



CHAPTER II

HISTORICAL

1) Chemical constituents of Rutaceae.

Essential oils are natural products of economic importance. They are indispensable ingredients of cosmetics, perfumes and they impart flavour to many foods. Their complex nature has stimulated analytical and structural chemistry ever since man became involved in the study of fragrance of plants. To plant chemotaxonomy, essential oils produce many valuable characters. In the order Rutales, essential oils are very common in Rutaceae which produced and accumulated them in lysigenous cavities of the tissue. The following reviews is focussed only on Thai rutaceous plants of which the chemical composition of essential oils have been previously worked on, the data of which is shown below.

| Plant part | Chemical constituents | Reference |
|------------|--|-------------------------------------|
| Leaves | <i>Aegle marmelos</i> Correa Monoterpene α -pinene (Z)- β -ocimene 3,5- β -para-menth-1-en-diol β -pinene <i>cis</i> -carveol γ -terpinene limonene linalool | Garge, Siddiqui, and Agarwal, 1995. |

| Plant part | Chemical constituents | Reference |
|------------|--|---|
| Leaves | <p>myrcene myrtenol myrtenol acetate <i>para</i>-menth-1,3,8-triene <i>para</i>-menth-4(8)-en-1-ol piperitol piperitone sabinene sabinol terpinene-4-ol trans-carveol</p> <p>Sesquiterpene α-elemene α-humulene <i>ar</i>-curcumene β-caryophyllene caryophyllene oxide</p> <p><i>Atalantia monophylla</i> Correa</p> <p>Monoterpene sabinene</p> <p>Phenylpropanoid <i>iso</i>-eugenol methyl ether</p> | <p>Sharma, Raina, Khanna, Sharma, and Singh, 1992</p> |

| Plant part | Chemical constituents | Reference |
|------------|---|---------------------------------|
| Leaves | <p data-bbox="487 378 848 415"><i>Citrus aurantifolia</i> Swing.</p> <p data-bbox="487 535 675 571">Monoterpene</p> <p data-bbox="487 591 675 628"><i>(E)</i>-β-ocimene</p> <p data-bbox="487 648 675 684"><i>(Z)</i>-β-ocimene</p> <p data-bbox="487 705 675 741">α-phellandrene</p> <p data-bbox="487 762 613 798">α-pinene</p> <p data-bbox="487 818 628 855">α-terpineol</p> <p data-bbox="487 875 597 911">β-pinene</p> <p data-bbox="487 932 613 968">citronellal</p> <p data-bbox="487 988 628 1025">δ-3-carene</p> <p data-bbox="487 1045 581 1081">decanal</p> <p data-bbox="487 1102 613 1138">dodecanal</p> <p data-bbox="487 1158 581 1195">geranial</p> <p data-bbox="487 1215 581 1251">geraniol</p> <p data-bbox="487 1272 675 1308">geranyl acetate</p> <p data-bbox="487 1329 597 1365">limonene</p> <p data-bbox="487 1385 581 1422">linalool</p> <p data-bbox="487 1442 597 1478">myrcene</p> <p data-bbox="487 1499 550 1535">neral</p> <p data-bbox="487 1555 550 1592">nerol</p> <p data-bbox="487 1612 644 1648">neryl acetate</p> <p data-bbox="487 1669 597 1705">sabinene</p> <p data-bbox="487 1725 660 1762">terpinene-4-ol</p> <p data-bbox="487 1782 628 1818">terpinolene</p> <p data-bbox="487 1930 675 1966">Sesquiterpene</p> <p data-bbox="487 1986 691 2023"><i>(E)</i>-β-farnesene</p> | Ibrahim, Abu and Abdul, 1996 |

| Plant part | Chemical constituents | Reference |
|------------|---|--|
| Leaves | <p>(Z)-β-farnesene</p> <p>(Z)-nerolidol</p> <p>α-bergamotene</p> <p>α-eudesmol</p> <p>α-guaiene</p> <p>α-humulene</p> <p>β-bisabolene</p> <p>β-caryophyllene</p> <p>β-elemene</p> <p>β-eudesmol</p> <p>δ-elemene</p> <p>elemol</p> | Sato, Asano, and Sato, 1990; Ibrahim <i>et. al.</i> , 1996 |
| | <p><i>Citrus hystrix</i> DC.</p> <p>Monoterpene</p> <p>(Z)-β-ocimene</p> <p>1,8-cineol</p> <p>1,8-epoxy-terpinolene</p> <p>α-phellandrene</p> <p>α-pinene</p> <p>α-terpinene</p> <p>α-terpineol</p> <p>β-phellandrene</p> <p>β-pinene</p> <p><i>cis-hydrate</i>-sabinene</p> <p><i>cis</i>-linalool 3-7-oxide</p> <p>citronellal</p> <p>citronellic acid</p> | |

| Plant part | Chemical constituents | Reference |
|------------|---|-----------|
| | citronellol acetate citronellyl acetate γ -terpinene geranial geraniol <i>iso</i> -menthone <i>iso</i> -pulegole limonene linalool linalool 3-6-oxide menthone myrcene neral nerol nerol acetone <i>para</i> -cymene <i>para</i> -menthane-1-8-diol sabinene terpin-4-ol terpinolene <i>trans-hydrate</i> -sabinene Sesquiterpene <i>2,6-dimethyl-hep-5-en-1-al</i> <i>2,6-methyl-hep-5-en-2-one</i> α -cadinene α -copaene α -curcumene α -eudesmol | |

| Plant part | Chemical constituents | Reference |
|------------|--|---|
| | α -humulene α -muurolene β -cubebene β -elemene β -eudesmol calamenene <i>cis-para</i> -farnesene cubenol δ -cadinene δ -elemene elemol <i>epi</i> -cubenol γ -cadinene germacrene D hexadecanoic acid <i>iso</i> -caryophyllene phytol safrole <i>trans</i> - α -farnesene <i>trans</i> -nerolidol | |
| Leaves | <i>Citrus medica</i> Linn. var. <i>sarcodactylis</i> (Noot.) Swing. Monoterpene (E)- β -ocimene (Z)- β -ocimene 3,4-methylacetophenone 6-methyl-5-hepten-2-one | Cotroneo., <i>et. al.</i> , 1986; Chen, Lin, and Jin, 1989; Nguyen and Nguyeu, 1996 |

| Plant part | Chemical constituents | Reference |
|------------|--|-----------|
| | α -limonene diepoxide α -pinene α -terpineol α -thujene β -pinene camphene camphor <i>cis</i> -linalool oxide citronellal γ -terpinene geranial geraniol geranyl acetate <i>iso</i> -geranyl acetate limonene limonene oxide I limonene oxide II linalool myrcene neral nerol neryl acetate nonanal <i>para</i> -cymene piperitone sabinene terpinene-4-ol terpinolene <i>trans</i> -linalool oxide | |

| Plant part | Chemical constituents | Reference |
|------------|---|--|
| Leaves | <i>trans-para-mentha-2,8-diene-1-ol</i> undecanone Sesquiterpene α -humulene α - <i>trans</i> -bergamotene β -bisabolene β -caryophyllene β -ionone caryophyllene oxide spathulenol | Ekundayo <i>et. al.</i> , 1990; Verzera <i>et. al.</i> , 1992 |
| | <i>Citrus reticulata</i> Blanco. Monoterpene α -phellandrene α -pinene α -terpinene α -terpineol α -thujene β -pinene camphene <i>cis</i> - β -ocimene <i>cis</i> -sabinene hydrate citronellal citronellol γ -terpinene geranial | |

| Plant part | Chemical constituents | Reference |
|-----------------------------------|--------------------------------------|---|
| Leaves | geraniol | Reisch, 1985; Ekundayo <i>et al.</i> , 1986; Okunnade, and Olaifa, 1987; Ivan, <i>et al.</i> , 1996 |
| | limonene | |
| | linalool | |
| | myrcene | |
| | neral | |
| | nerol | |
| | <i>para</i> -cymene | |
| | sabinene | |
| | terpinen-4-ol | |
| | terpinolene | |
| | thymol | |
| | <i>trans</i> - β -ocimene | |
| | <i>trans</i> -sabinene hydrate | |
| | Sesquiterpene | |
| | α -humulene | |
| | α -sinensal | |
| | β -caryophyllene | |
| | farnesene | |
| | <i>Clausena anisata</i> Hook. | |
| | Benzenoid | |
| | <i>para</i> -anise alcohol | |
| <i>para</i> -anisaldehyde | | |
| <i>1-4-methoxypheny</i> -ethanone | | |

| Plant part | Chemical constituents | Reference |
|------------|--|-----------|
| | <p>Phenyl propanoid</p> <p><i>dihydro-anethole</i></p> <p>chavicol</p> <p>estragole</p> <p><i>1-4-methoxyphenyl-propan-2-one</i></p> <p><i>(Z)-anethol</i></p> <p>methyl chavicol</p> <p><i>para-methoxy-cis-cinnamaldehyde</i></p> <p><i>tran-methoxy-trans-cinnamaldehyde</i></p> <p><i>para-methoxy-cinnamyl alcohol</i></p> <p>Monoterpene</p> <p><i>1,8-cineol</i></p> <p>α-phellandrene</p> <p>α-pinene</p> <p>β-phellandrene</p> <p>β-pinene</p> <p><i>cis-linalool oxide</i></p> <p>citronellal</p> <p>citronellol</p> <p>citronellyl acetate</p> <p>γ-terpinene</p> <p>geraniol</p> <p>geranyl acetate</p> <p>limonene</p> <p>linalool</p> <p>myrcene</p> <p><i>para-cymen-8-ol</i></p> | |

| Plant part | Chemical constituents | Reference | |
|------------|--|-----------|---|
| Leaves | <p><i>para</i>-cymene</p> <p>piperitenone</p> <p>sabinene</p> <p>terpinene-4-ol</p> <p><i>trans</i>-linalool oxide</p> | | |
| | Sesquiterpene | | |
| | <i>(E,E)</i> -farnesol | | |
| | <i>(Z)</i> - β -farnesene | | |
| | α -cadinol | | |
| | α -eudesmol | | |
| | β -bisabolene | | |
| | β -elemene | | |
| | β -eudesmol | | |
| | caryophyllene oxide | | |
| | δ -cadinene | | |
| | elemol | | |
| | γ -cadinene | | |
| | γ -eudesmol | | |
| | germacrene D | | |
| | humulene | | |
| | humulene epoxide | | |
| | spathulenol | | |
| | zingiberene | | |
| | <p><i>Clausena excavata</i> Burm.</p> <p>Benzenoid</p> <p>benzyl benzoate</p> | | <p>Leclercq, Nguyen, and Nhuyen, 1994</p> |



| Plant part | Chemical constituents | Reference |
|------------|--|-----------|
| | <p>Monoterpene</p> <p>α-phellandrene</p> <p>α-pinene</p> <p>α-terpineol</p> <p><i>cis</i>-β-ocimene</p> <p>cuminaldehyde</p> <p>γ-terpinene</p> <p>linalool</p> <p>myrcene</p> <p><i>para</i>-cymene</p> <p>sabinene</p> <p>terpinolene</p> <p><i>trans</i>-β-ocimene</p> <p>verbenone</p> <p>Sesquiterpene</p> <p>α-cadinol</p> <p>α-cedrene</p> <p>α-humulene</p> <p><i>allo</i>-aromadendrene</p> <p>aromadendrene</p> <p>β-bourbonene</p> <p>β-caryophyllene</p> <p>β-cubebene</p> <p>β-elemene</p> <p>β-eudesmol</p> <p>caryophyllene oxide</p> <p>δ-cadinene</p> <p>δ-cadinol</p> | |

| Plant part | Chemical constituents | Reference |
|------------|---|----------------------------------|
| Leaves | <p> δ-elemene germacrene B globulol <i>iso</i>-aromadendrene juniper camphor nerolidol nootkatone spathulenol terpinene-4-ol viridiflorol Alkene hex-cis-3-en-1-ol butanoate </p> <p> <i>Hesperethusa crenulata</i> Roem. </p> <p> Monoterpene 1,8-cineol β-pinene geraniol </p> | <p>Kumar, and Mukharya, 1989</p> |
| Flower | <p> <i>Murraya paniculata</i> Jack. </p> <p> Phenyl propanoid eugenol <i>iso</i>-eugenol </p> <p> Monoterpene 1,8-cineol </p> | <p>Wang, 1979.</p> |

| Plant part | Chemical constituents | Reference |
|-------------------|--|--|
| | β -pinene camphene geraniol <i>hydroxy</i> -citronellyl limonene linalool linalool acetate Sesquiterpene cadinene farnesol vomifoliol Benzenoid β -phenylethanol Sesquiterpene | |
| Leaves | bisabolene | Penfold, and Simonsen, 1925. |
| Flower and Leaves | Sesquiterpene cadinene | Penfold, and Simonsen, 1925.; Wang, 1979. |
| Leaves | <i>Toddalia asiatica</i> Linn. Monoterpene car-3-ene citronellal citronellol | Raju, and Rao, 1979 |

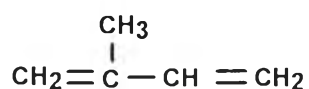
| Plant part | Chemical constituents | Reference |
|------------|--|--|
| Leaves | <p>geraniol</p> <p>geraniol acetate</p> <p>limonene</p> <p>ocimene</p> <p>Coumarin</p> <p>limettin</p> <p><i>Triphasia trifolia</i> P.Wils.</p> <p>Monoterpene</p> <p>α-terpineol</p> <p>camphor</p> <p>carvacrol</p> <p><i>cis-para</i>-menth-2-en-1-ol</p> <p><i>iso</i>-thujyl alcohol</p> <p>linalool</p> <p>myrtenol</p> <p><i>neo-iso</i>-thujyl alcohol</p> <p><i>para</i>-cymene-8-ol</p> <p>terpin-4-ol</p> <p><i>trans</i>-sabinene hydrate</p> <p>Sesquiterpene</p> <p>α-copaene</p> <p>β-elemene</p> <p>cadelene</p> <p>δ-cadinene</p> <p>γ-muurolol</p> | <p>Ameenah, Mala, and Fawzia, 1995</p> |

| Plant part | Chemical constituents | Reference |
|------------|-----------------------|-----------|
| | globulol valencene | |

1.1) Terpenoids

1.1.1) Chemistry and distribution.

Terpenoids are constructed from isoprene (2-methylbutadiene) units:



Terpenoids are widespread in microorganisms, plants, and animals.

The terpenes still contain the original carbon skeleton of the isoprene units. In other groups of isoprenoids the skeleton is altered by addition or loss of carbon atoms. The isoprenoids are categorized as given in Table 1 according to the number of isoprene units used as building blocks.

Table 1 Secondary products derived from activated isoprene

| Number of isoprene units | Group of compounds | Representative |
|--------------------------|--------------------|--|
| 1 | Hemiterpenes | Isoprene, 3,3-dimethylallyl alcohol, isopentenol, isoamyl alcohol, tuliposides |
| 2 | Monoterpenes | Constituents of essential oils, e.g., geraniol, menthol, and thymol |

| Number of isoprene units | Group of compounds | Representative |
|--------------------------|--------------------|--|
| 3 | Sesquiterpenes | Constituents of essential oils, e.g., farnesol, and bisabolol, and of sesquiterpene lactones, e.g., matricin; abscisic acid, juvenile hormone, sirenin |
| 4 | Diterpenes | Constituents of resins e.g., abietic acid; gibberellins, phytol, vitamin A, crocetin |
| 5 | Sesterterpenes | Constituents of unsaponifiable lipid extracts, waxes, etc.; ophiobilin, ircinin, variabilin |
| 6 | Triterpene | Squalene, steroids, pentacyclic triterpenes |
| 7 | Tetraterpenes | Carotenes, xanthophylls |
| >8 | Polyterpenes | Rubber, gutta, solanesol, spadicol, dolichols, betulaprenols, ficaprenols |

The basic structure of isoprenoids may be modified by the introduction of a wide variety of chemical groups, by isomerization, shift of double bonds, methyl groups, etc. Hence, a bewildering number of chemical structure arises. In addition, compounds derived from other biogenic pathways may contain isoprene residues. (Martin, 1990)

1.2. Monoterpenoids (C₁₀)

1.2.1 Introduction to monoterpenoids

These substance constitute a fairly large family of alcohols, hydrocarbons, ketones, etc., which are important components of the essential oil obtained from the leaves, root, and bark of various plants. They have pleasant odours, and many are of some industrial importance, though not necessarily as pure chemical individuals.

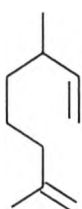
1.2.2 Classification of monoterpenoids (Bentley, 1990; Ikan, 1991)

The monoterpenoids may be divided into three classes having zero, one, or two rings; further subdivisions are made on the basis of carbon skeleton.

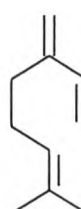
1.2.2.1 Acyclic monoterpenoids

Acyclic monoterpenoids are comparatively few in number but include some of the most important isolates in perfumery.

Among the important hydrocarbons are ocimene and myrcene.

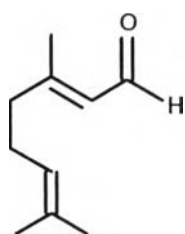


ocimene

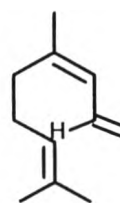


myrcene

Aldehydes

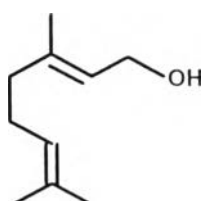


geranial

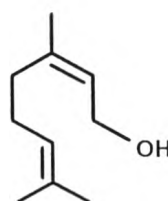


neral

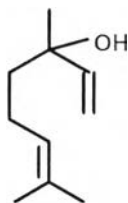
Alcohols



geraniol



nerol

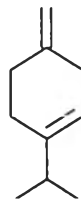
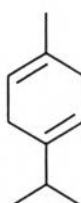


linalool

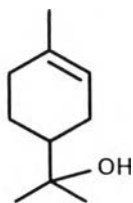
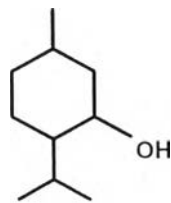
1.2.2.2 Monocyclic monoterpenoids

The great majority of these substances have *p*-menthane carbon skeleton. In addition there are a small group of methylated cyclohexanes and another small miscellaneous group including some derivatives of cyclopentane.

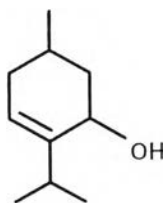
Important hydrocarbons are: (Ikan, 1991)

 α -limonene α -terpinene β -terpinene γ -terpinene α -phellandrene β -phellandrene

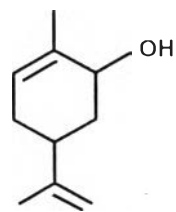
Alcohols

 α -terpineol

menthol

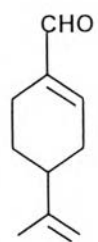


piperitol

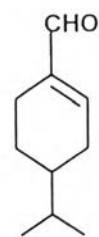


carveol

Aldehydes

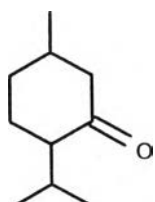


perillaldehyde

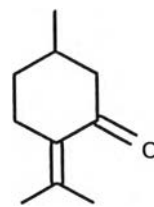


phellandral

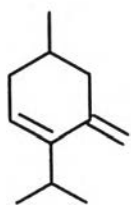
Ketones



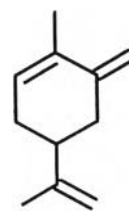
menthone



pulegone

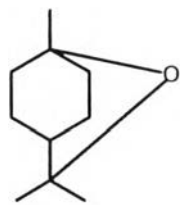


piperitone

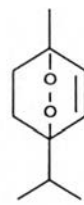


carvone

Oxides



1,8-cineol



ascaridole

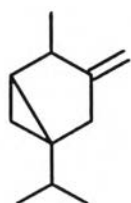
1.2.2.3. Bicyclic monoterpenoids

The bicyclic monoterpenoids may be divided into five groups.

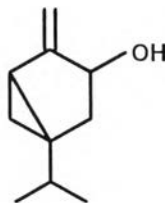
Thujane group.

 α -thujene

sabinene

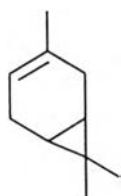


thujone

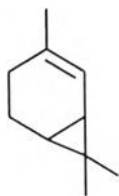


sabinol

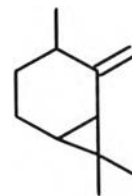
Carane group.



car-3-ene

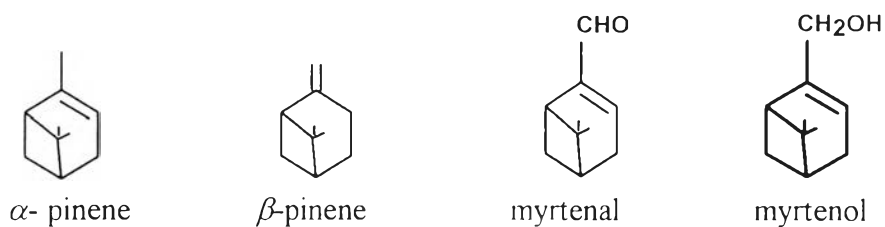


car-4-ene

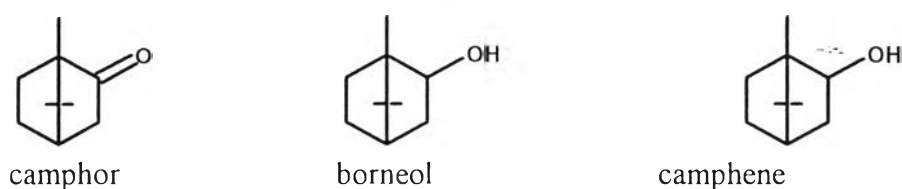


carone

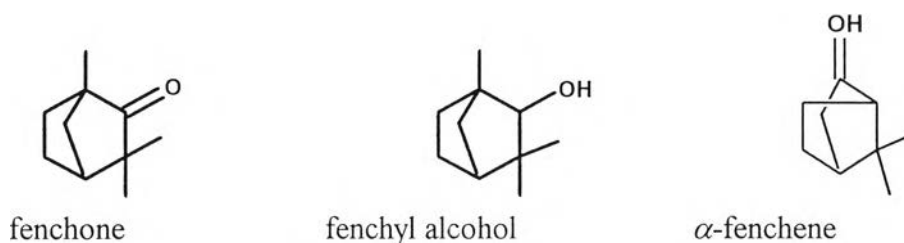
Pinane group.



Camphene group.



Fenchane



1.3. Sesquiterpenoids (C 15)

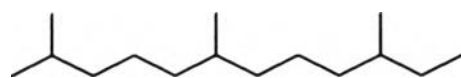
1.3.1 Introduction to sesquiterpenoids

Although the study of the sesquiterpenoids was begun in the early years of the nineteenth century, it was only after about 1920 that serious progress began to be made. Whilst Wallach, 1887 believed that the sesquiterpenoids, like the monoterpenoids, were built up from isoprene nuclei.

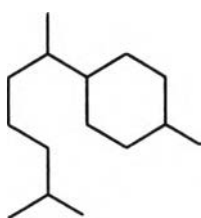
The sesquiterpenes form the higher-boiling fraction of the essential oils, They are formed by the union of three isoprene units. Sesquiterpenes are unsaturated compounds and may be acyclic, monocyclic, bicyclic, and tricyclic.(Ikan, 1991).

1.3.2 Classification of sesquiterpenoids

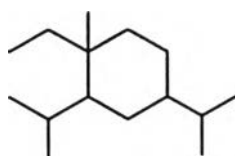
Simple farnesene sesquiterpenes.



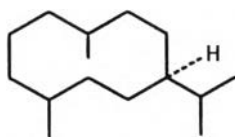
Bisabolanes



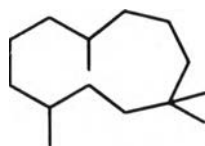
Elemans



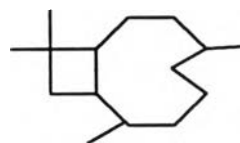
Germacranes



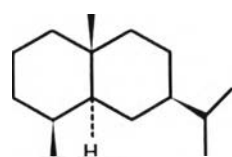
Humulanes

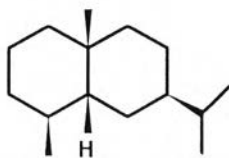
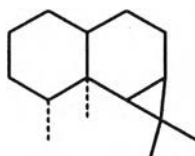
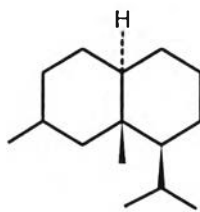
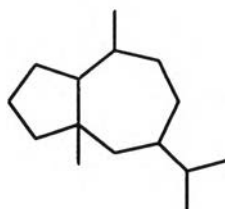
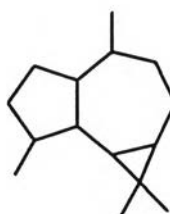
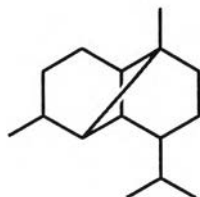


Caryophyllanes



Eudesmanes



Eremophilanes**Aristolanes****Cadinanes****Pseudoguianes****Aromadendranes****Copaanes****Thujosanes**