Essential oils and their development

RP Garry
JC Chalchat
Laboratoire de chimie
des huiles essentielles
ENS chimie, université
Blaise-Pascal de Clermont
Campus des Cézeaux
63177 Aubière
France

Essential oils and their development.

ABSTRACT
Different research focuses of the Essential Oils Chemistry Laboratory of the École nationale supérieure de chimie (Clermont-Ferrand, France) are presented. Interesting industrial applications of the research results in France and abroad are discussed.

Huiles essentielles et voies de valorisation.

RÉSUMÉ
Les différents pôles d'intérêt et de recherche du laboratoire de chimie des huiles essentielles de l'École nationale supérieure de chimie de Clermont-Ferrand sont présentés. La valorisation de ces études par des applications industrielles en France et à l'étranger est évoquée.

Aceites esenciales y vías de valorización.

RESUMEN
Los diferentes polos de interés y de investigación del Laboratorio de Química de los Aceites esenciales de la Escuela Nacional Superior de Química de Clermont-Ferrand son presentados. Se evoca la valorización de estos estudios por aplicaciones industriales en Francia y en el extranjero.

Fruits, 1995, p 453-458
***Version française* : p 485-487**

KEYWORDS
Essential oils, uses, non-food industries, chemical composition, chemical synthesis.

MOTS CLÉS
Huile essentielle, utilisation, industrie non alimentaire, composition chimique, synthèse chimique.

PALABRAS CLAVES
Aceites esenciales, usos, industria no alimentaria, composición química, síntesis química.

introduction

Some research topics investigated by the Essential Oils Chemistry Laboratory of the École nationale supérieure de chimie (Clermont-Ferrand, France) are:

– obtention and analysis of essential oils and aromatic and medicinal plant extracts;

– organic and bioorganic synthesis of essential oils and/or their constituents;

– correlations between the activities and compositions of essential oils and their constituents:

. antimicrobial and antifungal activity relative to this composition;

. stereochemistry-dependant odorant and aromatic activity;

– interesting industrial applications of the results in France and abroad.

These different topics are presented successively in the present paper.

essential oils

The importance of essential oils is partially illustrated in table I, within the framework of development-oriented agricultural research. Products extracted from turpentine, volatile constituents of resins, and those derived by solvent extraction of mosses and lichens, could also be considered under the essential oils category.

The tonnages seem low, but essential oil yields are often less than 1%. In addition, essential oils of rose, jasmine and neroli sell for more than 10 000 FF (before tax)/kg, which means that even relatively low quantities of these products have a high sales value.

These oils are mainly used in the perfume industry, with some used in the food industry. Note also that the quality, and thus the price, of an essential oil is dependent on the presence of trace quantities of special substances.

There are many economically interesting compounds with a wide range of different odours and flavours (fig 1). Hence, (+) and (-) limonenes, depending on their stereochemistry, have a hint of orange or lemon; p-menth-8-enes have orange (trans) or hydrocarbon (cis) characteristics; in the ketones, trans geranylacetone, menthones, isomenthone and nootkatone have hints of rose, round-leaved mint, and grapefruit, respectively.

Essential oil extraction (fig 2) is performed with aromatic plants, the raw material of this industry. Full description of these oils is essential for their regional, national or industrial development. Any oil that has not yet been described should be. If it has already been studied, its composition just has to be checked against that already described, according to certain standard parameters: genetics, soil, harvest period and distillation technique.

Table I
Data on the production, compositions and origins of the main essential oils.

Essential oils	*Tonnes /year*	*Plant raw materials*	*Main components*	*Producing countries*
Orange	12 000	Fruit peel	(+) Limonene	Brazil, USA, Israel, Italy
Lemon	2 300	Fruit peel	(+) Limonene	USA, Italy, Argentina
Citronella	2 300	Leaves/stems	(+) Ctironellal	China, Indonesia
Broad-leaved mint	2 200	Leaves	(–) Menthol	USA, France
Corn mint	2 100	Leaves	(–) Menthol	China, Brazil
Spearmint	1 400	Leaves	(–) Carvone	USA
Stock flowers	2 000	Buds	Eugenol	Indonesia, Tanzania, Madagascar
Eucalyptus globulus	1 500	Leaves	Cineol-1,8 ou eucalyptol	Spain, Portugal, Australia, China
Eucalyptus citriodora	800	Leaves	+/- Citronellal	Brazil, South Africa, India
Lavandin	1 000	Shrubs	Linalol, linalol acetate	France
Lavander	350	Shrubs	Linalol, linalol acetate	France, Bulgaria, Russia
Patchouli	500	Dried leaves	(-) Patchoulol	Indonesia, China
Sassafras	400	Tree	Safrol	
Turpentine	300 000	Tree	α and β-pinenes	USA, Canada, Russia, Morocco, Portugal, etc
Lichens	850	Lichens	Orcinols, β-orcinols	France, Morocco, Yugoslavia

organic and bioorganic syntheses

objectives

These syntheses are aimed at preparing compounds with novel extract properties, ie, fragrances, flavours, antimicrobial and antifungal effects.

syntheses

There is a wide range of different laboratory organic and bioorganic synthesis techniques, which can be classified in three categories:
– hydroformylations, hydroborations and acetalizations (enantioselective catalysts);
– oxygenations and photo-oxygenations;
– biotransformations.

These syntheses, generally chemistry-based, should be carefully performed when they concern development-oriented research, particularly with respect to problems of finding outlets for the created products, or the availability of field equipment. These second-level optimizations therefore have to be fully targeted before beginning to process the chosen aromatic or medicinal plants.

correlations between the chemical composition and the activity of these essential oils and/or turpentines (mono or sesqui)

The third topic could have more direct applications than the first two described earlier.

objectives

There are three objectives:
– to determine correlations between the activity and composition of essential oils, or between this activity and the molecular structure (stereochemistry);
– to obtain essential oils with high activity through auto- or photo-oxidation of the molecule; this study is being carried out in collaboration with a photochemical laboratory at université Blaise-Pascal (Clermont-Ferrand, France);
– to study monoterpenic models.

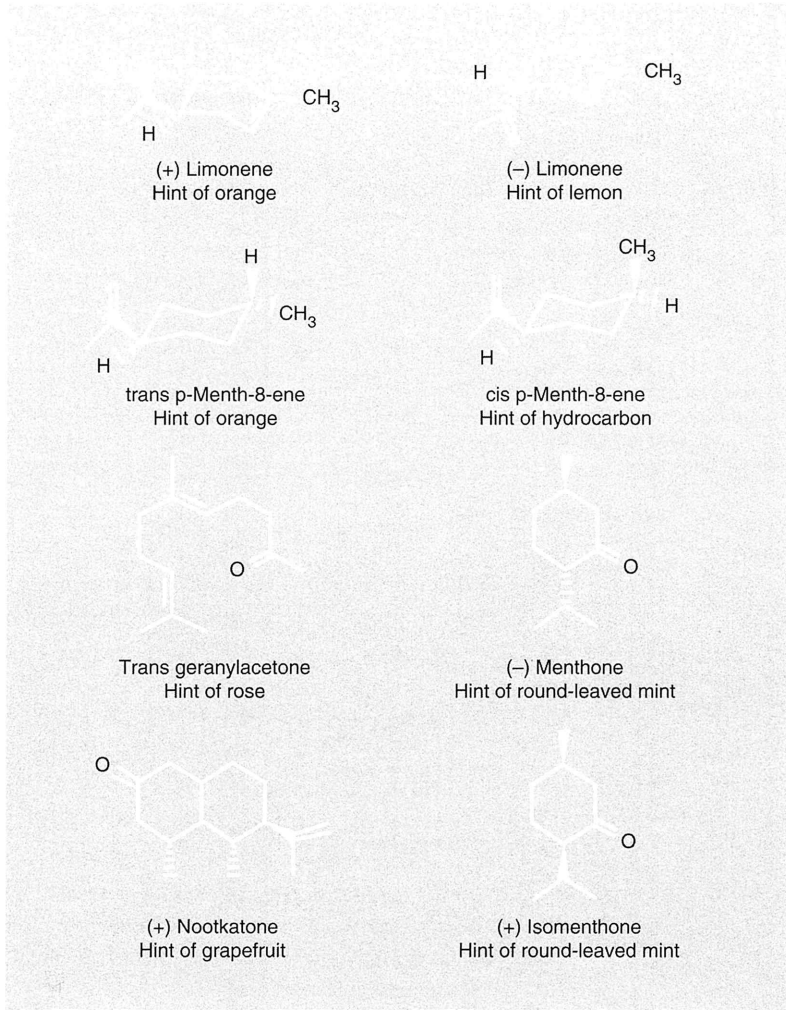

Figure 1
A few examples of molecules present in essential oils.

results

Various results have been obtained on this topic, such as:
– discovery of antimicrobial and antifungal activities which could be associated with the compositions of the essential oils concerned and their constituents; these studies were carried out in collaboration with two pharmaceutical laboratories of the université de Clermont I (France);
– stimulation of the activity of products through oxygenation of the essential oils.

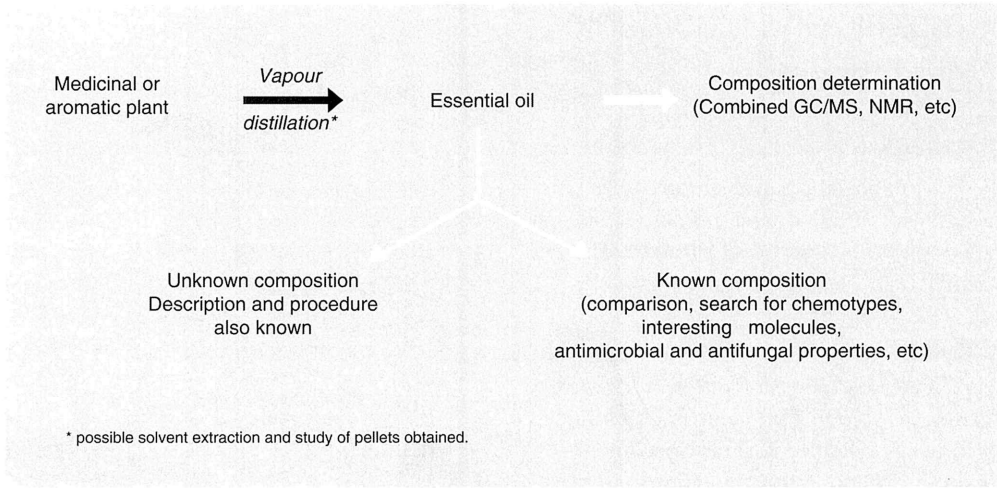

Figure 2
Procedure for studying essential oil composition from the raw material (an aromatic or medicinal plant).

Studies on relations between the structures of these molecules and their odours or flavours are under way.

optimal use of the results through applications

Optimal applications of the results as targeted by the laboratory, are on three levels, depending on the location of the partners concerned: regional, national and international.

regional applications

For the research laboratory considered here, located in the outskirts of Clermont-Ferrand, France, the Auvergne region is the closest area of activity.

The production and analysis of essential oils from plants that could be cultivated locally, eg, some conifers (pines, firs, spruces, Douglas firs, etc), and other species (eg, camomile, lovage, angelica, etc), in collaboration with farmers' and foresters' groups and associations, with the support of the Conseil régional, has prompted the creation of two small-scale essential oil production units: one is a cooperative (CUMA: Coopérative d'utilisation de matériel agricole) and the other a private limited company (SARL: Société à responsabilité limitée), and most of their production is exported abroad. The creation of such processing units provides an interesting development opportunity for this French rural area, thus stalling the depopulation process.

national applications

On the national scale, cooperation with AFOCEL (Association forêt-cellulose) was developed a few years ago, involving research on polyclonal varieties of common spruce, an ideal conifer for reforestation operations. Analytical identification of the recuperated essential oil is, in this case, associated with discriminating characters.

The laboratory research team has published a list of chemically-defined substances present in essential oils and extracts (86 oils described) (edited by the French Syndicat national des industries des arômes alimentaires, SNIAM, Paris). The laboratory has also been asked to investigate conditions required to obtain and to describe the composition of various essential oils that are currently major French imports.

international applications

Internationally, the concerns of essential oil-producing countries in Africa are often similar to those of French manufacturers, eg, the goal of producing an essential oil locally in order to reduce imports of perfume components used in soaps.

A 250 liters laboratory pilot processing unit makes it possible to quickly switch from the experimental to the industrial scale. This simple

technique can be readily adapted to meet the needs of developing countries.

More generally, many other research focuses of the Essential Oils Chemistry Laboratory of the École nationale supérieure de chimie (Clermont-Ferrand, France) also have interesting industrial prospects:
– organic and bioorganic syntheses, including auto- and photo-oxidation of essential oils or terpenes, for instance;
– enzymatic esterification of essential oil constituents: products prepared by this laboratory process can be called natural products;
– correlations between the chemical composition and antimicrobial and antifungal activities of essential oils are of considerable interest for African countries; a medicinal plant can thus be processed more quickly, but the activity of the resulting oil often differs from that of the whole plant, and its use should be carefully controlled.

conclusion

There are undoubtedly many other alternatives for the development of aromatic plants than extracting and processing their essential oils. The cases discussed here are only examples, basic and applied research thrusts; their potential applications were highlighted. Some of them are easier to achieve than others, but all projects require collaboration on a national and international scale. There are already close relations between research teams, particularly with the laboratory of Professor Lamaty at the Université de Montpellier II (coordinator), and with other laboratories, to undertake a census and promote the development of aromatic plants of sub-Saharan Africa.

There are three overall motives behind the Essential Oils Chemistry Laboratory of the École nationale supérieure de chimie (Clermont-Ferrand, France) within the framework of European or AUPELF (Association of partially or wholly French-language universities) contracts, in its programmes with African partners: training and research, since the laboratory is a university structure, as well as development based on potential industrial applications, carried out jointly with the concerned countries.

appendix 1

Documents published by the Essential Oils Chemistry Laboratory of the École nationale supérieure de chimie (Clermont-Ferrand, France), since 1990

Chalchat JC, Garry RP (1993) Pentan extracts of roots of *Angelica archangelica* L of France. *J Ess Oil Res*, 5, 447-449

Chalchat JC, Garry RP (1993) Bioconversions de terpènes: obtentions de molécules parfumantes ou aromatisantes. *Riv Ital EPPOS* 9, 29

Chalchat JC, Garry RP, Bastide P, Fabre F, Malhuret R (1991) Corrélation composition chimique / activité antimicrobienne. V. Contribution à la comparaison de deux méthodes de déterminations des CMI. *Plantes Méd Phytother* 25 (4), 184-193

Chalchat JC, Garry RP, Gorunovic MS (1994) Contribution à l'étude chimiotaxonomique des pins endémiques des Balkans: composition chimique de l'huile essentielle de *Pinus heldreichii* Christ, pinacées différentes selon le site, la partie et l'âge des individus étudiés. *Pharmazie* 49, 852-854

Chalchat JC, Garry RP, Gorunovic MS, Bogavac PM (1992) Composition of the Essential Oil of *Ferulago sylvatica* (Besset) Reichenb (*Apiaceae). Pharmazie* 47, 802-803

Chalchat JC, Garry RP, Lamy J (1994) The influence of harvest time on yield and composition of *Artemisia annua* oil produced in France. *J Ess Oil Res* 6, 261-268

Chalchat JC, Garry RP, Lecomte E, Michet A (1991) Hydro-formylations of some mono- and sesquiterpenes from essential oils. *Flavour Fragrance J* 6, 179-182

Chalchat JC, Garry RP, Mathieu JP (1994) Analytical study of the volatile fraction from Honduras styrax, *Liquidambar styraciflua* L. *J Ess Oil Res* 6, 73-75

Chalchat JC, Garry RP, Michet A (1991) Chemical composition of *Calendula officinalis* essential oil. *Flavour Fragrance J* 6, 189-192

Chalchat JC, Garry RP, Michet A (1992) Hydroborations of some mono and sesquiterpenes from essential oils. *Flavour Fragrance J* 7, 107-110

Chalchat JC, Garry RP, Michet A, Benjilali B (1994) Essential oils components in sawdust of Cedrus atlantica from Morocco. *J Ess Oil Res* 6, 323-325

Chalchat JC, Garry RP, Michet A, Benjilali B, Chabart P (1993) Essential oils of Rosemary (*Rosmarinus officinalis* L). Chemical compositions of oils of various origins (Morocco, Spain, France). *J Ess Oil Res* 5, 613-618

Chalchat JC, Garry RP, Michet A, Gorunovic M, Stosic D (1991) Contribution to chemotaxonomy of *Artemisia annua* L. *Acta Pharm Jugoslavia* 41, 233-236

Chalchat JC, Garry RP, Michet A, Peyron L (1990) Chemical composition of oils and extracts from *Juniperus* woods. *J Ess Oil Res* 2, 231

Chalchat JC, Garry RP, Michet A, Veschambre H (1992) Bioconversion of terpinolene and its 4,8-epoxide. *J Ess Oil Res* 4, 235-238

Garry RP, Chalchat JC, Michet A (1991) Huiles essentielles de résineux: nouvelles matières premières pour la parfumerie et l'aromathérapie. *Riv Ital EPPOS* 4, 37-49

Gorunovic MS, Bogavac PM, Chalchat JC, Garry RP (1992) Analysis of the essential oil of *Artemisia lobelii* All. *Pharmazie* 47, 803-804

Gorunovic MS, Chalchat JC, Garry RP (1995) Contribution à l'étude chimiotaxonomique des pins endémiques des Balkans: composition chimique de l'huile essentielle de pin noir illyrique, *Pinus nigra* Arnold ssp *nigra* (Arn, Hayek), pinacées d'origine locale, différentes selon la partie et l'âge des individus étudiés. *Pharmazie* 50, 281-283

Gorunovic M, Panov I, Chalchat JC, Garry RP, Michet A (1991) The quality of wild-growning carawey (*Carum carvi* L essential oil) from Montenegro. *Acta Pharm Jugoslavia* 41, 267-271

Menut C, Bessière JM, Lamaty G, Amvam Zollo PH, Boyom-Fekam F, Chalchat JC, Garry RP (1992) Aromatic plants of Tropical Central Africa. VII. A comparative study of the volatil constituents of the stem barck of *Enantia chloranta* Oliv and *Xylopia staudtii* Engl & Diels from Cameroon. *Flavour Fragance J* 7, 259-261