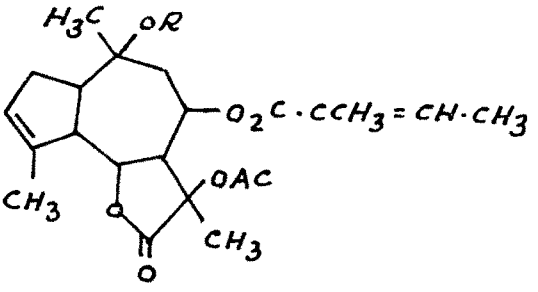
(73) R = CO · C(CH3) = CH · CH3



(74) R = CO · C(CH3) = CH CH3



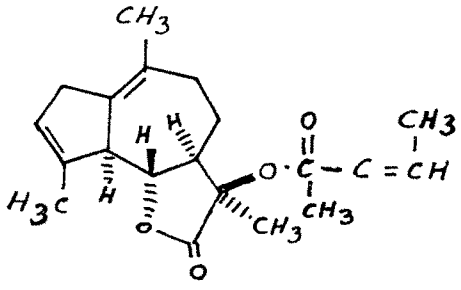
(75)



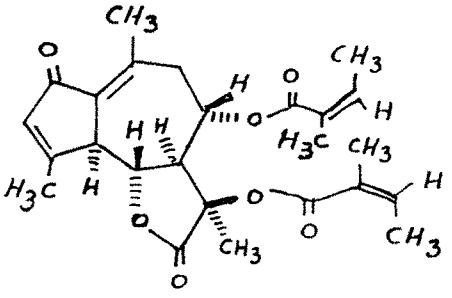
(76) R = H

(77) R = Ac

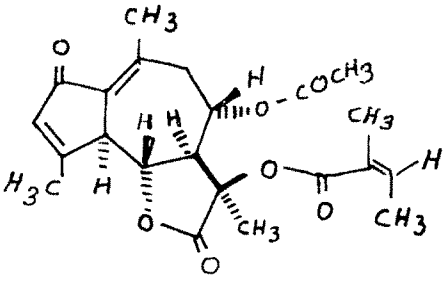
FIG. VII



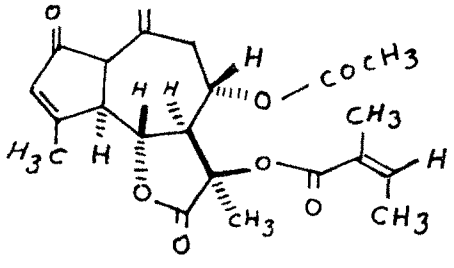
(78)



(79)



(80)



(81)

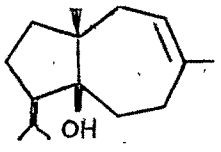
FIG. VIII

Tribe 8: Dauceae

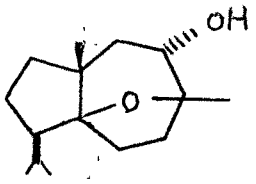
The tribe consists of only three genera and terpenic constituents have been reported from only one genus (i.e.Daucus)

Daucus L.: Daucus is a genus of north temperate zone and the species Daucus carota L is widely cultivated for its edible roots.

Sorm et al.[71] have examined the essential oil of the seeds of Daucus carota L and have isolated two major constituents carotol(82) and daucol(83).

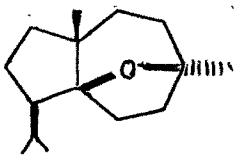


(82)



(83)

Kalsi et al.[72] have isolated a sesquiterpene oxide from the essential oil from the seeds of Daucus carota L. Structure(84) has been suggested for this compound.



(84)

Daucane Skeleton as a Chemotaxonomic Marker

The above survey has led to a distinct observation. It is of phylogenetic interest to note that, of all the species so far studied, of the different tribes of sub-family Apioideae, the daucane based sesquiterpenes occur only in the four tribes viz, Apieae, Peucedaneae, Laserpiteae and Dauceae. This distinct feature separtes these four tribes from the rest of the tribes belonging to the sub-family Apioideae. Thus, using daucane skeleton as a marker, it may be possible to segregate these four tribes of the sub-family Apioideae and group them under a separate sub-family. Of course this justification necessiates other supplementary evidences from other fields such as morphology, anatomy etc.

SUMMARY

The terpenic constituents of umbelliferae, with the restriction to the sub-family Apioideae of Europe and India have been presented. All the triterpenes occurring in this sub-family are pentacyclic and most of the sesquiterpenes have a five membered ring fused to a seven membered ring system.

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