Orange blossom

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Orange blossoms are the flowers from the bitter orange tree, *Citrus Aurantium Linnaeus*. Originating in China, the bitter orange tree was probably introduced to southern France somewhere between the tenth and eleventh centuries AD by the conquering Arabs. It remained the only orange known to Europeans for about five centuries. Since the fruit of this tree is so unpalatable (though more sour than bitter from this author's first hand experience) it is no wonder that products for fragrances were developed. Distilled oil of orange flower appeared as early as the sixteenth century, but only when it was used in 1680 by the Duchess Flavio Orsini, a member of a noble and powerful Roman family, did it emerge as a fashionable fragrance article.[1] Since this lady was also known as the Princess of Neroli, or Nerola, a town situated roughly thirty kilometers northwest of Rome, the name oil of neroli was adopted and remains in current use.

While this is probably the most glamorous tale of orange blossom use, it is by no means the only reason for the success of products from *Citrus Aurantium*. The peel of the fruit is used in marmalade, a bitter but popular jam. In Italy, for instance, where bitter-tasting products are more accepted than in the United States, the juice from the fruit is used in beverage flavors such as Chinotto[2] and Aranciata, both popular bitter orange sodas. Orange blossom and related products have been used in beverages, ice cream, ices, candy, baked goods, chewing gum, gelatins, and puddings. It may well be that orange flower water absolute became commercially available as a result of an effort to reduce the exported volume of orange flower water. This was done to decrease the cost of freight and custom duties levied on orange flower water.[3]

Along with esthetic uses came the pharmacological uses of neroli oil. It has a weak antiseptic effect, belongs to the group of cramp-inducing oils, and has a strong bactericidal effect on *Staphylococcus aureus*. Neroli water or eau de neroli is classified as a hypnotic, sedative, antispasmodic, and capable of calming heart rhythm.[4] For all those perfumers who have sleepless nights, it is a well-known remedy for insomnia.[5]

Overall, the citrus industry in Europe is literally built on the bitter orange tree. Since the roots of the tree are so resistant to disease, lemon, sweet orange, mandarin, grapefruit, and bergamot are commonly propagated on the root stock.[6] Figure 1 shows the products derived from the bitter orange tree for general reference.

Studies

Through the years, orange flower has been the subject of some study. There is some information in the literature on the composition of neroli. As early as 1928, Villavecchia identified d-pinene, l-camphene, dipentene, decanal, jasmone, l-linalool, linalyl acetate, geraniol, nerol, d-nerolidol, phenyl ethyl alcohol, d-terpineol, indole, methyl anthranilate along with esters of phenyl acetic acid, and benzoic acid.[7] Information on orange flower absolute is more obscure. For a perfumer, the composition of the natural flower is of paramount interest, and it is in the analysis of orange flower absolute that one might best look for that information. In Table I, analyses of orange flower absolute, neroli, and orange flower water absolute can easily be compared.[12] In theory, if one were to combine neroli and orange flower water absolute, one should arrive at the total fragrance composition that exists in the flower. Of course, this is

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unrealistic and does not take into account the changes introduced by processing.

As can be seen in Table I, some components vary in concentration due to their water solubility, such as phenyl ethyl alcohol and methyl anthranilate. Further, if we focus on linalyl acetate, we notice a reduction of this chemical in neroli and practically a complete loss in orange flower water absolute. This is probably a result of the harsh distillation process, which hydrolizes the ester. Overall, this may be an indicator of what may happen to other oils containing linalyl acetate that undergo steam distillation. Products such as lavender and lavandin may in fact have higher concentrations of linalyl acetate in the plant than the analysis of their essential oils would lead us to believe.

Table I

	Orange Flower Absolute %	Neroli %	Orange Flower Water Absolute %
alpha-pinene	trace	9.8	-
beta-pinene	0.4	15.0	1.1
myrcene	0.1	1.6	-
limonene + cis-ocimene	5.1	16.1	0.5
trans-ocimene	0.6	6.0	0.2
linalool	37.0	30.6	44.2
phenyl ethyl alcohol	4.5	-	1.9
alpha-terpineol	2.4	3.0	18.5
citronellol	0.5	0.2	0.2
nerol	0.9	0.5	2.8
linalyl acetate	16.8	9.1	-
geraniol	1.5	2.0	6.4
indole	1.0	0.1	0.1
methyl anthranilate	3.0	0.3	4.1
eugenol	0.3	-	0.5
neryl acetate	0.8	1.7	0.5
citronellyl acetate	0.1	-	-
geranyl acetate	0.6	2.9	0.5
nerolidol	7.6	4.0	1.7
farnesol	7.7	4.0	0.5

Odor contribution of constituents

With problems of processing aside, we can begin to examine the constituents for their odor contribution. As a guideline, I have listed the main characteristics of orange blossom below. Under each heading, I have placed the chemicals that contribute most to that character. Methyl anthranilate appears under two categories, floral and fruity. I feel that this particular chemical plays an important dual role in the overall fragrance of orange blossom.

Citrus

alpha pinene
beta pinene
myrcene
limonene
ocimene
linalool
linalyl acetate

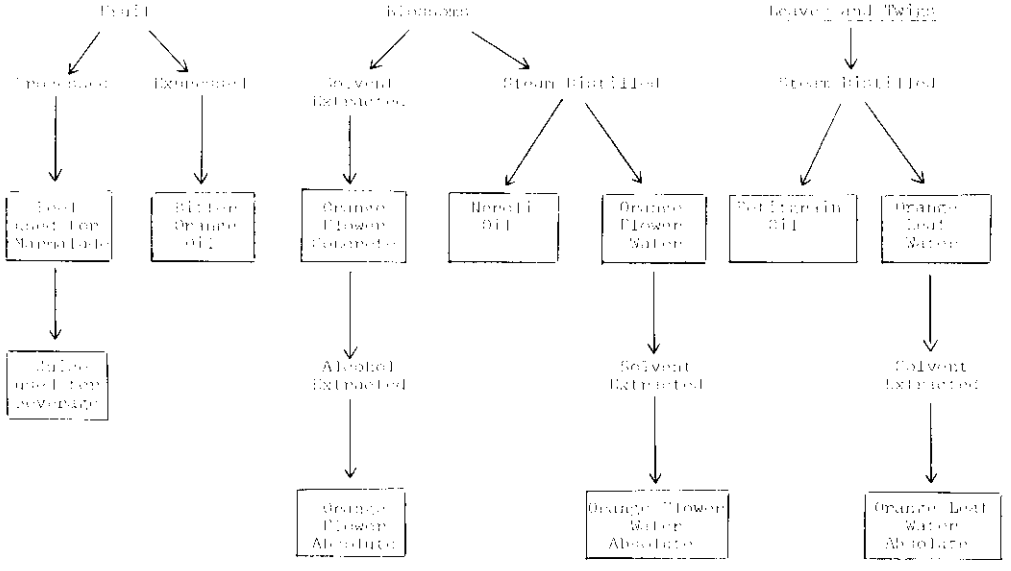
Fruity

neryl acetate
citronellyl acetate
geranyl acetate
methyl anthranilate

Floral

phenyl ethyl alcohol
alpha terpineol
citronellol
nerol
geraniol
indole
methyl anthranilate
nerolidol
farnesol

Figure 1



Spicy

eugenol

Green earthy

pyrazines

Chemical class of constituents

After categorization by odor, I have often found it helpful to examine the constituents with regard to their chemical class. While each component is different in its character and performance, examination by class can give an overall appreciation for the construction of the odor of orange blossom.

Hydrocarbons

alpha pinene
beta pinene
myrcene
limonene
ocimene

Alcohols

linalool
phenyl ethyl alcohol
alpha terpineol
citronellol
nerol
geraniol
nerolidol
farnesol

Esters

linalyl acetate
methyl anthranilate
neryl acetate
citronellyl acetate
geranyl acetate

Phenols

eugenol

Nitrogenous compounds

indole
methyl anthranilate

Hydrocarbons

This class provides the bright, fresh citrus character that is so characteristic of neroli. Collectively, the hydrocarbons represent about 40% of neroli oil and they are the reason neroli is so bright and diffusive, adding a fresh note to any composition. The role of hydrocarbons in the absolute is less important than in the distilled oil. Representing only about 6%, this group boosts the floralcy of the other components, giving the overall composition brightness and diffusion. The most important component in this class is ocimene, which provides a very fresh citrus note along with a subtle green nuance.

Alcohols

This group provides the floral body of orange blossom. As can be seen in Table I, this group is much more important to the character of the absolute than the distilled oil. Linalool is the major contributor to odor impact and character in this group. This chemical can be viewed as the link that bridges the citrus character with the floral character. Displaying characteristics of each, linalool, well-known as it may be in the industry, is a very important chemical to the odor of orange blossom.

Esters

While the esters can generally be characterized as fruity, the part they play in orange blossom can best be described as supporting and modifying the citrus character. The single most important member of this class is methyl anthranilate. It is both fruity and floral and is a major characterizing component in both the absolute and the distilled oil. Even though there is only one tenth the amount in the distilled oil, the presence of methyl anthranilate can be easily detected by odor.

Phenols

While eugenol in a minor constituent, the effect of this chemical should not be overlooked or underestimated. The spicy clove-like odor adds a particular brightness and natural character to orange blossom. Phenols as a class are extremely important odor contributors. They often occur at trace levels, and it is certain that more are waiting to be discovered in orange blossom.

Nitrogenous compounds

Indole and methyl anthranilate are very important character contributors to orange flower. Indole is a nitrogen-bearing molecule, and acts as a powerful floral chemical that can also be perceived as quite animalic when not in extreme dilution. While methyl anthranilate is listed along with the esters, it differs in one important aspect in that it is also an amino ester and as previously stated, is a major odor characterizer for orange blossom.

After all the previously discussed components are combined at their proper concentration, it becomes quite clear that the odor of neroli has been vaguely imitated but the unique character has not been captured. It is at this crucial point that we come to grips with the nature of orange blossom.

The occurrence of pyrazines in nature is well-known. The odor importance of this class of chemicals is just beginning to be understood and appreciated. In 1971, Duprey and James identified 2-methoxy-3-isopropyl, 2-methoxy-3-isobutyl, and 2-methoxy-3-isopropyl 5-methyl pyrazines in oil of petitgrain.[8] It would come as no surprise to find them in the blossoms of the flower. In my opinion, it is precisely that peculiar pyrazine-like note with the green yet dry and earthy character that is so characteristic of orange blossom. Granted, there may be many other unidentified constituents and many of them important to the aroma of orange blossom but I would suspect that pyrazines, along with thiazoles and other nitrogenous compounds, are the most important contributors to the unique somewhat bread-like character of orange flower. It is well-known to perfumers and flavorists alike that orange blossom has the ability to add a unique freshness to the top note while exhibiting a long-lasting character with surprising tenacity. This is a common characteristic of the performance of pyrazines. The pyrazines do for orange flower what damascenone and damascone do for rose.

If the rose can be dubbed "Queen of the Florals," I suppose we could call the orange blossom the princess. It is an expensive product but it finds its way into many creations. It has been used as a main theme in fragrances like L'Origan and Fidji, and appears extensively as top notes or modifiers in many colognes like Eau Sauvage and 4711.

Many commercially available chemicals have become successful because they impart orange flower notes quite economically. Nerone=1-(Para menthene-6-yl)-1-propanone is a green and somewhat earthy note reminiscent of petitgrain. This chemical is rather unusual in the sense that there are not many of this type or class exhibiting a character of orange flower or petitgrain.

An interesting group of chemicals are the various substituted naphthalenes: alpha methyl naphthyl ketone, beta methyl naphthyl ketone, nerolin, and yara-yara. They all bear a resemblance to each other and to methyl anthranilate, which is probably the reason they have come to be associated with the orange flower character initially.

There are a few other chemicals reported in the literature, for example, gamma terpinene, para cymene, alpha terpinyl acetate, sabinene, alpha phellandrene, terpinolene, terpinene-4-ol, cis-3-hexenol, decanal, neral, geranial, and thymol.[9] Guenther mentions benzaldehyde, an unidentified basic compound with a nicotinic odor, nitrile of phenylacetic acid, jasmone, and an unidentified nitrogenous compound.[10] Additionally, Corbier and Teisseire identified cis-8-heptadecene and 2,5-dimethyl 2, vinyl-4-hexenal.[11] Unfortunately, they did not characterize the odor or flavor of these components.

Many unidentified or discovered but not yet publicized chemicals exist in orange blossom, and in order to gain a proper understanding of the nature of orange blossom much additional work is needed.

References

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