Neroli in Perfumery

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A lthough introduced to perfumery in France in the seventeenth century by the Princess of Neroli, whence it received its name, neroli has not been appreciated as a fragrance per se, as are jasmin, rose, hyacinth and other florals.

As to the identity of this Princess of Neroli, there is conflicting information, one source quoting Anne-Marie de Trémoille, and another naming the Duchess Flavio Orsini, but we will leave this problem to the historians.

Botanical Origin

Neroli oil is obtained from blossoms of different varieties of orange and lemon trees:

Citrus Bigaradia, Risso, var. amara—the bitter orange tree

Citrus Aurantium, Risso, var. dulca—the sweet orange tree

Citrus Limonum, Risso—the lemon tree

The orange trees originated in Southeastern Asia, spreading to India and Persia (now Iran). The bitter orange tree was introduced to the Mediterranean countries (including Syria, Palestine, Egypt, and North Africa) by the Arabs in the tenth and eleventh centuries; the sweet orange trees appeared few centuries later.³

Later, the "spice route" and the crusades helped to disseminate the orange trees. Columbus introduced them to the New World. In due time, the colonists and missionaries introduced the trees to Brasil.

The origin of the lemon tree is more obscure. It

is believed that it is a native of Southeastern Asia. The tree was introduced to Persia (Iran) and Palestine in the twelfth century. It is assumed that the lemon tree was brought to Northern Africa by the crusaders. Later, it was introduced to the New World, West Indies, and Latin America.⁴

Mode of Production

Distillation of orange blossoms is the only method used to obtain neroli oil. The distillation yields neroli essential oil and orange flower water (also called neroli water).

Neroli oils are named according to their botanical origin:

- —Neroli Bigarade (from the bitter orange tree blossoms)
- -Neroli Portugal (from the sweet orange tree blossoms)
- —Neroli Citronier (from the lemon tree blossoms)

Of the three, the Bigarade is the most important and commercially available. At present, neroli is obtained mostly from orange tree blossoms grown in North Africa, and to a lesser extent in Spain.

In the past, orange flower water was used for the manufacture of colognes, but today it is no longer commercially available for export. In the beginning of this century, on extraction with solvents and subsequent purification, orange flower absolute was obtained, which is still used in Europe, especially in Italy.

Perfumery Notes

Steam distillation of 1 kg of orange flowers yields one liter of orange flower water, which in turn yields on the average 1 g of neroli oil, or about 0.1 percent.⁵

In discussing neroli, another essential oil, namely petitgrain must be mentioned. The bulk of this oil is obtained from leaves and petioles of the bitter-sweet orange tree, growing semi-wild in South America. Petitgrain oil is used as a base for synthetic neroli compounds.

Chemical Composition

Research work done in the end of the 19th century and in the first five decades of this century revealed the following components in the French Neroli Bigarade oil:6

beta Ocimene l-camphene alpha Pinene Dipentene Decyl aldehyde (probably) Linalool Linalyl acetate Phenyl ethyl alcohol alpha Terpineol Nerol and neryl acetate Geraniol Jasmone (probably) Nerolidol Farnesol Acetic acid, phenyl acetic acid, benzoic acid, palmitic acid (traces), all present in esterified form Phenols (traces) Methyl anthranilate Indole Paraffins

Some more recent research on neroli is available. A comparison of earlier and newly identified components of neroli oil is given in Table I.

Research work done on neroli Bigarade during the last two decades has also revealed the presence of cis-8-heptadecene and 2,5-dimethyl-2vinyl-4-hexenal. Although no pyrazine derivatives have been identified in neroli oil, polysubstituted pyrazines and trace amounts of cis-3hexenol have been found in petitgrain oil. 11

Table I. Components of Neroil Oil

<u>Compound</u>	Neroli Bigarade French ref. 7	Neroli Egyptian ref. 8	Neroli(origin unspecified) ref. 9
	<u> </u>		<u> </u>
alpha Pinene		4.26	0.8
Camphene	35.0	5.50	-
Dipentene		-	-
Paraffin C-27		_	-
Sabinene	-	2.55	-
beta Pinene	-	8.67	15.0
Myrcene	-	2.15	1.6
delta 3 Carene	-	2.46	-
Limonene	-	22.43	16.1 (limonene+cis-ocimene)
trans Ocimene	-	-	6.0
Terpinene	-	4.14	-
p-Cymene	-	trace	-
Terpineol	2.0(alpha)	1.87	3.0(alpha)
Linalool	30.0	2.52	30.6
Linalyl acetate	7.0	0.87	9.1
Geraniol	4.0	1.02	2.0
Nerol	•	6.97 incl. farneso unknown)	0.2 1,
Geranyl acetate	4.0	3.74	2.9
Neryl acetate		-	1.7
Citronellol	-	1.87	0.2
Citral	-	2.41	-
beta Citral	-	1.87	-
Nerolidol	6.0	-	7.6
Farnesol	see: last item	see: nerol	4.0
Methyl anthranilate	0.6	1.89	0.3
Indole	less than 0.1	-	0.1
Acetic, palmitic acid	is 0.1	_	_
Decyl aldehyde(probat	oly) \		
Phenyl acetic acid)		
Benzoic acid	11.2		
Farnesol	} '''2		
Jasmone	/		

The orange flower water is rich in phenyl ethyl alcohol and methyl anthranilate, associated with the nitrile of phenylacetic acid and traces of jasmone. It contains similar components as the neroli oil, but in different proportions, and it is obvious that the water soluble ingredients are found in a larger percentage, and terpenes and sesquiterpenes in lesser amounts. In addition, eugenol and benzaldehyde were identified among other ingredients. Is

Synthetic Compounds

Neroli compounds are based on the same ingredients as orange blossom compounds, but the heavier components, i.e., indole, aurantiol, phenyl acetates are used in smaller amounts, and a larger percentage of esters and alcohols is included.

The base of synthetic neroli compounds is petitgrain oil, linalool, linalyl acetate, rose al-

Formula 1. Neroli Base

Grams	
250	Petitgrain
200	Aurantiol
125	Linalyl acetate
100	Phenyl ethyl alcohol
50	Linalcol
50	Sweet orange oil
50	alpha Amyl cinnamic aldehyde
30	Aldehyde C-10 10%
25	Geraniol
25	Geranyl acetate
25	Terpineol
20	Methyl naphthyl ketone
20	Alcohol C-12
15	Indole
5	Phenyl ethyl acetate
000	

Formula 2. Neroli

Grams	
230	Petitgrain terpeneless
40	Phenyl ethyl acetate
40	Nerol
20	Linalyl acetate
20	Sweet orange oil
15	Linalool
10	Geranyl formate
6	Aldehyde C-10 10%
6	Methyl naphthyl ketone
6	Celery oil
393	

cohols and their acetates, and its Schiff base or methyl naphtyl ketone, depending on the end use of the compound. Bergamot, sweet orange oil, or sometimes lemon oil are used for the top note. Benzyl acetate, amyl cinnamic aldehyde, nonadienol acetate, eugenol and isoeugenol are used as modifiers. Alcohols C-8, C-9, C-10 and C-12, as well as corresponding aldehydes are included.

Small amounts of nerolidol, hydroxycitronellal or its replacements, methyl benzoate, phenyl ethyl anthranilate, indole and terpineol may be added. Among natural trace components, basil and celery oils may be mentioned.

Resinoids benzoin, tolu, labdanum, myrrh and civet, and such aromatics as benzyl cinnamate and phenyl ethyl acetate are considered good fixatives.

Ethyl cinnamate is a useful component of neroli synthetic for soap. More expensive neroli compounds may contain natural neroli oil or orange flower absolute.

Neroli shares common ingredients with jasmin, tuberose, narcissus (benzyl acetate, amyl cinnamic aldehyde, linalool, linalyl acetate, anthranilates, jasmone), and rose (phenyl ethyl alcohol, other rose alcohols and their esters, aldehyde C-10).

Dimethyl anthranilate and phenyl acetic acid have been used in neroli compounds. Phenyl

Formula 3. Neroli

Grams	
270	Petitgrain
130	Linalyl acetate
100	Linalool
50	Methyl anthranilate
50	Phenyl ethyl alcohol
40	Geraniol
30	Geranyl acetate
30	Bergamot
30	Lemon oil
20	Aurantiol
20	Linalcol
20	Terpineol
5	Basil
_2	Phenyl ethyl acetate
797	

Formula 4. Neroli

Grams	
400	Petitgrain
400	Methyl anthranilate
240	Linalyl acetate
140	Limonene
130	Pinene
40	Phenyl acetic acid
40	Palmitic acid
10	Benzoic acid
1400	

Perfumery Notes

acetic acid is a sensitizer, and it has been eliminated. Dimethyl anthranilate is a photoirritant and its percentage has been limited in perfumery use.

However, the natural neroli oil, among several other essential oils, is considered as having antimicrobial and antifungal activity against certain Gram-positive and Gram-negative organisms (among which is Vibrio cholerae and E. coli, as well as various fungi). 14,15

Attempts to reproduce neroli oil before the advent of dermatological consideration are illustrated in formula 4.

More recent neroli oil imitations as well as neroli compounds may include cis-3-hexenol and its esters, neroli oxide, methyl jasmonate, rose oxides, damascenones, as well as other new aromatics, some mentioned previously, as they become available. Small amounts of macrocyclic musks may be used as fixatives.

Application

Natural neroli oil is very expensive, and therefore is used only in deluxe fragrances. Synthetic neroli compounds are used to cut natural neroli oils in eau de colognes.

In smaller amounts, neroli is used in the following floral and non-floral compositions: acacia, carnation, cyclamen, fougère, gardenia, honeysuckle, jasmin, magnolia, new mown hay, hyacinth, lilac, lily of the valley, narcissus, orange flower, lilac, jonquil, sweet pea and tuberose.

Although used before World War II as an innovative perfume without alcohol, among other florals, neroli did not become popular as a fragrance per se.¹⁶

The main application of neroli is in classical eau de colognes. Portugal lotion, an eau de cologne based on orange terpeneless and neroli, containing no lavender or rosemary, fortified with aldehyde C-10, has been popular. ¹⁷ Of more recent innovative colognes, Eau Sauvage may be mentioned.

In eau de cologne compounds neroli acts as a fixative for bergamot because of the fixation effect of the lower boiling material (neroli) upon the higher boiling material (bergamot).¹⁸

Neroli is also used as component in various fragrances: lavender (especially English type), chypre, amber types (small amounts for top note), aldehydic compositions of neroli and rose combination. Among other established fragrances containing neroli or its components are: Chanel No. 5, Arpege, Fleurs de Rocaille, Fougere, Cuir de Russie, Vol de Nuit, Fleurs de Tabac, Cashemir, Origan, Miss Dior, and Fidgi.

Neroli is also used in better soap colognes, among them orange flower, fougere, lettuce, and opoponax type compounds as well as in newer fragrance types.

In the men's fragrance lines, woody types contained neroli. English Leather is a good example of neroli application.

Orange flower water (neroli distillation water) has been used in classical colognes, among them in Marina Farina type, and in various hair lotions, almond milks, stearate creams, as well as astringents.

Summary and Conclusions

Neroli oil is obtained from the bitter orange tree blossoms by distillation. Neroli plays an important role in classical and modern colognes. It is also used as a component in various women's and men's fragrances. Neroli is an expensive flower oil, and synthetic compounds are used to cut or to replace entirely the natural oil in less expensive fragrances and colognes.

It is difficult to reproduce the typical odor of the natural oil, although new research has been done on citrus flower oils and a few new aromatics are available.

Neroli, with its elusive top note and fixative properties, will remain an important note in both women's and men's fragrances.

References

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