

Beyond BRIC: Traditional and New Natural Raw Materials and Supply Issues

Ingredients and sourcing in Indonesia, Tahiti, Réunion and Maghreb—highlights from Journées des Huiles Essentielles and Congrès International Plantes Aromatiques et Médicinales

Jean-J. Etienne; photos by Patrick Pellerin, chairman of the APPAM scientific committee

The 30th Essential Oil Days (Journées des Huiles Essentielles [APPAM]) and International Congress of Medicinal and Aromatic Plants (Congrès International Plantes Aromatiques et Médicinales [PAM]), co-organized by APPAM and Pole PASS (competitive cluster for perfume, aroma, smell and flavors), were held jointly recently in Digne-les-Bains, France, serving as an opportunity to discuss ingredients produced in developing countries and broader issues surrounding ingredient trade and quality.

Jean-Pierre de Mattos (Mane) discussed various consumer preference trends. One style, dubbed “Tribal Forces,” will introduce spicy, leathery and woody notes for men, according to de Mattos, increasing the demand for patchouli, sandalwood and oud. The “Eco-Luxe” concept, meanwhile, will be characterized by new green and sparkling notes for men, including mature lemon, basil and fennel notes. For women, this trend will manifest with fresh grass, hyacinth and springlike notes. Female consumers will also seek out so-called “new chypres.”

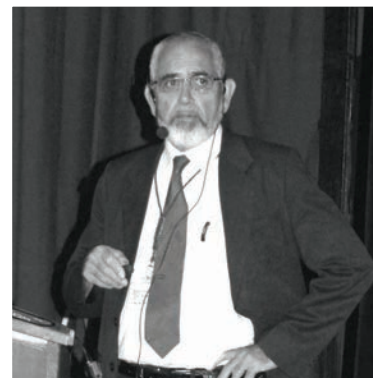
Inevitably, naturals associated with these fragrance trends will face new demands, and so de Mattos reviewed the present situation of several ingredients:

- The availability of Florida grapefruit is compromised due to parasitical illness and hurricanes in the years 2004–2005
- Cinnamon and nutmeg have been impacted by regulatory restrictions concerning safrole content
- Oud from Indonesia and Malaysia face extinction
- *Rosa centifolia* production is nearly limited to the Grasse region

De Mattos noted that there are solutions



J.P. de Mattos (Mane) discussed the challenges facing some key natural materials.



Gérard Bondoux (Waters) discussed a new method for detecting furocoumarins.



M. Langasque (Diffusions Aromatiques) explained the complexities of ingredients trading.



Hugues Brévard (Robertet) discussed aroma molecule analytical techniques.



Jacqueline Smadja (University of La Réunion) discussed the aromatic and medicinal plants on La Réunion (Bourbon) Island.



S. Zrira (Hassan II Institute, Morocco) discussed the aromatic and medicinal plants of the Maghreb region.



P. Raharivelomanana. (University of French Polynesia) gave a talk about the aromatic and medicinal plants in French Polynesia.



Didier Nicol (AFNOR) discussed the standardization of essential oils.



Farid Chemat (University of Avignon) discussed eco-extraction.

to overcome these sourcing difficulties, for example fractionation of cinnamon essential oil and development of oud growing in Laos. Appropriate solutions exist to face every particular case, he explained, and it is possible to anticipate risks linked to a source's disappearance, emerging regulatory requirements, wild cost variations, etc., allowing formulators to create with natural raw materials in a quieter climate.

In addition to securing traditional materials, de Mattos opened a window on new naturals developed for sustainability of source and social development of the people involved in their production:

- Namibia myrrh: This material is collected by the Himba people of the region, who are paid for their labor. The resulting essential oil is Ecocert-labeled.
- Palo Santo wood: This Ecocert-labeled material is collected by the Sancán people of Ecuador.

De Mattos concluded by noting that consumers' expectations are pushing the industry to find answers, while also "controlling the risks" for the vegetal world and the people who live in it.

Aromatic and Medicinal Plants of French Polynesia

French Polynesia comprises 120 islands distributed in five archipelagos that represent some 3,521 km² of land mass spanning 5 million km² of the Pacific Ocean.

According to Phila Raharivelomanana (University of French Polynesia), varied ecological conditions throughout the archipelagos induce a rich biodiversity both for vascular plants (900 indigenous species) and non-vascular plants, many of them still unclassified by botanists.

Tiaré: *Gardenia taitensis*, available all year long, is the symbol of Tahiti. The emblematic use stands in the preparation of Monoï oil, but Tiaré is also used in traditional medicine to combat headaches, pains, respiratory diseases, bleeding and trauma. More than 200 components have been identified in the concrete, particularly:

- Esters (28%), including dihydroconiferyl acetate (14.9%), phenylethyl, hexenyl, benzyl benzoates and salicylates
- Hydrocarbons (24%), including C₂₃, C₂₅, C₂₇, C₂₉ and n-alkanes
- Ethers such as 2,3-epoxysqualene (17%)

Dihydroconiferyl esters show interesting fragrant notes; for example, benzoate has a flowery/fruity note on a pepper base and salicylate imparts a smoked/sugary smell.

Sandalwood: *Santalum insulare*, which is a relatively small tree, has suffered from intensive and traditional commerce with China. This Polynesian sandalwood accompanies everyday life habits, is used to make handcrafted objects, and offers many uses in traditional medicine against otitis, joint pains and other disorders. Two chemotypes are known, one containing santalol and the other nuciferol. Levels of α - and β -santalol in *Santalum insulare*—respectively, 46–56% and 18–23% of the essential oil—are close to those of Indian sandalwood, *Santalum album*—respectively, 41–55% and 16–24% of the essential oil. *Santalum insulare* appears consequently to be a possible alternative to Indian sandalwood, while Australian sandalwood, *Santalum spicatum*, has a quite different profile—respectively, 0–22% and 0–9% of α - and β -santalol in the essential oil. This justifies an active development of growing the former variety.

Tamanu: *Calophyllum inophyllum* is a tree with delicately cut leaves and whose ovoid fruit contain an almond. This *tamanu* is a sacred tree, the wood of which is used to make sculptures. In traditional medicine, leaf decoction calms fevers and diarrhea, while bark decoction soothes ulcers. An oil, greenish-yellow in color with a nut aroma, is derived from the dried seeds of the plant via a crushing and filtering process. The oil reportedly possesses healing properties for cutaneous and mucous wounds (radio-dermatitis, hemorrhoids, etc.). Recent works have shown its efficiency in scab treatment. Studies about some antiviral (anti-HIV), anticancer, antibacterial and anti-inflammatory properties are forthcoming. The leaf extract and almond oil have been studied. New components (tamanolides) have been identified, along with neoflavonoids (catanolides), which present antioxidant and antielastasic properties.

Metuapua'a: This term refers to two members of Pteridophyta, Polypodiaceae: *Microsorium scolopendria* and *Microsorium membranifolium*. Interest in them stems from ecdysteroids, low-toxicity polyhydroxylated steroids found in their extracts, which display adaptive,

anabolic and antiaging, antiinflammatory, immunostimulating, healing, energizing and hepatoprotective properties. They stimulate the healing speed and a protection against senescence. The ecdysteroids are used in traditional medicine, including *raeu tabee* (purge for children), *raeu fati* (energy) and *raeu pihae* (antiemetic).

Vanilla: The vegetal cycle of *Vanilla tahitensis* Orchidaceae from flower to pollination to the growing of pods, takes nine to 11 months. GC analyses have been performed, showing different profiles for plants grown in the region. In addition to classical components, some long-chain monounsaturated fatty acids are present in the material, including C 24:1 (pervoric), C 26:1 (ximenic), C 28:1 and C 30:1.

Aromatic and Medicinal Plants in La Réunion (Bourbon) Island

La Réunion Island, also called Ile Bourbon and Bourbon Island, stands in the Indian Ocean and contains great biodiversity, according to Jacqueline Smadja (University of La Réunion). Preserving and commercializing the area's aromatic and medicinal plants has required a network of Botanical Associations (APN, APLAMEDOM), business associations (Coopérative Agricole des Huiles Essentielles de Bourbon [CAHEB], Provanille), botanical gardens (Jardin d'Eden), cosmetic brands (Run'Essence, Laboratoire Octans) and state organisms (ONF, National Park of La Réunion). CAHEB, created in the 1960s to regulate essential oils business and halt speculative exchanges, manages the technical requirements, the collection of products and their commercialization. Provanille, created in 1995, is an association of vanilla producers that collects green vanilla and develops a quality label. Research laboratories associated with this strategy include CIRAD—Agricultural Research for Development, LCSNAC, UMR 53 PVMBT and the Qualitropic Competitiveness Cluster, which coordinates the efforts of the MAP channel and is presently creating a collaborative platform for eco-extraction. The aromatic plant channel has been weakened for the last 30 years:

Vetiver Bourbon: Production of *Chrysopogon zizanioides* L. Robert has disappeared almost entirely. It currently totals about 50 kg/year, while it was as much as 35 tons/year in the 1970s. Escaping a nearly total disappearance in 1998, production started again in 2001 with 450 kg. Then, in 2002, Hurricane Dina destroyed crops. Today, the remaining production is simply devoted to tourists at a price of about €300/kg, while Haitian vetiver is sold for €100–150/kg.

Geranium Bourbon: *Pelargonium graveolens* L. production in the area decreased from 9 tons to 3.5 tons in 2002 in the wake of Hurricane Dina; it will reach 2 tons in 2011 at a price of €140/kg. Production comprises 110 growers on 110 ha; moreover, 50–80 kg of an organic, or "bio," quality will be available this year at a price of €200/kg.

Baie rose: *Schinus terebinthifolius* production varies between 40 tons and 120 tons and is extracted exclusively with supercritical carbon dioxide. In 2011 the production

totaled 30–40 tons due to the drought suffered on the island this year.

Newcomers: Citronella (*Cymbopogon citratus*) essential oil is an insect repellent (against mosquitoes). Production began in 2011 and will total 100 kg. Production of Ceylon citronella (*Cymbopogon nardus* L.) will begin this year with a production of 50 kg.

Scientific studies are underway to better understand the biology of plants grown in the area. A Vandor project aims to determine the impact of environment (growing locations and cultivation techniques) on the obtained vanilla quality. Studies of the essential oils of some varieties have revealed three new terpenes, molecules that could be taxonomic markers aiding in the understanding of the evolutionary relationship among these plants.

Following the registration of 15 plants of the island in the French Pharmacopoeia, systematic studies have been engaged to elucidate which components have a pharmacological effect. An Atem project is elucidating the antidiabetic properties of some traditional preparations. A Phytochik project seeks to find the active substances against Chikungunya: 180 species have been collected and 720 extracts tested for their antiviral properties in cell cultures, resulting in 13 “hits” (candidates), among which eight have been confirmed. To conclude, it can be considered that, if the field of aromatic plants is to go on showing its resistance to the financial crisis, the medicinal field, thanks to the collaborative projects now running, seems to promise a brilliant future.

Aromatic and Medicinal Plants in Maghreb

The Maghreb region is characterized by great biological diversity, noted S. Zrira (Hassan II Institute, Morocco). Morocco is home to 4,200 plants species, 800 of which have an aromatic and /or medicinal interest. Of these, 280 are cultivated, including rosemary, thyme, pennyroyal, white artemisia, oregano, myrtle, bay laurel, Atlas cedar and *Rosa damascena*. Carob, meanwhile, is cultivated for its seeds. Tunisia is home to 2,150 species, 200 of which have an aromatic/medicinal interest, including rosemary, myrtle, mint, thyme, oregano, pennyroyal, white sage, bitter orange, geranium and many spices. Algeria boasts 3,139 indexed species, 626 of which are of aromatic/medicinal interest, including pines, mastic and Djurdjura cedars. Agricultural cultivation of some materials, such as bitter orange in Tunisia, takes place in all three countries. Meanwhile the cultivation of wild plants is managed in several ways:

- An adjudication system is in place in Morocco.
- An auction system is in place for collectors in Tunisia.
- In Algeria, authorization is given by Directorate General of Forests, either for the steppe ecosystem or for the Saharan/oasitic ecosystem.

Among key materials are:

- Rosemary (*Rosmarinus officinalis*) is present in all three countries, with a production of 50 tons/year of essential oil in Morocco, making it the third largest

producer after Spain and Tunisia.

- Morocco produces 30 tons/year of *Artemisia herba-alba* essential oil, making it the single largest producer in the world.
- Tunisia exports 2–3 tons/year of myrtle essential oil; Morocco exports 1–2 tons/year.
- Morocco exports 11.5 tons/year of pennyroyal essential oil.
- Morocco produces 1,500 tons/year of thyme in the dry herb state.
- Morocco is the leading producer of Atlas cedar essential oil.
- Tunisia is the leading world producer of neroli essential oil, totaling 700 kg/year. Morocco produces 300–400 kg/year of the essential and derived products such as floral waters and petitgrain essential oil.
- Morocco's Ouarzazate district produces 5 tons/year of *Rosa damascena* essential oil and concrete.

Processing: From a technological point of view, cultivated materials (bitter orange, geranium, etc.) are treated on premises that are relatively well equipped, while products coming from wild sources are treated with rudimentary and mobile equipments. Herbs are still frequently dried in the open air and rarely in warehouses so that many products do not always fit the required commercial standards. Since the present business conditions tend to calm speculations, efforts must be concentrated on the technical field of the complete network in order to satisfy expectations of international customers.

Export figures: In Morocco, the spices and aromatic plant market exceeded 40,000 tons/year in 2008–2009, with Europe as the leading consumer (60% total). In Tunisia neroli, rosemary and myrtle contribute, respectively, 34%, 32% and 7% of exports, primarily to Europe. While Tunisia and Morocco are exporters, Algeria is an importer having only a domestic and greatly reduced production activity.

Eco-extraction

Eco-extraction presents a 21st century answer to complex extraction needs, said Farid Chemat (University of Avignon). Its aim is to combine an ecological approach with an economic one. The GREEN group (Groupe de Recherches en Eco-Extraction de produits Naturels) suggests the following definition translated from the French:

Eco-extraction is based on the discovery and conception of extraction processes that ensure energy consumption reduction together with the use of alternative solvents that are renewable/sustainable, proceeding from innovative sources, and producing reliable and qualitative extracts.

Many examples are reported showing the pathways to such eco-extracts:

- Yield improvement by turbo distillation
- Ultrasound extraction of carotene and its addition to an edible oil

- Rapid extraction by microwave treatment of *Rosmarinus officinalis* to obtain the essential oil

The next step, according to Chemat, is the creation of an eco-extract label.

A New Method to Determine Furocoumarins

Furocoumarins present a potential risk for health (in particular phototoxicity) and are already subject to restrictions (cf. SCCP opinion and Directive 95/34/EC), noted Gérard Bondoux (Waters). An International Fragrance Association proposition from 2008 suggests a maximum concentration of 5 μm for leave-on products and 50 ppm for rinsed-off products for the mix of the six concerned substances: 5 MOP (bergapten) bergamottin, epoxy bergamottin, byakangelicol, isopimpinellin and oxypeucedanin. The reference method is HPLC, which separates and detects furocoumarins accurately, but which is a burdensomely long process (60 min). To improve these conditions, a new method has been developed, ultra performance liquid chromatography (UPLC), which is characterized by columns filled with phases whose granulometry is $< 2 \mu\text{m}$, requiring higher flow rates and higher pressure. Several systems have been developed (Acquity UPLC, Acquity UPSFC) that are able to produce data three times faster than HPLC while using half the solvent.

A 30-year Evolution of Analytical Techniques for Aromatic Molecules

Analytical methods such as GC and TLC have emerged in the last 30 years, noted Hugues Brévard (Robertet). These have represented spectacular improvements in extraction/injection techniques, chromatography techniques, detection, and identification/authentication of separated compounds. Solid phase micro extraction (SPME) allows the analysis of headspace, thanks to the absorption from a gaseous volume by an adsorber, which desorbs at the head of the column (INDEX, SBSE systems, etc.). Mini absorbing traps have been created, the size of which allows them, for example, to be placed in a flower corolla to collect, without artifacts, the fragrant components that are present. These traps are desorbed and components analyzed. Some of these traps are even able to study a plant or an organ live (without cutting), with identification of effluents being done by FID, MS and even olfactometry.

In the field of GC itself, improvements concern the decreasing of the length and diameter of columns, stationery phases granulometry and gaseous flow. Separation has been improved via the addition of a second criteria (adsorption affinity), allowing a second separation with separated effluents leading to the so-called 2D, or bidimensional, chromatography. Among detectors, the emergence of mass spectroscopy (MS) has allowed researchers to associate separation and identification. More recently, the use of time of flight (MS ToF) has continued this evolution. TLC benefited also from developments with the use of high pressures (HP TLC) and

improvement of the detection of eluents. This method is enabling the characterization of many plant components, thanks principally to the identification of spots by MS and biological tests.

Standardization of Essential Oils

Didier Nicol (AFNOR; www.afnor.org) discussed the organization's role, established following the 1901 French law aimed at helping set voluntary industry standards and rules based on a reference collection. The AFNOR standard is not a law, though laws frequently refer to it. The same model of coordination is developed on the international level the ISO standards. These standards cover:

- The terms of a common language (vocabulary ISO 4720, prISO 9235 to be issued)
- Products monographs, 96 in number (amyris, vetiver, ylang-ylang, etc.)
- Analytical methods, 30 in number (benzene traces, GC determination)
- Protocols for sampling and labeling

In total there are 130 standards and several updating documents. At the ISO level, new standards have been already issued for materials such as geranium, hyssop, bitter orange and neroli, though not for others, including vetiver, tarragon and baie rose. The ISO/TC 54 Technical Committee comprises 17 countries and 30 observers; it is chaired by A. Bordas from Spain. The AFNOR T75 A Essential Oils groups 37 members and is chaired by H.P. Bodifée (Prodarom). An updated collection of AFNOR Standards is available on its website.

Raw Material Trading in the 21st Century

The profession of raw material trader is as old as that of the perfumer, said Marc Langasque (Diffusions Aromat-

iques). Within the profession, three main profiles can be identified:

- The classical trader who buys, stocks and sells: this individual has a great independence but has to face all financial risks in terms of quality and even regulatory changes
- The agent, whose risk is lower but who is more dependent upon sources and assumes stocks for clients
- The non-classical trader, who is free of stocks and QC compliance, but fully dependant of suppliers and thus subject to delivery uncertainties

In the last 50 years, said Langasque, changes have had a considerable impact on the trading profession due to communication facilities, direct sourcing, quick transportation and multiplication of suppliers sources; regulation requirements, which are in permanent evolution; the development of sophisticated analytical techniques (GC, GC/MS, etc.); and the shortening of production timelines (stocks held by the supplier and not in the client's warehouse). As a result, the 21st century trade is a reactive professional, fully responsible for the quality of its products and permanently watching over regulations that evolve continuously (REACH, for example) and who manages prices and offers in a permanently instable market.

The detailed Congress presentations are available at www.appam.online.fr.

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