Ketoximes

Black currant odorants are desirable olfactory agents for perfume compositions.

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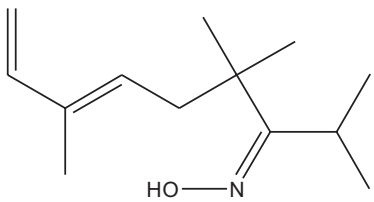
Oximes, which have been well-known for many years, have been used chiefly as derivatives to characterize aldehydes and ketones. Some oximes also possess desirable odors and other qualities that might make them desirable olfactory agents for use in perfume compositions. Several of these oximes are discussed herein.

For instance, cassis oxime **(F-1)** has a black currant, cassis, green, grapefruit, herbal and metallic odor. Not found in nature, this ingredient is used in many fragrances as a modifier; it blends well with accords where a fresh fruity, green aspect is required in citrus, modern lily-of-the-valley, lavender and other profiles.[b]

F-1. 2,4,4,7-Tetramethyl-6,8-nonadiene-3-one oxime (Cassis oxime; trade name: Labienoxime[a,b]; $C_{12}H_{23}NO$; CAS# 81783-01-9)



[a] Trademark of Givaudan
[b] Info derived from Givaudan

Physical Data for Cassis Oxime[7]

Appearance:	Colorless to pale yellow liquid to solid
M.W.:	209.3
Assay (min.):	10% in benzyl laurate, or in isopropylmyristate/triethylcitrate (9:1) mixture[b]
Flash point:	212°F TCC
LogP(o/w):	4.14 (estd.)
Vapor pressure:[2]	0.0016 hPa

Due to its strength, cassis oxime is offered as 10% solution in isopropyl myristate/triethyl citrate (9:1) mixture, and its recommended use level is from traces to 0.5%. Below is an example of a fragrance with a citrus-white grapefruit accord **(F-2)**[c].

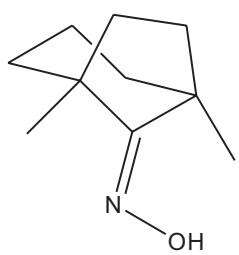
In this formulation, methyl laitone 10% lends a sweet volume while Velvione gives a rich, powdery musk body and dimethyl octenone adds a sparkling, juicy grapefruit note.

F-2. Citrus-white grapefruit formulation containing cassis oxime

Cassis oxime 10%	-	3
Methyl laitone[d] 10%	-	2
Velvione[e]	-	5
Citral	-	15
Petitgrain oil	-	15
Dihydromyrcenol	-	25
Linalool	-	30
Hedione	-	60
Dimethyl octenone	-	80
Orange terpenes distilled	-	765

Buchu oxime (**F-3**; bicyclo[3.2.1]octan-8-one-1,5-dimethyl oxime; Buccoxime[f]; CAS# 75147-23-8) has a very intense and substantive black currant odor that is green-metallic, fresh, fruity, herbal and typical of buchu leaf oil[g].

F-3. Buchu oxime



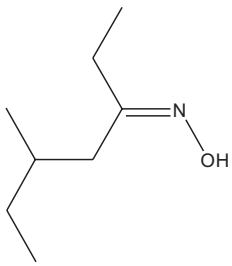
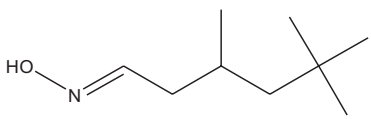
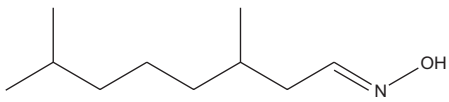
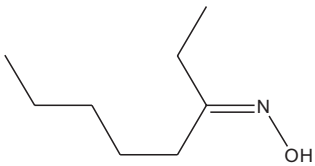
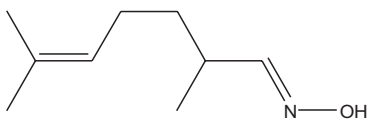
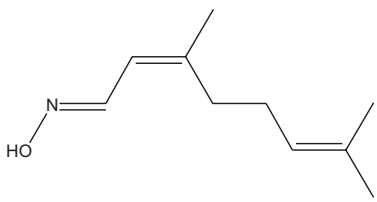
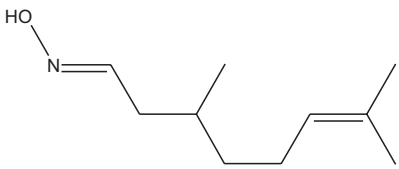
[c] The Perfumer's Apprentice; *http://store.perfumersapprentice.com;* Hedione is a trade name of Firmenich
[d] 8-Methyl-1-oxaspiro(4.5)decan-2-one, CAS #94201-19-1
[e] (5Z)-cyclohexadec-5-en-1-one, CAS #37609-25-9
[f] Trademark of Symrise AG
[g] Symrise spec. sheet

Bucchu oxime bonds between black currant and grapefruit accords in *Good Life* (Davidoff), a woody, floral, musk, citrus, fresh-spicy, sweet perfume for men. It's also used in fantasy notes such as the tomato leaf accord of *Les Belles* (Nina Ricci), a balmy, citrus, woody, floral, powdery, warm-spicy perfume for women.[1]

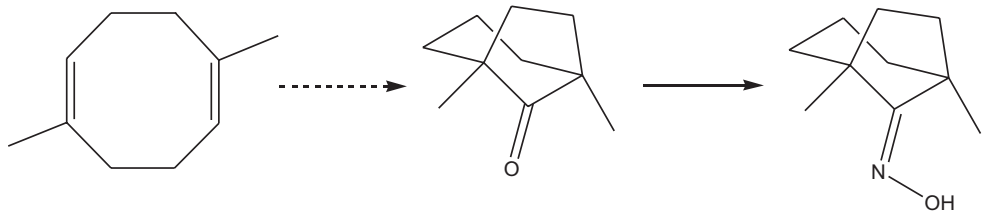
F-4 describes a list of oximes both of ketones and of aldehydes used mostly in fragrances.

One of the interesting applications of oximes is their ability to contribute to fragrance compounds that elevate liveliness and induce psychologically positive emotions. Such fragrance compounds contain fruit aroma-generating components and fruit aroma-enhancing components. For example, a mango aroma energizing composition was formulated containing Labienoxime (2,4,7,7-tetramethyl-6,8-nonadien-3-one oxime); use of a body

F-4. Oximes of ketones and aldehydes used mostly in fragrances

	Structure	Organoleptic Properties
5-Methyl-3-heptanone oxime Leafy oxime; Stemone [22457-23-4]		Intense green-leaf odor quite suggestive of crushed fig leaves[2]
3,5,5-Trimethyl-hexanal oxime [138915-31-8]		Green, vetiver, woody, earthy, orris, minty, camphoraceous, cassis and grapefruit aroma profile with minty, camphoraceous, green, herbaceous, vetiver and galbanum topnotes[1]
3,7-Dimethyloctanal oxime [22457-26-7]		Earthy-green-rosy character that gives a naturalness of odor resembling that of freshly cut flowers[g]
Octan-3-one oxime [7207-50-3]		Intense green-earthy odor suggestive of crushed twigs and moss[g]
2,6-Dimethyl-5-heptenal oxime [22457-24-5]		Floral odor suggestive of gardenia flower[g]
Citral oxime 3,7-Dimethylocta-2,6-dienal oxime [13372-77-5]		Diffusive musty odor quite suggestive of seaweed[g]
Citronellal oxime 3,7-Dimethyloct-6-enal oxime [22457-25-6]		Leafy-green-rosy-citrus odor[g]

F-5. Preparation of Buccoxime

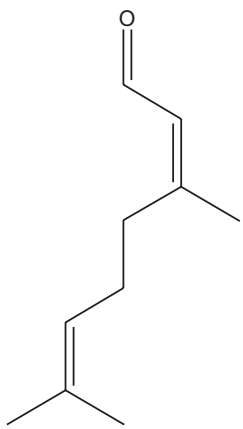


5-Dimethylcyclooctadiene

1,5-Dimethylbicyclo[3.2.1]-octan-8-one

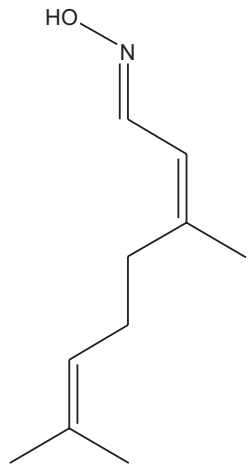
1,5-Dimethyl-bicyclo[3.2.1]octan-8-one oxime

F-6. Citral, citronellal, and their oximes and nitriles



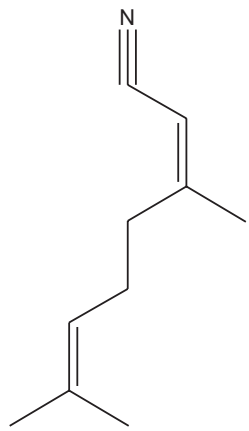
Citral

Fresh, juicy, lemon peel odor, with a sweet-tangy green nuance



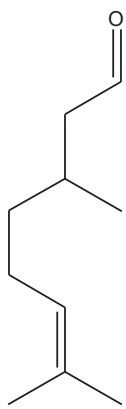
Citral oxime

Diffusive musty odor, quite suggestive of sea weeds



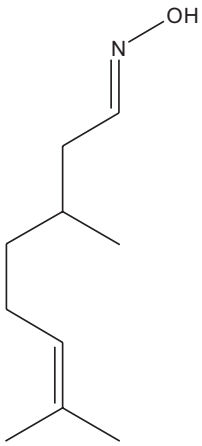
Geranyl nitrile

Citrus, lemon nitrile, aldehydic, metallic odor



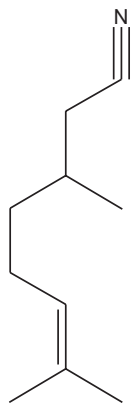
Citronellal

Sweet, dry, floral, herbal, waxy aldehydic citrus odor



Citronellal oxime

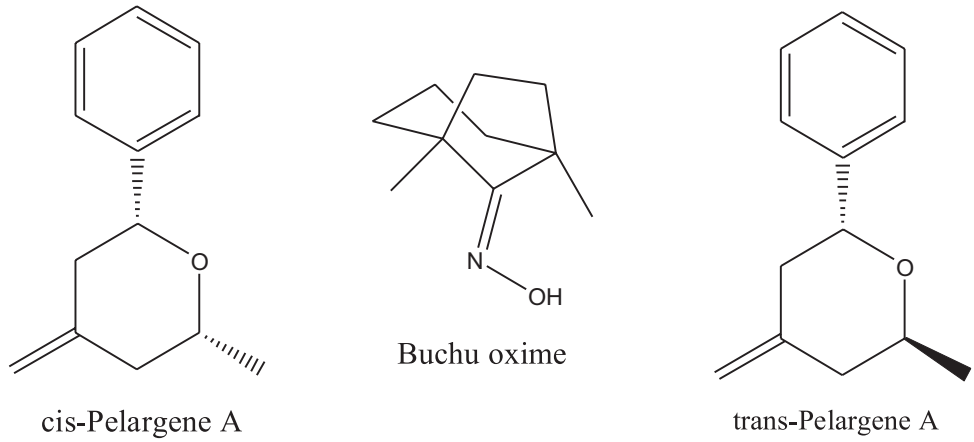
Leafy-green, rosy, citrus odor



Citronellyl nitrile

Fresh lemon, metallic, citrus, waxy, floral odor

F-7. (2S,6R)-*trans*-Pelargene A, Buchu Oxime and (2R,6R)-*cis*-Pelargene A



cis-Pelargene A | Buchu oxime | trans-Pelargene A

shampoo containing this composition significantly increased vivacity scores in volunteers in a fragrance study.[4]

Due to the fact that oximes are relatively chemically stable molecules, they can be used in cosmetic applications together with antimicrobial agents, like with triclosan (CAS# 3380-34-5), an antibacterial and antifungal agent, and with trichlorocarbanilide (CAS #101-20-2), a substance with antibacterial and antifungal properties that is used in disinfectants, soaps and other household products.[5]

Another advantage of oxime ingredients is their long-lasting odor stability (Labienoxime's tenacity on a blotter is one week)[h]. Due to this property, oximes can be used, for example, in long-lasting air fresheners. Buchu oxime (bicyclo[3.2.1]octan-8-one-1,5-dimethyl oxime) was used at 0.01%, together with other 1.99% perfumery ingredients in air freshener formulations consisting of 25% sodium carbonate, 15% sodium bicarbonate, 46% fumaric acid, 5% polyethylene glycol, 0.02% sucrose fatty acid ester and the balance dextrin.[6]

Oximes are prepared in general by reacting a ketone or an aldehyde with hydroxyl-amine. **F-5** shows the preparation of 1,5-dimethyl-bicyclo[3.2.1]octan-8-one oxime; Buccoxime[h].

This substance is produced by oximation of 1,5-dimethylbicyclo[3.2.1]octan-8-one, which is obtained by a two-step reaction starting from 1,5-dimethylcyclooctadiene.[7]

When trying to look at the structure-odor-relationship (SOR) of oximes, it seems there is no observed SOR between the original carbonyl and its oxime. **F-6** is an example of citral, citronellal and their oximes and their nitriles in comparison.[h]

All the other oximes mentioned above were studied for their odor in relation to the original carbonyl and there was no observed SOR between any couple of carbonyl-oxime. In his review Structure-Odor Relations: A Modern Perspective, Luca Turin mentions that oximes and aldehydes, for example, can be reliably identified once the odor character and the functional group character is known.[8]

John Leffingwell highlights another view in which totally different molecules, (2S,6R)-*trans*-Pelargene A (CAS #885479-94-7) and (2R,6R)-*cis*-Pelargene A (CAS # 885480-12-6; **F-7)**, have a buchu oxime-like odor[i].

To summarize, differently from the case of carbonyls and their nitriles, where there is an odor resemblance between both, from the observations mentioned above, it seems there is no detected SOR between the carbonyl molecule and its oxime.

[h] Part of data from The Good Scents Company database *www.thegoodscentscompany.com*

[i] Chirality & Odour Perception, John C. Leffingwell, PhD, The Pelargenes, *www.leffingwell.com/chirality/chirality.htm*

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8. L Turin, F Yoshii, *Structure-Odor Relations: A Modern Perspective, Handbook of Olfaction and Gustation 2nd ed*, Marcel Dekker, New York (2003)