Highlights From the XXXIst International Days of Essential Oils & Extracts

Raw materials from South America, fern aromas, floral waters, regulatory pressures, the evolution of perfumery and more

Jean-Jacques Étienne

The XXXIst International Days of Essential Oils & Extracts, which took place last fall in Digne, France, provided an opportunity to learn more about natural products, creativity and regulatory threats to the industry.

Jean-Claude Elléna (Parfums Hermès); all photos courtesy of Patrick Pellerin (president, scientific committee, APPAM).

Raw Materials From South America

Peru is the third largest country in South America in terms of surface area, explained Y. Seugnet and S. Dompnier (Uniquim), during their talk. Peru's 30 million inhabitants mainly derive their income from marine and agricultural resources. The two main aromatic plants in the country are Peruvian pepper (*Schinus molle*) and ambrette (*Abelmoschus moschatus*).

Schinus molle (Anacardiaceae), frequently called "false pepper," is a 6–15-meter-high tree with persistent, finely indented leaves that smell peppery, having the appearance of a weeping-willow. Blossom comes in small clusters of white flowers, which yield bunches that resemble mini grapes. These red grains are collected by hand, selected, passed through a sieve, washed and dried. Then they are placed in bags and they will have a 55-day boat trip, if they are sent to France.

The essential oil is obtained through steam distillation (7 h) with a yield of approximately 3–5% on dry matter. Its content is rich in hydrocarbons, particularly:

- α-phellandrene (21.3%)
- β-phellandrene (8%)
- myrcene (20.3%)
- (+)-limonene (9.1%)

The name ambrette is taken from the Arabic word *anbar*, meaning amber, due to its amber smell. The essential oil is obtained from *Hibiscus abelmoschus* moschatus (Malvaceae) seeds. This plant originates from India and its cultivation is quite difficult: the flower only lives one day and is highly dependent upon specific weather conditions. Seeds are collected at the end of November from capsules developed inside the flower. Oil yield is about 0.2–0.6% on dry matter for a 24-h distillation. The essential oil is of interest for amber fragrances (oil content of ambrettolide is up to 10%) that evoke ambergris and some musk notes from animal origin which are now unavailable.

Uruguayan *Eucalyptus globulus* and Petitgrain

In direct contrast to the mountainous country of Peru is the flat country of Uruguay. The country's 3.5 million inhabitants are primarily engaged in animal breeding—bovine and ovine—with a strong export commerce of beef and wool, while a growing tourist trade is in full development.

A single local distiller is in the country at the moment, according to presenter C. Monin (Acphytaroma). This distiller is mainly interested in *Eucalyptus globulus* essential oil. This tree, which requires large quantities of water and is subject to parasitic diseases, is grown for the paper industry, which requires trees with a 30–40-cm diameter, while younger trees (trunks with 7–8-cm diameter) are collected for distillation. Yield in essential oil is approximately 0.35% of the starting raw material, which can decrease by half in the case of excess dryness (composition can include as much as 78% 1,8-cineole). Production of the oil is around 70 t/year; the essence faces strong competition from Chinese-manufactured alternatives.

The country's Rìo Negro region grows many citrus species. The technical facilities available for eucalyptus have been used for the preparation of a petitgrain essential oil from buds and terminal branches. The oil yield is 0.20% and the quality of the essence obtained is very close to those of the Mediterranean sources (more than 46% limonene).

Many other products can be produced in Uruguay from stevia, mate, chamomile and marigold. These possibilities are under study in collaboration with the University of Montevideo. Could Uruguay become a new key supplier for essential oils?

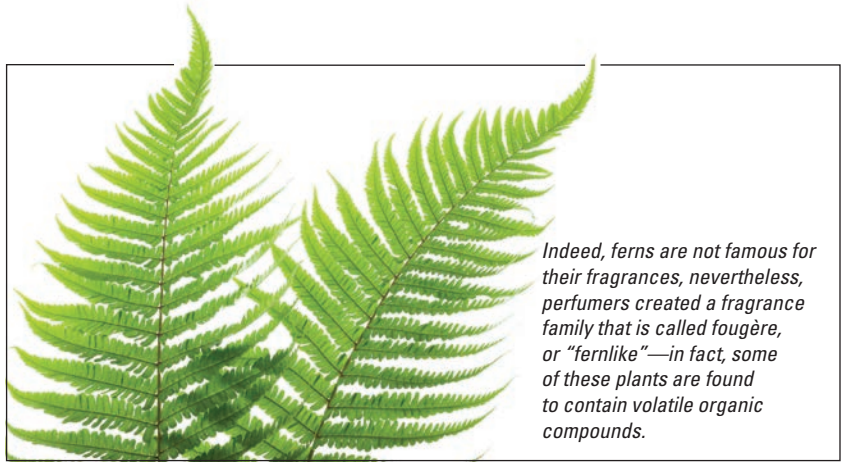
Ferns: Analysis of Scents and Perfumery

Indeed, ferns are not famous for their fragrances, noted F. Fons (Montpellier III University). Nevertheless, perfumers in their classifications, created a fragrance family that is called *fougère*, or "fernlike." In fact, some of these plants are found to contain volatile organic compounds. *Adiantum capillus-veneris* contains polyketide compounds, *Blechnum spicant* contains aromatic compounds, and *Dryopteris filix-mas* contains terpene

and sesquiterpene derivatives.

An exhaustive study leads one to consider several categories, in fact four profiles, according to their composition, according to Fons:

- Profile 1, in which fatty acid derivatives are dominating, for example *Adiantum capillus-veneris*, which shows nearly 88% of derivatives such as amides (lauric acid, nonanoic acid), aldehydes (heptenal, decenal, decadienal)—not very attractive, olfactorily, indeed.
- Profile 2, in which fatty acid derivatives and aromatic substances are present, including phenyl acetaldehyde (floral, hyacinth, lilac) and octane-3-ol (fungus), as in the case of *Athyrium filix-femina*.
- Profile 3, in which fatty acid derivatives and terpene derivatives dominate, as with *Dryopteris filix-mas* (filicinic acid, 16.7% and nerolidol, 38.7%).
- Profile 4, in which terpene derivatives dominate, as in *Oreopteris limbosperma*, which is rich in α-terpineol (13.5%), nerolidol (14.7%), β-caryophyllene (5.0%) and which expresses a citric-woody fragrance softened by benzaldehyde (3.6%).



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A great deal of aromatic structures are found in ferns, among which are terpene derivatives, aldehydes and alcohols derived from fatty acids—and even some carotenoid derivatives like α- and β-ionones.

"If God would have given a fragrance to ferns, they would have the smell of *Fougère Royale*," declared Paul Parquet (1862–1916), who was the creator, in 1882, of this fragrance for the brand Houbigant. Other "ferns" have included *English Fern* (Penhaligon) and *La Fougeraie Au Crépuscle* (Coty). The classification established by SFP (Société Française des Parfumeurs) considers *Jicky* (Aimé Guerlain, 1889) the emblematic scent in this category, around which are gathered fragrances with profiles as varied as floral, amber and spicy. They are frequently more masculine than feminine, as with *Monsieur Rochas*.

Thanks to the slightly mysterious plants, with images of nature and woodland atmosphere, perfumers found their inspiration, allowing them to reveal "the fragrant soul of ferns."

Floral Waters

Counter to conventional wisdom, the introduction of distillation should not be attributed to Arabs, but, 4,000 years previous, to inhabitants of Indus Valley, where a still of terra cotta, among other perfumery objects, has been discovered. Later, added P. Pellerin (president, scientific committee APPAM), the Virgin Mary, in Alexandria, created the so-called *bain-Marie* (French term for water-bath) and the *tribikos*, a kind of still equipped with three receiving flasks. Later still, Jabir Ibn Hayyan (also known as Geber), born in Iran in 721, reported his works using distillation.

Rose water is one of the ingredients named in the famous ointment formula, *Galien's cerate*, but when "perfumed waters" are referred to, it is not clear if they resulted from hydrodistillation. The development of floral waters took place in the Arab world and were spread to Europe by Crusaders.

A complex terminology can cause confusion. If "aromatic waters" generally refer to "distillate," "hydrolate," "flower water" or "floral water," they must be differentiated from "aromatized waters," either "natural" or "reconstituted."

These waters generally result from industrial hydrodistillation, but sometimes from family distillation with home stills. In these processes, matter is boiled in water, which will transfer odorants and finally lead to the floral water and the essential oil.

Modern methods presently under development aim at not adding water, but using the plant water itself. This is the VMHD (vacuum microwave hydrodistillation) process (patented by Archimex). In this method, the plant material alone (without addition of water) is heated with a microwave source under vacuum in order to lower the boiling point of the water. Several short cycles (some minutes) are repeated until total exhaustion of the source material. The interest of this process stands in the fact that the water recovered is the constitutive water of the plant. A similar process, DIC (*détente instantanée contrôlée*, or controlled instantaneous expansion), developed by K. Allaf, consists of heating the raw vegetal at 100°–120°C under pressure (4–5 bars), then subjecting the material to a vacuum phase which induces a quick bursting of material (some minutes), providing a water that is the constitutive water of the plant.

> The SCCS opinion clearly mentions that 1–3% of the public is affected by allergies originating in perfumes and that the situation for many years now seems to be stabilized. Is it appropriate, then, to implement such a restrictive regulation? We, as a population, do not face "a priority health problem."

Floral water components are polar, and mainly alcohols: their determination is usually done via an extraction with pentane, followed by solvent elimination. *Rosa damascena* water is richer (420 mg/l) than *Rosa centifolia* water (90 mg/l).

Housekeeping of such waters is somewhat delicate: They must be cleaned of every vegetal residue and preferably distributed in small content articles.

Mediterranean countries are the most important consumers of such classical waters. Their production is significant: for example, 1,500 t/year of orange flower water in Tunisia. Cosmetologists are interested by organic-certified waters or by constitution waters that are particularly rich in active ingredients, while perfumers look to them for new approaches to create non-alcoholic perfumery products.

Improving and Mechanizing Harvest Efficiency: Black Currant Buds, Narcissus Flowers and More

Keeping natural products economically viable remains a major priority, noted C. Sireyjol (IFF LMR). In Burgundy, black currant buds are available in winter (except when weather conditions are uncooperative). Cutting the branches and recovering the buds by hand allows one to obtain 1 kg of buds for 5 h of work. The application of harvesting equipment conceived for cereals allows for more efficient cutting of the branches and recovery of the buds, followed by a sieving of the buds, which nets 100 kg in the same 5-h period.

Narcissus is native to the French region of Massif Central (medium altitude: 1,000 m). Harvesting of the flowers was done by hand with a large comblike device; later, this tool was mounted on a cart that was pushed by peasant workers, which improved the recovery of flowers. Today, a machine that cuts just the flowers and deposits them immediately in bags has been developed. While the "primitive" comb was able to collect 30–50 kg of flowers per person per day, and the rolling cart 100–150 kg, contemporary equipment is able to collect between 500 kg and 1,000 kg of flowers per day. Similar approaches are being studied for other sources such as key materials, including iris, rose and geranium to ensure that naturals keep a competitive value in the coming years.

Meanwhile, B. Candaele (Crieppam) noted that the 19th century process of cutting lavender flowers and distilling them in the fields with stills transported on the back of mules was replaced in the 20th century with a more "sedentary" organization. The stills, initially placed in the open air, were progressively equipped with a grid in their bottom, then with independent heating equipment, and soon were gathered and sheltered in a dedicated building.

Cultivation moved from uncultivated and haphazard growing to organized, "square" growing, which allowed for the easiest cutting of the plants. Later, water-bath equipped stills appeared (Eysseric-type), followed by mechanized cutting.

In the 1990s, the "green process" appeared: The plant was cut, crushed and received in a mobile container equipped in order to be used as the distillation vessel. Today, improvements are to be found in the fields with high-performance machines (digging, grass cutting, planting, precise driving) and distillation techniques (heat-sparing, recycling of matter). In the industry's delicate present situation, products' competitiveness must be preserved. It is necessary to share equipment and develop business contracts/conventions between producers and clients/buyers.

Identity of Corsican Spirits: Liqueurs and Brandies From Myrtle and Citron

Two Corsican plants traditionally used for the preparation of liqueurs and brandies—myrtle (*Myrtus communis* L.) and citron (*Citrus medica* L.)—have been studied, said J. Paolini (Universita di Corsica P. Paoli). Myrtle (dried plant, essential oil of bays and leaves, hydrolates, extracts, etc.) has been used since antiquity as a disinfectant and an antiseptic; its antimicrobial and antioxidant properties have been studied recently. Spontaneous, uncultivated growth of the plant makes its supply vulnerable. An organized cultivation is now in the planning stages.

Two varieties of myrtle, one of which is primarily distributed on the north and northwest of the Mediterranean (Morocco, Portugal, Spain, France [Provence] and Albania), is characterized by its composition of 1-8 cineole, α-pinene and myrtenyl acetate. The other variety is found in the east (Corsica, Sardinia, Tunisia, Lebanon and Iran) and contains cineole and pinene, but no myrtenyl acetate.

Citron (*cédrat*) has also been used since antiquity in religious contexts (ex: Jewish Feast of Tabernacles) and pharmaceutical preparations (antiseptic, wound healing). Today, it is used for the preparation of brandies. The Corsican variety, with a sweet pulp, is characterized by γ-terpinene and limonene; the Calabrian variety, *diamante*, is characterized by geranial and neral.

The purpose of recent studies sought to determine if the chemical composition (phenols and terpenes) could stand as a quality marker. Appropriate analytical methods (GC-MS, GC-FID, SPME, etc.) performed on fruits, essential oils, liquors and brandies evidenced:

- For myrtle, a homogeneous composition of the essential oil (for 16 different locations in Corsica) in 1,8 cineole and α-pinene (and absence of myrtenyl acetate) was found in the volatile phase of liquors and brandies. These terpene markers are the signature of a Corsican-Sardinian origin; a distinction between Corsica/Sardinia is possible in comparison to other origins with the help of phenol markers.
- For citron products, terpene markers have been identified.
- Aging of products does not induce significant changes in the results obtained.

This chemical approach is able to show a signature of authentic local origin of products.

The Immense Threats of Legal Requirements Impacting Essential Oils: an Update

Depending upon the type of products to which they are added—pharmacy products, veterinary products, cosmetics, household products, aromas, phytosanitary products, aromatherapy preparations, etc.—essential oils have to satisfy the corresponding regulation, noted Catherine Gadras (Robertet). As far as the F&F industry's activities are concerned, the regulatory framework is as follows:

From left, Francis Thibaudeau (European Federation of Essential Oils/Robertet), Philippe Massé (Prodarom) and Jean-Jacques Étienne

- As chemical products, REACh regulation 1907/2006 and classification, labeling and packaging (CLP) requirements 1272/2008
- As cosmetic products, European Directive 76/768 and the new regulation "Reglement" 1223/2009
- And, in France, the Public Health code and ANSM (ex AFSSaPS) recommendations

These must also be taken into account:
- IFRA Code of Practices and recommendations
- The recently published European Commission's Scientific Committee for Consumer Safety opinion concerning allergens (*http://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_102.pdf*).

In the scope of REACh, essential oils have been classified UVCB (unknown or variable composition, creation products or biological materials) and must be registered from a production quantity above 1 t/year. To satisfy the CLP requirements, essential oils are considered mixtures of substances containing some dangerous components: This classification arrives frequently at an overestimation of real dangers.

For example, the following is the classification of laurel leaf essential oil:
- H226: flammable liquid and vapors
- H304: can be mortal in case of ingestion and penetration inside respiratory system
- H315: provokes cutaneous irritation
- H317: can provoke a cutaneous allergy
- H341: can induce genetic abnormalities
- H351: can provoke cancer
- H411: toxic for aquatic organisms, generates long-term ill effects

As far as the Cosmetics Directive 76/768 is concerned, it is necessary to take into account prohibitions of Annex II and restrictions of Annex III, including labeling of the 26 allergens. In France, Agence Nationale de Sécurité du Médicament (ANSM; previously AFSSaPS) published three recommendations about essential oils: May 2008, evaluation of cosmetic products containing essential oils; October 2008, about camphor eucalyptol and menthol; and in October 2010, evaluation of the risk due to essential oils in cosmetic products.

The IFRA Code of Practice has made it possible to give recommendations about the use of certain essential oils and to indicate appropriate concentrations according to products concerned (with the help of QRA method). These recommendations are updated in relation with newly established data. For example, massoia oil is forbidden (as massoia lactone was found as an allergen); jasmine absolutes (*grandiflorum* and *sambac*) are subject to restrictions; and *Rosa damascena* essential oil and absolute are restricted to take in count the presence of methyl eugenol.

Last, but not least, SCCS, which in 1999 (then known as SCCNFP) obtained the labeling of 26 allergens found in perfumes, has published an "Opinion" increasing to 179 the number of cutaneous allergens. Twelve molecules (already included in the previous 26) and eight natural products (cananga, clove, jasmine, santal, etc.) are of particularly high concern. Complete prohibition of HICC (Lyral) is required. For the eight natural extracts and the 12 molecules (including the esters of alcohols

C. Sireyjol (IFF LMR)

listed), the SCCS asks a limit of 100 ppm in the finished products put on the market. This level of 100 ppm is considered low enough neither to induce sensitization nor induce a reaction for already sensitized subjects.

Among the "12 molecules" are found eight substances (cinnamaldehyde, cinnamic alcohol, citral, coumarin, geraniol, eugenol, isoeugenol and farnesol), which are quite common components in essential oils—and, by extension, their esters—opens the way to very difficult approaches. To give a rough idea of the challenges, one can consider a cologne containing a 12% "classical" composition; to satisfy these requirements, it should only contain 0.6% concentration to satisfy the 100 ppm requirement in finished products.

These requirements, if implemented as-is, are consequently an immense threat to the perfumery industry.

This threat was the subject of a discussion moderated by this author and featuring Philippe Massé (Prodarom), Francis Thibaudeau (European Federation of Essential Oils/Robertet) and attendees.

The author noted that the introduction of the SCCS opinion clearly mentions that 1–3% of the public is affected by allergies originating in perfumes and that the situation for many years now seems to be stabilized. Is it appropriate, then, to implement such a restrictive regulation? We, as a population, do not face "a priority health problem."

Thibaudeau noted that a great risk stands in the fact that these SCCS requirements be introduced directly in the new Réglement (to be fully implemented from July 2013) by Directorate General SANCO without any step of reflection/discussion either with partners (industry, Cosmetics Europe (formerly Colipa), IFRA, etc.) or parliamentary bodies. Consequently, the highest level of exchanges seems necessary.

Meetings and exchanges are at present running between IFRA and DG SANCO in order to show that this question is not an urgent health problem and that the industry is among the most responsible ones, noted Massé. He added that the industry's decline would generate around 300,000 lost jobs.

Nevertheless, Jean-Claude Bayle (IFF-LMR) suggested that, beside all these major inconveniencies, these requirements can also be an impulse for creativity.

Can the "common sense" of all partners find a way to an acceptable outcome in this delicate situation?

ERINI Platform

The ERINI platform (European Research Institute on Natural Ingredients) has been created to be a center of excellence in the field of analytical chemistry, devoted to natural substances used in perfumery, cosmetology and food aromas, according to presenter C. Roy. ERINI has been created by Pôle de Compétitivité Parfums Arômes, Prodarom, Centre National de la Recherche Scientifique, UNICE (Nice University) and other partners. Its main targets are:

- investigating substance degradation mechanisms;
- identification of components; and
- natural substances authentication and traceability.

Its technical/scientific equipment comprises:

- GC-FID, GC-MS, for the analysis of essential oils;
- GC-MS/MS for the evaluation of pesticides in natural extracts; and
- UPLC-QTOF to identify phytochemical markers.

An example was described in detail showing how this last technique was able to evidence a phytochemical marker, anisatin (a toxic material), found to be present in the Japanese star anise samples, while absent in the Chinese star anise samples.

From the Molecule to the Smell, Aroma Perception

The physiological process for perceiving odors comprises three steps, according to speaker J. Golebiowski (Nice-Sophia-Antipolis University). First, the odorant combines with a protein—olfactory binding protein (OBP)—which stands in the depth of the nasal mucous and whose chemical affinity (lipophilic) and structural configuration permits it to play the role of a messenger. In a second step, the messenger will deliver the odorant to an olfactory receptor (OR), which induces an ionic reaction by the neuron, which is an electrical answer sent toward the olfactory bulb, either in the limbic region (memory) or the orbitofrontal cortex (emotions). The reaction of the receptor induces an increase of Ca^{++} that can be followed by fluorescent probes.

A single odorant is able to stimulate several olfactory receptors while a single receptor can be stimulated by several different odorants. The impact of several odorants has been studied; the results, which are extremely complex, can be elucidated thanks to computational microscopy.

The third step of odor perception deals with metabolism, which can modify the odorant itself, which consequently becomes able to stimulate another olfactory receptor in order to avoid an effect of saturation—a kind of cleaning effect.

Olfactory studies have tended to explore the relations between molecular structure and odor—the same smell of musk, for example, being observed for molecules with different structures, while some molecules with very similar structures can lead to different smells.

The perception of aromas is linked to the availability of smelling and/or palatable molecules, noted E. Guichard (INRA, CSGA). Recent studies aim at building a rational approach to obtain an aroma/sapid/flavorful effect. Odor molecules are identified by GC. The complex medium in which they stand is able to modify their properties according, for example, to the partition ratio (liquid/vapor) or the chemical interactions that can occur (ex: smelling molecule affinity with some macromolecules), or even physical circumstances (solubility in lipids). Also, when chewing, other interactions can also occur (saliva effects).

Expression of aromas in the mouth with cheese has been studied. This has led to the association of the perception of certain aromas (ethyl propanoate, 2-nonanone) with some physical characters (rigidity, pasty, gel). With the same approach, the influence of fatty matter content upon the expression of salt in the mouth and the effects of thickening agents on the perception of strawberry aroma in yogurts have been elucidated.

Consequently, a methodical comprehension of the universe of odors, which has, until now been seen as highly subjective, is increasingly quantifiable.

Perfume, the Art of Illusion

Is the perfumer an illusionist, an odor conjurer? As an introduction, Jean-Claude Elléna (Parfums Hermès) showed how perfume evolved from the 18th century—a period when only a few raw materials were available, making all perfumes nearly identical—to the 19th century, when chemistry developed and offered a great quantity of products. This process was similar to the explosion of available colors around 1850, which stimulated so deeply Degas and Monet.

To illustrate Pablo Picasso's dictate that, "Art is the lie that tells the truth," Elléna offered the example of *Diorissimo* by perfumer E. Roudnitzka. This, said Elléna, is the most beautiful lie about lily of the valley ever created.

Since the 1980s, the trend has been to escape from familiar fragrances (rose, lily of the valley, ylang-ylang, etc.) and explore further domains (papaya, caviar, truffles, etc.). The purpose was to change words into odors, to be closer to the smell evocated.

For the fragrance series *Un Jardin Sur*, Elléna explained how he conceived *Un Jardin sur le Toît* ("A Garden on the Roof"), combining white flowering plants and trees (pear and apple trees, magnolia, white rose, etc.) that grow on the flat roof of Hermès' main offices in Paris. Today, the expectancy for fragrances depends largely upon the culture of social groups, religion, their habits and customs, Elléna explained. For example, a comparison between Japanese and French expectancies is as follows:

French consumers	***Japanese consumers***
• mixing	• juxtaposition
• complexity	• simplicity
• richness	• naturalness
• strength	• presence

The reference to simplicity, counter to tastes among Europeans, is perceived and appreciated by Asian consumers and can be interpreted, for example, as a kind of "blank," a component that avoids intrusiveness.

As a result of these differences, Elléna noted there are still many new ways to explore olfactory arts

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