

1,1-Dimethoxy-2,2,5-trimethyl-4-hexene: The Grapefruit Acetal

Chemistry and application in fragrance

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1,1-Dimethoxy-2,2,5-trimethyl-4-hexene (CAS# 67674-46-8; **F-1**) is a colorless to pale yellow liquid with a fresh, citrus, grapefruit peel-like odor and a vetiveryl acetate aspect. 1,1-Dimethoxy-2,2,5-trimethyl-4-hexene, which is not reported as being found in nature, belongs to a series of natural and synthetic molecules, of which nootkatone is a key material, that can represent the grapefruit note in fragrances. Both molecules show some structure similarity. (**F-2**)

1,1-Dimethoxy-2,2,5-trimethyl-4-hexene can be prepared by condensation of 2-methylbut-3-en-ol and isobutanal to form 2,2,5-trimethylhexenal as an intermediate. The intermediate aldehyde is then converted to the dimethyl acetal using trimethyl orthoformate (**F-3**). Additional methods of preparation use rather similar chemistry, but some of the reagents are different.¹

1,1-Dimethoxy-2,2,5-trimethyl-4-hexene, with its fresh bitterness, blends very well with citrus bases. It can also be used as a booster for vetiver accords.^c This makes 1,1-dimethoxy-2,2,5-trimethyl-4-hexene a key ingredient in modern colognes such as *Pleasures for Men* (Estee Lauder), *Aqua Allegoria Pamplelune* (Guerlain), and *L'eau de Kenzo Masculine* (Kenzo), which contain ca. 3.5% of this ingredient.

Grapefruit odor ingredients have many aspects—hesperidic, citrusy, fruity, rhubarb and cassis-type, as well as green and woody tonalities. Many of these aspects can be found in the cologne *Good Life* (Davidoff), which is driven by an overdose of 8.5% 1,1-dimethoxy-2,2,5-trimethyl-4-hexene.²

1,1-Dimethoxy-2,2,5-trimethyl-4-hexene can be applied also for beauty care, soap, laundry care and other household products. Its recommended usage level is 0.1–10.0%.

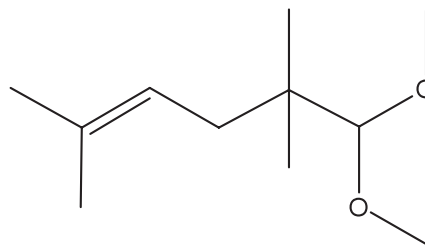
Additional important grapefruit ingredients are shown in **F-4**. Other grapefruit ingredients are based on sulfur-containing molecules, such as thiolimonene, thiocineole and thiogranol.

References

1. H Gebauer, M Regiert, Consortium Fur Elektrochemische Industrie GmbH, US Pat. 4,631,146 (1986).
2. P Kraft, JA Bajgrowicz, C Denis and G Frater, *Angew Chem Int*, **39**, 2980–3010 (2000).

1,1-Dimethoxy-2,2,5-trimethyl-4-hexene (Methyl Pamplemousse^a, Amarocit^b)

F-1



^a Methyl Pamplemousse is a trade name used by Givaudan.

^b Amarocit is a trade name used by Symrise.

Physical Data for 1,1-Dimethoxy-2,2,5-trimethyl-4-hexene

Appearance: colorless to pale yellow liquid

Molecular weight: 186.3

Molecular formula: C₁₁H₂₂O₂

Refractive index (n_{20/D}): 1.437–1.443

Specific gravity (D_{20/4}): 0.876–0.880

Purity (GC area): 96–98% (min.)

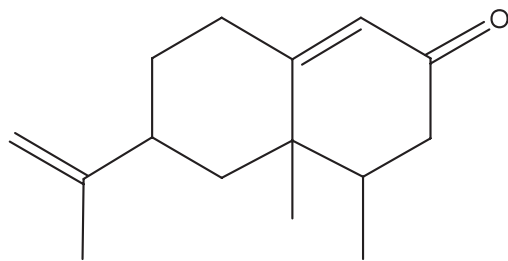
Flash point: 75°C

Solubility at 20°C: Ethanol 80 vol. %: 1:1 v/v;
diethylphthalate: 1:1 v/v; water: practically insoluble

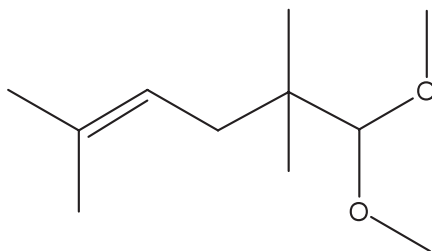
^c Information taken from Givaudan and Symrise specification sheets.

Nootkatone and 1,1-dimethoxy-2,2,5-trimethyl-4-hexene

F-2



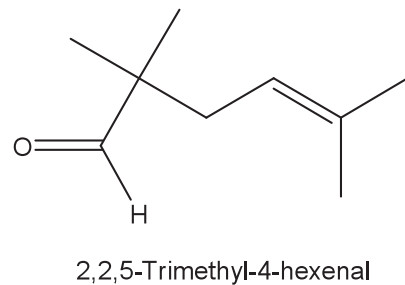
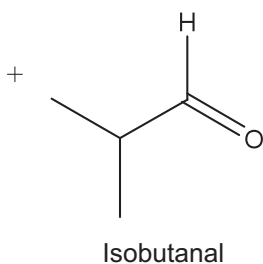
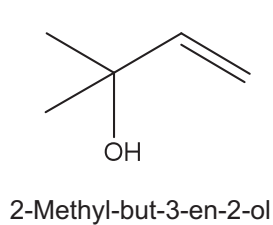
Nootkatone



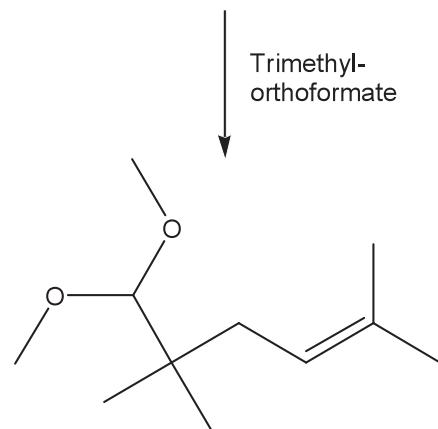
1,1-Dimethoxy-2,2,5-trimethyl-4-hexene

Preparation of 1,1-dimethoxy-2,2,5-trimethyl-4-hexene from 2-methylbut-3-en-2-ol

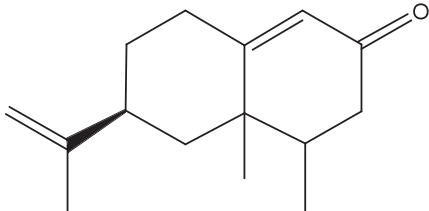
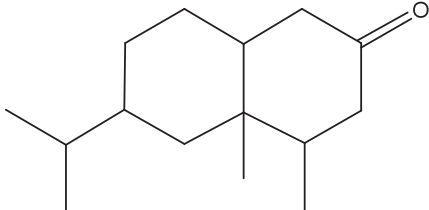
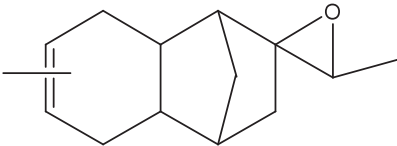
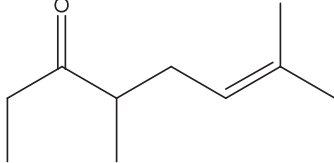
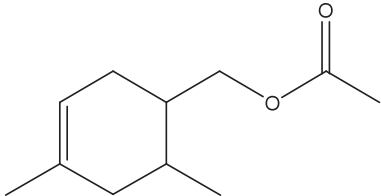
F-3



Trimethyl-orthoformate



1,1-Dimethoxy-2,2,5-trimethyl-4-hexene

Ingredient / CAS# / Trade Name (where applicable)	Organoleptic Characteristics
 <p>Nootkatone / 4674-50-4</p>	Extremely powerful grapefruit and citrus aroma
 <p>3,4,4a,5,6,7,8,8a-Octahydro-6-isopropyl naphthalene-2(1H)-one / 34131-98-1 / Decatone^d</p>	Citrus, woody, fresh, fruity
 <p>Spiro[1,4-methanonaphthalene-2(1H),2'-oxirane], 3,4,4a,5,8,8a-hexahydro-3',7'-dimethyl- / 418-03-9 / Rhubofix^e</p>	Complex woody, spicy, floral and fruity note. It has a zesty freshness and unique green rhubarb effect. ^f
 <p>2,5-Dimethyl-2-octen-6-one / 2550-11-0</p>	Bitter grapefruit, fresh, fruity
 <p>2,4-(3,5)-Dimethyl cyclohex-3-ene-1-methyl acetate / 67634-25-7/67634-26-8 / Floralate^g</p>	Citrus, grapefruit note also reminiscent of the dry notes of bitter orange oil and melon. ^h

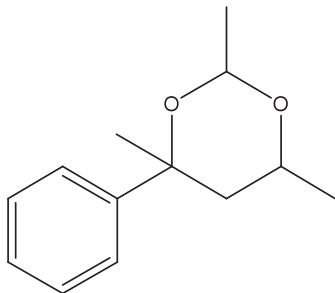
^d Decatone is a trade name used by Givaudan.

^e Rhubofix is a trade name used by Firmenich.

^f Information taken from Firmenich specification sheet.

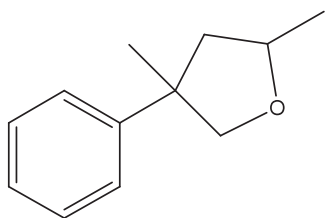
^g Floralate is a trade name used by IFF.

^h Information taken from IFF specification sheet.



2,4,6-Trimethyl-4-phenyl-1,3-dioxane / 5182-36-5 /
Floropal, Vertacetal coeurⁱ

Strong, herbal-fresh, green and
typical grapefruit



Furan, tetrahydro-2,4-dimethyl-4-phenyl / 82461-14-1 /
Rhubafuran^j

Intense tangy rhubarb character,
with a green eucalyptus heart
very suitable in citrus accords²

ⁱ Floropal and Vertacetal Coeur are trade names used by Symrise.

^j Rhubafuran is a trade name used by Givaudan.