Methyl 2,4-dihydroxy-3,6-dimethylbenzoate

Chemistry and application in fragrance

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Methyl 2,4-dihydroxy-3,6-dimethylbenzoate (CAS# 4707-47-5) is a white to off-white crystalline powder. It has an odor character impact of oak and treemoss. It is an excellent fixative, powdery and woody-sweet.

The material has excellent tenacity, and is stable at pH 1–9 (moderately alkali-stable) and fiber-substantive. It has a subsantivity of more than 10 days at 10% in DPG, and is used as a fragrance ingredient in fine fragrances, toiletries, and fragranced functional products such as fabric softeners, detergents and aerosoles, as well as in candles, potpourri and incense. Methyl 2,4-dihydroxy-3,6-dimethylbenzoate is an excellent fixative and can be used up to 7% of total concentrate.

Oakmoss products have a solidly established place in perfumery, being the cornerstone of two renowned accords, the chypre and the fougère. In the classical chypre accord, oakmoss is blended with patchouli, labdanum and other woody animalic and ambery notes, and also often with bergamot. These combinations are the foundation of a family of several leading fine fragrances: *Chypre* (Coty, 1917), *Mitsouko* (Guerlain, 1919), *Miss Dior* (Christian Dior, 1919) and *Ysatis* (Givenchy, 1984), and in the male category *Aramis* (Aramis, 1965) and *Macassar* (Rochas, 1980), to name but a few. In the fougère accord, striking examples of which include *Fougère Royal* (Houbigant, 1882), *Drakkar Noir* (Guy Laroche, 1982) and *Jazz* (Yves St. Laurent, 1998), oakmoss is blended with coumarin, lavandaceous notes and often with salicylates. Oakmoss products also find uses in colognes, pine fragrances, crepe de chine, oriental and fantasy bases, and so on.[1]

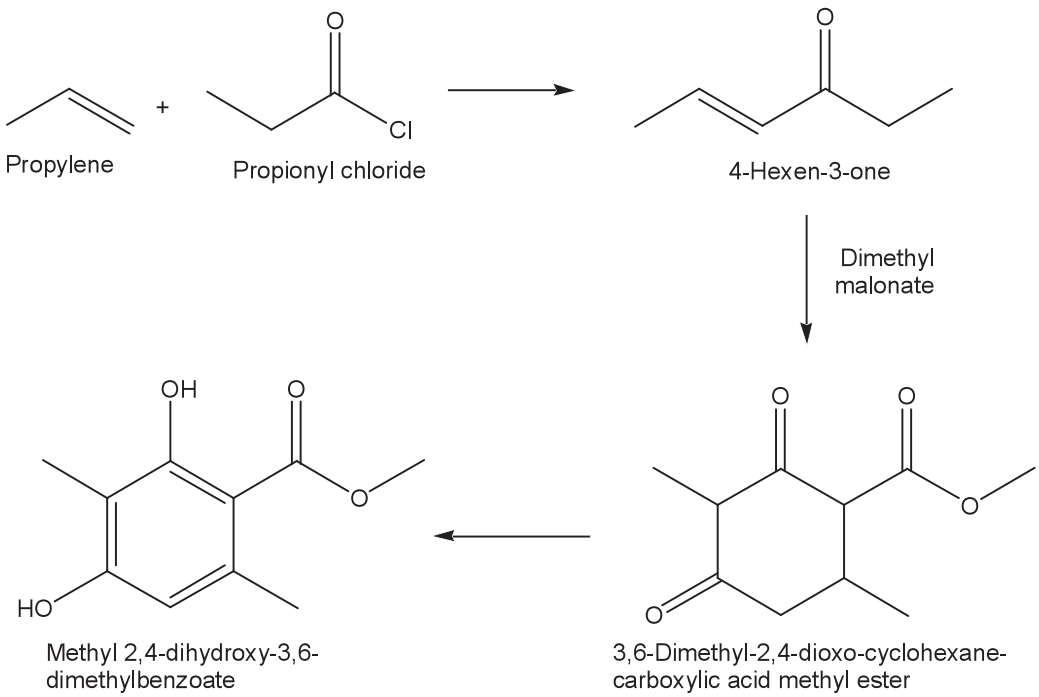
Methyl 2,4-dihydroxy-3,6-dimethylbenzoate can be prepared by reaction of dimethyl malonate with 4-hexene-3-one or analogues compounds, followed by cyclization with diethyl malonate and aromatization (**F-1**).[2,3,4]

The molecular base of the oakmoss odor can be extrapolated by structure modifications of the salicylic ester (CAS# 119-36-8) (**F-2**).[3] For example, the same olfactive impression can be obtained from the methyl ester of everninic acid (**F-3**). If the hydrogen-donating group of the bifunctional unit of everinic acid is blocked, there is corresponding loss of odor. It has been determined that the ethyl ester of everninic acid (**F-4**), and its corresponding acetophenone derivative 1-(2-hydroxy-4-methoxy-6-methylphenyl)-ethanone (**F-5**), have identical odors. The loss of methyl groups at

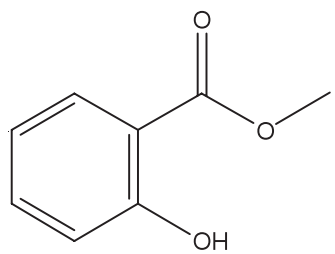
Physical Data for Methyl 2,4-dihydroxy-3,6-dimethylbenzoate

Appearance: white to off-white crystalline powder
Molecular weight: 196.2
Molecular formula: $C_{10}H_{12}O_4$
Melting point: 141–142°C
Solubility in water: Insoluble
Flash point: 100°C

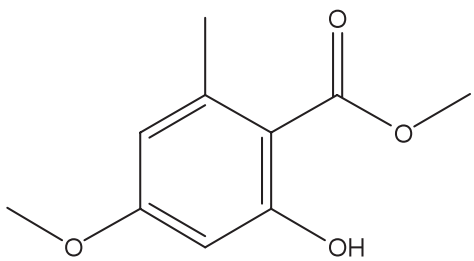
Preparation of methyl 2,4-dihydroxy-3,6-dimethylbenzoate F-1



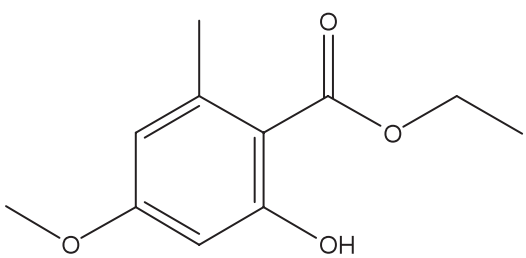
Salicylic ester F-2



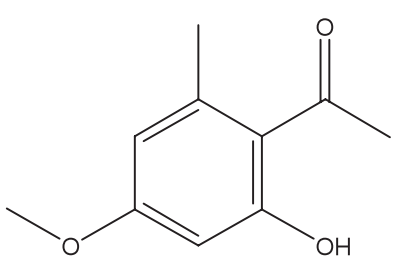
Everinic acid, methyl ester F-3



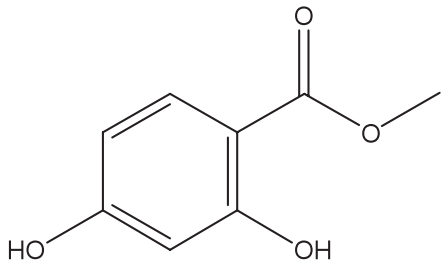
Everinic acid, ethyl ester F-4



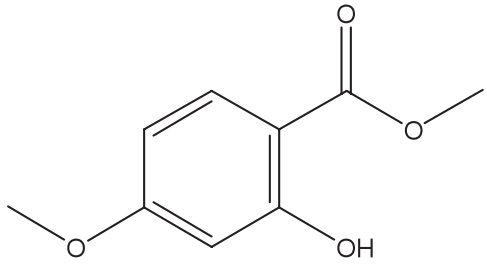
1-(2-Hydroxy-4-methoxy-6-methylphenyl)-ethanone F-5



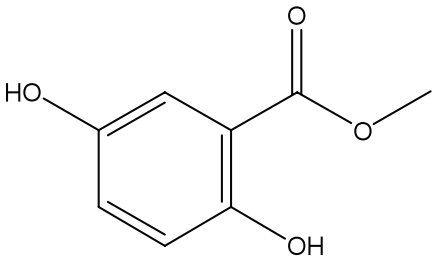
2,4-Dihydroxybenzoic acid methyl ester F-6



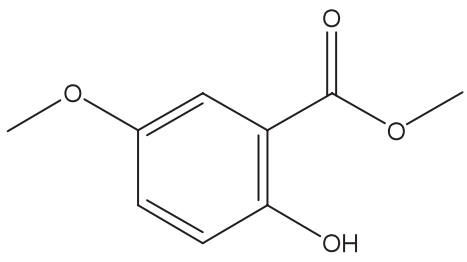
2-Hydroxy-4-methoxybenzoic acid methyl ester F-7



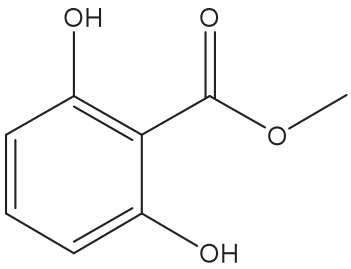
2,5-Dihydroxybenzoic acid methyl ester F-8



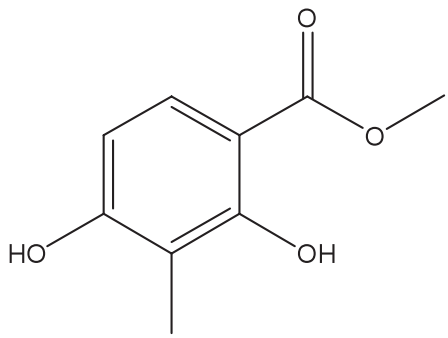
2-Hydroxy-5-methoxybenzoic acid methyl ester F-9



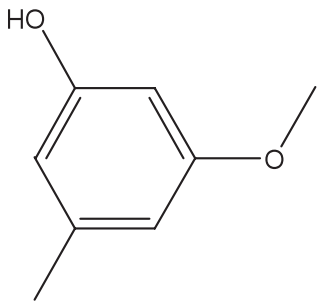
2,6-Dihydroxybenzoic acid methyl ester F-10



2,4-Dihydroxy-3-methylbenzoic acid methyl ester F-11



3-Methoxy-5-methylphenol F-12



the aromatic ring does not change the odor tonalitis of the compounds 2,4-dihydroxybenzoic acid methyl ester (**F-6**) and 2-hydroxy-4-methoxybenzoic acid methyl ester (**F-7**), it just leads to a weakening of the odor intensity. The regioselective derivatives 2,5-dihydroxybenzoic acid methyl ester (**F-8**) and 2-hydroxy-5-methoxybenzoic acid methyl ester (**F-9**) also have a much weaker odor than the hydrophobic compounds methyl 2,4-dihydroxy-3,6-dimethylbenzoate, which is the title molecule, and 2-hydroxy-4-methoxy-6-methylbenzoic acid methyl ester. Even so, the oakmoss character is still recognizable; in 2,5-dihydroxybenzoic acid methyl ester (**F-8**) it is more comparable to the salicycic ester (**F-2**) than to 2,6-dihydroxybenzoic acid methyl ester (**F-10**).

Another regioselective isomer of this series is 2,4-dihydroxy-3-methylbenzoic acid methyl ester (CAS# 33662-58-7) (Seamoss[a]) (**F-11**), having a strongly mossy, sea, oak and treemosslike olfactive character, and finally, a molecule of this series that totally lacks the carboxylic acid ester moiety—3-methoxy-5-methylphenol (CAS# 3209-13-0) (Orcinyl 3[b]) (**F-12**). This molecule has an oakmoss, sweet, phenolic odor. Due to its typical oakmoss note, 3-methoxy-5-methylphenol reinforces the character of this absolute in all compounds. It can be substituted for oakmoss when used together with methyl 2,4-dihydroxy-3,6-dimethylbenzoate (Evernyl[c]). It blends very well with chypre, leather, woody and tobacco accords.

[a]Seamoss is a trade name used by PFW Aroma Chemicals.
[b]Orcinyl3 is a trade name used by Givaudan.
[c]Evernyl is a trade name used by Givaudan.

References

1. T Burfield, Cropwatch Newsletter (2008).
2. RB Woodward, *J Am Chem Soc,* **74**, 4239 (1952).
3. US Patent 3944596, A. Cohen.
4. US Patent 4822910, G. Pelerin.
5. G Ohloff, *Scent and Fragrances*. Springer-Verlag, New York (1994).