Perfumery Notes

Muguet in perfumery a review of lily of the valley

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The odor character of the flowers of lily of the valley (Convallaria majalis L.) is appreciated by almost everyone. An essential oil of the flowers is not commercially available. Therefore, perfumers must create compositions of this odor type based upon their memory of the natural product, using other essential oils and synthetic fragrance materials.

Historical review

Lily of the valley belongs to the family of the Liliaceae, subfamily Asparagaideae, tribus Convallarieae. Two species are known of the genus Convallaria, Convallaria majalis L. (European lily of the valley) and Convallaria keisukei Miq. (Japanese lily of the valley). The species Convallaria transcaucasia Utkin and Convallaria manshurica Kom. can be regarded as polymorphic forms of the first two species.[1]

It is almost a tradition in publications about the composition of the flower oil of lily of the valley to reveal one characteristic substance. In 1836 Herberger studied the essential oil of lily of the valley for the first time and isolated a crystalline substance, which was very odoriferous.[2]

In 1913 Kerschbaum mentioned farnesol as an ingredient of the oil, and wrote, "For the preparation of farnesol, the expensive and difficult to obtain flower oils, in which it is present, like reseda etc., are not suitable. The odor characteristics of farnesol are very strange, in pure form the product is almost odorless. However, a very low concentration of the alcohol on a glass stick in the air develops after a short time a very intensive sweet, lily of the valley resembling odor, which lasts for several days."[3]

Sabetay, referring to the work of Kerschbaum, mentioned that this author had not given any experi-

0361-8587/80/0005-0101$02.00/0

Perfumer & Flavorist (ISSN 0361-8587)
Volume 5, Number 6

October/November 1980

mental proof of the occurrence of farnesol in the flower of the lily of the valley.[4] Sabetay himself extracted a concrete from the flowers, possessing a mild odor character, with muguet, rosy, neroli, and citrusy notes. By oximation he determined the presence of a notable amount of carbonyl derivatives and mentioned that "one already had supposed the presence of hydroxycitronellal in the flower of lily of the valley." As far as we know, there is still no evidence for the presence of this product today.

Cook discussed modern lily of the valley compositions. Apparently referring to the work of Sabetay, he wrote, "The lily of the valley flower or perfumer's muguet (Convallaria majalis L.) is found in the humid woods of southern France. A petroleum ether concrete has been made from the flowers and stalks. Farnesol was identified in the perfume."[5] It was just this statement which Sabetay had doubted.

In 1969, Wakayama and Namba published their thorough work on the constituents of the concrete from the flowers (Convallaria keisukei Miq.).[6] In this excellent investigation the authors for the first time used modern techniques. They revealed neither the presence of farnesol nor that of hydroxycitronellal. Moreover they did not find components that are characteristic for the muguet odor.

Mack and Kopsel published their results of an extensive investigation concerning odoriferous materials of the lily of the valley and lilac blossoms in 1973.[7] They mentioned that their olfactive judgment of the oil was that it represented the typical odor of the flowers. In one experiment by extraction of the condensed aqueous headspace of the flowers, leaves, and stalks with freon, the oil had a green odor of the leaves and stalks. This work was carried out very carefully, using the most up-to-date techniques. They did not demonstrate the presence of farnesol, as was suggested by their former colleague Kerschbaum.[3]

Although a series of odoriferous components were identified for the first time in the oil, no odor compound characteristic of muguet was found.

Some years ago, we studied the composition of the essential oil of the flowers and stalks of the lily of the valley (Convallaria majalis L.). We could partly repeat the results of Wagayama and Namba and of Mack and Kopsel and isolated some other components (see Table 1). Our essential oil consisted of about 70% citronellol, nerol, geraniol, and their acetates. No component with the characteristic muguet odor was isolated.

Isolation and analysis of the flower oil of lily of the valley

From 20,000 stalks with flowers of the lily of the valley, the flowers were carefully cut off. These flowers were extracted at ambient temperature for 1.5

Table I. Chemical composition of lily of the valley flower oil

Isoprenoid hydrocarbons	References
myrcene	7
ocimene	7
limonene	7,x
alpha-phellandrene	7
beta-phellandrene	7
alpha-terpinene	7
gamma-terpinene	7
terpinolene	7
p-cymene	
Ethers (cyclic)	
rose oxide	7
linalooloxide	7
2,2,6-trimethyl-6-vinyl-tetrahydrofuran	7
Alcohols	
n-pentanol	x
cis-3-hexenol-1	7,x
octene-1-ol-3	x/t
linalool	6,7,x
citronellol	6,7,x
nerol	6,7,x
geraniol	6,7,x
alpha-terpineol	x
beta-terpineol	x/t
farnesol	x
benzylalcohol	6,7,x
beta-phenylethanol	6,x
cinnamic alcohol	6,x
3-phenylpropanol	6,x
Aldehydes	
citral	6,x
citronellal	6,7,x
benzaldehyde	6,7,x
cinnamic aldehyde	x
Esters	
isoamylpropionate	x/t
cis-3-hexenylacetate	6,x
cis-3-hexenylpropionate	x/t
cis-3-hexenylbenzoate	x/t
linalylacetate	6
geranylformate	x
geranylacetate	6,7,x
geranylheptylate	x
nerylformate	x
nerylacetate	6,7,x
citronellylformate	x
citronellylacetate	6,7,x
farnesylacetate	x
benzylformate	x
benzylacetate	6,7,x
benzylcapronate	6
beta-phenylethylformate	x
beta-phenylethylacetate	7,x
cinnamylformate	x
cinnamylacetate	6,x
cinnamylcapronate	6
3-phenylpropylacetate	6
methyl anthranilate	6
methyl salicylate	6
Miscellaneous	
benzylcyanide	7,x
indole	7,x
phenol	x
p-cresylmethylether	x/t
creosole	6
methylnonylketone	x/t

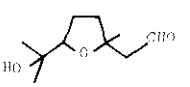
x = this publication; x/t = trace component

hours with about 28 liters of pentane (pro-analysis, redistilled). Subsequently the pentane was poured off and the flowers again extracted with about 11 liters of pentane. The collected pentane extracts were evaporated in distillation apparatus with 50 cm Vigreux column; there was obtained 200 ml of residue (with pentane). The residue was transferated (high vacuum distillation). The transferate was concentrated to 5 ml.

This concentrate was analyzed with the combined GC-MS technique. The identified components were checked on GC-retention time with reference substances. GC conditions: 50 M glass column, inside diameter 0.75 mm; Trennzahl 15; column temperature 70-180°C, 1°C/minute; injector temperature 160-240°C. Table I gives the identified components of the flower oil of lily of the valley from the referenced studies.

According to our perfumers, at least one peak in the olfactogram of the oil had a very strong character of muguet, with a floral note like hydroxycitronellal or Lilial, but even stronger and more natural. Lack of sufficient material prohibited isolation of this component. Moreover, from the olfactogram of the oil from flowers and stalks we got a strong indication of the presence of traces of substituted pyrazines, possibly together with cis-3-hexenol (and acetate) responsible for the green note of the stalks.

However, with regard to the occurrence of cyclic ethers and citral/citronellal in the essential oil we could imagine at least one characteristic compound in the natural essence, with the following structure.



We synthesized this product, which indeed has a fresh-floral odor, with a fruity-citrusy note.

We studied the commercially available chemicals with a muguet watery-floral odor character. The odor

character of muguet can be divided into two main aspects, e.g., the fresh-floral and the watery-floral.

The following remarks about structural features with respect to the compounds with a muguet odor type were made in 1973 (see Table II).[8]

1. All compounds do have an aldehyde group, and another functional group may also be present.
2. Many of the substances possess a double bond in the gamma-delta-position; this structure element can be replaced by an oxygen atom in the beta-position.
3. In the middle part of the molecules there are branched alkyl groups, cyclo-alkyl groups or a benzene nucleus (2.5-3.75 nm).[9]
4. At the opposite part of the molecule, in relation to the aldehyde function, the substances bear a bulky group, sometimes containing an essential hydroxyl group, which promote and modifies the odor.

Are these rules still valid today? We believe they need some modifications

1. The aldehyde function remains necessary.
2. An improvement over the gamma-delta double bond or the beta-oxygen atom is a relatively high electron density around the third carbon atom (-O-C_3,C_3=C, or C_3-C=C).
3. The branching of the carbon chain and the bulky group is not present in cis-4-decenal. However, all the molecules with a muguet odor possess a maximum length of 12-14 nm.

Materials for lily of the valley notes

Hydroxycitronellal—One of the oldest essential "building stones" for the lily of the valley fragrance. It has a characteristic floralcy, faintly reminiscent of citronellal with a slight woodiness in the background (like sawdust). The disadvantage of this aroma chemical is its aldehydic structure and because of that, it is instable in very high or very low pH ranges. Furthermore, it is a rather weak-smelling material.

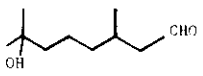
Bourgeonal (Naarden), Lilial (Givaudan), and *Bamca (UOP)*—These aroma chemicals have high impact and a typical strong and sweet lily of the valley note. They also possess a slightly green and watery character and are floral-waxy in the drydown. Bourgeonal is 2 to 3 times as strong as Lilial at the same concentration. Relatively small amounts (1% to 5%) in any given lily of the valley compound are very effective.

Cyclamal (Givaudan)—A traditional, effective high impact aroma chemical with the typical note of wild cyclamen flowers but also reminiscent of lily of the valley with a strong watery-fresh and slightly woody character. It is used frequently in lily of the valley compounds and has a better stability in soap than Lilial, but is somewhat lacking in the sweetness found in Lilial.

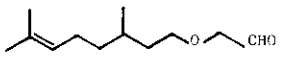
Dupical (Naarden)—One of the new lily of the valley components with extremely high odor impact. It has a strong lily of the valley connotation, is also green and at the same time sweet and much less watery than Cyclamal and Lilial. Amounts ranging from 0.5% to 2.5% used in a fragrance with lily of the valley note

Table II. Chemical structures of muguet aroma chemicals

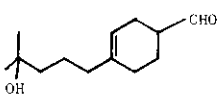
Hydroxycitronellal



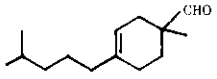
Citronellyloxyacetaldehyde



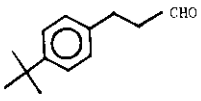
Hydroxyempetal/Lyral



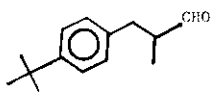
Vernaldehyde



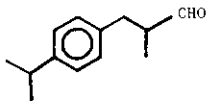
Bourgeonal



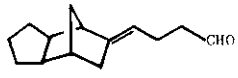
Lilial



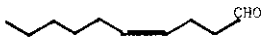
Cyclamal



Dupical



Cis-4-Decenal



Trimethyl Undecylenealdehyde

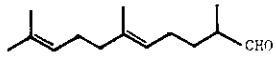


Table III. Evolution of muguet accords

Products	1926	1932	1949	1960	1970	1980
HO-citronellal	40%	29%	22%	30%	10%	5%
Terpineol	10	36	6	15	5	5
Citronellol	10	--	5	15	25	40
Citronellylformate	--	--	--	4	--	--
Citronellylacetate	--	--	--	--	--	10
Linalool	--	21	5	15	--	--
Tetrahydrolinalool	--	--	--	--	7	--
Tetrahydromyrcenol	--	--	--	--	--	10
Freesiol	--	--	--	--	--	1
Ionone	4	7	6	--	--	--
Farnesol	--	--	--	--	20	--
Benzylacetate	6	--	--	--	5	--
Benzylpropionate	--	--	--	2	--	--
Benzylbenzoate	20	--	--	--	--	--
Benzylsalicylate	--	--	--	5	--	--
Beta-phenylethanol	10	--	--	--	13	10
Phenylethylacetate	--	--	--	--	5	--
Anisylformate	--	--	--	4	--	--
Aubepine	--	--	4	--	--	--
Heliotropine	--	--	6	3	--	--
Vanillin	--	--	3	--	--	--
Musk ambrette	--	--	5	--	--	--
Astrotone	--	--	--	--	5	--
Ylang-ylang oil	--	7	3	2	--	--
Copaiva oil	--	--	--	--	5	--
Jasmin absolute	--	--	--	3	--	--
Civet tincture 3%	--	--	--	2	--	--
Muguet base	--	--	35	--	--	--
Cyclamen aldehyde	--	--	--	--	5	--
Bourgeonal/lilial	--	--	--	--	--	2-5
Lyral/HO-empetal	--	--	--	--	--	2-5
Dupical	--	--	--	--	--	1
TMU's	--	--	--	--	--	1
Aryl carbinol's	--	--	--	--	--	5
Hexenyl acetate	--	--	--	--	--	1

have a very good effect. Although this aroma chemical has an aldehydic structure, resulting in a certain loss in odor impact when used in media with a higher pH range, this is compensated for by its high impact value.

Cis-4-decenal (Bedoukian)—This aroma chemical is one of the newest items on the perfumer's palette. It has an extremely high odor impact and is generally used only in 1% to 10% solutions. Its odor characteristics can be described as strong lily of the valley, sweet, somewhat green, and pleasantly fatty. Used in a muguet compound at a level of 0.05% to 0.15%, it is very effective and adds life, lift, and radiation to the fragrance. However, this material is a top note only and because of its chemical nature it should be applied with caution.

Trimethyl undecylenic aldehydes, Farenal (Haarmann & Reimer), and *Oncidal (Dragoco)*—Out of all of the aforementioned materials these have the least characteristic lily of the valley note, though they are used quite frequently in muguet fragrances. Their odors are clearly fresh-watery, waxy, and aldehydic. Perfumers use these items to add certain freshness, real naturalness to lily of the valley and other floral compounds.

Freesiol (Haarmann & Reimer)—An item used more and more by perfumers because of its faint resemblance with linalool, which is one of the most important traditional muguet components. Freesiol is stronger than linalool but also more citrusy-fresh and has better stability in certain products with high or low pH value. In lily of the valley compounds, Freesiol works as a modifier and adds freshness and a sparkling top note.

Phenylethyl dimethyl carbinol—This item does not really belong in the group of aroma chemicals with a more or less typical lily of the valley note, but it is used in many lily of the valley compounds as a base note. Smelled by itself, its odor can best be described as slightly woody-fresh, generally floral, somewhat rose-like. It is a perfect material to round off a muguet fragrance.

Phenylethyl methyl ethyl carbinol—This also is not a real muguet-like smelling ingredient. Its warm-woody, floral (rosy), and slightly honey-like odor, however, gives richness and depth to any lily of the valley fragrance and is used accordingly.

Hydroxyempetal (Naarden) and *Lyral (IFF)*—These materials have a rich and warm lily of the valley character, which develops especially after about an hour and even more so towards the drydown. When added to a fragrance complex they give body and full floralcy.

Citronellyloxyacetaldehyde—A very strong aroma

chemical with a characteristic note of lily of the valley though also somewhat rosy-waxy and woody, it has a faint hint of citronellal. Perfumers use this item to accentuate the top note of a lily of the valley complex and lift up the rose notes used in those compounds.

History of muguet perfume compositions

The evolution of muguet accords since 1926 is shown in Table III. The authors have cited only the most important materials, which are mentioned in the literature.[5,12,13,15,16] In the original literature more components are given; Lazare mentions 19 materials,[12] Mann and Winter 10,[13] Ruemele 2,[15] and Jellinek 4.[16] Additional recent information regarding the compounding of muguet accords has been published.[14,17-20]

A rough analysis of the evolution of muguet accords shows us

1. The old fashioned hydroxycitronellal decreases, while the modern products like Bourgeonal, Lyral, Dupical, and TMU's increase.
2. The content of citronellol (Rhodinol) and esters increases, maybe due to the fact that about 70% of the natural isolate consists of citronellol, geraniol/nerol, and esters.
3. The ionones have disappeared.
4. Linalool came into use and then was replaced by the fresh notes of tetrahydrolinalool, tetrahydromyrcenol, and the aryl carbinols (benzyl-(phenylethyl)-dimethyl carbinol).
5. Farnesol was used incidentally.
6. Benzenoids except β-phenylethanol (and the aryl carbinols) appeared and then disappeared; however some aromatic aldehydes can be used in minor quantities as modifiers; β-phenylethanol remains necessary.
7. Musk chemicals have sometimes been used but do not seem to be necessary.
8. Natural products, like ylang-ylang oil, copaiba oil, jasmin oil, or tuberose abs., often are employed as modifiers and may be very useful.
9. Green notes such as cis-3-hexenylacetate or traces of 2-methoxy-3-isobutyl pyrazine can be used with success.[5]

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