Perfume Formulation

THE VIOLET GROUP

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Of the violet group, the violet fragrance and its related specialty effects are the most important to the perfumer; they are all based on the ionones.

Cassie and mignonette (Reseda) are classified with the violet because the ionones are used extensively in their make-up. As fragrances they themselves do not seem to have much attraction for the general public. This is probably because these flowers are not familiar in American gardens. Natural cassie and mignonette are used as adjuvants and modifiers in violet fragrances, and also find minor uses elsewhere in fantasies. The same is true of cassie and mignonette compositions. Of the two, cassie is used more frequently because of its closer resemblance to violet. Small amounts of cassie types are useful in aldehyde bouquets to help minimize the thinness of the aldehydes, and in fougeres and chypres for the interesting "twist" they can confer on these classic themes.

The Ionones

Tiemann's original ionone synthesis consists of two steps: the aldol-type condensation of citral with a ketone to make the so-called "pseudoionone"; and the cyclization of this product to form a citrylidene ketone. If the initial ketone is acetone, the end product would be the conventional commercial ionone. If the ketone is methyl ethyl ketone, then the result would be the familiar methyl ionone. "Methyl" is not correct nomenclature, but is used to indicate that the methyl group in the side chain of the parent ionone has been extended by one CH_2 group. "Ethyl" ionone would mean two CH_2 groups, and so on. Alpha and beta isomers exist for all the ionones, determined by the position of the double bond in the citrylidene ring. Thus, alpha ionone in Geneva nomenclature would be called: 4(2,6,6-trimethyl-2-cyclohexenyl) buten-3-one-2. Beta ionone would then be 1-cyclohexenyl structure, indicating the shift of the double bond in the foregoing nomenclature. The ionone structure on paper is a substituted and partially hydrogenated relative of the familiar benzylidene acetone.

Ionone and methyl ionone, made, respectively, from acetone and methyl ethyl ketone, have been conventional fragrance materials for decades. Few people—and this includes a substantial number of present day perfumers seem to realize there are other ionone derivatives available that have considerable novelty and utility. For example, carrying out Tieman's synthesis with diethyl ketone produces dimethyl ionone. This is a methyl ionone in which an additional methyl group is attached to the carbon adjacent to the ketone carbonyl group on the side-chain connected to the double bond. In Geneva nomenclature, this side-chain fragment would then be called: penten-4, 4-methyl-one-3. Because of the symmetry of the parent ketone, this so-called dimethyl ionone exists only as the alpha and beta isomers. It is available as the alpha-beta mixture, possessing a curious semi-fruity orris-like note. In perfumery its orris note is useful in conjunction with vanillin, heliotropine, coumarin and musk ketone to produce interesting "powdery" notes. It is also attractive as a modifier of the conventional methyl ionone note. In flavors, it finds its best use in raspberry to create the seed effect.

Another derivative, not well-known in America, is the so-called "acetyl" ionone, made by condensing acetylacetone in the Tiemann synthesis. Because of the symmetry of the parent ketone, acetylacetone, this exists only as alpha and beta isomers. This alpha-beta mixture has a peculiarly intense fruity-violet effect partially recalling the citrus notes. It provides a nuance in cologne designs when combined with the citrus oils. Although it blends well with all the citrus oils, it is most favorable with orange, mandarin and petitgrain. In flavor work it is especially interesting in conjunction with mandarin oil for the fruit flavors raspberry and strawberry. In cosmetic work this acetyl ionone will serve as a fruity modifier in place of the citrus oils, with consequent safety against deterioration, discoloration and irritation.

The various ionones can be hydrogenated at their double bonds, to produce a series of striking variation on the ionone themes. Hydrogenation usually produces an increase in the "precious wood" effect of the ionone, at the expense of its violet notes. This change makes these products extremely useful for creating the "expensive" finish in th lower-priced fragrances.

It is believed that many more of the unusual ionone derivatives have ben made, but are being held as "captive" chemicals because of their originality. The author feels that the secret of a certain world-famous rose specialty lies in one of these "captive" materials.

He has done some rather intricate work on the synthetic variation of the cyclocitrylidene ring structure ionone note may be altered strongly in the direction of the rose absolute odor. This is a fertile field for investigation, but not an easy one.

Because of the isomeric complexity of the ionones, it is suggested that the prefumer select ionones according to his artistic preference and then consistently buy from the same sources to avoid odor deviation.

Odor Characteristics of the Ionones

All of the commercially available ionones strongly resemble the fragrance of the violet flower. Their special and different nuances are produced by variation of the ketone structure in the side chain, coupled with the position of the double bond in the citrylidene ring.

The basic requirement of all the ionones is that they be free of "terpeny" by-odors. This grassy odor is derived from the lemongrass oil used in commercial ionone synthesis, and results from inefficient distillation during synthesis of either or both the initial pseudoionone or final ionone. This "terpeny" effect is most likely to be found in the soap grade ionones.

Commercial ionone (made from acetone) is available in three forms: ionone AB (the alpha-beta mixture), alpha ionone, and beta ionone. Ionone AB finds its principal use in soap and low-priced fragrance oils. It has a slightly coarse but nevertheless attractive violet note. This AB mixture may be chemically separated into pure alpha and beta ionones. Alpha ionone is intensely sweet but "thin." Artistically it is the better violet representation of the two isomers. Beta ionone, less important in fine perfumery than alpha, has a coarse violet note recalling a diluted raspberry fragrance.

Commercial methyl ionone (made from methyl ethyl ketone) is a mixture of four isomers, of which the iso-alpha is considered the finest in odor. Since this isomer has a boiling point differential from the others of nearly ten degrees, the various methyl ionones offered on the market under fancy names are usually redistillations of the initial methyl ionone, coupled with the reblending of various cuts, to provide a material rich in the artistically desirable alpha-iso fraction.

In general the methyl ionone note has a violet character with strong inflections of a "precious wood" effect. It is used in the violet group as a modifier of the thin ionone note, particularly the alpha ionone. This use is, however, relatively minor. Its "precious wood" effect makes it useful in a wide range of fantasies outside the violet group, to such an extent that its consumption for this purpose is many times that for violet production.

The ionone, "Ianthone" (made by condensing the unsaturated ketone mesityl oxide), was, and presumably still is, available in Europe. It possesses a most unusual pungency and is interesting both by itself and as a blend for fantasies with methyl ionone.

The dimethyl and acetyl ionones have been sufficiently discussed, and further comment is not necessary at this point.

The perfumer should be careful in his work with the ionones for two reasons: they are intensely provocative of olfactory fatigue, which makes it increasingly difficult to judge their effect in a composition as the work with them progresses; and they have a strong tendency to make the frangrances into which they are introduced flat. This quality is useful in softening the rough edges of compositions, particularly those containing aldehydes; but it can also cause an otherwise attractive fragrance design to flatten out and become dull.

The Ionone Specialties

The various ionones can be so well blended together as to produce a range of interesting effects that specific compositions have been built around them. Most of these specialties are built around methyl ionone, since it is the most versatile of the ionone series. Thre such products are shown below:

E.031 METHYL IONONE BOUQUET "A"

8	Vetyverol
6	Santalol
1	Oil labdanum distilled
1	"Veronol" aldehyde 10% in methyl ionone
984	Methyl ionone standard (rhodia)
1,000	

This composition, merely touched-up methyl ionone, has an odor remarkably more attractive than plain methyl ionone. It possesses a warm woody tone with a delightful iris and amber background. Furthermore, the presence of the vetyverol and santalol give it excellent stability. It will not go "sour" even after prolonged standing in a bottle under the adverse conditions of heat and light.

E.032 METHYL IONONE PARMA TYPE

3	Labdanum oil distilled
3	Aldehyde C-12 MNA 100%
5	"Veronol" aldehyde
10	Iris concrete
50	Vetyverol
50	Santalol
50	Tetrahydro methyl ionone
819	Methyl ionone standard (rhodia)
1,000	

This composition represents an elaborate modification of the methyl ionone fragrance for ultrafancy work. It is particularly effective in conjunction with

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Private industry should be subsidized only in cases where no non-profit organization can do the job. In such exceptional cases, however, full cooperation can be expected from a pharmaceutical firm approached by the Federal Government because of its unique qualifications.

PERFUME FORMULATION

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spice effects in the chypre class.

"ULTRAIONONE" E.033

2	"Cumin" ketone
4	Isobutyl quinoleine 5% in DEP
5	Labdanum oil distilled 10% in DEP
5	"Palatone" (Dow)
8	Vetyverol
8	Isopropyl quinoleine 5% in DEP
10	Hydratropyl alcohol
10	"Veronol" aldehyde 10% in DEP
20	Oil carrot seed 10% in DEP
34	Hydroxycitronellal
34	Eugenyl phenylacetate
30	Citronellyl oxyacetaldehyde
100	Alpha ionone
190	Methyl ionone standard (rhodia)
240	Dimethyl ionone
700	

This E.033 formula is an extreme composition based on three ionones with elaborate modifications. It is an all-purpose specialty base.

Violet

Because of the remarkable resemblance of the various chemicals of the ionone series to the violet flower, it would seem an easy matter to compound an artificial violet fragrance. Unfortunately this is not true. Although the ionones distinctly recall the violet fragrance, they are almost as difficult to manipulate effectively as the aliphatic aldehydes. Violet-type fragrances can readily be made, but a full rich fragrance that will simulate the violet flower without becoming tiresome is both difficult and costly to make.

The following are the "purpose" classifications of the violet components:

Basics. All the ionones and specialty compositions previously mentioned.

Blenders. Orris concrete, linalool, benzyl isoeugenol, eugenyl phenylacetate, hydroxycitronellal, "Cumin" ketone, isoeugenol, guaiac wood resin, guaiac wood acetate, heliotropine, benzyl acetate terpineol, diethyl hydroquinone, oil of bergamot, oil of lemon.

Adjuvants. Anisic aldehyde, hydratropyl propionate, phenylethyl acetate, allyl cyclohexane propionate, phenylethyl alcohol, tolyl alcohol; methyl heptine, methyl octine and phenylethyl heptine and octine

carbonates; methyl and ethyl myristinates, myristic aldehyde, aldehyde C-12 MNA, aldehyde C-12 lauric, eugenol, ylang Bourbon extra, ylang absolute, civet, indole, skatole, rhodinol, citronellol, dimethyl octanol, dimethyl octanyl acetate, oakmoss, "Veronol" aldehyde, citronellyl oxyacetaldehyde, geranyl oxyacetaldehyde, petitgrain natural and terpeneless, cuminic aldehyde.

Naturals. Cassie, mignonette, orange flower, rose and mimosa, jasmin absolutes.

Fixatives. Benzyl isoeugenol, eugenyl phenylacetate, benzyl salicylate, labdanum resin, costus resin, vanillin, coumarin, styrax resin, benzoin resin, vanillin Ethyl, musk xylol, musk ketone, oil sandalwood, santalyl acetate, vetyvert oil, vetyvert acetate, phenylethyl cinnamate, phenylethyl salicylate.

The following formula illustrates the design of a fully rounded violet fragrance.

VIOLETTE DE PARME E.034

250	"Ultraionone" E.033
50	Alpha ionone
40	Oil bergamot natural
20	Anisic aldehyde
10	Diethyl hydroquinone
10	Methyl heptine carbonate 10% in DEP
10	Methyl octine carbonate 10% in DEP
50	Ylang absolute
5	"Cumin" ketone
15	Isoeugenol
5	Eugenol
10	Vetyvert acetate
10	Santalyl acetate
10	Orris concrete
30	Heliotropine
5	Rose otto natural
5	Cassie absolute natural
10	Musk ketone
5	"Veronol" aldehyde 10% in DEP
5	Geranyl oxyacetaldehyde
5	Jasmin absolute
50	"Golden Jasmin" E.004
3	Civette absolute
1	Costus oil 5% in DEP
10	Hydroxycitronellal
20	Oil cedarwood terpeneless
56	Benzyl isoeugenol
700	

Cassie and Mignonette

The components of the cassie and mignonette very closely follow the violet and they need not be repeated. The principal difference is that cassie requires ethyl and isobutyl salicylates, whereas mignonette requires ethyl decine carbonate and methyl heptine carbonate, to a greater extent than is usually required by violet. Both mignonette and cassie rely heavily on the basic methyl ionone.

CASSIE E.035

10	Cassie absolute natural
15	Mimosa absolute natural
2	Rose absolute natural
10	Methyl ionone standard (rhodia)
10	Oil bergamot natural
10	Anisic aldehyde
2	Absolute labdanum extra
3	Methyl salicylate

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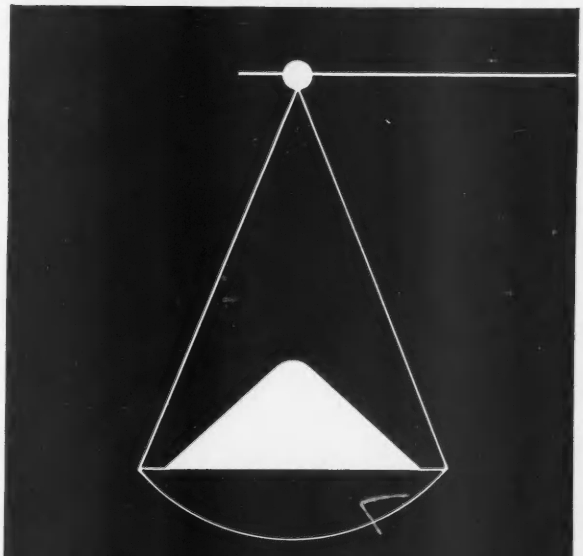

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10	Orris concrete
10	Linalool
3	Oil petitgrain terpeneless
10	Coumarin
1	Ethyl decine carbonate 100%
8	Isobutyl salicylate
10	Geraniol extra
4	Hydroxycitronellal
1	Alpha ionone
5	Dimethyl ionone
3	Oil cumin seed 10% in DEP
6	"Aurantiol"
6	"Acaciol"
8	Benzyl isoeugenol
3	"Cumin" ketone
150	

"Aurantiol" is the Schiff's base between hydroxycitronellal and methyl anthranilate. "Acaciol" is the Schiff's base between anisic aldehyde and methyl anthranilate.

MIGNONETTE E.036

110	Methyl ionone standard (rhodia)
40	"Resedalia" (Diphenylethyl acetal)
10	Benzyl acetate
50	Oil bergamot natural
30	Phenylpropyl alcohol
50	Oil standalwood East Indian
20	Oil petitgrain South American
10	Ylang Bourbon extra
12	Oil sweet basil
8	Isobutyl salicylate
1	Galbanum absolute
1	Labdanum resin
1	Lavender absolute
2	Methyl octine carbonate 100%
50	Amyl cinnamic aldehyde
30	Phenylpropyl acetate
20	Cinnamic alcohol
20	Heliotropine
50	Hydroxycitronellal
5	Ethyl decine carbonate 100%
30	Benzyl isoeugenol
550	

NATURE'S ANTIBIOTICS

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creted by such organs as the stomach, pancreas and intestines.

The control of unfavorable biochemical processes is best accomplished by seeding the intestines with a dominating flora of microbial antagonists. The same applies to the flora of enteropathogens where unfavorable growth and environmental factors act to inhibit reproduction, and with coincident decreased pathogenicity and virulence.

The Intestinal Pathogens

Fecal contamination of food and water is responsible for most gastro-intestinal diseases of microbial origin.

(1) Gastro-enteritis is caused by a group of organisms known as the pathogenic enterobacteriaceae. They include the *Salmonella typhi*, *S. paratyphi* A, B and C, *S. schottmuelleri*, and the *S. cholerae-suis* and *S. typhimurium*, which are pathogenic for both man