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3/2021

COSMETICS
TRENDS
TECHNOLOGY

COSSMA

SUSTAINABILITY

Finding resource-saving solutions
p 38

MARKET INSIGHT

Target group generation Z
p 46

“ECOLOGICAL OPTIMISATION WILL BE THE KEY FOR CONSUMER”

Christian Eisen, Vice President Global Sales & Innovation, Faber-Castell Cosmetics
p 58

NATURAL AND SAFE

Perfuming | Natural ingredients are not automatically without risk. Fragrances of a natural origin can have allergic potential or, on the other hand, be susceptible to contamination. Markus Nahrwold explains the approaches that green chemistry offers.

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Consumers often perceive aromatic plant extracts as "better" than synthetic fragrances. Yet, experts in the field of natural and chemical fragrances are well aware of the potential cocktail of allergens and sensitisers in natural extracts. To ensure safety in essential oils and stability in hydrolats, two solutions are proposed for natural fragrances in cosmetics:

1 Purification and green chemical transformation
2 Dilution combined with careful quality control

> "CATALYTIC HYDROGENATION IS A CHEMICAL STEP THAT IS IN LINE WITH THE TWELVE PRINCIPLES OF GREEN CHEMISTRY."
>
> Markus Nahrwold, Minasolve

Risks of natural fragrances in cosmetics

The most diverse type of natural fragrances are probably essential oils, whose long history dates back about 800 years to the golden Arabian age. Current annual production worldwide is estimated at 100,000t.[1]

Essential oils are traditionally obtained by steam distillation: hot water vapour is passed through fresh or dried plant material, thereby taking up the volatile components. The distillate is allowed to settle, and two phases are collected: A small lipophilic phase – the essential oil – and a large water phase, also known as hydrosol, hydrolat or "floral water" (figure 1).

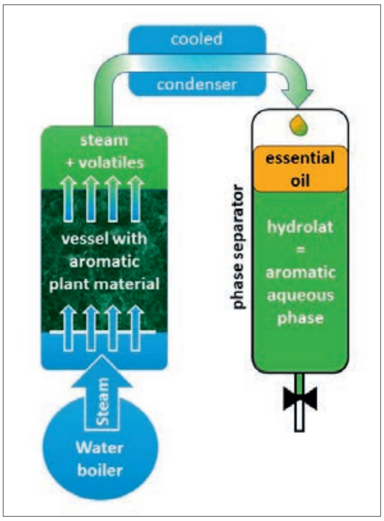

figure 1: Scheme of the traditional production of essential oils and hydrolats by steam distillation of plants.

Either phase can be used for perfuming personal care products. However, the problem is that the essential oil may contain sensitisers and can cause skin allergies. Hydrolats are often unstable and almost always sensitive to microbial contamination.

One **striking example of a safety risk** is "cinnamon bark oil", obtained by steam distillation from the bark of cinnamon or cassia trees. Its main component is cinnamaldehyde, a fragrance allergen listed in Annex III of the European Cosmetics Regulation, so limiting its concentration in products intended for use on human skin is recommended. In such cases, green chemical conversion offers advantages.

Minimizing risk with "green chemistry"

"Catalytic hydrogenation" is a chemical step that is in line with the twelve principles of green chemistry.[2] Such processes are typically short, selective, and atom-economic, hence generating little waste. Hydrogenation of cinnamaldehyde affords 3-phenylpropan-1-ol (INCI name: Phenylpropanol). The allergenic potential of phenylpropanol is much lower than that of cinnamaldehyde.[3] This makes phenylpropanol particularly attractive as an ingredient for personal care applications.

Phenylpropanol is found in nature, for example in hyacinths and ripe strawberries, and is therefore considered as a "natural" fragrance. Its odour is described as balsamic and flowery with an oriental note, reminiscent of hyacinths.

Its broad-spectrum antimicrobial properties can also help to generate self-preserving natural cosmetics. This activity is almost independent of the pH value, which is of interest for natural formulations with neutral or alkaline pH values.

Phenylpropanol is usually produced starting from petrochemically derived cinnamaldehyde. However, in recent times a version of phenylpropanol being produced directly from the natural essential oil is available (figure 2).

Isolation of cinnamaldehyde from cinnamon oil by fractional distillation is disturbed by formation of various azeotropic mixtures with other components of the essential oil.[4] ▶

figure 2: Production of phenylpropanol from cassia bark oil.

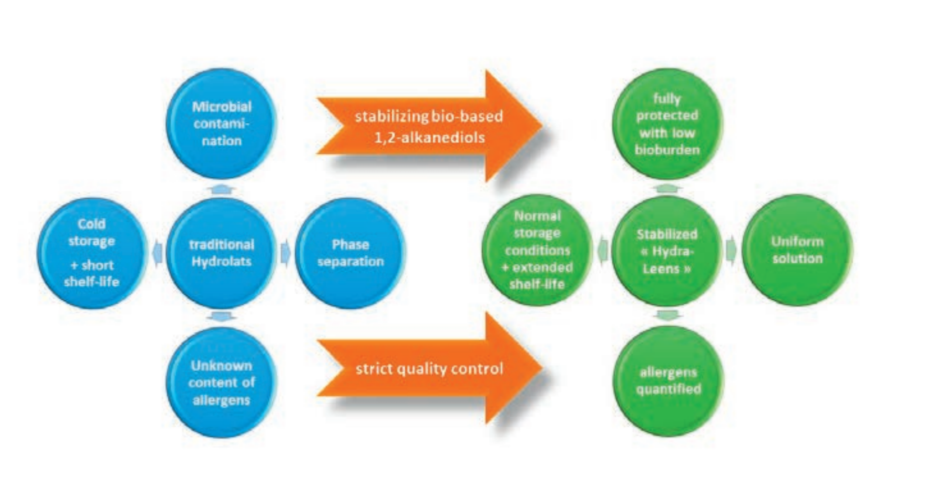

figure 3: The benefits of stabilised hydrolats.

Fortunately, all undesired impurities are "saturated" during the hydrogenation process, which simplifies their removal.

The obtained nature-derived phenylpropanol is therefore essentially free of listed allergens. The first of its kind natural phenylpropanol on the market, "A-Leen Aroma-3", is Cosmos and Natrue approved and USDA-certified bio-based. Its natural raw material is sustainably produced in cooperatives which cultivate the Cassia trees, isolate the essential oil, and valorise all remaining parts of the tree.

But it is just one example for the possibility of creating natural, yet low-allergen fragrance ingredients.

Minimizing risk with dilution

One can also directly use plant extracts as perfumes, without green chemical transformations, particularly when organic certifications are targeted. Here, hydrolats obtained via steam distillation of natural materials can be a convenient option.

One major advantage of hydrolats is paradoxically their low content of aroma ingredients. The high dilution makes an over-dosage almost impossible. Nonetheless, the content of fragrance allergens should be closely monitored and known hazardous contaminants should be also quantified. Prominent examples are furocoumarins inside orange extracts and methyl eugenol in rose water.

The composition of hydrolats is similar to the corresponding essential oils, with two major differences: The concentration of aroma components is as low as 0.1 %, and mainly the water-soluble components of the essential oil are enriched in the hydrolat.

As an example, the major aroma ingredient of rose water is the water-soluble phenylethyl alcohol (PEA), while rose oil contains almost no PEA. The aroma of natural rose water is therefore quite similar to rose flowers, while the odour of rose oil differs from the original flowers.[5]

Storage and stability risks of hydrolats

Despite being cost-effective and safe, natural perfumed waters are not always taken into consideration because of the risk for infections by microorganisms, which can represent a health risk and lead to olfactory off-notes. **While many hydrolats are self-preserving against bacteria, they are mostly not self-preserving against fungi.**

Cold storage may preserve the freshness of hydrolats for a while, but a short shelf-life of about six months is quite common – imposing an economic risk and a logistic constraint, if hydrolats are transported over longer distances or through tropical areas.

This is why hydrolats are often preserved with antimicrobial additives or subjected to sterile filtration or irradiation, which however need special equipment.

Hydrolat	Additive	TAMC	TYMC	Challenge test, ISO 11930
Cedrus atlantica (Cedar) bark water	–	> 1000	> 1000	Failed
Citrus aurantium amara (Neroli) flower water	–	> 1000	> 1000	Passed (B)
Rosa damascena (Rose) flower water	–	> 1000	> 1000	Failed
Hydra-Leen 5 Rose	Pentylene Glycol	< 10	< 10	Passed (A)
Hydra-Leen 8 Rose	Caprylyl Glycol	< 10	< 10	Passed (A)
Hydra-Leen 8 Cedar	Caprylyl Glycol	< 10	< 10	Passed (A)
Hydra-Leen 8 Neroli	Caprylyl Glycol	< 10	< 10	Passed (A)

table 1: Comparison of the bioburden and resistance to microbial contamination of unprotected and protected hydrolats (TAMC: Total Aerobic Microbial Count; TYMC: Total Yeast/Mould Count)

picture: polinaloves/Shutterstock.com, graphs and table: Minasolve

Another compounding problem linked to hydrolats is the **potential presence of excess essential oil**. The oil can form a separate phase, usually upon prolonged storage in a cold area.
This inhomogeneity can eventually lead to an overdose of the lipophilic fragrances, resulting in an inconsistent odour, incomplete solubility in water or even skin irritation or sensitisation.

Reducing risks

All the above risks can be avoided by using 1,2-alkanediols, such as bio-based 1,2-pentanediol or 1,2-octanediol. Such additives act as solubilizers and dispersing agents that keep the hydrolats homogenous.
Furthermore, the diols have anti-microbial properties and therefore avoid or even cure microbial contamination. The bio-based origin of the diol additives makes it possible to obtain eco-certifications such as Cosmos or Natrue.
Table 1 shows the differences in the bio-burden of stabilised versus non-treated hydrolats. Even microbial challenge tests according to ISO 11930 are passed, which enables a direct application on skin.

Rigorous testing of aromatic plant extracts

In summary, green chemical conversion and high dilution combined with strict quality control are two ways of obtaining natural fragrances with a low content of allergens. A detailed risk assessment according to the guidelines of the International Fragrance Association (IFRA) is recommended in any case. The reward of all this effort are safe and pleasant-smelling natural formulations. □

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5 H. S. Canbay, International Journal of Analytical Chemistry, 2017, Article ID 4870671.