Industrial use of Medicinal and Aromatic Plants (MAPs)

Unit 1. INTRODUCTION AND CONCEPTS

1.1 **Introduction.**
1.2 **Historic records and present day**
1.3 **Concepts.**
1.4 **Main application for MAP in industry.**

1.1 Introduction.

Many plants synthesize substances that are useful to the maintenance of health in humans and other animals. These include aromatic substances, most of which are phenols or their oxygen-substituted derivatives such as tannins. Many are secondary metabolites, of which at least 12,000 have been isolated — a number estimated to be less than 10% of the total. In many cases, these substances (particularly the alkaloids) serve as plant defense mechanisms against predation by microorganisms, insects, and herbivores. Many of the herbs and spices used by humans to season food yield useful medicinal compounds.

The demand for medicinal plants is currently increasing in both developed and developing countries for various reasons. For some it would be the growing recognition that natural products have fewer or even no side effects; for others it would be their accessibility and affordable costs that would tip the scales.

Medicinal and aromatic plants are used as plants themselves or parts of plants or can be processed by distillation to become essential oils. They are used in pharmacy, cosmetology, perfumes and the food industry among others.

With increased demands for the resources available, a number of important plant species have become scarce in areas where they were previously abundant. If their collection and use is not regulated, some species may become threatened with extinction.

In recent years, the use of medicinal and aromatic plants (MAPs) has increased greatly in western countries, but also in places such as India and China. In Europe, at least 2,000 MAP species are traded commercially, 1,200 to 1,300 of these being native to Europe.

The increase in demand for MAPs is putting pressure on natural resources. The European Plant Conservation Strategy (EPCS) states that 90% of MAP species native to Europe are still collected from the wild.

1.2 Historic records and present day

The origin of the Maps is as old as agriculture, as well as its essences and extracts. Its employment begins as an unselective wild-harvested of plants, moving into a selective collection of some other, to cultivate the most useful to its extension to crop.

The therapeutic utility of plants is traced from more than thousand years. The earliest known medical document is a 4000-year-old Sumerian clay tablet that recorded plant remedies of popular disease. From then on, it is found other antiques documents in Egyptian, in Chinese, in Indian and Western tradition. For example, the ancient Egyptian Ebers papyrus from 3500 year ago reported hundreds of remedies.

In the other hand, the legendary Chinese doctor LI-Shi-Chang, wrote down in the Pen-tsao, three hundred and sixty five (365) herbs, characterized as splendid, average and inferior plant. Among splendid/wonderful herb, it was ma-huang shrub (*Ephedra vulgaris*) recommended to applying to a lung sickness. In India, herbal medicine dates back several thousand years to The Rig-Veda, the collection of Hindu sacred verses. In addition, it also exists The Badianus Manuscript is an illustrated document that reports the traditional medical knowledge of the Aztecs

1.2.1 Early Greek and Romans

Western medicine can be traced back to the Greek physician Hippocrates, who believed that disease had natural causes and used various herbal remedies in his treatments Early Roman writings also influenced the development of western medicine, especially the works of Dioscorides, Galena and Avicenna.

Dioscorides (40-90 D.C.) compiled information on more than 600 species of plants with medicinal value in De Materia Medica

Dioscorides' work remained the standard medical reference in most of Europe for the next 1500 years, during Middle Age and Renaissance.

Galeno de Pergamo (130-200 A C) was a Greek doctor which work was a reference for Western medicine over the millennia.

On the other hand, it is pointed out the work of Abu Ibn Sina (980-1037 AC) known as Avicenna in Europe, was a doctor, scientist and philosopher from Persia which was very respected and recognized as one of the most important and influenced doctor.

During centuries, medicine and botany were strongly linked each other and plants were a basic element to medical application. From the seventeenth century, in western world botany and medicine drift apart, and prescription drug were little by little available for everybody, so the old application making up of whole plant disappeared.

1.2.2 Middle age

In the Middle Age, the use of medicinal plants was under threat of Spanish Inquisition; a huge amount of physicians were sentenced to death by burning in the fire. One of the most dangerous specie was *Claviceps purpurea* known as Ergot, a fungus, which infects grain and grass. Ergot contains alkaloids such as LSD whose hallucinated and convulsionary effects were believed to be provoked by evil demons. Only in monastery was preserved the previous knowledge by the translation of Greek and Roman documents about Medicinal Plants.

The beginning of the Renaissance saw a revival of herbalism, the identification of medicinally useful plants

This coupled with the invention of the printing press in 1450 ushered in the Age of Herbals

Many of the herbals were richly illustrated; all of them focused on the medicinal uses of plants, but also included much misinformation and superstition

The Doctrine of Signatures, for example, held that the medicinal use of plants could be ascertained by recognizing features of the plant that corresponded to human anatomy.

For example, the red juice of bloodwort suggests that it should be used for blood disorders; the lobed appearance of liverworts suggests that it should be used to treat liver complaints; the "humanoid" form of mandrake root suggests that is should be used to promote male virility and ensure conception

1.2.3 The New World

When European settlers reached to American land, they were fascinated with local knowledge about the common use of medicinal plant.

Aztecan had a medicinal herb inheritance of about more than 3000 species. In 1552 was written the first book about Mexican and America Medicine, *Medicinalibus, Indorum Herbis*, by Martín de la Cruz, Aztecan physician and translated into Latin by Juan Benardino.

Among species brought from American land to Europe was for example Quinine bark (Cinchona sp), coca (*Erythroxylum coca*) or tobacco (*Nicotiana tabacum*))

1.2.4 Modern prescription drugs

Many of the remedies employed by the herbalists provided effective treatments

Studies of foxglove for the treatment of dropsy (congestive heart failure) set the standard for pharmaceutical chemistry

In the 19th century, scientists began purifying the active extracts from medicinal plants (e.g., the isolation of morphine from the opium poppy)

In 1850, it was developed a new research movement to characterize vegetal composition and it supposed the born and beginning of pharmacologic, perfumery and seasoning industry.

Advances in the field of pharmacology led to the formulation of the first purely synthetic drugs based on natural products in the middle of the 19th century

In 1839, for example, salicylic acid was identified as the active ingredient in a number of plants known for their pain-relieving qualities; salicylic acid was synthesized in 1853, eventually leading to the development of aspirin

1.2.5 Herbal medicine today

While Western medicine strayed away from herbalism, 75% to 90% of the rural population of the rest world still relies on herbal medicine as their only health care.

Since seventies, in modern developing countries it appears a renewable interest for research, production and consumption of MAPs, apply to pharmacological, nutritious, perfumery and cosmetic field.

Traditional medicine, the awareness of health and improvement of standard of living has led to a research for alternative products with high quality and scientific demonstrated properties. In country such as German, the consumption of “natural” medicines is account for still 25 % of medical prescriptions. Nowadays, the offer of product with a natural origin is increasingly up.

Nowadays, western medicine is complemented with natural medicine, as well as oil and products with a medicinal plant origin are increasingly demanded.

In this moment, the big suppliers of medicinal plant are Eastern European country and Far East. They produce huge quantity. In many cases, quality property is less important than quantity, as a result of no stricter environmental regulation, products are used to getting contaminated by toxic substances.

The People’s Republic of China is the leading country for incorporating traditional herbal medicine into a modern health care system; the result is a blend of herbal medicine, acupuncture, and Western medicine

Plantations exist in China for the cultivation of medicinal plants, and thousands of species are thus available for the Chinese herbalist; prescriptions are filled with measured amounts of specific herbs rather than with pills or ointments (see fig. 19.3). In India, traditional systems have remained quite separate from Western medicine

Spain, with a high medicinal herb biodiversity has been a supplier of high quality material commonly from wild harvesting. The quality production of medicinal plant is a good alternative for little supplier in traditional agriculture, that they are currently dealing with serious economic problem. The development of the medicinal plant production requires a trade regulation framework that has been delayed by the lack of understanding between pharmacist and herbalist.

On the other hand, 150 species are threatened in Europe and especially in Albania, Hungary, Spain and Turkey by unselective collection and overuse. The most threatened species are Pheasant's eye**,** *Adonis vernalis,* Bearberry *Arctostaphylos uva-ursi,* Arnica, *Arnica montana,* Island moss *Cetraria islandica,* Sundew *Drosera rotundifolia,* Yellow gentian, *Gentiana lutea,* Liquorice *Glycyrrhiza glabra;* some species belong to *Gypsophila* spp (*Ankyropetalum gypsophiloides*), Bogbean *Menyanthes trifoliata*, orchid family , peony family, *Paeonia* spp., prímula family *Primula* spp., Butcher's broom, *Ruscus aculeatus*, some species of genus *Sideritis* spp., and species of genus of thyme and oregano (*Thymus* spp., *Origanum* spp., y *Thymbra* spp.)

1.3 Concepts

Firstly, it is pointed out the significance of a correct employment of botany taxonomy. All plants have a common name as they are known by local people. However, in different places a same plant can have different name or even a same name can use for identified different plant.

Secondly, to classify species, it is used a complete Latinized hierarchy sequence, which goes from more to less detail. This sequence is specie, genus, family, order, class and division. Therefore, the scientific or Latin name is composed of two names the first is the genus (beginning with a capital letter) and the second is the specific epithet (according to specie).

Finally, for example Chamomile can refer to different herbs and even to shrub.

- Roman Chamomile or common Chamomile (*Chamaemelum nobile*), perennial herb from Europe.
- German Chamomile or sweet chamomile (*Matricaria recutita* o *M. chamomilla*), an annual herb from Europe.
- Corn Chamomile (*Anthemis arvensis*), an annual herb from Europe.
- Mancineel (*Hippomane mancinella*), a very toxic American tree belongs to Euphorbiacea family.
- Monkey plum (*Ximenia americana*), a tropical tree belongs to Oleaceae family from Africa and America.

On the other hand, Aromatic and Medicinal plant term includes species with very different features and this same term can also include seasoning and tincture species.

Medicinal Herbs have curative powers and are used in making medicines because of their healing properties as a result of containing active ingredients. They represent one seventh of all known plant, around a 14,5% For instance, Valeriana officinalis has sedative properties.

The specific part of medicinal plant such as root, leaf, stem, flower, which is used for therapeutic purposes, is known as vegetal drug. For instance, in the case of Valerian or Ginseng, drug comes from root, while in the case of Liquorice, drug comes from bark.

Herbal material: is not only the whole plant itself but also its gums, fixed oils, essential oils, resins, extracts, etc In some countries, these materials may be processed by various local procedures, such as steaming, roasting, or stirbaking with honey, alcoholic beverages or other materials.

Active ingredients are the substances responsible for pharmacological action. In the example above mentioned, valepotriat and valerenic acid are principle actives from Valerian root.

Aromatic Plant: medicinal plants are those whose active ingredients are composed wholly or partly by essences. They represent a 0.66% of the medicinal plants.
Condiment or spice: are used for their organoleptic characteristics, which leads to food and drink certain aromas, colours and flavours that make them more appetizing, tasty and pleasing to smell, sight and taste. They are condiments plants, used in stews, dressings and liquor, such as: "ajedrea", "garlic", "anise", "saffron", "cilantro", "cumin", "fennel", "marjoram" , "mint", "oregano", "Rosemary", "pepper", "sage" and "thyme."

Honey Plants, melliferous, polinipher: Those that attract bees and those that collect nectar, pollen and honeydew, to feed the hive, or propolis for other uses in them. They contain active ingredients which are medicinal.

Tincture plants contains substances that are employed to dye material and fibre both vegetal and animal (wool, leather, cotton, linen) for clothes. For instance, Saffron, *Crocus sativus,* is used as tincture plant*.*

Essential oils: They are a mixture of volatile organic compounds extracted by physical means of odoriferous plant materials, for example: flowers, herbs, timber, fruits and roots.

Extracts are non volatile fraction that contains active ingredients extracted by physical means such as hot and cold solvent extraction.

Oleorresines spice: dried spices are obtained by extraction with a volatile non-aqueous solvent, followed by the elimination of solvent evaporation to moderate temperatures and a partial vacuum. The oleoresins contain the aroma and taste of the spice concerned (including the non -volatile principles, unlike the essential oils of spices) in concentrated form and are usually liquid or viscous substances Semi-solid.

1.4 Main application of Medicinal and Aromatic plant in industry.

The origin of the Maps is as old as agriculture, as well as its essences and extracts. Its employment begins as an unselective wild-harvested of plants, moving into a selective collection of some other, to cultivate the most useful to its extension to crop. MAPs are employed in nutritional industry, in home, in medicine and in cosmetic.

The following main industrial uses in order of importance, that used medicinal plants, are: big supplier to herborist, extraction of essential oil and industry. Species that have currently the most economic yield for its high consumption are Echinacea (*Echinacea purpurea*) and St. John's wort (*Hypericum perforatum*) (Moré, 1998) which in country such as German with a turnover of around $ 71,000 and $ 10,000 for each specie

According to European vegetal product turnover in 1996 (Gruenwald, 1998), German consume 50% of this kind of product, this is supposed a 42,9 $ annual per capita, following by France ($31,2) and Italy ($12,2). In Spain, the consumption is only $7,6 but it trends to grow in a future until reaching European consumption rate of the country such as German.

Essential oils are gaining importance in flavouring indoor environment in Japanese office, where is used different essences depending on the emotional state.

Aromatherapy, technical increasingly accepted in British hospital, is increasing the demand for essential oil. In addition, it is increasing its use as an antiseptic and it has illustrated its effect on some virus for which there is still not reliable medication.

Furthermore, the permanent replacement global synthetic for natural products has side effects, for instance citral aldehyde, which is toxic and has pure irritant effect on the skin, but it is very beneficial as lemon essential oil (or cedron)

The **seasonings** are used as preservative and natural antioxidants in the food manufacturing industry. For instance, oregano, rosemary and sage, which are used in meat and sausages.

They avoid the rancidness of products without the need of adding antioxidants and synthetic preservatives and stabilizers chemicals, which are becoming more limited in use in developed countries. Instead natives are safe.

Classified as **a food supplement** and do not require special licenses are not required restrictions on its use. In addition consumers tend to remove salt foods, replacing them with spices.

The preference for natural foods has sought to replace artificial **colours and flavours**, thus promoting the natural herbs.

The boom in the kitchen microwave, frozen foods and fast foods with new tastes, needs more **seasoning**.

The multinational **candy and cosmetics** have developed demand for all types of essences, essential oils and aromas.

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Unit 2. Classification of medicinal and aromatic plants.

2.1. According to their usage.
2.2. According to their active constituents.
2.3. According to their period of life.
2.4. Botanical Classification of Medicinal and Aromatic Plants.
2.5. Classification of Natural Products.

Classification of medicinal plants is organized in different ways depending on the criteria used. In general, medicinal plants are arranged according to their active principles in their storage organs of plants, particularly roots, leaves, flowers, seeds and other parts of plant.

These principles are valuable to mankind in the treatment of diseases. Reports on the classification of many plant species yielding vegetable oils used in cosmetics and body and skin care preparations are sporadic or lacking.

Herbs are classified in many ways. Some of them are

1. According to the usage
2. According to the active constituents
3. According to the period of life
4. According to their taxonomy

The classification system is discussed in detail under but we will describe the herbs as classified according to the period of the life.

2.1 According to the usage

The herbs are classified in four parts: Medicinal herbs, culinary herbs, Aromatic herbs, Ornamental herbs.

A. Medicinal Herbs

Medicinal herbs have curative powers and are used in making medicines because of their healing properties.

B. Culinary Herbs

Culinary herbs are probably the mostly used as cooking herbs because of their strong flavours like mint, parsley, basil.

C. Aromatic Herbs

Aromatic herbs have some common uses because of their pleasant smelling flowers or foliage. Oils from aromatic herbs can be used to produce perfumes, toilet water, and various scents. For e.g. mint, rosemary, basil etc.

D. Ornamental Herbs

Ornamental herbs are used for decoration because they have brightly coloured flowers and foliage like lavender, chives.

2.2 According to the active constituents.

Present in them, the herbs are divided into five major categories: Aromatic (volatile oils), Astringents (tannins), Bitter (phenol compounds, saponins, and alkaloids), Mucilaginous (polysaccharides), and Nutritive (food stuffs).

A. Aromatic Herbs

Aromatic Herbs, the name is a reflection of the pleasant odour that many of these herbs have. They are used extensively both therapeutically and as flavourings and perfumes. Aromatic herbs are divided into two subcategories: stimulants and nervines.

Stimulant Herbs increase energy and activities of the body, or its parts or organs, and most often affect the respiratory, digestive, and circulatory systems; e.g. fennel, ginger, garlic, lemon herb.

Nerving Herbs are often used to heal and soothe the nervous system, and often affect the respiratory, digestive, and circulatory systems as well. They are often used in teas or in encapsulated form, e.g. ginger, catnip.

B. Astringent Herbs

Astringent Herbs have tannins, which have the ability to precipitate proteins, and this "tightens," contracts, or tones living tissue, and helps to halt discharges. They affect the digestive, urinary, and circulatory systems, and large doses are toxic to the liver. They are analgesic, antiseptic, anti abortive, astringent, emmenaggogue, hemostatic, and styptic. For example, peppermint, red raspberry.

C. Bitter Herbs

Bitter Herbs are named because of the presence of phenols and phenol glycosides, alkaloids, or saponins, and are divided into four subcategories: laxative herbs, diuretic herbs, saponin-containing herbs, and alkaloid-containing herbs.

Laxative Bitter herbs include alterative, ant catarrhal, antipyretic, cholagogue, purgative, hypotonic, sialagogue, vermifuge, and blood purifier. For e.g. aloe, cascara, liquorice, pumpkin, senna, yellow dock, yucca, barberry, gentian, safflowers, and golden seal.

Diuretic Herbs induce loss of fluid from the body through the urinary system. The fluids released help cleanse the vascular system, kidneys, and liver. They are alterative, antibiotic, ant catarrhal, antipyretic, and antiseptic, lithotripter, and blood purifier in nature. For instance, asparagus, blessed thistle, burdock, butcher's broom, buchu, chaparral, chickweed, corn silk, dandelion, dog grass, grapevine, and parsley.

Saponin-containing Herbs are known for their ability to produce frothing or foaming in solution with water. The name "saponin" comes from the Latin word for soap. They emulsify fat soluble molecules in the digestive tract, and their most important property is to enhance the body's ability to absorb other active compounds.

Saponins have the ability to effectively dissolve the cell membranes of red blood cells and disrupt them. They are alterative, ant catarrhal, antispasmodic, and aphrodisiac, emmenagugue, cardiac stimulant, and increased longevity in nature. For e.g. yam root, schizandra, black cohosh, blue cohosh, devil's claw, liquorice, alfalfa, yucca, ginseng, and gotu kola.

D. Mucilaginous Herbs

Mucilaginous herbs derive their properties from the polysaccharides they contain, which give these herbs a slippery, mild taste that is sweet in water. All plants product mucilage in some form to store water and hydrates as a food reserve. Since most mucilage are not broken down by the human digestive system, but absorb toxins from the bowel and give bulk to the stool, these herbs are most effective topically as poultices and knitting agents, and are also used topically in the digestive tract. When used as lozenges or extracts, they have a demulcent action on the throat.

They eliminate the toxins from the intestinal system, help in regulating it and reduce the bowel transit time. They are antibiotic, antacid, demulcent, emollient, vulnerary, and detoxifier in nature. For e.g. althea, aloe, burdock, comfrey, dandelion, Echinacea, fenugreek, kelp, psylium, slippery elm, dulse, glucomannan from Konjak root, Irish moss, and mullein.

E. Nutritive Herbs

These herbs derive both their name and their classification from the nutritive value they provide to the diet. They are true foods and provide some medicinal effects as fibber, mucilage, and diuretic action. But most importantly they provide the nutrition of protein, carbohydrates, and fats, plus the vitamins and minerals that are necessary for adequate nutrition. For e.g. rosehips, acerola, apple, asparagus, banana, barley grass, bee pollen, bilberry, broccoli, cabbage, carrot, cauliflower, grapefruit, hibiscus, lemon, oat straw, onion, orange, papaya, pineapple, red clover, spirulina, stevia, and wheat germ.

2.3 According to the period of life, herbs also can be classified as annuals, biennials, and perennials. Annuals bloom one season and then die. Biennials live for two seasons, blooming the second season only. Once established, perennials live over winter and bloom each season.

Annual herbs complete their life cycle in one year; start them from seed. Annual herbs include

- Anise
- Basil
- Borage
- Calendula (Pot Marigold)
- Chamomile
- Chervil
- Cilantro/Coriander
- Dill Bouquet
- Dill Dukat
- Fennel, smoky
- Marjoram
- Parsley
- Shiso
- Saffron
- Summer Savoury

Biennial herbs are plants which live two season and bloom in the second season only.

- Caraway seeds
- Prime rose
- Bai Zhi
- Mullein
- Teasel
- Viper's Bugloss

Plants with aromatic foliage

- *Allium spp*, basal leaves smell of onions
- *Artemisia spp*, aromatic/pungent silvery foliage - spring & summer
- *Foeniculum vulgare*, aromatic leaves used in cooking
- *Helichrysum italicum*, 'Curry Plant', curry-scented aromatic
- *Helichrysum stoechas*, aromatic leaves smelling of curry

- *Hedychium gardnerianum*, fragrant lemon and red flowers
- *Lavandula spp & cvs*, all highly scented flowers and aromatic foliage
- *Origanum spp*, aromatic culinary herb
- *Pelargonium graveolen*s, *P. tomentosum* etc, scented leaves
- *Pistacia lentiscus*
- *Ruta graveolens*, aromatic herb with pungent foliage
- *Ruta graveolens* 'Jackman's Blue', aromatic leaves which are blue
- *Ruta chalepensis*, foetid rue, leaves very aromatic,
- *Ruta angustifolia*
- *Rosmarinus officinalis*, whole plant aromatic all year
- *Salvia officinalis*, aromatic all year
- *Satureja montana*, grown for aromatic foliage
- *Tagetes minuta*, whole plant has strong unpleasant odour
- *Thymus vulgaris*, grown for its aromatic foliage

Perennial herbs grow for more than one season and include sweet marjoram, parsley, mint, sage, thyme and chives. Most can be started from young plants except for parsley.

- Alfalfa
- Allspice
- Aloe Vera
- Angelica
- Acrimony
- Bee Balm
- Bay leaves
- Catnip
- Chives, Common
- Common Thyme
- Echinacea
- Fennel, Florence
- Lavender
- Lemon Balm
- Mints (Spearmint, peppermint, apple mint, orange mint)
- Marjoram
- Mitsuba
- Oregano
- Rosemary
- Sorrel
- Salad Burnet
- Sage
- Tarragon
- Thyme
- Watercress and Yarrow

2.4 Botanical Classification of Medicinal and Aromatic Plants

Modern Botanical Nomenclature.

A system to distinguish plants which is based purely on common names would be both ambiguous and confusing, and could group together plants which bear similar names, but are not related to each other e.g. here are some listings for Laurel (Mabberley 1998):

- Alexandrian Laurel *Calophyllum inophyllum* L.
- Bay Laurel *Laurus nobilis* L.
- Californian Bay Laurel *Umbellularia californica* (Hook. & Arn.) Nutt.
- Cherry Laurel *Prunus laurocerasus* L.
- Chinese Laurel *Antidesma bunius* (L.) Sprengel etc. etc.

So, today, plants are classified under the binomial system invented by Carl Linnaeus (1707-78), a Swedish botanist. In this system, the first name given is that of the genus, and the second, that of the specific epithet e.g. for creeping or Corsican mint Mentha requienii Bentham, the genus is Mentha, of the Labiatae family, M. requienii being one of some 25 species of aromatic herbs contained in this genus. The binomial ('two stages naming') system gives a precise classification of the particular plant, and these classifications are to be found Linnaeus's two definitive original works: Genera plantarum and Species plantarum. Botanists have further developed this system into a comprehensive diversely branched family tree of classifications, which includes all known plants. The complete ascending sequence is species, genus, family, order, class and division.

The meaning of the botanical name may be indicative of the history of the plant i.e. a genus may be named after a particular botanist e.g. the Kaempferia genus of some fifty herbal species withy rhizomes & tuberous roots which includes some lesser gingers, is named after the German physician Englebert Kaempfer 1651-1716. The name may also tell something of the habit or morphological characteristics of the plant e.g. in Gaultheria procumbens L., the latter name derives from ‘procumbent’ which describes the plant’s habit. A useful publication which is the standard reference for botanical Latin (& which includes comprehensive listings of the meaning of plant names) is listed below under Stearn (1992).

The Rules of Plant Nomenclature.

The rules pertaining to plant nomenclature have been set out in two publications: The International Code of Nomenclature for Cultivated Plants (first edn 1952 – the latest 6th edn. being published in 1995)

The International Code for Botanical Nomenclature (latest “the Tokyo Code: 1993).

Plants are divided into families in which similarly related plants are grouped together basic on the clear similarity of morphological characteristics.

Families may contain one genus or a large number. A **genus** may similarly contain one species or a large number of related individuals – for example the Rosmarinus genus contains just two species, Rosmarinus eriocalix Jord. & Fourr. and R. officinalis L. (although some workers recognise Rosmarinus tomentosus Huber-Morath & Maire, as a third species of the genus). Variations occur within a species and these are accommodated in the following manner: a **subspecies** (ssp.) is a distinct variant often arising because of evolution of plant **form** from geographic factors, **varieties** (var.) have small differences in morphology, and the form (forma), has very minor differences e.g. leaf or fruit colour. **Cultivars** offer further evidence of diversity and according to The International Code of Nomenclature for Cultivated Plants (1980), cultivars named since 1959 should be given vernacular names, which should be in roman type within quotes e.g. “Rosa”.

Hybrid plants arising from the sexual crossing of distinct species within the same genera are called interspecific hybrids and are indicated by a multiplication sign e.g. Lavandin plants Lavandula x intermedia are sterile hybrids between Lavandula angustifolia Mill. and Lavandula latifolia Medic. Less commonly met are plants arising from sexual crossings between different genera (intergeneric hybrids). Grafting one plant onto another can also produce hybridised plant growing onwards from the grafting point: these are indicated by a + sign linking the two involved species.

Chemotypes (ct.) are of especial interest in the world of essential oils. These are marked by differences in products of secondary metabolism (e.g. essential oil composition) which can occur even in morphologically stable species, such as Chamomilla recutita (L.) Rauschert. For example, four chemotypes of Ocimum sanctum L. from the highly varied Ocimum genus were described by Hegnauer (1966): a citral-type, a eugenol type, a methyl chavicol type and a chavibetonal type. The distinguishing criteria for chemotype identification are the major components only of the essential oil from a named specific part of the plant (seeds, leaves etc.). Genetic control of essential oil biosynthesis has been investigated and a bank of knowledge now exists for specific oil-bearing plants. It is probable however that many chemotypes of common aromatic plants have yet to be properly identified.

Most of the medicinal and aromatic plants belong to the following families:

- Compositae
- Labiatae
- Umbelliferae
- Leguminosae
- Roseaceae
- Rutaceae
- Solanaceae
- Cruciferae
- Liliceae
- Caryophyllaceae

- Boraginaceae
- Ranunculaceae
- Papaveraceae
- Malvaceae
- Cucurbitaceae
- Verbenaceae
- Scrophulariceae
- Phytolaccaceae

A. Medicinal plants of the Compositae family

The Compositae family, also known as the Daisy family, contains the highest number of medicinal plants as compared to other families. Medicinal plants belonging to this family include the chamomile, the field and pot marigolds, daisy, wormwood, chicory, thistles, ragwort and artichoke.

- Chamomile. *Matricaria chamomilla.*
- True chamomile, *Anthemis nobilis.*
- Marigold. *Calendula*.
- Daisy. *Bellis annua*,
- Wormwood. Also known as *Artemisia absinthium*,
- Chicory. *Cichorium intybus* and *Cichorium spinosa*
- Thistles. Milk thistle, known as *Silybum marianum*.
- Silver ragwort. *Senecio bicolour.*
- Artichoke, *Cynara cardunculus.*

B. Medicinal plants of the Labiatae family

A very important medicinal plant family is the Labiatae family, also known as the mint family. Plants in this family are herbs or shrubs often with an aromatic smell. They are common in the Mediterranean countries for the fact that some of them produce a high amount of essential oil that enables them to survive the hot summer season. Some examples from this family include horehound, lavander, balm, micromeria, the mints, thyme and rosemary.

The lavander is a term given to a group of plants that have similar shape and properties. In Spain there are several species and subspecies.

- *Lavandula officinalis*.
- *L. angustifolia* Miller
- *L. angustifolia* Miller subsp. *pyrenaica*
- *L. latifolia* Medicus
- *L. lanata* Boiss.
- *L. dentata L.*
- *L. stoechas* L.
- *L. pedunculata* Cav.
- *L. viridis* L'Hér.
- *L. multifida* L.

The mints constitute a large group of plants. Their scent varies from pungent to sweet. These properties are owned by the distinct mint species.

- Pennyroyal (*Mentha pulegium*).
- Water mint (*Mentha aquatica*).
- Peppermint (*Mentha piperita*)
- Spearmint (*Mentha spicata*)

Thyme has also many representatives is Europe.

- Mediterranean thyme (*Thymus capitatus*)
- *Thymus granatensis* (red thyme)
- *Thymus hyemalis* (sauce thyme)
- *Thymus longiflorus* (long flower thyme)
- *Thymus mastichina* (Mejorana)

- *Thymus serpylloides* (sierra thyme)
- *Thymus vulgaris* (common thyme)
- *Thymus zygis* (olive thyme)

Finally we can find rosemary (*Rosmarinus officinalis),* Horehound (*Marrubium vulgare*), Balm, also known as *Melissa officinalis*, Micromeria (*Micromeria microphylla*).

C. Medicinal plants of the Umbelliferae family

The Umbelliferae or carrot family consists of plants with a characteristic umbrella-arranged fruit. These plants usually produce an essential oil, an asset to survive during the hot summer days. In fact the oil has a cooling effect on the plant. Some examples from this family include bullwort (*Ammi majus*), wild celery (*Apium graveolens*), wild carrot (*Daucus carota*), sea holly (*Eryngium maritima*), fennel (*Foeniculum vulgaris*), anise (*Pimpinella anisum*), wild parsley (*Petroselinium crispum*), hemlock (*Conium maculatum*) and alexanders (*Smyrnium olusatrum*).

- Bullwort (*Ammi majus*).
- Wild celery (*Apium graveolens*).
- The wild carrot (*Daucus carota*)
- The sea holly (*Eryngium maritimum*)
- Fennel (*Foeniculum vulgare*).
- Parsley or *Petroselinum*.
- One of the most poisonous herbs is the spotted hemlock or *Conium maculatum*.
- Alexanders (*Smyrnium olusatrum*).

D. Medicinal plants of the Leguminosae family

The Leguminosae or pea family consists of large number of plants, both native and naturalised, that have been cultivated for fodder, food and ornamental purposes. Amongst these plants, those with medicinal virtues include the carob tree (*Ceratonia siliquia*), the pea (*Pisum sativum*), white and red clovers (*Trifolium repens* and *pratense*), false acacia (*Robinia pseudoacacia*), Judas tree (*Cercis siliquastrum*), alfalfa (*Medicago sativa*) and fenugreek (*Trigonella foenum-graecum*).

A group of closely related species in the Leguminosea family are the clovers. Two important species are the white and red clovers (*Trifolium repens* and *T. pratense*).

E. Medicinal plants of the Rosaceae family

A large of species in Rosaceae or rose family, have a medicinal value. Most of these are trees or shrubs with variable characteristics. This family is popular for its edible and juice fruit shrubs and trees. Some examples of this family include bramble (*Rubus ulmifolius*), rose (*Rosa gallica*), wood strawberry (*Fragaria moschata*), quince (*Cydonia oblongata*), round pear (*Pyrus amydaliformis*), loquat (*Eriobotrya japonica*), hawthorn (*Crataegus monogyna*), peach, almond and apricot (*Prunus persica, amygdalus* and *armeniaca*).

- Bramble (*Rubus ulmifolius*)
- The wild rose (*Rosa gallica*)
- Wood strawberry (*Fragaria moschata*)
- Quince (*Cydonia oblongata)*
- The round pear (*Pyrus amydaliformis*).
- Hawthorn (*Crataegus monogyna*)

The *Prunus* genus includes several stone fruits such as the peach, almond, apricot, plum and blackthorn. Most of these are cultivated for their fruit, as all have a local market. However, most have naturalised in valleys and gardens.

- Peach (*Prunus persica*)
- Almond (*Prunus amygdalus*).
- Blackthorn (*Prunus spinosa*)

F. Medicinal plants of the Rutaceae and Solanaceae families

The Rutaceae or rue family is a small family that consists of cultivated fruit trees and medicinal herbs. Plants in this family include the wall and garden rues (*Ruta chalepensis* and *graveolens*), orange (*Citrus aurantium*), lemon (*Citrus limon*), tangerine (*Citrus paradisi*) and grapefruit (*Citrus paradisi*).

The rues (*Ruta graveolens* and *R. montana*) are two related species that have different medicinal uses. A citrus tree with great medicinal value is the bitter orange tree (*Citrus aurantium*).

A family with several poisonous, but medicinally-important herbs is the Solanaceae or potato family. A species in this family that is widely cultivated (*Solanum tuberosum*). Other cultivated edible crops are the tomato (*Lycopersicum esculentum*) and the aubergine (*Solanum melongena*).

The potato is only edible when ripe, as green potatoes were found to be poisonous. Also although these three crops come from this poisonous family, through cultivation and experimentation, the genetic material that codes for the toxic compounds has been phased out, resulting in safer and non-toxic cultivars. Mediterranean natives in this family include the white henbane (*Hyoscyamus albus*), the Mediterranean withania (*Withania somnifera*) and garden thorn apple (*Datura metel*). Other important species include glaucous tobacco (*Nicotiana glauca*) and black nightshade (*Solanum nigrum*).

- White henbane (*Hyoscyamus albus*).
- Mediterranean withania (*Withania somnifera*).
- Garden thorn apple (*Datura metel*).
- Stramonium (*Datura stramonium*)
- Glaucous tobacco (*Nicotiana glauca*)
- Black nightshade (*Solanum nigrum*).

G. Medicinal plants of the Cruciferae family

The Cruciferae or cress family is characterised by plant that have flowers with cross-like petals. This family groups a large group of medicinal plants that include Wallflower (*Cheiranthus cheiri*), Bitter cress (*Cardamine hirsuta*), Shepherd's purse (*Capsella bursa-pastoris*), Black mustard (*Brassica nigra*), Horseradish (*Armoracia rusticana*), Hedge mustard (*Sisymbrium officinale*), White mustard (*Sinapis alba*), Wild radish (*Raphanus raphanistrum*), Watercress (*Nasturtium officinale*).

- Wallflower (*Cheiranthus cheiri*).
- Bitter cress (*Cardamine hirsuta*).
- Shepherd's purse (*Capsella bursa-pastoris*).

Although the *Brassica* plants are important crop, some of them have a medicinal value, such as the black mustard (*Brassica nigra*).

Other vegetable crops include cabbages and cauliflower.

- Horseradish (*Armoracia rusticana*).
- Hedge mustard (*Sisymbrium officinale*).
- White mustard (*Sinapis alba*).
- Watercress (*Nasturtium officinale*).
- Wild radish (*Raphanus raphanistrum*).

H. Medicinal plants of the Liliaceae family

The Liliaceae or lily family is composed of large number of plant with medicinal virtues. Most of these are herbs and rarely shrubs. Examples from this plant family include Asphodel (*Asphodelus aestivus*), Wild asparagus (*Asparagus aphyllus*), Seaside squill (*Drimia maritima*), Mediterranean smilax (*Smilax aspera*), Greater butcher's broom (*Ruscus hypophyllum*), Butcher's broom (*Ruscus aculeatus*), Tassel hyacinth (*Muscari comosum*), Madonna lily (*Lilium candidum*), Bluebell (*Hyacinthus orientalis*), Aloe (*Aloe vera*), Garlic (*Allium sativum*), Garden onion (*Allium cepa*), Mediterranean meadow saffron (*Colchium cupani*), Meadow saffron (*Colchium autunnale*)

- Asphodel (*Asphodelus aestivus*).
- Wild asparagus (*Asparagus aphyllus*).
- Seaside squill (*Drimia maritima*).
- Mediterranean smilax (*Smilax aspera*).

Two closely related species are Butcher's broom (*Ruscus aculeatus*) and greater butcher's broom (*Ruscus hypophyllum*).

- Tassel hyacinth (*Muscari comosum*).
- Madonna lily (*Lilium candidum*).
- Bluebell (*Hyacinthus orientalis*).
- Aloe (*Aloe vera*).
- Garlic (*Allium sativum*).
- Garden onion (*Allium cepa*).
- Mediterranean meadow saffron (*Colchium cupani*).
- Meadow saffron (*Colchium autunnale*).

I. Medicinal plants of the Caryophyllaceae and Boraginaceae families

The Caryophyllaceae or pink family group plants that usually have four to five petalled flowers that are usually white or pink in colour. Examples from this family include sandwort (*Arenaria serpyllifolia*), common chickweed (*Stellaria media*), sand spurrey (*Spergularia rubra*), nail wort (*Paronychia argentea*), smooth rupture-wort (*Herniaria glabra*), viscid sandwort (*Alsine tenuifolia*).

- Sandwort (*Arenaria serpyllifolia*).
- Common chickweed (*Stellaria media*).
- Sand spurrey (*Spergularia rubra*).
- Nail wort (*Paronychia argentea*).
- Smooth rupturewort (*Herniaria glabra*).
- Viscid sandwort (*Alsine tenuifolia*).

The Boraginaceae or borage family is made up of herbs or small shrubs with bristly stems and leaves. Examples in this family include borage (*Borago officinalis*), common comfrey (*Symphytum officinale*), purple alkanet (*Anchusa asurea*), yellow gromwell (*Neatostema apulum*), viper's bugloss (*Echium vulgare*) and southern hound's tongue (*Cynoglosum creticum*).

- Borage (*Borago officinalis*).
- Common comfrey (*Symphytum officinale*).
- Purple alkanet (*Anchusa azurea*).
- Yellow gromwell (*Neatostema apulum*).
- Viper's bugloss (*Echium vulgare*).
- Southern hound's tongue (*Cynoglosum creticum*).

J. Medicinal plants of the Ranunculaceae and Papaveraceae families

The Ranunculaceae or buttercup family is characterised by showy flowers that usually have 5 petals. Examples from this family include pheasant's eye (*Adonis annuus*), lesser celandine (*Ranunculus ficaria*), poppy anemone (*Anemone coronaria*), love in the mist (*Nigella damascena*), short-spurred larkspur (*Delphinium staphysagria*), larkspur (*Delphinium ajacis*), traveller's joy (*Clematis vitalba*), evergreen traveller's joy (*Clematis cirrhosa*).

- Pheasant's eye (*Adonis annua*).
- Lesser celandine (*Ranunculus ficaria*).
- Poppy anemone (*Anemone coronaria*).
- Love in the mist (*Nigella damascena*).
- Larkspur (*Delphinium ajacis*).
- Short-spurred larkspur (*Delphinium staphysagria*).
- Evergreen traveller's joy (*Clematis cirrhosa*).

The Papaveraceae or poppy family consists of a group of plant that contain a latex or water sap. There are four petals in a flower and these are cross shaped with two opposite petals above the other two. Plants with a medicinal value include greater celandine (*Chelidonium majus*), opium poppy (*Papaver somniferum*), common poppy (*Papaver rhoeas*), sea poppy (*Glaucium flavum*), fumitory (*Fumaria officinalis*) and fumitory (*Fumaria capria capreolata*)

- Greater celandine (*Chelidonium majus*).
- Opium poppy (*Papaver somniferum*).
- The common poppy (*Papaver rhoeas*).
- The sea poppy (*Glaucium flavum*).
- *Fumaria officinalis* and *Fumaria capria capreolata*. The Latin name *Fumaria* means smoke of the earth, as these have an unpleasant smoky smell.

K. Medicinal plants of the Malvaceae and other families

The Malvaceae or mallow family groups those plants that have five-petalled flowers and a nutlet-like fruit. Examples include common mallow (*Malva sylvestris*) hairless cotton (*Gossypium herbaceum*), hollyhock (*Althaea rosea*) and marsh mallow (*Althaea officinalis*).

- Common mallow, also known as *Malva sylvestris.*
- Hairless cotton (*Gossypium herbaceum*).
- Hollyhock (*Alcea rosea*).
- Marsh mallow (*Althaea officinalis*).

Other families that contain a very small number of medicinal plants include the following.

The Cucurbitaceae or cucumber family contains a large number of edible crops such as the cucumbers, melons and pumpkins. Two important medicinal plants in this family include the squirting cucumber (*Ecballium elaterium*) and the pumpkin (*Cucurbita maxima*).

Another family, called the Verbenaceae or verbena family contains three important medicinal plants; vervain (*Verbena officinalis*), chaste tree (*Vitex agnus-castus*) and the cultivated lantana (*Lantana camara*)

An important and common medicinal plant of the Scrophularia or figwort family is the snapdragon (*Antirrhinum majus*). It is a native of West Mediterranean and grows on rocky grounds and old walls. It flowers from January till October. Traditionally it was used as an astringent, diuretic, and hearmorrhoids. It contains several constituents such as alkaloids, amino acids and glycosides.

A characteristic plant of the pokeweed or Phytolaccaceae family is pokeweed itself (*Phytolacca americana*). Due to its poisonous properties, it was used externally only, for the treatment of rheumatism, withlow and skin inflammation. These are probably attributed to the saponins and the oleanolic acid derivative present in the plant. It contains a pokeweed lectin stimulates the white blood cells.

A member of the Euphorbiaceae family castor bean (*Ricinus communis*) is renowned for its medicinal and industrial purposes. It is a native of the tropics but has naturalised in some waste places and valleys. IT flowers between March and October.

Poisoning from seed ingestion has occurred in children. Traditionally, this plant was used as a laxative and to treat cradle-cap in babies. Castor oil is expressed from the seeds of the plant after they are peeled. Toxic albumins are present in the seed but these are removed by boiling with water. It is safe to use as a laxative and in baby skin products such as zinc and castor oil. It is used in industry as a lubricant to machinery and also in jet engines.

2.5 Classification of natural Products.

Natural products are compounds consisting essentially of carbon derived from natural sources (flora, fauna, land, etc.). And that generally have very diverse and interesting properties.

Some of the most relevant applications of the Natural Organic Products are using it as:

Fuels, plastics, fats, soaps, sugars.

Petroleum (Petra = stone; Oil = oil) is a naturally formed by liquid mixture of hydrocarbons, which are processed in the petrochemical industry through fractional distillation and cracking to gasoline, natural gas, etc.

Soap is the sodium salt of a fatty acid. Have a party hydrophyllic (dissolves in water) and other lipophyllic (fat dissolves dirt).

Sugars are natural polyhydroxialdehides or polyhydroxiketones with different functions: structure, energy storage components of the nucleic acids, etc. They are formed by photosynthesis in plants and are classified into monosaccharides (glucose), disaccharides (sucrose) and polysaccharides (cellulose, starch, etc.).

Sweeteners are natural or synthetic substance that gives a sweet taste to food. We can find natural sweeteners such as sucrose (cane and beet), fructose (sugar simpler and sweet, honey), lactose and galactose (sugars from milk, less sweet), and synthetic as: saccharin (300 times sweeter than sucrose), aspartame (160 times sweeter), etc.

Agro-chemicals: pesticides, plant growth regulators, etc.

Modifiers of animal behaviour (**pheromones**).

Flavours and perfumes. Food Additives (flavours, colours, antioxidants, etc.)

Drugs: Product to be administered for curative purposes. Although there are many natural source products that are used as drugs, the synthesis of drugs is well developed and provides a large amount of chemicals that are used as such. For example: sedatives, antiinflammatories, diurethics, antiviral, hepatoprotectors, etc.

Regulators: like dopamine, used for Parkinson´s sindrome (only L-Dopa is active)

Antibiotics: chemical products able to inhibit the growth of microorganisms and even destroy them.

Analgesics: drug that relieves pain without causing loss of consciousness. Painkillers are a large group that ranges from the derivatives of opium (solid product obtained drying the milky juice of the opium poppy "*Papaver sommiferum*" with a 25% alkaloids), and morphine (potent analgesic, very toxic and produces dependence), codeine (anticoughing, produces no habit), heroin (synthetic derivative obtained by acetylation of morphine, good analgesic with less depression than morphine addiction but more addiction), methadone (synthetic substitute for heroin with analgesic properties but also cause addiction) to opiates, such as aspirin, which is derived from the Silicilina (glycoside from the bark of willow formerly used as an analgesic), Paracetamol and ibuprofen. The application of topical analgesics include all anti-inflammatories, such as hydrocortisone and derivatives, and the general and local anesthetics at low doses.

A. Natural Products classification based on their chemical structure.

It is based on the type of chemical skeleton. So there are

- Aliphatic or non aliphatic fatty compounds of open chain as: fatty acids, sugars and a great amount of amino acids.
- Acyclic and cycloaliphatic compounds as terpenoids, steroids and some alkaloids.
- Aromatic or benzoic compounds as phenols, quinones, etc.
- Heterocyclic compounds such as alkaloids, flavonoids and nucleic acid bases.

Many natural products belong to more than one of these categories. For example, geraniol, farnesol and scualene belong to class 1, and thymol to class 3, but because of the biogenetic considerations they are treated as class 2.

B. Natural Products classification based on their physiologic activity

Approximately one half of the medicines used today are natural products, i.e. alkaloids, antibiotics or synthethic analogs. For that it is usually employed a classification that represents the physiologic activity, such as hormones, vitamins, antibiotics ad mycotoxins.

Even though the compounds belonging to each group have different structures and biogenetic origins, a narrow relationship is occasionally between those aspects and activity.

C. Natural Products classification based on their taxonomy

This classification is based on morphological studies of plants, or plant taxonomy. In animals and some of the microorganisms, final metabolites are generally excreted outside the body, while in plant metabolites are stored inside the plant. While it was thought that some metabolites were specific of some plants, we know today that are widely distributed in the plant kingdom and many constituents of plants such as alkaloids and isoprenoides have been isolated from species, genera, families or specific plant. For example, the "opium" of Papaver somniferum contains twenty alkaloids such as morphine, thebaine, codeine, and narcotine. they are all biosynthesized from precursor 1-bencilisoquinolina by oxidative coupling.

So, alkaloids that have similar structures are characteristic are constituents of this kind of plants and are designated as alkaloids opiates. Similarly, frequently appears in the literature names representing genera and families such as ergot alkaloids, iboga alkaloids, and menispermaceae alkaloids. Our knowledge of the constituent plant has been expanded to a dramatic rate in recent years due to progress in the methods of isolation and microcharacterization. This has led to a new field called "chemotaxonomy" or "chemosystematics", which tries to study the constituents of plants according to their taxonomy. Ultimately, the phytochemical constituents are considered as markers to understand the evolution and classification of plants.

However, the number of compounds known for each plant is still quite limited and, moreover, all plants have not yet studied. Undoubtedly, a meticulous and laborious study from a large amount of plant material, will lead to a clearer idea of its constitution and allow the isolation of products even if they have no known biological activity whatsoever. Still organized knowledge of the constituent plant according to the taxonomy is an area of great interest and importance at the present time.

D. Natural Products classification based on their biogenesis

Although "biogenesis" and "biosynthesis" are terms that are used sometimes indiscriminately, it is customary to use the first term for a hypothesis, and the last for a synthetic route tested experimentally.

The constituents of all plants and animals are biosynthesized in organisms through enzymatic reactions. The most commonly source of carbon used is the glucose, which is photosynthesized in green plants (autotrophic organisms) or obtained from the environment heterotrophic organisms. The relatively recent advances in biochemistry have greatly clarified the interplay between enzymatically catalyzed reactions of the "primary metabolites (such as sugars, amino acids and fatty acids) and biopolymers (such as lipids, proteins and nucleic acids). These metabolites lead to "secondary metabolites," so called because it is obvious his role in the metabolism of many organisms.

When in the years 30 our understanding of the chemistry of natural products had some size, some organic chemicals began to develop routes biogenetic theories of natural products in living organisms on the basis of its structural regularity.

There are at present three known major routes or routes that enable key biosynthesis of the vast majority of different types of natural products known:

- Mevalonic acid route: from it, prenyl units are formed, an after successive links they led to isoprenoids (terpenoids, steroides, carotenoids)
- Shikimic acid route: From it, amino acids are formed and from them, and other aromatic compounds more complex (phenylpropanoids, flavonoids, alkaloids)
- Acetate – Malonate Route (polyketide route): From malonate and acetate are formed polyketides (Ketogenines) and fatty acids are formed.

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Topic 3. Cultivation of MAPS

3.1. Why to cultivate Medicinal and aromatic plant?

All cultures from ancient times to the present day have used medicinal and aromatic plants which are still harvested from the wild. Little by little consumers have increasingly demanded more both quality and supply of MAPS. Nowadays, direct collection from the wild supposed a risk for many MAPs survival in its natural habitats. Therefore, it is recommended to ensure its conservation, a suitable MPAS cultivation and a regulation of its collection from the wild.

The main reasons to cultivate aromatic and medicinal plants are:

Quality tests and products homogenization: purchasers of raw material (dry or fresh material), such as herbal industry or laboratories are more demanding with MAPs quality. If the herb is purchased by herbal industry, homogenization and visual test are required. If material is purchased by laboratory, as well as, it is required homogenization and even active constituent richness and purity in the case of essential oil.

Conservation of local species and its natural habitat: Thyme, rosemary, lavender, labdanum, bearberry, Gentian are collected from the wild. Among of them it is currently selling a no sustainable volume, which is leading to depletion and destruction of their natural habitat. Some of them, such as Gentian (*Gentiana lutea*), Bearberry (*Arctosthaphyllos uva-ursi*), bogbean (*Menyanthes trifoliata*) and Arnica (*Arnica montana*), are in a critical state, so it is necessary to take serious conservation action.

In addition, the implementation of MAPs in agriculture land should be taking into account as a real alternative in land with poor benefits. According to future guidelines for **Common Agriculture Policy (CAP)** which are aimed to reducing surpluses crop production, MAPs cultivation could be an alternative and suitable extensive agriculture. On the other hand, during centuries MAPs have being very well adapted to hard Mediterranean edafo-climate conditions, especially dryness and poor nutritional soil. It is pointed out that many aromatic, medicinal and seasoning plants belong to local native Mediterranean species.

3.2. Characteristic of MAPS cultivation

When it aims to cultivate aromatic plant, it is important to take into account production target, selection of suitable seed, yield and quality. Cultivation cares and managements especially involve irrigation, fertilization and control against weeds, pests and diseases.

In general, producers of medicinal plant are in charge of selection, harvesting, processing and commercialization processes. Therefore, harvesting schedules should be related to industry requirement.

3.2.1 Product quality

Product quality depends on the kind of agriculture:

- Organic agriculture
- Conventional agriculture

Organic agriculture is a production system which avoids or excludes the use of synthetic preparations-artificial fertilizers, pesticides, growth accelerator and fodder additives. The plant receives nutrients by using natural organic or mineral fertilizers and weeds or pests are controlled and prevented by stimulating the population of useful insects.

It is pointed out that the higher quality of this product in organic agriculture involves more dedication than in conventional agriculture; as a result it is necessary more both manual and mechanical workforce. Therefore the final product should be a price higher.

3.2.2. Selection of specie

Selection of specie is undoubtedly linked to the future success of the exploitation. It is necessary not only to take into account climate and soil requirement but also available equipments, workforce and facilities, so as the maximal yield and efficiency will be able to reach.

Therefore it is necessary to find the optimal balance among the following data:

- Market requirement
- Field characteristic/features
- Specie requirement in its cultivation, its processing, available and suited equipment such as farm machinery, facility and workforce.

3.2.3. Market requirement

Industry determines the kind of specie that is admitted. The plant production can lead to pharmacy, herbal industry, cosmetics and perfumery, and finally nutritional industry.

- In pharmaceutical laboratories, the most demanded species are valerian, bearberry, St John's wort, Milk thistle, Opium poppy, Meadow saffron.
- In herbal industries: mint, peppermint, lemon balm, chamomile, lavender, salve, thyme,
- In cosmetics and perfumery: lavender, mint, chamomile, rose, aloe vera, arnica.
- In nutritional or seasoning industry: laurel (bay tree), rosemary, mint, gencian, parsley, sweet basil and juniper.

As soon as, we have been assessed all data and we have chosen species, the next step should be to provide vegetal material and then dealing with: cultivation technical and specific farm machinery and finally with processing of harvested material.

3.2.4. Cultivar field features

3.2.4.1 Water supply

It is especially important to choose the right place for the cultivation of a given culture and to irrigate it properly by not allowing the formation of swamps or stagnant waters. Medicinal plants cannot be cultivated in heavy and water-retaining soils.

According to water supply, we can have different kind of land:

- High water supply: irrigated land (sprinklers) or big volume of rainfall
- Low water supply: dry land (trickle irrigation)

Dry zones are the most suited for the cultivation of Medicinal and aromatic plant. The quality and richness of essential oils is better in dry land than in irrigated land; for instance, lavender, thyme, rosemary and St John’s wort. In addition, we can also have good yield in cumin, fennel, aniseed.

In irrigated land, it can be cultivated more number of species, such as mint, basil, peppermint, valerian and especially when it is necessary the whole plant, either their leaves or its root.

3.2.4.2 Altitude

Average altitude restricts the number of species. Altitude has a double effect on plants: firstly temperature decreased as a rate (dry adiabatic lapse rate or wet adiabatic lapse rate) of around one degree C per 200m of altitude (-1 ºC/200m) and secondly it can affect the active constituents concentration. It has been proved that high altitude increases rancidness of active constituents such as Gentian and also decreases the richness of active constituents in mint and thyme.

Plants which can be adapted to grow in high altitudes are valerian, angelica, mint, sweet balm, St John’s wort, Great burdock, Cone flower.

Low altitude, especially under Mediterranean influence, is very suited for cultivating species such as thyme, salve, lavender and rosemary because it is extracted essential oil with more quality and better yield.

3.2.4.3. Edafo-climate condition

Edafo-climate condition also plays an important role in the election of species.

When choosing the climate one should take into consideration the duration of daylight, the amount of rainfalls and the temperature range. These factors together with the day and night temperature amplitudes directly affect the physiological and biochemical processes in plants, especially the ones which involve enzyme reactions. These factors will inevitably influence their growth and the synthesis of organically active substances.

Medicinal plants require different climatic conditions to grow depending on their natural origin. These conditions need to be identical or at least similar to the conditions of their natural habitats. If one ignores climate, it is quite possible that yields would be very low and the percentage of active substances – much reduced. Most medicinal plants require sunny, aerated places sheltered from strong winds and late winter frosts.

It is also recommended that rooted specie should be cultivated in sandy, deep and light soil; for instance Great burdock, St John’s wort, arnica, Gentian, valerian, dandelion.

3.2.4.4. Field face

It is advisable to choose lands with a south-facing slope and no shaded, better than north facing. South-facing slopes receive the most solar energy, which is maximal when the slope grade equals the sun’s angle from the zenith point. North-facing slopes receive the least energy, especially when the slope grade equals or exceeds the angle of sun rays.

Frost is also a limiting factor for some species, but most of them withstand or tolerate common temperature below zero.

3.3. Cultivation technicques

Cultivation characteristic depends on the water needs of individual medicinal plant species, which can be classified as drought tolerant plant (thyme, rosemary) and demanding water plant (Mint, balm lemon). In addition, cultivation technical also depends on the final product target (leaves, whole plant, dry herb, essences and frozen herb). Therefore water supply, orientation, altitude are limiting factors.

Plants can be cultivated by direct seeding or planting. Seeding reduce plantation cost and space requirement, whereas planting is a successful application for low germination rate in plants, such as Labiatae family, and a way to control weeds as well as. In dry land, planting density is around twelve and fifteen plants per hectare, although in irrigated land it may be twice more. Planting density also depends on plant structure and harvest and processing machinery.

In Fertilization, plants with big biomass are more demanding in nitrogen, but Labiatae family are less demanding and even an nitrogen excess can produce more weakness and less active constituents in plant. Before plantation it is recommended fertilization with manure or mature compost.

Only a little irrigated land is able to provide medicinal plants for household needs, for example in 20 meter square. The plantation season should start from August to November.

3.3.1 Plantation characteristics

After selecting the most suited specie, according to all above mentioned aspects such as climate, soil condition and plant requirement, the following step is planning density plantation and space requirement.

Therefore, the planning should take into account:

- Harvesting and processing machinery
- Plant requirement
- Available workforce during cultivation and following processing
- The main target is maximized: equipment and facilities

Therefore it is recommended to plant species which have different blossoming stage or at least harvest and processing season doesn’t occur at the same time.

Spring is a stressful moment because harvest season is starting for thyme, oregano, Sweet balm, Mint, Save, St John’s worn, basil.

It is also recommended to test and analyse your soil and water not only to know initial field situation and fertility rate, but also to plan better plant requirement and future production.

In plantation establishment, it can be used the next vegetal material:

Seeding: is only suitable for species with a high germination rate. Seeds are collected after summer and then covered with a fine layer of soil. For instance, direct seeding in field for aniseed, calendula, parsley, valerian.

Seedling: comes from bare-root or container stock (in nursery), for instance Mint, Sweet balm, lavender, save, thyme, St John’s wort, rosemary,fennel, ajedrea.

Transplant from wild plant; for instance passion flower, borage, nettle, common mallow.

Coppicing mother plant: young buds are extracted with a little root, for instance Mint.

Sprout propagation: young branch around 30 cm, below a nude. After cutting leaves, sprout is buried around 70 percent. For instance, rosemary, save, etc

Selecting one or another method depends on the kind of cultivation, whether is a conventional or organic agriculture. The latest mentioned, organic agriculture, involves in employing all the preventive methods to control weeds (especially when they compete with our plants). For this reason, it is recommended to use seedling for successful plantation establishment, as well as preparing soil before cultivation.

According to **period of life**, plants can be classified as annuals[1], biennials[2] and perennials[3]. Annual plant can spring from its underground seeds if they are not removed. It is advisable to group species in sector, taking care that each specie have enough space to develop itself and then keeping the soil covered with straw. Previously brush and weeds have been removed.

Another important criterion is the **ecological behaviour** of the species. In addition, farmer should take into account seed viability, germination capacity and species hybridization to select one or another method to propagate material vegetal, such as seeding or seedling.

Price of vegetal material affects directly to cost of plantation establishment, for instance seeds can cost from 15 to 80 euros per kilogramme and prices of a plant are around five cents of euros per unit.

Plantation density depends on the plant specie and field conditions. It is used an initial stocking rate (density) from 4 to 7 kg/ha for seeding. The plantation density is linked to length of plant and cultivation conditions.

Irrigation

- large size and shape plant 35,000 pl /ha
- small size and shape plant 50,000 pl /ha

Dry land

- large size and shape plant 15,000 pl/ha
- small size and shape plant 25,000 pl/ha

Plantation can be established by using a cultivator.

3.3.2 Planting design

Planting density is usually in simple or multiple rows, according to size of plants and machinery.

Density (plants per hectare) depends on plant specie and supply of water, either dry land or irrigated land.

It can be used a density of 14,000 or 15,000 plants of lavenders and salvia per hectare.

It can be used a density of 45,000 pl/ha for species such as thymes or ajedrea in irrigated land.

Plantation can be programmed in spring or in autumn according to the kind of plantation (bare-root or container stock), conventional or organic agriculture.

[1] Annuals complete their life cycle in one year, Start them from seed.

[2] Biennials: complete their life cycle in two year, so they live for two season and blooming the second season only.

[3] Perennials: live more than one season.

3.3.3. Soil preparation

- Deep ripping
- Organic fertilizing (20 or 30 t /ha of manure)
- Ploughing
- Disking or rolling

It is important to reduce as much as possible weed seed bank, with deep ripping and herbicides.

Plantation costs depend on all the aspects above mentioned such as specie, cultivation, seed or seedling, irrigation system, employment of plastic. Cost plantation should share out between years of cultivation for 3 to 8.

3.3.4. Cultivation task

They are divided into:

- Weed control/blind cultivation
- Fertilization

Weeds can be removed mechanically in row cultivation by using rod weeder, disking whereas weeds should be removed by hand pulling, hoeing within the row, especially if it is organic agriculture.

If it is conventional agriculture it can be applied some authorized standard herbicides, carrying out the stipulated dose and frequency.

During the first year of cultivation and until rows are not closed, weed control is necessary.

During the second year of cultivation, weeds control may reduce until third part.

It is used straw cover or bark for Reducing weeds control

MAPs are not very nutrients and demanding but it is very important to carry out a fertilizing program. A peak in production plant has been illustrated in Sweet balm and Mint field, after winter fertilization.

Fertilization is very helpful after plant coppicing, because plant springs stronger and healthier.

Yield crop is increasing for any specie under irrigated condition, although it should be taken into account that some species don’t tolerate excess of moisture in soil or damp condition, for instance Salve.

It may be difficult to cultivate Sweet balm, mint and borage without irrigation. The most recommended is localized irrigation by Dripper, sprayer or micro-sprinkler because a small discharge of water is applied for each plant. However, it is the most demanding in management.

3.3.5. Cultivation maintenance

Maintenance is carrying out with fertilizing and weed control. According to the kind of cultivation, organic or conventional, maintenance would be different.

Weed control can be done between rows or in rows plantation. In conventional agriculture, it can be applied suited herbicide for MAPs. In organic agriculture, weeds control can be done in row cultivation by rod weeder and by hand pulling in plant rows. During the first year, this task requires a lot of time, but the following years are less as a result of plant shading in soil.

Fertilization is also a task that needs a special attention. In spite of being low nutrient demanding plant, it is recommended to apply nutrients (mineralise) that have been removed during the crop, to avoid soil depletion.

3.3.6. Cycle and cultivation timetable

- Selection of plant Spring
- Management of nursery Autumn
- Soil preparation Autumn
- Selection of seed Autumn
- Sprout Winter
- Plantation Winter
- Fertilization Spring
- Maintenance task Spring
- Harvest Summer
- Distillation Summer
- Package Summer
- Storage autumn

3.4. References

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TOPIC 4. ACTIVE CONSTITUENTS IN AROMATIC AND MEDICINAL PLANTS

KEY IDEAS

Pharmacological activity in plant-based drugs is centred on the presence of chemical compounds which we call active components

The main chemical groups are heterosides, polyphenols, terpenoids, and alkaloids. These in turn are sub-divided into other groups according to their chemical structure

4.1. Introduction and definition

Active constituents are substances which are found in different parts and organs of plants, and which change or modify the functions of human and animal organs and systems. Scientific research has allowed us to discover a wide range of active constituents, of which the most important –as far as health is concerned- are essential oils, alkaloids, glycosides or heterosides, mucilage and gums, and tannins. Other relevant active constituents in plants, such as vitamins, minerals, amino acids, carbohydrates and fibres, some sugars, organic acids, lipids, and antibiotics, are called essential nutrients

Active constituents are classified in groups according to their chemical structure:

Products resulting from primary metabolism (chemical processes which are directly linked to survival, growth and reproduction): glucides, lipids, amino acid derivations.

Products derived from secondary metabolism (these are not essential for the metabolism, but are synthesised as defences, adaptation, etc…). These are the most important active constituents, which will be introduced through this course.

***Heterosides**. Anthraquinones, cardiac glycosides, cyanogenics, coumarins, phenols, flavonics, ranunculosides, saponosides, sulphurides*

***Polyphenoles**. Phenolic acids, cumarins, flavonoids, lignans, tannins, quinones*

***Terpenoids**. Essential oils, iridoids, lactones, diterpones, saponins.*

Alkaloids.

For each of these groups we shall look at basic chemical structure, distribution in the plant world, and industrial uses.

Although heterosides belong to several groups, we shall group them in their own, separate category. Given their importance, we shall study essential oils as a separate topic.

4.2. Heterosides

Glycosides or heterosides are compounds which are made up of two parts: one is a sugar moiety (e.g. glucose) and the other a non-sugar moiety or aglycone. The bond between the two parts (moieties) involve a hydroxyl group, which can form an O-glycoside, (C-glycosides), (N-glycoside) or (S-glycoside).

Glycosides are broken down upon hydrolises with enzymes or acids, releasing the aglycone, the truly active constituent. This break is catalysed by ferments contained in the plant itself. They are classified according to the nature of the non-sugar or aglycone as we can see in the table below. The names end in –oside, although some prefer to use the traditional names ending –ine (e.g. digoxin).

They make up the active constituents of many plants, and their pharmacological activity is basically due to the non-sugar part.

Type	**Properties**	**Species**
Anthraquinones	Purgatives	Holy peel, Sen
Cardiac glycoside	Diuretic. Heart tonic	Digital
Cyanogenics	Anaesthetics. Anti-spasmodic. Hypo-tenser.	Cherry tree. Almond tree.
Coumarine	Antibacterial. Anti-coagulant. Protection from the sun.	Oats.
Phenol	Anti-pyretic and febrifugues.	Pear tree, willow.
Flavonoids	Weak capillaries. Vitamin C.	Sunflower, rude.
Ranunculosides	Irritation of the skin.	Berry plants.
Saponins	Hemolytic anemia. Emolients. Dermatitis.	Fir tree. Maize. Liquorice. Saponaria. Violet.
Sulphurates	Antibiotics.	Garlic. Onion. Radish.

The most important groups are the Anthraquinonics, Cyanogenics, cardiotonics, and cumarinics. Also the phenolics, because in this group we find salicin, the fore-runner of salicylic acetyl acid or aspirin.

c. Anthraquinonic Heterosides.

Anthraquinones are yellow-brown pigments, most commonly occurring as O-glycosides or C-glycosides. Their aglycone portions consit of two or more phenols linked by a quinine ring (anthracene derivative). They are used as laxatives and purgatives. They can be found in the following plants:

- *Aloes (aloe juice, especially liliacs).*
- *Rhubarb (rhizomes from Rheum especially F .Polygonaciae).*
- *Senna (leaves and pods of Cassia, especially F. Caesalpinaceae leguminous plants).*
- *Buckthorns (bark of the Rhamnus catharticus and R.frangula. F. Rhamnaceae).*
- *Cascara sagrada (bark of the Rhamnus pursiana. F. Rhamnaceae).*

b. Cardiac glycosides /Heterosides

This group contains a number of active constituents which act directly on the cardiac muscle, and thus exert therapeutic influence on congestive cardiac insufficiency, or on cardiac arrhythmia. However, given the gravity of this affliction, and also the special characteristics of these active constituents, whose therapeutic margin is extremely narrow, many of the drugs which contain them are not now used directly as phyto therapeutic products, even though their active constituents in isolation are still indispensable for therapy.

Some of the plants which contain this type of substance are:

- *Digitalis purpurea and D.lanata (F. Scrophulariaceae) whose pharmacological effects were described by Whitering in the 18th Century. Cardiac heterosides are also known as digoxin, which is actually a derivative of lantoside C, one of the glycoside in Digitalis*

- *Adonis vernalis (F. Ranunculae).*
- *Urginea maritima also known as escila (F. Liliaceae).*
- *Nerium oleander (F. Apocynaceae).*
- *Strophanthus (F. Apocynaceae). Its active principle, ouabaine, is used as a tool for pharmacological research.*

They share a common characteristic by acting specifically on the heart; no synthetic substitute has been currently found for some of them. Cardiotonic based on drugs are highly toxic (10 g of dried leaf or 40 g of fresh leaf are lethal). Strophants were used as poison for both hunting and warfare.

- *Digital: dried leaf of Digitalis purpurea*
- *Strophant: seeds of two different types of the species, Strophantus gratus and Strophantus kombe (Apocinaceae).*
- *Scila: dried scales of bulbs of Urginea maritime or Scilla maritime (Liliaceae).*

c. Cyanogenic Heterosides

Some plants give off hydrocyanic acid (a process known as cyanogenesis). A number of amino acids are known precursors of these glycosides (amydalin and prunasin).They have caused lethal poisoning.

Properties. The only drug which is used for fitotherapy because it contains these substances is the wild cherry laurel (*Prunus serotina)*, which contains prunasin. It is used as distilled water, as an anti-spasmodic, to stimulate breathing, and as an aromatic.

They are found mainly in

- *Rosaceae.*
- *Fabaceae (leguminous plants)*
- *Euforbiaceae.*
- *Poaceae less common gramineae.*

Organs include:

Roots: manioc (Manihot utilissimo,) belonging to Euforbiaceae, gives starch and tapioca.

Bark: the wild cherry laurel.

Leaves: elder (Sambucus nigra).

Seeds: bitter almonds (Prunus dulcis) and the kernel of apricot, peaches and plums. The sweet variety is edible, the bitter variety contains amygdalin, a cyanogenic heteroside. The bitter variety also differ in taste and because when crumbled and mixed with water, they give off a smell like benzaldehyde. If eaten they are toxic because they contain cyanide ions. 20-50 almonds are enough to kill an adult. They are used to make oil for use in cosmetics.

d. Coumarinic Heterosides

Coumarin is an aromatic. These plants contain vitamins, diminish capillary permeability, and increase the resistance of capillary walls (they protect us from capillary weakness and act as a tonic for the veins). Some have sedative properties, such as angelican. They may have hypnotic properties.

Gentian contains amarogentin. Because they are bitter, they stimulate appetite and digestion, and excite the taste-buds of the tongue. As a reflex reaction, they act on the stomach, increasing motility and helping to increase secretion. They should not be used when lactating as the active constituents pass into mother's milk.

The bark of the Indian chestnut also contains them. Both the bark and the seeds act similarly, but the active constituents are different. Only the bark contains coumarins.

Ash leaves *Fraxinus excelsior* (fraxina). They have diuretic, anti-rheumatic, and anti-arthritic properties. They are used to treat the kidneys and the bladder, or in cases of urine retention.

4.3. *Polyphenoles*

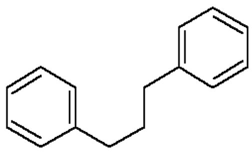
These are substances with a benzene nucleus supporting a hydroxile group. They usually bond with sugars to form heterosides, but they may be found separate. They range from very simple substances to very complex ones such as lignines and tannins. The main groups in this category are phenolic acids or phenols, cumarines, flavonoids, lignanes, tannins, and quinines.

a. Phenolic acids.

These are aril-carboxilics, and contain one or more OH groups in the aril. They have various pharmacological properties and uses: anti-oxidant, analgesics, choleretic… Eugenol, for example, is an antiseptic and also a local anaesthetic used in dentistry. Unbonded phenols provide important constituents of essences, such as timol and its isomer, carvacrol (essence of thyme). Many phenols are found in an oxidized ether state in essences. These include estragol, miristicine, apiol, and anetol.

b. Flavonoids

Flavonoids are yellow pigments derived from phenil-benzo γ pirona or phenil cromome. They are frequently found in the vegetable kingdom, usually in the form of heterosides. Their molecular structure is of the type C6-C3-C6. They are a very varied family of compounds, although all the final products are typically polyphenolic and soluble in water. There are 6 main classes, chalcons, flavones, flavonols, anthocyanidins, and condensed tannins, as well as two others, xantones, and aurones. The figure shows the basic structure of flavonoids.



These compounds are important for plants, because they are responsible for the colouration of many flowers, fruits and leaves, thus helping pollination by attracting insects. They also take an active part in the plant's life, acting to protect it from the harmful effects of UV radiation, and acting as an efficient anti-oxidant.

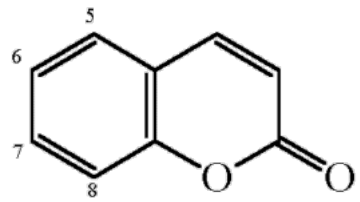
Of all these, the most interesting in terms of pharmacology fall within the group of flavonoids: flavones, flavonols, and flavones, and their correspondent heterosides and anthocyanosides. Many of them act on the vascular system, for example rutoside or citroflavanoids, which are thus named because they have been isolated in species belonging to the citrus family.

They act on the vascular system by dilating blood vessels. Furthermore, they are able to trap free radicals. Among the medicinal plants whose activity is related to flavonoid content are the passion flower (*Passiflora incarnate)* with approximately 2% of flavonoids; roman camomile (*Chamaemelum glabra*) and aquilea (*Achillea millefolium*); liquorice (*Glycyrrhiza glabra*) and gingko (*Ginkgo biloba)*; the Marian thistle (*Sylibum marianum*) and the white thorn (*Crataegus*). Isoflavones have fitoestrogenic properties so they are used treat menopausal symptoms (e.g. soya).

We must make special mention within the flavonoid group, of the antocyanoside group, the red and blue pigments in flowers, which have special characteristics and are highly soluble in water. For example, the cranberry *Vaccinium mirtyllus* (Ericaceas), and the blackcurrant *Ribes nigrum* (Saxifragaceas).

c. Coumarins

These are benzo - α pyrones. The name cumarines refers to large group of phenolic active constituents found in medicinal plants, which share a chemical structure 2H-1-benzopiran-2-ona known as cumarin. Substitutes of different chemical nature follow this structure which gives us different types of cumarins: simple and complex.



Practically all cumarins, with the exception of cumarin itself, have a hydroxilic substitute (OH) at number 7, be it free, as in umbelipherone or in combination (methyle, sugars, etc…).

As a group, it's not particularly interesting in pharmacological terms. Nevertheless, we must mention its effects on the vascular system (both on arteries and veins) and its use as a treatment for certain ailments of the skin such as psoriasis, due to its photosensitizing properties. Some of them are:

Cumarin, found in extracts of the melilotus (Melilotus oficinalis), which is used to treat veno-lymphatic insufficiency.

Esculoside, found in Indian chestnuts (Aesculus hippocastanum). It is both a tonic for the veins and a protector of the cell wall.

Visnadine is a dilator of the blood vessels found in the fruit of the visnaga, Amni visnaga.

Dicumarol is an anti-coagulant which forms in melilotuses when conditions for conservation are bad.

Furanocumarins are photosensitizing and are used to treat psoriasis. Sometimes they are used in sun creams as they enhance melanin production (photodynamic), for example, essence of bergamot (*Citrus bergamia)*.

d. Lignanes

These are molecules whose structure is the union of two units of phenile propane (C6-C3). They are very common in the plant world. Podophilotoxin, for example, is found in the podophylle rizome *(Podofilum peltatum)* and is the fore-runner of two substances (etoposide and teniposide) used for anti-tumor therapy. Silimarin too, a protector of the liver obtained from the marian thistle (*Sylibum marianum)*.

e. Tannins

These are complex substances which we cannot classify under one single chemical structure. They are non nitrogenised polyphenolic hydro-soluble substances of vegetable origin, having a molecular weight between 500-3000. Apart from reacting in the classic phenol way, they precipitate gelatine, alkaloid salts, and heavy metals. They can be both hydrolizable and condensed.

Tannin is found mainly in the roots, bark, and sometimes in the leaves of plants. These compounds have antibacterial, astringent, and antiseptic properties. They are found especially in the Ericaciae, Legume, Rosaceae, and Salicaceae families.

Historically, they are substances used for tanning leather as they form hydrogen bridges with the fibres of collagen in the skin. External pharmacological properties are astringent, constriction of blood vessels (for treating haemorrhages), and cicatricizing (burns). Internal properties: anti diarrhea, and, as they precipitate alkaloids, antidote to intoxication.

f. Quinones

These are aromatic dicetones which come from the oxidising of phenols. There are several types:

Para-benzoquinones: benzene derivates. Highly active (anti-microbacterial, antifungal).

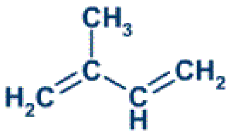
Naphthoquinones: naphthalene derivates. Anti-bacterial and antifungal. Junglone, from the walnut tree (*Juglans regia)*. Lawsona, from henna *(Lawsonia inermis)* used as a dye and as shampoo. Plumbagona, from the drosera (*Drosera rotundifolia)*, which is anti-expectorant. Vitamin K1 is found in alfalfa (*Medicago sativa*).

Anthracicflaxnes: naphtacene derivates. They are the nucleus of important antibiotics such as daunomicine and doxorubicine, as well as tetraciclines.

Anthraquinones and fenanthraquinones: antrhracene and fenantrene derivates, they act as laxatives and purgatives, when in heteroside form (see anthraquinonic heterosides).

4.4. Terpenoids

Terpenoids are made up of a whole number of isoprene (C5) units. Depending on this number, they are classified as:



Isoprene unit (C5)

- *Monoterpenes (2 units of isoprene = C10)*
- *Sesquiterpenes (3 units of isoprene=C15)*
- *Diterprenes (C20)*
- *Triterpenes (C30)*
- *Carotenes (C40)*
- *Polyterpenes (Cn)*

They include essential oils as we shall see in the next lesson (lesson 7), iridoids, lactones, sesquiterpenics, saponins, and cardiotonic heterosides (see above).

a. Iridoids

These are monoterpenic compounds and the name comes from a type of Australian ant *(Iridomirmex*) whence iridodial, the simplest compound in this group, was first isolated. They are usually found in plants in the form of heterosides, in the Gencianaciae and Valerianaciae families.

They are part of the active principle of some plants, such as the valepotriates of the valerian root (*Valeriana officinalis*), harpagosides of the harpagophite (*Harpagophytum procumbens)*, oleuropeoside in olive leafs *(Olea europea*), and genciopicroside in the roots of the genciana (*Gentiana lutea*).

b. Sesquiterpenic lactones

These are found in abundance in the Composite, Lauraceae and Magnoliaceae families, and are responsible for the bitter taste of many drugs; the holy thistle (*Cnicus benedictus)*, absinthe

(Artemisia absinthium), or dandelions (*Taraxacum officinale*). They are antibacterial and antifungal. Some produce dermatitis as they cause the formation of allergens.

c. Saponins

Or saponosides, from the Latin *sapo* = soap. They are substances which produce foam in water solutions, and are naturally tenso-active. Many have haemolytic properties (disintegration of erithrocites), and are highly toxic when injected into the blood. Their toxicity is less when taken orally. They are toxic to cold-blooded animals.

There are triterpenic and steroidal types. The former are found in the seed of the Indian chestnut, in liquorice *(Glycyrrhiza glabra*), the Asian centella (*Centella asiatica*), and in ginseng (*Panax ginseng*). The latter in Ruscus (*Ruscus aculeatus*), agave *(Agave sisalana*), and in dioscorea (*Dioscorea)*.

4.5. Alkaloids

a. General characteristics

This is a group of natural products of particular interest to pharmacology. Within this group we can find substances which are toxic even in small doses. The first alkaloid to be isolated was morphine (Sertüner 1805). The name 'alkaloids' was hit upon in 1819, because of their basic nature. Although they were first isolated in the 19^{th} century, their complexity meant that their structure was not established until later.

This was the case with strychnine (vomic nut seed). It was isolated in 1819. In 1870 its structure was established approximately. In 1889 it was produced synthetically. In 1946 its structure was finally determined.

Our knowledge of natural alkaloids has progressed thanks to the development of new techniques of separation and identification. In 1930, more than 300 were isolated and the structure of 200 was established. In 1950 more than 1,000 were isolated, in 1973, between 5 and 6,000.

They are sensitive to light and to heat and can be stabilized with inorganic acids. In nature, they are found in the form of salts, although they can also be found free. In plants, they were thought to be products obtained by extraction and not particularly soluble in typical extraction solvents because of their polarity. They undergo isomerisation (lysergic and isolysergic acid) and racemization (hiosciamin and atropine).

There are several types, depending on the molecule from which they derive (tropane, quinoleine or isoquinoleine).

b. Alkaloid drugs derived from tropane:

These are parasympathemimetic substances or antagonists of acetyl coline (synaptic transmitters). They have the following effects on the central nervous system:

In large doses, vertigo, delirium, hallucinations

In very large doses, death by respiratory paralysis

The drugs potency is Hiosciamine>Atopine>Escopolamine

Some examples of these drugs are:

Cocaine. A powerful local anaesthetic. Sympaticomimetic (it lengthens the effects of anaesthesia by constricting blood vessels). It excites the central nervous system. In extreme doses, it causes death by respiratory paralysis. Leaves of the *Erythroxylum coca* (Eritroxilaceae).

Lysergic acid. This drug is obtained from a fungus, *Claviceps purpurea,* which grows around the ovary of rye.

Caffeine. This drug is the almond or grain of the Caffea seed. The Coffee tree originated in Africa.

Teine. The drug is the young leaves of the *Camelia thea*. They are typical of Southeast Asia. Nowadays it comes from plants grown in India, China and Sri Lanka.

Atropine. In leaves and flowers of *Atropa belladonna* (Solanaciae)

Daturin. In stramonium leaves *Datura stramonium* (Solanaciae)

Hiosciamin. In belenium leaves. *Hyoscyamus niger* (Solanaciae). It is used to treat Parkinson's disease.

c. **Drugs with alkaloids derived from quinoleine (Quinine)**.

The drug is the dried bark of the trunk, branches and roots of the *Cinchona* (Rubiaceae). The most important species are:

- *Cinchona succiruba (red quine)*
- *Cinchona leogeriana (leogerine quine)*
- *Cinchona Calisaya (yellow quine)*
- *Cinchona Hybrida*
- *Cinchona robusta*

Their main effect is anti-malarial due to the quinine, which is toxic to the protozoa and paramecia especially for the plasmodium genre which produce malaria (*Plasmodium vivax, Plasmodium malariae*). It acts against asexual or schizontic forms.

d. Drugs with alkaloids derived from isoquinolein:

Opium. This is dried latex obtained from incising unripe pods of the different varieties of *Papaver somniferum* (paveracea). We obtain morphine from it. Even in low doses it is analgesic, and decreases the perception of pain; particularly useful against persistent, acute pains. Its properties are:

- Sedative to the central nervous system, leading to an unpleasant drowsiness.
- It produces a sense of wellbeing and euphoria. Repeated administration causes addiction, tolerance, and physical and psychological dependence.
- It causes respiratory depression and bradicardia.
- In the intestines it is an emetic and diminishes peristalsis.
- Overdoses cause death by cardiac and respiratory arrest.

4.6. Other active Constituents

Mucilage and gums

These are heterogeneous polysaccharides, formed by different sugars. In general, they contain uronic acids. They are characterised by the formation of viscous colloidal dissolutions, in water, jellies. The difference between mucilage and gums is difficult to ascertain and normally, everything is treated as gum. Nowadays, the difference is thought to be in the fact that mucilage are normal constituents of plants, whereas gums are products which only appear under certain circumstances, via the destruction of cellular membranes and exudation. The most important are in the leguminous plant family.

Properties

- They swell and form gels in water
- They dissolve forming viscous solutions
- They easily lose some monosaccharides in hydrolysis, but a more resistant nucleus which needs more energetic enzymes always remains.

Uses

Emollients and demulcents: anti-inflammatory. They can be used externally (haematomas), as cataplasms (respiratory). Internal uses: anti-inflammatory treatment of the respiratory system, mechanical laxatives. Laxative effects are due to their capacity for water retention, which makes them lubricants, thus aiding passage through the intestine. Because they retain water, they swell and press against the intestine wall, thus increasing peristalsis. They protect gastric mucus ant act against diarrhea, especially those caused by bacterial toxins.

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Topic 5. Chemical analysis of aromatic and medicinal plants.

5.1 **Introduction**
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5.1 Introduction

The chemical analysis of aromatic and medicinal plants consists in determining the chemical structure and composition of certain parts of the plant. Nowadays, it is regarded as an indispensable reference for establishing their quality for use in fitotherapic medicines or pharmaceutical specialities.

At the same time, it is a useful tool for establishing the extent of absorption of toxic substances by plants, such as the remains of pesticides, and the possible effects of atmospheric, soil, or water pollution. It enables us to chemically identify species and chemotypes in plant taxonomy.

The process for obtaining and analysing extracts of medicinal plants consists of these stages:

- Obtaining a sample from the raw material. The sample we analyse may be a whole plant, a chopped up or pulverised plant, essential oils, or extracts.
- Establishing the vegetable matter contained in water, ash, dry residual material, etc…
- Obtaining and analysing volatile parts (essential oils)
- Obtaining and analysing non-volatile parts (nutrients, minerals, extracts<9
- Quantitative and qualitative physical and chemical analysis
- Expressing results

Our end goal is to establish:

- Identification of the sample
- Content in water
- Content in minerals or ash
- Identification and quantification of active principles
- Calculate performance of oils and extracts
- Establish physical characteristics (specific weight, repart index, rotational power, and solubility in ethanol) and chemical characteristics (acid, ester, and saponification indices) of the constituents analysed.

This lesson refers to the methods described in the Pharmacopoeia. Law 25/90 on medicaments defines the Royal Spanish Pharmacopoeia (RFE) as “the code which must be respected to ensure uniformity of the nature, quality, composition, and richness of medical substances and excipients”.

The Pharmacopoeia includes monographs on different medicinal species and the minimum criteria to be observed regarding:

- Characteristics of the medicinal substance
- Excipients
- Methods for testing and analysing
- Procedures for preparing, sterilizing, conserving and equipment

The RFE is made up of:

- Specifically Spanish monographs
- Monographs from the European Pharmacopoeia (FE)

The RFE is directed, basically, towards the pharmaceutical industry.

5.2 Obtaining and preparing samples

Samples of vegetable matter are collected in the season chosen, before, during, or after flowering. A complete sample is obtained, leaves, flowers, stalks, and (if we wish to study active principles contained in them) roots.

They are left to dry in air until they have a constant weight, and leaves, flowers and stalks are separated and weighed separately. If necessary, the plants are chopped up in a blender, although this can also be done by hand, breaking the plant into small pieces.

When we analyse vegetable matter with a view to using it in pharmacology, quality control of samples is very important, and we must follow the guidelines established by the Pharmacopoeia, or those of the World Health Organisation (WHO, 1998), also bearing certain parameters in mind; for example, the degree of division the vegetable matter presents, the thickness of the same, the number of containers… And also we must establish measurements from a sample which is representative of the whole.

Essential oils make up the volatile part of active principles contained in a plant, and are therefore obtained through techniques of distillation, where the active principles are volatilised by heating, are condensed by cold, and are then collected (although we have seen that other techniques are sometimes used, like squeezing o *enfleurage*).

Extracts are the non-volatile part of active principles, i.e. those which cannot be volatilised or which are unstable depending on temperature. These cannot be obtained by distillation, but are obtained by means of various extraction techniques which we see later.

In general, the volatile part or essential oil is analysed afterwards using GC (or GC-MS), as this technique is valid for volatilizable compounds, whereas the extracts or the non-volatile part is analysed using HPLC, as this technique is valid for non-volatilizable or termolabile substances.

5.3. Methods for obtaining essential oils: distillation.

Essential oils make up the volatile part of the study of aromatic and medicinal plants. They are composed of terpens and derivates, benzene derivates, and others. They are analysed using gas chromatography GC and mass spectrometry if necessary, after extraction via distillation by steaming at atmospheric pressure.

Distillation consists in separating constituents of a sample depending on the different pressure of the steam and boiling point.

The boiling point is the temperature at which, at a certain pressure, a liquid becomes a steam, or the temperature at which the pressure of a liquid is equivalent to that of the gas around it.

When distillation is carried out at atmospheric pressure, it is the equivalent of a column of 760 mm Hg. A reduction in pressure also reduces the boiling point, while an increase in pressure increases it.

A mixture of constituents has not got a boiling point, but a range. Different essential oils have a wide variety of compositions and boiling points, and distillation is carried out depending on them. Different oils have different boiling points, so their distillation takes place at a range of temperatures, which varies, usually between 150-300 degrees.

When distillation separates constituents giving rise to two non-miscible phases, it is known as hydro-distillation, and is carried out in a glass distiller if the sample weighs less than 1 kg, and in a stainless steel dish if it is heavier.

First of all, we must prepare the plant so that the oils come out of the glands which contain them; to this effect they are ground, depending on the type of sample (leaves, flowers, and non-fibrous parts or fruits and seeds).

The sample is placed on the grill of the dish and steam is passed through it. This drags out the oils, which condense in the condenser. Hydro-distillation has the effect of diffusing the oils from the membranes (Hydro-diffusion), hydrolysing certain constituents, and decomposing others due to heat. The three phenomena occur simultaneously, and affect one another.

Hydro-diffusion: only a small part of the oils is present in the surface of plants and available for steaming. The remainder reaches the surface by diffusion through the plant tissues, either freely or by osmosis through permeable membranes for all or one of the constituents. During distillation, the steam does not usually penetrate membranes, so the process depends on osmosis. Conditions for this are good because the temperature and movement of the water speed up the force of diffusion.

Heat: the temperature is at a minimum at the beginning of distillation, and the constituents with the lowest boiling point are steamed. Temperature increases until it reaches that of steam saturation at a given pressure. For a better quality of oils, temperature should be kept as low as possible or the minimum time possible at high temperature.

Hydrolysis: this is a chemical reaction between water and the components of the plant, and of the oils, usually esters. It tends to produce the corresponding acids and alcohols. The amount of water used and the amount of time water and oils are in contact are important.

The principles of distillation are to keep temperature as low as possible without forgetting that the degree of production depends on temperature. We should use the minimum of water or steam possible in contact with the plant, while at the same time aiding diffusion. We should be careful when grinding and packing samples but not too much so.

The advantage of this method of extraction is the low original investment needed to acquire the equipment and accessories. It is a simple, versatile, flexible process, which enables us to work with large quantities of prime matter in each cycle, even without treating these in advance. The time of extraction does not change, but the yield does.

The drawbacks we find are that thermal degradation occurs in the essential oils obtained. I.e., unsought for chemical changes occur, such as oxidisation, hydrolysis, and olygomerysation, and also that operating costs per load of prime matter high, because of the energy needed to produce steam.

5.4**. Methods for obtaining vegetable extracts. Extraction.**

Among the processes of extraction for different fito-chemicals, essential oils, etc..., new extraction technologies such as the extraction of super-critical fluids stand out. However, other, traditional processes of extraction are still sometimes used, such as steam distillation, extraction by solution, and extraction by centrifugation.

a. SFE, supercritical fluids

If we want to extract caffeine from coffee, obtain cholesterol-free foods, or purify natural anti-oxidants using aromatic plants, these processes of extraction can be achieved using super-critical fluids.

A super-critical fluid is a substance, mixture, or element, which under certain operative conditions of pressure and temperature, and thanks to mechanical operations, is above its critical point but below the pressure needed to condense it into a solid.

Extraction via super-critical fluids is better for the environment than conventional methods of extraction, because it uses gases such as CO 2 at high pressure, in a liquid or super-critical state, instead of chlorinated solvents which produce toxic waste.

CO2 is what we call an ecological solvent (normally referred to as a green solvent). It is not toxic, it does not pollute, it is not inflammable, it is economic, easily recycled, and therefore, is not an environmental problem in terms of waste management.

The following aspects super-critical fluids stand out:

- They are powerful solvents and have a great capacity of penetration in solids, which allows a rapid and almost complete exhaustion of extractable solids.
- They can easily be completely separated from extracts, simply by modifying pressure or temperature, up to the point, if necessary, that the fluid becomes a gas.

The main drawback is the time of extraction, which is usually long. In fact, in some cases, it can take as much as 24 hours. With normal fluids, extraction can be speeded up by mechanical shaking, but this presents problems when using super-critical fluids, which limits industrial use.

In Spain, a team of researchers at the CSIC, the Polytechnic University of Valencia (UPV), and the AINA technological centre, have investigated and experimented applying high frequency ultrasound to speed up the process of extraction with super-critical fluids. The process is already in use for the extraction of oils from whole and ground natural almonds at different particle sizes.

b. Extraction by solution.

This requires a greater investment than extraction by steam distillation, but results in a yield which is almost double compared with previously mentioned processes. Furthermore, “practically all” the compounds found in the vegetable sample are obtained: volatiles, fats, waxes, pigments, etc…

On the other hand, it requires vacuum equipment to obtain absolute oils, meaning high operational costs compared with extraction via distillation or SFE. And specially, because we have to use organic solvents such as alcohols, hydrocarbonss, ethers, etc…

If the product or essence is to be used for human hygiene, it is also necessary to determine additional stages of purification. This restriction has meant that new solutions have had to be found, and that recovery has had to be optimised, and this too has increased cost and usage.

To this end, extraction is done using organic solvents, which penetrate vegetable matter and dissolve substances, which evaporate and condense at low temperature.

Afterwards, the solvent is eliminated leaving the part we require. When we choose a solvent, we try to find one that dissolves all the active principles quickly, but also the minimum amount of inert matter; it should have a low and uniform boiling point, so that it can be eliminated quickly, while also preventing losses due to evaporation; it should be non-soluble in water and chemically inert to prevent reaction with the components of the oils; also cheap and not inflammable.

This ideal solvent does not exist, so petroleum ether, which has a boiling point of 30-70 degrees, evaporates easily and is inflammable, benzene, which also dissolves waxes and pigments, or alcohol, which is soluble in water, are the most commonly used.

Extraction may be solid-liquid or liquid-liquid depending on the state of the sample.

- Solid-liquid extraction

When a sample is solid, we pulverize it and then extract the analytes using a solvent in which the former are highly soluble, and which distinguishes them from the substances present in the sample, which should be highly insoluble in the solvent.

This process is usually done by shaking, temperature, or ultrasound, to ensure maximum efficiency. They are usually centrifuged after extraction to eliminate any remaining solids.

- Liquid-liquid extraction

This process is the extraction of analytes from a liquid sample by means of a solvent which is immiscible in it, for example an aqueous phase with an organic immiscible solvent.

pH is essential for a good yield.

c. Extraction by centrifugation.

Extracts and oils obtained using this process, have superior aromatic qualities than those obtained using steam distillation.

As this is not a thermal process, properties are more stable, due to the natural anti-oxidants present. Even so, internal friction of the prime matter causes an uncontrollable increase in temperature which may mean a thermal degradation and a darkening of the extract.

This change requires additional, very expensive, purification equipment, which raises the final cost of the product.

d. Extraction in a solid phase.

We use columns or cartridges capable of retaining the analyte, which is later extracted using a small volume of solvent.

5.5. Morphological, anatomical, and organoleptic tests.

These tests serve to confirm the identity of the plant or drug, give us an idea about their conservation, and detect possible adulterations and falsifications.

A. Organoleptic analysis.

Organoleptic indicators include smell, colour, taste and texture.

Smell. Aromatic, garlicky, camphorated, nauseous, unpleasant, spicy, etc… Many plants and drugs have characteristic smells, e.g. mint, aniseed, cinnamon…

Colour. Uniform or not. When the drug is in powdered form, colour can give us an idea of the part of the plant we have before us. Green, for example, indicates that the drug comes from the leaves or aerated parts; brown from bark, stalks, or roots; white from rubbers or starches.

Taste. Sweet, bitter, astringent, acid, salty, tart, nauseous, aromatic.

B. Macroscopic analysis.

Macroscopic characteristics are observed with the naked eye or using a magnifying glass. We observe such characteristics as shape, size, hairiness, variegation, surface, fracture, section, thickness, and hardness of the whole plant or of parts of it.

- Stalks: type, section, leaf distribution.
- Leaves: form, variegation, hairs, texture.
- Inflorescences: Flower distribution, bractea.
- Flowers: calyx, corolla, stamens, carpels.
- Fruits: type, shape, and size.
- Seeds: size, colour, shape.
- Bark: colour, striations, wrinkles.
- Trunk: growth areas, vessels, medullar radia.
- Underground organs: shape, appearance, consistency.

Careful observation of the morphological characteristics of each organ allows us to identify the majority of drugs correctly.

C. Microscopic analysis.

Microscopic characteristics and histological cross-sections are also important. We use a microscope to observe cellular elements such as hairs, vessels, esclereids, stoma, and acellulars like crystals and grains of starch. We can thus establish the nature of the drugs when macroscopic analysis is insufficient. We also use this process to eliminate the possibility of adulteration.

Histological cross-sections. These are not always possible, only in whole drugs or fragments, not in powders. We can observe cellular content and structure.

Powdered drugs. Organoleptic and macroscopic characteristics are not enough for identification, so a microscopic examination is needed. We observe cellular content (grains of starch and aleurone, crystals, fats, and essences), cellular elements (vessels, tracheids, epidermic cells, stoma, parenquima, colenquima, suber, esclerenquima, petrified cells, fibre, and hairs or tricoma).

5.6. Physical tests – quantitative and qualitative chemicals.

We use the term to describe tests carried out on whole, powdered, or extracts of plants. They are qualitative or quantitative tests which allow us to ascertain the composition of the plant or drug, typify active principles, and recognise falsifications.

The tests are carried out with qualitative objectives (identification of substances), and quantitative objectives (establish level of concentration), or both.

Quantitative tests are:

- Humidity
- Ashes
- Dry residue
- Extractable material

- Physical parameters (density, rotational capacity, refractory index)
- Chemical indices (acidity, saponifisation, especially for essential oils)
- Swelling indices (for mucilages)
- Foam index (for saponines)
- Pollutants. Heavy metals, pesticides, aflatoxins
- Reaction identification. Colours, precipitation, fluorescence, micro-sublimation, etc…, which enable us to detect certain characteristic constituents in plants (flavanoids, alkaloids…)
- Chromatographic methods. These enable us to separate the different components of an extract, essence…
- Spectroscopic methods. These enable us to identify substances.

5.7 Quantitative tests

a. Humidity

By humidity we mean the water freely contained in vegetable matter. For good quality conservation, this should be less than 10% to prevent enzymatic processes, and to express the value of active principles compared with dry matter. There are several ways of determining humidity.

Gravimetric method. An exact quantity of dry matter is weighed, pulverised or broken in pieces, and placed in an oven at about 110 degrees, weighing it every 30 minutes until a constant weight is achieved. The difference between the initial and final weight is the water content or apparent humidity. Volatile substances may be lost, so this method cannot always be used.

Volumetric method (photo). Water content is determined by azeotropic drag. A specific quantity of vegetable matter is placed in a balloon flask with benzene, toluene or xylene, and is distilled in a closed circuit. The water steam condenses, and as it is immiscible, forms a separate and visible phase, with which volume is established.

Karl-Fisher method. This is very useful in samples with a low moisture content, and is based on the quantitative reaction of water and sulphur dioxide and iodine in an anhydrous atmosphere in presence of a base. Iodine and sulphurous anhydride react in the presence of water, forming sulphuric and iodhydric acid. To change the balance, we use a base such as pyridine.

b. Measuring ashes.

Ashes represent the mineral salt or inorganic matter content of the drug. In rigorous conditions, it is a constant and allows us to find falsifications due to other drugs, soils, or minerals.

Ashes give us an idea of the mineral matter contained in a plant, usually around 5%. Measuring it is important, because mineral matter may be the cause of a pharmacological effect (potassium salts, for example, have a diuretic effect on equiset, dandelion, and ortosiphon). If the content is high, this can indicate pollution due to the addition of mineral matter or soil, especially in roots.

Complete ashes. The process is based on calcinations until they are white. The residue corresponds to the ashes derived from vegetable tissue (physiological ash) and to those of extraneous matter (non-physiological matter).

Sulphuric ashes. H_2SO_4 is added before calcinations, obtaining the sulphates of the cations. They are much more stable than complete ashes.

Ashes which are insoluble in HCI. These are the residue left after extracting complete or sulphuric ashes using HCI. Silica is insoluble in HCI, which indicates the presence of sand or soil.

c. Nutrients.

Nutrients are analysed from complete ashes, in 1g samples, calcined at 400 degrees for 24 hours and dissolved in chlorhydric acid (1:1). The analytic measure of metals and minerals such as K, Na, Mg, Ca, Fe, Cu, Zn and Mn, are analysed by flame atomic absorption spectrophotometry.

d. Dry residues.

A specific weight of extract is dried in a oven at 100 degrees for a specific time. The result is expressed as % (m/m) of the original extract.

e. Matter which is extractable using solvents.

When no suitable methods for evaluating active principles a drug by means of physical or chemical tests are available, the amount of extractable matter is measured using water, alcohol, ether, or organic solvents.

f. Fito-sanitary products residues.

These are measured by TLC, GC, or HPLC (further on).

g. Microbiologic contamination.

In general, the plant is contaminated at the moment of collection, which diminishes yield at the time of extraction. Nevertheless, the process of manipulating the plant (grinding, packing, storage, etc…) can cause additional contamination. With certain exceptions, a maximum of 10^6 bacteria and 10^5 yeast is allowed per gram.

h. Radioactive contamination.

European regulations allow a maximum level of 600 beq/kg, although this refers to food products and not specifically to medicinal plants.

i. Nature and amount of extraneous matter.

Normally, pharmacopoeias permit up to 2%.

j. Heavy metals.

The following pre-established criteria are accepted for foodstuffs of vegetable origin:

Lead	Max. 0.5 ppm in fruit and roots Max. 1.2 ppm in green vegetables
Cadmium	Max. 0.1 ppm in fruit and green vegetables Max. 0.05 ppm in roots
Mercury	Max. 0.03 ppm in cereals

k. Swelling index.

This is applied to drugs with mucilage. It is defined as the volume in ml taken up by 1 gram of the drug and mucilage after swelling due to being in contact with an aqueous liquid. Agar, for example, is >15, flax seeds >4 if it is the complete drug, and >4.5 if it is powdered.

l. Refractory index.

This is given by the relation between the speed of light in air, and the speed of the substance being tested. It is measured using Abbe's refractometer. It is a useful measure for establishing the purity of essential oils, as their values appear in many pharmacopoeias.

m. Rotational capacity.

The rotational capacity of a liquid is the angle of rotation of its plane of light polarisation when a ray of polarised light is passed through a sample of said liquid. This rotation may be clockwise or anticlockwise.

n. Measuring essential oils.

The basic methods for analysing essential oils are as follows.

- Physical measurements
    - aroma
    - specific weight
    - refractory index
    - optical deviation (rotational capacity)
    - solubility in alcohol-water mixtures (reduced alcohols)
- Chemical measurements
- free acidity index
- saponisation and ester indices
- aldehide and cetone measures
    - phenilhydrazone formation
    - oxyme formation
    - semi-carbazone formation
    - bisulphite method
- acetyl index
- chromatographic techniques (FLC, GC, HPLC)
- spectroscopic methods (UV, IR, -MS, NMR)

5.8. Qualitative analysis

a. Colouration and precipitation reactions

These are simple reactions specific to an active principle or characteristic component of a drug, which serve to identify it. They are used for alkaloids, heterosides, saponins, flavonoids, tannins, etc…

These tests are not always applicable, due to the interference of other substances present in the drug, but they are very simple and quick. In general, they are done directly on a plant extract, usually of alcohol extraction.

For example, the appearance of a red colour when a holy peel (*Rhamnus purshiana*) is dissolved in an ammoniac solution is due to its anthraquinone content; the colour identifies it, if there is no red, it is something else.

Similarly, visnaga (*Amni visnaga*) produces a purple colouration when KOH is added to the residue of evaporating its alcoholic extract, because it contains furochromes.

Cyanogenic heterosides in bitter almonds (*Prunus amigdalus amar* variety) are determined using picroside paper, which turns reddish. This differentiates them from the sweet variety (*Prunus amigdalus dulcis*).

Finally, we should point out Liebermann's reaction, specific to steroids, which gives us a bluish-greenish hue.

b. Fluorescent reactions

The rhubarb root (*Rheum palmatum, R. officinale*), for example, can be distinguished from a falsification using the root of the rapontic (*R. rhaponticum*) because the latter produces a blue-violet fluorescence at 366 nm, due to the fact that it contains raponticine, a substance absent in the official drug.

c. Chromatographic analysis

Chromatographic techniques are based on separating the substances present in a complex mixture by putting it in contact with a mobile phase (liquid or gas) and another static one (solid or liquid) which is fixed.

The substances migrate through the static phase dragged by the mobile one, at different speed depending on affinity to or solubility in one phase or the other. Substances with a greater affinity to the static phase migrate more slowly, and those with greater affinity to the mobile phase, faster. If we adjust the chromatographic parameters, we manage to separate all the components. Three most common types are thin layer chromatography (TLC), gas chromatography GC, and liquid chromatography (HPLC).

d. Thin layer chromatography (TLC)

This is used in all types of control on natural products, having established itself as a very important analytical method in modern pharmacopoeias. It enables us to identify the components present in specific vegetable matter at a low cost and quickly. It can also be used as a semi-quantitative method.

e. Gas chromatography GC

Gas chromatography or gas-liquid chromatography GC is used with volatile or volatilizable substances, such as essential oils. A gas is used as the mobile stage, and a liquid in a capillary column (of very small diameter and several metres in length) is used in the static stage. The column is rolled up inside the chromatograph. High temperatures are used so that the components of the mixture remain volatilised.

This is the most selective technique, and is recommended by the European Pharmacopoeia as the standard method for analysing them. It allows us to separate and identify essential oils, camphor, vegetable acids, certain alkaloids such as opium or tobacco, cannabis resin, and compound steroids such as sapogenins and cardiotonic heterosides.

It is both quantitative and qualitative. This technique, together with Mass spectrometry (GC-MS), allows us to obtain the mass spectrum of each component, whence we can find the molecular weight and structural information. There are databases with the mass spectrum of many components. More recently, chiral chromatographic columns have been developed for separating optically active constituents.

f. High pressure liquid chromatography (HPLC)

HPLC are the English initials for this technique, a technique which enables us to separate and identify molecules of very similar chemical structure and even isomers. It is used with non-volatile compounds, such as heterosides, alkaloids, lipids, steroids, glucides, flavonoids, and thermo-labile substances like proteins and vitamins. Both the mobile and static phases are liquid, of different polarity, so the separation of substances occurs depending on this parameter. It is carried out at room temperature, but the mobile phases are pressure-pumped. The result, in both cases (GC and HPLC), is a chromatogram, which shows the separate compounds and the peak area of each one, which is in proportion to its concentration.

g. Spectrophotometric methods.

Many active principles can be chemically typified using the gas chromatography and mass spectrum data, as we explained above. However, when doubts as to character arise, we resort to spectral methods such as infra-red, ultraviolet, and nuclear magnetic resonance.

h. Infra-red spectrum

The infra-red spectrum enables us to detect the presence of hydroxile and carbonile, aromatic rings, double bonds C=C, etc… To establish the spectrum, we need only place a drop of the component in an NaCl cell and put it in the spectrophometer. The IR spectrum of a molecule is like its ID card, unique to it alone, and it can be compared against a spectrum database.

i. Ultraviolet spectrum

The ultraviolet (UV) spectrum allows us to recognise functional and chromophorous groups (chemical groups which can absorb UV). The lemon tree, for example, can absorb a maximum of 262 nm. On the whole, ultraviolet spectrophotometry has limited applications in the study of most terpenic essential oils, as few terpens contain chromophorous groups. Nevertheless, we find carotenoid constituents or constituents with oxygenated heterocyclic nuclei in the non-volatile part of citric essential oils (cumarins, substituted furocumarins, and polymethoxiflavones), which gives these substances a characteristic behaviour under UV. This characteristic has been used to fine tone methods which enable us to evaluate quality and authenticity, identify the geographical origin of a sample, and the technology used for its extraction, or the season when the oil was produced.

j. Nuclear Magnetic Resonance

Thanks to developments in NMR we have databases of spectra, especially C^{13} (^{13}C-NMR) for the most common monoterpens and sesquiterpens.

k. Mass Spectrometry

In connection with the study of essential oils, the combination of gas chromatography GC with mass spectrometry (GC-MS) is the one which has received most attention since its inception. The combined GC-MS technology allows us to obtain the mass spectrum of each component separately by GC. We can get structural information and obtain molecular weight. There are databases with mass spectra data for the chemical identification of many constituents of essential oils and other types of substance.

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Topic 6: **The industrial use of aromatic and medicinal plants**

6.1. Introduction

Aromatic and medicinal plants (MAPs) share the common characteristic of having a high content of active ingredients or substances with very specific chemical, biochemical or organoleptic properties, which allows us to use them for therapeutic purposes (medicinal plants), aromatic purposes (aromatic plants or essences), and dietetic or gastronomic purposes (condimental plants). The importance of their use depends not only in the richness of their active ingredient content, but also on the scarcity of their presence in the natural world and the difficulty their extraction entails.

The origin of the use of essences and aromas is as ancient as agriculture itself. It started with the gathering of all or any plant, before moving on to a more selective collection process, which eventually led to the domestication and cultivation of the most useful plants. Nowadays, they are used in the food industry, at home, in medicine, and in cosmetics.

The possibilities for using aromatic plants in food, cosmetics, medicines and products for the home are practically limitless.

These are the kinds of plants used in the several industries.

Aromatic plants: these contain essential oils, especially in the leaves. Examples include Rosemary (*Rosmarinus officinalis*), Citronella (*Cymbopogon nardus*), and Patchouli (*Pogostemon cablin*). All are widely grown in tropical and subtropical areas.

Spices: substances present in plants with antiseptic qualities used to season foods. Examples include Cinnamon (*Cinnamomum verum*), and Nutmeg (*Myristica fragrans*). These are typically found in the tropics, but also in other bio-geographical regions.

Colouring agents: these contain chemical constituents (carotenes, antocyanes, etc.) which can stain tissues, foodstuffs, and cosmetics. Examples include Curcuma (*Curcuma longa*), and liana fierro (*Arrabidaea chica*). They are widely grown in tropical and subtropical areas.

Bitter plants: these are plants which contain bitter-tasting substances and are used in the liquor industry. Examples include Quinine (*Cinchona spp*), Quassia (*Quassia amara*), Bitter palus (*Picrasma sp*), and Cedron (*Simaba cedron*).

Resins: these plants contain exudates, mainly in the trunk, which are used in the incense industry and for other purposes. For example, *Protium spp* and *Colophonia* (of the *Pinus* genre).

6.2. Industrial sectors which use MAPs

The main industrial sectors which use aromatic and medicinal plants are, in order of importance: medicine and herbal, foodstuffs, and cosmetics. Within these sectors we find the following industries: pharmaceutical and herbal, food, conditioning, essential oil manufacture, and extraction and formulation industries,

Purpose	Type of product	Uses
Pharmacological activity	Pulverised plants Simple extracts Essential oils Isolated active ingredients	Phytotherapy Homeopathy Aromatherapy Preparation of medicines Models for synthesis Molecules for semi-synthesis
Raw materials for industrial use	Pulverised plants Essential oils Extracts Isolated products	Nutritional complements Foodstuffs Perfumes Cosmetics

A. Herbal and medicinal sector

The Pharmaceutical Industry.

Within the herbal and medicinal sector we find the Pharmacy and Phytotherapy industries, which use dried plants, extracts, or isolated active ingredients to manufacture medicines.

Aromatherapy.

This is another important branch which has created a market, generating a demand for essential oils of a higher quality than traditionally accepted. Among those produced in Spain we find Thyme (*Thymus vulgaris* and *zygis*), Oregano (*Origanum vulgare*), Lavenders (*Lavandula angustifolia* and *latifolia*), Rosemary (*Rosmarinus officinalis*), and Spanish Salvia (*Salvia lavandulifolia*).

Herbal.

A study of the herbal market and consumption of herbs in Spain by the Gremi D'Herbolaris de Catalunya (2002), states that this sector retailed 751 million Euros in 2001, and that sales of herbal-dietetic products rose 52.8% between 1997 and 2001.

Veterinary Phytotherapy.

Medicinal plants are increasingly used in prophylaxis in animals which are being fattened. They are used particularly as background treatments or as complements to livestock feeding.

B. The bone-meal industry and animal feed

Their products in general have recently undergone the effects of the ban on many synthetic additives, to prevent the negative effects on health and productivity. Many of the banned substances can be substituted using these plants or derivates of them, which act against certain animal diseases of a bacterial, viral or fungal nature (Costa *et al.* 1999).

Cosmetics and parapharmacy.

This industry is a major consumer of vegetable derivates and of aromatic and medicinal plants such as oils, essential oils, waxes, etc… for the manufacture of cosmetic products, bath gels, deodorants, mouthwashes, toothpastes, elixirs, etc… Over the past few years, demand has increased considerably due to a rise in the use of natural products.

6.3. Raw materials for industrial use

This group includes all uses which are not of a pharmacological nature. Thus, we have grouped here plants that are used for the preparation of food complements and also those which are used because of their organoleptic properties (flavour enhancers, aromatic enhancers), or because of their physical-chemical properties, which help to create an appropriate “format” for the presentation of medicines, foodstuffs, and perfumes or cosmetics (solvents, gels, suspension stabilisers, etc…). (From Arco Ortiz de Zárate, 2001).

a. Food sector

Products for direct use by the consumer

According to figures for foreign trade in dry grains in Spain, in the nineties imports were greater than exports for the following products: laurel leaves, liquorice roots, mint leaves and stalks, lime-tree leaves and flowers, oregano, salvia and others (dry, fresh, and frozen), for use of their antioxidant and antibacterial properties.

Products for industrial use.

There are many areas in which the food industry can use aromatic plants and their derivates, among them the enhancement of quality. Precooked meals are increasingly taking the place of home-cooked food, and the preparation of the former requires the use of antioxidants, preservatives, flavour enhancers, and colouring agents, all of natural origin.

The food-farming industry is increasingly using natural condiments rather than synthetic ones. For example, the leaves and florid roots of oregano are used to flavour, to enhance aroma, and to conserve foodstuffs in the meat, pork products, and precooked meals industries. (Lalourcame *et al.* 1994).

Apart from preserving foods, complementary effects include their anti-oxidant, germicidal, and fungicidal action, due to their volatile constituents such as phenols, carvacrol and timol, and certain other standard constituents, among others, rosmarinic phenolic acid and chlorogenic phenolic acid, and also different oligoelements. (Nakatani and Kizukazi. 1987).

b. Perfume and cosmetics sector

World trade in essential oils amounts to around 1,000 million dollars a year, including both wild and farmed sources. Spain stands out as a major exporter of the essential oils of the lemon-tree, lavender, and lavandine. However, Spain imports more essential oils of mint, eucalyptus, rosemary, oregano, thyme, fennel, salvia, etc…

c Industrial perfumes

Air-fresheners and detergents use large quantities of essential oils, as do also a wide range of products which contain aromatic composites or essential oils in pure form: bath gels, soaps, lotions, creams, etc… High quality perfumes have an important content of essential oils and other extracts of vegetable matter.

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Topic 7. The medicinal and herb sector.

7.1. MAPs in the pharmaceutical industry

The pharmaceutical industry is the most important user of MAPs. We include, in this group, all therapeutic and preventive uses, i.e., the use of medicinal plants for their pharmacological activity.

The pharmacological activity of medicinal plants is obviously conditioned by the presence in them of certain active molecules, which are able to bond with different structures in living beings, thus modifying them. Synthetic drugs do the same.

The main difference lies in the concentration of these molecules in the drug. This is generally less in the plant, which produces significant differences of action, but also important differences as far as side-effects go. Phytotherapeutic drugs have a less intensive pharmacological action, take longer to act, but also have fewer adverse effects than synthetic ones.

Some species stand out above the rest because of a specific compound responsible for the pharmacological activity. However, it is frequently the case that the effects of administering a medicinal plant are different to those of administering just the constituents in isolation. There therefore exists a possibility that the final effect may be due to synergism (enhancing of activity) or to antagonism (reducing of activity) between the different active ingredients which the plant contains.

On the other hand, some constituents may interfere in the pharmacological activity of the active ingredients by modifying their pharmacokinesia, increasing or reducing their bio-availability. This is why the efficiency of certain phytotherapeutic medicines has not been bettered by the administration of isolated active ingredients, as in the cases of the roots of *Valeriana officinalis* (a sedative), or the roots of the ginseng, *Panax ginseng* (a stimulant).

The European Union recognises the importance of phytotherapy, especially in terms of treatment and prevention of minor ailments, but also for certain chronic afflictions. Phytotherapy may be used as an alternative therapy in cases where intolerance to or inefficiency of synthetic drugs are manifest, and also as a complementary treatment for serious diseases. The WHO, on its part, recommends the use of phytotherapy and takes it as the only form of therapy possible in Third World countries.

The drug or medicine comes with a leaflet which explains the composition, stipulates the concentration of the main active ingredient, defines the therapeutic effects, dosage, and recommended uses, as well as possible interactions and side-effects.

Medicinal plants are also used in the preparation of two other types of therapeutic products: those used in homeopathy, and those used in aromatherapy.

In the case of homeopathy, both medicinal species and toxic plants are used to prepare what are known as “mother tinctures”, from which we obtain the infinitesimal dilutions for homeopathic drugs.

In aromatherapy, essential oils are obtained from raw materials by distillation or pressure. These are administered by inhalation or as external rubs or topically and have several different beneficial effects for human beings.

7.2. Operation tecno-pharmaceutical.

These are the processes usually used to prepare a drug:

A. Drying.

Drying allows us to preserve vegetable matter adequately. As we have already seen, it consists in eliminating water, which prevents the metabolic decomposition processes from continuing.

B. Pulverisation.

This is used to homogenise the size of the particles and to improve preparation of medicines. It helps to free the active ingredients in the drug, increasing contact surface and breaking down cell structures. Resulting products may be lumps or powders of the drug.

C. Sieving and straining.

After pulverising the vegetable matter, we obtain particles of very different sizes. To obtain particles of a specific size, we need to separate them from the others. To this effect, we use light-sieves with decreasing mesh sizes, which separate drug particles according to size.

D. Mixing.

Medicines made with medicinal plants may be made up of a single vegetable drug or of mixes of several different drugs, which enhance or complement their performance. Excipients may also be added. An adequate homogenous mix of the different components is needed.

E. Extraction.

There are many products made by using plant extracts. An extract is a preparation of a vegetable drug which contains only the soluble active ingredients in the extraction medium used. As we have seen earlier, extracts are usually prepared by putting the drug into contact with a solvent. The soluble active ingredients of the drug remain in the solvent. Once we have obtained an extract, it can be used directly as a medicament or used to prepare a pharmaceutical form.

7.3. MAP preparations.

There are many medical preparations from medicinal plants. They can be classified according to their administration or to their consistency.

A. By way of mouth.

The most widely used medical preparations from medicinal plants are orally administered. This method is particularly used to administer liquid forms resulting from extraction processes to the vegetable matter. The following liquid forms may be highlighted:

- **Infusions**. As we have seen before, they are prepared by adding hot water to vegetable matter, and allowing the mix to brew for a few minutes. Infusions are usually prepared using soft drugs, such as flowers or leaves. They are probably one of the oldest preparations in existence, and were already in use in prehistoric times.
- **Ebullitions or decoctions**. These are obtained by boiling vegetable matter in water for a longer period of time than for infusions. They are basically used with drugs in seed, bark, or root form.
- **Clovesrations**. These are prepared by putting the drug in a solvent at room temperature. Depending on the solvent we use we can prepare:
- **Tinctures**. The solvent used is alcohol. The percentage proof of the alcohol depends on the drug itself. As a general rule, we use 70° alcohol. However, in the

case of resinous drugs we must use 90° alcohol, whereas for drugs rich in saponins it should not exceed 45°. It is best to dilute these before taking them, adding 15-25 drops (about 1 ml) to a glass of water. The presence of alcohol in these preparations limits their use with certain patients such as children or people with alcohol-related problems. Tinctures keep well, due to their alcohol content, which prevents bacterial growth. Nevertheless, they can be unstable, and at times become turgid or precipitate.

- **Glycerolates**. Glycerolates are prepared using glycerol instead of alcohol, which means they can be used with patients for whom alcohol is not recommended. They should also be diluted before use.

B. External or local administration.

In the past external or local administration was very common. However, preparation is more complex and nowadays it is less common. These preparations are either liquids or semi-solids. Examples are:

a Liquids

- **Medicinal oils**. These are oils which contain active ingredients of a drug dissolved in them. They are prepared by clovesrating the drug in a common oil for a period of several weeks. They may be applied directly via massage, or used as the main ingredient for preparing ointments. The oil acts as the vehicle for transmitting the active ingredients and also as an emollient and moisturiser for the skin, helping it to function and enhancing the absorption of active ingredients.
- **Essential oils**. These are oily liquids obtained by steam extraction from aromatic plants. Their active ingredients are volatile, so they should be stored in hermetic containers to prevent the loss of medicinally active substances. These essential oils are administered externally by bathing areas affected arthritic and muscular pains, although they may also be inhaled or by way of mouth if diluted.
- **Gargles**. Gargles are preparations which are administered to the mouth/larynx and consist of an infusion which has been slightly concentrated by evaporating water. They are used at a warm temperature and are retained in the throat without swallowing. They are used to treat laryngitis or wounds to the larynx, so they are usually prepared using astringent plants such as agrimony, emollients such as mallow, antiseptics such as thyme, or anti-inflammatories such as camomile.
- **Compresses or plasters**. These are liquid forms which are applied to the skin by means of a cotton gauze which is then covered. They can be applied either warm or cold. In the former case, the compress must be changed when it cools down. They are inconvenient because the patient must be lying down during their application to stop them from falling off. They are mainly used to treat dermatitis, and lesions to the skin which scar (cicatricise) badly, so they are prepared using astringent plants; they are also used for the treatment of mialgia and to relieve pain in contusions.
- **Eye washes**. These are extractive liquid solutions which are used cold directly on the ocular conjunctiva and palpebral. They are used to cleanse eyes and eyelids, to administer active ingredients to treat conjunctivitis, styes, and blepharitis. Astringent and antiseptic plants such as euphrasia, or anti-inflammatory plants such as camomile are used in their preparation. In spite of all this, eye washes are on their way out due to the possible risk of allergic reactions which aggravate conjunctivitis due to the presence of pollen in the infusions.

b Semi-solids.

- **Balsams**. Balsams are very oily, and made from the trunks of certain plants after treating their bark. The most frequently used include Tolu and Peru, of the species *Myroxylon balsamum*, and the banguy, from different species of the *Styrax* genre. Thanks to its great viscosity and adhesiveness to the skin (which can be enhanced by adding beeswax) they are administered for treating dermatological afflictions as they are both antiseptic and cicatricising.
- **Cataplasms**. Cataplasms are semi-solid preparations obtained by mixing ground vegetable drugs with hot water until a viscous paste is formed. Linseed or potato flour may be added to thicken. The paste is wrapped in a cloth and applied as hot

as possible to the patient's skin (without actually burning it). Then it is covered with a woollen cloth to keep the heat in. mud has at times been used to apply vegetable drugs. Cataplasms are locally emollient, analgesic, and anti-inflammatory, and are therefore used to treat rheumatic pains or skin problems.

7.4. Pharmaceutical forms and medicinal plants.

Adding a medicinal substance of medicinal plant origin to a pharmaceutical form, gives us a plant medicament. A plant medicament has a definite form and a specific, measured dosage.

Pharmaceutical forms have an advantage over traditional forms of administering (physician's preparations on sale in herbal medicine shops), and this is basically their high quality. This is because they are produced following perfectly standardised processes, and undergo quality control to ensure that they are safe and of a high standard.

Furthermore, the active ingredient content can be standardised, and this allows an equality of effects for each dose taken. In addition to this, because they contain preservatives and anti-oxidants, and thanks also to the technological processes used to obtain them, pharmaceutical forms are very stable, and can therefore be kept for long periods of time.

Finally, it is much easier to administer pharmaceutical forms, and they also mask (disguise) unpleasant organoleptic features.

We should highlight, however, a major disadvantage which is that they are more expensive. Also, these products lead more frequently to an overdose, as they are administered with greater quantities of active ingredients than traditional preparations.

Pharmaceutical forms, as with traditional preparations, may be classified according to how they are administered and also to their state. Again like traditional preparations, the most commonly used pharmaceutical drugs are taken by way of mouth, although at times, certain treatments require external, local or topical use.

A. Oral pharmaceutical forms.

A. Solids by way of mouth.

- **Tablets**. These are pharmaceutical forms made by compressing a powder or granules.
- **Capsules or pills**. These are pharmaceutical forms made up of a gelatine container filled with a solid matter (powder, granules), or even a liquid. They may be hard –with a gelatine container- or soft (also known as pearls) –with a glycerogelatine container.

B. Liquid forms by way of mouth.

- **Syrups**. This is an aqueous solution of the active ingredients of the plant saturated with saccharose, to help preserve it. Its pleasant taste makes it particularly suitable for children. What's more, the sugar has a demulcent effect on the mucus of the larynx, so they are often used to treat respiratory problems. They may be administered directly, using a spoon, or diluted in water. Given their high saccharose content, they should not be used to treat diabetic patients, unless the saccharose is substituted by another sweetener such as sorbitol.
- **Elixirs.** These are solutions diluted in a hydro-alcoholic solution. They keep for a long time thanks to their alcohol content. Nevertheless, they should not be used to treat children or alcoholics.

B. External or localised (topical) pharmaceutical forms.

Topical forms are also widely used to treat skin problems or localised ones. Some of the most common topical pharmaceutical forms used to make medicine from plants include:

a. **Semi-solid topical forms.**
   - **Ointments.** These are emulsions with an oily external phase. They are highly viscous and form a paste. They are very adhesive to the skin due to their viscosity, so they allow the active ingredients to penetrate the corneal layers of the skin.
   - **Hydrophilic gels**. These are formed by dispersing acrylic acid polymers in and aqueous solution or a hydrochloric solution. Compared to ointments, they are much more extendable (they spread over a greater area) and because the solvents evaporate, the skin feels a fresh, cooling sensation, so they are used to treat burns or skin wounds. What's more, they are pleasant to look at. They are used particularly to treat varicose veins and heavy legs. The major drawback is that they are often incompatible with cationic substances.

b. **Liquid topical forms.**
   - **Eye-drops (colliriums).** These are sterilised solutions or suspensions for use on the corneal mucus. They are used as decongestants and as antiseptics in cases of conjunctivitis. We need to try and keep the solution sterile, so it is recommended that the nozzle of the bottle should not touch the eye. Once we open the container, these products last a short time.
   - **Colutories**. These are hydro-alcoholic solutions which are administered as gargles or as mouthwashes. They are normally used to treat problems with teeth, the mouth, or the larynx. The product should not be swallowed.
   - **Nasal sprays and drops**. These are preparations which are applied to the cavities of the nose either as drops or as a spray. They act as nasal decongestants.

Although these pharmaceutical forms are now the most common, we should not forget others that were widely used in past times, such as liniments, lotions, enemas, and suppositories. Nowadays, very few medicines are presented in these forms.

7.5. Definitions.

Raw material: any substance (active or inactive) used to prepare a medicament, whether it is unchanged or modified, an even if it disappears altogether during the preparation.

Active ingredient (active ingredient): any matter, whatever its origin (human, animal, vegetable, chemical, or others), with the appropriate activity for the preparation of a medicament (active substance, medicinal substance, or pharmaceutical drug).

Excipient: matter which is added to active ingredients or their derivates (including traditional preparations) to act as a vehicle, to facilitate preparation and stability, to modify organoleptic properties, and to determine the physical and chemical properties and the bio-availability of the medicament.

Traditional (physician's) form and pharmaceutical form: the way in which active ingredients and excipients are adapted to prepare medicaments. They are defined according to the format in which the pharmaceutical product is presented and according to how they are administered.

Intermediate products: these are products destined for later industrial modification by an authorised manufacturer.

Medicaments for human use: any substance or combination of substances which is seen to have properties for the treatment or prevention of disease in human beings, or which can be used with or administered to humans, so as to restore, correct, or otherwise modify physiological functions by exerting a pharmacological, immunological, or metabolic action, or so as to establish a medical diagnosis.

Master formula: this is a medicine designed for an individual patient, prepared by a pharmacist (or under a pharmacist's directions) specifically to complement the active ingredients of a medical prescription. In observance of the pertinent regulations and quality controls, it includes the active ingredients and is dispensed in a chemist's or pharmacy service once the patient has been suitably informed of its contents and effects.

Officinal preparation: any medication prepared according to the pertinent regulations and quality control and guaranteed by a pharmacist (prepared by the former or under a pharmacist's directions) which is dispensed in a chemist's or pharmacy service, having a registration number and description in the National Formula Register, and which is given directly to the patients who are customers of said chemist's or pharmacy service.

Generic medication: all medicines which share quantitative and qualitative composition in terms of active ingredients and pharmaceutical forms, and whose bio-equivalence to the reference medication has been suitably proved by bio-availability studies.

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Topic 8. The food sector.

8.1. The spice and condiment industry.

The spice and condiment sector is a traditional one in which small and medium-sized business coexists with multinational companies.

At present, about 110 companies that produce and commercialise species are at work in Spain. Castilla - La Mancha and the Comunidad Valenciana are the autonomous communities where we find the majority of working spice companies. They are followed by Murcia, Aragon, Catalonia, and Andalusia.

Imports have a significant impact, given that Spain does not produce several of the principal spices, such as pepper, cinnamon, nutmeg, cloves, curry, etc…

Spanish spice exports are, however, also important. Two obvious cases are saffron and paprika, whose quality and repute bring a high added value. They are mainly exported to the European Union, the United States, and to Arab countries.

A. Definition.

Spices and condiments are vegetable substances which are used in small quantities to flavour and preserve food. Spices come from dried aromatic roots, bark, buds, seeds, and berries and other fruits.

Spanish legislation defines spices and aromatic condiments as *plants or parts of plants, either fresh or dried, whole, chopped or ground, whose characteristic colour, taste or smell cause them to be used to prepare foodstuffs or drinks, with the aim of incorporating said characteristics so as to make products tastier or more appetising thus ensuring a better use of the same.*

- They stimulate the appetite by increasing the taste and smell of dishes.
- They preserve foodstuffs well.
- They may be used instead of salt as a condiment when preparing food.

B. Most common spices in Spain. Characteristics and qualities.

Garlic. *Allium cepa* (*Alliaceae* family).

This is a bulbous plant with plain leaves originally from central Asia and which grows in warm countries. It contains vitamins A,B, and C, and reduces cholesterol levels in the blood. It can be used to treat infections to the digestive and respiratory systems, and it stimulates circulation. It contains aliine, a sulphoxide which gives it its smell.

Basil. *Ocinum basilicum* (*Labiatae* family). The leaves, either fresh or dried, are used. There are more than 40 different types of basil. Basil contains methylchavicol, linalool, cineol, and eugenol. Apart from these compounds, saponins are part of its composition.

Aniseed. *Pimpinella anisum*. (*Umbelliferae* family). There are two varieties of aniseed: green aniseed (*Pimpinella anisum*), and starred aniseed (*Illicium verum*. *Magnoliaceae* family). Spain is one of the major producers of green aniseed. Its medicinal properties are especially due to its essence, anetol, which, however, when isolated from the other active ingredients of the plant and in concentration, loses its curative properties and can even be toxic.

Saffron. *Crocus sativus* (*Liliaciae* family). Christened “red gold” because it is the most expensive spice of all. It is used as a dye, an aphrodisiac, and a perfume, but its most important uses are culinary and medicinal. Spain has a long tradition of saffron production, and is recognised as being the country that produces the best quality saffron. Saffron contains a bitter ingredient (picrocine), a colouring agent (crocine), and an essential oil.

Cinnamon. *Cinnamomun zeylanicum.* (*Lauraceae* family). Cinnamon is extracted from the inner bark of the cinnamon tree. It is one of the most widely used spices in the world. Cinnamon bark contains essential oil, cynamic aldehyde, tannins, terpenes, calcium oxalate, starch, and mucilage. The effect of all these substances together is to give it digestive properties, making it a stomach tonic and an appetiser.

Coriander. *Coriandrum sativum*. (*Umbelliferae* family). Originating in the region of the Mediterranean, coriander is grown all over the world nowadays. Its medicinal and culinary uses date back 3,000 years. Its name appears in papyruses from 1550 BC, in Sanskrit literature, and in the Bible. Hippocrates used coriander as a medicine, and the Romans spread its use all over Europe. It was one of the first spices to reach the Americas, and it was already being grown in Massachusetts before 1670. Its fruit contains an essential oil, linalool, whose active ingredient gives it eupeptic and carminative properties.

Cloves. *Syzygium aromaticum*. (*Mirtaceae* family). Cloves are the unopened flowers (buds) of a tropical tree which is dried in the sun. Aromatic cloves are found in the cuisine of Europe, Africa, Arab countries, and The Americas. Cloves contain an abundance of essential oil, are rich in eugenol, acetile eugenol, cariofilene, pinene, cariofiline, and methyle salicilate. They also contain tannins, mucilage, and other compounds less used in clinical applications.

Cumin. *Cuminum cyminum.* (*Umbelliferae* family). This is one of the most widely used spices in the world. Cumin is the basic ingredient of curry, it contains 10% oil whose main active ingredient is cuminic or cuminal aldehyde. It is an appetiser, and is both digestive and carminative.

Dill. *Anethum graveolens.* (*Umbelliferae* family). It is used to condiment the well-known pickled gherkin. Chewing dill grains prevents bad breath. Its essential oil is rich in limonene, eugenol, and atenol, among others, which give it carminative-type effects. It is also rich in cumarines, flavonoids, and caffeic and chlorogenic acisds.

Estragon. *Artemisia dracunculus*. (*Asteraceae* family). This is a perennial herb with a moderate resistance to the cold. It contains an essential oil that is rich in estragol, felandrene, and ocimene, and also has a high hydoxicumarine content.

Mint. *Mentha spp.* (*Labiatae* family). There are many varieties of mint. The best known and most commonly used variety is piperite mint (*Mentha piperita*). It contains menthol, which stimulates nerve endings sensitive to cold, creating a sense of freshness. In extreme cases, the same mechanism produces a mild local anaesthesia which used to be used to treat toothache. Menthol is used to aromatise and as an antiseptic.

Nutmeg. *Myristica fragrans.* (*Myristicaceae* family). The part we use for cooking with is the fruit. Its constituents include several terpenes (eugenol, borneol, geraniol, safrol), and 3-4% myristicine, which is toxic at high dosages.

Oregan. *Origanum vulgare.* (Labiatae family). This is a wild plant which originated in the Mediterranean basin. It is normally used dried. The whole plant is rich an essential oil which contains timol and carvacrol, whose effects are sedative, anti-spasmodic, and carminative. In addition to this, they are biocidal substances, and have been (are) used for the preservation of food products, especially meat and cured meat. It also contains flavonoids and ursolic acid, which give it anti-rheumatoid properties.

Paprika. *Capsicum anuum.* (*Solanaceae* family). Paprika is the result of grinding the dried fruit of peppers. Christopher Columbus claimed to have discovered it on his voyages to America. It is used as a condiment and also to preserve food, especially meat. At an industrial level, it is commercialised as oleoresin. Paprika's main active ingredient is capsaicine, whose chemical name is methylenonenic acid vanililamide.

Pepper. *Piper nigrum*. (*Piperaceae* family). Pepper grains can be green, black, or white, depending on the different stages of ripening. The main fact about the origins of pepper is a mention in ancient Indian texts. From India, trade spread pepper to Malaya and Indonesia. Later it reached the New World too.

At the beginning of the XV century, Venice controlled the commercial pepper routes from Alexandria. This monopoly encouraged the Portuguese to seek a western sea route. After adventures and discoveries along the coast of Africa, an expedition led by Vasco de Gama reached Calcutta towards the end of the year 1400, and Portugal took control of the pepper market.

At the beginning of the XVII century, England established the East India Company and Portugal lost control of the pepper monopoly.

Later on, due to a fall in price, pepper became a spice that everyone could afford and trade became more fluent.

It contains an essential oil (1-4%): pinenes, cariofilene, limonene, felandreone; resin: piperine, and other secondary aminoes (piperiline, piperitine, piperinine).

Rosemary. *Rosmarinus officinalis*. (*Labiatae* family). This is a perennial plant which can grow to 2 metres in height. Its leaves are needle shaped, and its flowers a pale blue colour. It originated in the Mediterranean area, but spread into Northern Europe for use medicinally.

Among other substances, the essence is made up of camphor. The flower cavity contains caffeic and rosmarinic acids. It also contains flavonoids.

Salvia. *Salvia officinalis*. (*Labiatae* family). This plant originated in Southern Europe and grows well in warm climates, although it is quite resistant and survives in regions such as the Alps. It is also widely grown in North America.

Salvia has a strong taste, which is spicy and aromatic, with a subtle hint of camphor, so it should be used in moderation. Its essential oil is rich in tuyona, cineol, and borneol. It also contains tannic material, and bitter substances, resins, starch, albumenoids, phosphoric acid, and traces of asparagin have been found in the roots.

Thyme. *Thymus vulgaris*. (*Labiatae* family). This is one of the most typical Mediterranean spices. Its taste and smell is spicy and reminiscent of oregano. Traditionally, it was recommended as a digestive aid and to relieve coughs, sore throats, etc… mixing thyme with honey.

The essence of thyme varies greatly depending on geographical location and altitude, or on season of collection. Dried, it has a maximum effect of 3%. Its essence is basically made up of timol. Apart from its essence, this aromatic plant contains flavonoids and certain phenolic acids, such as caffeic or rosmarinic. Its essence gives the plant antiseptic and anti-fungal properties, which are enhanced by phenolic acids.

8.2. Food additives. Preservatives and colouring agents.

Food additives are chemical substances which are added in small quantities to frozen or canned foodstuffs to preserve them, and to improve their texture, taste, appearance, and smell. There is a wide variety of additives, but mainly preservatives and colouring agents.

A. Natural preservatives of plant origin.

Preservatives are natural and artificial substances used to conserve foodstuffs against the effects of micro-organisms, so as to stop them deteriorating for a certain period of time and under certain storage conditions. Basically, they have bacterio-static and bactericidal properties.

Some studies have shown that for meat products, the best combination is a mix of essential oil of oregano, capsicum oleoresin, and curcuma oleoresin, applied at 0.1%.

They are obtained from essential oils and oleoresins. These extracts are complex natural mixtures, extracted from carefully selected raw vegetable matter, and prepared using special extraction technology. They reproduce the characteristic smell and taste of the raw material whence they come, but are completely different to it in terms of physical-chemical behaviour.

Firstly, essential oils are compounds that are made up of a few volatile constituents, which means that they generally have a clearly defined chemical formula.

Because of the extraction technology used, oleoresins, on the other hand, are defined as the non-volatile potentially extractable fraction of a certain plant, and their chemical formula is complex. These characteristics make oleoresins more stable.

The use of these extracts as natural preservatives is related to these specific chemical structures, present in the original plant. They include:

- Carvacrol and timol in oregano.
- Carnosic acid in rosemary.
- Capsaicine in spicy ajies.
- Curcumin in curcuma.
- Eugenol in aromatic cloves, laurel, and basil.
- Other compounds found in plants (coriander, garlic and foengreek among others).

Some of these compounds have antibacterial properties, others have anti-fungal properties, and others are anti-oxidants. Furthermore, some are found in the volatile fraction, such as carvacrol, timol, and eugenol, whereas others are found in the non-volatile fraction, such as curcumin, capsaicine, and carnosic acid. i.e., the constituents with antimicrobial and/or anti-oxidant properties are found in different fractions.

In the case of meat products, such as frozen hamburgers, where the main cause of deterioration is oxidation, we can apply a mixture with a high rosemary oleoresin content. In the case of semi-cured meats such as sausages, we use a combination to prevent contamination on the surface during the process of putting them in skins. With bakery and cake products, we use a mix with a high antibacterial activity, which also adds some colour.

B. Natural colouring agents of plant origin.

Colouring agents are natural or artificial substances which are used to enhance the colour of foodstuffs, either because the food product has lost colour during industrial treatment, or to make it look tastier and more attractive to the consumer.

Colouring agents are also substances which are added to return colour to foodstuffs, and these include natural constituents derived from foodstuffs or other natural sources, which are consumed as foodstuffs in their own right, and which are not normally used as separate ingredients.

Colouring agents are split into two main groups: natural agents and artificial (synthetic) agents. They all have an identification number. In Europe, this number is preceded by the letter E. some natural colouring agents are:

Curcumin. It is used in ice-cream, sauces, soups, cakes, desserts, pre-cooked meals, cheeses, drinks, condiments, etc… It is usually in a hydro-soluble liquid, lipo-soluble liquid, or hydro-soluble powder form. It has good stability in the presence of acids, medium stability to heat, and little stability to light. It gives a yellow or yellowy-orange colour.

Riboflavin. It is used in ice-cream, cakes, drinks, yoghurts, etc… It is presented in a hydro-soluble liquid or hydro-soluble powder form. It has good stability to heat, and medium stability to light or in the presence of acids. It gives a yellow colour.

Chlorophyl. It is used in ice-cream, cakes, drinks, condiments, vinaigrettes, etc… It is presented in a hydro-soluble liquid, lipo-soluble liquid, or hydro-soluble powder form. It has medium-to-good stability in the presence of acids, and medium stability to light and heat. It gives a green colour.

Cochinilla carmine. The word carmine defines both a shade of colour and a colouring agent. In fact, carmine is the name usually given to a natural red colouring agent extracted from the female cochinilla (*Coccus cacti*), an insect that lives in the branches of cactuses, especially in the *Opunctia coccinillifera* found mainly in Peru and the Canary Islands (Spain).

This colouring agent has been in use since ancient times to treat cloth, vinegar, alcohols, and meat products. More recently it is used in cosmetics. It is very expensive.

Carmine gives a bright red colour in an acid medium, and a violet colour in an alkaline medium. This is because carmine belongs to the antiocianin group, which are pH indicators depending on the medium.

8.3. Functional foodstuffs. Phytobiotics and phytochemicals.

Nowadays, a very important commercial demand for MAPs is for Functional foodstuffs. Only Japanese legislation has a clear definition of what is (and what is not) a functional foodstuff. The most commonly accepted definition of a functional foodstuff is: *a foodstuff that is similar in appearance to a traditional foodstuff, which is eaten as part of a normal diet, and which goes beyond its nutritional value because it has been scientifically proven to reduce the risk of getting a particular illness and/ or to have physiological benefits*. There are three kinds:

- Probiotic
- Prebiotic
- Photobiotic or photochemical

Phytochemicals are secondary metabolites of plants. They are termed secondary because they have no direct influence on basic activities such as growth or reproduction, but give rise to many chemical constituents:

- Carotenoids: betacarotene, licopene, luteine.
- Glucosinolates
- Phyto-estrogens
- Poly-phenols: lignanes, phenolic acids, tannins, flavonoids, etc…

Some of these substances function by facilitating the elimination and dis-intoxication of toxins or carcinogenic products present in the organism, by modulating the action of certain enzymes.

Others act as antioxidants, by neutralising free radicals, which are the cause of cardiovascular diseases, arteriosclerosis, or anti-immune reactions. Phytochemicals are not the only antioxidants, as certain vitamins (C and A) and certain oligo-elements (selenium and manganese) also have this property.

8.4. The liquor industry.

Aromatic and medicinal plants are used to prepare a wide range of liquors (cordials). From the XV-XIX centuries, these were used for medicinal purposes. Among the many vegetable species used we find:

- Juniper berries (*Juniperus communis*).
- The roots and seeds of Angelica (*Angelica archangelica*).
- Starred aniseed seeds (*Illicium verum*).
- Aniseed seeds (*Pimpinela alisum*).
- Cinnamon bark (*Cinnamomum zeylanicum*).
- Cardammon seeds (*Elettaria cardamomum*).
- Coriander seeds (*Coriandrum sativum*).
- Cloves buds (*Eugenia cariophylata*).
- Curcuma roots (*Curcuma longa*).
- Gentian roots (*Gentiana lutea*).
- Fennel seeds and leaves (*Foeniculum vulgare*).
- Hyssop leaves (*Hyssopus officinalis*).
- Marjoram leaves (*Origanum majorana*).
- Melissa leaves (*Melissa officinalis*).
- Mint leaves (*Mentha piperita*).
- Oregano leaves (*Origanum vulgaris*).
- Thyme leaves (*Thymus vulgaris*).
- Vanilla pods and seeds (*Vanilla perifolia*).

A. Production methods

There are three basic methods of elaborating liquors, two cold, and one using heat. The method used depends on the plants, the aroma and the taste. Fruits are best extracted cold, whereas seeds, peels, and flowers are usually extracted hot. The parts of the plant used are seeds (almonds), fruits or berries (juniper), peels (citrus), roots (liquorice), flowers (orange flowers), and leaves (mint). Natural concentrates are also used.

B. Classifying liquors.

Liquors may be classified according to their main constituents.

a. Herb and spice liquors.

They contain herbs such as basil, rosemary, salvia, mint. Examples include:

- **Benedictine** (it was used as a remedy for malaria).
- **Chartreuse** (it contains more than 130 plants).
- **Drambuie** (it contains liquorice, herbs and whisky).

b. Liquors made from seeds.

They contain seeds like aniseed, hazelnuts, or almonds. Examples include:

- **Aniseed.** Very popular in Spain. It contains aniseed seeds. Distilled it is between 40-60% proof.
- **Ouzo**. Greek liquor which contains aniseed seeds, liquorice, mint, fennel, and hazelnuts.
- **Pernod**. French liquor which is a variety of traditional absinthe. It is a herbal elixir containing 15 different herbs, among which is absinth (*Artemisia absinthium*).

c. Other liquors from plants.

- **Gin.**

In 1650, Franciscus de la Boe, a Dutch doctor and Professor at Leyden University, discovered the diuretic and hepatic qualities of the juniper berry, and developed a medicinal tonic using liquors and said berries. He named it Geniévre (juniper in French). It also contains coriander, angelica roots, liquorice, cassia bark (*Cinammomum cassia*), and orange and lemon peel. The Bombay variety contains Moroccan coriander seeds, Chinese liquorice, Spanish almonds, angelica from Saxony, iris roots (*Iris germanica*), Italian juniper, cassia bark from Indochina, Javanese cubeba pepper (*Piper cubeba*), and paradise grains (*Aframomum melegueta*) from Africa.

- **Vermouth.**

The word “vermouth” is the French equivalent to the German “wermut” or English “wormwood” (absinthe, *Artemisa absinthium*). It is a fortified wine, with herbs and spices. The main ones being angelica, aloe juice, cinnamon, cloves, coriander, gentian, hyssop, melissa, marjoram, sweet and sour orange peel, quinine, salvia, thyme, and absinthe.

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Topic 9. The perfume and cosmetic sectors.

9.1. The perfume and cosmetic sectors

Plants generate a considerable amount of antioxidants, preservatives, and synthetic colours. There is much demand for these both in the food industry (as we have seen before) and in the cosmetics industry. The perfume sector also uses important quantities of aromatic plants.

We can define phyto-cosmetics as the use of the active ingredients of plants for the care and appearance of skin and hair.

The use of different plants is determined by their physiological activity, which varies from plant to plant, so we can find a plant for nearly all our aesthetic needs.

The dermatological properties of plants are many and varied: tonics, astringents, anti-inflammatory, antiseptics, anti-scarring, cleansers, moisturisers, relaxants, emulsifiers, decongestant, refreshing, etc…

There is also a wide range of formats of cosmetic preparations. We can find preparations of plant extracts in creams, emulsions, lotions, gels, oils, soaps, deodorants, etc… cosmetics include the following type of products:

- essential oils
- perfumes and colognes
- beauty treatment, make-up, skin treatment
- sun-block and tanning preparations
- products for manicure and pedicure
- products for hair
- dental and mouth hygiene products
- products for shaving and aftershaves
- body deodorants
- bath products
- depilatory products
- other preparations

Spices used.

We are going to see some of the regulations edited by AENOR in December 2006 applied to raw materials for use in cosmetics. They also refer to the vegetable extracts used in the manufacture of cosmetic products.

- hydroglicolic extract of camomile (*Chamomilla recutita* L. Rauschert).
- hydroglicolic extract of calendula (*Calendula officinalis L*).
- hydroglicolic extract of rosemary (*Rosmarinus officinalis L*).
- hydroglicolic extract of ivy (*Hedera helix L*).
- hydroglicolic extract of green tea (*Camellia sinesis L*).
- hydroglicolic extract of butcher´s broom (*Ruscus aculeatus L*).
- hydroglicolic extract of oats (*Avena sativa L*).
- hydroglicolic extract of aloe (*Aloe vera L*).
- hydroglicolic extract of Indian chestnut (*Aesculus hippocastanum L*).

Other frequently used plants include:

- **Soya.** A Chinese plant known for over 5,000 years. It has been recovered by cosmetic laboratories because of its anti-ageing effects. It is rich in isoflavones.
- **Green tea**. An antioxidant against free radicals. Recently, white tea has also been incorporated into the cosmetics industry as it is thought to be more effective against free radicals.
- Botanical extracts of ***Gingko biloba*****, ginseng, lavender,** and **aloe vera**.
- **Camomile**, which is used to make creams for sensitive skins.

9.2. The cosmetic industry. The perfume sector

A A brief history of perfume.

To find the origins of perfume we must travel back to Ancient Egypt. Incense (the word is of Latin origin and means "through smoke") and myrrh were the basic ingredients used by the Egyptians to aromatise ceremonies, healing rituals, but also as a beauty complement for women. Furthermore, they had a complete process for the preparation of perfumes which consisted in impregnating rose leaves with oil to preserve their fragrance. They would also macerate aromatic plants in oil and then drain the oil onto a cloth.

Later, the **Greeks** inherited these techniques and proceeded to improve them. The Romans imported raw materials such as **myrrh and incense from Arabia** and brought other substances from **India**.

The fall of the **Roman** Empire brought about a decline in use of perfumes in the West. The custom lived on only in **Arabia**, where plant distillation techniques were developed. **Baghdad** became the city of fragrances. Other ingredients were discovered such as **musk,** which they mixed into the **mortar** used to build palaces and mosques.

During the **Middle Ages**, the **Crusader** period saw a rise in commerce and trade between **East and West** and perfume was rediscovered. However, its general use did not come until the **XVI** century when **Catalina de Medici** imposed the perfume fashion in **Paris**.

Later on, the **Industrial Revolution** saw large-scale commercialisation of perfume. Perfumiers specialised in chemistry so as to develop better products, and perfumes stopped being a fashion to become a basic requisite for the beauty criteria of the times.

At the beginning of the **XX** century, perfumes were given away in clothes shops, but gradually they began to be sold until the first exclusive perfume companies appeared.

With time, better techniques developed, and new ingredients for the making of perfumes were discovered. Nowadays, it is an important industry with millions of dollars in turnover and which designers depend on more even than on clothes.

B The structure of perfumes (the pyramid system).

For a long time, perfumes were thought to be evolving. But their fragrance and intensity were only due to evaporation, by this we mean volatility, and therefore to their gradual wearing off.

The **XX century** saw the start of perfume preparation using several fragrances. The first person to introduce this system of perfume preparation was André Guerlain in **1899**. From then onwards, a system known as the **"pyramid**" or **"three layer system**" was generally used. This structure divides a perfume's fragrances into three types: **high, medium, and low**.

High note: this corresponds to fragrances which are quicker to evaporate because they come from more volatile substances. They last a very short time and are used to make a first impression.

Middle note: this emerges when the high note has disappeared and is basically the "heart" of the perfume. It lasts about four hours and contains the main fragrances of a perfume.

Finally**, the low note**: this corresponds to the least volatile fragrances. Its purpose is to "fix" the perfume and give it a global harmony. It is the longest lasting and may last up to two days.

How long a perfume lasts depends on the environmental temperature and on body chemistry as well as on fragrance concentration. The higher the concentration of essential or fragrant oils, the more expensive the perfume is.

Perfume. This is the highest concentration of a fragrance. It usually contains 20% of active ingredients, essential oils or fragrances. It lasts from 4 to 7 hours.

Eau de perfume. These contain about 10% of essential oils or fragrances and once applied to the body, last between 3 and 5 hours.

Eau de toilette. These contain approximately 5% concentration and, on the body, last less than 3 hours.

Cologne. These are very light concentrations -2 or 3%- and last up to 2 hours on the body.

C **Raw materials in the perfume industry**.

a. Raw materials of vegetable origin.

Barks. A typical example is cinnamon, without forgetting the sassafras root (*Sassafras albidum*). Both contain safrol, which is used in the synthesis of aromatic compounds.

Flowers. These are the principal source of aromas. Such species as jasmine, roses, fragrant olive (*Osmanthus fragrans*), mimosa, nard, and orange flowers and ylang-ylang buds are all examples.

Leaves and shoots. We should highlight patchouli, salvia, violets, rosemary, and citrus leaves. Sometimes the leaves are valued because of their "green" aroma, as with tomato leaves.

Fruits. Fresh fruits like apples, strawberries, or cherries, do not give the required aroma when extracted, so they are synthesised. Some exceptions are Verbena exotica (*Litsea cubeba*), vanilla, and juniper berries. The most frequently used fruits concentrate aroma in their peel, for example oranges, lemons, limes, and pomegranates.

Resins. They have been highly valued since ancient times, incense being a good example. They are very aromatic and have antiseptic qualities. Many civilisations and cultures have used them as medicines or as condiments for food. Some resins used in perfume-making include laudanum, incense, myrrh, and Peruvian balsam. Pine and fir resins are a valued source of terpenes, which are used in the organic synthesis of other synthetic aromatic substances.

Roots, ryzomes, and bulbs. These sub-soil parts of the plant are also used in perfume, for example vetiver or ryzomes of the ginger family.

Seeds. For example, coriander, aniseed, cocoa, nutmeg and cardamom seeds.

Wood. Oils and distillations obtained from wood are basic to perfume-making. They provide the perfume's base. For example, sandalwood, birch, jacaranda, cedar, juniper, and pine.

These are some of the vegetable species used in perfume-making:

- Angelica (*Angelica archangelica*)
- Arnica (*Arnica montana*)
- Aromatic retama (*Spartium junceum*)
- Atlas cedar (*Cedrus atlantica*)
- Azahar (*Citrus aurantium*)
- Bitter orange (*Citrus aurantium* Amara)
- Blackcurrant buds (*Ribes nigrum*)
- Bladder wrack (*Fucus vesiculosus*)
- Camomile (*Chamomilla matricana*)
- Camphor(*Cinnamomum camphora*)
- Carrot seeds (*Daucus carota*)
- Celery (*Apium graveolens*)
- Cinnamon (*Cinnamomum zeylanicum*)
- Cloves (*Eugenia caryophyllata*)
- Estragon (*Artemisia dracunculus*)
- Eucalyptus (*Eucalyptus globulus*)
- Fennel (*Foeniculum vulgare* Dolce)
- Fir balsam (*Abies balsamea*)
- Hyacinth (*Hyacynthus orientalis*)
- Jasmine (*Jasminum grandiflorum*)
- Lemon (*Citrus limonium*)
- Marjoram (*Origanum majorana*)
- Mimosa (*Acacia cecurrens*)
- Mint (*Mentha viridis, M.spicata, M.piperita*)
- Mountain rue (*Ruta montana*)
- Narcissus (*Narcissus poeticus*)
- Nard (*Polianthes tuberosa*)
- Pennyroyal (*Mentha pulegium*)
- Peruvian balsam (*Myroxolon pereirae*)
- Sweet lime (*Citrus aurantifolia*)
- Tolu balsam (*Myroxolon toluiferum*)
- Tuya (*Thuya occidentalis*)
- Ylang-ylang (*Cananga odorata*)

Diamonds (Emporio Armani©):

- Raspberry
- Lychee
- Rose
- Patchouli
- Amber
- Violet
- Geraniol
- Linalool
- Eugenol
- Cinnamal
- Farnesol
- Limonene
- Citronellol
- Citral

b. Raw materials of animal origin.

Ambergris (grey amber). This substance is found in the entrails of cachalot whales. It is solid and opaque, grey in colour with yellow and black veins. It smells like musk. In perfume-making it is called amber, but we should not confuse it with the yellow amber used by jewellers. (Definition from the Real Academia Española dictionary).

Castoreum. A crass, pomade-like substance, of a chestnut colour and resinous appearance, having a strong and unpleasant smell. It is secreted by two glands found in the abdomen of beavers. It is an anti-spasmodic medicine.

Civet/ algalia. This is a sticky substance, having a consistency like honey's, which is originally white but turns brown. It has a strong smell and an acrid taste. It is produced by a feline of the *Viverridae* family, related to *Herpestes edwardsi*.

Musk. A greasy, sticky substance, of an intense hue, it is secreted through glands by certain mammals. Because of its spreadableness and aroma, musk is used as the base material for several cosmetic products and perfumes. Nowadays it is protected, so a synthetic form is used. Before, musk was obtained from the male *moschus moschiferus* (muskrat), but this meant killing the animal.

Although musk is only usually produced by young males, hunters were not usually very particular about the age and sex of the animals they killed. This led to a serious drop in numbers of the muskrat population and eventually led to a ban on hunting them. Because of its rarity and high price, and also for legal and ethical reasons, many perfume businesses will only use the synthetic component in their products.

However, the synthetic form stays in the environment for a long time, and residues have been found in human fat, mother's (breast) milk, and even at the bottom of the Great Lakes.

c. Other natural sources.

Lichens. For example, *Evernia prunastri* and *Pseudoevernia furfuracea*.

Algae. *Fucus vesiculosus*, commonly called Sargasso. They are not used very much because they are expensive and have a lesser yield than their synthetic equivalents.

d. Industrial perfume-making.

Another important sector in terms of the amount of raw materials it uses and the market it creates is industrial perfume-making. This industry manufactures all sorts of products such as detergents, air-fresheners, floor-cleaners, soaps, washing-up liquids, etc… These are some of the spices and constituents used:

The essential oils of lemons, bergamot, cedar, cypress, citronella, juniper, lavender blossoms, eucalyptus, geraniums, jasmine, lavender, lilac, linalool, marjoram, pine, rosemary, salvia, sandalwood, terpineol, thyme.

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