

Lily of the Valley (Muguet) in Perfumery

By Danute Pajaujis Anonis, Consulting Chemist Perfumer,
Ridge Park, New York

Lily of the valley is an important floral odor in perfumery. The natural flower oil is not commercially available although attempts have been made to obtain the concrete of lily of the valley.

In the early part of this century, a product called Muguet de Mai was commercially available, but it was a lily of the valley-like extract produced in Grasse from the hyacinth-like freesia.¹

The advent of aromatic chemicals paved the way for synthetic lily of the valley compounds which are now being used in perfumery.

Botanical Origin

Lily of the valley, *Convallaria maialis* L. (fam. Liliaceae) originated in Asia Minor, or Persia (now Iran), and is known in Europe as a wild growing plant.² Another species of lily of the valley is *Convallaria keikusei* Miq. (Japanese lily of valley).³

Mode of Production, Yield, Type of Oil

Steam distillation can not be applied to obtain the lily of the valley oil.

Attempts have been made to extract the flower oil with petroleum ether. The yield of the concrete obtained from the flowers and stalks was 0.42 to 0.55 per cent. Extraction of the flowers alone gave 0.9 to 1.05 per cent of the concrete.⁴

Another method which tried to obtain the concrete was butane extraction of the flowers.⁵

Lily of the valley oil produced by these methods was and still is being used only for scientific research.

Chemical Composition

As early as 1836, a crystalline substance possessing a strong odor was reported in a study on the composition of the lily of the valley.⁶

At the beginning of this century in another study, the presence of farnesol was indicated.⁷ This was later disputed.

In the last three decades, new research work in lily of the valley was done in Japan,⁸ in Germany,⁹ and in Holland,¹⁰ and over fifty components were reported. Previously identified main components were confirmed, and a number of new components present in low concentrations were found. Some of these are significant to the odor of lily of the valley.

Components found in both species reported in the above studies are listed in Table I; additional components found only in *Convallaria Maialis* L. are shown in Table II; those found only in *Convallaria kekusei* Miq. are shown in Table III.

Synthetic Compounds

As no natural lily of the valley flower oil was commercially available, synthetic compounds had to be developed. The base of the early lily of the valley compounds consisted of hydroxycitronellal combined with jasmin and rose components to which linalool, terpineol and ionone were added. Cinnamic alcohol, farnesol, methyl heptin- and octin carbonates, guaiacwood acetate, indol and cresol esters, nonalactone, aldehydes C-8, C-9, C-11 (enic), and C-12(MNA) were used in smaller amounts to add nuance.

Table I. Identical Components of *Convallaria malalis* L. and *Convallaria kekusei* Miq.

Components	Japan(8)	Germany(9)	Holland(10)
Benzaldehyde	+	+	+
Citral	+	+	-
Citronellal	+	+	+
Benzyl alcohol	+	-	+
Cinnamic alcohol	+	-	+
Citronellol	+	+	+
Geraniol	+	-	+
Linalool	+	+	+
Nerol	+	-	+
Phenyl ethyl alcohol	+	+	+
Phenyl propyl alcohol	+	+	+
Creosol	+	+	-
Benzyl acetate	+	+	+
Cinnamyl acetate	+	-	+
Citronellyl acetate	+	-	+
Geranyl acetate	+	+	+
Cis-3-hexenyl acetate	+	+	+
Methyl anthranilate	+	+	-
Methyl salicylate	+	+	-
Neryl acetate	+	+	+
Neryl formate	+	+	+
Phenyl propyl acetate	+	+	-

Table II. Additional Components of *Convallaria malalis* L.

Components	Germany(9)	Holland(10)
Limonene	+	+
α -Phellandrene	+	-
Farnesol	-	+
Cis-3-hexenol	+	+
Octene-1-ol-3	-	tr
n-Pentanol	-	+
α -Terpineol	-	+
β -Terpineol	-	tr
α -Terpinene	+	-
Phenol	-	+
Cinnamic aldehyde	-	+
Benzyl caproate	+	-
Benzyl formate	+	-
Cinnamyl caproate	+	-
Cinnamyl formate	-	+
Farnesyl acetate	-	+
Geranyl formate	-	+
Geranyl heptylate	-	+
Cis-3-hexenyl benzoate	-	tr
Cis-3-hexenyl propionate	-	tr
Isoamyl propionate	-	tr
Methyl nonyl ketone	-	tr
Neryl formate	-	+
Phenyl ethyl acetate	+	+
Phenyl ethyl formate	-	+
Linalool oxide	+	-
Rose oxide	+	-
Benzyl cyanide	+	+
Indole	+	+
2,2,6-trimethyl-6-vinyl hydrofuran	+	-

* not specified

Table III. Additional Components of *Convallaria kekusei* Miq.

Components	Japan(8)
Benzyl capronate	+
Cinnamyl capronate	+
Linalyl acetate	+
3-Methyl propyl acetate	+

For the green note, phenylacetaldehyde dimethyl acetal was important. Later, aromatic carbinols and their acetates were used. Phenyl propyl aldehyde and dimethyl octanol were some of the other aromatics used.

Fixatives were civet, olibanum, balsam tolu and styrax resinoid, as well as crystalline aromatics, i.e., musk ketone and vanillin. Later, musk and civet specialties were used as fixatives, replacing natural civet and musk.

Among trace components, are cardamon, celeri, clary sage, coriander, cuminic aldehyde, neroli and ylang. Of the absolutes, cassie, mimosa, orange flower, rose, reseda, tuberose and violet leaves may be cited.

As new aromatics became available, they were used in lily of the valley compounds.

Glycol derivatives became important, for example, phenyl glycol acetate, phenyl glycol acetal of phenylacetaldehyde and propylene glycol acetal of phenylacetaldehyde.

The following are among less common aromatics that have been used to capture the elusive odor of lily of the valley: anisyl acetate, anisyl formate, cinnamyl acetate, cinnamyl butyrate, citronellyl formate, linalyl isobutyrate and phenyl ethyl salicylate.

The following percentages of less known aromatics have been recommended in lily of the valley compositions:¹¹

citronellyl cinnamate (1-3%)
dimethyl octanyl phenyl acetate (3%)
geranyl cinnamate (0.5%)
linalyl anthranilate (2%)
neryl isovalerate (4%)

Examples of few conventional illustrative lily of the valley compounds are shown in Formula 1-3.

New research on lily of the valley has shown that its main constituents are rose alcohols (geraniol, citronellol and nerol), and their acetates, comprising 70 per cent of the flower oil.³

Accordingly, modern lily of the valley compounds are being reformulated to include a higher percentage of rose alcohols and their esters, and smaller amounts of hydroxycitronellal. The later has not been identified in the lily of the valley flower oil. As more stable aromatic chemicals became available, i.e., cyclamen aldehyde, Lilial and Lylal, they were used in lily of the valley compounds. More recent aromatics in the hydroxycitronellal odor type are: Dupical (Naarden), cis-dihydro shiseol (Mayol-Firmenich), and Bourgeonal (Naarden) among others. The use of ionones has also declined.

Hexenol and nonadienol and their esters brought a new gamut of green and folial odors. Several green type aromatics are cited:¹² trans-2-hexanyl acetate, cis-hexenyl ethyl acetal of phenylacetaldehyde, dihydrodicyclopentadienyl acetate, and acetaldehyde ethyl phenylethyl acetal, to mention but a few, encompass fruit-, flowery-, herbal-, cucumber- and violet-green odor types.

Cis-r-decenal, trimethyl undecylenic aldehyde are among the newer aldehydes available. Oxy-acetaldehydes, including cis-hexenyl oxyacetaldehyde, bring new possibilities.

Dihydrolinalool and piperonyl propanal are few examples of replacements for older aromatic chemicals.

Methyl dihydrojasmonate (Hedione), jasmolactone and derivatives of cyclopentenone, among others, are used per se or as components of jasmin compounds in lily of the valley formulas. Analogically, rose oxides and damascenones are used for the rose note, and neroli oxide in the orange flower. Two more recent groups of aromatics used in perfumery are furan and pyrazine derivatives. Among the later, 2-methoxy-3-isobutyl pyrazine of a green odor tonality may be mentioned, and 2,2,6-trimethyl-6-vinyl hydrofuran (listed in Table II) was newly discovered in lily of the valley oil.

The majority of components of modern lily of the valley compounds being rose alcohols presents no problems of stability in alkali. The same may be said of most hydroxycitronellal replacements.

In regard to sensitization, several perfume materials previously used in lily of the valley compounds have been eliminated; others are used in purified form, in limited concentration or in conjunction with quenchers. Among the first are coumarin, farnesol, heliotropin, methyl heptene carbonate, musk ambrette, orris concrete and balsam Peru. Bergamot and styrax resinoid belong to the second group. Cinnamic alcohol, isoeugenol, and phenylacetaldehyde may serve as examples of the third group.

Lily of the Valley Formula 1

	Parts
Hydroxycitronellal	150
Geraniol	30
Ylang	30
Linalool	30
Terpineol	30
Rose synthetic	15
Benzoin resinoid, 20%	15
Coriander	0.4

Lily of the Valley Formula 2

	Grams
Hydroxycitronellal	350
Jasmin synthetic	100
Rhodinol	100
Terpineol	30
Geraniol	20
Linalool	20
Cyclamen aldehyde	7
Phenyl ethyl alcohol	5
Guaiacyl acetate	5
a-Ionone	5
Rose absolute	3
Geranyl acetate	2
Cuminic aldehyde	0.5

Lily of the Valley Formula 3

	Parts
Hydroxycitronellal	320
Benzyl acetate	70
Phenyl ethyl alcohol	30
Ionone	25
Linalool	25
Jasmin synthetic	20
Rose synthetic	15
Rhodinol	12
Terpineol	10
Citronellyl oxyacetaldehyde	10
Geranyl acetate	6
Rose absolute	5
Bergamot, desensitized	5
Sweet orange, terpeneless	4
Rose Otto	2
Guaiacyl acetate	2
Orange flower absolute	1.5
Ylang	1
Isoeugenol	1
Isopropyl hydratropic aldehyde	1
Musk ketone	0.5

Application

In the beginning of this century, synthetic lily of the valley compounds were produced by the German chemical industry. Lily of the valley (known as muguet) was offered in the form of a

straight perfume oil, along with jasmin, rose, carnation, heliotrope, and violet in small vials as fragrance. Another application was to mix these perfume oils with a specified amount of eau de cologne or alcohol to obtain what were known at that time as "triple extraits".¹³

Before World War II, innovative perfumes without alcohol, adaptable for export, were available in Germany. Diethyl phtalate, castor oil and others were used as solvents. Lily of the valley was included among other floral fragrances.¹⁴

Among single lily of the valley fragrances of the past, Muguet (Coty), Premier Mai (Houbigant), and Muguet de Chaville (Cheramy) may be cited.

Lily of the valley compounds were valuable components of past perfumes, as they still are in modern fragrances. Among the early perfumes, containing lily of the valley or its components, Quelques Fleurs, Amour Amour, Chanel 5, Arpège and Je Reviens may be mentioned.

In the 1940s and 1950s, White Shoulders, Réplique, Chantilly, L'air du Temps, Wind Song, Intimate, and especially Diorissimo—a reborn muguet fragrance—are good examples.

Among fragrances of the 1960s and 1970s, Fidgi, Madame Rochas, Rive Gauche, Charlie, Aliage, White Linen and Adolfo may serve as examples.

Of the newer modern fragrances we cite two examples, in Première, lily of the valley is blended with gardenia and honeysuckle; in Armani—with jasmin, orange flower and hyacinth.

In general, lily of the valley is osmotically compatible with many floral notes, among them, besides the above mentioned, jonquil, reseda, rose and violet; it also blends well with aldehydic and green, as well as folial notes.

Lily of the valley cream perfumes, containing undecalactone, aldehyde C-12(L), vetyver acetate, and benzyl salicylate have a good coverage of the lanolin odor. Dihydrocitronellal, terpineol, and phenylacetaldehyde dimethyl acetal are other aromatics used in traditional lily of the valley type of cream perfumes.

Lily of the valley is also used to perfume lotions. Some lily of the valley compositions contained lilac compounds, older ones were fixed with musk and civet infusions and tolu resinoid, and some contained methyl heptene carbonate.

Lily of the valley fragrances for powder contain terpineol, linalool, benzyl acetate and hydroxycitronellal as base, and among other components are heliotropin, coumarin, musk ambrette, tolu balsam, cinnamic alcohol, ylang and aldehyde C-12(L).

Conclusion

In spite of a number of new aromatics identified in the lily of the valley oil, none of them suggests the basic scent of the flowers.

The unique characteristic of the lily of the valley flowers, as observed by the writer, is that the dry blossoms, while losing part of the ethereal green-floral odor, retain a musky sweetness with a light green note for weeks when enclosed in a plastic envelope. In contrast, lilac blossoms lose all odor and change to a rusty color when wilting. Present aromatic research concentrates mostly on analyzing head space constituents of the flower oils. Perhaps new residual components of the lily of the valley would help to better reproduce the elusive odor of lily of the valley.

Lily of the valley has not lost its importance in perfumery. It has found a more universal application. Previously there was a clear division of two main groups of fragrances: the heavier sultry orientals and chypre-derived types, and the light floral-aldehydic-green types. Lily of the valley belonged to the latter group of fragrances and found extensive application in the "green" type fragrances of the 1970s. In the last decade, semi-oriental, fruity-floral-green fragrance types have evolved, and lily of the valley became part of these fragrances.

As men's line fragrances became more sophisticated, lily of the valley components found their way into these fragrances.

References

Address correspondence to Ms. Danute Pajaujis Anonis, 98-41—64th Road, Rego Park, NY 11374, U.S.A.

1. O. Gerhardt, *Das Komponieren in der Parfumerie*, Akademische Verlagsgesellschaft, M.B.H., Leipzig (1931), p. 62
2. *Ibid.*, p. 62
3. M. Boelens, H. J. Wobben and J. Heydel, *Perfum. Flavor.*, **5**(5), 1-8, October/November 1980
4. Naves and Mazuyer, *Les Parfums Naturels*, Paris (1939), p. 250
5. M. Meunier, *Ind. Perfum.*, **5**, 26, 1950
6. B. Herberger, *Rept. Pharm.*, **2**, 397, 1836
7. M. Kerschbaum, *Chem. Ber.* **46**, 1732, 1913
8. S. Wakayama and S. Namba, *Nippon Kagaku Zasshi* **90**(11) 1160-3, 1969
9. H. Mack and M. Köpsel, *Parf. Kosm.*, **54** 8/73, 233, 1973
10. M. Boelens et al., *ibid.*
11. E. S. Maurer, *Perfumes and their Production*, United Trade Press, Ltd., London, 1958, 125-160
12. A. F. Morris, *Perfum. Flavor.*, **6**(1), 1-7, February/March 1981
13. *Le Nouveau Bréviaire de la Beauté*, G. Clarks, Paris, 89, 176
14. H. Fouquet, *La Technique Moderne et les Formules de la Parfumerie*, Paris & Liège, Librairie Polytechnique Ch. Béranger, 1951, p. 141.

