Urged by the global demand of safe and natural ingredients, the fragrance industry is undertaking profound changes. This study investigates the origins of change, and speculates on the direction that will lead to massive diffusion of safe fragrance ingredients based both on natural fragrant molecules as well as on microencapsulated fragrances that, we argue in conclusion, will be widely used in the cosmetic, cosmeceutical and personal care industries.

INTRODUCTION

Sustainability has become a central business topic in the fragrance industry, namely one of the world’s wealthiest and oldest, with 2014 revenues exceeding $13 billion, estimated above $17 billion by 2017 (with more than 5% annual growth) (1). The 2016 World Perfumery Congress conference program, for instance, will focus on the theme “Scents & Sustainability: A Responsible Future for Fragrance” (2).

The reason for this shift is simple: consumers wish to buy naturally derived fragrances widely perceived as beneficial to health, avoiding synthetic ingredients which, among other adverse health effects, are often allergenic.

Fragrances are small volatile molecules with pleasant scent widely used in cosmetic, personal and home care products (3), adding scent to human body and living spaces, providing favorable effect on our emotional perception (4). The word perfume derives from “per fumum” (Latin for “through smoke”), as Romans learned that by throwing flowers, leaves, and aromatic resins onto burning coals, all these botanical species released their scents.

Starting with Persians, Indians and Egyptians, for >4,000 years, human civilization has relied on plants as source of a wide variety of fragrances. The first distillation units found in the Indus valley are estimated to go back to 4,000 years ago. The Persians developed the technique of extracting essential oils (EOs) from flowers, especially from rose, and plants through steam distillation.

The fragrance and flavor industry has given eminent contributes to the progress of chemistry and even to protect the environment. The headspace technology (namely the needle made of a special silicone fiber to extract the odorous molecules from the living flower) pioneered in the late 1980s by Braja Mookherjee (5), former chief scientist at a leading flavor and fragrance company, made it possible for scents to be captured and studied without the need to kill the plant, enabling better understanding of the chemistry of plants, including what Ormancey, another eminent organic chemist working in the same industry, has called the language of flowers (6): namely the fact that plants communicate through fragrant volatiles.
The perfume industry profoundly changed with the advent of modern synthetic organic chemistry. A turning point was the discovery of the vanillin synthesis from coniferin in 1874 (the Reimer-Tiemann chemical reaction), which led to the foundation in Germany of what is today one of the world’s largest fragrance suppliers (Symrise).

In 1889, Aimé Guerlain used synthetic vanillin as the “base note” of his commercial perfume Jicky introducing the concept of a perfume with a top note, a middle note and a bottom note. Recognized immediately upon application of the perfume, the top notes of a fragrance are generally comprised of the most volatile molecules such as d-limonene in citrus (lemon, orange zest, bergamot). Abundant in lavender and jasmine, the middle notes are those sensed once the top notes evaporate. They last longer than the top notes and have a strong influence on the bottom notes such as vanilla and musk, namely on the fragrance notes that appear once the top notes are completely evaporated which, mingling with the bottom notes to create the full body of the fragrance, provide the perfume lasting impression lingering on the skin for hours after the top notes have dissipated [3].

Today, more than 3000 different fragrance ingredients - most of which are synthetically derived from oil - are available to perfumers to formulate their compositions [7]. In 1986 the US National Academy of Sciences noted that 95 percent of chemicals used in synthetic fragrances are derived from crude oil, and a vast majority from benzene.

Unfortunately, a survey of asthmatics found that perfume chemicals can trigger attacks in nearly three out of four individuals [8]. Only in Denmark, fragrance mix allergy causing dermatitis doubled in frequency from 4.1% in 1985 to 9.9% in 1997 [9]. In addition, several polycyclic synthetic musks are endocrine disruptors (disrupting hormones), and bioaccumulate in fat tissue, breast milk, and umbilical cord blood [10].

In 2012 a US-based coalition of over 100 groups seeking transparency about chemicals in cosmetics commissioned independent laboratory tests that revealed 38 chemicals not listed on the label in 17 leading fragrances. The average fragrance product tested contained 14 secret chemicals among which some are associated with hormone disruption and allergic reactions [11].

These sad findings may not be surprising considering that only a few fragrances have been tested for toxicity, alone or in combination, leading to a prevalence and burden of fragrance sensitization in the general population that was clearly identified as significant [12].

Consumers in the Internet era, especially those with multiple chemical sensitivities, are increasingly aware of the hazards posed by cosmetics, perfumes and personal care products, and are actively seeking safer alternatives.

CHANGING REGULATION AND TRANSPARENCY

In Europe, Regulation 1223/2009 (fully enforced since July 2013) on the safety of cosmetic products includes a list of approved ingredient and the conditions for using them [13], such as maximum concentration.

According to said regulation, the presence of 26 potential fragrance allergens must be indicated in the label (list of ingredients), if concentration exceeds 0.001% in leave-on product. Substances classified as carcinogenic, mutagenic or toxic for reproduction are prohibited and will be reviewed by the Scientific Committee on Consumer Safety (SCCS) before use is granted.

To date, for example, the SCCS consider data insufficient to ban diethyl phthalates (DEP) and 4-hydroxybenzoic acid derivatives (parabens) from cosmetics [14], even though the European Commission on Endocrine Disruption has listed DEP as a Category 1 priority substance, based on evidence that they interfere with hormone function, decrease sperm counts in man, inducing early puberty in girls, and reproductive defects in the developing fetus [15].

Indeed, besides fragrances several other perfume ingredients are used to enhance the performance of perfuming agents (adjuvant) or protect them against microbial growth for maintaining product quality (preservatives). Perhaps, the most controversial fragrance adjuvant and preservative agents are, respectively, cheap and versatile DEP and parabens.

In the US, the composition of the bouquet in any perfume is a trade secret, and as such manufacturers are not required to disclose the list of ingredients which makes very difficult, according to health and environmental activists, to avoid side effects “even to the most scrupulous customer” [16].

This regulatory obsolescence is all the more surpassed when one considers that today’s perfumes, like today’s cosmetics, are required to do more than just add beauty or scent; but rather act as truly personal care products, with several health beneficial effects, namely true cosmeceuticals [17].

Large companies are reacting to the demand of transparency. In June 2012, for example SC Johnson expanded its WhatsInsideSCJohnson.com program launched in 2009 to make more information readily accessible to consumers, with the introduction of its Exclusive Fragrance Palette, providing consumers with a comprehensive list of fragrance ingredients found in the company’s products, down to 0.09 percent of the product formula.

In another example of new industrial commitment to ingredient transparency, in 2014, Clorox expanded its Ingredients Inside program to include specific fragrance components.

On the other hand, building part of their success on the prolonged lack of label transparency mentioned above, hundreds of manufacturers of naturally derived perfumes in North America, Europe and Asia voluntarily disclose the composition of their mixtures, often seeking third party certification of the lack of petrochemicals in their products.

THE SHIFT TOWARDS GREEN CHEMISTRY AND TRANSPARENCY

The shift of the global fragrance and cosmetic industry towards natural products started the early 1980s, best epitomized perhaps by the The Body Shop spectacular growth across Europe and North America, lately has further accelerated [18].
Not only certifying bodies exert pressures to restrict or prohibit petrochemical extraction of botanical extracts, but suppliers of natural extracts sourced from endangered aromatic plants seek third party certification to show commitment to protection of biodiversity.

For example, pure sandalwood essential oil obtained from Australia’s new plantations managed in a sustainable way, allows a company to position itself as an ethical provider of the oil to the global fragrance market (19). In the US, the Natural Products Association requires that to be labeled “natural” essential oils need not to be derived using an hydrocarbon solvent.

Indeed, pointing out to the obsolescence of most conventional solid-liquid extraction with oil-derived solvents such as hexane or petroleum ether, Denzil Phillips was recently asking how the public would react “If they read Charles Sell’s excellent book The Chemistry of Fragrances which clearly shows that the production of many natural essential oils consumes more fossil fuel, produces more carbon dioxide, more effluent and has more negative environmental impacts than many synthetic aroma chemicals” (20).

Accordingly, large fragrance companies have started to invest in new plantations and new extraction plants using novel extraction technology, acquiring control of the whole value chain in the sourcing country. Symrise, for example, lately opened a large (3,500 m2) facility in Madagascar for making high quality vanilla extracts working directly with vanilla farmers (7,000 in 90 villages) in northeastern Madagascar in order to ensure the sourcing of natural vanilla as well as guarantee its high quality and seamless traceability (21).

More than 30,000 people benefit directly and indirectly in terms of income, health, education and training. In addition, Symrise reinvests 10% of its yields from vanilla operations into Madagascar in the form of education and training, reforestation and the sustainable cultivation of various agricultural raw materials on the island.

All this creates new room for the two cleanest extraction technologies, namely supercritical fluid extraction (SFE) and microwave-assisted extraction (MAE), whose applicative potential had remained largely unfulfilled.

Odorless, colorless, non toxic and non flammable supercritical carbon dioxide (scCO2) allows the high yield recovery of intact lipophilic compounds such as essential oils from many plant matrices, thereby replacing solvent extraction and steam distillation at lower operational cost (22).

The numerous advantages of scCO2 extraction of plant flavors and fragrance, when compared to conventional extractions with organic solvent, include rapidity, selectivity, and unprecedented cleanliness, leaving the extract devoid of any contaminants (23).

Similarly, microwaves can be effectively used on industrial scale to rapidly extract all sort of valued natural compounds using water as unique dispersing medium, with significant energy savings (24). The biological matrix is placed in a vessel (typically comprised of PTFE) inside the MW oven, without adding water or organic solvents. Hydrodiffusion and gravity extraction occur due to release of internal water of the matrix. Essential oils and other valued solid components are recovered from the bottom of the reactor via condensation of the distillate (25).

MICROENCAPSULATION

The increasing utilization of essential oils in place of highly stable (actually, too stable and bioaccumulating) synthetic fragrances and musks is creating demand for another technology whose potential had remained unfulfilled, namely microencapsulation of essential oil (EO) natural fragrances.

In general, in terms of ecotoxicology, most EOs tested rapidly biodegrade and, in contrast to some synthetic fragrances, do not bioaccumulate (26), even though allergic reactions to some constituents of EOs are known, such as in the case of sun sensitivity due to bergaptene in bergamot oil (27).

In perfumery, one main objective is to create perfumes whose scent can last longer when compared to the non encapsulated EO. Microencapsulation, indeed, allows the isolation and protection of fragrances from evaporation, oxidation as well as degradation caused by heat, light and moisture; thus eliminating the need for hazardous preservatives.
Similarly, it is highly desirable maintaining the fragrance in shampoo, shower gel or body lotion for the entire day. New microencapsulation technologies, such as the sol-gel microencapsulation in silica-based microcapsules, allow such extended endurance of fragrances opening the route to what we called truly sustainable fragrances and aromas (28).

The sol-gel process, indeed, offers unique benefits because it allows the preparation of monodisperse capsules with unprecedented high load (up to >90% in weight), excellent physicochemical stability, lack of toxicity and biocompatible nature. Furthermore, true control of the microcapsule size, textural and surface (hydrophilic-lipophilic balance) properties allows truly full control of the release profile of the encapsulated fragrance.

In brief, fragrances were not amongst the microencapsulated payload required by the customers of the new microencapsulation companies using different encapsulants (organic polymer, biopolymer, and inorganic oxides) and methods targeting the cosmetic market in 2007 (29).

Ten years later, perhaps not surprisingly, several microencapsulation companies include fragrant microcapsules in their offerings. An ample variety of microencapsulated perfume odorants for laundry (to smell fresh for longer), and fabric have been successfully launched on the marketplace.

Here, we focus on microencapsulated fragrances for cosmetic use, showing selected early products that are likely to be shortly found in mass market cosmetics.

In France, in 2015 Microcapsules Technologies developed a silicone copolymers microcapsule (Microsil) suitable for encapsulation of natural oils and showing an excellent skin acceptance and flawless toxicity. In the same year, Tagra Biotechnologies in Israel launched the Release on Demand RND Microencapsulation Technology, an efficient and controlled method which enables the production of encapsulated ingredients for a wide range of formulations specifically designed for the cosmetic industry.

In India, Natural Odours & Polymers commercializes essential oils entrapped in Agar (Sphera) microspheres. In Israel BotanoCap technology uses interfacial polymerization to synthesize hypoallergenic polymer microencapsules enabling controlled release of essential oils.

In Quebec, Materium Innovations, a small company which just left the enterprise incubator, has developed a proprietary technology for the production of hollow silica microspheres (Matspheres 424) for perfume extended release.

Many other companies, including large cosmetic and flavor and fragrance enterprises, own and use proprietary fragrance microencapsulation technologies. The ones mentioned above give a quick idea of the ample variety of approaches synthetic molecules made available by synthetic organic chemistry, the global fragrance industry is slowly but inevitably changing towards sustainable fragrances.

Rather than defending the status quo for which activists wrote as of the end of 2015 about the need to “unpacking the industry” (16), and expose policy failures and public health aspects, the industry has started to invest in new plantation and extraction plants using new extraction technology to lower supply costs, and meet the rapidly increasing demand of natural ingredients entirely free from petrochemicals.

As the natural fragrance market will continue to advance, technologies like microencapsulation that for decades remained limited to low value added applications such as microencapsulated ink, will rapidly find widespread diffusion in the high valued added cosmetic sector, including perfumery.

Young chemical researchers and chemical engineers should feel motivated to work in the rapidly evolving fragrance industry. Chemistry scholars, on the other hand, need to undertake renewed educational efforts in both nanochemistry (30) and green chemistry applied to the fragrance industry (31), which continue to act as today’s main barrier to the industry’s adoption of greener technology.

Overall, this renaissance will lead to propagation of better strains, optimal planting techniques to conserve water and minimise soil erosion, and optimal contour cultivation strategies to dispense with the need for insecticides. Farmers, even in remote areas and in small land surface, benefit from revenues of highly valued essential oil cultivation; whereas the supplier-producer proximity, minimises transportation costs and adds benefits, including training and joint development efforts, meeting the truly triple-bottom-line approach to business of sustainability, which combines social and environmental objectives with the main economic objective: profit.

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ProBioBalance CLR™ NP
Healthy nutrition for the skin

ProRenew Complex CLR™
Probiotic approach to skin renewal and resurfacing

Repair Complex CLR™ PF
Immune strengthening against photoaging

Probiotic active ingredients for sustainable and effective skincare