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# DIPLOMARBEIT

„Essential Oils of Japanese and Austrian Liverworts  
and  
of Selected Japanese Higher Plants“

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# CONTENTS

Acknowledgment .....	6
Abstract .....	7
Zusammenfassung .....	8
<b>1. INTRODUCTION .....</b>	<b>9</b>
<b>1.1. Liverworts (Hepaticae) .....</b>	<b>9</b>
1.1.1. Anatomical and morphological characteristics .....	9
1.1.2. Chemical components of Liverworts and their biological activity .....	10
1.1.3. Systematic of liverworts .....	13
<b>1.2. Japanese higher plants .....</b>	<b>15</b>
1.2.1. Compositae (Asteraceae) .....	15
1.2.1.1. <i>Artemisia vulgaris</i> L. var. <i>vulgaris</i> .....	15
1.2.1.2. <i>Farfugium japonicum</i> .....	16
1.2.1.3. <i>Petasites japonicus</i> .....	16
1.2.1.4. <i>Solidago altissima</i> .....	16
1.2.1.5. <i>Solidago virgaurea</i> .....	17
1.2.2. Umbelliferae (Apiaceae) .....	17
1.2.2.1. <i>Angelica keiskei</i> .....	17
1.2.3. Labiatae (Lamiaceae) .....	17
1.2.3.1. <i>Perilla frutescens</i> .....	18
1.2.4. Zingiberaceae .....	18
1.2.4.1. <i>Curcuma zedoaria</i> .....	18
1.2.5. Platanaceae .....	19
1.2.5.1. <i>Platanus occidentalis</i> .....	19
1.2.6. Lauraceae .....	19
1.2.6.1. <i>Cinnamomum sieboldii</i> .....	19

1.2.7. Amaranthaceae .....	19
1.2.7.1. <i>Chenopodium ficifolium</i> .....	20
1.2.8. Rutaceae .....	20
1.2.8.1. <i>Zanthoxylum piperitum</i> .....	20
1.2.8.2. <i>Citrus junos</i> .....	20
1.2.9. Verbenaceae .....	21
1.2.9.1. <i>Lantana camara</i> .....	21
1.2.10. Cupressaceae .....	21
1.2.10.1. <i>Thujopsis dolabrata</i> .....	21
1.2.10.2. <i>Chamaecyparis obtusa</i> .....	21
1.2.10.3. <i>Cryptomeria japonica</i> .....	22
<b>2. MATERIALS .....</b>	<b>23</b>
2.1. Liverworts .....	23
2.2. Higher plants .....	24
<b>3. METHODS .....</b>	<b>25</b>
3.1. Preparation of the volatile Compounds .....	25
3.2. Methods used for the analysis of the compounds .....	25
<b>4. RESULTS AND DISCUSSION .....</b>	<b>28</b>
<b>4.1. Liverworts .....</b>	<b>28</b>
4.1.1. Austrian liverworts .....	28
4.1.1.1. <i>Conocephalum Conicum</i> .....	28
4.1.1.2. <i>Marchantia polymorpha</i> L. ....	29
4.1.1.3. <i>Radula</i> sp. ....	30
4.1.1.4. <i>Lophocolea heterophylla</i> .....	31
4.1.1.5. <i>Ptilidium</i> sp. ....	32
4.1.1.6. <i>Lepidozia reptans</i> .....	33
4.1.1.7. <i>Scapania</i> sp. ....	34
4.1.1.8. <i>Preissia</i> sp. ....	35

4.1.1.9. <i>Pellia epiphylla</i> .....	36
4.1.2. Japanese liverworts .....	37
4.1.2.1. <i>Conocephalum conicum</i> .....	37
4.1.2.2. <i>Marchantia polymorpha</i> .....	39
4.1.2.3. <i>Pellia endiviifolia</i> .....	40
4.1.2.4. <i>Reboulia hemisphaerica</i> .....	41
4.1.3. New Caledonian liverworts .....	42
4.1.3.1. <i>Bazzania</i> sp. ....	42
4.1.3.2. <i>Leptolejeuna</i> sp. ....	43
4.1.4. Liverworts of the La Réunion Island .....	44
4.1.4.1. <i>Gottschelia schizopleura</i> .....	44
4.1.4.2. <i>Plagiochila boryana</i> .....	44
4.1.4.3. <i>Jamesoniella purpurascens</i> .....	45
<b>4.2. Higher plants .....</b>	<b>47</b>
4.2.1. Compositae (Asteraceae) .....	47
4.2.1.1. <i>Artemisia vulgaris</i> L. var. <i>vulgaris</i> .....	47
4.2.1.2. <i>Farfugium japonicum</i> .....	58
4.2.1.3. <i>Petasites japonicus</i> .....	61
4.2.1.4. <i>Solidago altissima</i> .....	62
4.2.1.5. <i>Solidago virgaurea</i> .....	66
4.2.2. Umbelliferae (Apiaceae) .....	68
4.2.2.1. <i>Angelica keiskei</i> .....	68
4.2.3. Labiatae (Lamiaceae) .....	72
4.2.3.1. <i>Perilla frutescens</i> .....	72
4.2.4. Zingiberaceae .....	75
4.2.4.1. <i>Curcuma zedoaria</i> .....	75
4.2.5. Platanaceae .....	77
4.2.5.1. <i>Platanus occidentalis</i> .....	77
4.2.6. Lauraceae .....	80

4.2.6.1. <i>Cinnamomum sieboldii</i> .....	80
4.2.7. Amaranthaceae .....	81
4.2.7.1. <i>Chenopodium ficifolium</i> .....	81
4.2.8. Rutaceae .....	82
4.2.8.1. <i>Zanthoxylum piperitum</i> .....	82
4.2.8.2. <i>Citrus junos</i> .....	83
4.2.9. Verbenaceae .....	84
4.2.9.1. <i>Lantana camara</i> .....	84
4.2.10. Cupressaceae .....	85
4.2.10.1. <i>Thujopsis dolabrata</i> .....	85
4.2.10.2. <i>Chamaecyparis obtusa</i> .....	86
4.2.10.3. <i>Cryptomeria japonica</i> .....	88
<b>5. CHEMICAL STRUCTURES .....</b>	<b>89</b>
<b>6. CONCLUSION .....</b>	<b>105</b>
6.1. Liverworts .....	105
6.2. Higher plants .....	109
<b>REFERENCES .....</b>	<b>114</b>
<b>APPENDIX .....</b>	<b>118</b>
TLC, maps and other Photographs .....	118
GC-Spectra .....	123
Curriculum vitae.....	157

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## **Abstract**

The work of this master thesis is based on the analysis of volatile components of liverworts collected in Austria, Japan, New Caledonia and La Réunion Island, and of several Japanese higher plants, which have different medical and economical use.

The aim of this thesis was to extract and analyze the volatile compounds from lower plants, whose vascular system is not trained, which are very small, but were used by the people for a long time in various medical fields, on the one hand; and those compounds from higher plants that possess a vascular system, which also have been investigated, on the other hand.

The results presented in this thesis have been obtained by using different analytical methods. For the manufacture of the "extracts" from the plants, two methods were used: extraction with diethyl ether or n-hexane, and steam distillation. The separation of the components was achieved by gas chromatography and the identification of each compound was made by their mass spectrometry.

The experimental part of this master thesis was done during the winter term 2008/2009, at the Faculty of Pharmaceutical Sciences, Tokushima Bunri University, in Tokushima, Japan, under the administration of **Prof. Dr. Yoshinori Asakawa**.

The research and the written work prior and after the stay in Japan have been coordinated by **Prof. Dr. Gerhard Buchbauer**, at the Vienna University.

## **Zusammenfassung**

Die vorliegende Diplomarbeit beruht auf der Analyse von flüchtigen Verbindungen aus verschiedenen Lebermoosen, die in Österreich, Japan, Neukaledonien und in La Réunion-Insel gesammelt wurden; und aus höheren japanischen Pflanzen, die in verschiedenen medizinischen und alltäglichen Bereichen eingesetzt werden.

Ziel dieser Diplomarbeit war es auf der einen Seite, die flüchtigen Verbindungen aus niederen sehr kleinen Pflanzen, die kein vaskuläres System ausbilden, aber vom Menschen seit sehr langer Zeit in verschiedenen medizinischen Bereichen eingesetzt wurden, und auf der anderen Seite jene Verbindungen aus höheren Pflanzen, die ein vaskuläres System besitzen, die aber auch viel eingehender untersucht worden sind, zu extrahieren und ihre Zusammensetzung zu analysieren.

Die Ergebnisse, die in dieser Diplomarbeit gezeigt werden, sind durch den Einsatz verschiedener analytischer Methoden gewonnen. Für die Herstellung des zu analysierenden „extracts“ wurde die Extraktion mit Diethylether und n-Hexane vorgenommen und die Wasserdampfdestillation herangezogen. Für die Trennung der einzelnen Komponenten kam die Gaschromatographie zum Einsatz und die Identifikation der einzelnen Verbindungen wurde durch die Massenspektrometrie erreicht.

Der praktische Teil wurde im Wintersemester 2008/2009 an der pharmazeutischen Fakultät der Tokushima Bunri University in Tokushima, Japan unter der Leitung von **Prof. Dr. Yoshinori Asakawa**, durchgeführt.

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# 1. Introduction

## 1.1 Liverworts (Hepaticae)

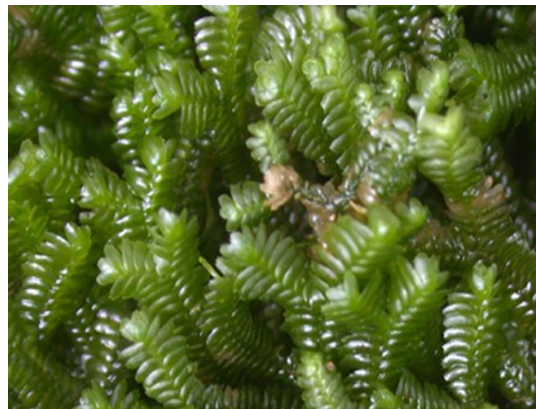
### 1.1.1. Anatomical and morphological characteristics

Hepaticae (Liverworts) is one of three divisions of the bryophytes, which are taxonomically placed between algae and pteridophytes. There are about 24.000 species of bryophytes in the world and are divided as mentioned in three classes: Musci (mosses, 14.000 species), Hepaticae (liverworts 6.000 species) and Anthocerotae (hornworts 300 species) [Asakawa, 1999].

Liverworts are also called Marchantiophyta. They consist of small, terrestrial, nonvascular plants and grow closely packed together on rocks, soil or trees. Thus almost all of them grow in humid and shaded places. Some of them are xerotolerant even though the availability of liquid water is essential for their development and metabolism (ex. gametophyte needs water to allow the motile, biflagellate spermatozoids or antherozoids to swim to the female organ where the egg is located) [Asakawa, 1999]. They are thought to be the oldest terrestrial plants, although in the literature is not yet evidenced about it [Gradstein].

Marchantiophyta are morphologically very small and the species are highly variable, so that their identification and classification is very difficult.

Thus, the two main types of Liverworts are: leafy liverworts and thallose liverworts. Leafy liverworts are made up of stem (differentiates in cortex resp. hyalodermis and medulla), branches (intercalary or thecal and terminal or athekal), leaves (generally two lateral rows and a ventral row called underleaves or amphigastria).



*Bazzania* sp.

Leafy liverworts possess 4 types of oil bodies that are characteristic for different species, or they may have the so-called, ocelli, cells with a large oil body and no

chloroplast. The attachment of these low plants is possible of the rhizoids, in different forms, only *Calobriales* lack them. There are superficial cells in stem and branches. They produce the reproductive organs, the antheridia and archegonia.

For the thalloid liverworts is the thallus structure a very important characteristic for the identification. *Metzgeriales* have an internally simple and multistratose throughout or a single layer of cells while they have a multistratose central, resembling a midrib. The thallus of the *Marchantiales* is internally differentiated, dorsal side is green and the chlorophyllous tissue is in air chambers with specialized pores, ventral side is composed of colorless storage tissue.



*Marchantia polymorpha*

*Metzgeriales* have chloroplasts and oil bodies on their thallus cells, while *Marchantiales* and *Monocleales* have specialized cells for the oil bodies. Thalloid liverworts produce also reproductive organs (antheridia and archegonia), which are produced from the thallus cells. Their rhizoids are smooth or tuberculate, or smooth and tuberculate, as well. The sporophytes of thalloid and leafy liverworts are quite similar. The main differences are in the seta and capsule valve [Gradstein].

#### 1.1.2. Chemical components of Liverworts and their biological activity

Hepaticae contain - as already mentioned - oil bodies, while the other two classes of Bryophytes do not contain such cell structures. These are special cell organelles in which mono-, sesqui- and diterpenoids and lipophilic aromatic compounds (bibenzyls, bis-bibenzyls, benzoates, cinnamates, long chain alkyl phenols, naphthalenes, phthalides and isocumarines) are stored. Due to their chemical compounds, they have different pharmacological activities and show characteristic fragrant odors, an intense hot and bitter or saccharin-like taste or cause allergenic contact dermatitis and are not damaged by insects, snails, slugs, and other small animals. Generally, the chemical constituents of Musci, Hepaticae and Antherozetae differ from each other. Thus Bryophyta have been used in China more than 400 years

ago, e.g. *Fussidens* and *Polytrichium* were known as plants with diuretic activity and their ashes as promoter of hair growth on the human head. Medical decoctions or the powder of Bryophytes were applied, too, such as to cure cuts, burns and external wounds. North American Indians used to use *Philonotis* sp. and *Polytrichium juniperum* to cure burns, bruises and wounds. In Europe, *Marchantia polymorpha* was used as a diuretic drug: Patient drank the white liquor with which the fresh plants, has been soaked before [Asakawa, 1999].

Some of the important components and their activities:

Acetogenins: Sesqui- and diterpenoids most of *Lejeunaceae* species, *Cheiloloejenea imbricate*, *Marchantia pleacea* var. *diptera*: (R)-dodec-2-en-1,4-olide and (R)-tetradec-1-en-5,6-olide mixture, milky fragrance.

Monoterpenoids: characteristic smell, *Jungermannia hattoriana*: Cyclocitral, *Conocephalum conicum*: (-)-sabinene, (+)-bornyl acetate and methyl cinnamate.

Sesquiterpenoids: *Mniaceae* mosses: Hemostatic activity and induce allergic contact dermatitis, *Plagionium acutum* (Musci): ent-sesquiterpene hydrocarbons, ent- $\beta$ -cerdrene,  $\alpha$ -cerdrene,  $\alpha$ -acoradiene, *Rebouilia hemisphaerica*: gymnomitrane-type sesquiterpene, gymnomitrol, rebouliadienol, *Cholchaphus polyanthus* and *Lepidozia vitrea*: Eudesmane-type sesuiterpenoids; *Frullania tamarisci*: monomer eudesmanolides and eudesmanol and its dimer, *Frullania densiloba*: eudesmanolides, densilobalides A and B,  $\alpha$ -cyclodihydrocostunulide, *Porella parrottetiana*: eudesmanol.

Biological and pharmacological activities [Huneck, 1983], [Asakawa, 1990].

- Antibiotic and antifungal activities: Extracts from 18 mosses and liverworts are active against 8 different fungi: *Diplophyllum albicans*, *Pogonatum aloides*, *Plagiothecium denticulatum* etc. antimicrobial activity: Bibenzyls of *Radula* species. *Frullania*, *Marchantia*, *Porella* and *Plagiochila* show also antimicrobial and antifungal activity, they also contain bibenzyls.
- Antitumor activities: ethanolic extract of *Polytrichium juniperinum* against Sarcoma 37; diplophyllin against human epidermal carcinoma and

frullanoide, tulipinolide and diplophyllin indicated cytotoxicity against KB cells. Marchantin-, riccardin-, plagiochin-, isomarchantin-, isoriccardin and perrottetin-type bis (bibenzyls) that are produced by some liverworts possess cytotoxicity against KB cells and 5-lipoxygenase and calmodulin inhibitory activity, especially marchantin A.

- Plant growth regulatory activities: Lunaric acid found in *Lunaria criciata*, *Marchantia polymorpha*, other compounds; stilbenes, drimenol, gymnocolin, longiborneol, longifolene, scapanin.
- Allergenic activities: contact dermatitis caused by *Frullania* and *Radula* species: Frullanolide seemed to be responsible for the active allergenic principle.
- Insect antifeeding activities: pinguosone, tadeonal and plagiochilin A against the African army worms *Spodoptera littoralis* and *S. exempta*.
- Piscicidal activities: costunolide against the killie-fish (*Oryzias latipes*), sacculatal and polygodial possess a stronger activity against the "killie-fish".
- Irritancy and tumour promoting activity: polygodial, sacculatal, plagiochiline A and C are potential tumor promoters. (+)-Frullanolide (*Frullania dilatata*) possess an inhibitory activity.

Other pharmacological activities are the hot and bitter taste which is due to the presence of polygodial (a few *Porella* sp., *Jamesoniella autumnalis*), sacculatal (*Pellia endiviifolia*) or plagiochiline A, I and B (pungent *Plagiochila* sp.). Furthermore some liverworts emit characteristic odor when crushed; e.g. the sweet mushroomy odour of *Conocephalum conicum* (particularly the male thalli) and *Wisnerella denudata* comes due to the presence of (+)-bornyl acetate, (-)-sabinene, methylcinnamate, 1-octen-3-ol and its acetate, from the former and (+)-bornyl acetate,  $\alpha$ - and  $\beta$ - pinene, camphene,  $\alpha$ - terpinene from the latter one. Since some species of *Frullania*, *Jungermannia*, *Lejeunea*, *Plagiochila* and *Porella* show the presence of mixtures of monoterpenes, they emit a strong terpenin-like odour, similar to that of the conifer-leaves.

### 1.1.3. Systematics of liverworts

Bryophytes are morphologically very small and their systematic classification is very difficult. For this reason the study of the secondary metabolites is extremely important in assigning species. The knowledge of their chemical constituents might serve to delineate also the evolutionary relationship within the Hepaticae at genus or family level. For example, *Isotachis* used to be a separated family since it was found that the chemical constituents, isotachin A and B were present also in the family of Balantiopsidaceae. The outcome was the suggestion of a common ancestor and later than *Isotachis* has been added on [Asakawa, 2004].

Hepaticae are divided in 2 subclasses: Jungermannidae and Marchantiidae. Jungermanniadae are divided in the orders: Metzgeriales, Takakiales, Calobryales, Jungermanniales and Marchantiidae are divided in Monocleales and Marchantiales [Asakawa, 1999].

#### Subclass: **Jungermannidae**

Liverworts that are adapted to moist climates, their gametophytes and spores are not very strongly drought-tolerant. They have green cells with oil bodies.

#### Order: Metzgeriales

- Aneuraceae(=Riccardiaceae)
- Pelliaceae (=Dilaenaceae)
- Pallaviciniaceae
- Blasiaceae
- Fossombroniaceae
- Hymenophytaceae
- Metzgeriaceae

#### Order: Takakiales

- Takakiaceae

#### Order: Calobryales

- Haplomitraceae

#### Order: Jungermanniales

- Jungermanniaceae
- Lophoziaceae
- Gymnomitriaceae (=Marsupellaceae)
- Arnelliaceae
- Plagiochilaceae
- Geocalycaceae
- Acrobolbaceae

- Scapaniaceae
- Balantiopsidaceae
- Adelantaceae
- Lepidolaenaceae
- Schistochilaceae
- Antheliaceae
- Lepidoziaceae
- Calypogeiaceae
- Cephaloziaceae
- Isotachidaceae
- Trichocoleaceae
- Ptilidiaceae
- Lepicoleaceae
- Herbertaceae
- Radulaceae
- Pleuroziaceae
- Porellaceae
- Frullaniaceae
- Jubulaceae
- Lejeunaceae

Subclass: **Marchantiidae**

Liverworts, which are mostly adapted to grow in dry climatic regions, thereby they have developed special devices, e.g. subterraneous tubers, a fleshy thallus, large end thick-walled spores, to survive long periods of desiccation. They have, contrary to Jungermanniidae, either cells with chloroplasts or with an oil body, never with both [Zinsmeister, 1990].

Order: Monocleales

- Monoclealaceae

Order: Marchantiales

- Targionaceae
- Aytoniaceae (=Grimaldiaceae)
- Conocephalaceae
- Lunulariaceae
- Marchantiaceae
- Ricciaceae

[Asakawa, 2004].

## 1.2. Japanese higher plants

### 1.2.1. Compositae (Asteraceae)

The sunflower family consists of 1528 genera and 22750 species. The plants grow as herbs, shrubs, trees or vines. They have been classified into at least ten subfamilies with a worldwide distribution. The Compositae are economically important. Some of them are important as food additive, ornamental cultivars, and some of them have different local or industrial use [Simpson].

#### 1.2.1.1. *Artemisia vulgaris* L. var. *vulgaris*

*Artemisia vulgaris* also called yomogi in Japan has different economical and medicinal uses in different countries. In the European traditional medicine the plant is used as a choloretic, for amenorrhoea and dismenorrhoea while in Japan is it used for bruises and other external injuries and as food additive in the "mochi" (rice sticky sweets) and bread. In the Austrian traditional medicine *Artemisia vulgaris* is used in cases of stomach troubles and absence of appetite.



In the Indian traditional medicine the plant is used for diabetes and the extract of the whole plant for a few other injuries such as: single extract epilepsy, in combination with other plant it is used for psychneurosis, depression, irritability etc. Aerial parts of the plant are used in the herbal medicine as an anthelmintic, an antiseptic, an antispasmodic, as tonic for vital organs and different disorders including hepatitis. The antibacterial activity and the efficacy in the correction of breech presentation of *A. vulgaris* have been showed in various studies. It is found that artemisin that was extracted from *A.vulgaris* showed an antimalarian activity. Furthermore the crude extract of the plant has been used as antimalarial agent for thousands of years. Other usages of *A. vulgaris* are skin diseases, inferior substitute for cinchona for treating fever, leucorrhoea, haemoptysis, colitis, vomiting, rheumatism etc. The compounds responsible for the effects of *A. vulgaris* are: flavonoids, coumarins, sesquiterpene



lactones, volatile oils, inulin and traces of alkaloids [Govindaraj, 2008].

#### 1.2.1.2. *Farfugium japonicum* (L.f.) Kitamura

*Farfugium japonicum* belongs to the Asteraceae family. It is a perennial herbaceous plant which grows in moist meadows and along streams in Korea, China and Japan. All parts of this plant have been used in Korea in folk remedies for antipyretic, eczema, cough, wounds healing, bronchitis, lymphadenitis, diarrhea and antidote of fish poison.



It has been found that the essential oil of *F. japonicum* possesses antioxidant effects and antimicrobial activity against several microorganisms. Nowadays although, the usage of *F. japonicum* is limited as ornamental plant with its bold and attractive foliage [Kim].

#### 1.2.1.3. *Petasites japonicus* (Maxim.) Fr. Schmidt

*Petasites japonicus* is the Japanese butterbur and it is native to Japan. The Japanese name for this plant is fuki. The Japanese butterbur is widely spread. It is used as vegetable in the Japanese cuisine after pre-treating with salt and soaking with water [Iwamoto].



#### 1.2.1.4. *Solidago altissima* L.

The tall goldenrod is native to North America and it is the most common alien plant species in Japan. It has been brought to Japan about hundred years ago [Wu, 2007], but is native to U.S.. It grows very high, over 2 m, that is why the species name *altissima* which means “very tall” or “the tallest”. Native North-American Indians used to use the tall goldenrod in teas to relieve cramps and the roots were used for boils after grinding and moistening [Simpson].



#### 1.2.1.4. *Solidago virgaurea* L.

*Solidago virgaurea* belongs to the Asteraceae family and it is widely distributed in North America. It can be found in almost every state of the USA and throughout Canada. The flowers were used in the traditional medicine of the Amerindians for pains, burns and ulcers treatment, febrifuge, gastrointestinal and liver aids. The genus *Solidago* contains chemical secondary components such as: essential oil, flavonoids, phenolic acids, sesquiterpenes, diterpenes and saponins [Bradette-Herbert].

### 1.2.2. Umbelliferae (Apiaceae)

The carrot family has a worldwide distribution and consists mostly of herbs, but also (rare) shrubs or trees. Umbelliferae include 446 genera and 3540 species. They are economically important as herbs, food and spice plants. Some species are poisonous [Simpson].

1.2.2.1. *Angelica keiskei* (Miq.) Koidz is called ashitaba in Japanese. The antioxidant and antigenotoxic activity of several extracts of this plant has been verified and published. The substances contained in *A. keiskei* have a complementing insulin action, induction of the adipocyte differentiation and the enhancement of glucose uptake [Enoki, 2007].



The plant is eaten in Japan as vegetable and it has also a potent anti-tumor promoter activity [Okuyama, 1991].

### 1.2.3. Labiatae (Lamiaceae)

The mint family consists of 6700 species in 251 genera. The plants belonging to this family may appear as herbs, shrubs, or rarely trees. They have often glandular trichomes which are short stalked and which produce aromatic ethereal oils. They have a worldwide distribution. They are economically important as medicinal and culinary herbs (e.g. Mentha, Rosmarinus, Salvia, Thymus etc), fragrance plants (e.g. Lavaendula) and a few ornamental cultivated plants [Simpson].

#### 1.2.3.1. *Perilla frutescens* (L.) Britton

*Perilla frutescens* also called shiso in Japanese is an ornamental plant. The dried stems are used in the traditional Chinese medicine because of the analgetic activity, leaves are used for cold and headaches and fruits for severe diseases of the respiratory organs.



Activities: Aldose-reductase-inhibitor, allergenic, analgesic, antibacterial, anticancer, antidote, crab and fish, antiseptic, antipyretic [Duke].

#### 1.2.4. Zingiberaceae

The ginger family includes ca. 1300 species ordered in 50 genera. The Zingiberaceae are a large family and consist of perennial plants. They are an important source of spice plants especially *Curcuma* spp. and *Zingiber* spp., some species are cultivated as ornamentals [Simpson].

#### 1.2.4.2. *Curcuma zedoaria* (Christm.) Rosc.

*Curcuma* plants including *Curcuma zedoaria* are used as herbal drugs because of their antiinflammatory, antihepatotoxic and neuroprotective activity. In the Asian medicine they were used due to obstruction of blood circulation and retention of blood stasis such as arthralgia and dysmenorrhoea. More than 10 species are distributed or cultivated in China and Japan.



The Chinese herbal literature prescribes specific ailments for each *Curcuma* sp., their clinical application is complicated though. The leaf blades of the Japanese *C. zedoaria* have a purple-colored band (purple-cloud type) [Sasaki].

### 1.2.5. Platanaceae

The plane tree family includes ten species and varieties ordered in two subgenera. The genus *Platanus* is spread in the northern hemisphere and is the only extant representative of the Platanaceae.

1.2.5.1. *Platanus occidentalis* also called American maple tree is native to North-America but is widely spread in Japan as well. According to Nixon and Poole [2003], who recognized two species groups, *P. occidentalis* belongs to the second group which according to their taxonomy is purely American [Grimm].



### 1.2.6. Lauraceae

The laurel family includes 2200 species which are ordered into 45 genera. They consist of trees or shrubs and contain aromatic oil glands. They are distributed in tropical to warm temperate regions like south-east Asia and tropical America. Their economical use consists of several timber plants, spice and other flavoring plants, as well as food plants [Simpson].

1.2.6.1. *Cinnamomum sieboldii* Meisn.

Methanol extracts of *C. sieboldii* show insecticidal activities [Kim]. The essential oil of *C. sieboldii* showed an acaricidal activity against *Dermatophagoides farinae* and *D. pteronyssinus* [Cho].

### 1.2.7. Amaranthaceae

The amaranth family includes Chenopodiaceae and consists of 2050 species ordered in ca 174 genera with a worldwide distribution. The economical use of the plants of this family is as vegetable crops (beet, spinach), pseudograin crops (*Amaranthus*, *Chenopodium* spp.), cultivated ornamentals, cockscomb, detrimental weeds and local firewoods and medical plants [Simpson].

#### 1.2.7.1. Chenopodium ficifolium

*Chenopodium* includes 120 species and their wide application in folk medicine includes the usage as a diaphoretic, as an antihelmentic, as a stomachic, emmenagogue for the pain of amenorrhoea, antispasmodic, as an abortifacient, and for the relief of asthma, migraine and catarrh. The plants which belong to this genus are reported to contain essential oils, flavonoids, sterols and steroidal estrogen-like substances, alkaloids, and coumarins. They are used for the treatment of many ailments [Gobar, 1997].

*Chenopodium* spp. were ordered in a separated family called Chenopodiaceae. The compounds found in *Chenopodium ficifolium* are triterpene saponins, kaempferol-3,7-dirhamnoside. Compounds found in the *Chenopodium* genus/ Chenopodiaceae are alkaloids, phenolic acids, saponins, glycosides and glycorunides. The saponins found in these plants have the effect to exhibit the hypoglycemic activity [Gobar, 2002].

#### 1.2.8. Rutaceae

The citrus family contains 1800 species ordered in 153 genera. They consist of trees, shrubs, lianes or rarely herbs. They have a worldwide distribution mostly in tropical regions.

##### 1.2.8.1. Zanthoxylum piperitum

*Zanthoxylum piperitum* is native to the Japanese Islands, mainland of China and the Korean peninsula. It is a deciduous shrub which belongs to the Rutaceae family. It is also called the Japanese pepper. The dried fruits and fresh young leaves are used in the Japanese cuisine as a spice to allow a fresh flavor or to suppress any unpleasant fishy and meaty odor in dishes. They are also used as diuretics and stomachics in traditional Chinese and Japanese medicine [Asakawa].

##### 1.2.8.2. Citrus junos Tanaka

*Citrus junos* is also called yuzu in Japanese. The fruits of citrus are widely cultivated. It is one of the most important crops because of its pleasant taste, odor and fragrance [Satake].

### 1.2.9. Verbenaceae

#### 1.2.9.1. *Lantana camara* LINN

*Lantana camara* is a hairy shrub and it is native to tropical America. It has been cultivated in other countries as an ornamental or hedge plant. The medicinal usages of the different parts of the plant are the treatment of various human ailments: itches, cuts, hurts, ulcers, malaria, anemia, bilious fever, tumor, influenza, eruptions, rheumatism, toothache, scabies and leprosy and as antiseptic for wounds. There have been isolated various terpenoids, steroids and flavonoids, from different parts of the plant [Begum].

### 1.2.10. Cupressaceae

1.2.10.1. *Thujopsis dolabrata* is endemic in Japan and it is called: Hiba arborvitae. It belongs to the Cupressaceae. It is proved that it contains tropolone and some hinokitol-related compounds that are known to have a strong antimicrobial and insecticidal activity. Due to the mentioned compounds it is used in agriculture, clinical products, cosmetics and other areas [Saniewski]. *T. dolabrata* is also used in Japan as ornamental plant.



Another usage is diced heartwood of the tree as odor dispenser, probably for religion reasons. Totarol was isolated from its seeds and it is proved that it has a fungi select activity for the seedling. [Yamaji, 2007]

1.2.10.2. *Chamaecyparis obtusa* also called the Japanese cypress is an evergreen conifer. It contains also tropolone and some hinokitol-related compounds. It is used in agriculture, clinical products, cosmetics and other areas [Saniewski].



1.2.10.3. Cryptomeria japonica (L. f.) D. Don

*C. japonica* is distributed mainly in Asia. It is also called the Japanese cypress and the Japanese name for the tree is *sugi*. Economical usage of the plant is mostly as ornamental plant and as a source to obtain the essential oils [Wiersema].



Prof. Dr. Yoshinori Asakawa, October, 5<sup>th</sup> 2008, Tokushima exhibition

## 2. Materials

This master thesis is based on working with fresh or dried plants which contain volatile compounds and essential oils. The main objects were to extract and to identify their volatile compounds, based on the TLC analysis and on the resulted mass spectra. A small amount of all plants has been washed with water, crushed and extracted with diethyl ether or n-hexane. The essential oil of *Thujopsis dolaborata*, *Artemisia vulgaris* and the red leaves of *Platanus occidentalis* have been obtained by steam distillation.

### 2.1. Liverworts

Austrian liverworts were collected at the mountain at Stuhleck (Spital am Semmering, A-8684), Tirolstrasse (Neuburg an der Mürz, A-8692), and St. Pölten (A-3100) by Mag.pharm.Thomas Schweiger and Vlora Mehmeti. The Japanese liverworts were collected in Tokushima-prefecture and Tokyo by Prof. Asakawa. The Japanese as well as the Austrian liverworts have been identified by Prof. Asakawa. The New Caledonian liverworts have been collected in Noumea. They were also collected and identified by Prof. Asakawa. Liverworts of La Réunion Island have been collected and identified by Prof. T. Pócs. The information about the place and the date of collection as well as the amount that has been used for the analysis is listed in the table below:

Table I : Liverworts

Liverworts	Place	Habitat	Coll.date:	A (g)
Austrian liverworts				
<i>Marchantia polymorpha</i>	Stuhleck (A-8684)	Soil	28.09.2008	0.1
<i>Conocephalum conicum</i>	Sankt Pölten	Sandy ground	23.09.2008	0.9
<i>Lepidozia reptans</i>	Stuhleck (A-8684)	Soil	28.09.2008	0.2
<i>Radula sp.</i>	Tirolstr. (A-8692)	Wood	28.09.2008	0.1
<i>Ptilidium sp.</i>	Stuhleck (A-8684)	On wood	28.09.2008	0.3
<i>Scapania sp.</i>	Tirolstr. (A-8692)	Rock	28.09.2008	0.8
<i>Lophocolea heterophylla</i>	Stuhleck (A-8684)	Soil	28.09.2008	0.1
<i>Pellia epiphylla</i>	Stuhleck (A-8684)	Soil	28.09.2008	0.1
<i>Preissia sp.</i>	Tirolstr. (A-8692)	Rock	28.09.2008	0.8
Japanese Liverworts				
<i>Marchantia polymorpha</i>	Tokushima	Soil	23.11.2008	0.4
<i>Marchantia polymorpha</i>	Tokyo	Soil	25.11.2008	0.2
<i>Conocephalum conicum</i> big	Tokushima	Chalky soil	23.11.2008	0.4

thalloid				
<i>C. conicum</i> small thalloid	Tokushima	Chalky soil	23.11.2008	0.3
<i>Rebouilla hemisphaerica</i>	Tokushima	Sandy ground	23.11.2008	0.2
<i>Pellia endivifolia</i>	Tokushima	Soil	23.11.2008	0.2
New Caledonian liverworts				
<i>Bazzania</i> sp.	Noumea	Decayed wood	8.11.2008	0.15
<i>Leptolejeuna</i> sp.	Noumea	Fern leaves	8.11.2008	0.1
La Réunion Island				
<i>Jamesionella puppurescense</i>	Foret de Beleuve	Decayed wood	12.09.2008	0.1
<i>Plagiochila boryana</i>	Le Petit Col	On ground	16.09.008	0.15
<i>Gottschelia schizopleura</i>	Foret de Beleuve	Mossy forest	13.09.2008	0.15

## 2.1. Higher plants

There have been 17 plants used for analyzes, all of them have been collected in Tokushima prefecture. The plants have been separated into leaves, stem, flowers, roots or rhizome. The crude extracts of the plants or the parts of the plants have been used (see the table below). The essential oils of *Thujopsis dolabrata*, *Artemisia vulgaris* and *Platanus occidentalis* have been obtained by steam distillation.

Table II: Higher Plants

Plant name	Leaves	Stem	Flowers	Roots	Other
<i>Artemisia vulgaris</i> (n-Hex)	0.5 g	1.0 g	0.9 g		
<i>Artemisia vulgaris</i> (ether)	0.7 g	1.2 g	0.8 g		Cortex: 1.52 g
<i>Artemisia</i> sp.- young plant	5.0 g	2.8 g			
<i>Solidago altissima</i>	0.7 g	1.0 g	0.7 g	0.5 g	
<i>Solidago virgaurea</i>	0.8 g	0.7 g	0.5 g	1.2 g	
<i>Chenopodium ficifolium</i>					Herba: 0.7 g
<i>Chamaecyparis obtusa</i>	1.7 g				
<i>Angelica keiskei</i>	0.5 g	1.0 g	1.0 g		
<i>Platanus occidentalis</i>	2.1 g				Red Leaves: 2.6 g
<i>Petasites japonicus</i>	1.8 g				Rhizome: 5 g
<i>Lanata camara</i>	1.5 g	3.0 g			
<i>Farfugium japonicum</i>	5.2 g	2.7 g	6.2 g		
<i>Curcuma zedoaria</i>	3 g			5.4 g	
<i>Cinnamomum sieboldii</i>					Cortex: 5.2 g
<i>Thujopsis dolabrata</i>		Crushed wood: 3.5 kg			
<i>Perilla frutescense</i>	1.2 g	1.5 g	0.9 g		Corrolle: 0.6 g
<i>Zanthoxylum piperitum</i>	2.1 g				
<i>Citrus junos</i>	A drop of the pressed EO diluted with ether				
<i>Cryptomeria japonica</i>	1.5 g				



### 3. Methods

#### 3.1. Preparation of the volatile compounds

##### Extraction

Two solvents have been used to extract the volatile compounds from the plants: diethyl ether and n-hexane. A small amount of each plant or each part of the plant has been crushed in a mortar and then extracted with ether or n-hexane, respectively. After that the obtained liquid has been filtrated through a pipette which was prepared with a piece of cotton and silicagel powder. Magnesiumsulfate was used to absorb the water that was contained in the sample and which would disturb the measurement. Final step was the evaporating of the solvent so that the concentration of the extracted material has the ideal concentration as required for the TLC and GC-MS.

##### Steam distillation

For this method an automatically working steam distillation apparatus was used. The concept of this method is to obtain the pure essential oil by using the steam. The plants have been cut in small pieces before the distillation. This equipment has a grid-cage into which the sample has been measured. The essential oils of the crushed wood of *Thujopsis dolaborata*, the dried and cut *Artemisia vulgaris* and the red leaves of *Platanus occidentalis* have been obtained in such a way.



The essential oils were obtained by heating the water in the main cage at a temperature of 100°C for 6 hours. The preheating time was 1 hour.

#### 3.2. Methods used for the analysis of the compounds

Thin layer chromatography (TLC) is a simple and speed method to detect the compounds of a mixture or an extract. The advantage of this method includes versatility, speed and sensivity. Different adsorbens (cellulose, silicagel etc) can be

spread on to a glass plate, aluminium sheets or plastic and employed for chromatography. This method allows a diversity of the adsorbents e.g. with or without a fluorescent indicator which allows the detection of compounds that quench the fluorescence. However the detection of the compounds is usually carried out by spraying.

The preparative TLC used for this thesis was carried out on glass-plates with a thin layer of silicagel 60 F254 as absorbent (0.25 mm) and eluted with a solvent mixture of n-hexane: ethylacetate, 4:1. The running distance was 8 cm and the running time was approx. 14 min. The plates have been detected under UV-light after the solvent was completely evaporated. After that the plates have been sprayed with sulfuric acid and heated at 120°C.

#### Gas chromatography-Mass spectrometry (GC-MS)

Gas liquid chromatography is a sophisticated and expensive method which provides both quantitative and qualitative data on plant substances. The GC apparatus has four main components: the column, the heater, gas flow and the detection device. The column is a long narrow tube usually made of metal and is packed with the stationary phase on an inert powder. The rapid evaporation of the sample as soon as it is passed on the column is necessary. The heater is necessary to heat the column progressively from 50 to 250°C which is also necessary. An inert carrier gas (nitrogen or argon) will be passed through the column at a controlled rate to achieve the separation of the compounds on the column. The compound will be swept through the column and the measurement is made by detection device which is connected to a potentiometric recorder. The results of the separation are shown in a GC trace of a series of peaks of varying intensity. These results can be expressed in terms of retention volume (R<sub>v</sub>) or in terms of retention time (R<sub>t</sub>).

The GC is mostly automatically linked to mass spectrometry (MS). MS allows the detection and the identification of the different compounds that are present in the analyzed mixture. The vaporized and separated components diffuse to a low pressure system of the mass spectrometer. The ionisation of the compounds is made with a sufficient energy to cause the fragmentation of the chemical bonds. The positively

charged ions which are accelerated and dispersed in a magnetic field allow relative abundance measurements of ions of the given mass-to-charge ratio. The resulted mass spectral graph consists of a series of lines of varying intensity at different mass units.

The analysis of the many structurally complex components with the combination of the GC with MS permits a qualitative and quantitative identification at one run. 1  $\mu\text{l}$  of the extracts obtained by direct extracting or steam distillation has been injected in a coupled liquid gas chromatograph with a mass spectrometer system.

The GC-system used was a HP 6890. The column was a silica gel fused column and had a length of 30 m. Its diameter was 0.25 mm (internal) and the thickness of the column film was 0.25 mm. Helium was used as carrier gas with a floating rate of 1.0 ml/min during the process of measurement. The temperature at the time of injection was 50°C which was kept constant for 5 min. From the 6<sup>th</sup> min the temperature increased for about 5 °C per min until the column attained the temperature of 250°C. The temperature was than kept this high for 15 min. After passing the column the compounds were detected by a MS using the TIC (Total Ion Corrent). Due to their mass spectra it was possible to identify the separated compounds by searching them through the mass finder or the literature.



## 4. Results and discussion

### 4.1. Liverworts

#### 4.1.1 Austrian Liverworts

##### 4.1.1.1. *Conocephalum conicum* (Conocephalaceae)

*Conocephalum conicum* was collected by Mag.pharm. T. Schweiger in Sankt Pölten, on September 23<sup>rd</sup>, 2008. A small amount has been cut and crushed in a mortar in order to extract it with diethyl ether. A plenty of 1 µl has been injected into the GC-MC apparatus. The GC showed the main peak after 26.7 min. Which according to the mass spectra, could be a calamene-derivative. Sabinene (**28**) as a characteristic compound of *Conocephalum conicum*, appeared after 11.5 min in the GC. The area extension was not that high, though. Other compounds that have been detected with a higher area percentage are:  $\alpha$ -cubebene (**59**),  $\gamma$ -cadinene (**51**), cadina-3,5-diene (**55**), cadina-1,4-diene (**54**), cubebol (**76**), and ent-epicubenol (**147**). Meanwhile 1-oct-3-enylacetate (**262**), sencyunolide (**160**),  $\alpha$ -copaene (**60**), aristolene (**62**), eudesm-3-ene-7-ol (**90**), 7 $\alpha$ H,10H-cadina-1(6),4-diene (**53**), guaia-6,9-diene (**183**), (Z)-nerolidol (**10**),  $\gamma$ -calacorene (**63**), 4 $\alpha$ -hydroxy-germacra-1(10),5-diol (**117**), tetradecanal (**260**), 1-oxo- $\alpha$ -longipenene (**216**) and hexadecanoic acid (**258**), were also detected with a lower area percentage than 1%. The retention time and the calculated area-percentage are shown in the table below. There are some unidentified peaks as well.

Retention time (min)	Area %	Compound
11.458	0.564	Sabinene ( <b>28</b> )
15.605	0.549	1-Oct-3-enylacetate ( <b>262</b> )
22.006	0.497	Unknown
22.348	5.232	$\alpha$ -Cubebene ( <b>59</b> )
22.733	0.373	Sencyunolide ( <b>160</b> )
23.051	0.577	$\alpha$ -Copaene ( <b>60</b> )
23.432	8.683	$\gamma$ -Cadinene ( <b>51</b> )
24.176	0.800	Aristolene ( <b>62</b> )
24.953	3.037	Cadina-3,5-diene ( <b>49</b> )
25.268	0.511	Eudesm-3-ene-7-ol ( <b>90</b> )

25.402	0.615	7 $\alpha$ H,10 $\beta$ H-Cadina-1 (6),4-diene ( <b>53</b> )
25.494	2.362	Selina-3,6-diene ( <b>73</b> )
25.559	1.721	$\beta$ -Copaene( <b>61</b> )
25.712	0.761	Unknown ( <b>51</b> )
26.014	5.036	cis-Muurolo-4 (15),5-diene ( <b>64</b> )
26.113	2.601	$\alpha$ - Cadinene ( <b>49</b> )
26.497	1.130	$\gamma$ -Cadinene ( <b>51</b> )
26.637	5.202	Cubebol ( <b>76</b> )
26.717	9.555	Calamenene-derivative
26.939	3.651	Cadina-1,4-diene ( <b>54</b> )
27.035	0.567	Guaia-6,9-diene ( <b>183</b> )
27.179	0.406	$\gamma$ -Calacorene( <b>63</b> )
27.495	0.380	(Z)-Nerolidol ( <b>10</b> )
27.954	0.969	4 $\alpha$ Hydroxygermacra-1 (10),5-diol ( <b>130</b> )
29.136	2.939	ent-Epicubenol ( <b>147</b> )
29.428	0.538	Unknown
29.519	0.56	$\gamma$ -Cadiene ( <b>45</b> )
30.757	0.41	Tetradecanal ( <b>260</b> )
33.322	2.737	Unknown
33.804	0.733	Unknown
33.871	0.696	1-Oxo- $\alpha$ -Longipinene ( <b>216</b> )
34.171	1.202	Unknown
34.316	1.412	Unknown
35.105	0.867	Unknown
35.359	0.869	Unknown
35.840	3.406	Hexadecanoic acid ( <b>258</b> )

#### 4.1.1.2. *Marchantia polymorpha* L. (Marchantiaceae)

There have been three samples of *Marchantia polymorpha* used to analyze for this master thesis. They were collected at Stuhleck, Tokushima-Prefecture and in Tokyo.

The main compound of the Austrian *M. polymorpha* shown in the GC-spectra appears at a time of 28.3 min with an area-percentage of 26.8%. Other characteristic and important compounds such as  $\beta$ -chamigrene (**211**), thujopsene (**80**), isobazzanene (**203**) and  $\gamma$ -cuprenene (**207**) appeared in much lower percentage, 6.6%, 3.2%, 1.1%, and 2%. Another characteristic compound,  $\beta$ -barbetene (**165**), was detected, even if in a very low percentage, the peak appeared at the beginning of the 26<sup>th</sup> min.

Retention time (min)	Area%	Compound
24.297	0.606	Unknown
24.697	3.220	Thujopsene ( <b>80</b> )
24.800	1.110	Isobazzanene ( <b>203</b> )
25.038	0.857	$\beta$ -Barbetene ( <b>165</b> )
25.125	1.654	Selina-5,11-diene ( <b>74</b> )
25.534	1.405	$\gamma$ -Cuprenene ( <b>207</b> )
25.718	2.625	Maaliene ( <b>85</b> )
25.850	6.672	$\beta$ -Chamigrene ( <b>211</b> )
26.367	2.081	$\gamma$ -Cuprenene ( <b>207</b> )
26.778	0.949	Unknown
27.098	2.240	Unknown
27.403	3.107	$\delta$ -Cuprenene ( <b>208</b> )
28,319	26.822	(-)-Cyclopropenecuparenol ( <b>210</b> )
28.889	0.668	Unknown
29.357	1.450	Unknown
29.541	2.293	Unknown
30.535	2.930	Maaliol ( <b>84</b> )
30.708	1.554	Unknown
30.977	1.373	1-Oxo- $\alpha$ -Longipenene ( <b>216</b> )
33.051	1.171	Widdrol ( <b>152</b> )
33.481	3.892	Unknown
33.975	0.875	Unknown
34.337	1.943	Unknown
37.635	2.037	$\alpha$ -Cadinol ( <b>52</b> )
39.404	1.114	Phytol ( <b>286</b> )
42.121	0.478	Methyloleate ( <b>267</b> )
44.741	0.747	Tetradecanal ( <b>260</b> )

#### 4.1.1.3. *Radula* sp. (Radulaceae)

*Radula* sp. has been collected in Tirol. A small amount has been crushed and extracted with ether. The GC of the ether extract showed a number of peaks which could be identified as different types of bibenzyls. The main peak appeared after 46.9 minutes with an area extension of 33.7 % and has been identified as radulanin K (**178**). Another big peak detected after 45.4 min, 6.2 area % was not exactly identified but according to the mass spectra, it should be a radulanin derivative or at

least a bibenzyl type component. The next lower peak that appeared as the last peak in the GC was identified as 3-methyl-4-(3-methyl-2-butenyl)-4'-hydroxybibenzyl (**158**). A second radulanine type bibenzyl has been also detected and it has been identified as radulanin I (**177**) (after 44.9 min and 2.2 area %). One chromene type component appeared after 43.5 minutes and an unidentified sesquiterpene alcohol has been also found after 46.5 minutes in the GC.

Retention time (min)	Area %	Compound
32.365	5.537	3-Methoxybibenzyl ( <b>175</b> )
33.614	0.866	Neophytadiene isomer I ( <b>288</b> )
34.106	0.239	Neophytadiene isomer II ( <b>289</b> )
34.468	0.524	Neophytadiene isomer III ( <b>290</b> )
43.558	0.858	2,2-Dimethyl-5-hydroxy-7- (2-phenylethyl)-chromene ( <b>181</b> )
43.931	1.066	Bibenzyl derivative
44.348	0.951	3,5-Dihydroxy-2 (2,3-epoxy-3-methyl)-bibenzyl ( <b>180</b> )
44.876	2.230	Radulanin I ( <b>177</b> )
45.453	6.234	Radulanin deriveative
45.870	0.821	Unknown
46.175	7.600	3,5-Dihydroxy-2- (3-methyl-2-butenyl)-bibenzyl ( <b>176</b> )
46.496	17.275	Sesquiterpene alcohol
46.954	33.668	Radulanin K ( <b>178</b> )
47.535	0.640	Frullanolide ( <b>162</b> )-type comp.
49.631	0.731	Unknown
55.032	19.529	3-Methyl-4- (3-methyl-2-butenyl)-4'-hydroxybibenzyl( <b>179</b> )

#### 4.1.1.4. *Lophocolea heterophylla* (Geocalycaceae)

*Lophocolea heterophylla* has been collected at Stuhleck, Austria. The GC-MS analysis of the ether extract showed the main peak after 36 minutes and it was identified as ent-diplophyllolide (**164**). Another big peak appeared in the GC after 43 minutes and it was identified as squalene (**287**). One bibenzyl-type compound was identified. The peak that appeared after 38.3 minutes was identified as 3-methoxybibenzyl (**175**), the area extension of which was 3.9 %. Other identified components of the diethyl ether extract were isoalantolactone (**161**), 14-methylpentadecanoate (**268**),  $\alpha$ -selinene (**68**), amorpho-4,7(11)-diene-8-one (**79**),  $\beta$ -barbetene (**165**) and neophytadiene isomers (**288**), (**289**) and (**290**).

Retention time (min)	Area %	Compound
25.55	0.298	$\beta$ -Barbetene ( <b>165</b> )
26.22	0.248	Amorpha-4,7 (11)-diene-8-one ( <b>79</b> )
26.728	1.072	$\alpha$ -Selinene ( <b>68</b> )
33.910	1.789	Neophytadiene isomer I ( <b>288</b> )
34.396	0.369	Neophytadiene isomer II ( <b>289</b> )
34.760	0.704	Neophytadiene isomer III ( <b>290</b> )
35.599	2.989	14-Methylpentadecanoate ( <b>268</b> )
36.346	2.164	Isoalantolactone ( <b>161</b> )
36.593	32.075	ent-Diplophyllolide ( <b>164</b> )
38.355	3.899	3-Methoxybibenzyl ( <b>175</b> )
43.121	24.600	Squalene ( <b>287</b> )
43.359	5.974	Unknown
45.215	2.656	Unknown
46.858	5.053	Unknown
47.614	2.640	Unknown
50.120	1.017	Unknown
53.944	2.059	Unknown

#### 4.1.1.5. *Ptilidium* sp. (Ptidiliaceae)

The main peak showed in the GC appeared after 41.3 minutes and was identified as an not exactly identified pinguisaninelactone. The peaks that appeared in the GC after 34.4, 36.1 and 36.5 minutes showed MS spectra of unidentified pinguisanine (**142**) derivatives. A peak which appeared after 33.3 minutes was identified as 5-epi-pinguisenol (**140**). Another pinguisanine-type component was detected after 37.7 minutes and was identified as dehydropinguisenol (**145**). Petasitene (**191**) and davanafurane (**165**) have also been detected. Their peaks appeared in the GC after 29 and 36 minutes. Other identified components were  $\alpha$ -pinguisene (**139**), drim-8-ene (**88**) and one aliphatic compound: n-eicosane (**235**).

Retention time (min)	Area %	Compound
5.986	0.432	$\alpha$ -Pinguisene ( <b>139</b> )
27.495	3.810	Unknown
28.970	1.902	Drim-8-ene ( <b>88</b> )
29.274	1.219	Petasitene ( <b>191</b> )



29.935	0.600	Unknown
32.347	0.790	Pinguisanine ( <b>142</b> )
33.064	0.696	Drim-8-en-7-one ( <b>89</b> )
33.266	6.416	5-epi-Pinguisenol ( <b>140</b> )
34.314	3.845	Neophytadiene isomer I ( <b>288</b> )
34.373	3.983	Pinguisanine derivative
34.807	1.019	Unknown
35.937	9.577	Pinguisanine derivative
36.147	1.939	Davana furan ( <b>165</b> )
36.578	2.903	Pinguisanine derivative
37.053	0.361	Unknown
37.670	1.475	Dehydropinguisenol ( <b>145</b> )
39.913	0.840	Eudesma-3,11-diene-8-one ( <b>105</b> )
41.316	52.552	Unidentified Pinguisanin lactone
43.716	1.093	Unknown
45.714	0.971	n-Eicosane ( <b>235</b> )
47.449	1.162	Unknown

#### 4.1.1.6. *Lepidozia reptans* (Lepidoziaceae)

*Lepidozia reptans* was collected at Stuhleck in Austria. After the purification a small amount has been extracted with diethyl ether. The GC showed the main peak after 30.7 minutes which has been identified as 1(10)-spirovetivene (**166**). A big peak that appeared after 33.9 minutes has been identified as eudesm-3-en-6,7-oxide (**92**). Another big peak which was detected at the 31<sup>st</sup> minute was identified as 1(10)-valencene-7 $\beta$ -ol (**94**). Other compounds that were identified in the GC were:  $\beta$ -barbatene (**185**), bicyclogermacrene (**127**),  $\gamma$ -curcumene-17-al (**96**). A lot of peaks that appeared after 44 minutes could not be identified.

Retention time (min)	Area %	Compound
26.348	1.427	$\beta$ -Barbatene ( <b>185</b> )
27.490	1.389	Bicyclogermacrene ( <b>127</b> )
30.703	33.875	1 (10)-Spirovetivene ( <b>166</b> )
30.917	7.300	1 (10)-Valencene-7 $\beta$ -ol ( <b>94</b> )
33.218	1.333	$\gamma$ -Curcumene-15-al ( <b>96</b> )
33.953	12.47	Eudesm-3-en-6,7-oxide ( <b>92</b> )
34.102	2.261	Unknown
34.466	8.014	Neophytadiene isomer I ( <b>288</b> )

35.316	2.333	Neophytadiene isomer II ( <b>289</b> )
42.372	1.096	Neophytadiene isomer III ( <b>290</b> )
44.839	1.503	Unknown
45.916	1.237	Unknown
47.692	7.753	Unknown
48.012	1.875	Unknown
52.388	1.975	Unknown
57.245	1.061	trans-Methyl-trans farnesoate ( <b>272</b> )
57.314	1.342	Unknown

#### 4.1.1.7. *Scapania* sp. (Scapaniaceae)

*Scapania* sp. was collected at Stuhleck, Austria. A small amount of the sample has been crushed and extracted with diethyl ether. The main peak detected in the GC was a not identified labdane type compound. The peak that appeared after 37.8 minutes in the GC was identified as 2(3), 5(6)-fusicoccadiene (**192**). Fusicogigantepoxide (**194**) as a characteristic compound of *Scapania* sp. was detected after 42 minutes. A big peak that appeared after 49.1 minutes with 14.6 % of the area percentage could not be identified. Another unidentified compound appeared after 54.4 minutes in the GC with an area extension of 3.4 % of the area.

Retention time (min)	Area %	Compound
24.725	0.458	$\beta$ -Elemene ( <b>108</b> )
26.144	4.552	$\beta$ -Barbetene ( <b>165</b> )
26.752	0.844	Germacrene type sesquiterpene
26.938	3.628	Germacrene D ( <b>123</b> )
27.040	7.072	Isobicyclogermacrene ( <b>128</b> )
27.290	2.425	Bicyclogermacrene ( <b>127</b> )
27.782	4.306	Sesquisabinene ( <b>105</b> )
27.865	0.775	$\beta$ -Bazzanene ( <b>202</b> )
29.830	1.031	Labdane-type compound
30.237	29.407	Labdane-type compound
33.638	0.687	Longipinanol ( <b>148</b> )
34.303	3.909	Neophytadiene isomer I ( <b>288</b> )
35.148	1.320	Neophytadiene isomer III ( <b>290</b> )
37.445	0.652	Isogymnomitrol ( <b>188</b> )
37.879	1.195	2 (3),5 (6)-Fusicoccadiene ( <b>192</b> )
39.021	0.471	$\beta$ -Eudesmol ( <b>113</b> )

41.193	1.353	Furanoeremophilone ( <b>167</b> )
41.656	0.588	Aphidicol-15-ene ( <b>222</b> )
41.894	1.327	Sclarene ( <b>230</b> )
42.613	4.612	Fusicogigantepoxide ( <b>194</b> )
42.752	1.044	unknown
46.145	2.215	Gymnomitr-3(15)-en-4 $\beta$ -ol ( <b>187</b> )
49.099	14.612	Unknown
54.451	3.431	Unknown

#### 4.1.1.8. *Preissia* sp. (Marchantiaceae)

*Preissia* sp. has been collected at Stuhleck and 0.8 g of the sample has been used for the analysis. The major compound that has been detected in the GC appeared after 27.6 minutes and has been identified as cubebol (**76**). Sabinene (**28**) appeared in the GC after 11.8 minutes and has an area extension of 1.1 %. Bornyl acetate (**45**) was also detected. It appeared after 21.8 minutes in the GC. Other identified compounds were  $\gamma$ -cadinene (**51**), germacrene D (**123**),  $\alpha$ -muurolene (**87**), and a few aliphatic compounds: tetradecanal (**260**), n-tetracanoic acid, oleic acid (**265**), n-tetracosane (**242**) and octadecanal (**259**).

Retention time (min)	Area %	Compound
11.792	1.129	Sabinene ( <b>28</b> )
21.836	1.606	Bornylacetate ( <b>45</b> )
24.554	2.184	Selina-3,6-diene ( <b>73</b> )
26.037	0.845	cis-Muurola-4 (15)5-diene ( <b>64</b> )
26.776	0.895	$\gamma$ -Cadinene ( <b>51</b> )
27.059	1.087	Germacrene D ( <b>123</b> )
27.140	1.349	$\alpha$ -Muurolene ( <b>87</b> )
27.641	15.745	Cubebol ( <b>76</b> )
27.921	0.618	Cadina-1,4-diene ( <b>54</b> )
28.437	1.578	n-Dodecanoic acid ( <b>263</b> )
28.968	2.891	$\alpha$ -Hydroxygermacra-1 (10),5-diene ( <b>130</b> )
29.303	1.035	Unknown
30.107	1.801	ent-Epicubenol ( <b>147</b> )
31.670	0.639	Tetradecanal ( <b>260</b> )
32.701	1.062	n-Tetracanoic acid
34.229	21.664	Neophytadiene isomer I ( <b>288</b> )
34.338	1.227	2-Hexadecene ( <b>245</b> )

34.694	3.296	Neophytadiene isomer II ( <b>289</b> )
35.058	6.621	Neophytadiene isomer III ( <b>290</b> )
35.218	0.950	Unknown
36.021	0.773	Unknown
36.622	0.364	Methyloleate ( <b>260</b> )
42.795	0.924	Oleic acid ( <b>265</b> )
45.564	1.628	n-Tetracosane ( <b>242</b> )
48.003	1.366	Unknown
49.385	3.442	Octadecanal ( <b>259</b> )
56.502	1.968	Squalene ( <b>287</b> )

#### 4.1.1.9. *Pellia epiphylla* (Pelliaceae)

*Pellia epiphylla* showed no pungency after chewing it which means it probably contained no sacculatal (**231**) which is typical for *Pellia* sp. After analyzing the GC-MS-GC no sacculatal (**231**) could be identified.  $\gamma$ -Cuprenene (**207**), (1E,4Z)-germacrene B (**126**) and elemenone (**109**) were identified they appeared in the GC after 26.7, 28.6 and 32.2 minutes.

Retention time (min)	Area %	Compound
26.724	1.116	$\gamma$ -Cuprenene ( <b>207</b> )
28.678	1.294	(1E,4Z)-Germacrene B ( <b>126</b> )
32.199	2.262	Elemenone ( <b>109</b> )
34.344	51.835	Unknown
34.262	1.869	3,7,11,15- Tetramethyl-2-Hexadecene ( <b>270</b> )
34.823	8.312	Unknown
35.186	17.046	Unknown
40.441	1.054	Phytol ( <b>286</b> )
41.237	1.692	Unknown
56.928	1.655	Unknown

## 4.1.2. Japanese liverworts

### 4.1.2.1. *Conocephalum conicum* (Conocephalaceae)

*Conocephalum conicum* has been collected in the Tokushima prefecture on October 24<sup>th</sup>, 2008, and considered of two sorts of thallus, a bigger and a smaller one. These have been separated and then separately extracted with diethyl ether. TLC and GC-MS were carried out. The results are shown in the table below. Both seemed to have a lot of unidentified compounds, even if not in such a high percentage.

#### Big-thalloid *C. conicum*

The main peak of the GC was identified as a neophytadiene isomer (**288**), a decomposition product of chlorophyll. Another big peak that appeared after 22 minutes with an area extension of 21.2% has been identified as bornyl acetate (**45**).  $\beta$ - Elemene (**107**) and 1 (15)E,5E-germacradien-11-ol (**116**) have also been detected. A big peak has been detected after 28.5 minutes in the GC. This peak was identified as 1,8-oxido-cadine-4-ene (**57**) with an area extension of 13.4 %.

Retention time (min)	Area %	Compound
9.226	1.945	Unknown
15.831	4.143	1-Oct-3-enylacetate ( <b>262</b> )
22.014	21.252	Bornylacetate ( <b>45</b> )
27.397	2.431	$\beta$ - Elemene ( <b>107</b> )
28.556	13.424	1,8-Oxido-cadine-4-ene ( <b>57</b> )
29.100	5.495	Unknown
30.999	1.658	Unknown
31.993	1.821	1 (15)E,5E-Germacradien-11-ol ( <b>116</b> )
34.823	2.845	Unknown
36.198	24.316	Neophytadiene isomer I ( <b>288</b> )
36.732	3.343	Neophytadiene isomer II ( <b>289</b> )
37.128	7.712	Neophytadiene isomer III ( <b>290</b> )
40.518	1.561	Unknown
51.387	4.050	Unknown
55.565	4.002	Unknown

### Small-thalloid *C.conicum*

The main peak in the GC which appears after 6.2 minutes has been identified as a short chain aliphatic alcohol, 2-heptanol (**254**), which is probably a decomposition product of monoterpenes by heating it [Asakawa]. Bornyl acetate (**45**) has been detected after 22.2 minutes in the GC-MS GC of the small thalloid Japanese *Conpcephalum conicum*. The small peak that has been detected after 10.9 minutes has been identified as sabinene (**28**). A big peak that appeared in the GC after 37.5 minutes could not be identified. Actually a number of peaks that appear between 37.5 and 56 minutes could not be identified.

Retention time (min)	Area %	Compound
6.238	22.629	2-Heptanol ( <b>254</b> )
10.919	0.379	Sabinene ( <b>28</b> )
16.545	0.814	1-Oct-3-enylacetate ( <b>262</b> )
22.246	3.400	Bornylacetate ( <b>45</b> )
24.711	0.373	Unknown
28.587	2.807	1,8-Oxido-cadine-4-ene ( <b>57</b> )
30.487	1.152	Unknown
36.192	15.258	Neophytadiene isomer I ( <b>288</b> )
36.727	2.159	Neophytadiene isomer II ( <b>289</b> )
37.134	8.266	Neophytadiene isomer II ( <b>290</b> )
37.557	19.868	Unknown
46.706	1.385	Unknown
49.780	4.148	Unknown
51.413	5.586	Unknown
52.688	2.051	Unknown
55.689	7.655	Unknown

#### 4.1.2.2. *Marchantia polymorpha* (Marchantiaceae)

*Marchantia polymorpha* was collected in Tokyo prefecture on November 23<sup>rd</sup>(2008), 0.4 g have been used for the analysis. The GC showed a big peak after 29 minutes which was identified as (-)-cyclopropenecuparenol (**210**) and has an area extension of 16.8 %. Thujopsene (**80**) was also detected. The peak appeared in the GC after 26.2 minutes. Another characteristic compound for *Marchantia polymorpha* is  $\beta$ -chamigrene (**211**) which appeared after 27.9 minutes in the GC with an area

extension of 6.1 %. Other compounds that could be identified are isobazzanene (**203**) (Rt: 26.8 min),  $\beta$ -barbetene (**165**) (Rt: 27.1 min)  $\alpha$ -cuprenene (**206**) (Rt: 28.5 min),  $\gamma$ -cuprenene (**207**) (Rt: 29.3 min),  $\delta$ -cuprenene (**208**) (30.8 min), thujopsan-2 $\alpha$ -ol (**82**) (Rt: 31.4 min),  $\epsilon$ -cuprenene (**209**) (Rt: 35.9 min). Phytol (**286**) and other decomposition products of chlorophyll were detected after 36.2 minutes.

*Marchantia polymorpha*, Tokyo prefecture

Retention time (min)	Area%	Compound
26.243	3.075	Thujopsene ( <b>80</b> )
26.796	0.950	Isobazzanene ( <b>203</b> )
27.108	1.651	$\beta$ -Barbetene ( <b>165</b> )
27.199	1.195	Unknown
27.602	0.701	$\gamma$ -Cuprenene ( <b>207</b> )
27.797	1.087	Unknown
27.988	6.119	$\beta$ -Chamigrene ( <b>211</b> )
28.546	1.809	$\alpha$ -Cuprenene ( <b>206</b> )
29.357	1.063	$\gamma$ -Cuprenene ( <b>207</b> )
29.714	16.874	(-)-Cyclopropenecuparenol ( <b>210</b> )
30.818	1.523	$\delta$ -Cuprenene ( <b>208</b> )
31.427	0.707	Thujopsan 2 $\alpha$ -ol ( <b>82</b> )
32.166	2.251	Unknown
33.215	0.912	$\alpha$ -Bisabolol ( <b>100</b> )
33.684	0.483	Thujopsenone ( <b>81</b> )
35.961	2.01	$\epsilon$ -Cuprenene ( <b>208</b> )
36.125	1.664	Unknown
36.254	17.258	Neophytadiene isomer I ( <b>288</b> )
36.792	2.419	Neophytadiene isomer II ( <b>289</b> )
37.193	5.411	Neophytadiene isomer III ( <b>290</b> )
38.057	0.630	Geranylinalool ( <b>282</b> )
44.167	1.300	Phytol ( <b>286</b> )
50.847	1.057	Aliphatic compound
52.823	2.384	Unknown

The second *Marchantia polymorpha* that was collected in the Tokushima prefecture showed almost the same spectra. The identified compounds were almost the same but with another area extension compared to the sample that was collected in Tokyo. The major compound was (-)-cyclopropenecuparenol (**210**) which appeared in the GC after 30.7 minutes with an area extension of 20.6 %. Thujopsene (**80**) was detected

after 26.67 minutes and  $\beta$ -chamigrene (**211**) appeared in the GC after 27.9 minutes. Isobazzanene (**203**),  $\beta$ -barbetene (**165**),  $\alpha$ -cuprenene (**206**),  $\gamma$ -cuprenene (**207**),  $\delta$ -cuprenene (**208**) were also identified from the GC of *M. polymorpha* that has been collected in Tokushima.

M.polymorpha Tokushima prefecture

Retention time (min)	Area%	Compound
26.667	7.844	Thujopsene ( <b>80</b> )
26.758	2.185	Isobazzanene ( <b>203</b> )
27.069	1.086	$\beta$ -Barbetene ( <b>165</b> )
27.159	1.176	Unknown
27.569	0.108	$\gamma$ -Cuprenene ( <b>207</b> )
27.775	1.735	Unknown
27.950	10.465	$\beta$ -Chamigrene ( <b>211</b> )
28.516	11.223	$\alpha$ -Cuprenene ( <b>206</b> )
29.314	2.376	$\gamma$ -Cuprenene ( <b>207</b> )
29.676	3.085	$\delta$ -Cuprenene ( <b>208</b> )
30.753	20.673	(-)-Cyclopropenecuparenol ( <b>210</b> )
32.112	3.250	Citronellylacetate ( <b>5</b> )
33.173	1.483	$\alpha$ -Bisabolol ( <b>100</b> )
36.217	5.764	Neophytadiene isomer I ( <b>288</b> )
37.156	1.787	Neophytadiene isomer III ( <b>290</b> )
39.145	0.922	Unknown
44.144	2.307	Phytol ( <b>286</b> )
50.547	4.814	Unknown
52.832	1.547	Unknown

4.1.2.3. *Pellia endiviifolia* (Pelliaceae)

A small amount *Pellia endiviifolia* has been used for the analysis. The detected compounds are shown in the table below. The most compounds could not be identified. Thus the major compound was identified as sacculatal (**231**). The peak was detected after 48 minutes and the calculated area extension was 32.8 %. The peaks that appeared in the GC after 50; 51.2; 52.3 and 57.2 minutes have also been identified as derivatives of (**231**).



Retention time (min)	Area %	Compound
36.226	4.670	Neophytadiene isomer I ( <b>288</b> )
36.765	0.519	Neophytadiene isomer II ( <b>289</b> )
37.162	1.459	Neophytadiene isomer III ( <b>290</b> )
42.481	1.688	unknown
42.481	2.676	Unknown
43.128	1.578	Unknown
44.389	1.391	Unknown
46.528	1.442	Unknown
48.088	32.852	Sacculatal ( <b>231</b> )
48.500	2.354	Unknown
48.802	2.944	Unknown
50.158	5.721	Sacculatal derivative
50.707	6.166	Unknown
51.251	6.718	Sacculatal derivative
52.367	19.463	Sacculatal der.-lactone type
53.128	1.361	Unknown
57.209	3.201	Sacculatal derivative

#### 4.1.2.4. *Reboulia hemisphaerica* (Aytoniaceae)

The GC-MS analysis of the *Reboulia hemisphaerica* which has been crushed and extracted with diethyl ether, showed a big peak after 48 minutes. The area extension was 7.8% and the peak was identified as 16-kaurene (**223**).  $\gamma$ -Cuprenene (**207**) was identified in the GC after 24.6 minutes and had an area extension of 3.3 %. The peak detected after 27.9 minutes was identified as  $\beta$ -chamigrene (**211**). Other identified components were cadina-1,4-diene (**54**), cadina-4,11-diene (**56**) and acorenol (**214**). They had a low area extension, though.

Retention time (min)	Area %	Compound
24.602	3.359	$\gamma$ -Cuprenene ( <b>207</b> )
26.598	0.297	Cadina-1,4-diene ( <b>54</b> )
27.518	0.994	Cadina-4,11-diene ( <b>56</b> )
27.904	3.861	$\beta$ -Chamigrene ( <b>211</b> )
28.602	3.793	Unknown
29.282	0.645	Acorenol ( <b>214</b> )
30.79	2.907	Unknown
36.244	18.391	Neophytadiene isomer I ( <b>288</b> )

36.785	2.282	Neophytadiene isomer II ( <b>289</b> )
37.185	5.528	Neophytadiene isomer III ( <b>290</b> )
48.104	7.762	16-Kaurene ( <b>223</b> )
52.388	1.474	Unknown
52.779	2.347	Unknown

### 4.1.3. New Caledonian liverworts

#### 4.1.3.1. *Bazzania* sp. (Lepidoziaceae)

*Bazzania* sp. was collected in Noumea. The GC-MC analysis showed a number of unknown compounds. The mass spectra of a lot of the peaks that appeared in the GC could not be identified. Anyway, the major peak was identified as selina-4,7-diene (**75**) which appeared after 24 minutes. Pogostol (**201**) and  $\beta$ -patchoulene (**197**) were also identified; their peaks have been detected after 32 and 33.5 minutes respectively. A big peak that appeared in the GC after 24.6 minutes was identified as anastreptene (**196**). Other identified compounds from the diethyl ether extract of *Bazzania* sp. were isopatchoula-3,5-diene (**198**) (Rt:25.8min),  $\alpha$ -caryophyllene (**133**) (Rt:27.2min), bicyclogermacrene (**127**) (Rt:28.3min), cuparene (**204**) (Rt:28.9min) and germacrene B (**125**) (Rt:30.2min).

Retention time (min)	Area %	Compound
6.168	0.914	t-Butanol ( <b>253</b> )
23.889	0.959	Unknown
24.038	12.514	Selina-4,7-diene ( <b>75</b> )
24.679	5.774	Anastreptene ( <b>196</b> )
24.821	2.729	Unknown
25.414	0.835	Unknown
25.860	0.715	Isopatchoula-3,5-diene ( <b>198</b> )
25.357	10.24	Unknown
27.061	0.605	$\beta$ -Barbatene ( <b>185</b> )
27.248	1.956	$\alpha$ -Humulene ( <b>133</b> )
28.373	0.613	Bicyclogermacrene ( <b>127</b> )
28.934	1.486	Cuparene ( <b>204</b> )
29.356	1.966	Unknown
30.285	0.568	Germacrene B ( <b>125</b> )

32.036	6.228	Pogostol ( <b>201</b> )
33.498	6.083	$\beta$ -Patchoulene ( <b>197</b> )
35.426	5.768	Unknown
36.214	3.986	Unknown
36.737	1.005	Unknown
37.145	1.324	Unknown
39.799	2.562	Unknown
40.296	5.450	Drimenol ( <b>114</b> )
44.868	2.779	Unknown

#### 4.1.3.2. *Leptolejeuna* sp. (Lejeunaceae)

*Leptolejeuna* sp. was also collected in Noumea. It has a very strong smell upon crushing it. It was grown on the leaves of ferns. The GC-MS analysis of the diethyl ether extract of *Leptolejeuna* sp. showed a main peak after 35 minutes which was identified as menthothiophene (**21**). 4-Ethylphenol (**20**) was also identified. Its peak appeared in the GC after 21.5 minutes. Other compounds found in the ether extract of *Leptolejeuna* sp.:  $\beta$ -caryophyllene (**134**) which was detected after 26.2 minutes, pinguisenene (**126**) after 29.7 minutes, deoxopinguisone (**144**) after 30.4 minutes, ptychanolide (**154**) after 36.3 minutes and dehydropinguisenol (**145**) which appeared in the GC after 40 minutes. The other peaks could not be identified.

Retention time (min)	Area %	Compound
6.675	67.477	2-Heptanol ( <b>254</b> )
21.536	1.090	4-Ethylphenol ( <b>20</b> )
26.285	2.441	$\beta$ -Caryophyllene ( <b>134</b> )
27.219	0.492	$\alpha$ -Humulene ( <b>133</b> )
28.583	1.425	Unknown
29.782	2.598	Pinguisanene ( <b>141</b> )
30.443	4.880	Deoxopinguisone ( <b>144</b> )
35.105	8.409	Menthothiophene ( <b>21</b> )
36.209	2.061	Unknown
36.376	1.473	Ptychanolide ( <b>154</b> )
37.618	1.052	Unknown
38.313	3.405	Unknown
40.057	1.809	Dehydropinguisenol ( <b>145</b> )

#### 4.1.4. Liverworts of the La Réunion Island

##### 4.1.4.1. *Gottschia schizopleura* (Jungermanniaceae)

*Gottschia schizopleura* was collected at Foret de Beleuve on La Réunion Island. The biggest peak that appeared in the GC after 32.8 minutes could not be exactly identified but according to the mass spectra it could be a sesquiterpene alcohol. The compounds found in the ether extract of the *Gottschia schizopleura* are bicyclogermacrene (**127**) (Rt: 23.8min),  $\beta$ -elemene (**107**) (Rt:25.4min), isobazzanene (**203**) (Rt:26.7min),  $\beta$ -barbatene (**185**) (Rt:27min), valencene (**93**) (Rt:27.4min), germacrene D (**123**) (Rt:27.9min), bicyclogermacrene (**127**) (Rt:28.4min),  $\beta$ -bazzanene (**202**) (Rt:29min), viridiflorol (**153**) (Rt:30.3) and  $\beta$ -phenylethylcinnamate (**228**) (Rt:43.5min). A big peak that was detected after 56.2 minutes could not be identified.

Retention time (min)	Area %	Compound
23.832	1.557	Bicycloelemene ( <b>111</b> )
25.400	0.658	$\beta$ -Elemene ( <b>107</b> )
26.769	1.187	Isobazzanene ( <b>203</b> )
27.096	5.783	$\beta$ -Barbatene ( <b>185</b> )
27.448	1.895	Valencene ( <b>93</b> )
27.972	2.623	Germacrene D ( <b>123</b> )
28.401	3.955	Bicyclogermacrene ( <b>127</b> )
29.030	0.627	$\beta$ -Bazzanene ( <b>202</b> )
30.555	0.797	Viridiflorol ( <b>153</b> )
32.801	27.056	unidentified sesquiterpenealc.
43.525	1.682	$\beta$ -Phenylethylcinnamate ( <b>228</b> )
56.253	11.378	unknown

##### 4.1.4.2. *Plagiochila boryana* Gottsche in Steph. (Plagiochilaceae)

*Plagiochila boryana* has been collected at Le Petit Col on La Réunion Island and it showed pungent taste by chewing it. Plagiochilin C (**169**) and A (**151**) have been detected in the GC after 40 and after 42.7 minutes, respectively. The GC of the diethyl ether extract showed a main peak after 28.3 minutes which was identified as bicyclogermacrene (**127**) and the area extension of it was 13.4 %. Two peaks which

have been identified as fusicocca-2,5-diene (**192**) and fusicocca-3,5-diene (**193**) were detected in the GC-data. The first peak appeared after 36.7 minutes and after 42.2 minutes, respectively. Another characteristic compound for *P. boryana*, fusicogiganteopside (**194**), was also detected. The peak appeared after 45.8 minutes in the GC-data. A peak with a higher area extension appeared after 39.5 minutes and could not be identified. A few peaks that appeared after 42.9 minutes could not be identified. Thus spathulenol (**199**) and ent-spathulenol (**200**) were identified from the diethyl ether extract of the *P. boryana*.

Retention time (min)	Area %	Compound
23.829	5.311	Bicycloelemene ( <b>111</b> )
28.390	13.474	Bicyclogermacrene ( <b>127</b> )
30.535	0.939	ent-Spathulenol ( <b>200</b> )
36.707	1.163	Fusicocca-2,5-diene ( <b>192</b> )
39.589	8.076	Unknown
39.787	2.898	Unknown
40.086	1.081	Plagiochilin C ( <b>169</b> )
42.265	1.516	Fusicocca-3,5-diene ( <b>193</b> )
42.744	1.468	Plagiochiline A ( <b>170</b> )
42.941	3.090	Unknown
44.437	3.221	Unknown
44.734	4.414	Unknown
44.849	2.092	Unknown
45.817	5.706	Fusicogiganteopside ( <b>194</b> )
46.099	1.673	Spathulenol ( <b>199</b> )

#### 4.1.4.3. *Jamesoniella purpurascens* (Jungermanniaceae)

*Jamesoniella purpurascens* belongs to Jungermanniales, it was collected in Foret de Beleuve. A small amount has been used for the extraction with diethyl ether. The GC-MS analysis showed a characteristic big peak after 43.5 minutes, the area extension of the peak was 49.5 %. The mass spectra were not identical to any of the known mass spectra but it showed that the major compound of the *Jamesoniella purpurascens* is a diterpene alcohol. The next peak according to the retention time showed a diterpene alcohol. The compounds that could be identified from the extract

of *J. purpurascens* were 1-oct-3-enylacetate (**262**), bicyclogermacrene (**127**), anastreptene (**196**), and  $\beta$ -barbatene (**185**):

Retention time (min)	Area %	Compound
16.525	0.553	1-Oct-3-enylacetate ( <b>262</b> )
23.812	0.965	Germacrene-type sesquiterpene
24.408	3.543	Unknown
24.852	2.409	Anastreptene ( <b>196</b> )
27.025	0.814	$\beta$ -Barbatene ( <b>165</b> )
28.385	2.633	Bicyclogermacrene ( <b>127</b> )
36.593	2.372	Unknown
43.563	49.474	Diterpene alcohol
44.013	18.122	Diterpene alcohol
45.478	1.385	unknown
45.840	1.846	Unknown

## 4.2. Higher plants

### 4.2.1. Compositae (Asteraceae)

#### 4.2.1.1. *Artemisia vulgaris* L. var. *indica* Maxim

A large quantity of *Artemisia vulgaris* L. var. *indica* has been collected at the riverside of Akiigawa, Tokushima prefecture. The crude extract of a small amount of the plant has been used for the analysis therefore two extracting agents have been used: n-hexane and ether. The essential oil of this plant has been also analyzed. The essential oil has been obtained by steam distillation of a bigger amount of the plant which has been cut into small pieces.

A small amount of the fresh plant was separated into leaves, stem and flowers. Each part has been divided in two different mortars, than crushed and extracted with n-hexane and ether, respectively. A TLC of all extracts has been carried out. The TLC plate showed many interesting spots. After that, 1  $\mu$ l has been injected in the GC-MS apparatus. The obtained data showed a lot of peaks, every one of them has been compared to the mass spectra of known volatiles, though many of them could not be identified. Anyhow, no chamazulene was detected in any one of the plant parts.

#### -) n-Hexane extracts

##### Leaves

A small amount of the leaves has been cut, crushed in a mortar and extracted with n-hexane. The main peak on the GC-MS data was identified as  $\gamma$ -cadinene (**51**) with an area extension of 38.9% which appeared in the GC after 27 minutes. The next peak according to the area percentage was  $\beta$ -caryophyllene (**134**) whose area extension was 27.5%. These were by far the major components of the n-hexane extract of *Artemisia vulgaris* leaves. Monoterpenes found in this extract were camphene (**30**),  $\beta$ -pinene (**30**), sabinene (**28**), limonene (**2**), 1,8-cineole (**23**), camphor (**32**) and  $\alpha$ -pinene (**29**). Only the last two have an appearance of more than 6% and 1% of the area extension. A number of sesquiterpenes were found, predominantly germacrene type components and  $\alpha$ -humulene (**133**).

Retention Time (min)	Area %	Compound
10.402	1.365	$\alpha$ -Pinene ( <b>29</b> )
10.938	0.360	Camphene ( <b>30</b> )
11.957	0.724	$\beta$ -Pinene ( <b>30</b> )
12.409	0.665	Sabinene ( <b>28</b> )
13.806	0.450	Limonene ( <b>2</b> )
13.908	1.797	1,8-Cineole ( <b>23</b> )
17.159	0.349	iso-Chrysanthenone ( <b>33</b> )
17.931	6.425	Camphor ( <b>31</b> )
18.922	0.065	Unknown
22.248	0.227	Lavandylacetate ( <b>10</b> )
23.780	0.133	Bicycloelemene ( <b>111</b> )
24.835	0.597	$\alpha$ -Copaene ( <b>60</b> )
25.217	1.074	$\beta$ -Elemene ( <b>107</b> )
26.125	27.502	E- $\beta$ -Caryophyllene ( <b>134</b> )
26.321	0.165	Thujopsene ( <b>80</b> )
26.669	2.593	trans- $\beta$ -Bergamotene ( <b>116</b> )
26.866	7.714	$\alpha$ -Humulene ( <b>133</b> )
27.627	38.858	$\gamma$ - Cadinene ( <b>51</b> )
27.841	3.324	Bicyclogermacrene ( <b>127</b> )
28.298	0.205	Calamenene-derivative
28.999	0.181	Dodecanoic acid ( <b>263</b> )
29.063	0.143	Farnesal isomer I ( <b>278</b> )
29.594	2.396	5 $\alpha$ -Hydroxy-germacra-1 (10)5-diol ( <b>117</b> )
29.790	0.350	Caryophyllenoxide ( <b>136</b> )
30.074	0.223	Unknown
30.271	0.302	Cedrol ( <b>151</b> )
30.918	0.166	Germacra-4 (15)5,10 (14)triene-1 $\alpha$ -ol ( <b>118</b> )
32.118	0.770	Unknown
57.828	0.533	Squalene ( <b>287</b> )

## Stem

Fresh, mostly green stems of *Artemisia vulgaris* have been hacked and extracted with n-hexane. The peak with the biggest extension that appeared in the GC after a time of 27.3 min with an extension of 33.4% has been identified as germacrene D (**123**).  $\beta$ -Caryophyllene (**134**) has been detected at the time 25.9 min, 18.6% of the area. The highest area percentage of monoterpenes can be attributed to  $\alpha$ -pinene (**29**) which appeared after 10,3 in the GC with a 6.2 % of the area percentage. Other



components identified from the n-hexane extract of the *A. vulgaris* stem were: camphene (**30**), sabinene (**28**) (small amount),  $\beta$ -pinene (**30**), limonene (**2**), 1,8-cineole (**23**), camphor (**31**), lavandulyl acetate (**12**), and bicyclogermacrene (**127**).

Retention Time	Area %	Compound
10.360	6.197	$\alpha$ -Pinene ( <b>28</b> )
10.912	0.305	Camphene ( <b>30</b> )
11.808	0.329	Sabinene ( <b>28</b> )
11.936	4.496	$\beta$ -Pinene ( <b>26</b> )
12.396	1.084	Unknown
13.788	2.749	Limonene ( <b>2</b> )
13.885	0.996	1,8-Cineole ( <b>23</b> )
17.849	2.615	Camphor ( <b>31</b> )
22.243	1.059	Lavandulylacetate ( <b>12</b> )
25.117	0.769	Unknown
25.907	18.611	$\beta$ -Caryophyllene ( <b>134</b> )
26.509	4.718	(E)- $\beta$ -Farnesene ( <b>273</b> )
26.717	7.100	$\alpha$ -Humulene ( <b>133</b> )
27.363	33.405	Germacrene D ( <b>123</b> )
27.702	1.780	Bicyclogermacrene ( <b>127</b> )
29.489	1.128	4 $\alpha$ -Hydroxygermacra-1 (10)5-diol ( <b>130</b> )
46.054	1.291	Unknown
47.859	3.771	Unknown
52.180	1.120	Heptacosane ( <b>245</b> )
57.624	4.350	Squalene ( <b>287</b> )

## Flowers

Flowers of *Artemisia vulgaris* have been separated from leaves and stem than crushed and extracted with n-hexane. Camphor (**31**) is the major compound which appears after 17.9 minutes in the GC. Other compounds with a high area extension in the GC are  $\gamma$ -cadinene (**51**) (17<sup>th</sup> minute, 10.1 area %), helifolene (**48**) (27.8 min, 7.3 area %), (E)- $\beta$ -farnesene (**273**) (after 27 min, 6.8 area %),  $\beta$ -caryophyllene (**134**) (26<sup>th</sup> min 6.4 area %). Some aliphatic components were found as well. They appeared after 42.2 minutes in the GC. Nonadecane (**237**), tricosane (**239**), hexacosane (**238**) and heptacosane (**245**) could be identified. Many small peaks could be found in this GC, some of them could not be identified. The identified as

well as the unknown components are shown in the table bellow, listed according to their retention time.

Retention Time	Area %	Compound
10.386	1.020	$\alpha$ -Pinene ( <b>28</b> )
10.938	1.642	Camphene ( <b>30</b> )
11.950	0.476	$\beta$ -Pinene ( <b>29</b> )
12.403	0.623	$\beta$ -Myrcene ( <b>1</b> )
13.813	0.633	Limonene ( <b>2</b> )
13.914	4.321	1,8-Cineole ( <b>23</b> )
15.198	0.686	$\beta$ -Terpineol ( <b>14</b> )
16.306	0.856	Unknown
17.169	0.708	iso-Chrysanthenone ( <b>33</b> )
17.992	27.392	Camphor ( <b>31</b> )
19.996	1.081	Unknown
20.170	0.997	trans-Piperitol ( <b>16</b> )
22.251	1.206	Lavandylacetate ( <b>10</b> )
23.805	0.416	$\gamma$ -Terpineol ( <b>15</b> )
24.109	0.332	$\delta$ -Elemene ( <b>108</b> )
26.355	6.373	$\beta$ -Caryophyllene ( <b>119</b> )
26.789	1.24	trans- $\beta$ -Bergamotene ( <b>116</b> )
27.062	6.903	(E)- $\beta$ -Farnesene ( <b>273</b> )
27.275	1.544	$\alpha$ -Humulene ( <b>133</b> )
27.825	7.304	Helifolene ( <b>48</b> )
28.054	10.147	$\gamma$ -Cadinene ( <b>51</b> )
28.201	1.495	$\beta$ -Selinene ( <b>69</b> )
28.410	0.714	Bicyclogermacrene 2 ( <b>127</b> )
30.337	1.277	4 $\alpha$ -Hydroxygermacra-1 (10)5-diol ( <b>130</b> )
41.882	0.732	Unknown
42.192	4.588	Unknown
43.262	0.738	Tricosane ( <b>239</b> )
44.225	1.319	Unknown
47.240	2.52	Nonadecane ( <b>237</b> )
49.871	0.967	Hexacosane ( <b>238</b> )
53.342	6.652	Heptacosane ( <b>245</b> )

## -) Diethyl ether extracts

### Leaves

The ether extract of the *Artemisia vulgaris* leaves showed the main peak after 19 min with 19 % of the area, this peak has been identified as  $\gamma$ -cadinene (**51**). Peaks with a high extension were also detected after 26.3, 27.2, 28.6, and 44.7 minutes. The first two peaks were identified as  $\beta$ -caryophyllene (**134**) and  $\alpha$ -humulene (**133**) and the second two peaks were unknown compounds.  $\beta$ -Caryophyllene (**134**),  $\alpha$ -humulene (**133**) and (E)- $\beta$ -farnesene (**273**) appeared in the GC at a higher percentage. Other identified compounds with a lower percentage were: 1,8-cineole (**23**), camphor (**31**),  $\gamma$ -cuprenene (**207**), curcumene (**95**),  $\beta$ -acoradiene (**112**), caryophyllenoxide (**136**), 4 $\alpha$ -hydroxygermacra-1(10)5-diene (**130**),  $\beta$ -bisabolol (**102**) and guaia-3,7(11)10(14)-triene-6,12-olide (**184**). Phytol (**286**) and other decomposition products of chlorophyll were also detected. The peaks that appeared in the GC after 44.7 minutes could not be identified.

Retention Time (min)	Area %	Compound
13.886	1.346	1,8-Cineole ( <b>23</b> )
17.853	2.379	Camphor ( <b>31</b> )
26.322	18.290	$\beta$ -Caryophyllene ( <b>134</b> )
27.011	4.552	(E) $\beta$ - Farnesene ( <b>273</b> )
27.252	5.128	$\alpha$ -Humulene ( <b>133</b> )
27.752	1.698	$\gamma$ -Cuprenene ( <b>207</b> )
27.828	1.113	Curcumene ( <b>95</b> )
27.984	19.036	$\gamma$ -Cadinene ( <b>51</b> )
28.144	1.514	$\beta$ -Acoradiene ( <b>112</b> )
28.383	1.375	Bicyclogermacrene ( <b>127</b> )
28.616	6.519	Unknown
30.476	2.692	4 $\alpha$ -Hydroxygermacra-1(10)5-diene ( <b>130</b> )
30.707	1.834	Caryophyllenoxide ( <b>136</b> )
35.120	0.791	$\beta$ -Bisabolol ( <b>102</b> )
35.861	6.163	Neophytadiene isomer I ( <b>288</b> )
36.318	0.915	Neophytadiene isomer II ( <b>289</b> )
36.658	1.854	Neophytadiene isomer III ( <b>290</b> )
41.697	1.797	Phytol ( <b>286</b> )
42.278	2.542	Guaia-3,7 (11)10 (14)-triene-6,12-olide ( <b>184</b> )
44.728	6.092	Unknown

44.909	4.013	Unknown
47.258	1.062	Unknown
47.803	1.398	Unknown
49.291	3.085	Unknown
54.162	1.934	Unknown

## Stem

The GC-MS analysis of the *A. vulgaris* stem showed a lot of peaks. Thus a lot of them could not be identified. The unknown components appeared in the GC after the 41<sup>st</sup> min. The main peak appeared after 44 minutes and which could neither be identified. Two big peaks appeared in the GC after 26 and 27 minutes. They were identified as  $\beta$ -caryophyllene (**134**) and  $\gamma$ -cadinene (**51**).  $\alpha$ -Humulene (**133**) and (E)- $\beta$ -farnesene (**273**) were also found in this data. Their peaks appeared both on the 28<sup>th</sup> minute.  $\beta$ -Pinene (**29**), camphor (**31**), fenchylacetate (**47**) and pimaradiene (**220**) were also found in the GC, in a very low percentage, though. Neophytadiene isomer I (**288**), and the isomeres II (**289**), III (**290**) and Phytol (**286**) (3,7,11,15-Tetramethyl-2-hexadecene-1-ol) appeared between the 35<sup>th</sup> and the 37<sup>th</sup> minute in the GC.

Retention Time	Area %	Compound
4.306	9.306	2-Heptanol ( <b>254</b> )
11.926	0.438	$\beta$ -Pinene ( <b>29</b> )
17.854	0.866	Camphor ( <b>31</b> )
26.316	9.159	$\beta$ -Caryophyllene ( <b>134</b> )
27.011	2.233	(E)- $\beta$ -Farnesene ( <b>273</b> )
27.248	2.785	$\alpha$ -Humulene ( <b>133</b> )
27.977	8.664	$\gamma$ -Cadinene ( <b>51</b> )
28.613	9.89	Unknown
30.371	0.606	Fenchylacetate ( <b>47</b> )
35.429	4.917	Neophytadiene isomer I ( <b>288</b> )
35.555	0.398	Neophytadiene isomer II ( <b>289</b> )
35.898	0.895	Neophytadiene isomer III ( <b>290</b> )
36.238	1.514	3,7,11,15-Tetramethyl-2-hexadecene-1-ol ( <b>275</b> )
38.256	0.748	Pimaradiene ( <b>220</b> )
43.601	1.141	Unknown
43.688	1.195	Unknown
43.983	1.161	Unknown
44.335	12.971	Unknown

44.724	1.341	Unknown
45.032	1.177	Unknown
45.646	1.195	Unknown
45.937	1.279	Unknown
46.085	1.259	Unknown
46.323	1.212	Unknown
46.736	1.430	Unknown
46.917	2.928	Unknown
47.376	1.972	Unknown
47.457	2.184	Unknown
48.906	4.250	Unknown
53.655	2.820	Eicosane ( <b>235</b> )

## Flowers

Flowers of *A. vulgaris* have been crushed and extracted with diethyl ether. The GC-MS data showed a high presence of aliphatic compounds which appeared after 44 minutes. Anyhow the biggest peak in the GC was identified as squalene (**287**). Its peak has been detected after 40 minutes and the area extension was 15.6%. Compounds with a higher area percentage that have been detected were  $\gamma$ -cadinene (**45**),  $\beta$ -caryophyllene (**134**) and guaia-3,7(11),10(14)-triene-6,12-diole (**184**). Other identified components from the diethyl ether extract of *A. vulgaris* flowers were 1,8-cineole (**23**), borneol (**44**), bornyl acetate (**45**), camphor (**31**),  $\alpha$ -humulene (**133**),  $\beta$ -bisabolol (**102**) etc.

Retention Time	Area %	Compound
13.730	0.510	1,8-Cineole ( <b>23</b> )
17.778	3.495	Camphor ( <b>31</b> )
19.400	0.359	Borneol ( <b>45</b> )
22.247	0.246	Bornylacetate ( <b>45</b> )
26.307	5.933	$\beta$ -Caryophyllene ( <b>119</b> )
26.763	0.233	(E)- $\beta$ -Farnesene ( <b>273</b> )
27.246	2.082	$\alpha$ -Humulene ( <b>133</b> )
27.976	5.366	$\gamma$ -Cadinene ( <b>51</b> )
28.143	0.424	cis- $\alpha$ -Bergamotene ( <b>115</b> )
28.381	0.435	Bicyclogermacrene ( <b>127</b> )
28.613	4.223	Unknown
30.472	1.024	4 $\alpha$ -Hydroxygermacra-1 (10)5-diene ( <b>130</b> )

30.703	1.652	Caryophyllenoxide ( <b>120</b> )
35.357	0.618	$\beta$ -Bisabolol ( <b>102</b> )
35.530	0.502	7-epi-Bisabolol ( <b>101</b> )
36.213	0.930	Neophytadiene isomer I ( <b>288</b> )
37.132	0.345	Neophytadiene isomer III ( <b>290</b> )
40.219	15.589	Squalene ( <b>287</b> )
40.905	1.447	Unknown
42.805	5.904	Guaia-3,7 (11),10 (14)-triene-6,12-diole ( <b>184</b> )
43.117	2.748	4 (15)-Dehydroglobulol ( <b>190</b> )
44.195	1.473	n-Octadecane ( <b>240</b> )
44.412	1.620	Unknown
44.561	1.489	Unknown
44.887	1.389	Unknown
45.286	7.415	Unknown
45.486	12.722	n-Heneicosane ( <b>239</b> )
48.418	3.335	Eicosane ( <b>235</b> )
49.968	2.863	Unknown
51.318	1.159	Unknown
55.035	8.516	Unknown

## Cortex

The cortex has been scratched down by a knife and extracted with diethyl ether. A strong smell was present during scratching by the knife. There have been 12 g used for the extraction which were divided in small amounts. Each one of them has been given into an Erlenmeyer-flask with ca. 20 ml of ether. The mixture was treated with an ultrasonic bath for 5 min. After an extracting time of 5 days the mixtures were filtrated. TLC and GC-MS were carried out. The major component found in the data was  $\beta$ -longipinene (**150**). Its peak appeared after 28.1 minutes and has an area extension of 27.2 %. Other components identified from the GC-MS data are:  $\beta$ -caryophyllene (**134**) (Rt: 26.3 min; 5.6 %), (E)- $\beta$ -farnesene (**273**) (Rt:27min; 4.5%), (E)- $\beta$ -bisabolene (**98**) (Rt:27.3 min;3.4%), ar-curcumene (**95**) (Rt:27.8min; 2.8%) and 4 $\alpha$ -hydroxygermacra-1(10),5-diol (**130**). A few peaks could not be identified.

Retention Time	Area %	Compound
26.372	5.616	Caryophyllene ( <b>119</b> )
27.070	4.522	(E)- $\beta$ -Farnesene ( <b>273</b> )
27.308	3.435	(E)- $\beta$ -Bisabolene ( <b>98</b> )
27.895	2.830	ar-Curcumene ( <b>95</b> )
28.117	27.203	$\beta$ -Longipinene ( <b>150</b> )
28.672	4.489	Unknown
30.531	1.213	4 $\alpha$ -Hydroxygermacra-1 (10),5-diol ( <b>130</b> )
32.453	1.923	Unknown
36.282	9.180	Neophytadiene isomer I ( <b>288</b> )
36.811	2.687	Unknown
37.213	3.520	Unknown

### Essential oil

The essential oil of the *A. vulgaris* was obtained by steam distillation. 16.7 kg of the dried and hackled plant were steam-distilled in 18 days. The obtained oil had a very strong smell and its color was dark green. The color did not change to blue as expected. A drop of the essential oil that has been diluted with ether has been used for the GC-MS analysis. TLC has been also carried out. The main peak appeared after 26 minutes and was identified as  $\beta$ -caryophyllene (**134**). A big peak appeared after 27 minutes with an area percentage of 10 % which has been identified as germacrene D (**123**). Caryophylleneoxide (**120**) was also detected. The peak appeared in the GC after 29.8 minutes. Other components found were: camphene (**30**), 1,8-cineole (**23**), camphor (**31**), artemisyl acetate (**234**), bornylacetate (**45**), germacrene B (**125**) etc. All peaks detected on this data could be identified, however no chamazulene was found.

Retention Time	Area %	Compound
10.340	0.702	$\alpha$ -Pinene ( <b>28</b> )
10.895	1.104	Camphene ( <b>30</b> )
11.919	0.652	$\beta$ -Pinene ( <b>30</b> )
13.88	2.325	1,8-Cineole ( <b>23</b> )
17.871	3.401	Camphor ( <b>31</b> )
18.560	2.058	Artemisylacetate ( <b>234</b> )
21.471	0.962	cis-Chrysantenylacetate ( <b>34</b> )

22.260	1.424	Bornylacetate ( <b>45</b> )
24.054	1.218	Germacrene B ( <b>125</b> )
25.217	0.638	$\gamma$ -Gurjunene ( <b>155</b> )
26.127	27.501	$\beta$ -Caryophyllene ( <b>134</b> )
26.340	1.603	Thujopsene ( <b>80</b> )
26.646	4.712	(E)- $\beta$ -Farnesene ( <b>273</b> )
26.867	7.685	$\alpha$ -Caryophyllene (133)
27.297	3.274	$\beta$ -Acoradiene ( <b>112</b> )
27.516	11.983	Germacrene D ( <b>123</b> )
27.602	2.045	Zingiberene ( <b>104</b> )
27.799	2.039	cis- $\alpha$ -Bergamotene ( <b>115</b> )
28.320	1.469	Calamene-derivative
28.597	1.901	Caryophylla-3 (15),7 (14)-diene-6-ol ( <b>135</b> )
29.072	0.469	E-Nerodiol ( <b>11</b> )
29.809	4.907	Caryophyllenoxide ( <b>136</b> )
30.279	0.947	Cedrol ( <b>151</b> )
30.341	0.818	Humulenepoxide II ( <b>137</b> )
30.967	0.820	Cubebol ( <b>76</b> )
31.253	2.100	T-Muurolol ( <b>67</b> )
32.163	0.540	Hexadecanal ( <b>258</b> )

### *Artemisia* sp. -the young and fresh plant

The young plant of *A. vulgaris* plant has been collected in Tokushima prefecture. After separating it in leaves and stem, a small amount of each part has been extracted with diethyl ether. The GC-MS analysis showed a high presence of mono-and sesquiterpenes.

#### Leaves

The ether extract of leaves showed the main peak after 27 minutes with a high area percentage. This peak was identified as germacrene D (**123**) and has an area extension of 20.5%. According to the area percentage the next peak was  $\beta$ -caryophyllene (**134**), it appeared after 26 min and had an area percentage of 11.2%. Two big peaks which appeared after 21 and 42 minutes were identified as cis-chrysanthenacetate (**34**) (7.7 area %) and phytol (**286**) (6.8 area %). Another big peak was detected after 43.7 minutes but could not be identified. The decomposition product of chlorophyll, neophytadiene and its isomers (**288**), (**289**) and (**290**) were



detected after the 36 minutes. Many other mono- and sesquiterpenes have been found, they are listed in the table bellow.

Retention Time	Area %	Compound
11.941	0.570	$\beta$ -Pinene ( <b>30</b> )
13.672	0.756	Unknown
13.883	2.587	1,8-Cineole ( <b>23</b> )
18.860	3.075	cis-Chrysanthenol ( <b>32</b> )
21.078	7.670	cis-Chrysanthencetate ( <b>34</b> )
26.300	11.243	$\beta$ -Caryophyllene ( <b>134</b> )
27.000	5.851	$\beta$ -Farnesene ( <b>273</b> )
27.236	2.715	$\alpha$ -Humulene ( <b>133</b> )
27.969	20.556	Germacrene D ( <b>123</b> )
28.131	1.494	$\beta$ -Selinene ( <b>69</b> )
28.374	1.511	Unknown
30.455	3.591	4 $\alpha$ -Hydroxygermacra-1 (10),5-diol ( <b>130</b> )
30.796	3.367	Unknown
36.208	6.808	Neophytadiene isomer I ( <b>288</b> )
36.745	1.229	Neophytadiene isomer II ( <b>289</b> )
37.145	2.182	Neophytadiene isomer III ( <b>290</b> )
41.479	2.455	Unknown
42.605	6.811	Phytol ( <b>286</b> )
43.746	8.929	Unknown
45.982	4.783	Unknown

## Stem

The green stem of *Artemisa* sp. has been cut in small pieces than crushed in a mortar and extracted with ether. A big peak with a high area extension appeared after 27.9 minutes with an area percentage of 9.1 % which was identified as germacrene D (**123**). Monoterpenes detected in the GC were identified as  $\alpha$ - (**29**) and  $\beta$ -pinene (**30**). Their peaks appeared after 10.4 and 11.9 minutes. The methyl ester of the elaidic acid (**269**) appeared in the GC after 44.3 minutes and has a very low area extension. (E)- $\beta$ -Caryophyllene (**134**) was also detected, retention time 26.3 minutes.

Retention Time	Area %	Compound
6.227	8.039	2-Heptanol ( <b>254</b> )
10.368	5.688	$\alpha$ -Pinene ( <b>29</b> )
11.939	4.870	$\beta$ -Pinene ( <b>30</b> )

26.292	4.644	(E)- $\beta$ -Caryophyllene ( <b>134</b> )
27.958	9.078	Germacrene D ( <b>123</b> )
36.203	31.500	Neophytadiene isomer I ( <b>288</b> )
36.744	3.243	Neophytadiene isomer II ( <b>289</b> )
37.139	10.251	Neophytadiene isomer III ( <b>290</b> )
44.315	0.132	Elaidic acid methyl ester ( <b>269</b> )
52.667	10.420	Unknown

#### 4.2.1.2. *Farfugium japonicum* (L.) Kitam

*Farfugium japonicum* was collected on October, 24<sup>th</sup>, 2008 in Tokushima prefecture. Leaves, stem and flowers were separated and extracted with diethyl ether.

##### Leaves

The ether extract of the leaves of *F. japonicum* showed a lot of peaks in the GC which in total could not be identified. 1-Nonadecene (**244**) showed the main peak. It was detected after 16 minutes and it has an area extension of 18.5%.  $\beta$ -Caryophyllene was also detected, its peak appeared in the GC after 26 minutes.  $\gamma$ -Cadinene (**51**) appeared after 28 minutes in the GC. The peaks of the unknown components appeared on the date after 36.2 minutes except for the peak that was detected after 40 minutes, which was identified as diplophillin (**163**).

Retention Time	Area %	Compound
6.247	3.638	2-Heptanol ( <b>254</b> )
15.928	18.555	1-Nonadecene ( <b>244</b> )
26.357	9.053	$\beta$ -Caryophyllene ( <b>133</b> )
28.015	3.089	$\gamma$ -Cadinene ( <b>51</b> )
36.261	16.530	Unknown
36.797	2.446	Unknown
37.199	4.750	Unknown
40.092	2.904	Diplophillin ( <b>163</b> )
41.571	3.340	Unknown
41.954	3.466	Unknown
42.188	2.643	Unknown
42.977	6.435	Unknown
44.885	5.059	Unknown
46.994	3.246	Unknown

48.902	5.650	Unknown
51.888	9.195	Unknown

## Stem

A small amount of *F. japonicum* stem has been cut in small pieces than crushed in a mortar and extracted with diethyl ether. There were a lot of peaks detected in the GC. Most of these peaks could not be identified. They appear mostly after 40 minutes though. Diplohillin (**163**) was identified at a retention time of 40.1 minutes. Furanopolyhydronaphthalene derivatives were detected after 40.5 minutes. It was not possible to find out the exact structure of the compound. Sesquiphellandrene (**103**) was detected after 43 minutes. Two aliphatic components, non-1-ene (**243**) and E-2-octanal (**256**) were found after 8.7 and 15 minutes.

Retention Time	Area %	Compound
6.179	13.025	2-Heptanol ( <b>254</b> )
8.784	4.711	Non-1-ene ( <b>243</b> )
15.929	5.904	E-2-Octanal ( <b>256</b> )
28.661	1.862	Unknown
35.609	1.309	Unknown
40.172	1.614	Diplohillin ( <b>163</b> )
40.508	1.919	Furanopolyhydronaphthalene derivative
41.467	1.474	Unknown
42.971	4.006	Sesquiphellandrene ( <b>103</b> )
43.289	1.743	Unknown
43.576	1.189	Unknown
43.860	1.425	Unknown
44.138	12.399	Unknown
44.399	2.469	Unknown
44.588	3.379	Unknown
44.831	1.376	Unknown
45.398	1.199	Unknown
46.033	3.804	Unknown
47.302	4.218	Unknown
48.111	1.464	Unknown
48.291	6.595	Unknown
48.485	1.893	Unknown
48.556	1.848	Unknown

48.882	9.117	Unknown
49.075	2.560	Unknown

## Flowers

The major compound of the volatile components of the *F. japonicum* flowers was identified as isopingiusanine (**143**), which appeared in the GC after 43 minutes and has an area extension of 43.8%. The peaks which appeared in the GC after 26.3, 28, 34.8 and 44.3 minutes were identified as  $\beta$ -caryophyllene (**134**),  $\gamma$ -cadinene (**51**), furanoeremophyllone (**167**) and acutifolene A (**146**).

Retention Time	Area %	Compound
15.600	3.171	1-Undecene ( <b>238</b> )
26.334	1.013	$\beta$ -Caryophyllene ( <b>134</b> )
28.008	0.756	$\gamma$ -Cadinene ( <b>51</b> )
34.056	2.258	Unknown
34.799	1.079	Furanoeremophyllone ( <b>167</b> )
35.841	3.580	Unknown
43.077	1.254	Unknown
43.507	1.156	Unknown
44.047	1.045	Unknown
44.295	1.851	Acutifolene A ( <b>146</b> )
44.417	3.820	Unknown
44.722	14.645	Unknown
45.882	1.018	Unknown
47.443	43.819	Isopingiusanine ( <b>143</b> )
47.951	2.835	Unknown
48.256	4.247	Nonadecane ( <b>237</b> )
49.591	8.382	Unknown
54.816	2.533	Heptacosane ( <b>245</b> )

#### 4.2.1.3. *Petasites japonicus* F. Schmidt

*Petasites japonicus* was collected in Tokushima prefecture. After the separation into leaves and rhizome, a small amount of each part of the plant has been crushed and extracted with ether. A characteristic smell was present during the crushing and the extraction of the rhizome.

##### Leaves

The ether extract of the leaves of *P. japonicus* showed a lot of unknown components in the GC. Though,  $\beta$ -caryophyllene (**134**),  $\gamma$ -cadinene (**51**) and (E)- $\alpha$ -bisabolene (**97**) were identified and their retention time was 25, 27 and 26.7 minutes. A low percentage of cis-cadine-4,6-diene-11-ol (**58**) was also found. Its peak appeared in the GC after 46.7 minutes. The peaks that were detected after 48.6 minutes were unknown components. The biggest peak in the GC appeared after 53 minutes which was neither identified.

Retention Time	Area %	Compound
25.040	0.916	$\beta$ -Caryophyllene ( <b>134</b> )
27.037	1.136	$\gamma$ -Cadinene ( <b>51</b> )
28.699	0.718	(E) $\alpha$ -Bisabolene ( <b>97</b> )
36.248	1.612	Neophytadiene isomer I ( <b>288</b> )
37.188	0.604	Neophytadiene isomer III ( <b>290</b> )
46.702	0.676	cis-Cadina-4,6-diene-11-ol ( <b>58</b> )
48.633	0.761	Unknown
49.316	3.024	Unknown
51.954	1.438	Unknown
53.670	84.315	Unknown
56.024	2.294	Unknown
56.645	1.005	Unknown

##### Rhizome

The subterranean part of the plant has been purified from soil, other plant parts and other impurities and after that crushed and extracted with diethyl ether. Pinguisanene (**141**) was detected after 37 minutes and it had an area extension of 9.5%. Another peak with a high area extension was detected after 46.1 minutes which was not

exactly identified but according to the mass spectra, it could be a pinguisanine (**142**) type derivative. A big peak appeared after 37.8 minutes which has been identified as muurola-4,10(5)diene-8 $\alpha$ -ol (**66**). The peak with the highest area extension was detected after 48.5 minutes and could not be identified. A big peak found after 38.4 minutes was identified as isopatchuola-3,5-diene (**198**).

Retention Time	Area %	Compound
8.591	1.882	1-Hexanol ( <b>246</b> )
10.657	5.010	Unknown
28.120	0.396	Valencene ( <b>93</b> )
37.033	9.550	Pinguisanene ( <b>141</b> )
37.813	13.364	Muurola-4,10(5)-diene-8 $\alpha$ -ol ( <b>66</b> )
38.436	11.096	Isopatchuola-3,5-diene ( <b>198</b> )
42.880	1.019	Unknown
44.093	0.883	Unknown
44.874	0.402	Unknown
45.02	0.535	Unknown
45.248	0.739	Unknown
46.151	16.381	Pinguisanine derivative
46.405	1.222	Unknown
46.756	1.935	Unknown
47.578	1.531	Unknown
48.571	28.883	Unknown
53.356	5.171	Unknown

#### 4.2.1.4. *Solidago altissima*

*Solidago altissima* was collected in the riverside of Akuigawa, Tokushima. The plant was separated into leaves, stem, flowers and roots. The leaves showed a high percentage of germacrene B (**125**), whose peak appeared after 28 minutes in the GC and has an area extension of 77.5%. Other identified compounds from the diethyl ether extract of *S. altissima* leaves were  $\alpha$ -pinene (**29**), limonene (**2**),  $\beta$ -elemene (**107**),  $\gamma$ -cadinene (**51**),  $\beta$ -ylangene (**117**), germacrene D (**110**) and (Z)- $\gamma$ -bisabolene (**99**) which had a higher area extension. Meanwhile sabinene (**28**) and isobornylacetate (**46**) were also found, in a low area percentage, though. An unidentified peak appeared after 28.6 minutes in the GC.

Retention Time	Area %	Compound
10.401	3.488	$\alpha$ -Pinene ( <b>29</b> )
11.851	0.964	Sabinene ( <b>28</b> )
13.833	1.481	Limonene ( <b>2</b> )
22.316	0.980	Isobornylacetate ( <b>46</b> )
23.879	1.786	$\beta$ -Elemene ( <b>107</b> )
25.436	2.712	$\gamma$ -Cadinene ( <b>51</b> )
26.324	3.679	$\beta$ -Ylangene ( <b>117</b> )
26.597	1.469	Germacrene D ( <b>123</b> )
27.289	1.422	(Z)- $\gamma$ -Bisabolene ( <b>99</b> )
28.038	77.539	Germacrene B ( <b>125</b> )
28.652	1.240	Unknown
35.886	3.239	Neophytadiene isomer I ( <b>288</b> )

## Stem

The stem of *Solidago altissima* that was almost lignified was hackled into small parts and then extracted with diethyl ether. The major compound of this extract seemed to be  $\gamma$ -cadinene (**51**) with 50.8 % of the area percentage. The first peak in the GC was identified as  $\alpha$ -pinene (**29**). it appeared in the GC after 10.4 minutes and had an area extension of 7%. Sabinene (**28**) and limonene (**2**) were also found in the GC. Their peaks appeared after 11.8 and 13.8 minutes and their area extensions were 3% each.  $\beta$ -Ylangene (**117**) was detected after 26.3 minutes. An unknown peak was detected after 39 minutes in the GC.

Retention Time	Area %	Compound
10.400	7.035	$\alpha$ -Pinene ( <b>29</b> )
11.849	3.139	Sabinene ( <b>28</b> )
13.827	3.097	Limonene ( <b>2</b> )
26.313	5.135	$\beta$ -Ylangene ( <b>117</b> )
28.032	50.887	$\gamma$ -Cadinene ( <b>51</b> )
39.064	5.763	Unknown
56.581	0.873	Nonadecane ( <b>237</b> )

## Flowers

The yellow colored flowers were separated from stalk and leaves. The extract had an intensely yellow color. In analogy to the stem, the major compound was identified as  $\gamma$ -cadinene (**51**) its percentage in the flowers is much lower than in the stem extract, although.  $\alpha$ -Pinene (**29**), sabinene (**28**),  $\beta$ -pinene (**30**),  $\beta$ -myrcene (**1**), limonene (**2**) and other components were found in the GC. Their retention time and the area extension are listed in the table below. Two peaks of aliphatic compounds appeared in the GC, after 48.2 and 54.7 minutes.

Retention Time	Area %	Compound
10.380	9.879	$\alpha$ -Pinene ( <b>29</b> )
11.833	1.142	Sabinene ( <b>28</b> )
11.963	0.662	$\beta$ -Pinene ( <b>30</b> )
12.427	3.788	$\beta$ -Myrcene ( <b>1</b> )
13.820	5.869	Limonene ( <b>2</b> )
23.881	0.588	2-Carene ( <b>25</b> )
25.442	0.705	Unknown
26.320	1.330	$\gamma$ -Ylangene ( <b>117</b> )
26.605	0.515	Unknown
28.030	29.804	$\gamma$ -Cadinene ( <b>51</b> )
28.658	0.700	Unknown
36.104	0.480	Neophytadiene isomer I ( <b>288</b> )
40.531	6.068	Neophytadiene isomer II ( <b>289</b> )
40.565	4.214	Neophytadiene isomer III ( <b>290</b> )
40.706	1.072	Unknown
40.895	8.944	Unknown
40.919	14.03	Unknown
48.225	5.543	Eicosane ( <b>235</b> )
54.795	3.925	Unidentified aliphatic compound

## Roots

A small amount of roots was purified from soil and other impurities. After washing the roots were cut in small pieces and extracted with diethyl ether. The identified components of the diethyl ether extract of the *S. altissima* roots were  $\gamma$ -cadinene (**45**), limonene (**2**), cadina-3,5-diene (**55**), muurola-4,10(5)-diene-8 $\alpha$ -ol (**66**),  $\alpha$ -cubebene



(**59**) and  $\alpha$ -pinene (**29**). Nevertheless, the most of the detected peaks could not be identified, the major component included (Rt.: 43.2 min).

The main compound and a lot of other compounds of this extract could not be identified. The major peak appeared in the GC after 43 minutes with an area extension of 25.1%. Another big peak which appeared in the GC after 32.1 minutes could not be identified. All mass spectras of the peaks that have a higher retention time as 31.5 minutes were not found in the MS-library.

Retention Time	Area %	Compound
10.397	0.561	$\alpha$ -Pinene ( <b>29</b> )
13.821	3.082	Limonene ( <b>2</b> )
24.223	0.937	$\alpha$ -Cubebene ( <b>59</b> )
25.417	2.456	Cadina-3,5-diene ( <b>55</b> )
27.748	1.055	Valerene-type comp.
28.007	4.531	$\gamma$ -Cadinene ( <b>51</b> )
28.638	1.474	Unknown
30.389	2.412	Muurola-4,10(5)-diene-8 $\alpha$ -ol ( <b>66</b> )
31.584	1.779	Unknown
32.128	22.439	Unknown
41.583	5.464	Unknown
42.82	0.707	Unknown
43.173	25.162	Unknown
43.487	2.420	Unknown
44.362	9.404	Unknown
44.736	1.008	Unknown
45.088	1.307	Unknown
46.562	1.954	Unknown
47.146	3.582	Unknown
47.517	2.080	Unknown
48.122	3.829	Unknown
51.713	1.645	Unknown

#### 4.2.1.5. *Solidago virgaurea*

*Solidago virgaurea* was collected in a small field near Tokushima Bunri University on October, 31<sup>st</sup> 2008. The plant was separated into leaves, stem, flowers and roots. Leaves were purified, crushed and extracted with diethyl ether. Main compound of the leaves extract was germacrene B (**125**) with an area extension 61.94%. Other compounds, sesquiterpenoids such as  $\beta$ -caryophyllene (**134**) germacrene D (**110**),  $\beta$ -cadinene (**50**), and the monoterpenes  $\alpha$ -pinene (**29**),  $\beta$ -myrcene (**1**), limonene (**2**) and bornylacetate (**45**) were also found in much lower percentage although. Two peaks detected after 32 minutes and three other peaks detected after 37.2 minutes were unknown components.

#### Leaves

Retention Time	Area %	Compound
6.315	2.882	2-Heptanol ( <b>254</b> )
10.430	1.036	$\alpha$ -Pinene ( <b>29</b> )
12.456	0.652	$\beta$ -Myrcene ( <b>1</b> )
13.844	0.724	Limonene ( <b>2</b> )
22.317	2.313	Bornylacetate ( <b>45</b> )
25.461	2.146	$\beta$ -Elemene ( <b>107</b> )
26.346	4.888	$\beta$ -Caryophyllene ( <b>134</b> )
26.601	1.174	Germacrene D ( <b>123</b> )
27.929	1.499	$\beta$ -Cadinene ( <b>50</b> )
28.133	61.935	Germacrene B ( <b>125</b> )
28.529	0.958	$\alpha$ -Humulene ( <b>133</b> )
32.024	0.858	Unknown
33.712	1.141	Unknown
36.265	3.968	Phytol derivatives
37.195	0.956	Unknown
42.707	9.198	Unknown
53.455	3.761	Unknown

#### Flowers

Flowers of *S. virgaurea* were purified, cut, crushed in a mortar and extracted with diethyl ether. The main compound appeared after a retention time of 28.1 minutes with 62.7 % of the area extension and the mass spectra was identical to the one of

germacrene B (**125**).  $\alpha$ -Humulene (**133**) was detected after 26.3 minutes and its area extension was 10.2%. Other peaks identified from the data were the peak after 10.4 minutes identified as  $\alpha$ -pinene (**29**), after 12.4 minutes identified as  $\beta$ -myrcene (**1**), after 13.8 minutes identified as limonene (**2**), the peak after 22.3 minutes identified as bornylacetate (**45**), after 25.4 minutes  $\beta$ -elemene (**107**), etc. Isogermacrene D (**124**) was also identified and its peak appeared in the GC after 28.5 minutes. Eicosane (**235**) was the only one aliphatic compound found in the GC.

Retention Time	Area %	Compound
6.311	5.204	2-Heptanol ( <b>254</b> )
10.413	0.721	$\alpha$ -Pinene ( <b>29</b> )
12.450	2.486	$\beta$ -Myrcene ( <b>1</b> )
13.842	1.179	Limonene ( <b>2</b> )
22.326	1.950	Bornylacetate ( <b>45</b> )
25.475	3.912	$\beta$ -Elemene ( <b>107</b> )
26.366	10.202	$\beta$ -Caryophyllene ( <b>82</b> )
26.611	2.362	$\gamma$ -Cadinene ( <b>51</b> )
27.032	0.956	Unknown
27.300	2.243	Valencene ( <b>93</b> )
27.548	0.906	Unknown
28.129	62.699	Germacrene B ( <b>125</b> )
28.536	2.509	Isogermacrene D ( <b>124</b> )
28.662	1.091	Unknown
50.875	1.582	Eicosane ( <b>235</b> )

## Roots

A small amount of the *S.virgaurea* roots were purified and extracted with diethyl ether. The identified components were  $\alpha$ -pinene (**29**) (two peaks after 10.4min and after 12 min), sabinene (**28**) (Rt:11.8min), a very low percentage of  $\beta$ -myrcene (**1**),  $\beta$ -caryophyllene (**134**), anastreptene (**196**), limonene (**2**) (Rt:13.8min),  $\gamma$ -cadinene (**45**) (Rt:25.4) and  $\alpha$ -guaiene (**182**) (Rt:27.7min). The mass spectra of the major components of the *S.virgaurea* roots did not match to any of the mass spectra from the MS-library.

Retention Time	Area %	Compound
6.410	1.104	2-Heptanol ( <b>254</b> )
10.428	1.028	$\alpha$ -Pinene ( <b>28</b> )
11.870	0.220	Sabinene ( <b>28</b> )
12.005	1.289	$\beta$ -Pinene ( <b>29</b> )
12.453	0.308	$\beta$ -Myrcene ( <b>1</b> )
13.893	4.444	Limonene ( <b>2</b> )
25.458	0.451	$\gamma$ -Cadinene ( <b>45</b> )
26.35	0.218	$\beta$ -Caryophyllene ( <b>134</b> )
27.793	0.801	$\alpha$ -Guaiene ( <b>182</b> )
28.064	1.492	Unknown
29.248	0.278	Anastreptene ( <b>196</b> )
32.171	1.856	Unknown
52.677	4.496	Unknown
43.393	9.922	Unknown
43.654	1.857	Unknown
44.601	4.070	Unknown
45.300	1.247	Unknown
46.324	3.225	Unknown
46.752	2.319	Unknown
50.380	48.610	Unknown

#### 4.2.2. Umbelliferae

##### 4.2.2.1 *Angelica keiskei*

*Angelica keiskei* was collected in Tokushima prefecture on October 24<sup>th</sup>, 2008. The plant was divided into leaves, stem and flowers. Each part has been purified and a small part of it has been crushed in mortar and extracted with diethyl ether. The excrement of the larvae of swallowtail butterfly that ate this plant has also been extracted with ether, in order to check if any of the volatile compounds of *Angelica keiskei* have been bio-transformed.

##### Leaves

A small amount of the leaves, stem and flowers has been extracted and studied on the GC-MS. The extract of the leaves showed the presence of some monoterpenoids as well as sesquiterpenoids. One diterpene type compound has been detected, abieta-8(14)13(15)-diene (**227**) even though in a low percentage.  $\gamma$ -Terpinene (**3**) appeared

in the GC after 14.9 minutes and has the highest area extension of the monoterpenes detected from the *A. keiskei* leaves. Other components detected in the GC were 3-carene (**26**), 2-carene (**25**),  $\beta$ -caryophyllene (**134**), bicyclogermacrene (**127**) and helifolene (**48**). They are shown in the table below. An unidentified benzopyran derivative has been detected after 35.5 minutes with an area extension of 2.8%.

Retention Time	Area %	Compound
6.215	5.253	2-Heptanol ( <b>254</b> )
13.172	4.969	3-Carene ( <b>26</b> )
14.892	9.272	$\gamma$ -Terpinene ( <b>3</b> )
15.930	1.452	2-Carene ( <b>25</b> )
26.368	3.948	$\beta$ -Caryophyllene ( <b>134</b> )
26.610	1.668	Unknown
27.806	1.031	Helifolene ( <b>48</b> )
28.032	5.969	cis-Muurolo-3,5-diene ( <b>65</b> )
28.668	3.400	Unknown
29.002	1.323	trans-Bergamotene ( <b>116</b> )
35.579	2.820	Benzopyran derivative
36.283	40.701	Neophytadiene isomer I ( <b>277</b> )
36.416	1.409	Unknown
36.811	4.286	Neophytadiene isomer II ( <b>289</b> )
37.213	9.076	Neophytadiene isomer III ( <b>290</b> )
43.125	1.871	Phytol ( <b>286</b> )
45.966	0.877	Unknown
50.057	0.669	Abieta-8(14)13(15)diene ( <b>227</b> )

#### Stem

The compounds found in the GC obtained from the stem of *A. keiskei* were 3-carene (**26**),  $\gamma$ -terpinene (**3**),  $\gamma$ -cadinene (**51**),  $\gamma$ - (**78**) and  $\delta$ -amorphene (**77**),  $\alpha$ -humulene (**133**)  $\alpha$ -muurolene (**87**) and isobicyclogermacrene (**128**). However,  $\gamma$ -cadinene (**51**) was the major compound identified from the crude extract of the stem. The highest area percentage showed a peak which appeared in the GC after 35.5 minutes and were not identified. A few other peaks could not be identified.

Retention Time	Area %	Compound
6.177	4.281	2-Heptanol ( <b>254</b> )
13.165	3.076	3-Carene ( <b>26</b> )

14.889	2.648	$\gamma$ -Terpinene ( <b>3</b> )
25.474	0.521	$\beta$ -Elemene ( <b>107</b> )
26.611	8.076	Unknown
27.827	0.911	$\gamma$ -Amorphene ( <b>78</b> )
28.032	10.160	$\gamma$ -Cadinene ( <b>51</b> )
28.433	0.823	$\alpha$ -Muurolene ( <b>87</b> )
28.669	2.228	Unknown
28.860	0.973	Unknown
29.041	1.540	$\delta$ -Amorphene ( <b>77</b> )
29.461	0.892	$\alpha$ -Humulene ( <b>133</b> )
30.068	3.672	Isobicyclogermacrene ( <b>128</b> )
35.517	18.095	Unknown
36.273	4.035	Neophytadiene isomer I ( <b>288</b> )
37.212	1.124	Neophytadiene isomer II ( <b>289</b> )
43.187	5.090	Neophytadiene isomer III ( <b>290</b> )
45.959	2.706	Unknown
50.855	1.574	Unknown
55.596	13.171	Unknown
56.035	15.749	Unknown

## Flowers

The light yellow-green coloured flowers of *A. keiskei* have been separated from stem and leaves. The major compound was  $\gamma$ -terpinene (**3**) which appeared after 13.7 minutes in the GC and has an area extension of 26.2%. Other monoterpenes detected in the GC were 3-carene (**26**) and terpinolene (**4**). Long chain aliphatic compounds were detected after 50 and 53 minutes.

Retention Time	Area %	Compound
11.676	4.226	3-Carene ( <b>26</b> )
13.738	26.263	$\gamma$ -Terpinene ( <b>3</b> )
14.940	2.493	Terpinolene( <b>4</b> )
26.229	2.895	$\beta$ -Caryophyllene ( <b>134</b> )
26.502	2.646	Unknown
27.717	1.252	Helifolene ( <b>48</b> )
27.937	8.959	cis-Muurolo-3,5-diene ( <b>65</b> )
28.359	3.844	(E,E)- Farnesene ( <b>275</b> )
28.592	0.788	Unknown
28.927	1.109	Sesquisabinene ( <b>109</b> )

29.716	0.710	Elemol ( <b>110</b> )
29.998	1.876	Isobicyclogermacrene ( <b>128</b> )
36.253	5.592	Neophytadiene isomer I ( <b>288</b> )
36.790	0.746	Neophytadiene isomer II ( <b>289</b> )
37.191	1.575	Neophytadiene isomer III ( <b>290</b> )
43.013	5.300	Phytol ( <b>286</b> )
44.427	3.547	Falcarinol ( <b>285</b> )
45.528	1.315	Nonadecene ( <b>244</b> )
45.949	2.524	Unknown
47.030	12.624	Squalene ( <b>287</b> )
50.846	9.475	Eicosane ( <b>235</b> )
52.754	4.582	Unknown aliphatic compound

### The excrements of the swallowtail butterfly larvae

The larvae of the swallow butterfly ate the leaves, leafstalk and the flowers of *Angelica keiskei* was brought to the laboratory together with the plant and its excrement was collected and purified from plant residues. The black coloured excrement was crushed in a mortar and extracted with diethyl ether. TLC and GC-MS were carried out to check its compounds in order to compare them with the compounds found in leaves, stem and flowers and to suggest if any compound has been bio-transformed by the worm. The GC-MS data showed higher peaks at the end of the spectra, most of them were unknown components, though. A big peak which appeared in the GC after 47.8 minutes was identified as the diterpene (E)-15,16-bisnorlabda-8(17)12-diene-14-al (**218**). Another peak with a higher area extension was detected after 28 minutes and was identified as  $\gamma$ -cadinene (**51**)  $\alpha$ -Humulene (**133**), germacrene B (**125**), (Z)- $\gamma$ -bisabolene (**99**),  $\alpha$ -sesquiphellandrene (**103**) were also detected.

Retention Time	Area %	Compound
5.746	17.055	2-Heptanol ( <b>254</b> )
12.922	1.143	3-Carene ( <b>26</b> )
14.694	1.585	2-Carene ( <b>25</b> )
26.297	3.722	$\alpha$ -Humulene ( <b>133</b> )
26.551	3.507	Germacrene B ( <b>125</b> )
27.968	14.527	$\gamma$ -Cadinene ( <b>51</b> )
28.370	1.821	(Z)- $\gamma$ -Bisabolene ( <b>99</b> )

28.603	1.682	Unknown
28.942	1.979	$\beta$ -Sesquiphellandrene ( <b>103</b> )
29.999	1.740	(1E,4Z)-Germacrene B ( <b>126</b> )
33.611	1.748	Germacra 4(15)5,11(14) triene-1 $\alpha$ -ol ( <b>131</b> )
36.219	21.861	Unknown
36.748	3.125	Unknown
37.149	6.292	Unknown
47.803	14.012	(E)15,16-Bisnorlabda-8(17)12-diene14-al ( <b>218</b> )
50.794	18.213	Unknown

#### 4.2.3. Labiatae (Lamiaceae)

##### 4.2.3.1. *Perilla frutescense* Britton var. *acuta*

The plant was collected in Tokushima near the University campus. After separating it in leaves, stem and flowers, each part has been reduced in small parts, crushed and extracted with diethyl ether. The compounds that were found and identified by their mass spectra are listed below.

#### Leaves

The color of the leaves was a mixture of green and purple, with a slightly domination of the purple color. The first peak in the GC that appeared after 19 minutes has been identified as elzholtzia ketone (**171**), the area extension was 3.9%. Next identified component was E- $\beta$ -caryophyllene (**134**) whose peak appeared after 26.3 minutes in the GC. Other identified compounds were (Z,E)  $\alpha$ -farnesene (**276**) (Rt:27.8 min), 3,7,11,15-tetramethyl-hexadecene (**270**) (Rt:35.1 min) and phytol (**286**) (Rt:40.5 min). Two big peaks that appeared after 35 minutes were identified as neophytadiene isomers III (**290**). A lot of the detected peaks could not be identified.

Retention Time	Area %	Compound
19.667	3.916	Elzholtzia ketone ( <b>171</b> )
26.286	1.394	$\beta$ -Caryophyllene ( <b>134</b> )
27.822	1.798	(Z,E) $\alpha$ -Farnesene ( <b>276</b> )
28.367	5.550	Unknown
35.033	56.295	Unknown
35.138	1.151	3,7,11,15-Tetramethyl-hexadecen ( <b>270</b> )



35.484	8.301	Neophytadiene isomer I ( <b>288</b> )
35.839	16.948	Neophytadiene isomer III ( <b>290</b> )
38.667	0.929	Unknown
39.507	0.659	Unknown
40.538	1.672	Phytol ( <b>286</b> )
48.435	1.338	Unknown

## Stem

The stem-color was also a mixture of green and violet tones. It has been hackled and then extracted with ether. The major components could not be identified after comparing their mass spectra to the library data. The major components appeared after 27.8 and 34.5 minutes, their mass spectra were unknown although. Identified components from the ether extra of *P. frutescense* were  $\beta$ -caryophyllene (**134**), geranylinalool (**282**), methyloleate (**267**), striatol (**173**) and a few aliphatic compounds: hexadecene (**245**), nonadecene (**244**), nonandecane (**237**) and n-heneicosane (**239**). Squalene (**287**) was also detected. Its peak appeared in the GC after 57.5 minutes. A lot of other compounds were detected, their mass spectra was unknown, though.

Retention Time	Area %	Compound
25.873	0.552	$\beta$ -Caryophyllene ( <b>134</b> )
27.858	22.508	Unknown
34.557	22.516	Unknown
34.677	0.682	Hexadecene ( <b>245</b> )
35.034	4.460	Neophytadiene isomer I ( <b>288</b> )
35.393	8.762	Neophytadiene isomer II ( <b>289</b> )
39.821	1.307	Neophytadiene isomer III ( <b>290</b> )
40.284	5.364	Nonadecene ( <b>244</b> )
43.019	0.839	Geranylinalool ( <b>282</b> )
43.128	1.024	Methyloleate ( <b>267</b> )
44.798	0.686	Striatol ( <b>173</b> )
45.679	2.393	Nonandecane ( <b>237</b> )
46.015	2.961	Unknown
47.818	10.922	Unknown
48.587	1.092	Unknown
51.351	1.019	Unknown
52.103	1.836	n-Heneicosane ( <b>239</b> )
57.535	8.407	Squalene ( <b>287</b> )

## Flowers

Flowers were cut from the stalk and extracted with ether. The main peak which appeared in the GC after 27 minutes has been identified as cis-bergamotene (**115**). Two big peaks were detected after 19.6 and 25.5 minutes, they have been identified as elzholtzia ketone (**171**) and  $\beta$ -caryophyllene (**134**). Other components that were identified from the data were linalool (**6**), neral (**7**), geranial (**9**), piperitoneoxide (**24**) etc.

Retention Time	Area %	Compound
16.275	1.518	Linalool ( <b>6</b> )
19.576	9.196	Elzholtzia ketone ( <b>171</b> )
20.683	0.959	Neral ( <b>7</b> )
21.48	1.126	Geranial ( <b>8</b> )
23.655	1.757	Unknown
24.245	1.364	Piperitoneoxide ( <b>24</b> )
25.515	10.143	E- $\beta$ -Caryophyllene ( <b>134</b> )
26.314	0.911	$\alpha$ -Humulene ( <b>133</b> )
26.515	1.041	1 $\alpha$ ,10 $\alpha$ -Epoxyamorph-4-ene ( <b>172</b> )
27.006	15.567	Cis-Bergamotene ( <b>115</b> )
27.309	1.014	Bicyclogermacrene ( <b>127</b> )
27.524	4.584	Unknown
34.351	13.571	Neophytadiene isomer I ( <b>288</b> )
34.822	2.612	Neophytadiene isomer II ( <b>289</b> )
35.186	4.952	Neophytadiene isomer III ( <b>290</b> )
40.255	5.908	n-Eicosane ( <b>235</b> )
43.125	0.813	1-Oxo- $\alpha$ -Longipinene ( <b>216</b> )
45.448	1.497	n-Pentacosane ( <b>241</b> )
46.218	2.222	Unknown
47.477	1.499	Unknown
47.957	5.806	Nonacosane ( <b>237</b> )
51.683	6.261	Heptacosane ( <b>245</b> )
54.404	2.496	Nonadecane ( <b>237</b> )

## Corolla

Petals were separated from the other parts of the plant. Only corolla was taken for this measurement (no stalk and no sepals). The main peak of this data could not be found in the mass spectra library. The GC showed the presence of many aliphatic

compounds such as 1-octadecene (**247**), n-tricosane (**239**), 1-nonadecene (**244**) and methyloleate (**267**). They appeared after 39 minutes in the GC.

Retention Time	Area %	Compound
19.614	2.455	Elzholtzia ketone ( <b>171</b> )
25.527	1.023	(E)- $\beta$ -Caryophyllene ( <b>134</b> )
27.014	1.718	cis-Bergamotene ( <b>115</b> )
27.572	28.871	Unknown
34.332	0.593	Neophytadiene isomer I ( <b>288</b> )
36.836	1.478	Neophytadiene isomer II ( <b>289</b> )
38.058	0.335	Neophytadiene isomer III ( <b>290</b> )
39.670	0.548	1-Octadecene ( <b>247</b> )
42.428	0.515	Selina-2,4-diene ( <b>72</b> )
42.578	0.392	n-Tricosane ( <b>239</b> )
42.934	1.140	1-Nonadecene ( <b>244</b> )
45.263	0.858	Methyloleate ( <b>267</b> )
45.756	2.865	Unknown
46.236	3.157	Unknown
47.540	12.899	Unknown
48.013	13.018	Pentacosane ( <b>241</b> )
48.241	1.434	Unknown
51.746	11.997	Unknown
54.510	11.265	Unknown
56.933	2.020	Squalene ( <b>287</b> )

#### 4.2.4. Zingiberaceae

##### 4.2.4.2. *Curcuma zedoaria* Roscoe

The collected *Curcuma zedoaria* was separated in leaves, rhizome and roots.

#### Leaves

The major compound of the leaves of *C. zedoaria* has been identified as albicanol (**122**). The peak appeared in the GC after 49 minutes and it has an area percentage of 72.4%. Monoterpenes found were  $\beta$ -pinene (**30**) and 1,8-cineole (**23**), thus in a very low percentage. The peak that appeared in the GC after 25.2 minutes with an area extension of 1.4% was identified as methylcinnamate (**42**). The isomers of neophytadiene (**288**), (**289**) and (**290**) were detected on the 37<sup>th</sup> and 38<sup>th</sup> minute.

Three peaks after 44.6 minutes and two other peaks after 48.7 minutes were unknown components.

Retention Time	Area %	Compound
5.873	2.283	2-Octanol ( <b>255</b> )
11.785	0.310	$\beta$ -Pinene ( <b>30</b> )
13.790	0.581	1,8-Cineole ( <b>23</b> )
25.250	1.424	Methylcinnamate( <b>42</b> )
36.272	4.918	Neophytadiene isomer I ( <b>288</b> )
36.795	0.672	Neophytadiene isomer II ( <b>289</b> )
37.203	1.487	Neophytadiene isomer II ( <b>290</b> )
41.217	0.448	Unknown
44.654	2.473	Unknown
46.571	4.589	Unknown
46.968	1.751	Unknown
48.060	72.389	Albicanol ( <b>122</b> )
48.708	3.827	Unknown
52.228	1.192	Unknown

#### Rhizome

The rhizome of *C. zedoaria* was purified from the soil, roots and other impurities. A small amount of it was cut and extracted with diethyl ether. Most of the found components could not be identified by their mass spectra. The identified components were benzylacetone (**41**), cinnamaldehyde (**40**), bicyclofarnesal (**168**) and albicanol (**122**). The major component appeared in the GC after 48.4 minutes and could not be identified.

Retention Time	Area %	Compound
6.354	1.486	2-Heptanol ( <b>254</b> )
21.076	0.217	Benzylacetone ( <b>41</b> )
21.991	0.525	Cinnamaldehyde ( <b>40</b> )
35.997	0.411	Bicyclofarnesal ( <b>168</b> )
43.110	1.987	Unknown
44.178	1.307	Unknown
44.711	3.067	Unknown
46.791	3.685	Unknown
47.016	1.604	Albicanol ( <b>122</b> )
48.480	81.188	Unknown

## Roots

Roots of *Curcuma zedoaria* showed a major compound after 47.9 minutes, whose percentage was by far higher than that of the other compounds (42.7%). This peak was identified as albicanol (**122**). Coronarin E (**233**) could also be identified. The peak of it appeared after 42.5 minutes, in a very low percentage though. Fenchylacetate (**47**), furanogermacrene (**132**), (E)15,26-bisnorlabda-8(17),12-diene-14-al (**218**) and isopimara-7,15-diene (**221**) were identified. The GC showed a lot of peaks of unknown components.

Retention Time	Area %	Compound
6.029	18.595	1-Octanol ( <b>251</b> )
10.717	0.231	Fenchylacetate ( <b>47</b> )
20.198	1.436	Unknown
27.466	0.325	Unknown
28.603	1.238	Unknown
37.009	1.173	Unknown
37.483	6.136	Unknown
38.170	1.251	Unknown
41.704	1.231	Nonadecane ( <b>237</b> )
42.592	0.473	Coronarin E ( <b>233</b> )
43.019	0.665	Unknown
46.099	1.102	Furanogermacrene ( <b>231</b> )
47.897	42.704	Albicanol ( <b>122</b> )
48.219	2.705	E15,26-Bisnorlabda-8 (17),12-diene-14-al ( <b>218</b> )
48.964	0.539	Isopimara-7,15-diene ( <b>221</b> )
49.874	0.768	Unknown
52.103	5.037	Unknown
52.732	7.717	Unknown
53.282	5.332	Unknown

### 4.2.5. Platanaceae

#### 4.2.5.1. *Platanus occidentalis*

*Platanus occidentalis* is also called American maple tree. Green and red leaves of the American maple tree have been collected at the Tokushima Bunri University campus. They have been crushed in a mortar and extracted with diethyl ether.

## Green leaves

Limonene (**2**) appeared in the GC after 13.8 minutes and had an area percentage of 13.5 %. The peak was detected after 13.8 minutes and has an area extension of 13.4%. A big peak with an area extension of 11.4% which appeared in the GC after 37.1 minutes could not be identified. Thus a few other compounds were detected from the data.  $\alpha$ -Pinene (**29**),  $\beta$ -pinene (**30**),  $\alpha$ -humulene (**133**), germacrene D (**123**) and abietal (**219**) showed a higher peak area.  $\beta$ -Caryophyllene (**133**), dimethylnonanol (**280**) and docosane (**242**) were also found, in much lower percentage though.

Retention Time	Area %	Compound
10.397	7.791	$\alpha$ -Pinene ( <b>29</b> )
11.972	2.584	$\beta$ -Pinene ( <b>27</b> )
13.823	13.477	Limonene ( <b>2</b> )
26.353	0.841	$\beta$ -Caryophyllene ( <b>134</b> )
27.291	2.003	$\alpha$ -Humulene ( <b>133</b> )
28.014	3.456	Germacrene D ( <b>123</b> )
33.790	0.889	4,8-Dimethylnonanol ( <b>280</b> )
35.0158	0.499	Docosane ( <b>242</b> )
36.256	28.617	Neophytadiene isomer I ( <b>288</b> )
36.401	0.912	Neophytadiene isomer II ( <b>289</b> )
36.793	5.685	Neophytadiene isomer III ( <b>290</b> )
37.193	11.396	Unknown
45.055	2.152	Unknown
48.872	3.357	Abietal ( <b>219</b> )
52.749	5.492	Unknown
53.812	4.030	Unknown

## Red leaves

The ether extract of the red leaves of *P.occidentalis* showed many big peaks in the first 14 minutes of the GC. Monoterpenes such as  $\alpha$ -pinene (**26**), sabinene (**28**) and limonene (**2**) were identified. Limonene (**2**) seemed to be the major compound, the peak area was almost 31 % and it appeared in the GC after 13.8 minutes.  $\alpha$ -humulene (**133**) was identified in the GC after 27.3 minutes. Neophytadiene (**288**) and its isomers (**289**) and (**290**) appeared in the GC between 36.2 and 36.8 minutes.

Their peak area was much lower as the area extension of their peaks from the ether extract of the green leaves.

Retention Time	Area %	Compound
6.252	5.137	2-Heptanol ( <b>254</b> )
10.424	15.623	$\alpha$ -Pinene ( <b>29</b> )
11.867	0.675	Unknown
11.995	6.797	Sabinene ( <b>28</b> )
13.840	30.996	Limonene ( <b>2</b> )
26.354	0.935	Unknown
27.300	2.066	$\alpha$ -Humulene ( <b>133</b> )
28.025	3.484	Unknown
28.656	2.283	n-Tetracosane ( <b>242</b> )
36.260	9.6401	Neophytadiene isomer I ( <b>288</b> )
36.407	0.992	Neophytadiene isomer II ( <b>289</b> )
36.795	2.047	Neophytadiene isomer III ( <b>290</b> )
37.198	3.889	Unknown
47.617	8.226	Unknown
50.844	1.893	Unknown
52.797	1.562	Unknown
53.838	2.470	Unknown
54.476	2.026	Unknown

### Essential oil

Red leaves of *Platanus occidentalis* had a strong smell by crushing it, which happens to be due to the high presence of the monoterpenes. In order to know more about the composition of these compounds, a bigger amount of *P. occidentalis* leaves has been collected and steam distilled. After two runs the steam distillation was cancelled because of the small amount of the essential oil that could be yielded from the leaves. Thus, a drop of the obtained oil was diluted with ether and used for the GC-MS analysis. Three big peaks which appeared in the GC after 26.3, 28 and 28.3 minutes were identified as  $\beta$ -caryophyllene (**134**) (15.5%),  $\gamma$ -cadinene (**51**) (16.7%) and isobicyclogermacrene (**128**) (17.2%).  $\alpha$ -Humulene (**133**), globulol (**190**) and T-murolol (**67**) were also detected, in a lower area percentage though. Three of the detected peaks were unknown compounds. No monoterpenes were found in the GC.

Retention Time	Area %	Compound
26.298	15.517	$\beta$ -Caryophyllene ( <b>134</b> )
27.255	3.479	$\alpha$ -Humulene ( <b>133</b> )
27.99	16.702	$\gamma$ -Cadinene ( <b>51</b> )
28.387	17.201	Isobicyclogermacrene ( <b>128</b> )
28.646	6.05	Unknown
28.815	5.236	Unknown
29.016	11.007	Unknown
30.761	3.606	Globulol ( <b>190</b> )
32.11	8.18	Unknown
32.453	7.316	T-Muurolol ( <b>67</b> )

#### 4.2.6. Lauraceae

##### 4.2.6.1. *Cinnamomum sieboldii*

The cortex of *Cinnamomum sieboldii* was collected on October, 24<sup>th</sup>, 2008 in Tokushima prefecture. The brown colored cortex has been cut in small pieces and extracted with diethyl ether. The peak of the major compound appeared in the GC after 54.9 minutes with an area extension of 17.5% and could not be identified. A compound with a lower area percentage was found after 39.1 minutes (13.3%) which was identified as the diterpenoid 8(14), 15-pimaradiene (**220**). A lower peak with a percentage of 6.8 % appeared after 22 minutes and was identified as cinnamaldehyde (**40**). Other compounds found in the GC were  $\gamma$ -cuprenene (**207**), (E,Z)- $\alpha$ -farnesene (**274**), (E)-biformene (**232**), abietatriene (**225**) and abieta-7,13-diene (**226**). The peaks that appeared in the GC after 43.5 minutes, including the major component, could not be identified.

Retention Time	Area %	Compound
5.014	9.827	2-Heptanol ( <b>254</b> )
22.132	6.843	Cinnamaldehyde ( <b>40</b> )
28.169	2.659	$\gamma$ -Cuprenene ( <b>207</b> )
28.523	0.509	(E,Z)- $\alpha$ -Farnesene ( <b>274</b> )
28.627	2.723	Unknown
36.223	2.951	Neophytadiene isomer I ( <b>288</b> )
37.064	1.368	Neophytadiene isomer III ( <b>290</b> )
39.117	13.339	8,(14),15-Pimaradiene ( <b>220</b> )



39.829	1.314	(E)-Biformene ( <b>232</b> )
40.628	4.255	Abietatriene ( <b>225</b> )
41.127	5.084	Abieta-7,13-diene ( <b>226</b> )
43.548	5.455	Unknown
44.695	3.504	Unknown
45.027	3.589	Unknown
45.891	4.505	Unknown
54.991	17.57	Unknown

#### 4.2.7. Amaranthaceae

##### 4.2.7.1. *Chenopodium ficifolium*

*Chenopodium ficifolium* was collected in the riverside of Akuigawa on October 10<sup>th</sup> 2008. This plant has been analysed as a mixture of stem, leaves and flowers since this plant is used as herba. The vast majority of the analysed part was made of flowers. Leaves were very rare and hard to find. The plant has been cut in small pieces and extracted with diethyl ether. The major compounds found were pinocarvone (**37**) and the reduced form of it, pinocarveol (**35**), namely the trans isomer. Other monoterpenes detected were  $\alpha$ -pinene (**29**), myrtenal (**39**), myrtenol (**38**) and isobornylacetate (**46**). A big peak detected after 23 minutes was identified as 4,8-dimethyl-1,4,7-nonatriene (**281**). Another peak with a high area extension appeared in the GC after 47.5 minutes and was identified as seline-5,11-diene (**74**). Cedrol (**151**) was also identified and appeared in the GC after 36.2 minutes. A few peaks with lower area extensions were identified as aliphatic components: nonadecene (**244**), eicosane (**235**). The results of the identified as well as unknown components of the diethyl ether extract of the herbal *C. ficifolium* are listed in the table below.

Retention Time	Area %	Compound
9.871	3.960	$\alpha$ -Pinene ( <b>29</b> )
17.810	9.183	trans-Pinocarveol ( <b>35</b> )
18.341	16.928	Pinocarvone ( <b>37</b> )
18.625	3.098	Unknown
19.470	0.438	Myrtenal ( <b>39</b> )
20.579	0.794	Myrtenol ( <b>38</b> )

21.895	0.808	Unknown
22.241	1.217	Isobornylacetate ( <b>46</b> )
22.992	17.511	4,8-Dimethyl-1,3,7-nonatriene ( <b>281</b> )
23.440	0.670	trans-Pinocarveoyl-acetate ( <b>36</b> )
24.167	1.960	2E-Decanal ( <b>252</b> )
24.960	0.348	1-Oct-3-enylacetate ( <b>262</b> )
36.239	1.000	Cedrol ( <b>151</b> )
41.559	0.649	7,11-Dimethylheptadecene ( <b>271</b> )
42.852	0.808	Unknown
44.724	1.277	Nonadecene ( <b>244</b> )
45.512	1.877	Unknown
47.231	10.590	Unknown
47.533	11.732	Selina-5,11-diene ( <b>74</b> )
49.666	1.597	Unidentified aliphatic compound
50.808	2.283	Eicosane ( <b>235</b> )
51.158	4.047	Unknown
53.384	1.192	Unknown

#### 4.2.8. Rutaceae

##### 4.2.8.1. *Zanthoxylum piperitum*

The leaves of *Zanthoxylum piperitum* were collected in Tokushima prefecture. The GC showed a big peak after 6.6 minutes which was identified as t-butanol (**253**). Another big peak that appeared after 13.9 minutes could not be identified. Peaks with a lower area extension appeared after 10.4, 24.1, 26.3 and 36.3 minutes which were identified as  $\alpha$ -pinene (**29**), 2,3-dehydro-1,4-cineole (**22**),  $\beta$ -caryophyllene (**134**) and farnesyl acetate (**283**). Other volatile compounds found, were: sabinene (**28**),  $\beta$ -myrcene (**1**), linalyl acetate (**19**),  $\alpha$ -humulene (**133**).

Retention Time	Area %	Compound
6.647	39.804	t-Butanol ( <b>253</b> )
10.418	2.231	$\alpha$ -Pinene ( <b>29</b> )
11.859	0.742	Sabinene ( <b>28</b> )
12.445	0.809	$\beta$ -Myrcene ( <b>1</b> )
13.940	26.829	Unknown
21.247	0.878	Linalyl acetate ( <b>19</b> )
24.147	3.430	2,3-Dehydro-1,4-cineole ( <b>22</b> )
26.360	4.038	$\beta$ -Caryophyllene ( <b>119</b> )

27.288	0.501	$\alpha$ -Humulene ( <b>133</b> )
30.741	0.728	Unknown
33.784	0.556	1-Nonadecene ( <b>244</b> )
36.356	4.628	(2E,6E)-Farnesylacetate ( <b>283</b> )
42.661	5.674	Unknown
45.529	0.613	Unknown
46.491	2.498	Unknown
47.930	0.850	Tetracosane ( <b>242</b> )
50.847	1.818	Eicosane ( <b>235</b> )

#### 4.2.8.2. *Citrus junos* Siebold ex Tanaka

##### Pericarp (Flavedo)

A small part of the pericarp of the *Citrus junos* fruit has been squeezed into a vial and then diluted with ether. The GC-MS analysis showed that limonene (**2**) was the major compound by far. The peak appeared in the GC after 13.8 minutes with a very high area extension (83.7%). Most of the other components were also monoterpenes such as  $\alpha$ - (**29**), and  $\beta$ -pinene (**30**),  $\beta$ -myrcene (**1**), 3-carene (**26**) and linalool (**6**). Linalool (**6**) and  $\gamma$ -cadinene (**51**) were also detected in very low percentage though. Their peaks appeared in the GC after 16.2 and 27.9 minutes.

Retention Time	Area %	Compound
6.250	1.774	t-Butanol ( <b>253</b> )
10.309	0.517	$\alpha$ -Pinene ( <b>29</b> )
11.893	0.882	$\beta$ -Pinene ( <b>30</b> )
12.363	0.734	$\beta$ -Myrcene ( <b>1</b> )
13.853	83.681	Limonene ( <b>2</b> )
14.412	1.386	Unknown
14.831	8.515	3-Carene ( <b>26</b> )
16.223	1.787	Linalool ( <b>6</b> )
27.949	0.724	$\gamma$ -Cadinene ( <b>51</b> )

#### 4.2.9. Verbenaceae

##### 4.2.9.1. *Lantana camara* L.

The stem and leaves of *Lantana camara* have been used for the analysis, they have been cut and extracted with diethyl ether. The ether-soluble compounds found and identified from the ether extract of both parts of *L. camara* is listed in the tables below.

##### Leaves

Monoterpenes found in the ether extract of the *Lantana camara* leaves were 1,8-cineole (**23**) and linalool (**6**) whose peaks appeared in the GC after 13 and 15 minutes, respectively.  $\gamma$ -Cadinene (**51**) was detected after 27.9 minutes and had an area extension of 7.8%.  $\beta$ -Caryophyllene (**134**) was also detected. Its peak appeared in the GC after 26 minutes. Other identified components were isopulegol acetate (**18**), geraniol (**279**), cembrene (**284**) and a few aliphatic components.

Retention Time	Area %	Compound
13.094	1.361	1,8-Cineole ( <b>23</b> )
15.735	2.150	Linalool ( <b>6</b> )
19.613	1.954	Isopulegol acetate ( <b>18</b> )
21.624	2.336	Geraniol ( <b>279</b> )
23.431	6.517	2,6-Dimethyl-1,5-E 7-trien-3-ol ( <b>8</b> )
25.385	1.701	Cembrene ( <b>284</b> )
26.282	3.119	$\beta$ -Caryophyllene ( <b>134</b> )
26.538	1.450	Unknown
27.971	7.866	$\gamma$ -Cadinene ( <b>51</b> )
28.621	0.851	Isobicyclogermacrene ( <b>128</b> )
30.030	1.039	Muurola-4,10 (15)dien-8-ol ( <b>66</b> )
34.294	0.696	Unknown
35.573	27.332	Neophytadiene isomer I ( <b>288</b> )
35.690	1.086	Dodecanol ( <b>252</b> )
36.032	3.507	Neophytadiene isomer II ( <b>289</b> )
36.375	8.304	Neophytadiene isomer III ( <b>290</b> )
53.802	4.490	Eicosane ( <b>235</b> )

#### 4.2.10. Cupressaceae

##### 4.2.10.1. *Thujopsis dolabrata*

*Thujopsis dolabrata* also called hiba in Japan has been collected at Shikoku Island. The wood was reduced in small pieces and then used for steam distillation to obtain the essential oil. 3.485 kg of the wood have been steam distilled in 6 days. The obtained essential oil showed a red-brown color, thick consistence and it used to smell very strong. A small drop of the oil has been diluted with ether and 1  $\mu$ l has been used for the GC-MS analysis. The GC showed two big peaks which appeared after 26.6 and 30.6 minutes. Their area extensions were 16.5 % respectively 13.8 % and these two peaks have been identified as thujopsene (**80**) and widdrol (**152**). Two smaller peaks have been viewed in the GC, with in the 31<sup>st</sup> (3.2 and 30.8) minute and both have been identified as cedrol (**151**). Other peaks that appear in a higher extension were identified as cuparene (**204**) (after 28.3 min, 4.9 area %), valeranal (**159**) (after 32.3 min, 5.5 area %), palustrol (**186**) (after 32.5 min, 4.8 area %),  $\beta$ -costol (**120**) (after 32.8 min, 5.3 area %) and  $\beta$ -herbertenol (**205**) (after 34.6 min, 4.7 area %). A few other compounds were identified such as  $\alpha$ -cuprenene (**206**),  $\alpha$ -microbiotene (**212**),  $\alpha$ -longipinene (**149**),  $\delta$ -cuprenene (**208**) etc.

Retention Time	Area %	Compound
18.941	0.260	Terpinene-4-ol ( <b>13</b> )
22.780	0.419	Carvacrol ( <b>17</b> )
25.675	0.145	$\alpha$ -Longipinene ( <b>149</b> )
26.059	0.837	$\alpha$ -Cedrene ( <b>195</b> )
26.263	0.706	$\gamma$ -Cadinene ( <b>51</b> )
26.675	16.515	Thujopsene ( <b>80</b> )
27.306	0.576	Ylanga-2,4(15)-diene ( <b>118</b> )
27.436	0.184	Unknown
27.539	0.174	Unknown
27.627	0.458	$\beta$ -Chamigrene ( <b>211</b> )
27.789	0.232	$\beta$ -Longipinene ( <b>150</b> )
28.152	2.856	$\alpha$ -Cuprenene ( <b>206</b> )
28.320	4.958	Cuparene ( <b>204</b> )
28.530	1.127	$\alpha$ -Microbiotene ( <b>212</b> )
28.664	0.274	(Z)- $\gamma$ -Bisabolene ( <b>99</b> )
28.829	1.054	$\alpha$ -Longipinene ( <b>149</b> )

29.151	1.306	$\delta$ -Cuprenene ( <b>208</b> )
29.770	0.616	Unknown
30.262	2.095	Unknown
30.654	13.833	Widdrol ( <b>152</b> )
30.713	5.563	Cedrol ( <b>151</b> )
30.952	1.050	Unknown
31.043	0.535	$\beta$ -Acorenol ( <b>215</b> )
31.131	0.785	Unknown
31.339	0.765	Pogostol ( <b>201</b> )
31.573	1.781	Sclareolide ( <b>174</b> )
31.735	1.805	Cyperenal ( <b>156</b> )
31.917	1.338	African-1-ene ( <b>157</b> )
32.124	3.116	$\alpha$ -Bisabolol ( <b>100</b> )
32.274	5.534	Valerenal ( <b>159</b> )
32.473	4.770	Palustrol ( <b>186</b> )
32.610	2.471	Unknown
32.809	5.306	$\beta$ -Costol ( <b>120</b> )
33.686	3.046	Unknown
34.010	0.987	$\alpha$ -Costol ( <b>119</b> )
34.134	2.802	$\gamma$ -Costol ( <b>121</b> )
34.588	4.676	$\beta$ -Herbertenol ( <b>205</b> )
34.761	1.326	Unknown

#### 4.2.10.2. *Chamaecyparis obtusa*

A small amount of the foliage of *Chamaecyparis obtusa* has been used for the extraction. The GC showed a lot of peaks and most of them were known components. The highest area extension showed the peak which appeared in the GC after 29.8 minutes. It was identified as elemol (**110**). Components with a high area percentage found were sabinene (**28**), 2,3-dihydro-1,4-diene (**21**), thujopsene (**70**). The peak that appeared in the GC after 46 minutes was identified as totarol (**224**). The area extension was 5.8 %. Other components found in the GC were  $\beta$ -myrcene (**1**), limonene (**2**), 3-carene (**26**),  $\alpha$ -pinene (**29**), bornyl acetate (**45**),  $\gamma$ -cadinene (**51**) and selina-4(15),5-diene (**70**). They are listed on the table below according to their retention time.

Retention Time	Area %	Compound
10.356	0.380	$\alpha$ -Pinene ( <b>29</b> )
11.821	6.097	Sabinene ( <b>28</b> )
12.402	1.763	$\beta$ -Myrcene ( <b>1</b> )
13.793	1.755	Limonene ( <b>2</b> )
14.849	0.714	3-Carene ( <b>26</b> )
21.221	0.474	endo-Isocamphanyl acetate( <b>43</b> )
22.295	3.821	Bornyl acetate ( <b>45</b> )
24.143	6.844	2,3-Didehydro-1,4-cineole ( <b>22</b> )
25.436	0.539	$\beta$ -Elemene ( <b>107</b> )
26.194	0.944	(Z,Z)- $\alpha$ -Farnesene ( <b>277</b> )
26.422	0.526	Unknown
26.689	3.659	Thujopsene ( <b>80</b> )
27.014	1.719	$\gamma$ -Cadinene ( <b>51</b> )
27.510	2.187	Unknown
27.991	1.746	Selina-4 (15),5-diene ( <b>70</b> )
28.362	0.571	$\alpha$ -Cuprenene ( <b>206</b> )
28.528	0.928	Unknown
28.633	1.005	Unknown
29.022	0.986	$\beta$ -Longipinene ( <b>150</b> )
29.339	2.039	$\alpha$ -Longipinene ( <b>149</b> )
29.835	27.37	Elemol ( <b>110</b> )
30.514	1.285	4 $\alpha$ -Hydroxygermacra-1 (10),5-diol ( <b>130</b> )
30.761	0.658	Unknown
30.920	1.696	Thujopsane-2 $\beta$ -ol ( <b>83</b> )
31.332	2.563	Cedrol ( <b>151</b> )
31.901	1.100	Microbiotol ( <b>213</b> )
32.456	0.714	Eudesm-3en-7-ol ( <b>90</b> )
32.624	0.177	$\alpha$ -Bisabolol ( <b>100</b> )
33.950	1.034	Unknown
34.489	2.009	Unknown
35.920	1.176	Unknown
36.238	0.937	Neophytadiene isomer I ( <b>288</b> )
37.177	0.344	Neophytadiene isomer II ( <b>289</b> )
37.570	0.879	Neophytadiene isomer III ( <b>290</b> )
38.052	1.607	$\beta$ -Oplopenone ( <b>138</b> )
38.905	5.760	Unknown
46.020	3.110	Unknown
46.615	5.802	Totarol ( <b>224</b> )

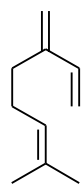
#### 4.2.10.3. *Cryptomeria japonica*

A small part of the Japanese cypress leaves were crushed and extracted with diethyl ether. The two major compounds which appeared at a time of 46.07 and 48.41 min, could not be identified by their mass spectra. Presumably they are catabolism products of phytol (**286**). Their area percentage is very high. Sabinene (**28**) and camphor (**31**) were present at a very low percentage. The peaks that appeared after the 41<sup>st</sup> and the 43<sup>rd</sup> minute were presumably derivatives of phenanthrene which were not possible to identify exactly. Another peak detected after 50 minutes could be a derivative of the oxygenated form of phenanthrene, phenanthrone.

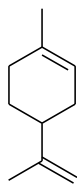
Retention Time	Area %	Compound
11.794	0.569	Sabinene ( <b>28</b> )
17.880	0.239	Camphor ( <b>31</b> )
18.028	0.364	3,7-Dimethyl-6-octenal ( <b>261</b> )
27.477	1.274	Unknown
32.656	0.692	(2E,6E) Farnesyl acetate ( <b>283</b> )
34.299	3.336	Neophytadiene isomer I ( <b>288</b> )
34.782	0.673	Neophytadiene isomer II ( <b>289</b> )
35.143	1.266	Neophytadiene isomer III ( <b>290</b> )
38.779	0.945	Phenanthrene derivative
40.194	2.197	Nordextromethorphan ( <b>229</b> )
40.760	1.232	Unknown
41.115	0.662	Phenanthrene derivative
41.335	1.536	Geranylinalool ( <b>282</b> )
41.559	1.665	(E)-Biformene ( <b>232</b> )
42.324	2.340	Unknown
42.483	9.580	Unknown
43.459	7.660	Phenanthrenol derivative
43.935	2.194	Unknown
44.732	1.148	Unknown
46.069	28.252	Unknown
48.410	25.587	Unknown
50.080	1.571	Phenanthrenone derivative
56.822	0.834	Squalene ( <b>287</b> )



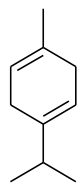
## 5. Chemical Structures



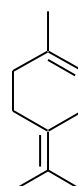
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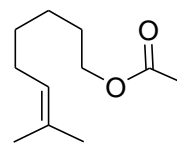
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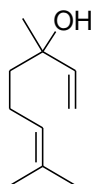
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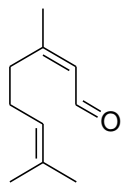
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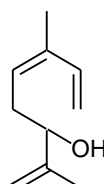
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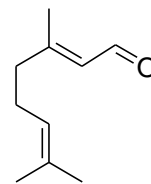
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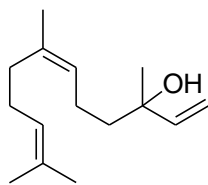
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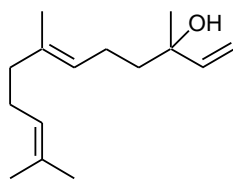
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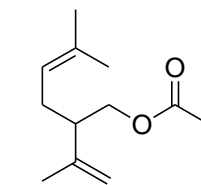
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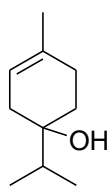
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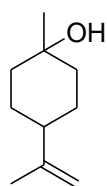
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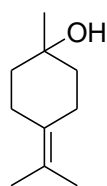
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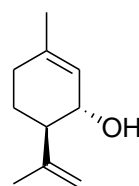
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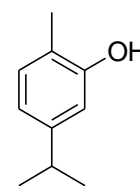
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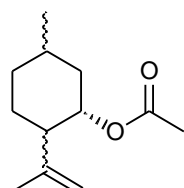
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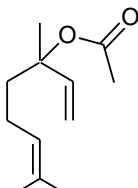
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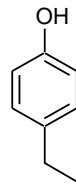
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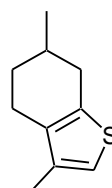
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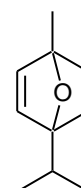
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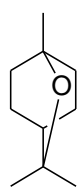
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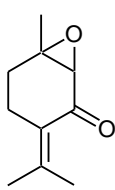
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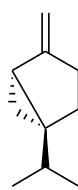
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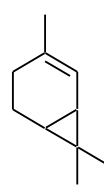
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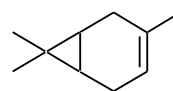
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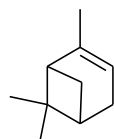
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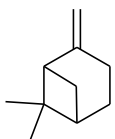
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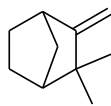
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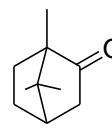
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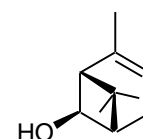
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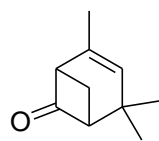
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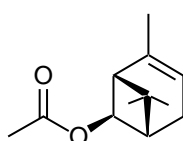
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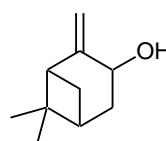
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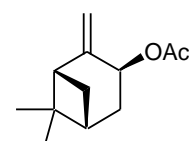
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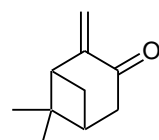
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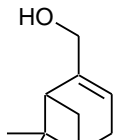
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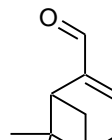
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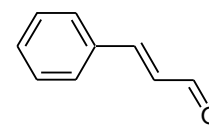
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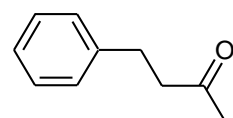
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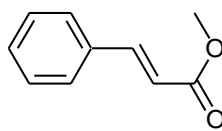
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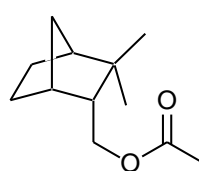
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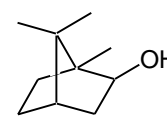
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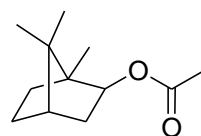
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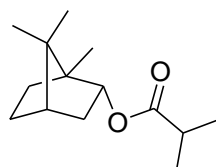
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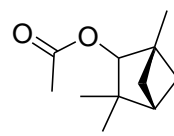
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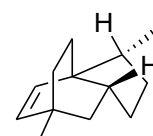
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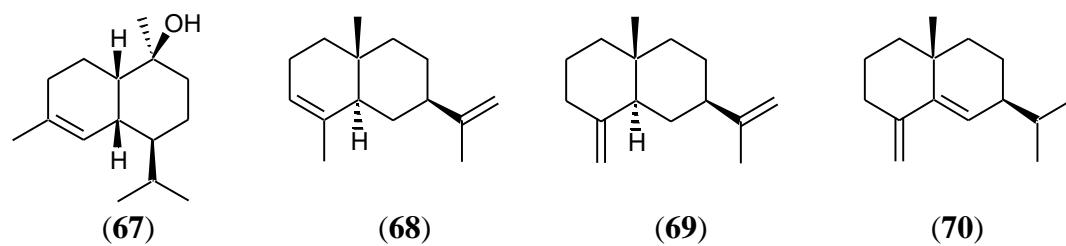
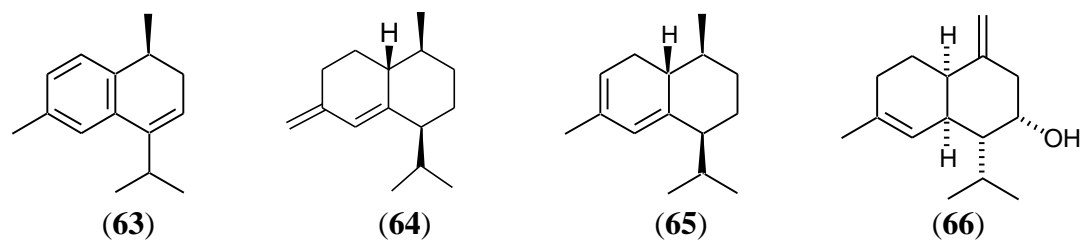
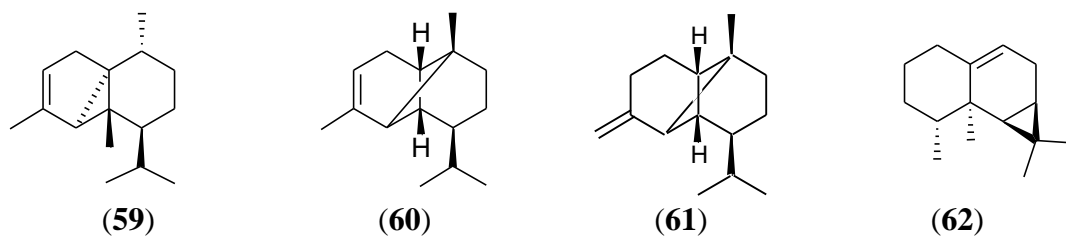
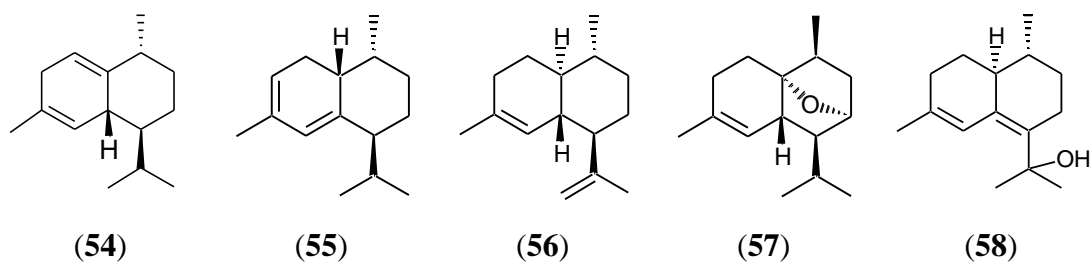
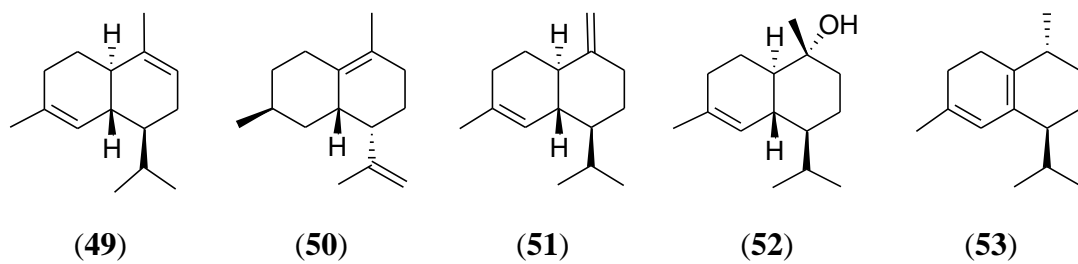
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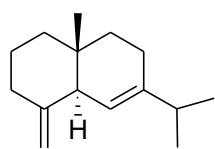


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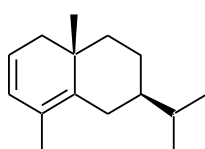


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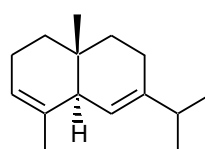




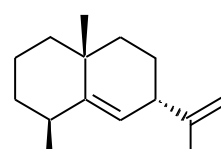
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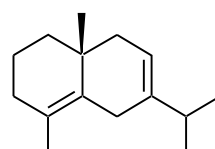
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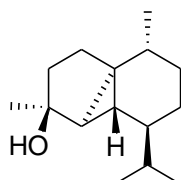
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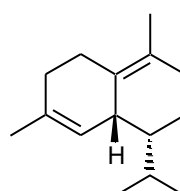
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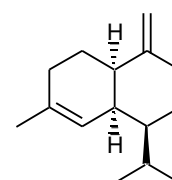
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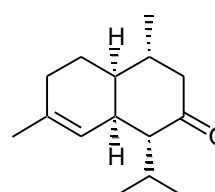
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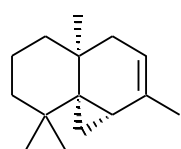
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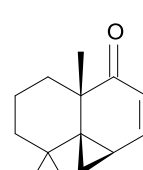
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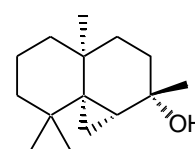
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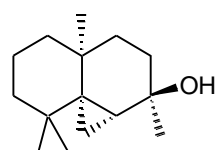
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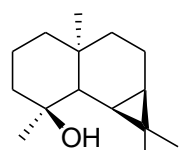
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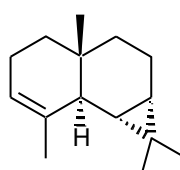
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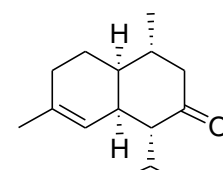
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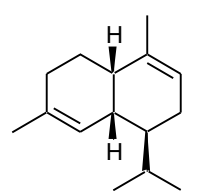
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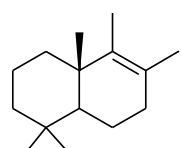
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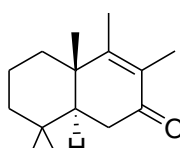
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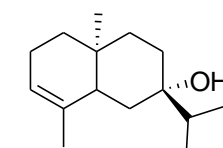
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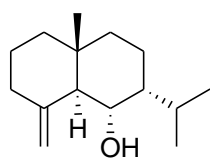
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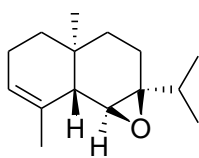
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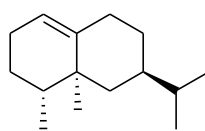
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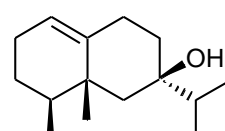
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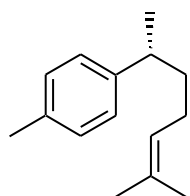
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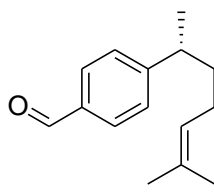
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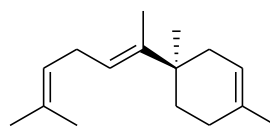
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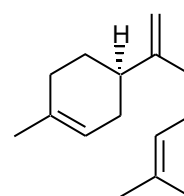
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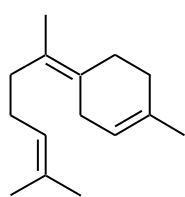
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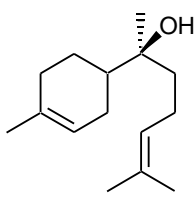
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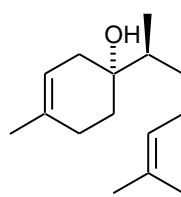
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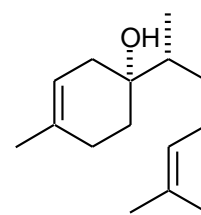
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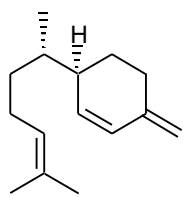
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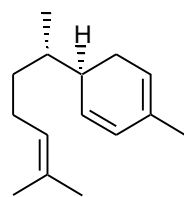
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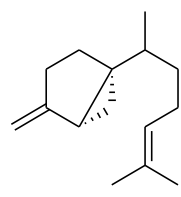
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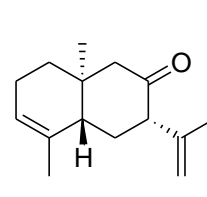
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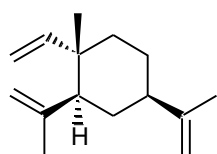
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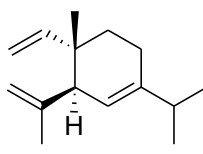
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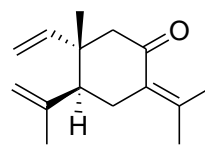
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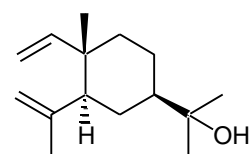
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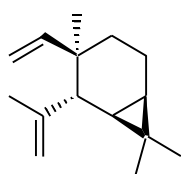
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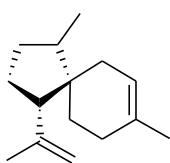
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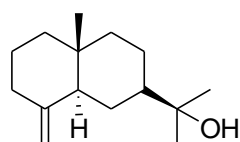
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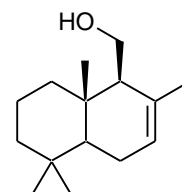
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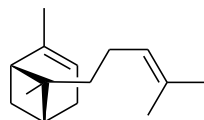
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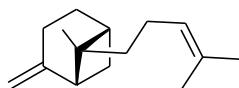
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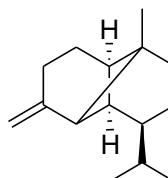
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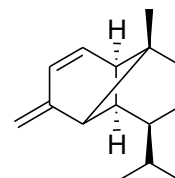
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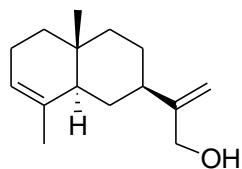
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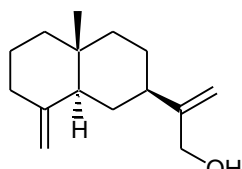
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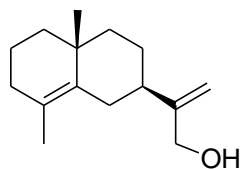
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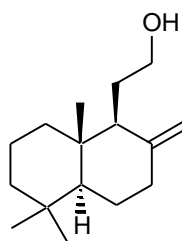
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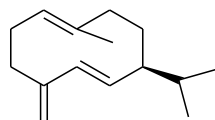
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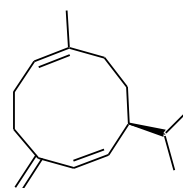
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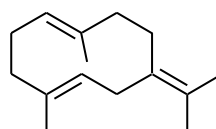
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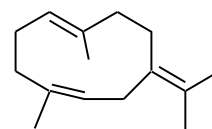
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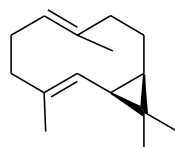
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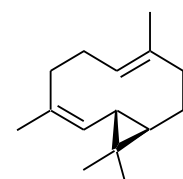
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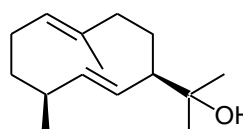
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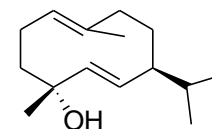
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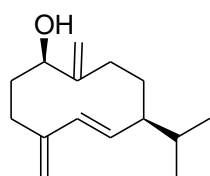
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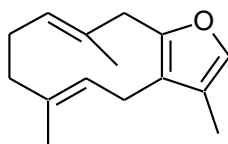
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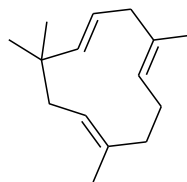
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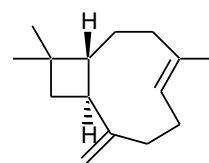
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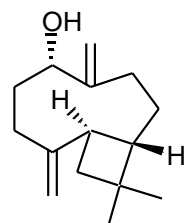
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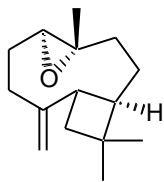
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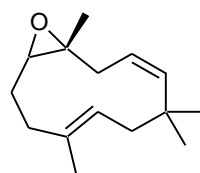
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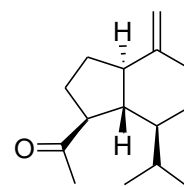
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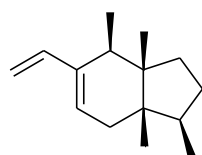
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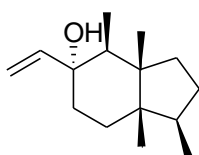
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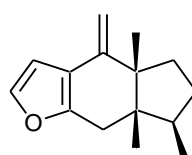
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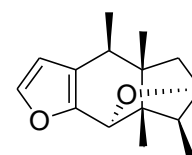
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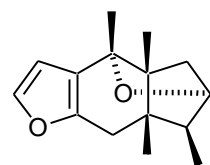
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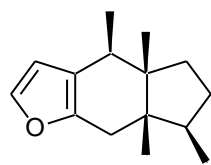
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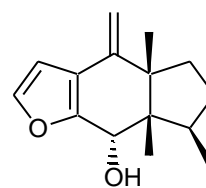
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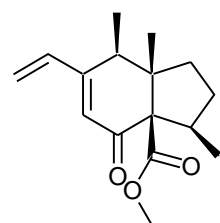
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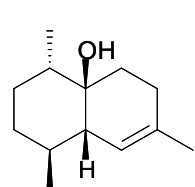
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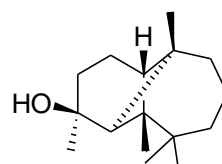
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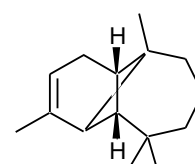
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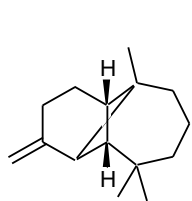
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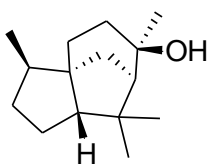
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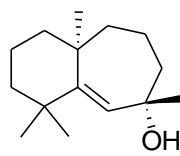
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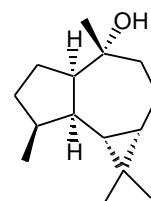
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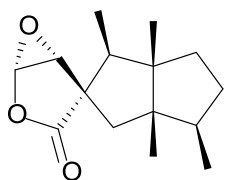
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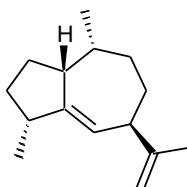
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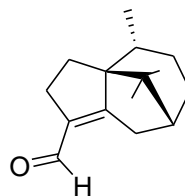
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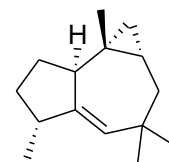
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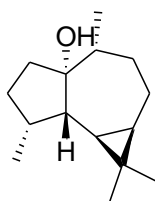
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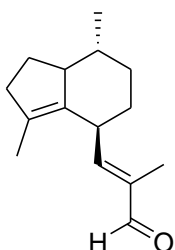
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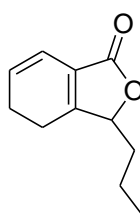
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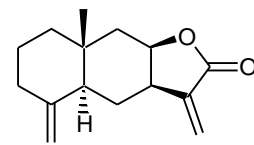
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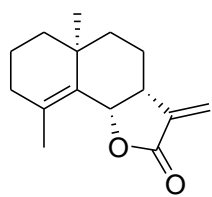
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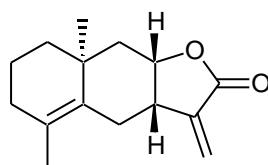
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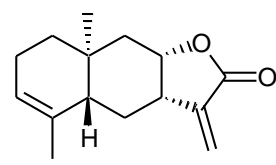
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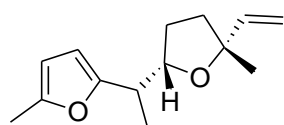
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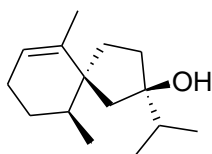
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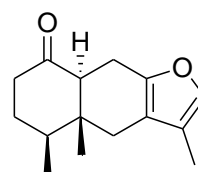
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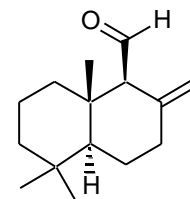
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(166)

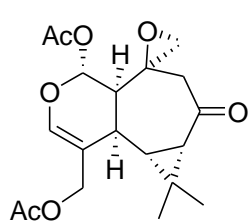


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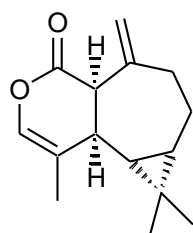


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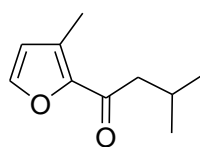




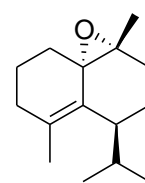
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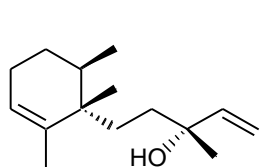
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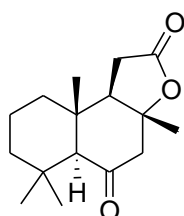
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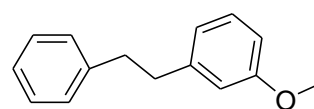
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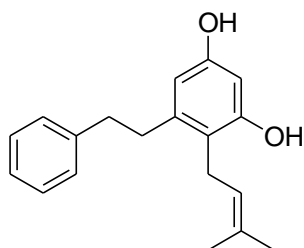
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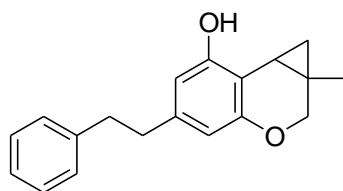
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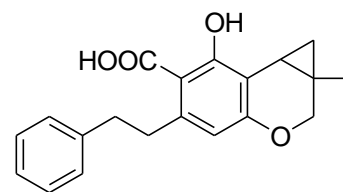
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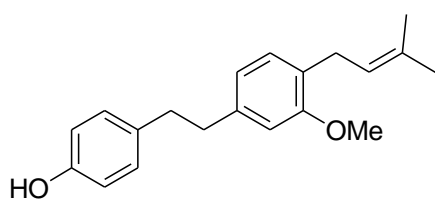
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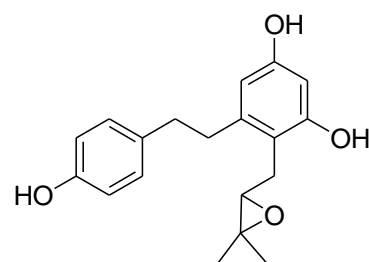
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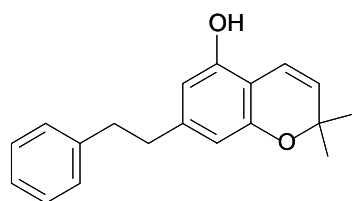
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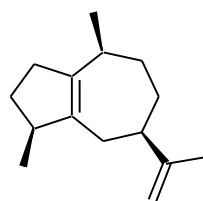
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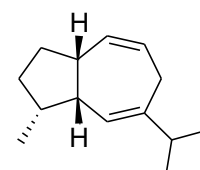
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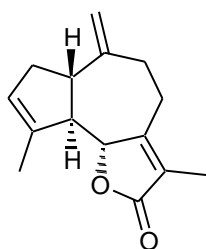
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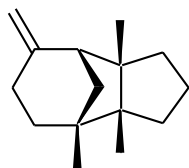
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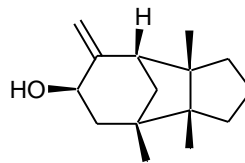
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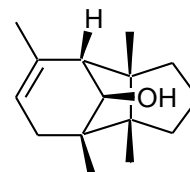
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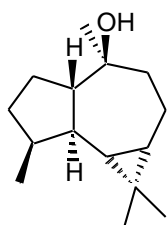
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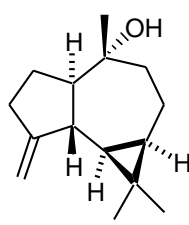
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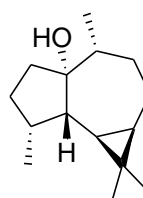
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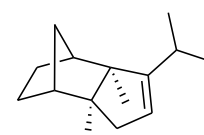
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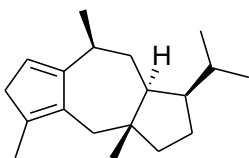
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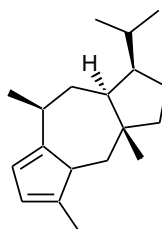
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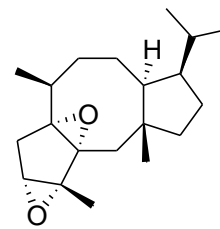
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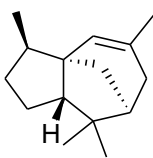
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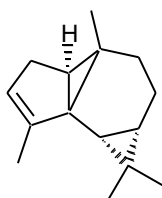
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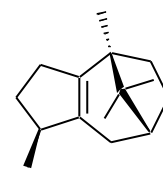
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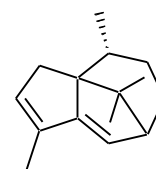
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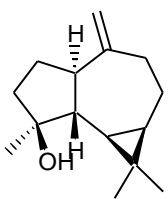
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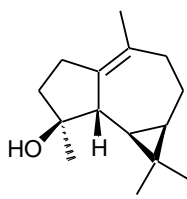
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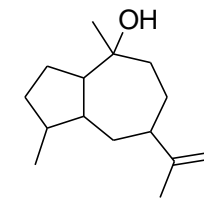
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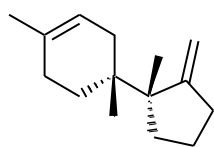
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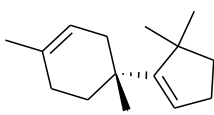
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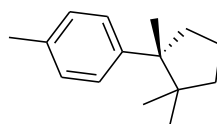
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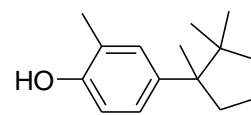
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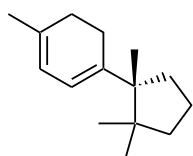
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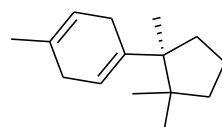
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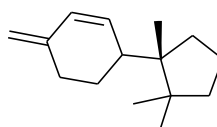
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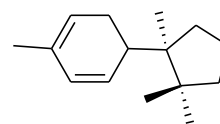
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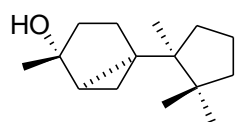
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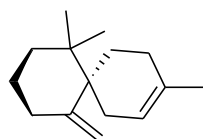
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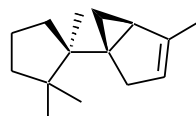
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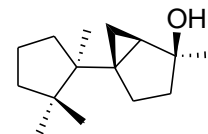
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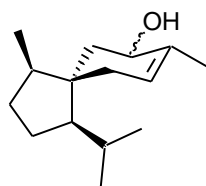
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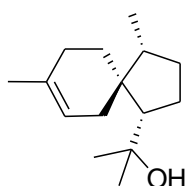
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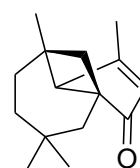
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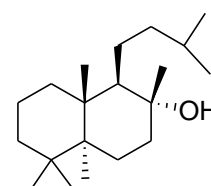
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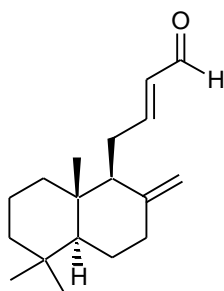
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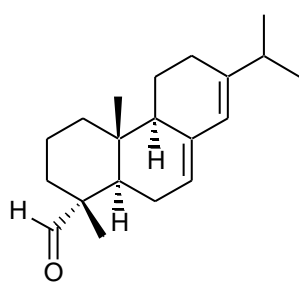
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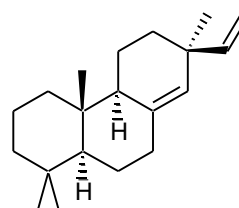
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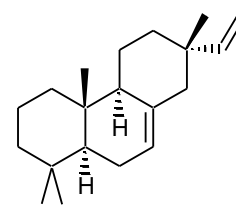
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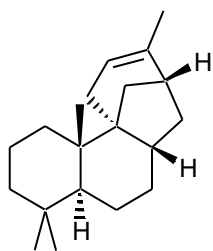
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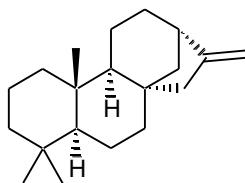
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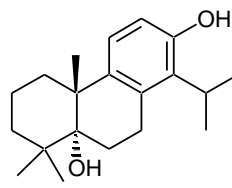
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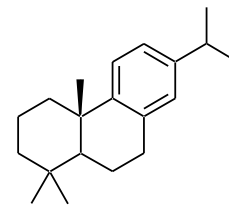
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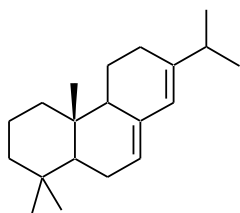
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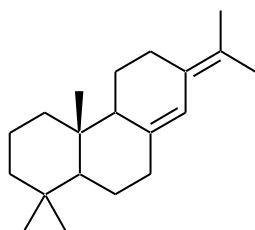
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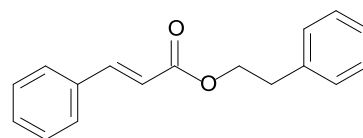
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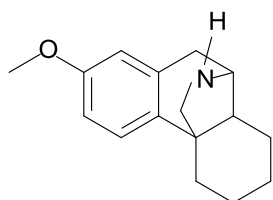
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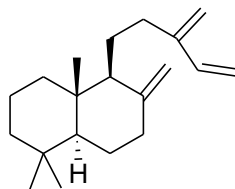
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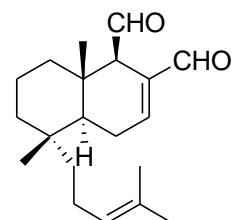
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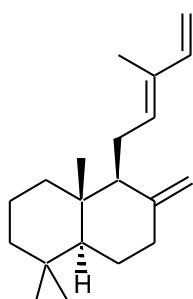
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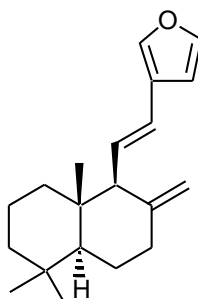
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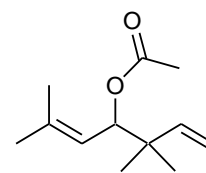
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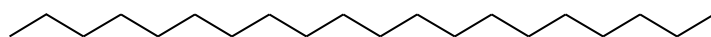
(232)



(233)



(234)



(235) Eicosane (C-20)

(236) Nonadecane (C-19)

(237) n-Octadecane (C-18)

(238) 1-Undecene (C-11)

(239) n-Heneicosane (C-21)

(240) Docosane (C-22)

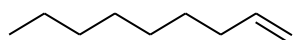
(241) Tricosane (C-23)

(242) Tetracosane (C-24)

(243) Pentacosane (C-25)

(244) Hexacosane (C-26)

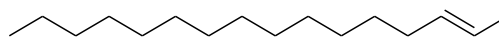
(245) Heptacosane (C-27)



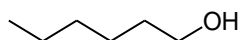
(246) Non-1-ene (C-9)

(247) 1-Octadecene

(248) 1-Nonadecene (C-19)



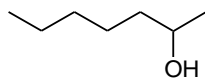
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(250) 1-Hexanol (C-6)

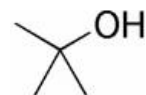
(251) 1-Octanol (C-8)

(252) Dodecanol (C-12)

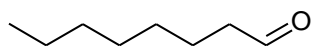


(254) 2-Heptanol (C-7)

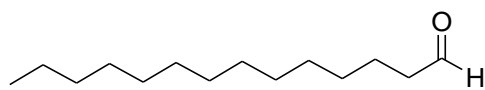
(255) 2-Octanol (C-8)



(253)



(256) E-2-Octanal (C-8)

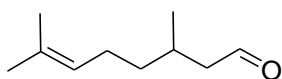


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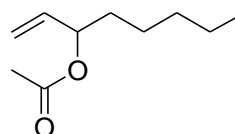
(257) 2E-Decanal (C-10)

(258) Hexadecanal

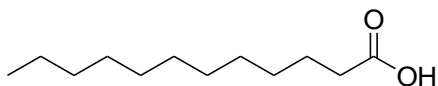
(259) Octadecanal (C-18)



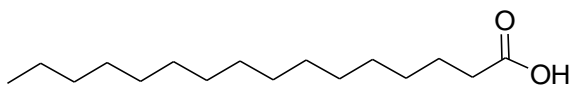
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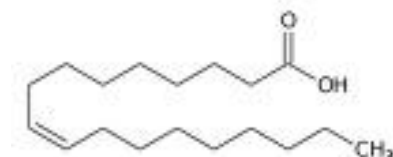
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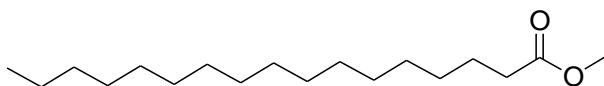
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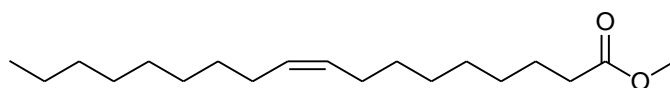
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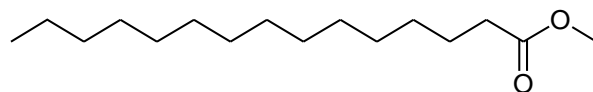
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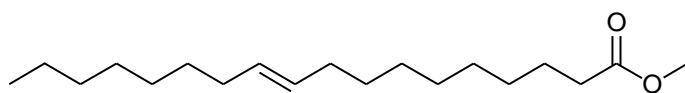
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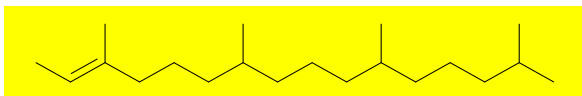
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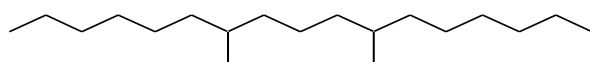
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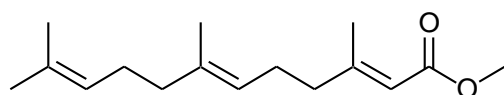
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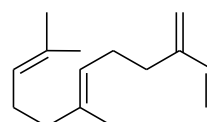
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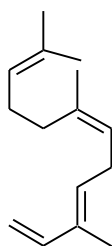
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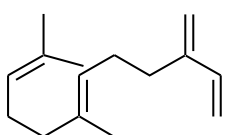
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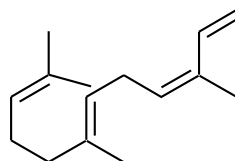
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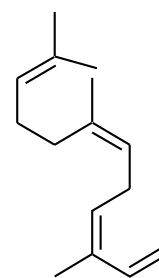
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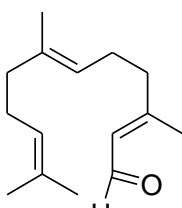
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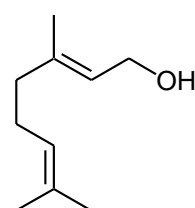
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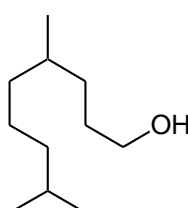
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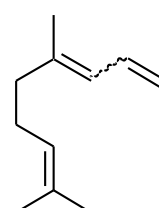
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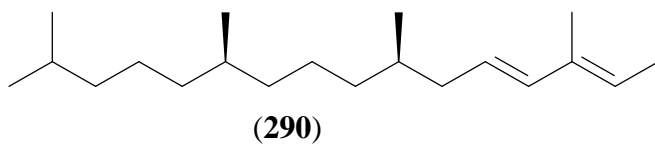
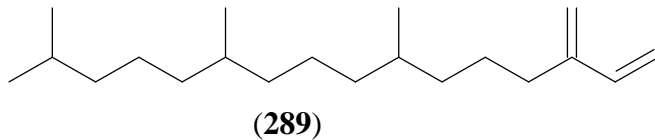
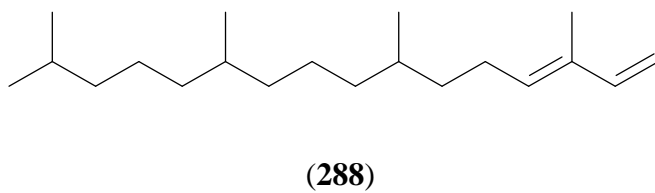
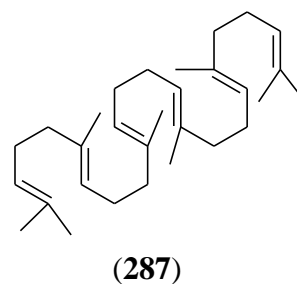
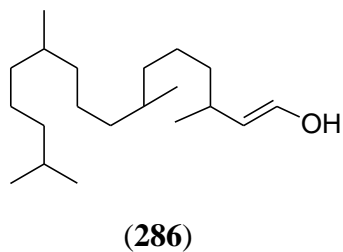
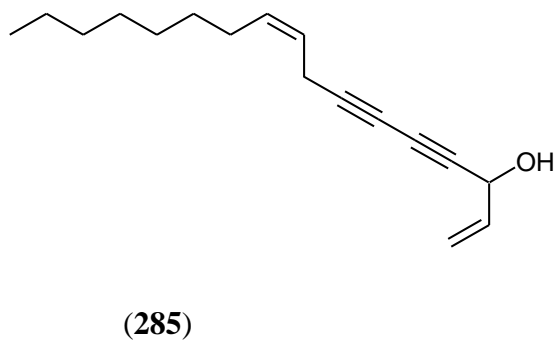
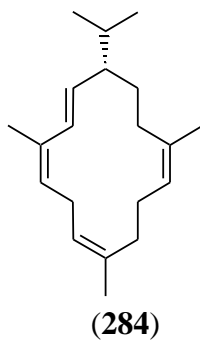
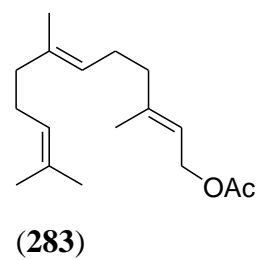
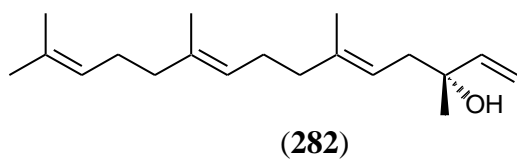
(279)



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(281)





## 6. Conclusion

### 6.1. Liverworts

The liverworts that have been used for this study were collected in four different places: Austria, Japan, New Caledonia and La Réunion Island.

It is known that the pattern of terpenoids and aromatic compounds of the liverworts depends on their development stage, the season of collection, on sexual forms (male, female and sterile) of some species and on the altitudinal distribution [Asakawa, 2004]. Same is shown in the specimens of *Conocephalum conicum* and *Marchantia polymorpha* collected in different places.

The Japanese and the Austrian *Conocephalum conicum* seemed to be morphologically similar but chemically very different. The Austrian *C. conicum* showed  $\gamma$ -cadinene (**51**) and an unknown calamenene derivative as major components while the Japanese *C. conicum* comprised 1,8-oxido-cadine-4-ene (**51**) which is the second major component of the big-thallus *C. conicum*. The latter showed bornyl acetate as major compound which corresponds to the chemo-type II of the three *C. conicum* chemo-types (I, II, III), that have been found in Tokushima [Toyota, 1997]. Whereas, sabinene (**28**) and 1-oct-3-enyl acetate (**256**), as characteristic compounds of *C. conicum*, were detected from the ether extract of the Austrian and the Japanese *C. conicum* specimens, in different quantities though. The small thalloid *C. conicum* showed a higher amount of components with higher molecular weights. Their peaks which appeared in the GC after 32 minutes were not identified. The appearance of 2-heptanol (**254**) in such a high amount, corresponds probably to the presence of a thermolabile compound in the crude extract prior heating it [Asakawa].

According to Prof. Dr. Asakawa, the European *C. conicum* contains usually (-)-thujanol and its epimer [Asakawa, 1995]. The Austrian sample used for this thesis, contained neither (-)-thujanol nor its epimere, it is rich on sesquiterpenes, though.

(-)-Cyclopropanecuparenol (**210**) was found to be the major component of all three samples of *M. polymorpha*, collected in Austria and two places of Japan, the

Austrian *M. polymorpha* showed the highest amount of it. Furthermore both Japanese specimens seemed to contain  $\alpha$ -bisabolol (**100**), which was not present in the Austrian *M. polymorpha*. The latter one showed the presence of widdrol (**152**) though. *Marchantia* species are known for their characteristic secondary metabolites, the (bis)-bibenzyls, such as marchantin or riccardin which are not soluble in ether though [Asakawa].

Sacculatal (**231**), sacculatallactone- and other derivatives are predominant in the composition of volatiles of the pungent *Pellia endiviifolia* collected in Tokushima. The pungency of *Pellia endiviifolia* comes due to the high presence of this pungent component and its derivatives. Moreover, sacculatal is the most significant chemical marker of *P. endiviifolia* even though it has been found in other Metzgeriales like *Pallavicini* and *Riccardia* species. The volatile components  $\gamma$ -cuprenene (**207**), germacrene B (**125**) and elemene (**109**) were detected from the Austrian *P. epiphylla*, which on the other side does not contain sacculatal (**231**) or any of its derivatives. The genus *Pellia* belongs to Metzgeriales which lack the oil bodies, this could explain the few volatile components that have been found in the two specimens [Asakawa, 2004].

The presence of terpenoids in *Radula* sp. is extremely rare [Asakawa]. Compounds that have been found are all bibenzyls and prenylbibenzyls: radulanin K (**177**), radulanin I (**178**), 3-methoxy-4-(3-methyl-2-butenyl)-4-hydroxybibenzyl (**179**), 3,5-dihydroxy-2-(2,3-epoxy-3-ethyl)-bibenzyl (**180**), 3,5-dihydroxy-(3-methyl-2-butenyl)-bibenzyl (**176**). It is worth mentioning that (**178**) was by far the predominant component. It is also worth mentioning that the compound, which is the most important marker of *Radula* sp., 2,2-dimethyl-5-hydroxy-7-(2-phenylethyl)-chromene (**181**), has also been identified, even if in a low area percentage.

Pinguisanine-type sesquiterpenoids are the major constituents of *Ptilidium* sp. They are also the most characteristic components of the genus *Ptilidium* [Asakawa, 1995 and 2004]. Similar to the Austrian *Ptilidium* sp., of which the GC-MS-data showed the presence of:  $\alpha$ -pinguisene (**139**), 5-epi-pinguisenol (**140**), dehydropinguisenol

and other derivatives. Petasitene (**191**) was also found in the ether extract of the Austrian *Ptilidium* specimen.

The components: 1(10)-valencene-7 $\beta$ -ol (**94**) and 1(10)-spirovetivene (**166**) are characteristic chemical markers of *Lepidozia reptans* which belongs to the family of Lepidoziaceae. The latter one is the major compound of the analyzed specimen.

A few germacrene-type sesquiterpenoids were found in the ether extract of the Austrian *Scapania* sp.. Meanwhile the major component was an unknown labdane-type sesquiterpene. Fusicogigantepoxide (**194**) and 3,5-fusicocadiene (**193**), that are thought to be very characteristic for this genus, were also detected.

The major constituent of the Austrian *Preissia* sp. was cubebol (**76**). Other volatile components detected were: ent-epicubebol (**147**), sabinene (**28**) and bornyl acetate (**45**).

The Japanese *R. hemisphaerica* differs from the European species because it produces mainly aristolan-type sesquiterpenoids [Toyota, 1999]. But no aristolane-type sesquiterpenes could be detected on the data of the sample used for this study. Some of the the components found in the GC were  $\gamma$ -cuprenene (**207**),  $\beta$ -chamigrene (**211**), cadina-4,11-diene (**56**), 16-kaurene (**223**).

$\beta$ -Patchoulene (**197**), drimenol (**114**), selina-4,7-diene (**75**), germacrene B (**125**) and pogostol (**201**) have been identified from the New Caledonian *Bazzania* sp. Meanwhile menthathiophene (**21**) and 4-ethylphenol (**20**) could be found in the GC-MS spectral data of the strong smelling *Leptolejeuna* sp.. Menthathiophene was also described as being partly responsible for the smell of buchu leaf oil obtained from the higher plant *Agathosma* sp.( buchu plant, Rutaceae).

The liverwort *Plagiochila boryana* had a pungent taste by chewing it, which is due to the presence of plagiochiline A (**170**) or rather plagiochilal B which comes as result of the transformation of plagiochiline A (**170**) to the intensive pungent dialdehyde plagiochilal B through amylase or saliva. Plagiochilal B was found and isolated from *Plagiochila fruticosa* [Asakawa, 1995].

The major component of *Gottschelia schizopleura* was possibly a sesquiterpene alcohol the structure of which could not be exactly identified.  $\beta$ -Barbatene (**185**), germacrene-type sesquiterpenes and  $\beta$ -phenylethyl cinnamate (**228**) were also detected in the GC of this liverwort, in much lower percentage though. The former was also detected in the GC of the liverwort *Jamesionella purpurascens* which also contained anastreptene (**196**) and bicyclogermacrene (**127**). The major component was an unknown diterpene alcohol though.

Only about 10 per cent of total bryophytes have been chemically studied. Since they are morphologically very small and the chemotaxonomy is very important, it is necessary to continue the chemical study especially the oil bodies which contain lipophilic terpenoids with very various carbon skeletons as well as aromatic compounds and phenolics. About 90 per cent of the bryophytes, investigated so far, possess oil bodies. A few of the compounds found in the liverworts are peculiar to these and were not found in higher plants [Asakawa, 2004]. Furthermore, 80 % of the sesquiterpenes found in Hepaticae are the enantiomers of those found in the higher plants.

In summary, the secondary metabolites of the liverworts are very interesting and show a lot of biological and pharmacological activities. Though liverworts are morphologically very small, it is very difficult to collect, purify and identify large amounts of liverworts in order to guarantee pure samples. For this reason they are considered to be useless for the use in the human diet. Although they have been used to cure cuts, burns, external wounds, pulmonary tuberculosis, fractures, neurasthenia, scalds etc. and to isolate a number of new terpenoids and aromatic compounds which showed interesting biological activity and which were not found in any other plant. For example the bis-bibenzyls, phenolic compounds that are one of the most characteristic chemical constituents of the liverworts, have not been found in any other organisms, except for the Japanese fern called *Hymenophyllum barbata*.

## 6.2. Higher plants

17 higher plants have been investigated for this study. All of them were collected in Tokushima some of which are endemic to Japan. Their usages were different beginning from ornamental to medical plants, due to their chemical constituents.

The GC-MS data obtained from the ether and the n-hexane extracts of *Artemisia vulgaris* var. *indica* leaves showed a lot of interesting peaks.  $\gamma$ -Cadinene (**51**) showed the highest peak extension followed by  $\beta$ -caryophyllene (**134**). Whereas the major compound of the n-hexane extract of the stem, has been identified as germacrene D (**123**). Furthermore, the n-hexane extract of the flowers showed as major compound camphor (**31**), which appeared in the GC also of the ether extract though in a low percentage. The sesquiterpenes (**51**), (**134**) and (**123**) seemed to be present in every plant part of *A. vulgaris*, independent from the solvent used for the extraction, in a quiet high percentage.

A higher amount of *A. vulgaris* has been steam distilled and the obtained essential oil had a dark green color. The color of the oil did not change as expected from green to blue therefore the plant used for the analysis contained no chamazulene which characteristically changes the color from green to blue by heating it [Asakawa]. The absence of chamazulene was also approved by analyzing the GC-MS data. Moreover, an unknown yellow-orange colored fungus grew on the residue after the steam distillation. It is assumed that the essential oil of *A. vulgaris* might have a fungicide or at least a fungistatic activity. The presence of mono- and sesquiterpenes in the GC of the ether extract of *A. vulgaris* var. *indica* very high before the steam distillation. The GC data of the *A. vulgaris* herba also extracted with ether, after the steam distillation, showed a very low presence of limonene (**2**) and some aliphatic compounds: tricosane (**239**), docosane (**242**) and pentacosane (**241**). The appearance of  $\beta$ -caryophyllene (**134**) in the data was a bit higher, no other volatile components were detected. Besides the GC spectral data of the essential oil of *A. vulgaris* showed a predominance of  $\beta$ -caryophyllene (**134**). 1,8-Cineole (**23**), camphor (**31**). Some germacrene-type sesquiterpenes were also detected.

The GC-MS data obtained from the crude extract of the young plant of *Artemisia vulgaris* showed as major components: germacrene D (**123**) in the ether extract of the leaves, and a lot of decomposition products of chlorophyll. Furthermore the ether extract of the young plant showed the presence of cis-chrysanthenol (**32**) and its acetate (**34**), they were also present in the GC of the essential oil, but not in any of the plant parts of the one year old *Artemisia vulgaris*.

The analysis of the *Farfugium japonicum* GC-MS data showed a lot of unknown components as well as a lot of aliphatic components. The unknown compounds appeared in the GC mostly after 42 minutes, probably too big molecules to be identified by the MS detector. The aliphatic compounds found in the GC are probably decomposition products. Based on the obtained data it was suggested that *F. japonicum* contains a lot of diterpenes and thermo labile secondary products. Anyhow, diplohillin (**163**) was identified in the GC, obtained from the leaves and the stem. Furthermore, the major compounds of the roots have been identified as isopinguisanine (**143**) and furanoeremophyllone (**167**) both characteristic components of the roots of *F. japonicum* [Asakawa], the latter was also identified in the ether extract of the stem.

The leaves and the rhizome of the pungent *Petasites japonicus* that has been collected in Tokushima prefecture have also been analysed to study the composition of the volatile components. The data obtained from the rhizome extract showed a high presence of pinguisanine (**142**) and its derivatives. Isopatchoula-3,5-diene (**198**) seemed to be another characteristic compound of the rhizome. Unfortunately, a number of the biggest peaks registered in the GC could not be identified.

Two *Solidago* sp. have been analyzed in this study: *Solidago altissima* and *S. virgaurea*. *Solidago altissima* has been collected in the riverside of Akiugawa, near Tokushima prefecture and the plant was more than 2 meters tall; while the second species was collected in the Tokushima city. Germacrene B (**125**) seemed to be the major component of the leaves of both species. The GC of the stem of *S. altissima* showed  $\gamma$ -cadinene (**51**) as the major component, though the presence of the monoterpene,  $\alpha$ -pinene (**28**) appeared also in a high area percentage.

The GC of the flowers of the two different species of *Solidago* showed similarity in the pattern of the components but different major compounds. *S. altissima* flowers seemed to have  $\gamma$ -cadinene (**51**) above all other components while the predominant component of the flowers of *S. virgaurea* was germacrene B (**125**). Furthermore the flowers of the former showed a higher percentage of monoterpenes than the flowers of the latter. The analysis of the roots of both specimens, showed a lot of unknown components. Many peaks were found but an exact identification according to the registered mass spectra was not possible.

Ether soluble components like:  $\beta$ -caryophyllene (**134**), 3-carene (**26**),  $\gamma$ -cadinene (**51**) and other mono- and sesquiterpenes were identified from the ether extract of the stems, leaves and flowers of *Angelica keiskei*. These compounds were also found in the spectral data of the excrements of the larvae of the swallowtail butterfly that ate this plant.  $\gamma$ -Terpinene (**3**) appeared in the GC obtained from the ether extract of the leaves and flowers in high percentage. Furthermore, this component appeared on the GC-MS data-sheet of the stem as well, in lower percentage although, whereas the analysis of the excrements of the swallowtail butterfly larvae showed no presence of  $\gamma$ -terpinene (**3**) at all. A biotransformation to an unknown component might have occurred. The compounds found on the data obtained from the stems of the same plant were  $\gamma$ -cadinene (**51**) (major compound),  $\gamma$ - (**78**) and  $\delta$ -amorphene (**77**) which have not been detected from the ether extract of the leaves.

The analysis of the leaves, flowers and the stem of *Perilla frutescense* Britton var. *acuta* belonging to the Labiateae family, showed a few unknown components. Furthermore the major components of the leaves and stems could not be identified whereas the major compound of the flowers was identified as cis-bergamotene (**115**). Elzholtziaketone (**171**) seemed to be a characteristic chemical constituent of this plant, since it appeared in the ether extract of the leaves, flowers and corolla. The highest amount was in the extract of the flowers, though.

Albicanol (**122**) appeared at a very high percentage in the GC obtained from the ether extract of roots and leaves of *Curcuma zedoaria* and at a low percentage in the data of the rhizome. The major component of the rhizome and a lot of the peaks

detected from the ether extract of the roots of *C. zedoaria* could not be identified. Coronarin E (**233**) which is also a characteristic secondary metabolite of *C. zedoaria*, was found in the ether extract of the roots.

The American maple tree belongs to Platanaceae and is called *Platanus occidentalis*. Its leaves change the color during end of November-beginning of December, from green to yellow or/and red. It is a very common plant in Japan. The ether extracts of red and green leaves of *P. occidentalis* collected from the campus of the Tokushima Bunri University, showed the presence of almost the same compounds, only the extension of the peaks was different. The ether extract of red leaves showed a higher amount of monoterpenes and a smaller amount of chlorophyll catabolism products. The leaves of *P. occidentalis* seemed to lose the chloroplasts and the ability to produce chlorophyll. The red color of the leaves was not soluble in diethyl ether even by using ultrasound. Abietal (**219**) which was present in the ether extract of the green leaves, did not appear in the GC of the red leaves. The essential oil obtained from the red leaves showed a high concentration of bicyclogermacrene (**127**),  $\beta$ -caryophyllene (**134**) and  $\gamma$ -cadinene (**51**). Globulol (**190**) and T-muurool (**67**) were also found in the GC of the essential oil, moreover they were not present in any of the ether extract obtained from the green and red leaves, respectively.

8(14),15-Pimaradiene (**220**) is the major component identified from the yellow-brownish colored cortex of *Cinnamomum sieboldii* (Lauraceae). Other characteristic compounds of this plant seemed to be the abietane-type diterpenes and cinnamaldehyde (**40**).

Pinocarvone (**37**), trans-pinocarvol (**35**) and selina-5,11-diene (**74**) appeared in the GC obtained from the dried herbal mixture of *Chenopodium ficifolium* (Amaranthaceae) in a high percentage. The biggest peak in the GC was identified as 4,8-dimethyl-1,3,7-nonatriene (**281**), though pinocarvone-derivatives seemed to be characteristic chemical constituents of this plant.

*Citrus junos* and *Zanthoxylym piperitium* belong to the family of Rutaceae. Even though the parts that have been used for the analysis were different, the composition of the essential oils extracts showed similarities.  $\alpha$ -Pinene (**28**) and  $\beta$ -myrcene (**1**)



appeared in the spectra obtained from the pericarp of *C. junos* as well as from the leaves of *Z. piperitium*. Limonene (**2**) was the major compound of *C. junos* pericarp, while the major compound of the *Z. piperitium* leaves could not be identified. Linalool (**6**) and its acetate were detected from the pericarp of *C. junos* as well as from the leaves of *Z. piperitium* respectively. t-Butanol was found in a high amount in the GC data of *Z. piperitium*, which is supposed to be the decomposition product of linalool (**6**) [Asakawa].

The GC-MS analysis of the leaves and the stems of *Lantana camara* furnished very different data. The data obtained from the stems showed a number of mostly unknown components. Linalool (**6**) seemed to be present in both parts of the plant.  $\beta$ -Caryophyllen (**134**), cembrene (**273**), geraniol (**268**) and  $\gamma$ -cadinene (**51**) were found in the GC obtained from the ether extract of the leaves.

The essential oil of *Thujopsis dolabrata* (Cupressaceae) that was obtained by the steam distillation of the crushed wood had a viscous consistency and its color was red-brownish. The GC-MS analysis showed thujopsene (**80**) as the major component. Widdrol (**152**), cedrol (**151**) and the isomers of pogostol seemed to be also characteristic for the essential oil of this plant. The majority of the identified components were sesquiterpenes though.

The GC-MS analysis of the scale-like leaves of *Chamaecyparis obtusa* (Cupressaceae) furnished a number of monoterpenes and sesquiterpenes. Elemol (**110**), a sesquiterpene alcohol, showed the highest peak. The monoterpenes: sabinene (**28**), 2,3-didehydro-1,4-cineole (**22**) were also found in a higher percentage.

Phenanthrene derivatives were the major identified components from the ether extract of the leaves of the Japanese cedar (*Cryptomeria japonica*). Many peaks, including two major components, with a very high area extension, could not be identified.

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**Collection places of liverworts**



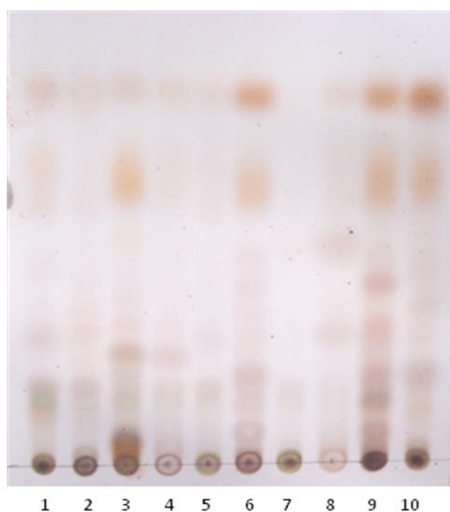








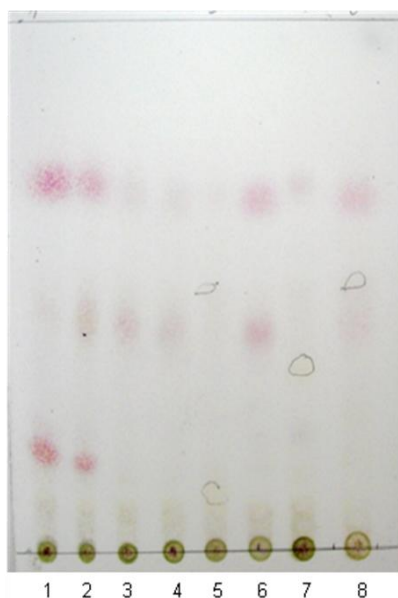
## TLC- Plates



### Austrian Liverworts:

1. *Conocephalum conicum*
2. *Marchantia polymorpha*
3. *Radula* sp.
4. *Lophocelae heterophylla*
5. *Preissia* sp.
6. *Ptilidium* sp.
7. *Pellia epiphyta*
8. *Lepidozia reptans*
9. VM1(unknown liverwort)
10. *Scapania* sp.

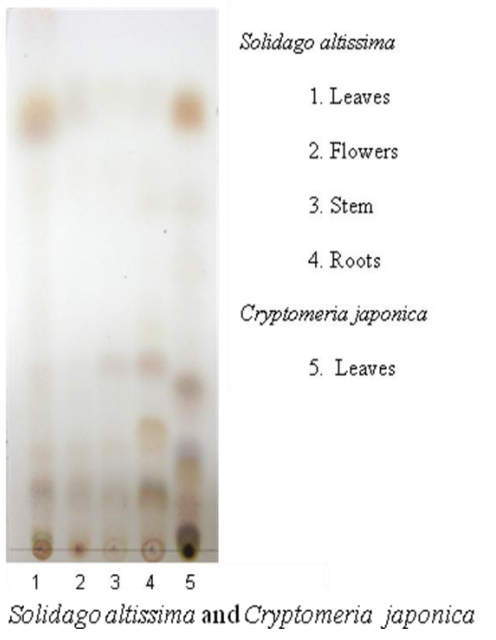
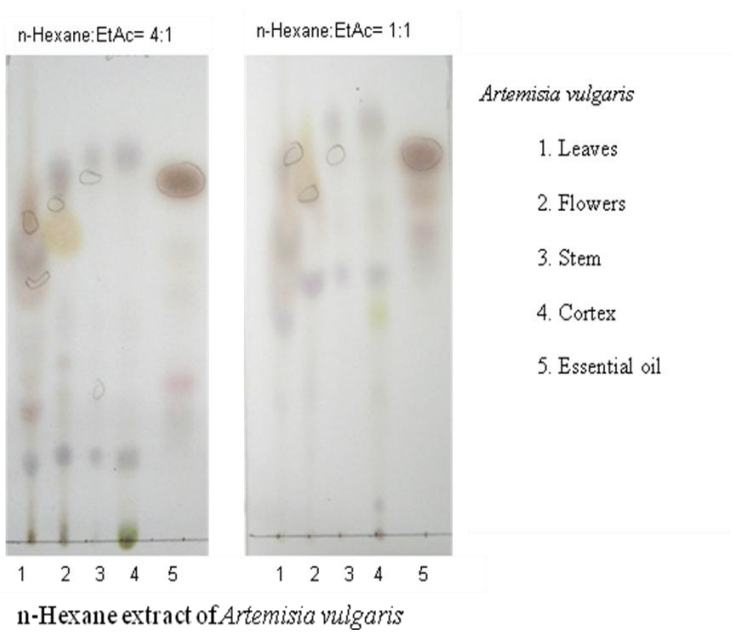
TLC plate of the liverworts collected in Austria



### Japanese Liverworts:

1. *M. polymorpha*, Tokushima
2. *M. polymorpha*, Tokyo
3. *C. conicum*, big thalus
4. *C. conicum*, small thalus
5. *Pellia endivifolia*
6. *Reboulia hemisphaerica*
7. *Corsinia coreandrina*
8. VM2

TLC plate of the Japanese liverworts





*Perilla frutescense*

1. Leaves
2. Stem
3. Flowers
4. Corolle
5. Essential oil of *Thujopsis dolabrata*

1 2 3 4 5  
*Perilla frutescense*



*Petasites japonicus*

1. Leaves
2. Leaf-stalk
3. Rhizome

1 2 3  
*Petasites japonicus*



*Angelica keiskei*

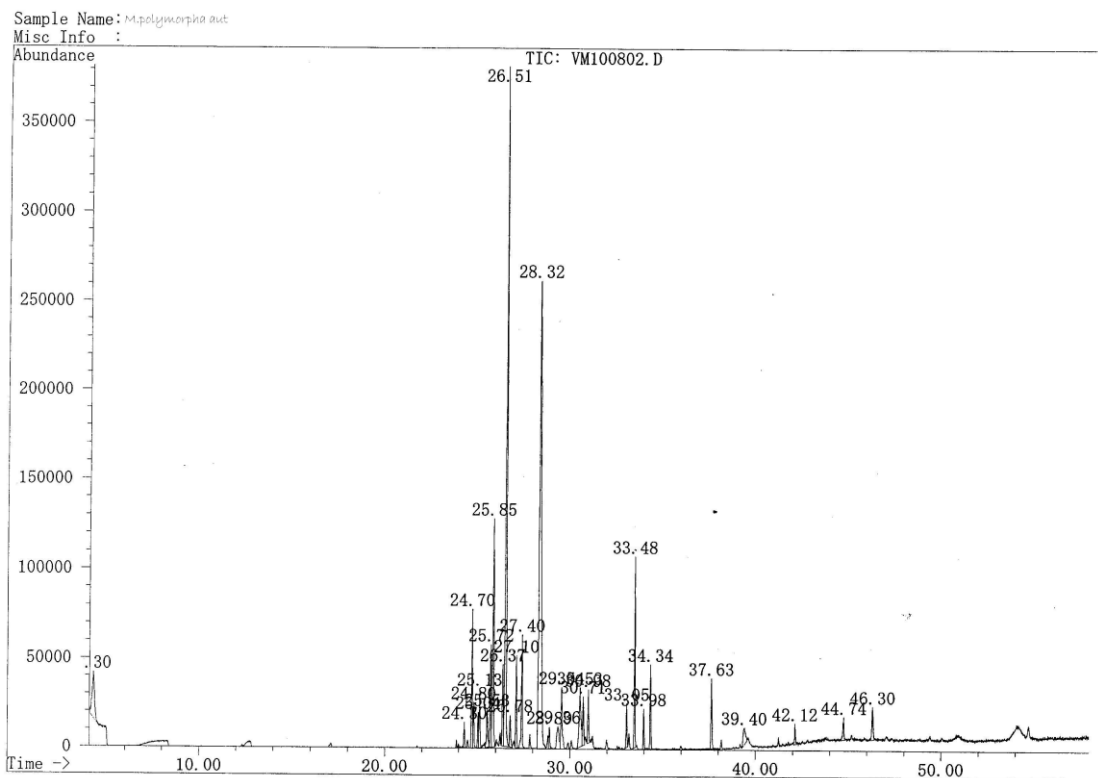
1. Leaves
2. Stem
3. Flowers

*Platanus occidentalis*

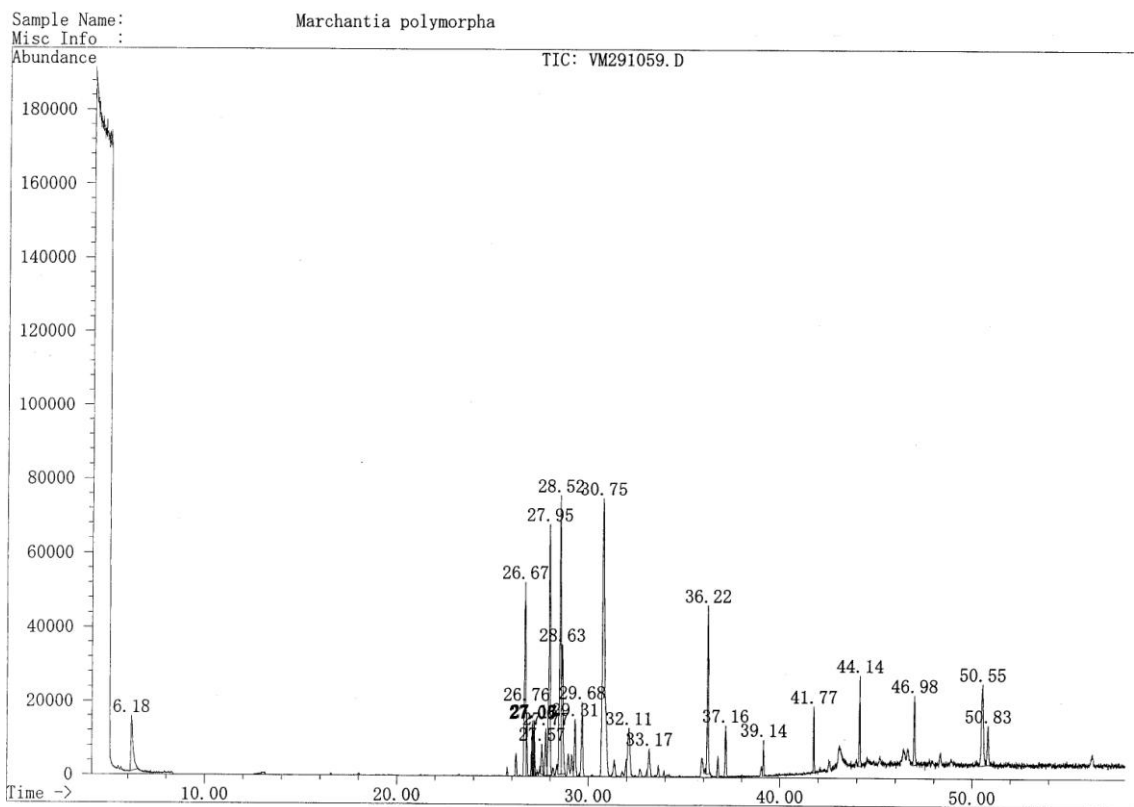
4. Red leaves
5. Green leaves

1 2 3 4 5  
*A. keiskei and P. occidentalis*

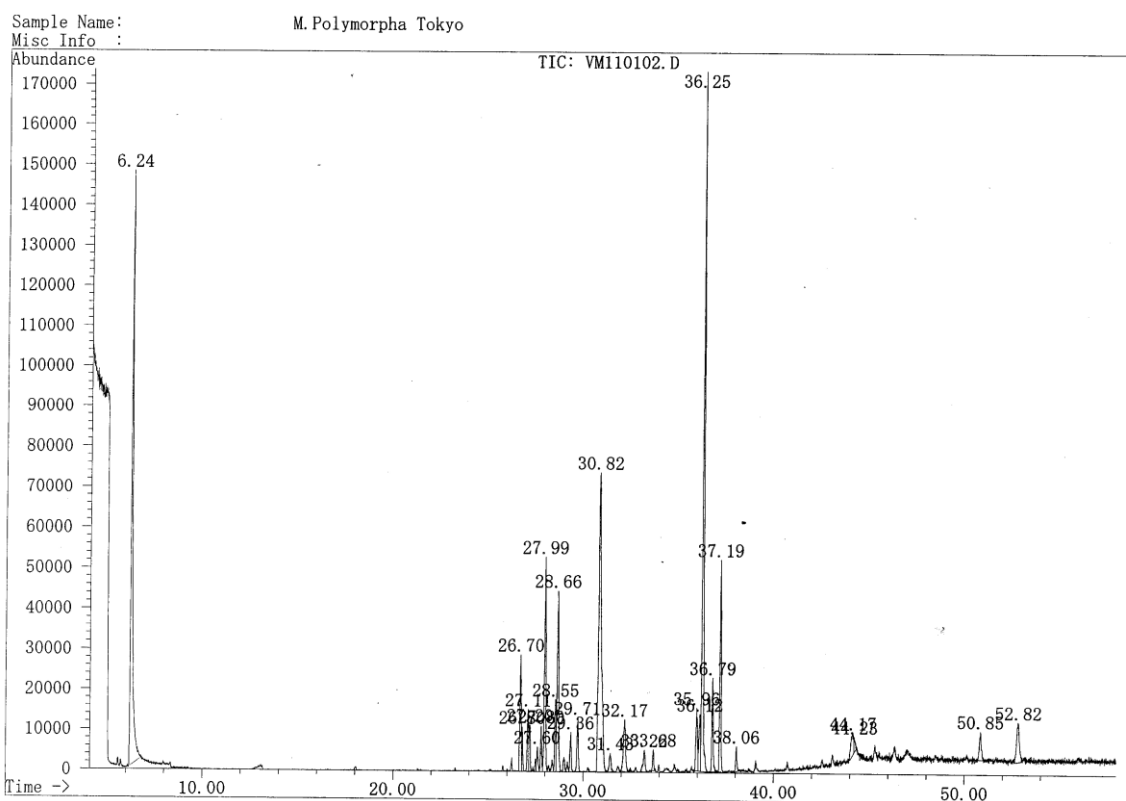
## GC- Spectra- Liverworts



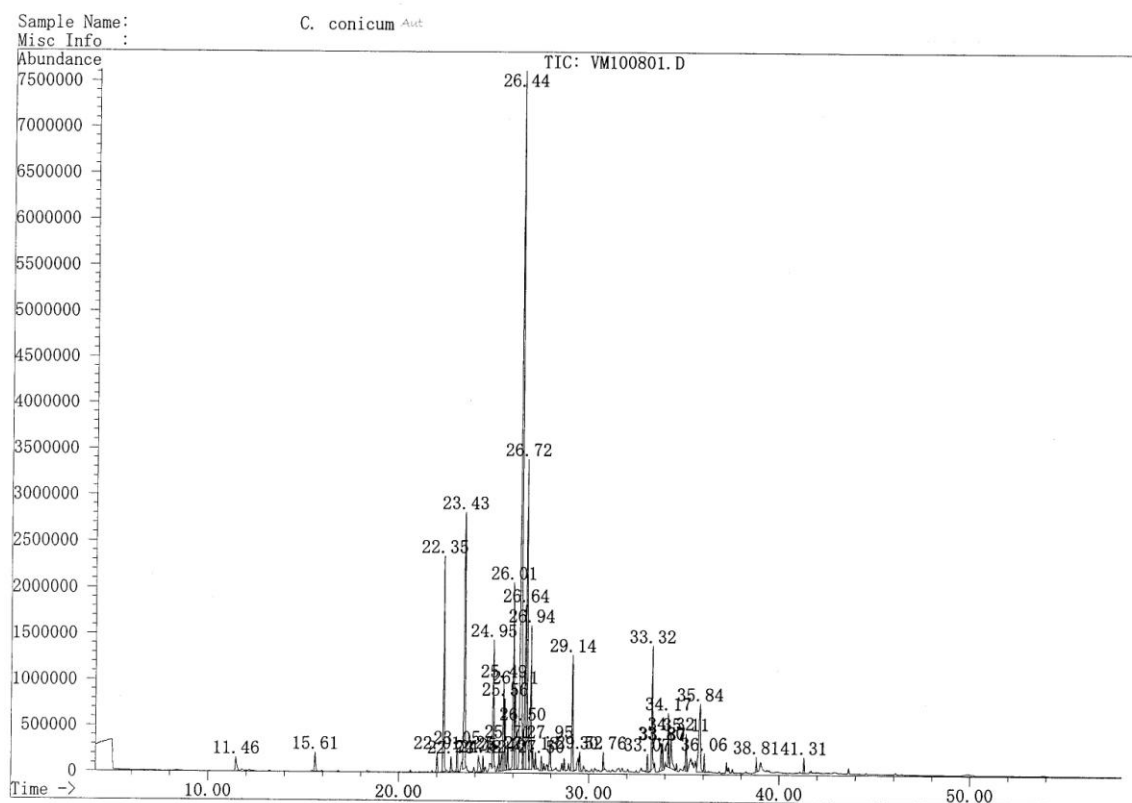
*Marchantia polymorpha*, Stuhleck



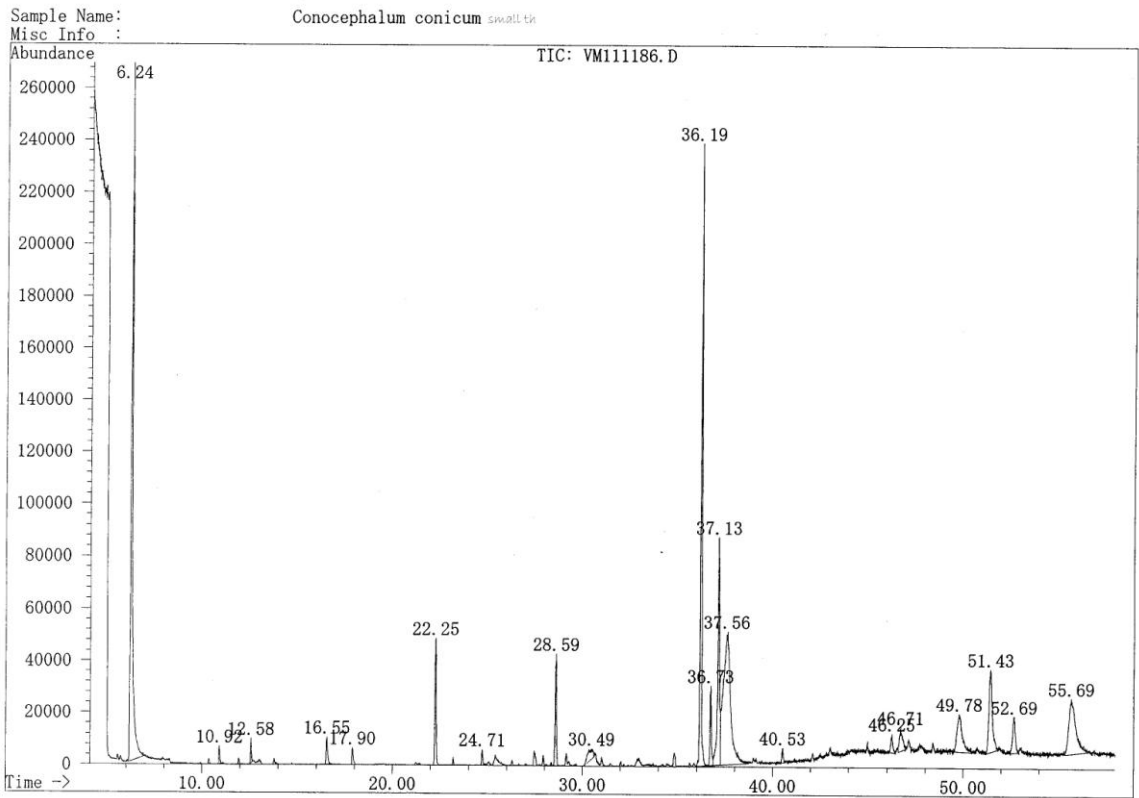
*Marchantia polymorpha*, Tokushima



*Marchantia polymorpha*, Tokyo

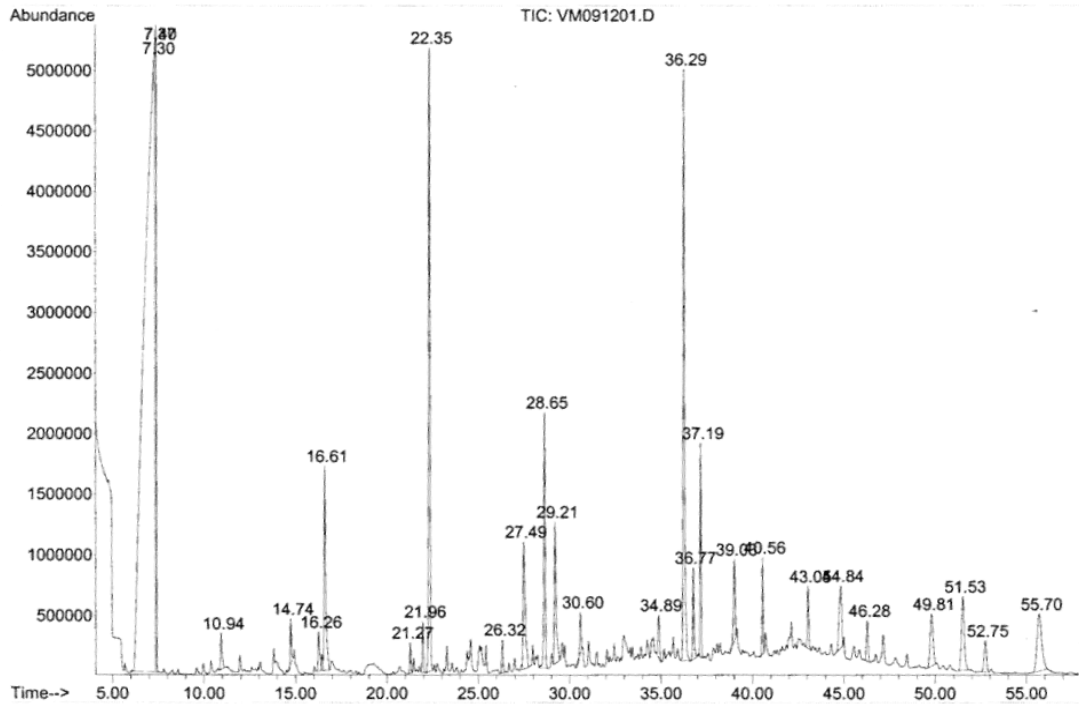


*Conocephalum conicum*, St. Pölten

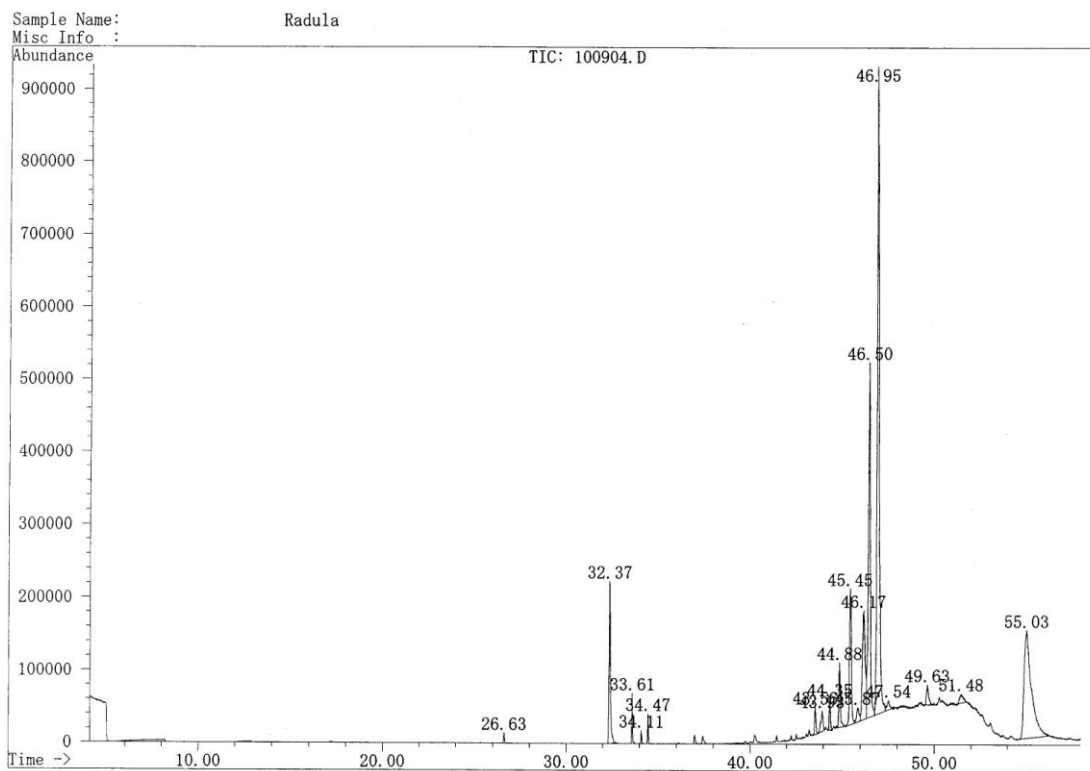


*Conocephalum conicum*, small thaloid, Tokushima

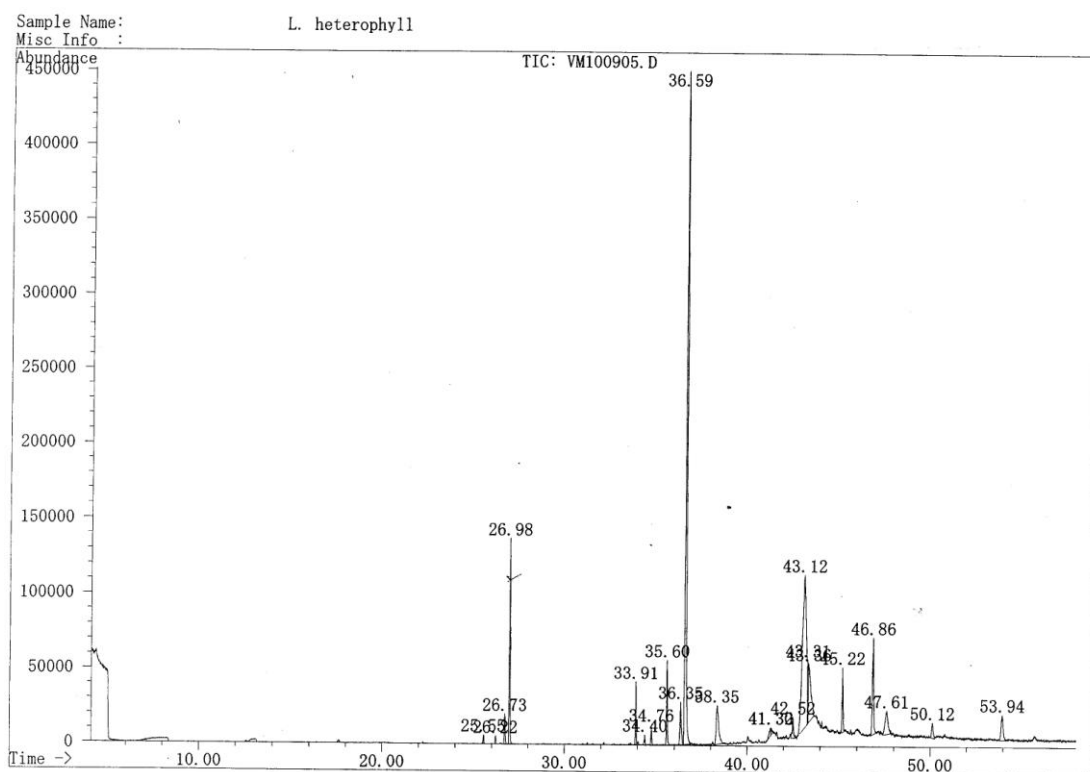
Sample Name: C.conicum big th  
 Misc Info :  
 Vial Number: 1



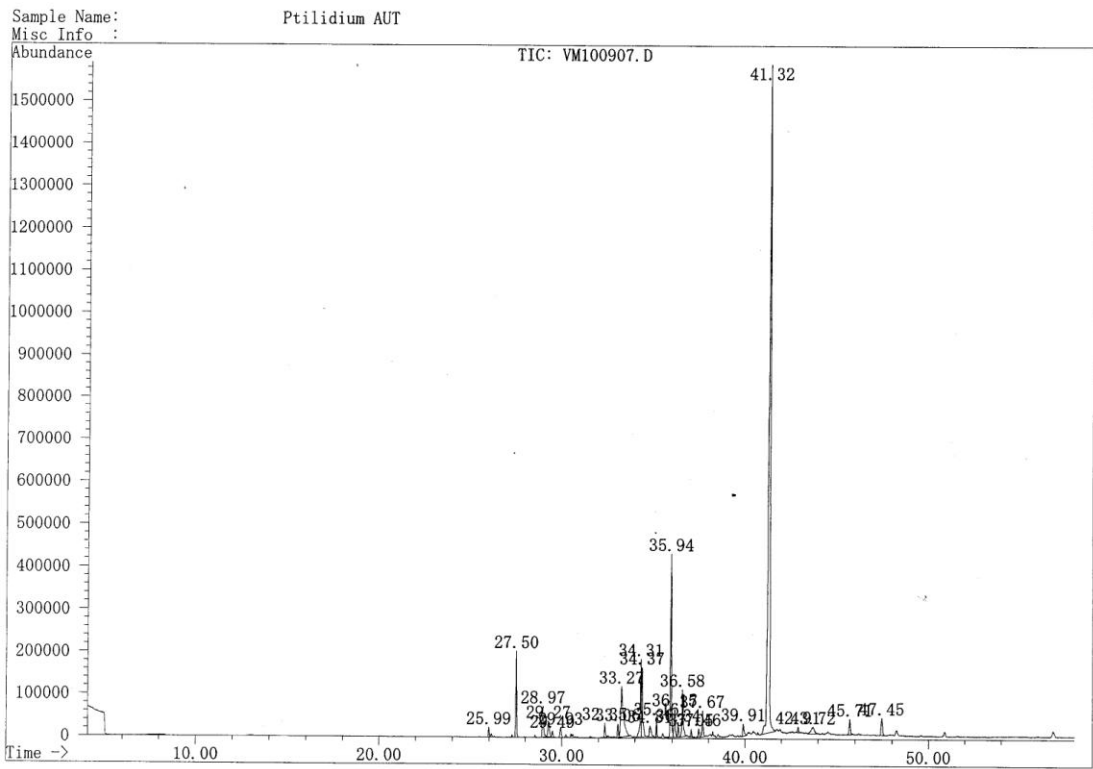
*Conocephalum conicum*, big thaloid, Tokushima



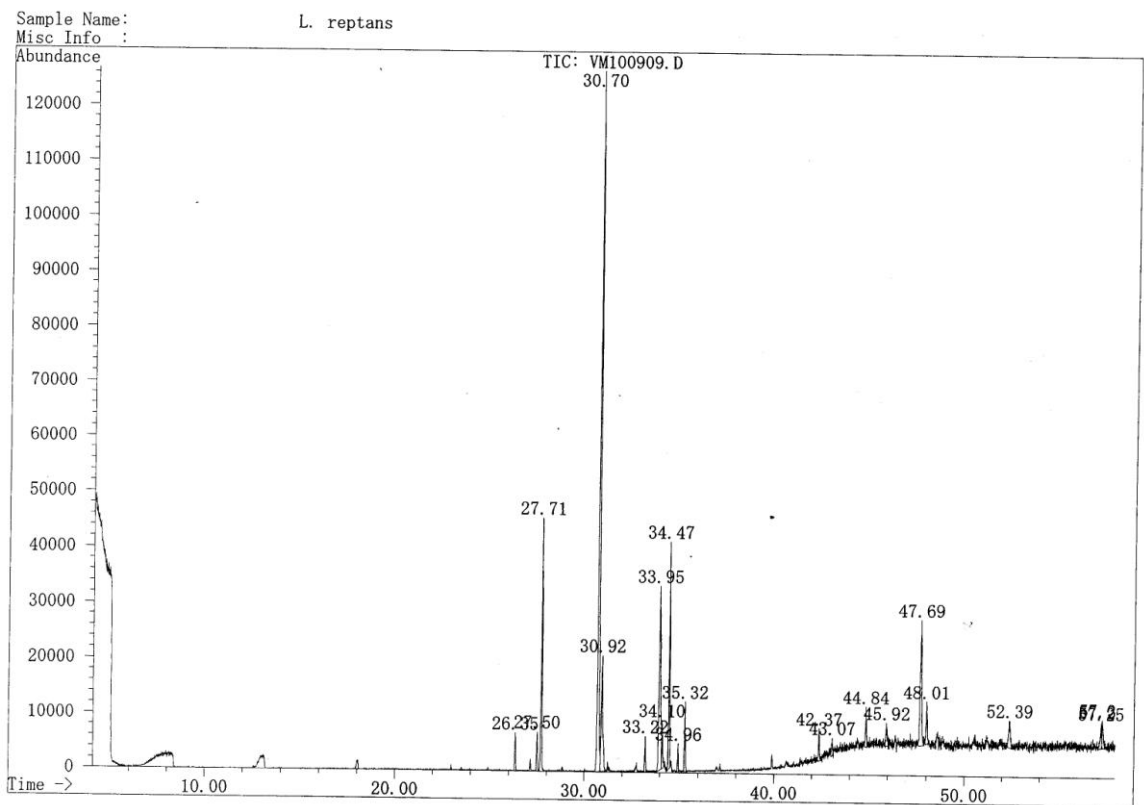
*Radula* sp. Stuhleck



*Lophocolea heterophylla*, Stuhleck

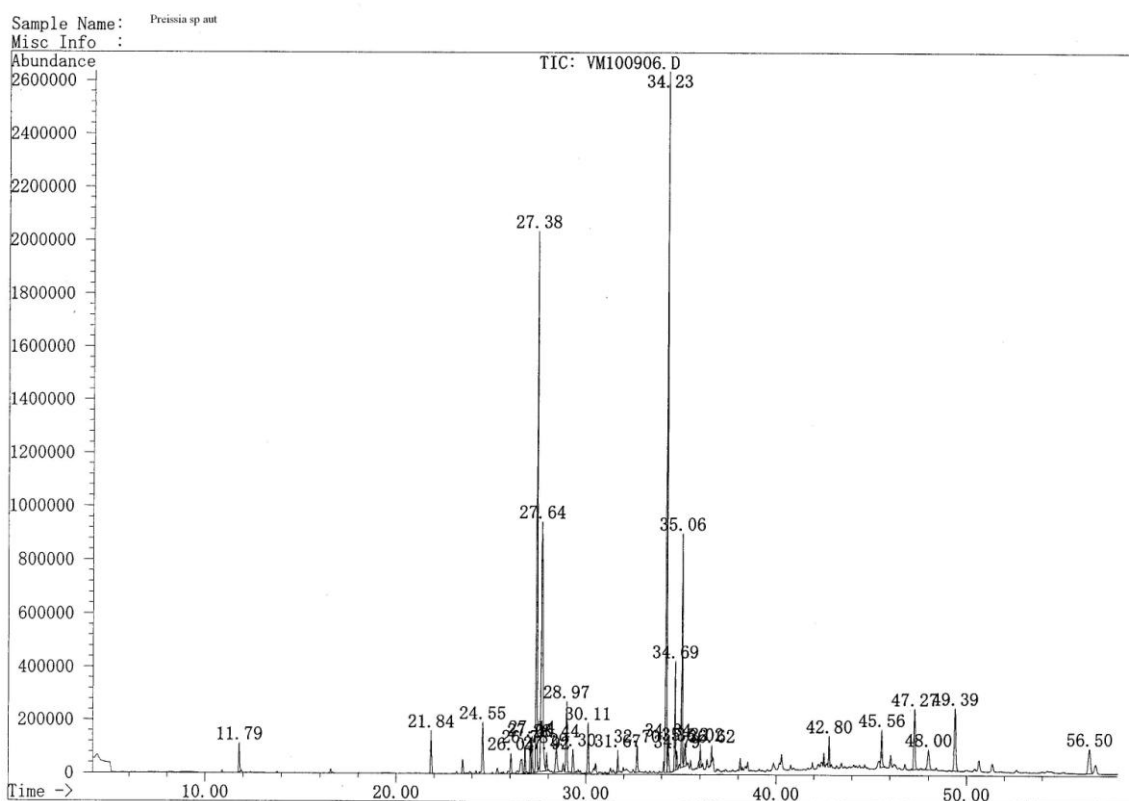


*Ptilidium* sp, Stuhleck

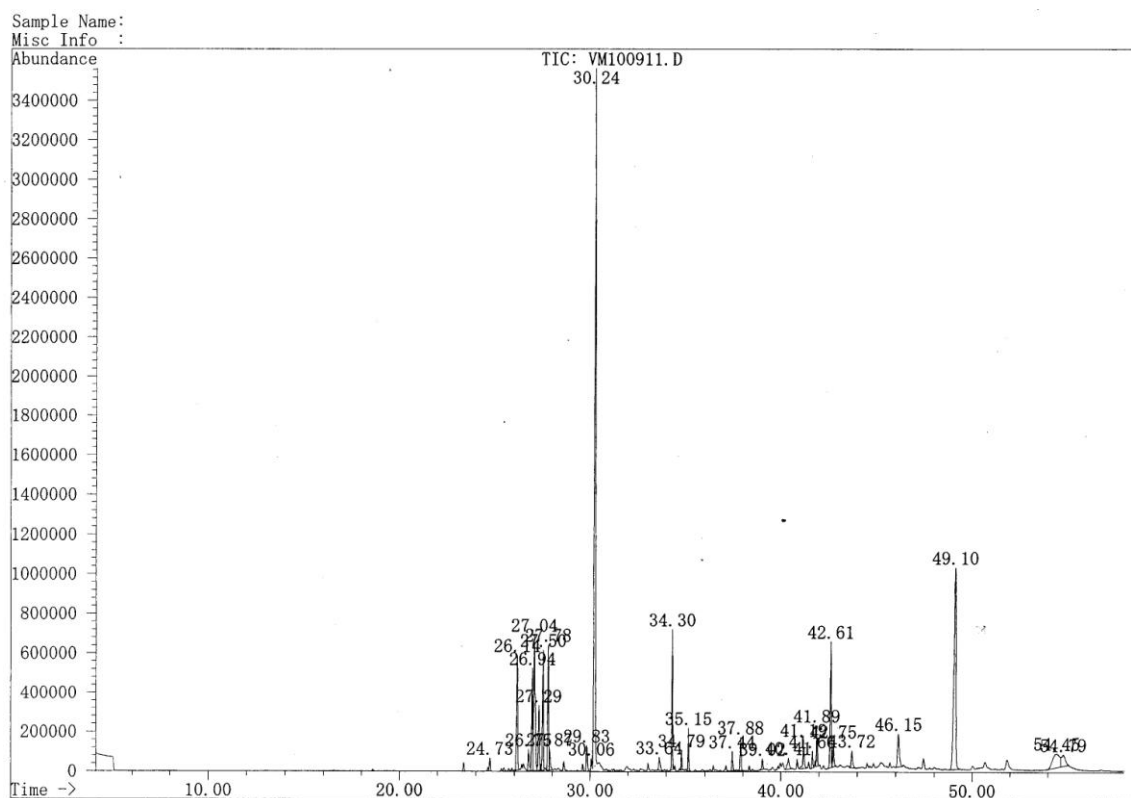


*Lepidozia reptans*, Stuhleck



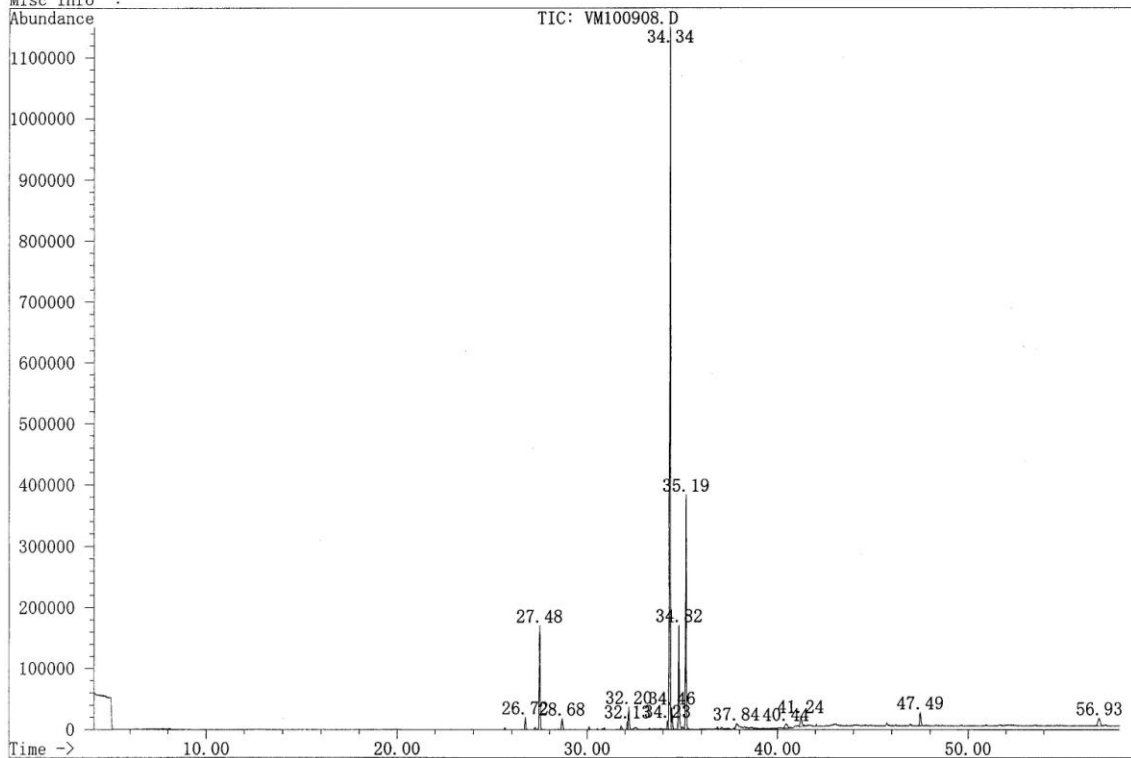


*Preissia* sp., Stuhleck



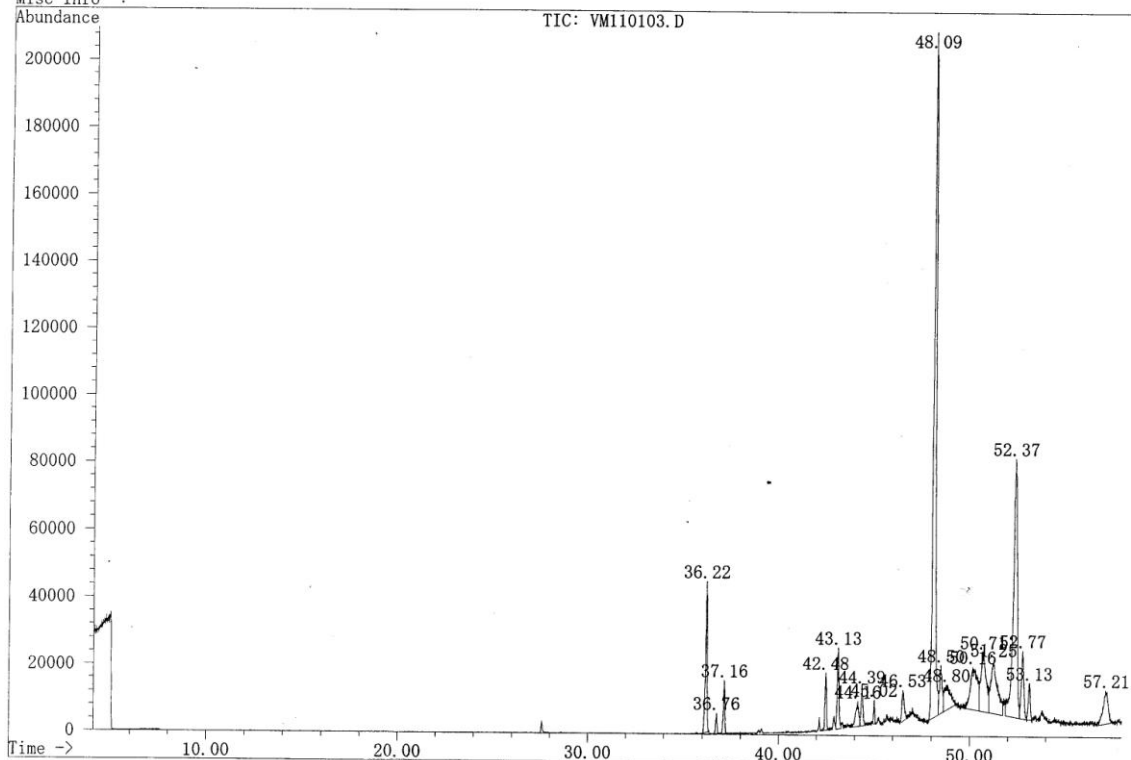
*Scapania* sp., Stuhleck

Sample Name: Pellia epiphylla Aut  
Misc Info :

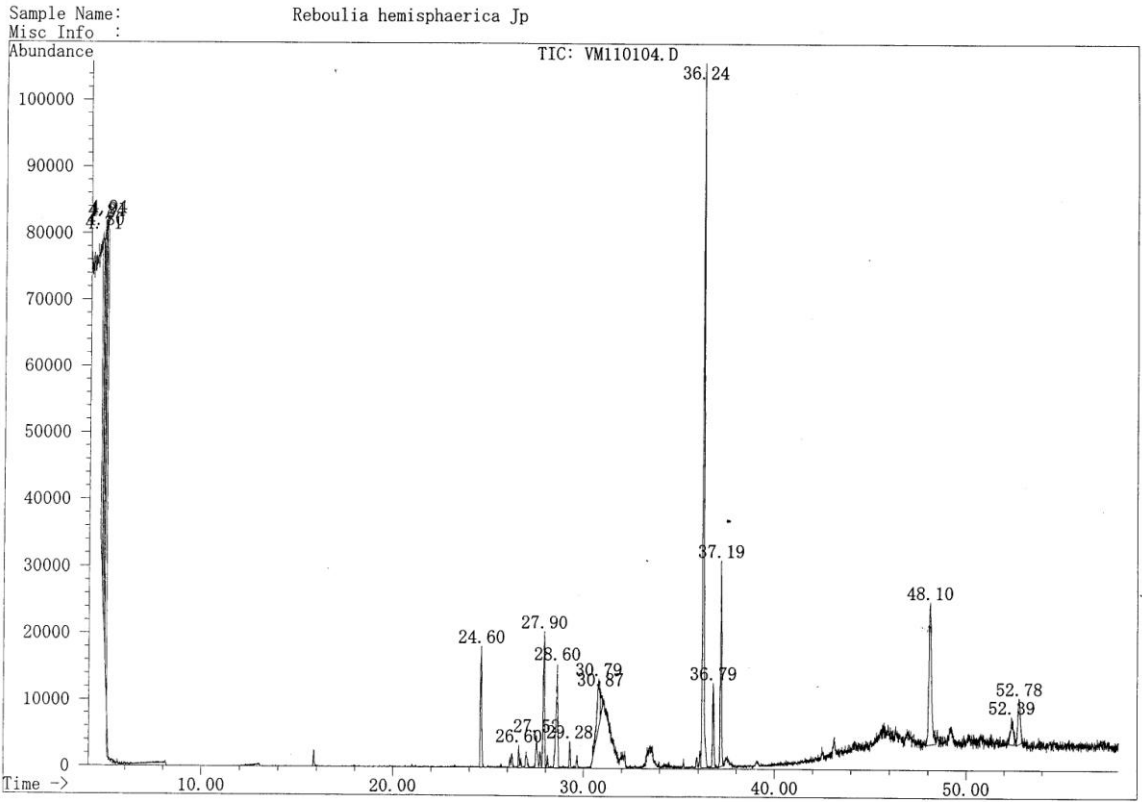


*Pellia epiphylla*, Stuhleck

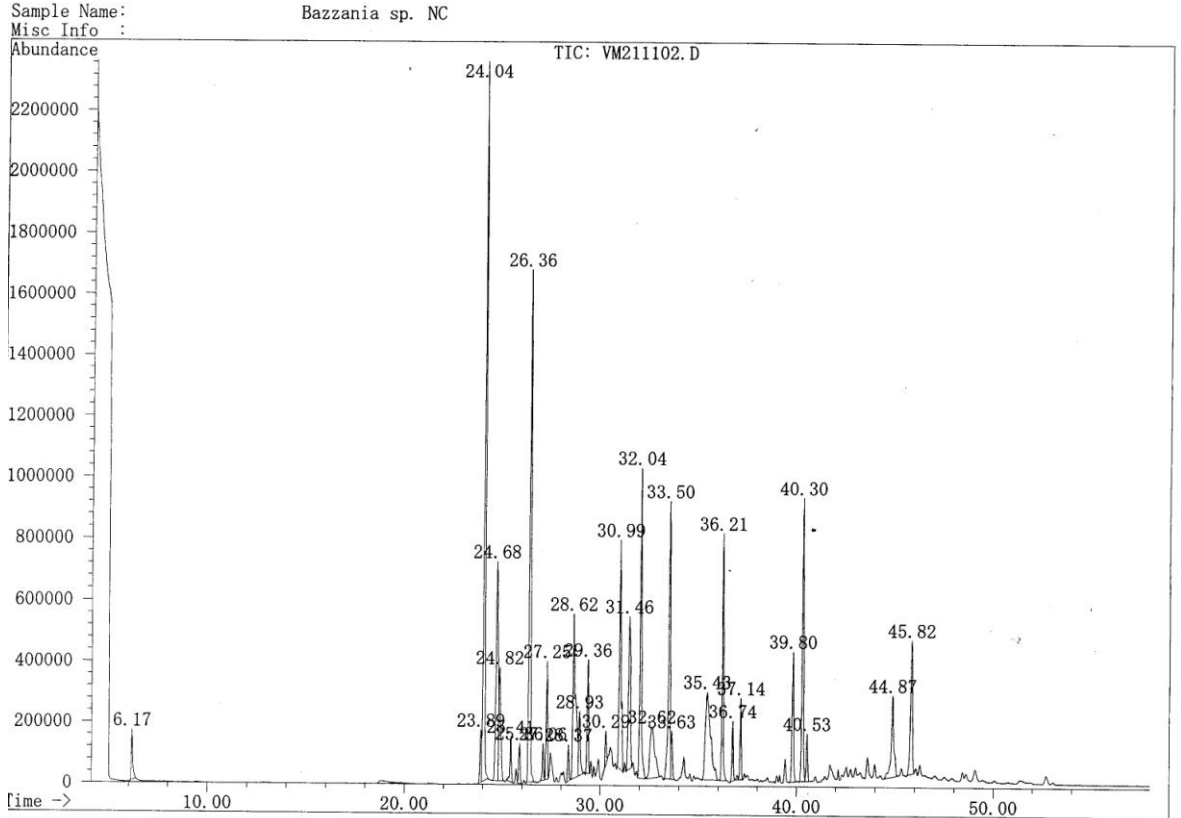
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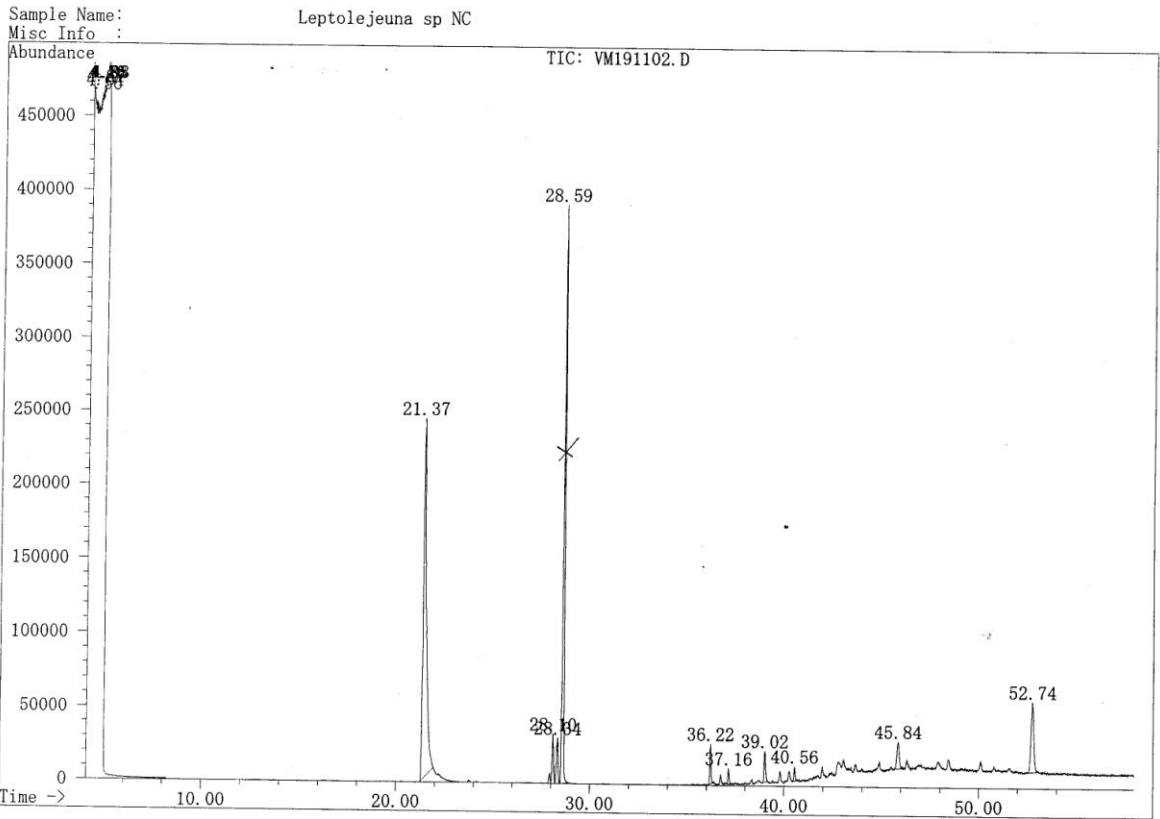
*Pellia endivifolia*, Tokushima



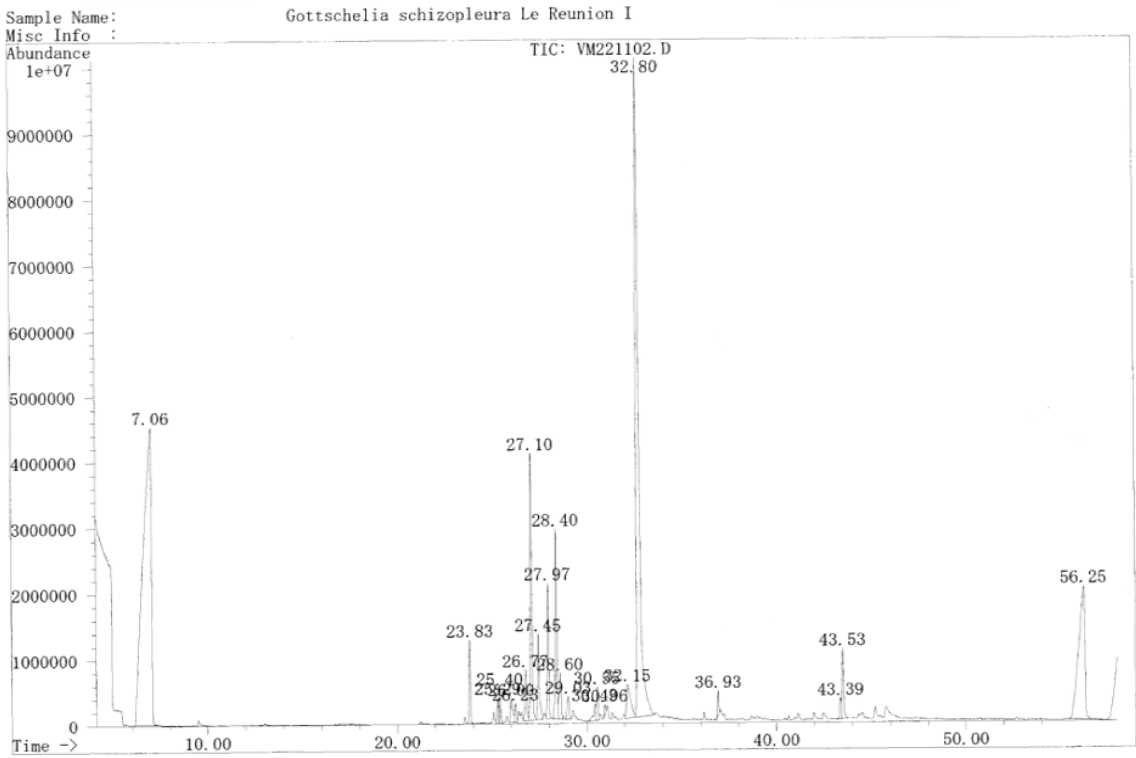
*Reboulia hemisphaerica*, Tokushima



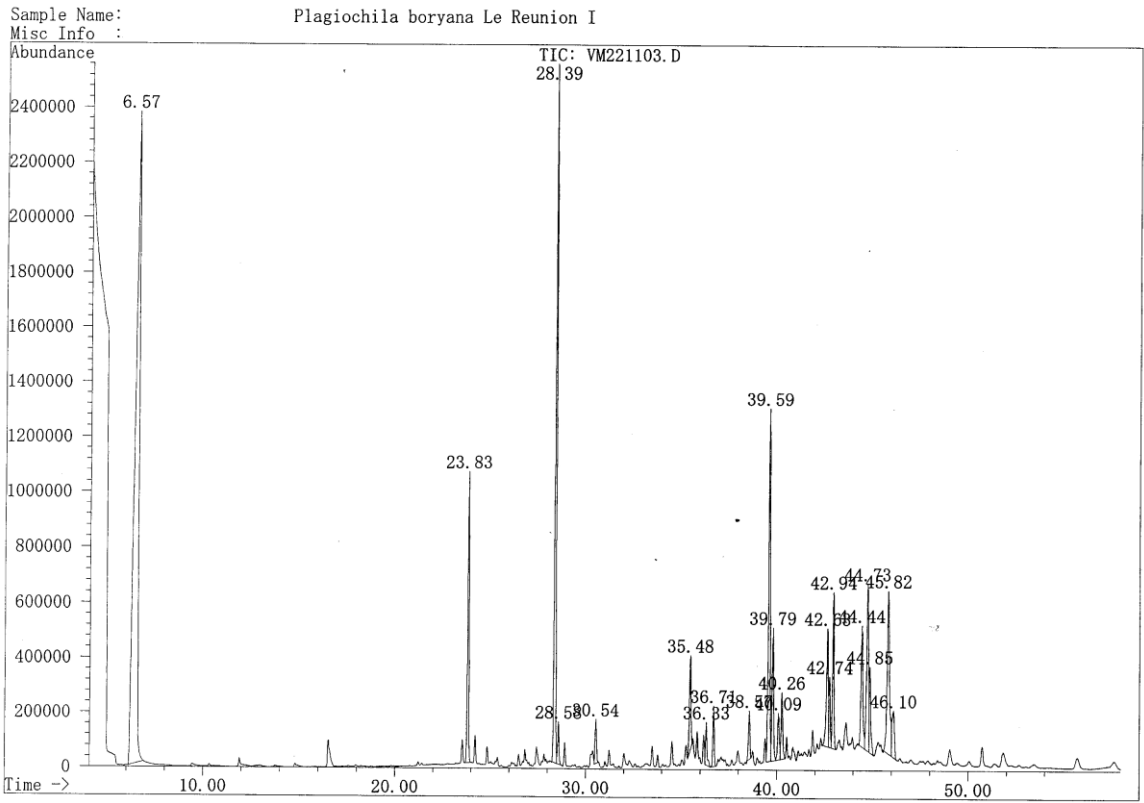
*Bazzania* sp., Noumea



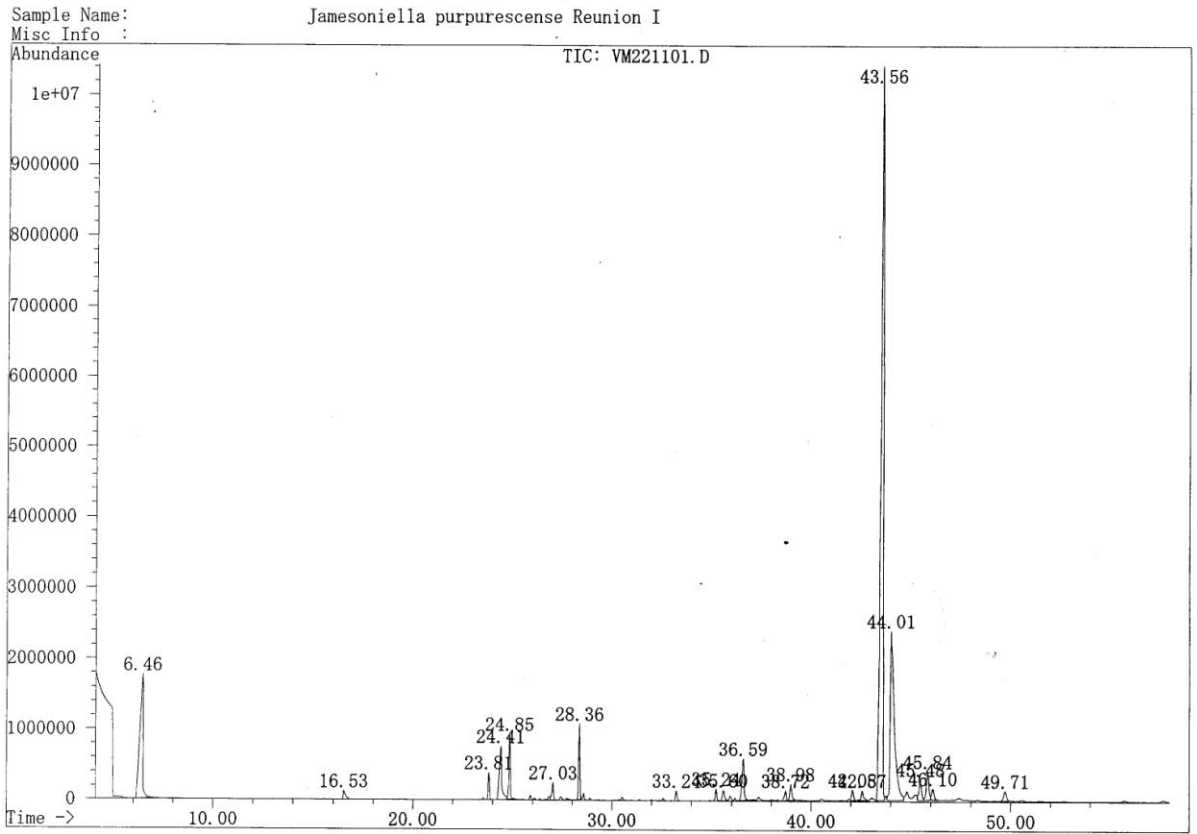
*Leptolejeuna* sp., Noumea



*Gottschelia schizopleura*, Le Reunion Islands



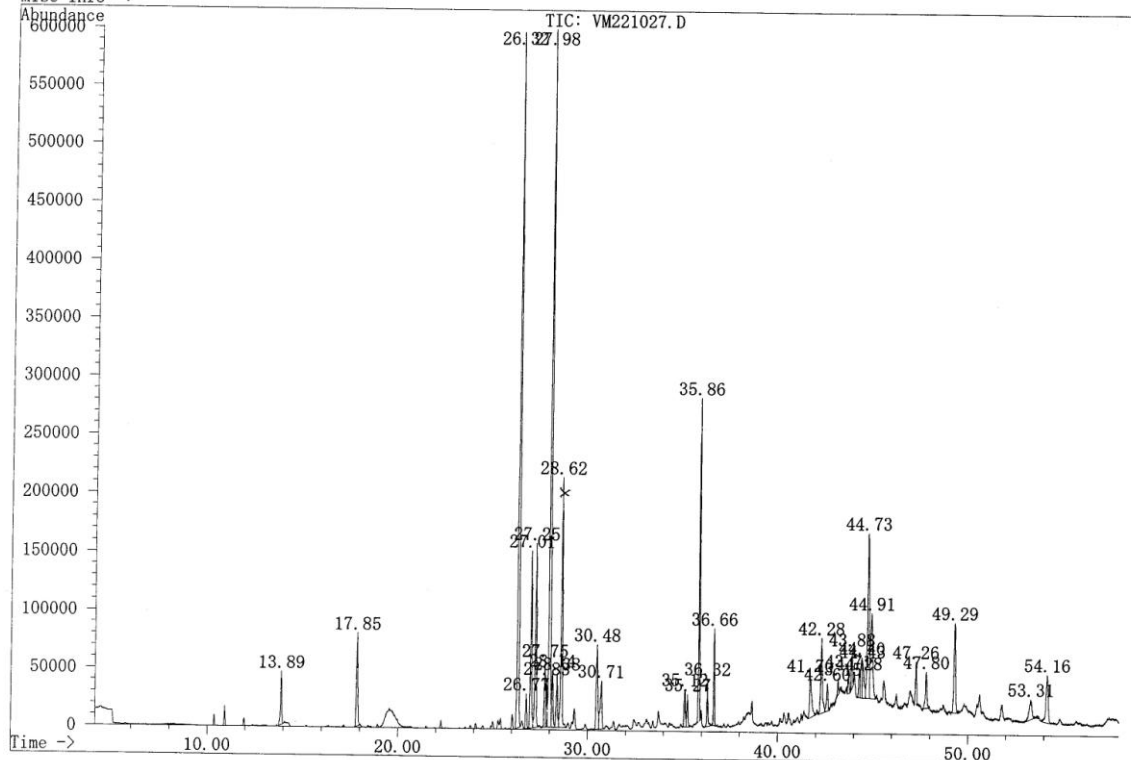
*Plagiochila boryana*, Le Reunion Islands



*Jamesionella purpurascens*, Le Reunion Islands

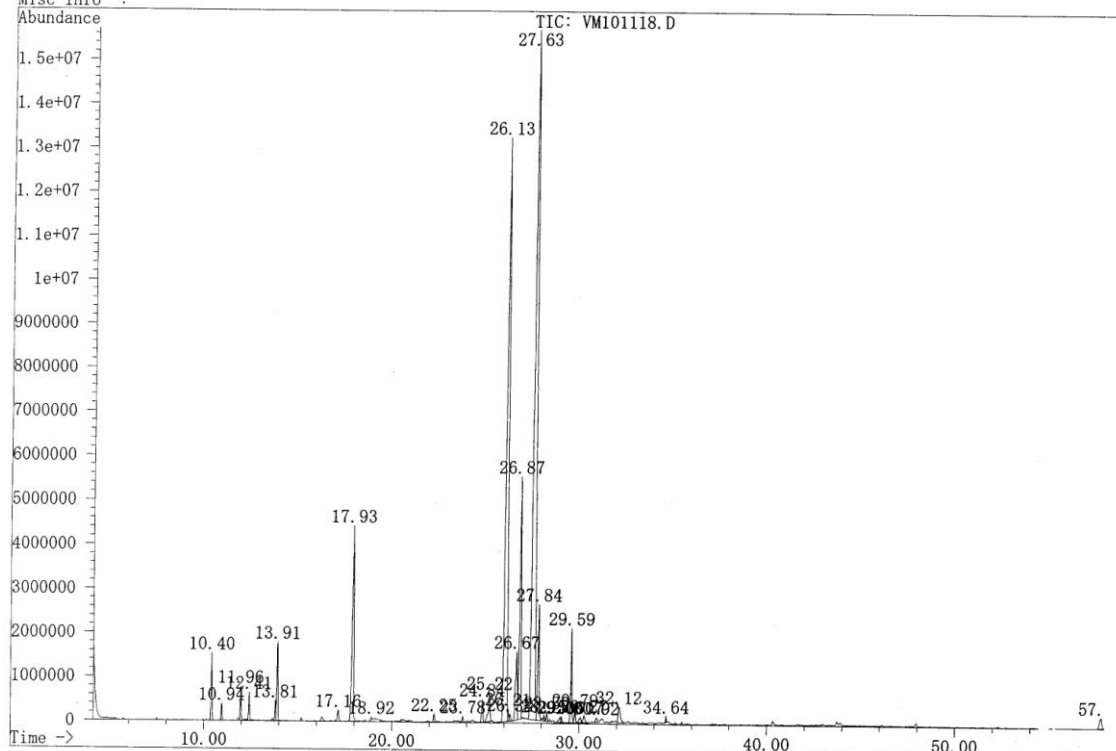
# Higherplants

Sample Name: Artemisia vulgaris, leaves ether extr  
 Misc Info :



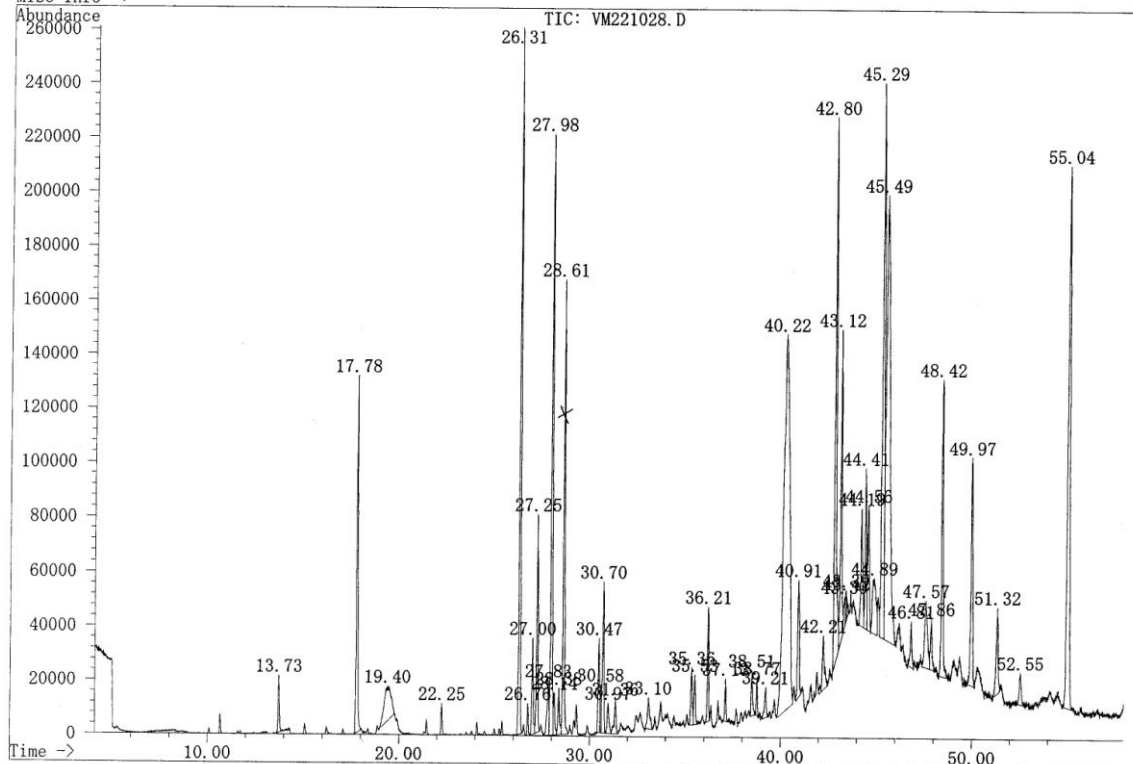
Ether extract of the leaves of *Artemisia vulgaris*

Sample Name: Artemisia vulgaris, leaves, n-hexane  
 Misc Info :



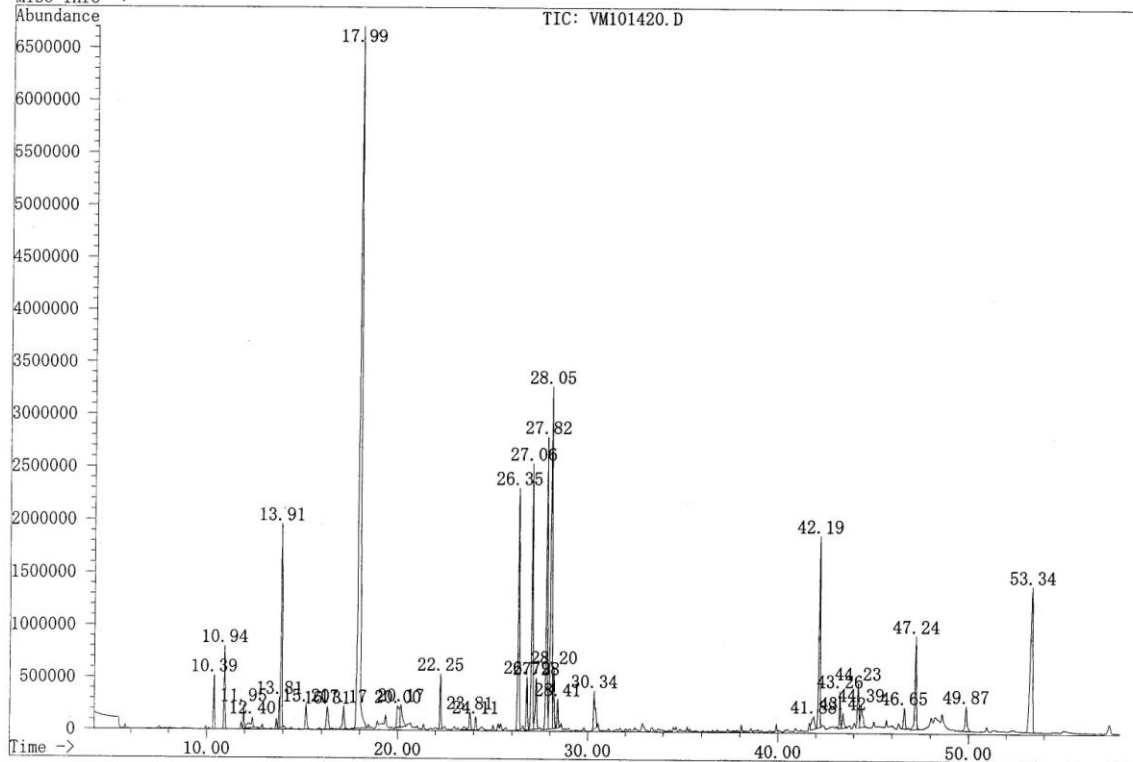
N-Hexane extract of the leaves of *Artemisia vulgaris*

Sample Name: Artemisia vulgaris, flowers, ether extr  
Misc Info :

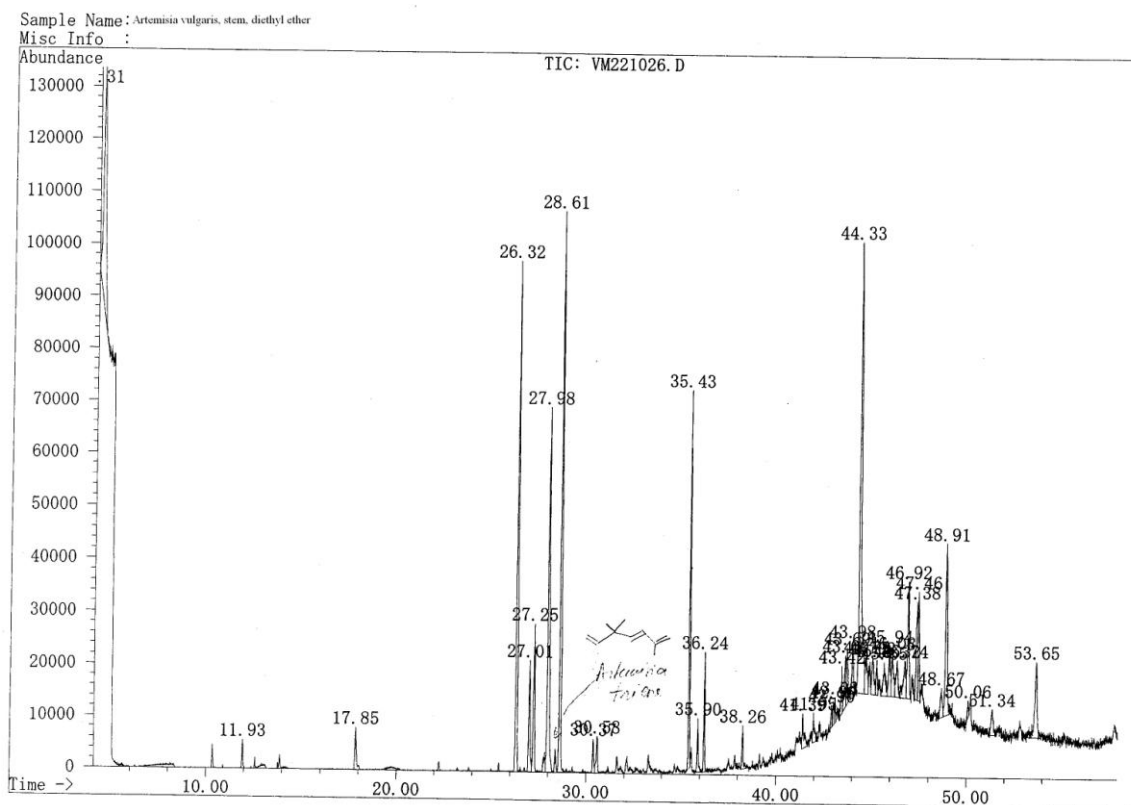


Ether extract of the *Artemisia vulgaris* flowers

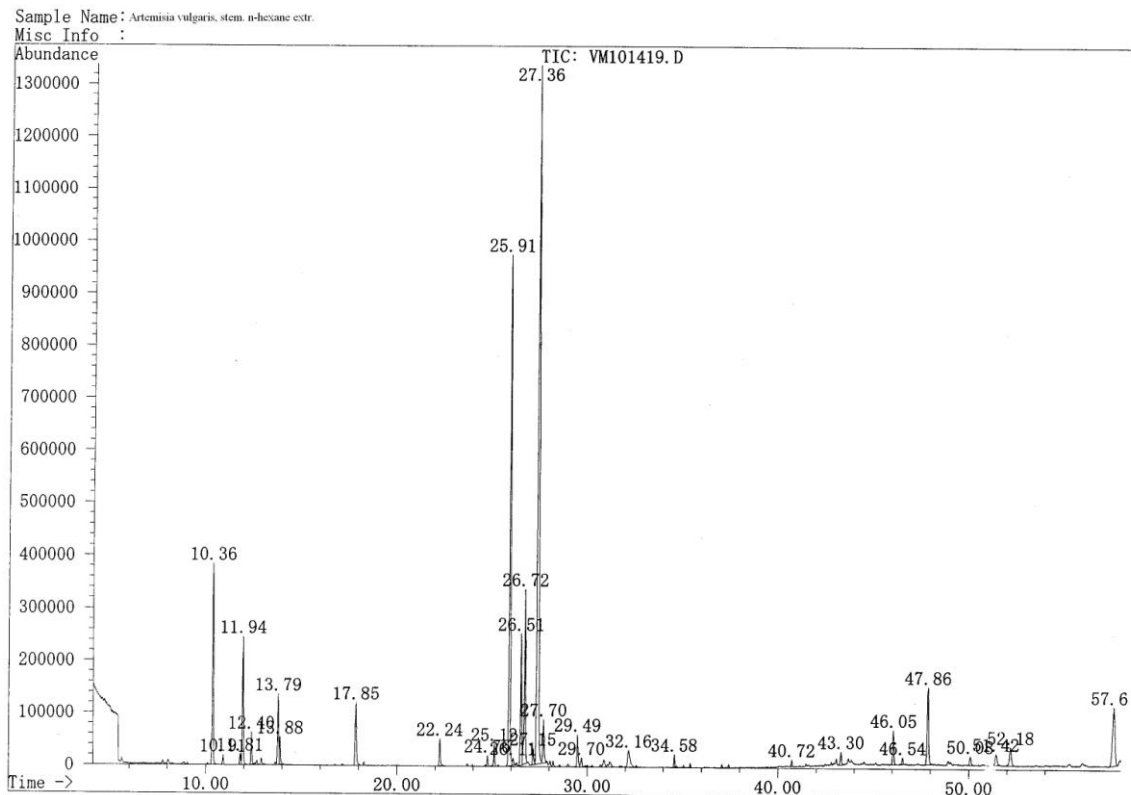
Sample Name: Artemisia vulgaris var. vulgaris, flowers, n-hexane extract  
Misc Info :



n-Hexane extract of the *Artemisia vulgaris* flowers

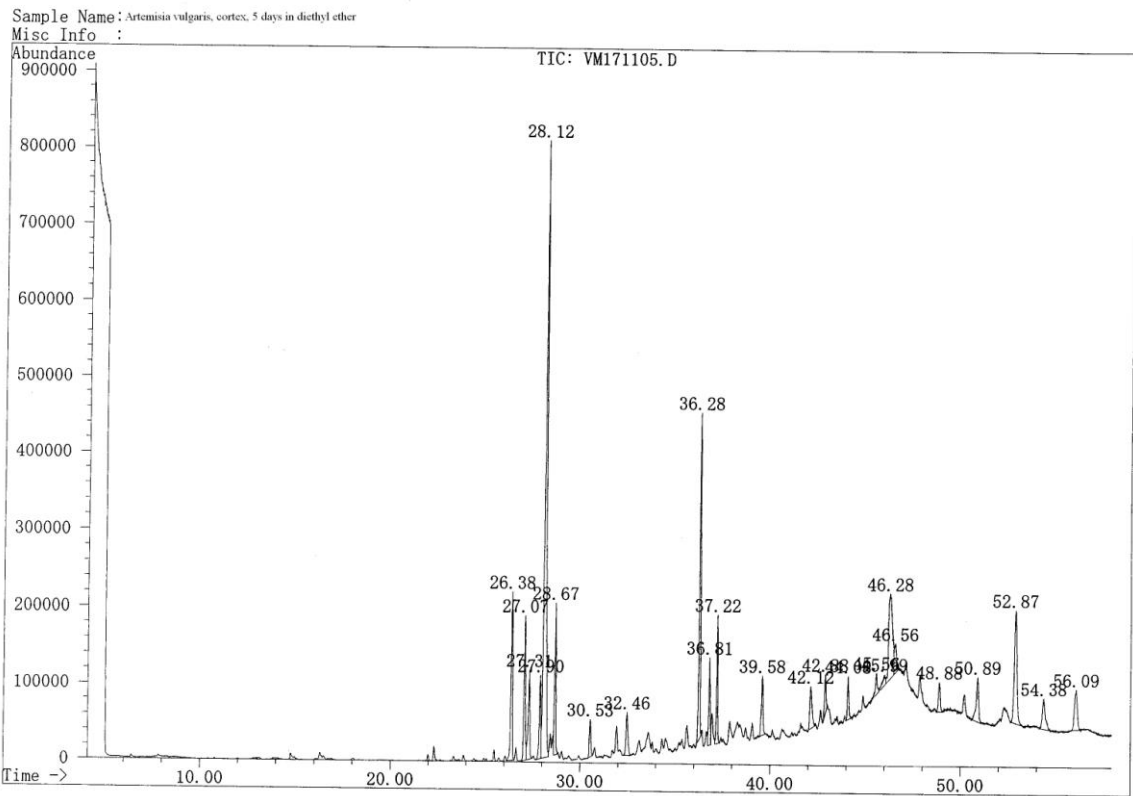


Diethyl ether extract of the *Artemisia vulgaris* stem

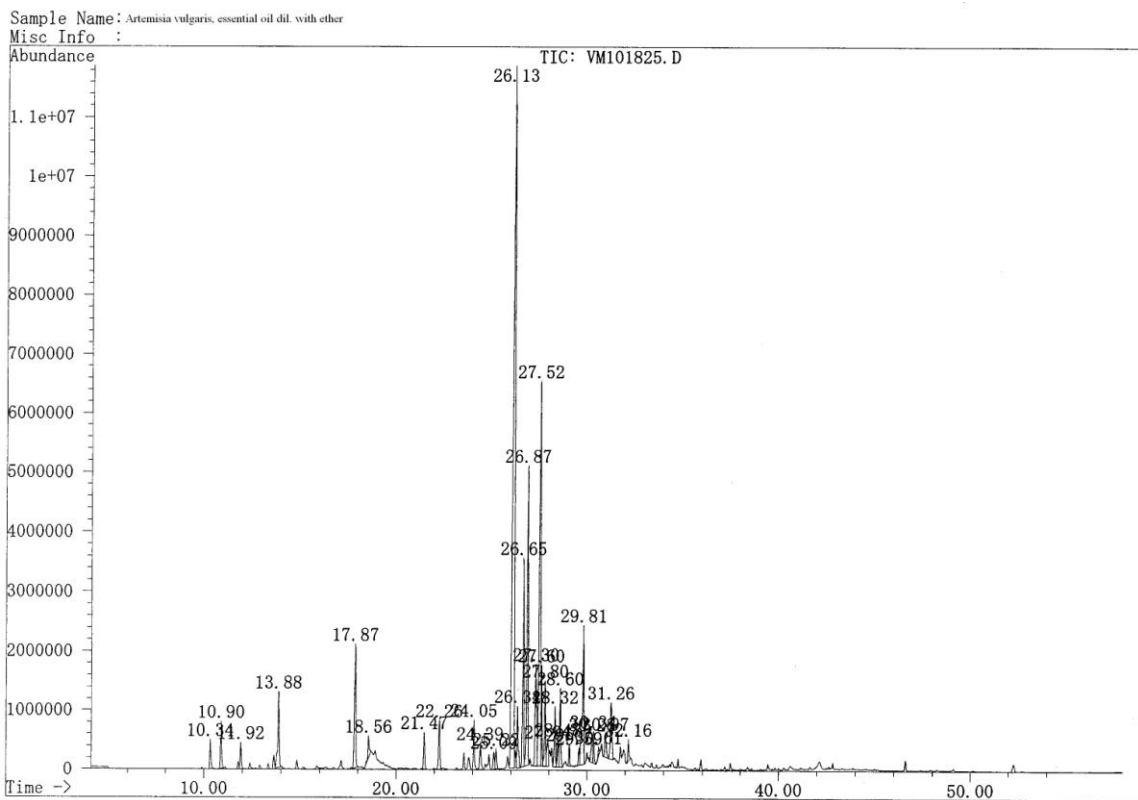


n-Hexane extract of the *Artemisia vulgaris* stem

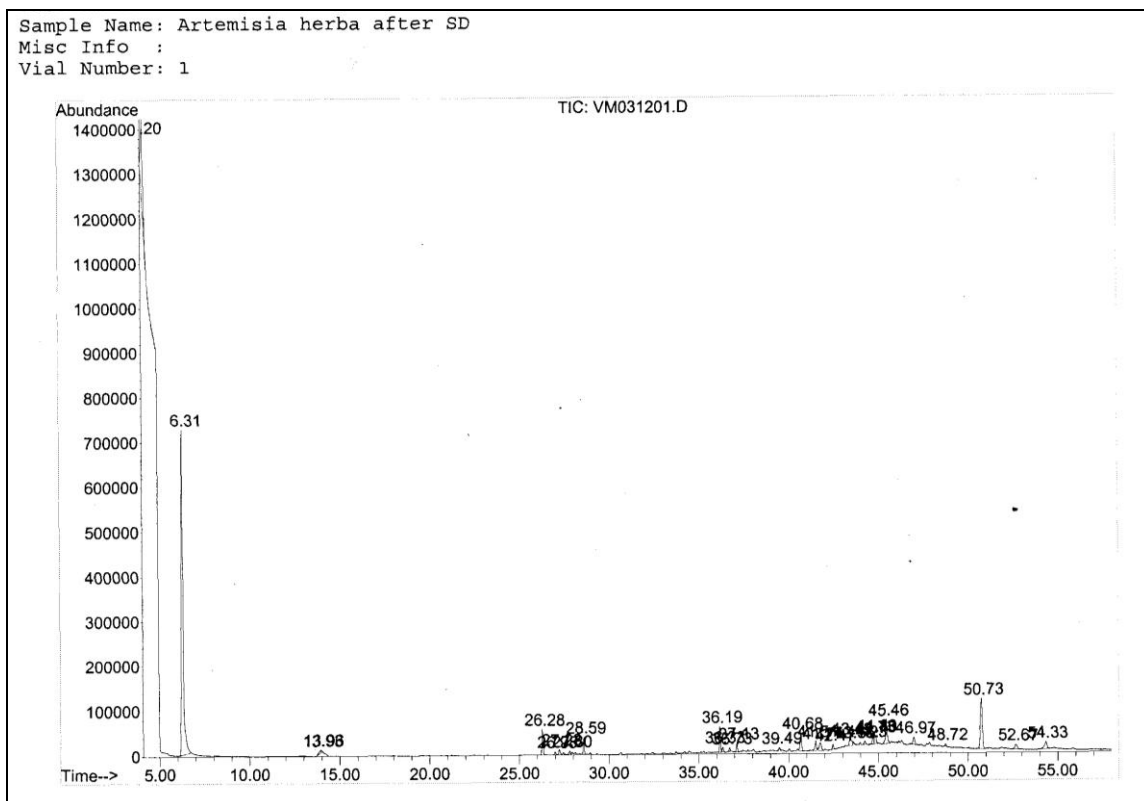




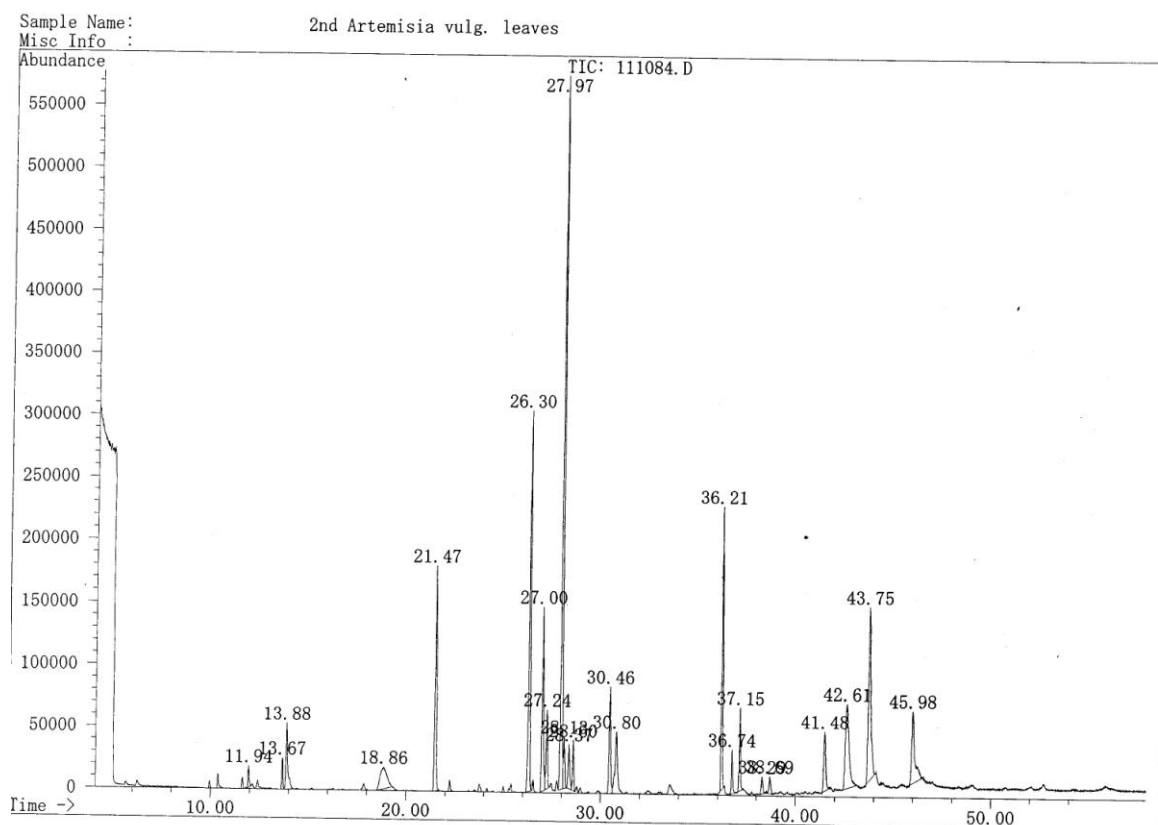
*Artemisia vulgaris* cortex extracted 5 days with diethyl ether.



Essential oil of *A. vulgaris* diluted with ether



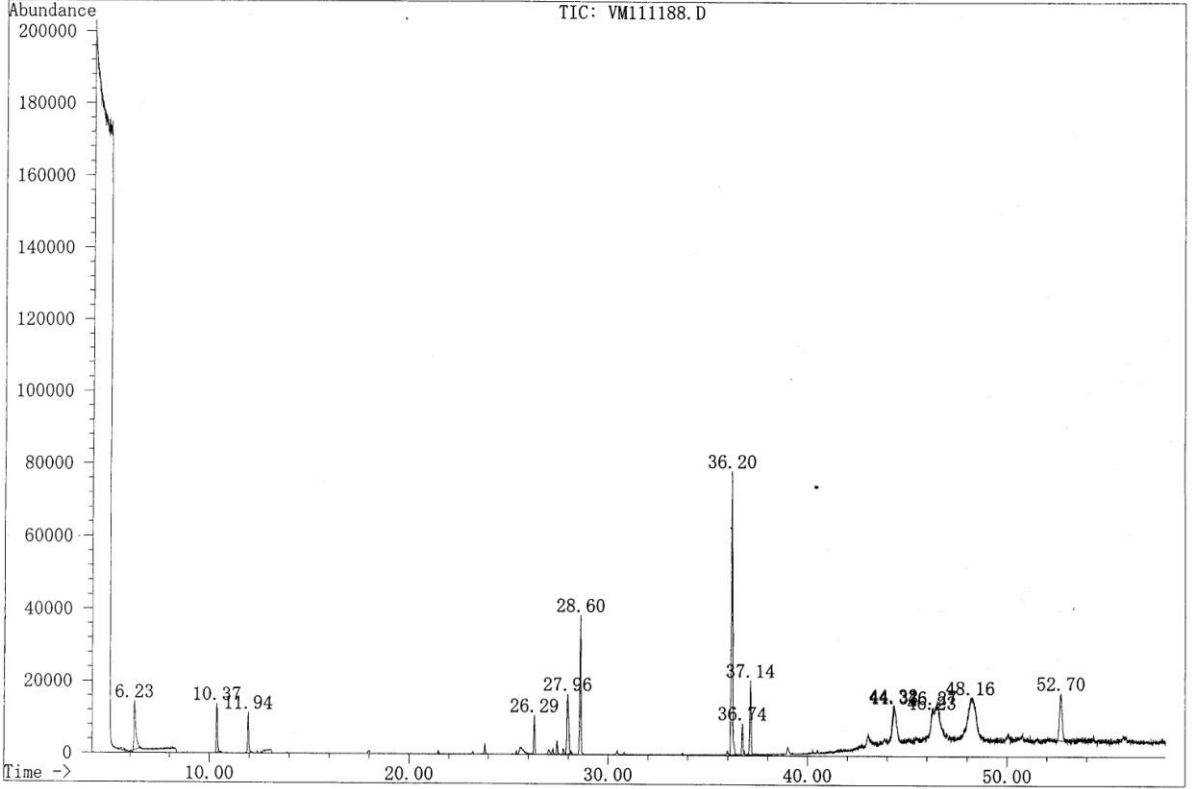
*A. vulgaris* extracted with diethyl ether after the steam distillation



Leaves of the young, fresh plant of *Artemisia vulgaris*, ether extract

Sample Name: A. vulgaris young p stem

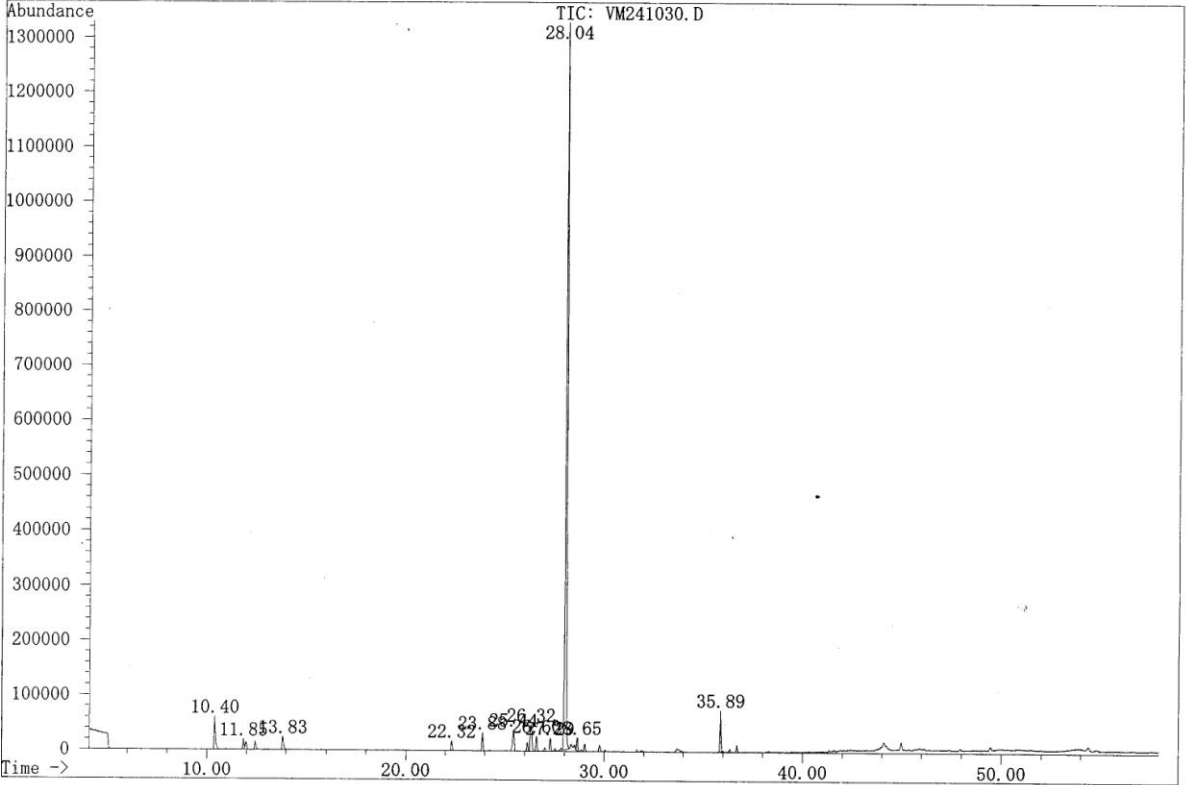
Misc Info :



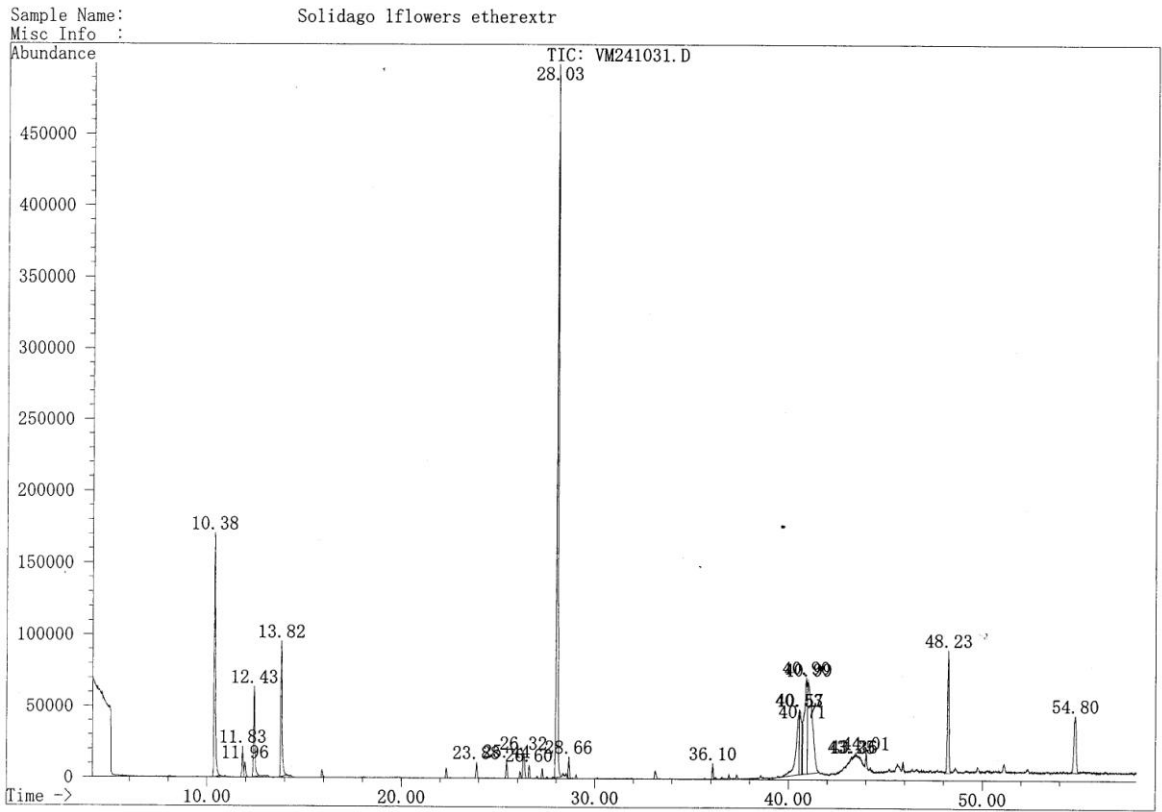
Stem of the young, fresh plant of *Artemisia vulgaris*, ether extract

Sample Name: Solidago leaves etherextr

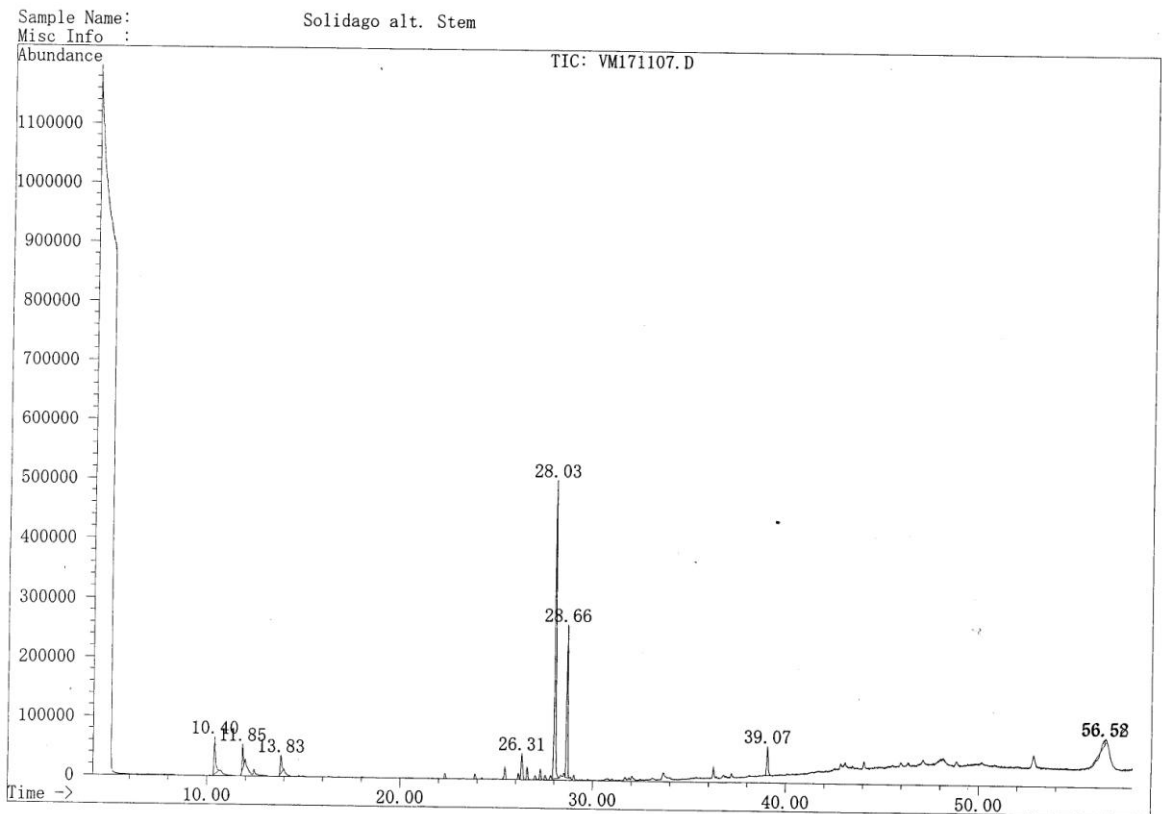
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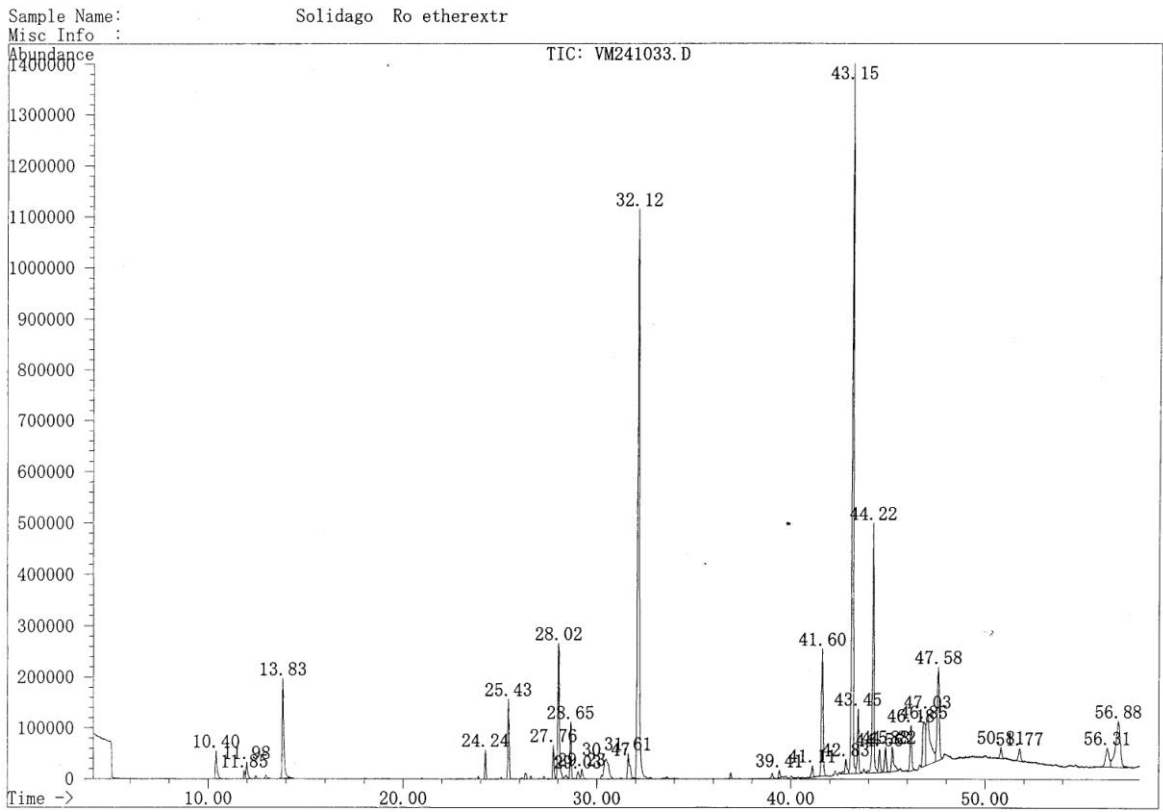
*Solidago altissima*, leaves, ether extract



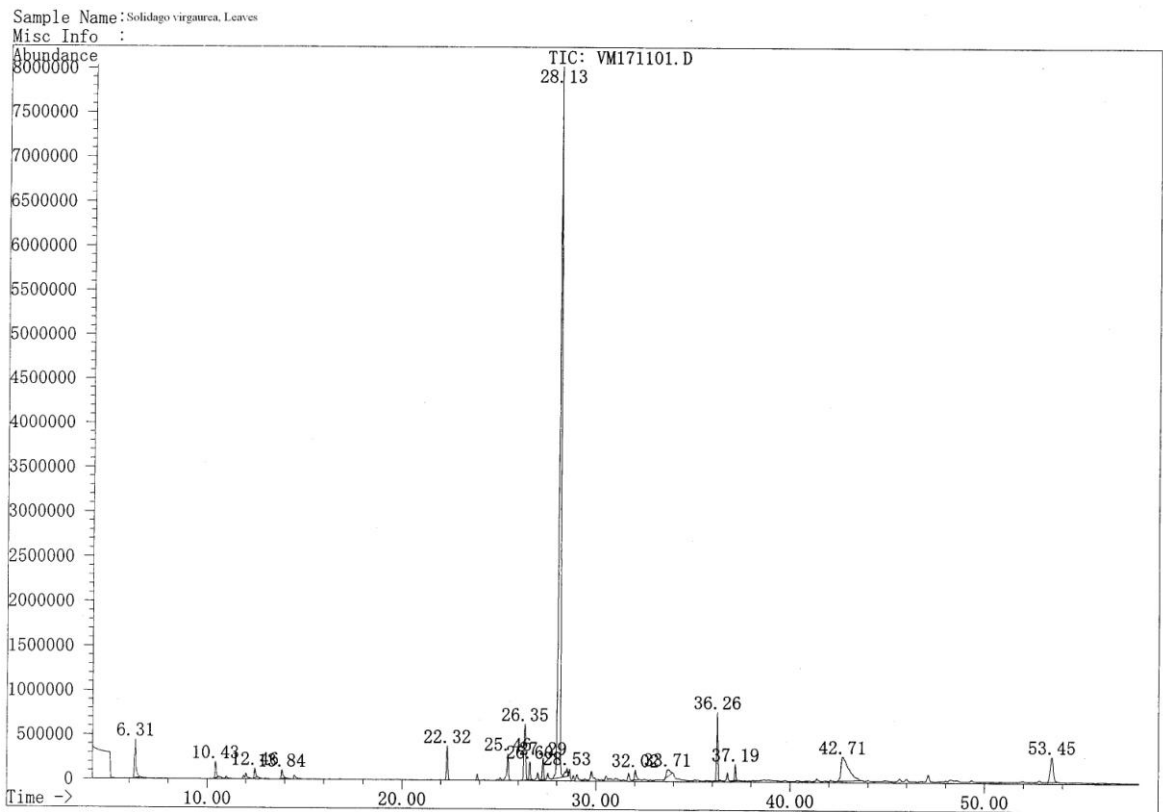
*Solidago altissima*, flowers



*Solidago altissima*, stem, diethyl ether extract

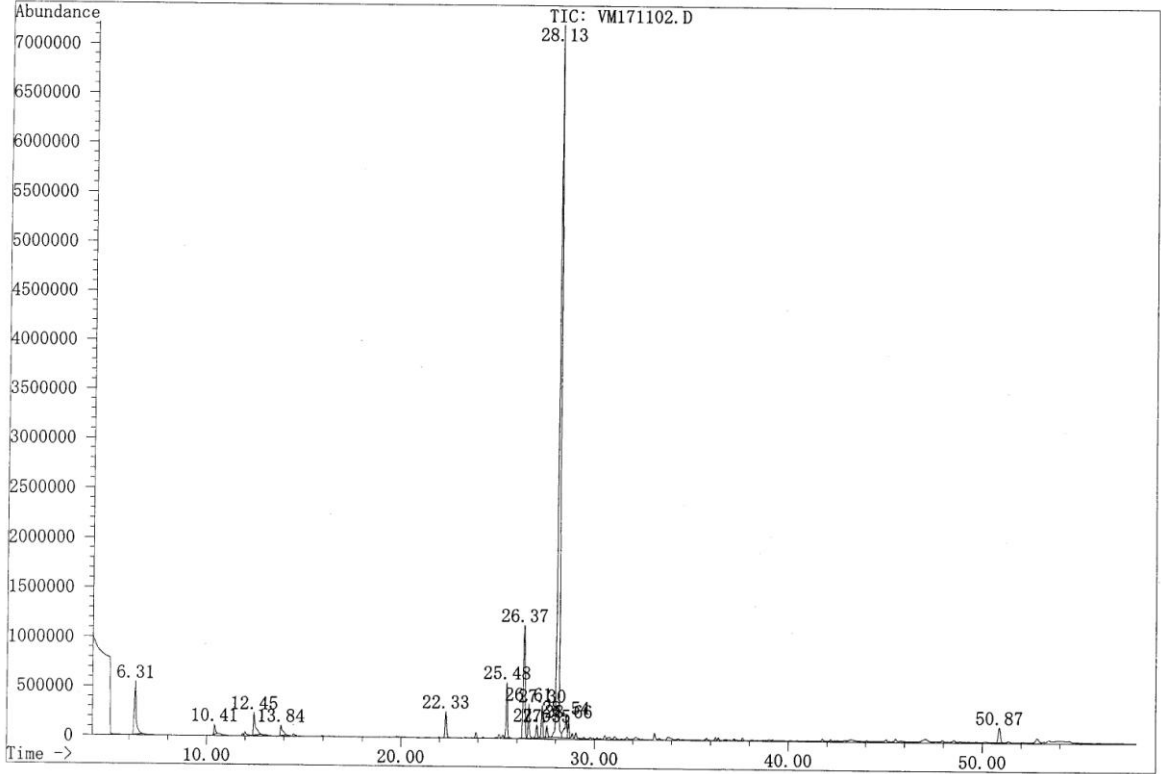


Roots of *Solidago altissima*



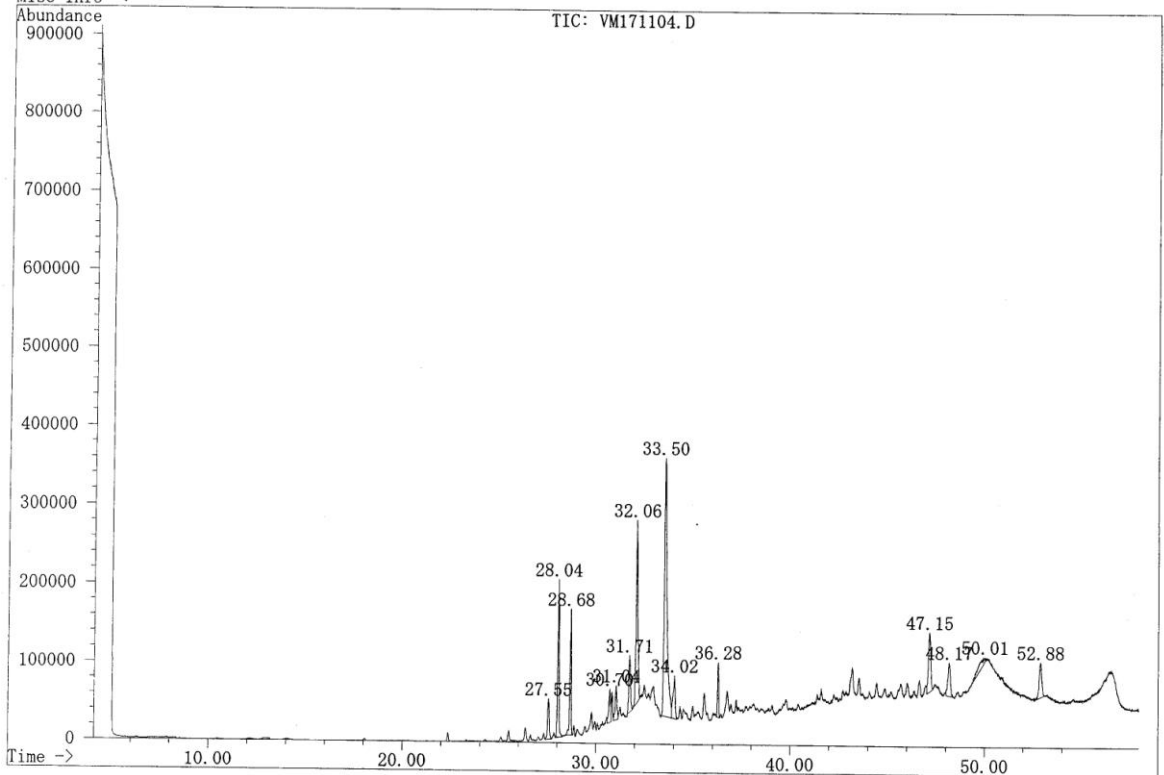
Diethyl ether extract of *Solidago virgaurea* leaves

Sample Name: Solidago virgaurea, flowers  
Misc Info :



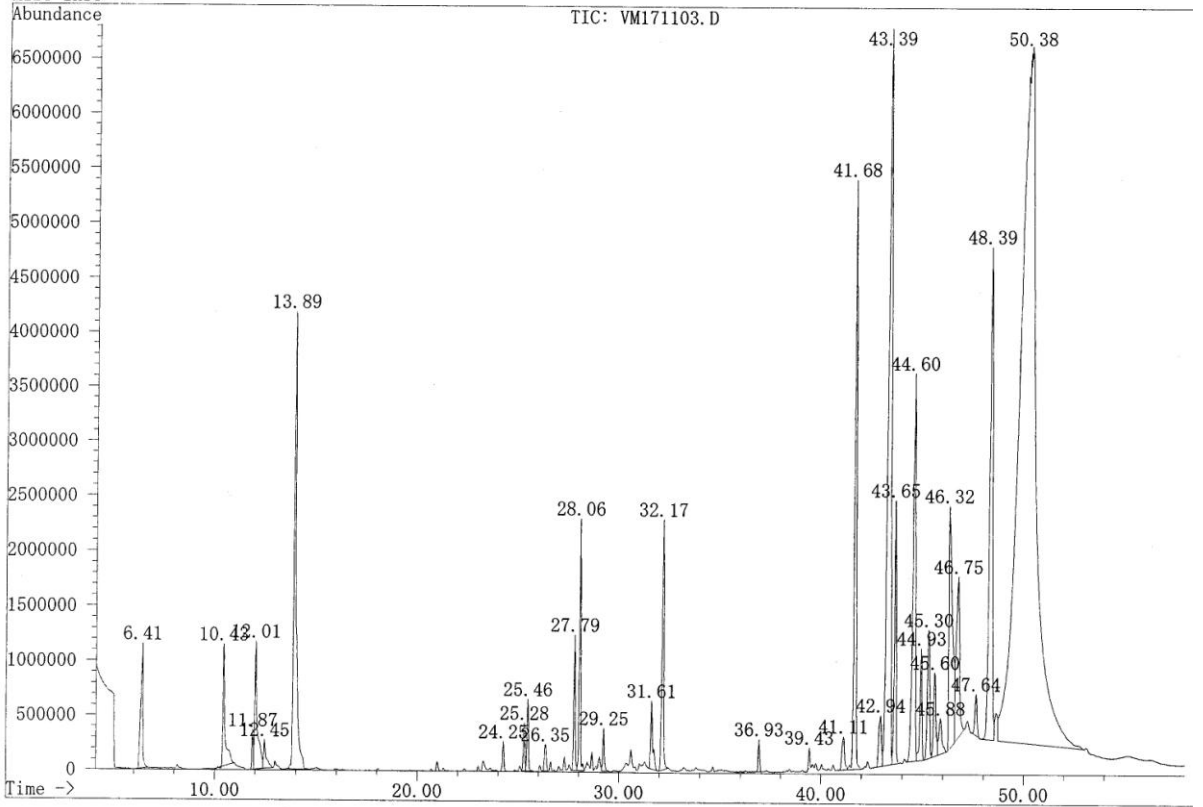
Flowers of *Solidago virgaurea*

Sample Name: Solidago virgaurea, stem  
Misc Info :



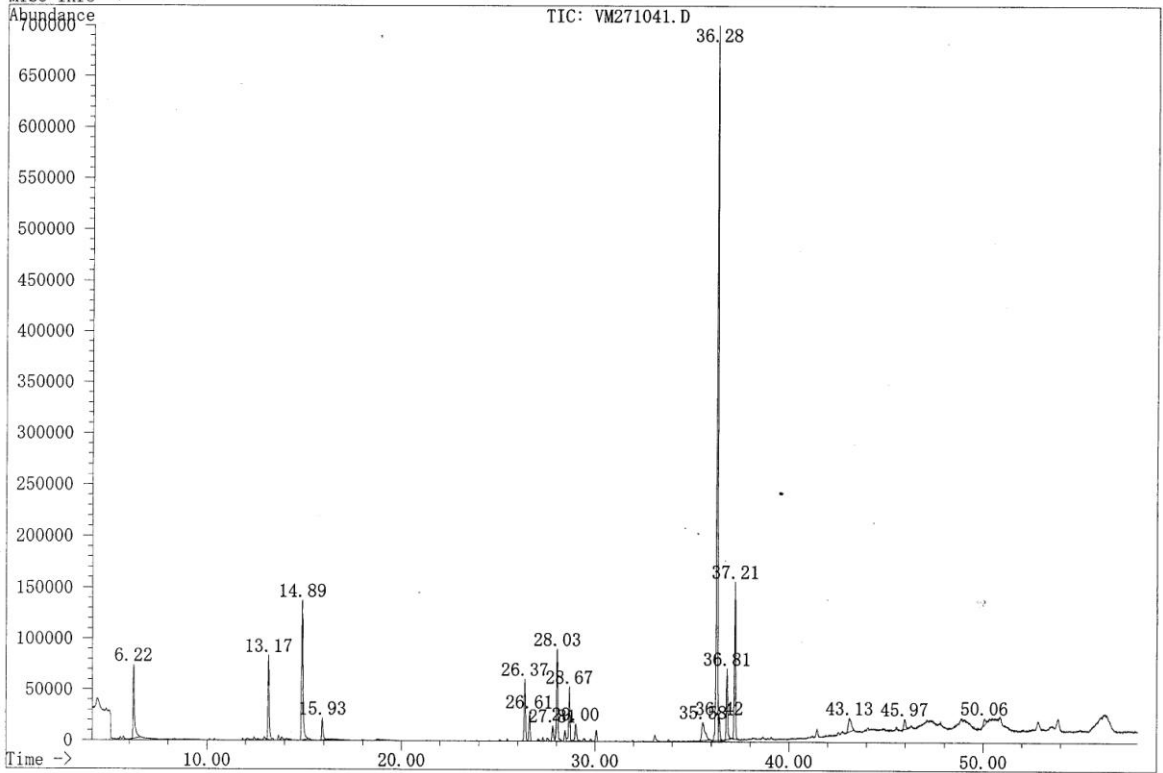
Stem of *Solidago virgaurea*

Sample Name: Solidago virgaurea, roots  
Misc Info :



Roots of *Solidago virgaurea*

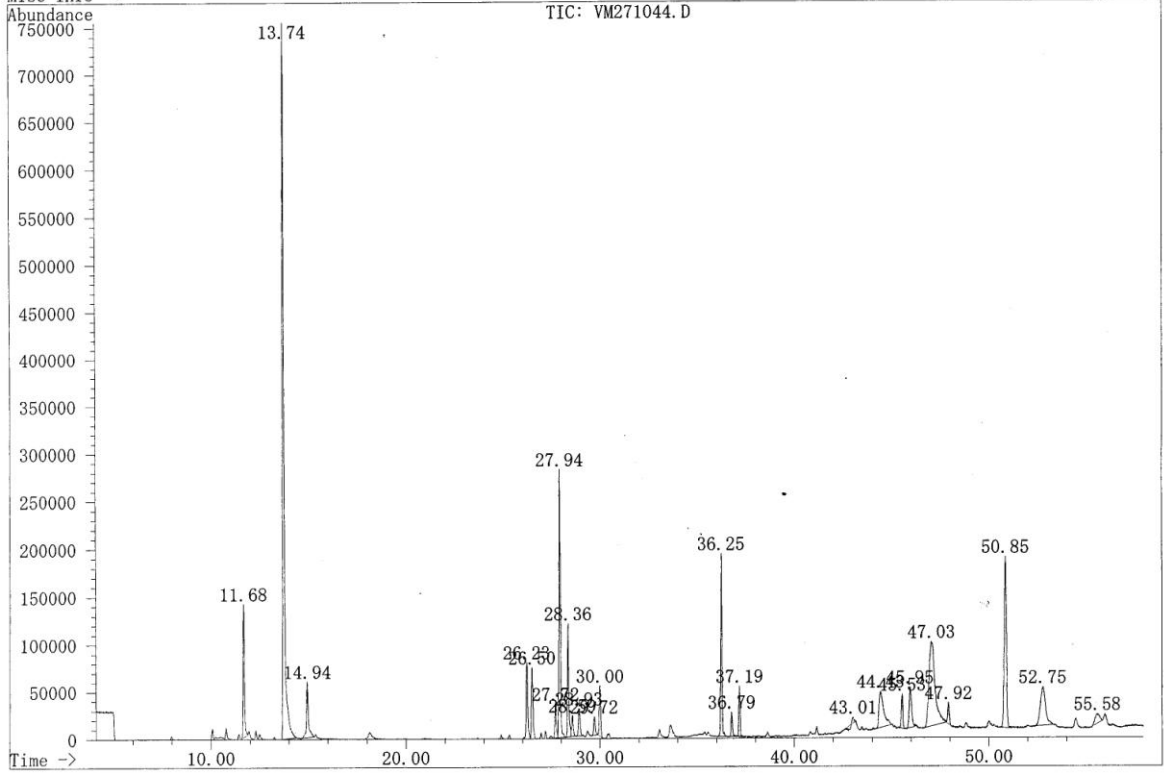
Sample Name: Angelica keiskei leaves  
Misc Info :



Ether extract of *Angelica keiskei* (ashitaba) leaves

Sample Name: Angelica keiskei flowers

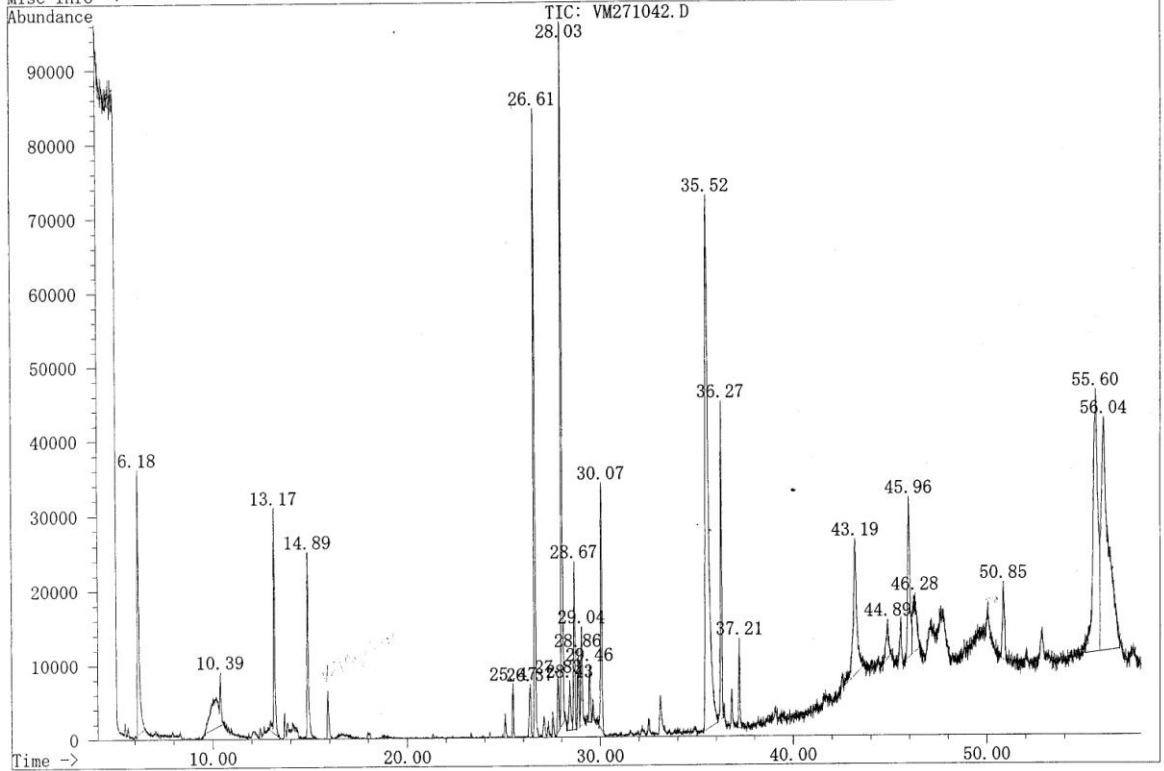
Misc Info :



Flowers of *A. keiskei* (ashitaba)

Sample Name: Angelica keiskei stem

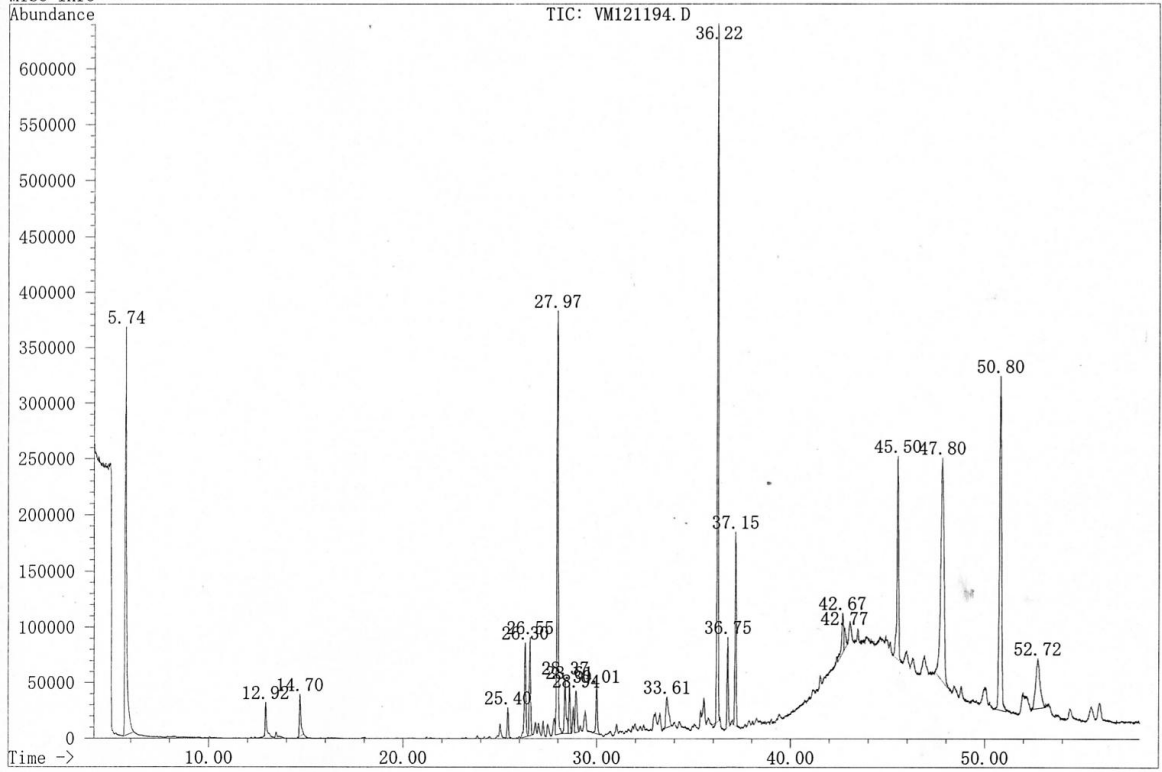
Misc Info :



Diethyl ether extract of *A. keiskei* (ashitaba) stem

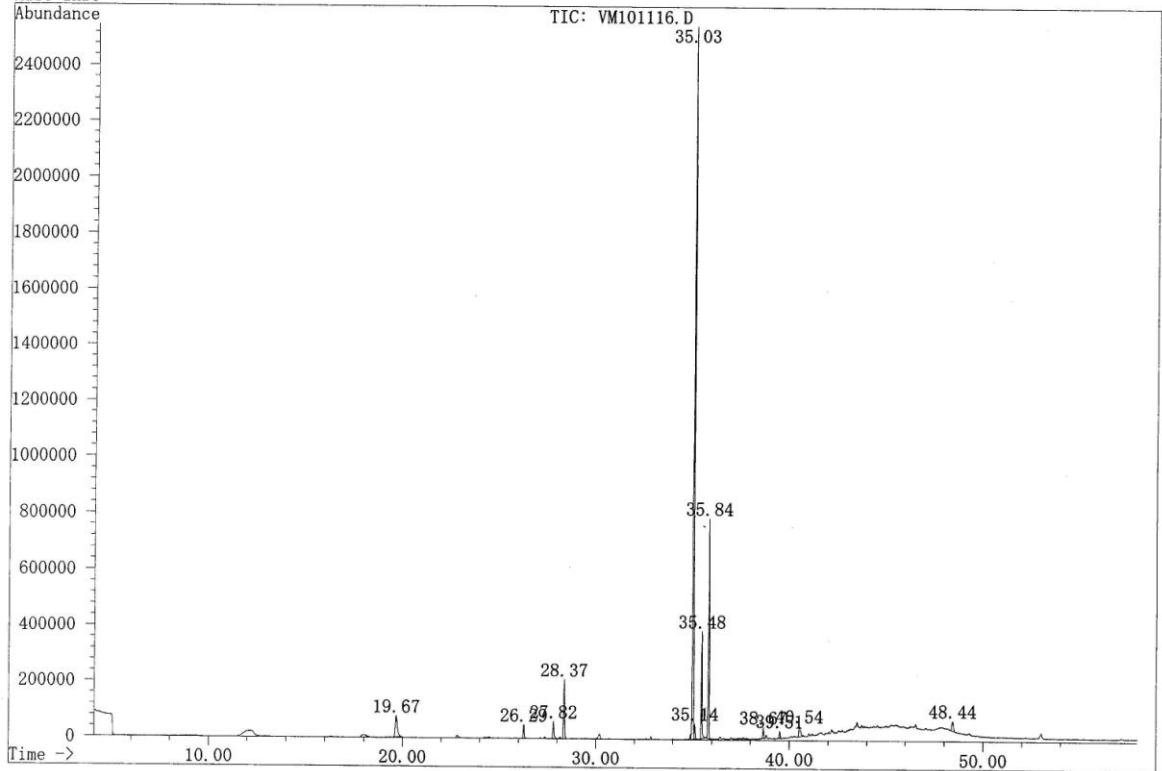


Sample Name: Worms excrement  
Misc Info :



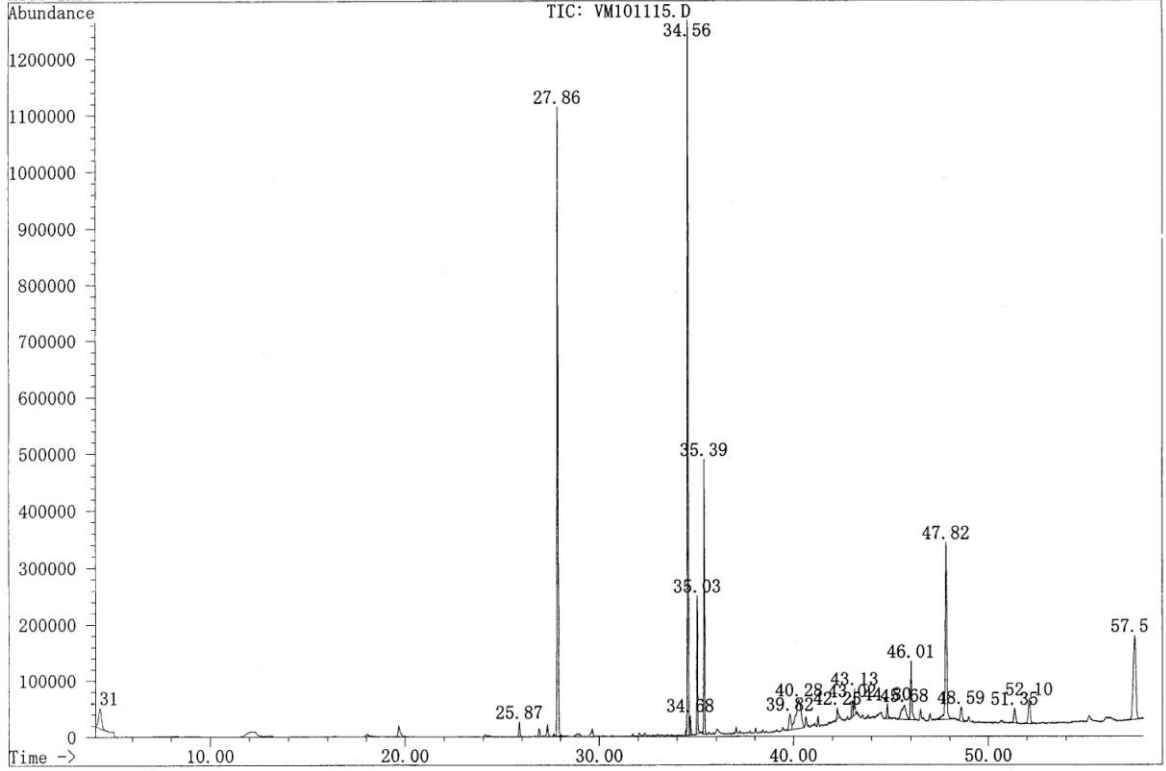
Ether extract of the excrement of the swallowtail butterfly larvae

Sample Name: Perilla frutescens leaves  
Misc Info :



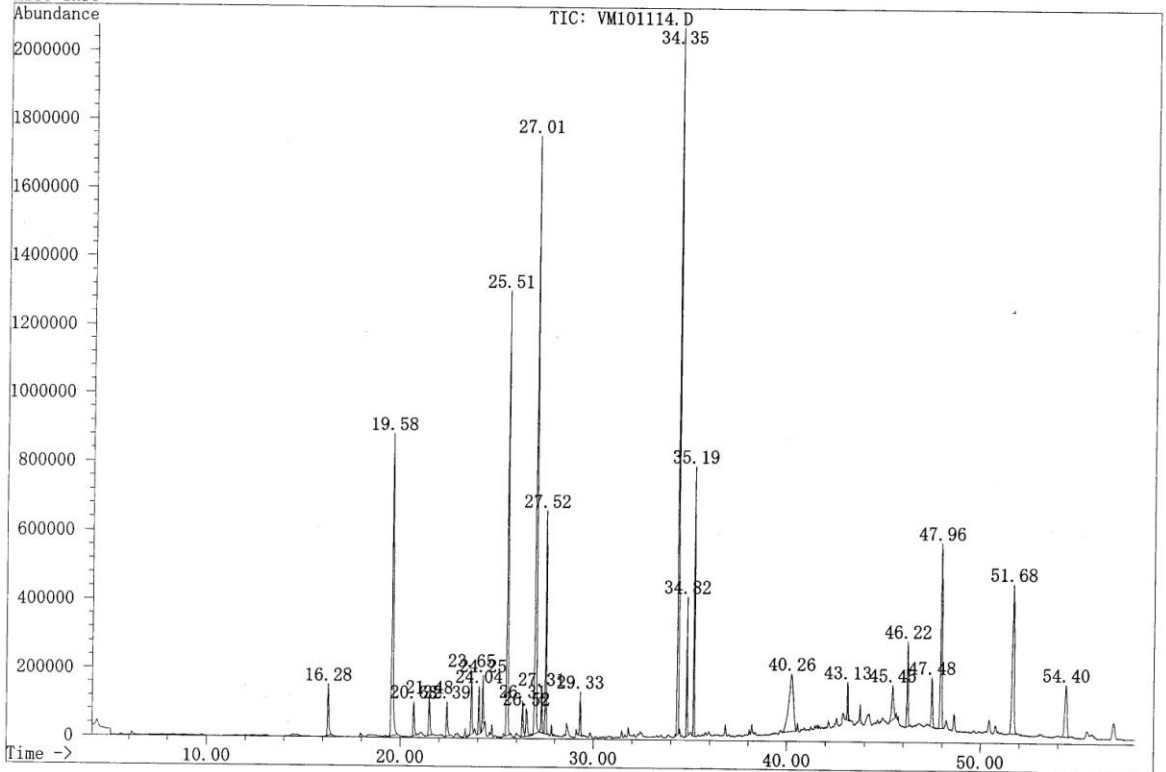
*Perilla frutescens*, leaves

Sample Name: Perilla frutescense stem  
Misc Info :



*P. frutescense*, stem

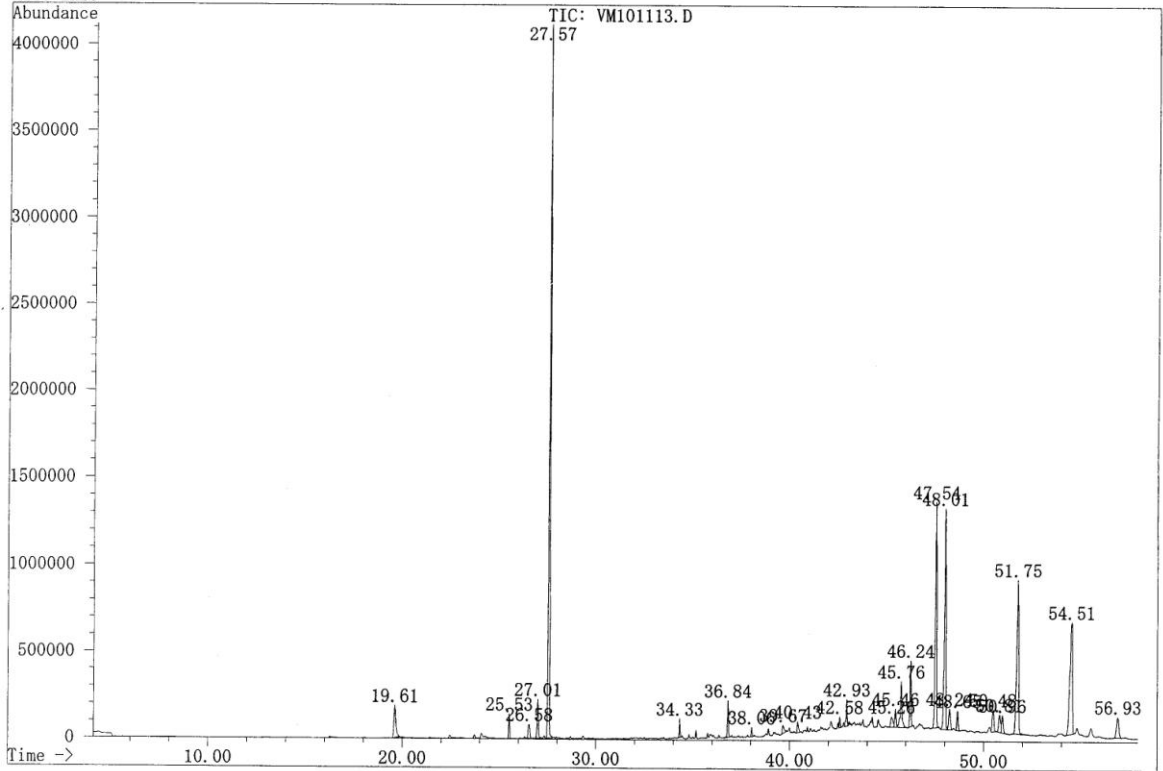
Sample Name: Perilla frutescense flowers  
Misc Info :



*P. frutescense*, flowers

Sample Name: Perilla frutescens corolle

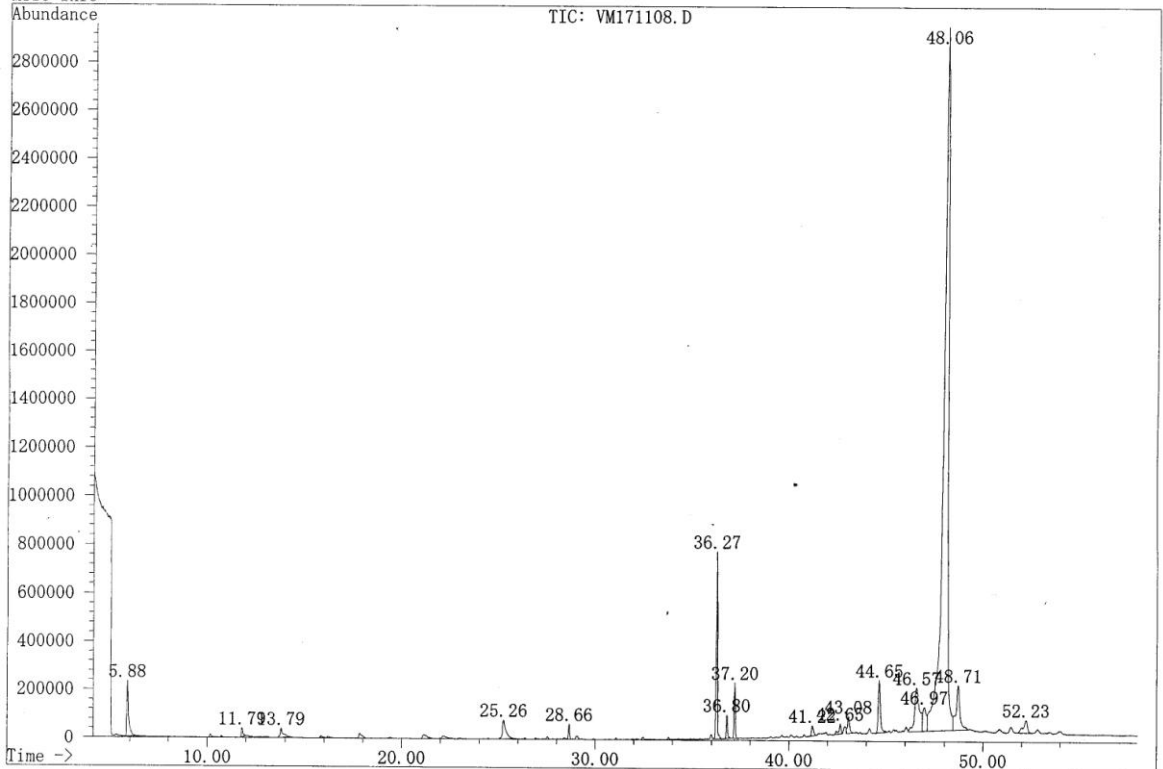
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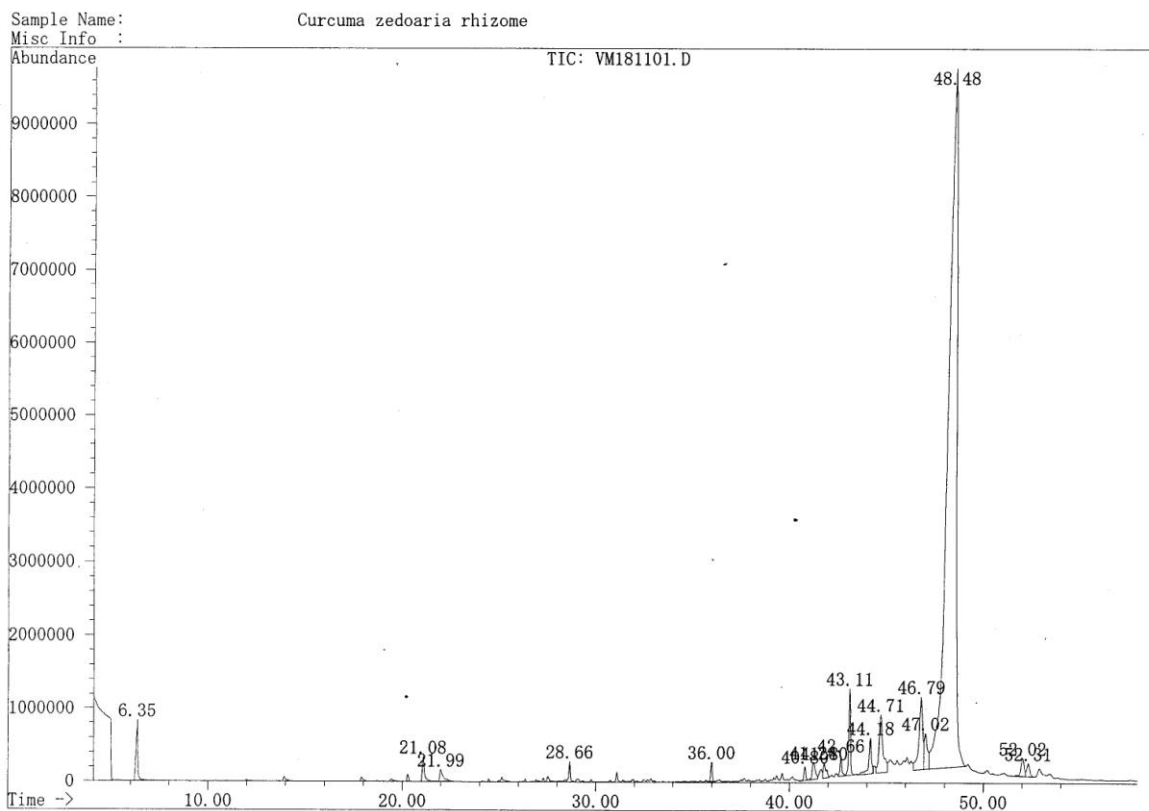
*P. frutescens*, corolle

Sample Name: Curcuma zedoaria leaves

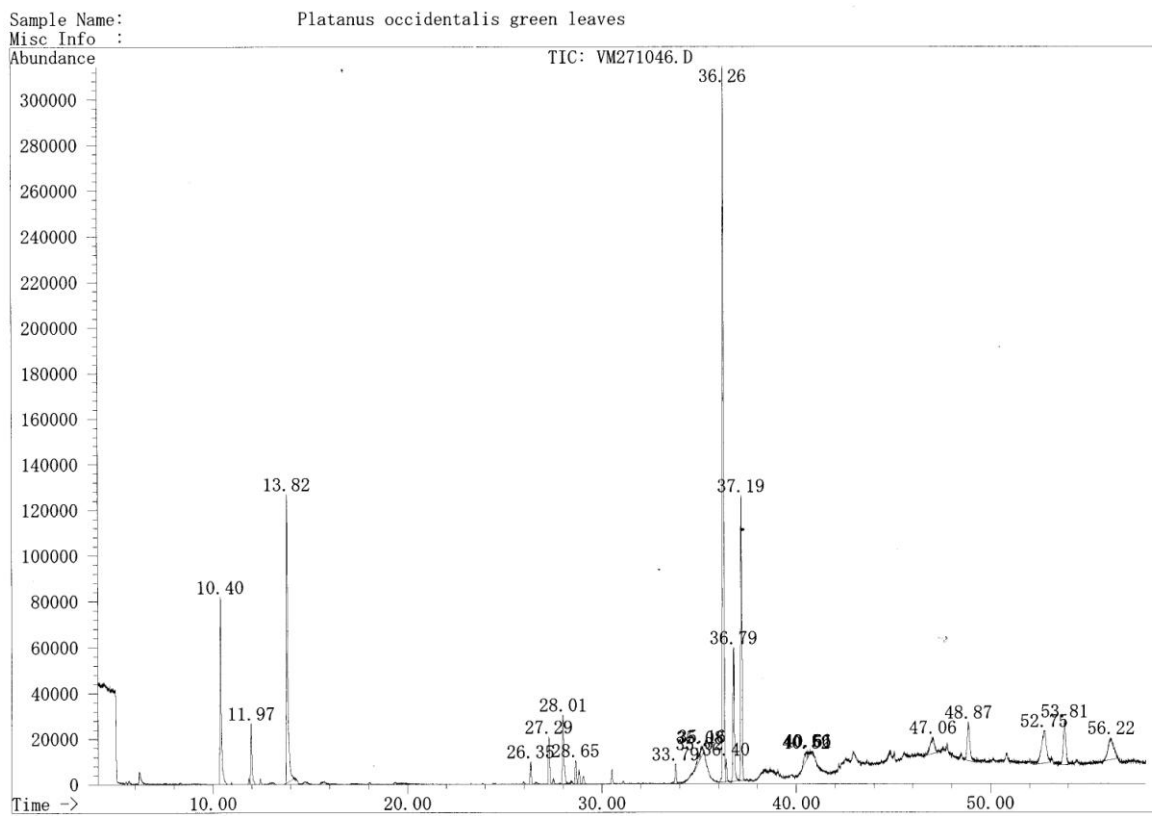
Misc Info :



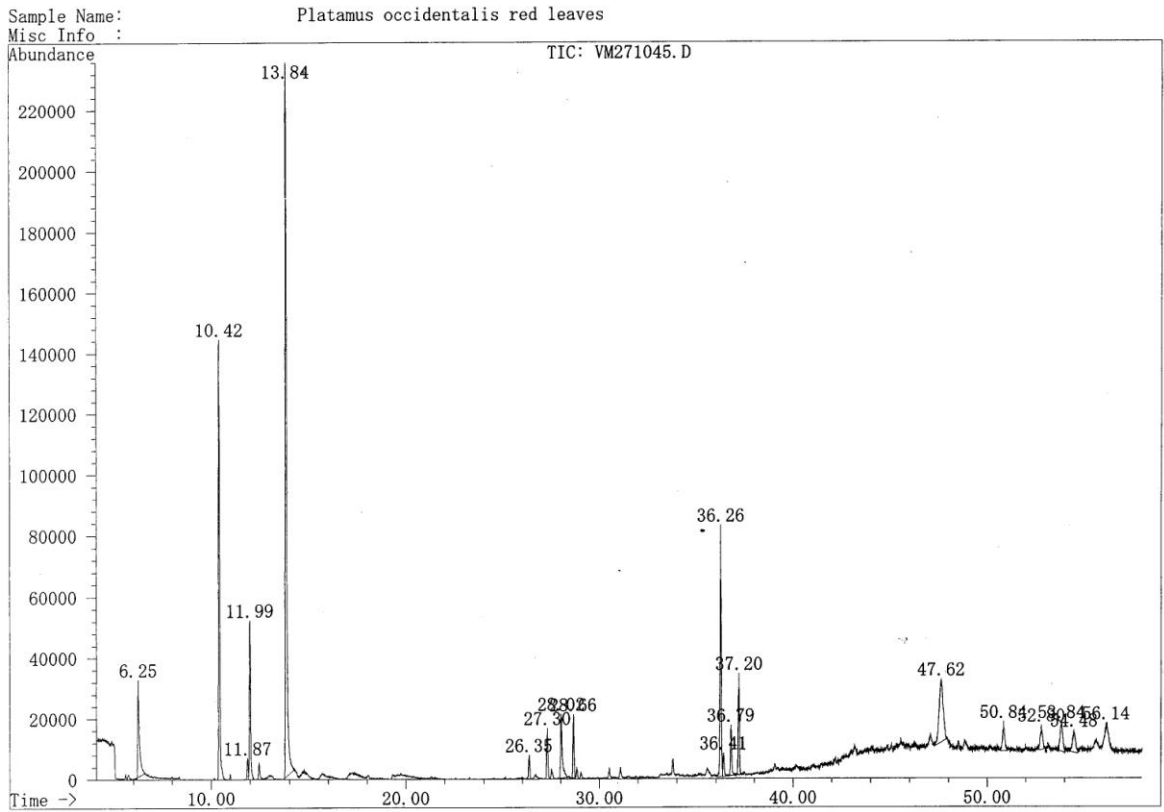
Ether extract of *Curcuma zedoaria* leaves



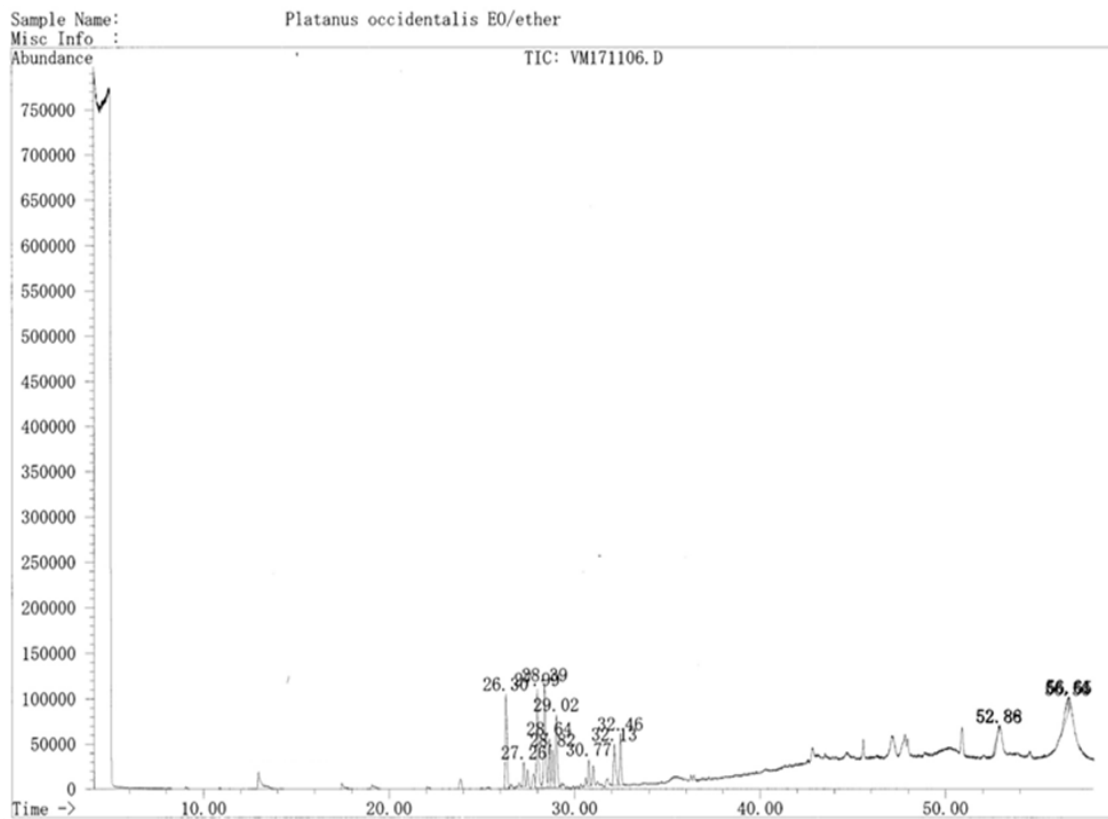
Ether extract of *Curcuma zedoaria* rhizome



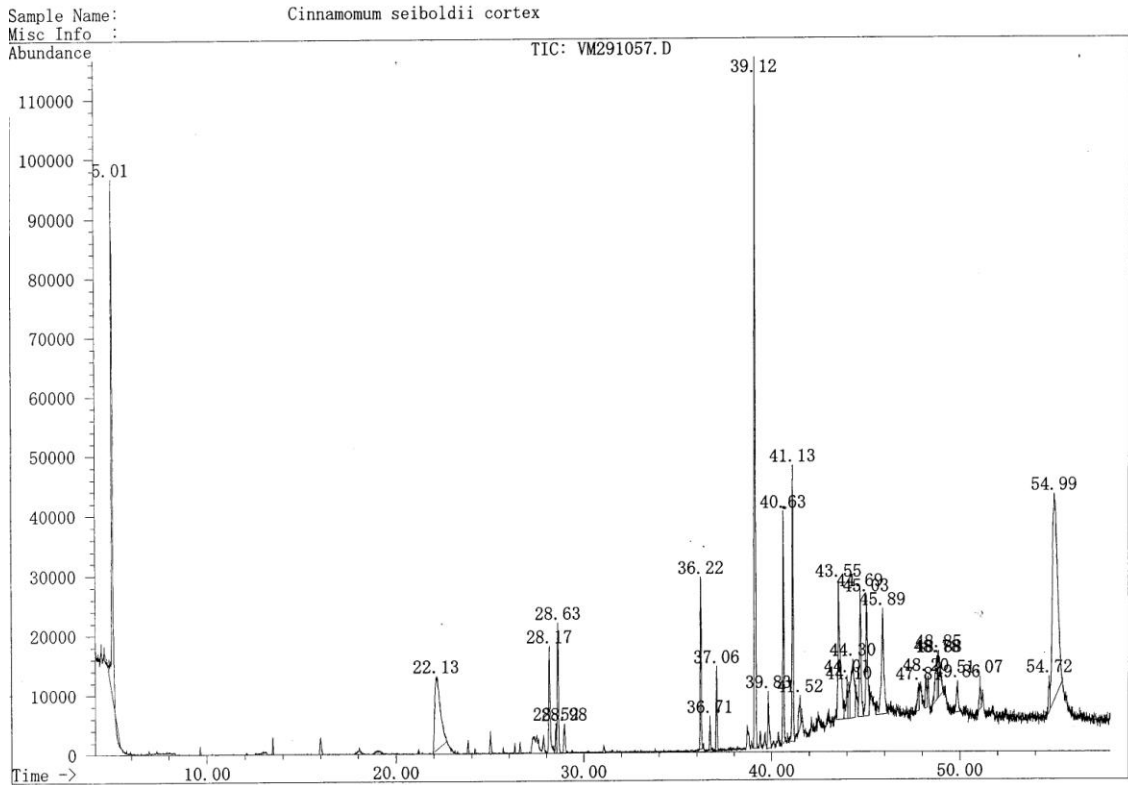
Green leaves of *Platanus occidentalis*



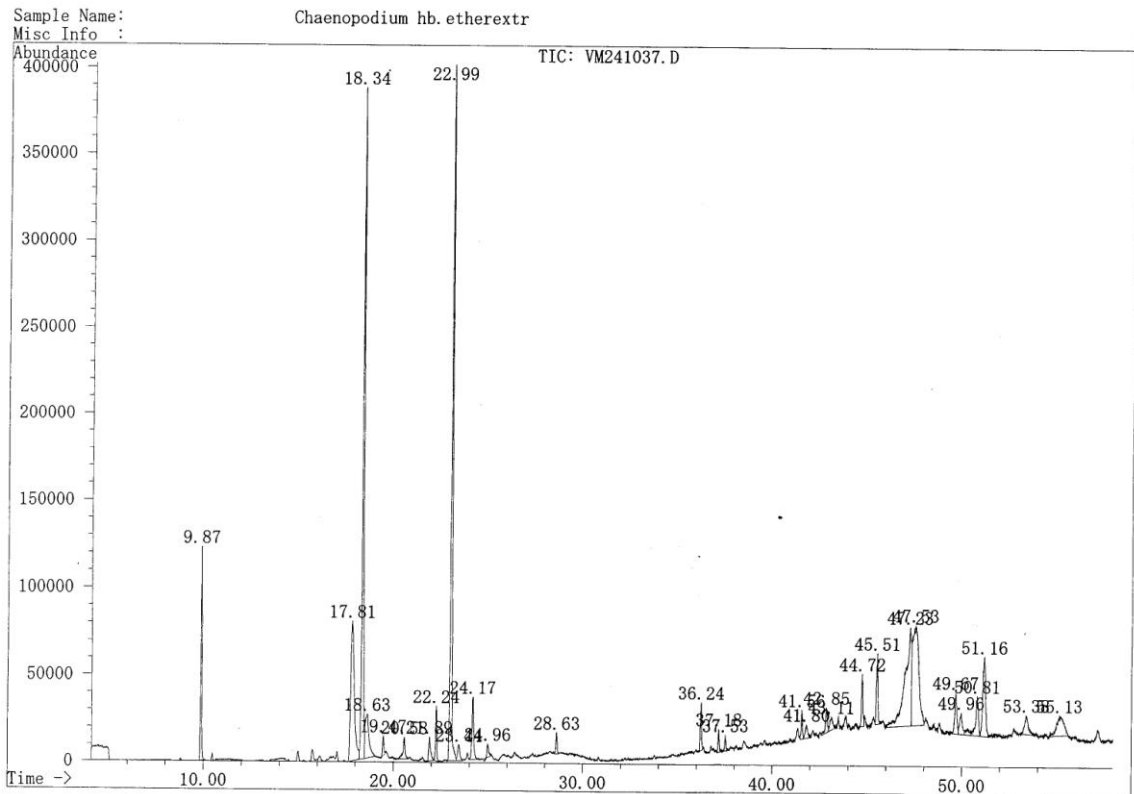
*Platanus occidentalis*, red leaves



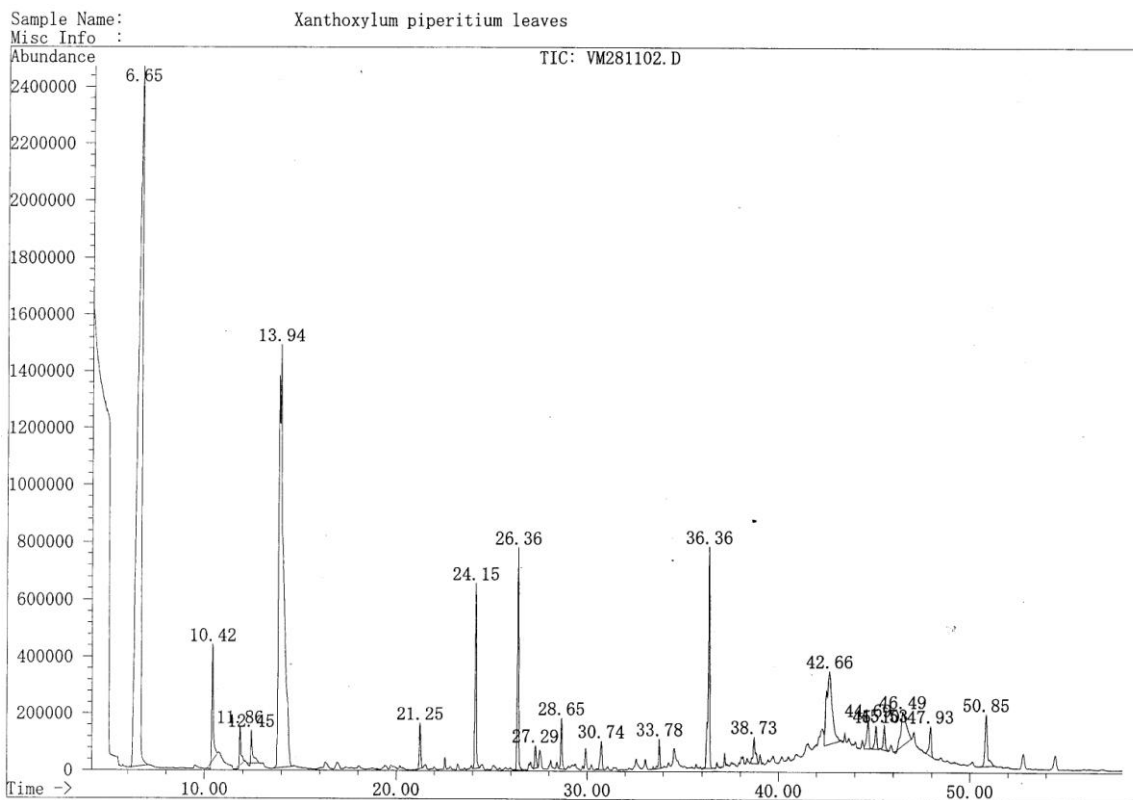
*P. occidentalis*, essential oil diluted with ether



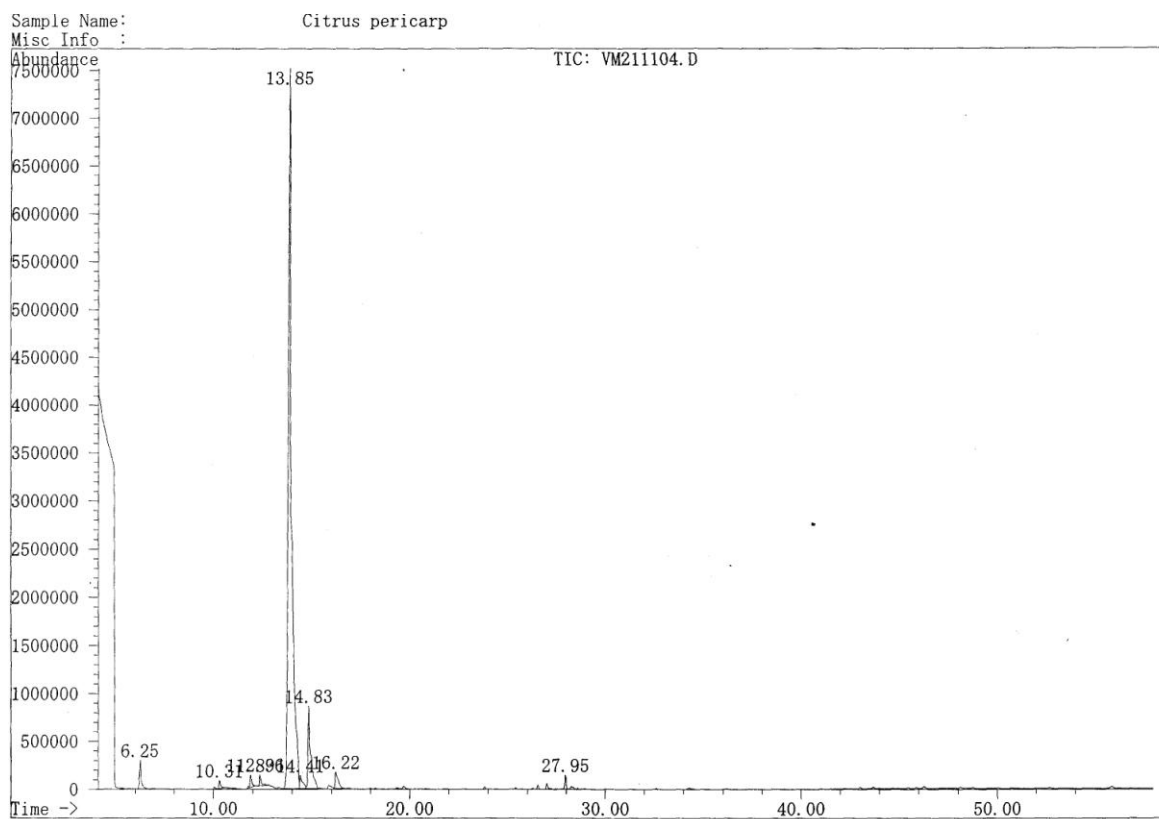
Ether extract of the cortex of *Cinnamomum sieboldii*



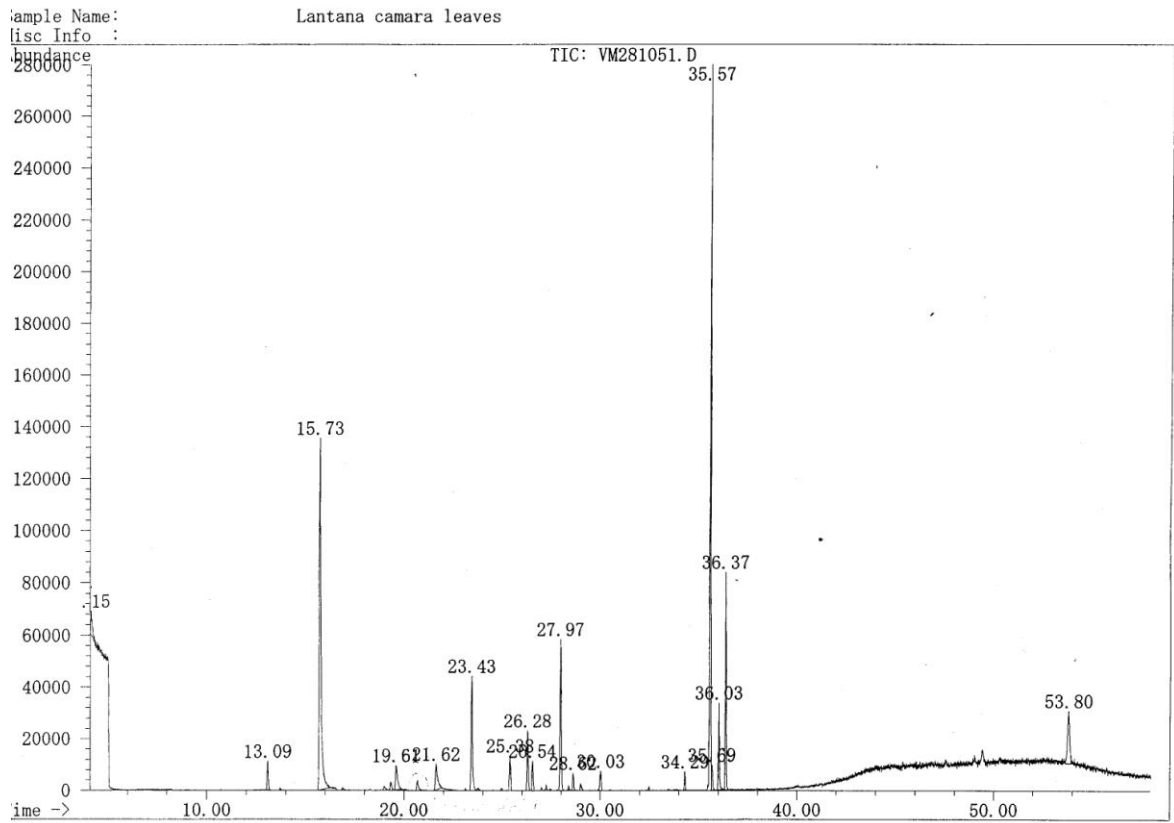
Diethyl ether extract of the *Chaenopodium ficifolium* herba



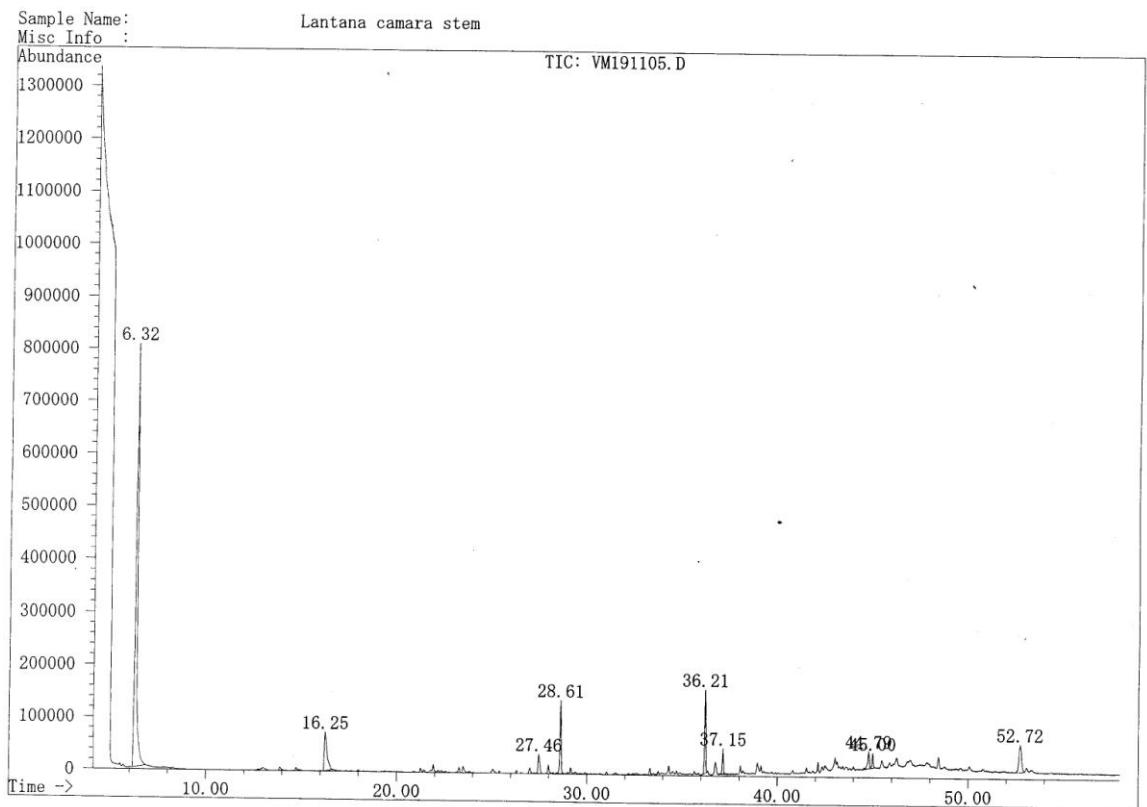
*Zanthoxylum piperitum*, leaves



Pericarp of the fruit of *Citrus junos*

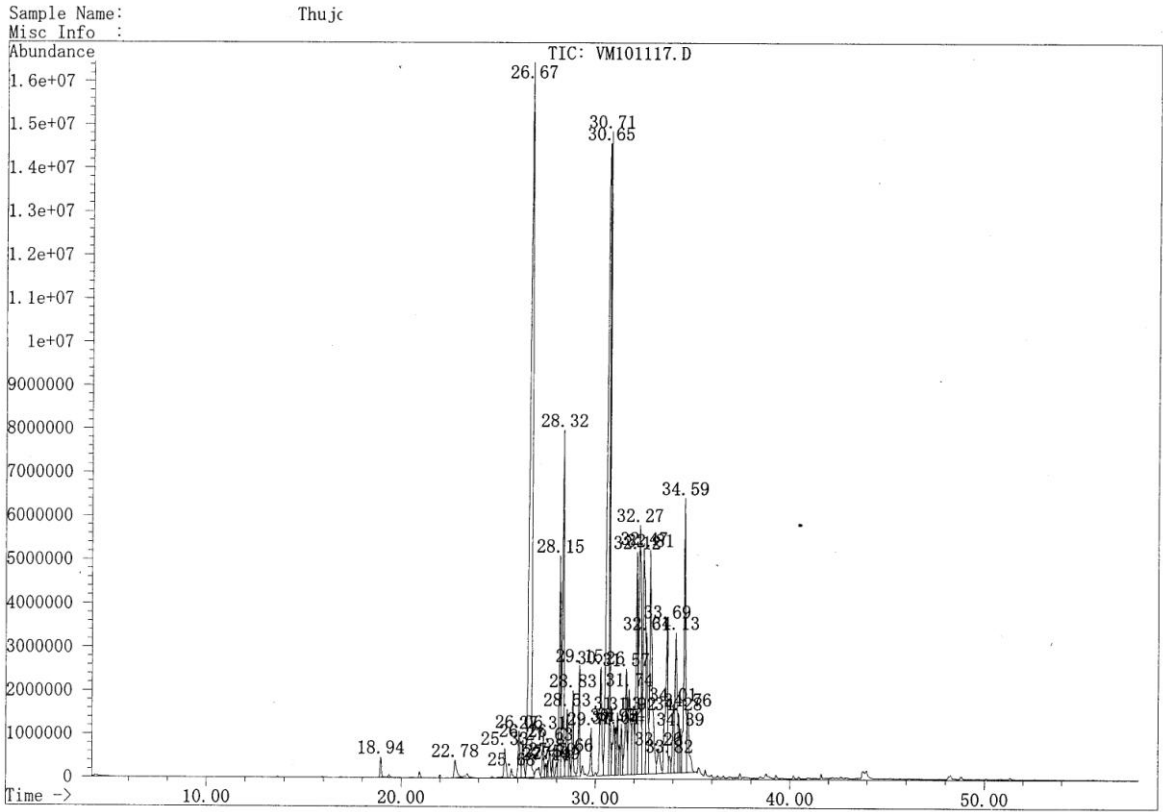


*Lantana camara*, leaves

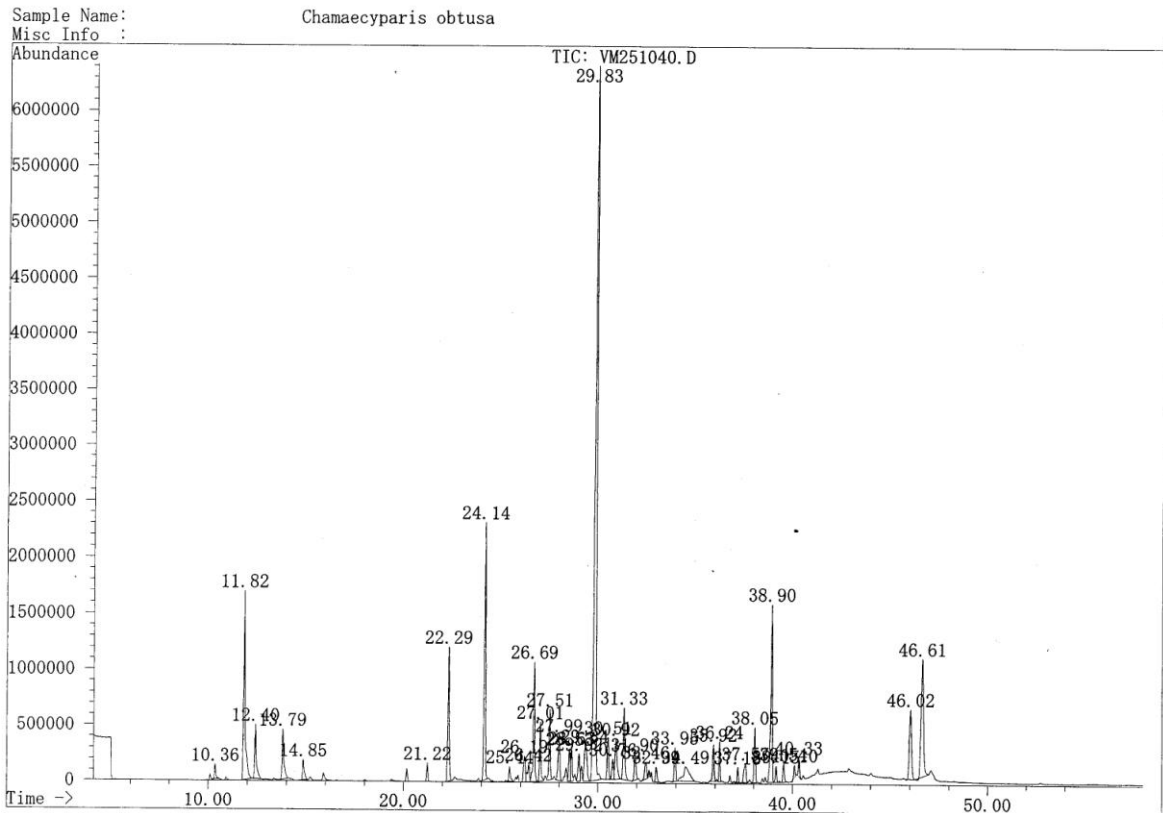


*Lantana camara*, stem

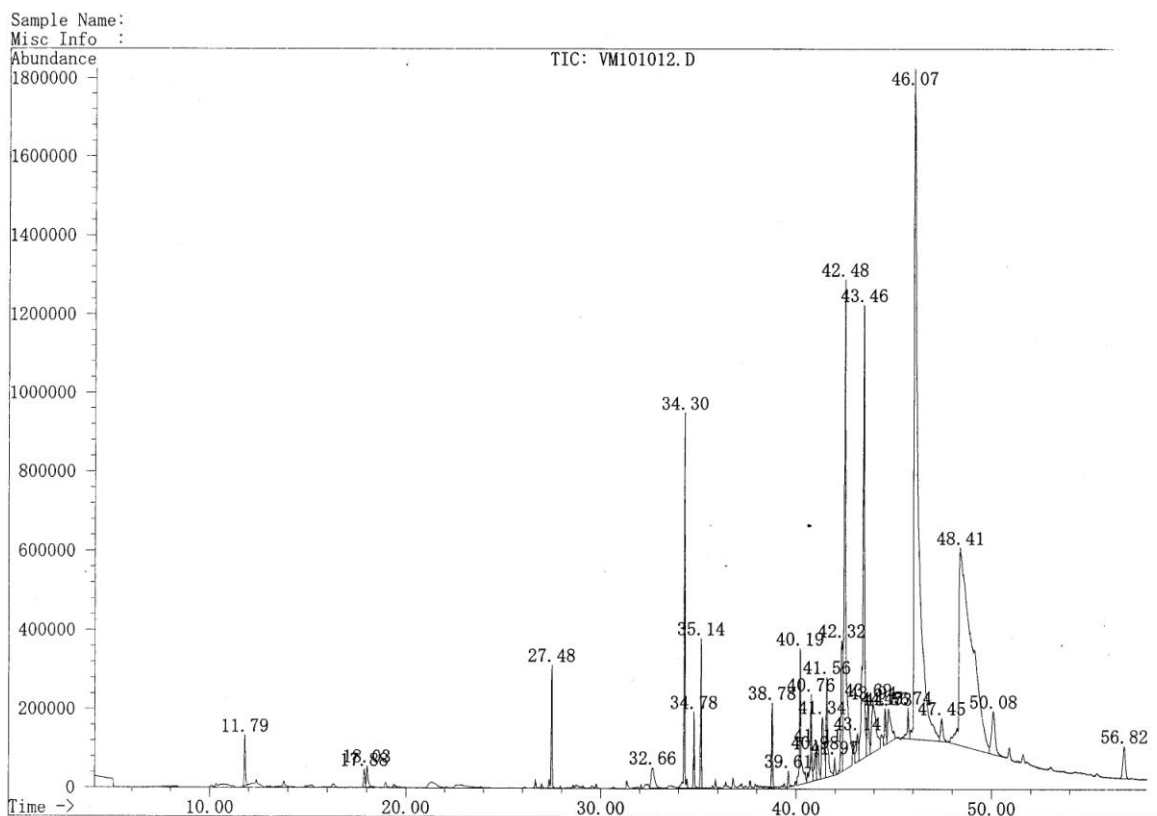




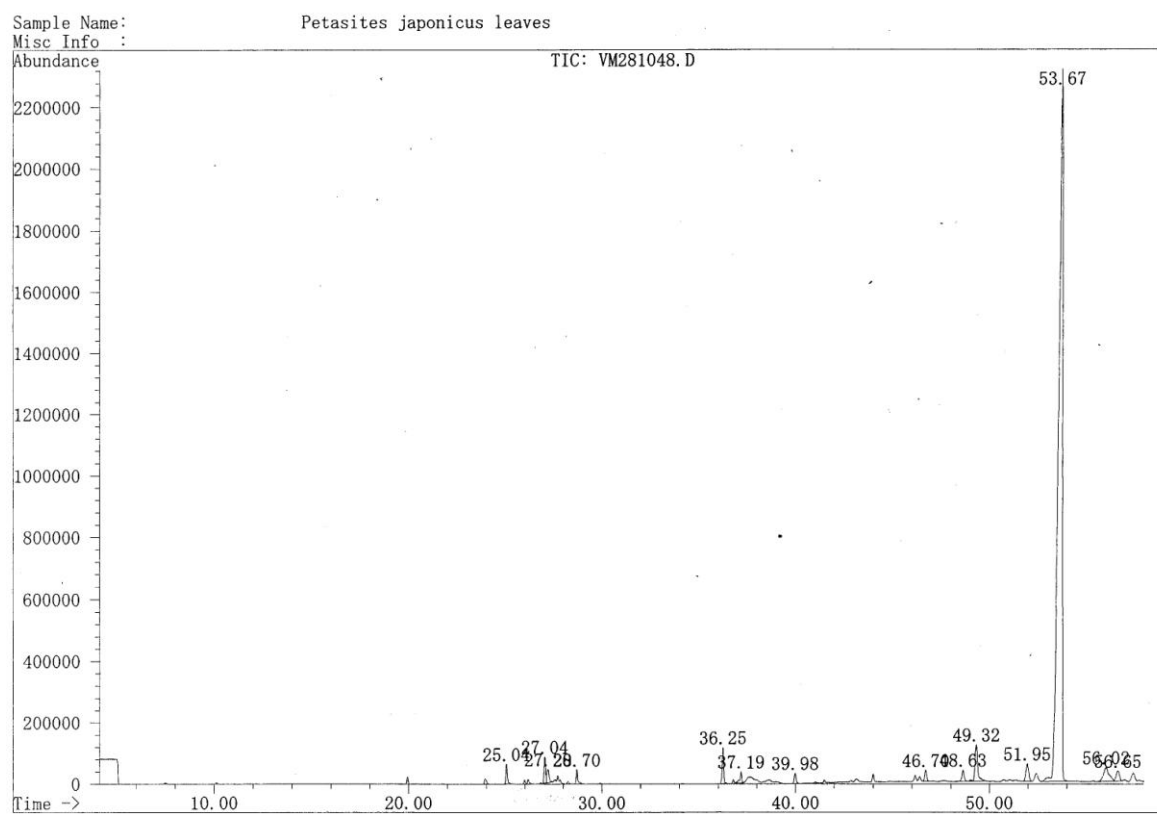
*Thuja dolabrata*, essential oil



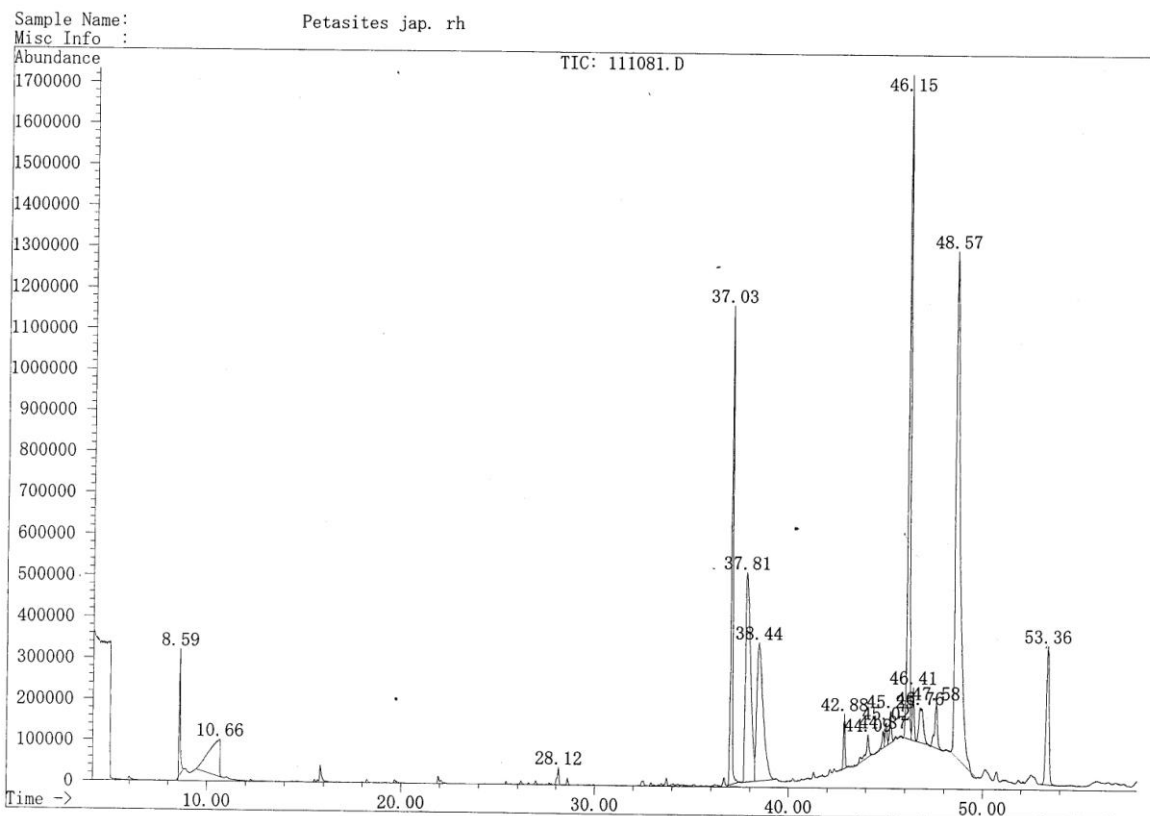
*Chamaecyparis obtusa*, leaves



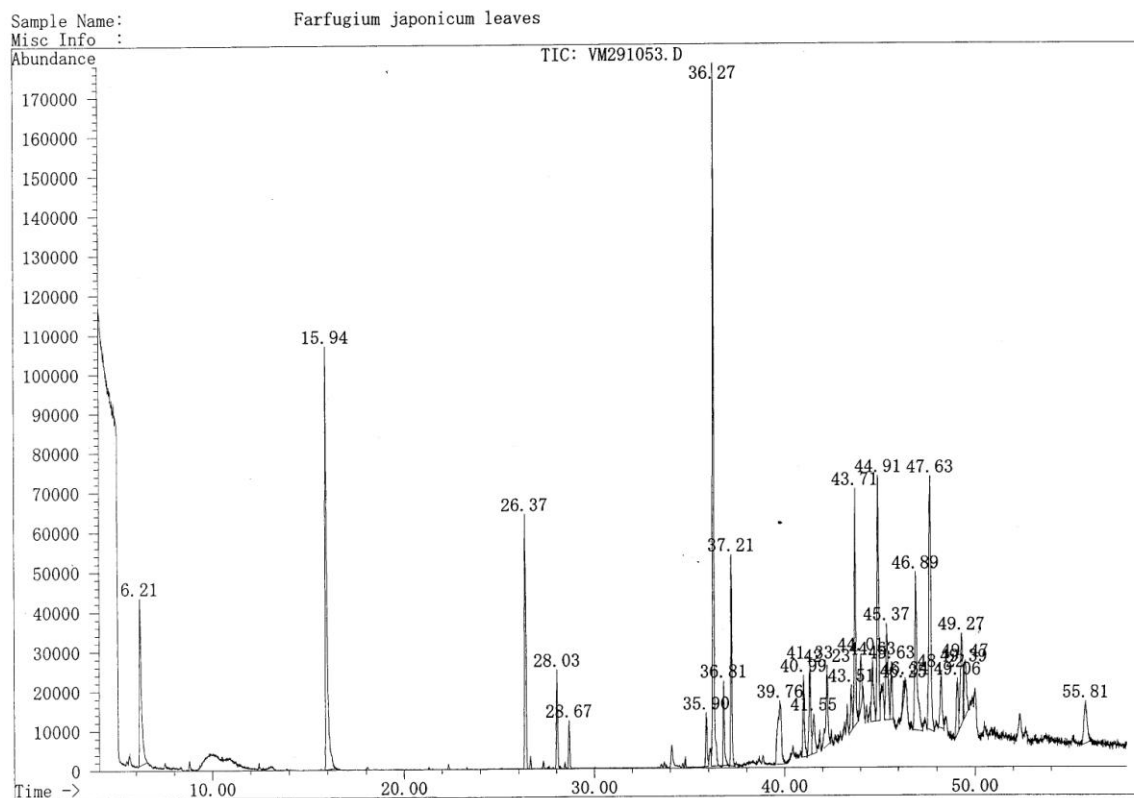
*Cryptomeria japonica*, leaves



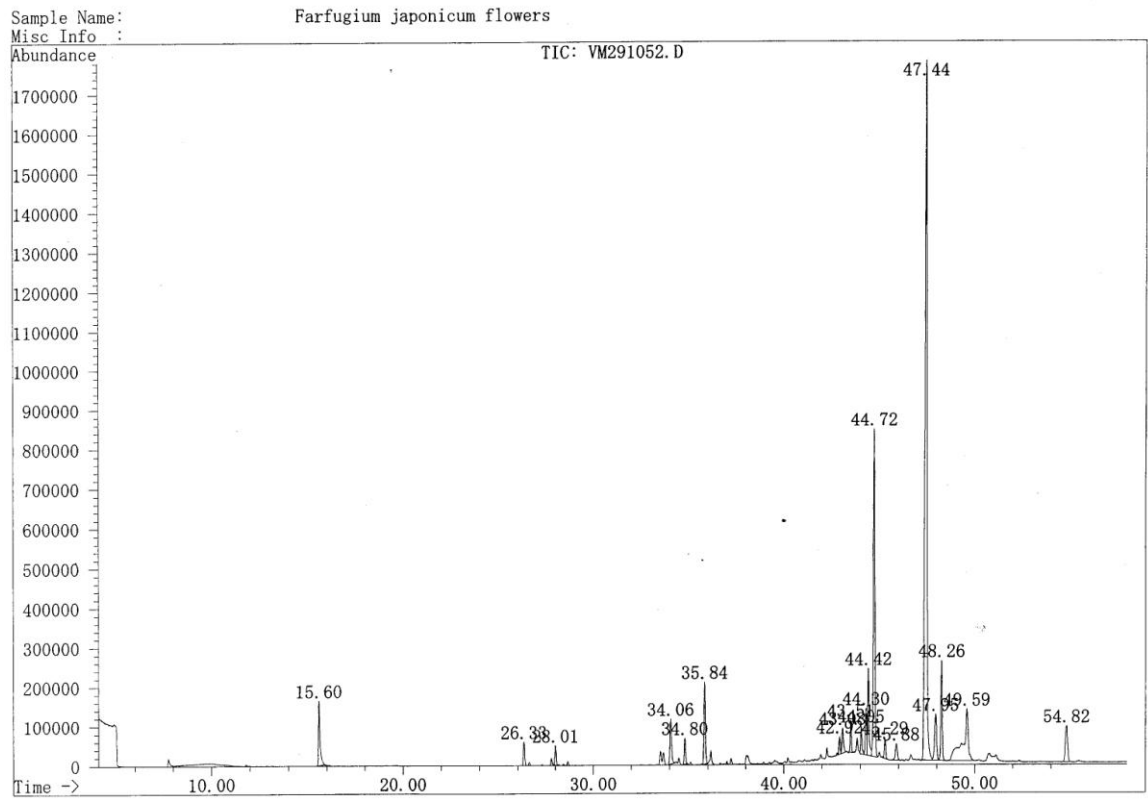
*Petasites japonicus*, leaves



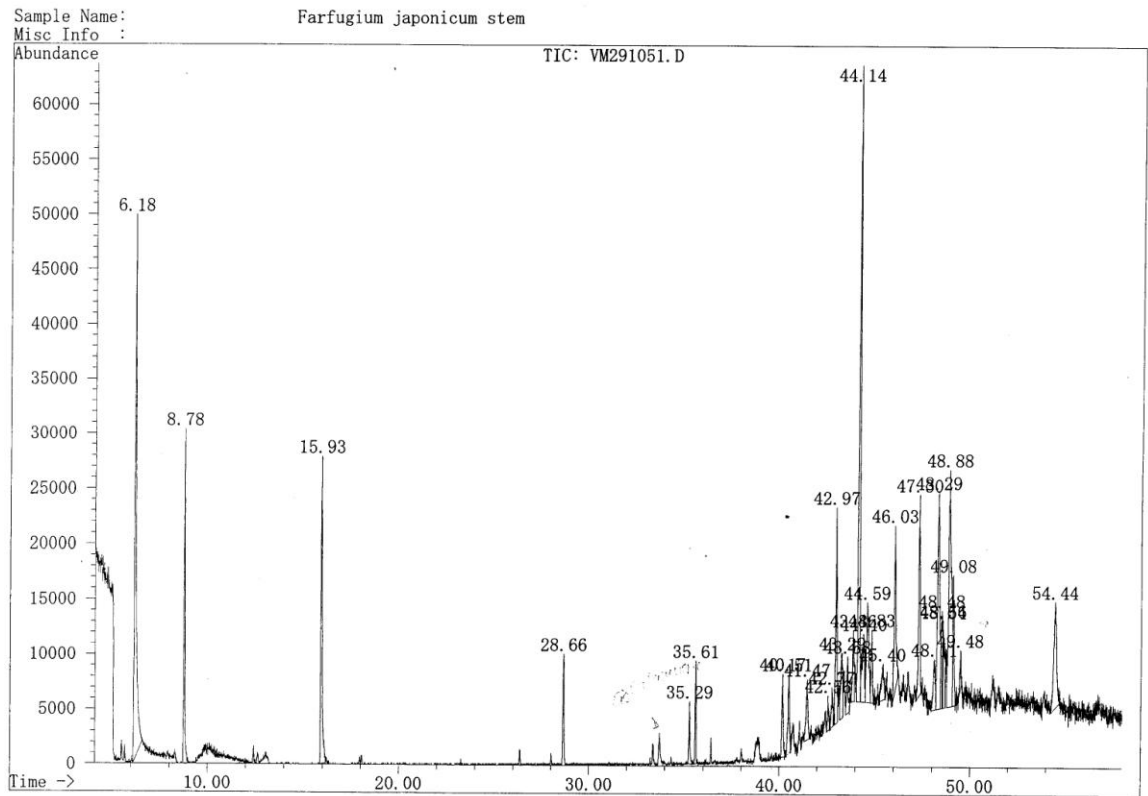
*P. japonicas*, rhizome



*Farfugium japonicum*, leaves



*Farfugium japonica*, flowers



*Farfugium japonicum*, stem

## Curriculum Vitae

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### Personal Information:

Place of Birth: Kosovo

Citizenship: Austrian

Gender: female

### Education:

1.10.1988-15.06.1996 Elementary school / Kosovo

1.10.1996-30.06.2000 High School / Kosovo –Vienna

October 2000 Notification for Pharmacy  
and medical study at Vienna-University

1.10.2001-20.06.2001 Supplementary lecture and closing exam:  
“Latin for medical sciences”

28.05.2008-2.06.2008 “1<sup>st</sup> international congress of medical sciences”  
Prishtina, Kosovo

22.12.2008 1<sup>st</sup> Research Symposium “Innovation of  
Medicinal Materials by Using the Methods of  
Purification and Organic Synthesis of Natural  
Products”, Tokushima Bunri University,  
Tokushima, Japan

6.09.2009-9.09.2009 40<sup>th</sup> International Symposium on Essential Oils (ISEO), Poster presentation of the master thesis at the "GC-MS analysis of essential oils of selected liverworts and Japanese medicinal plants" Savigliano, Italy

**Employment History:**

10.08.2003-4.04.2007 Part-time job as a counsel  
Zara GmbH, Vienna

11.08.2007- 15.09.2008 Part-time job as a counsel and organizer Billa GmbH, Vienna  
Area of responsibility: assistance of the branch management

Since 14.07.2008 employed as an assistant at the Haydn-Pharmacy and health center, 1050 Wien  
Area of responsibility: Identification of substances, Preparation of different pharmaceutical and cosmetic products, consultant.

**Particular skills:**

MS word, MS Excel, power point, intermediate level

Perfect Team-work, reliability, responsibility

**Languages:**

Albanian, English, German

**Hobbies and interests:**

Volleyball, traveling, reading