

## An Aroma-Chemical Profile

# Methyl Salicylate, or Oil of Wintergreen

By George Stuart Clark IV, Cameron & Stuart Inc., Easton, Maryland

**M**ethyl salicylate is an aromatic ester whose principal natural source is wintergreen (*Gaultheria procumbens*) and sweet birch (*Betula lenta*) plants. Its history is intertwined with that of salicylic acid and its other derivatives, all of which were recognized by early man as having therapeutic values (see sidebar).

Its organoleptic nature is viewed positively in North America. Wintergreen is still referred to as "mountain tea" in some areas of the US.<sup>5</sup> Its use as a refreshing and medicinal beverage carried over into that country's popular soft drinks: birch beer, root beer and sarsaparilla. With the demise of sassafras oil (due to its safrole content), methyl salicylate was employed to re-construct America's uniquely flavored national beverages. In the world's soft drink market, North America is the only place where these three beverages are consumed. Outlanders usually find the taste of these soft drinks repulsive!

This different attitude toward methyl salicylate reflects itself in differences in organoleptic description of this aroma chemical, depending on whether the describer is an American or a European cousin. These cultural orientations have resulted in wintergreen-based oral hygiene products finding acceptance in North America and the Philippines, and to a lesser extent in Great Britain, while the rest of the world shuns them. Almost 50% of the North American toothpaste flavor market is wintergreen-based, versus nil in the rest of the world.

### Health Benefits of Methyl Salicylate

The folk use of methyl salicylate and salicylic acid for cures goes back into the dawn of the human race. More than 2400 years ago, the Greeks were using extracts of the willow tree (*Salix alba*) to treat pains and gout. Hypocrites recommended the juice of the poplar tree, rich in salicin, for eye diseases. The North American Indians used the willow tree to treat pain and fever prior to the arrival of the Europeans. Moreover, they introduced the colonists to the custom of drinking wintergreen and bitter wintergreen tea as a refreshment and a remedy. They also taught the use of birch sap as a cure for warts.<sup>5</sup>

### Methyl Salicylate

**Mwt:** 152, C<sub>8</sub>H<sub>8</sub>O

**CAS:** 119-36-8

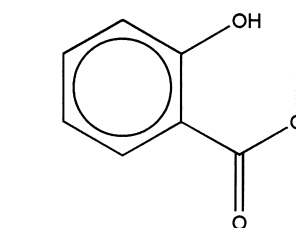
**Harmonized**

**Tariff No.:** 2918.23.20

**FEMA-GRAS:** 2745

**Classification:**

**Additional Names:**<sup>1,2</sup>



Aromatic ester

2-hydroxy methylbenzoate; methyl ortho-hydroxybenzoate; salicylic ether; artificial oil of wintergreen; oil of bitter wintergreen; checkerberry oil; mountain tea oil; Prince's Pine Oil; oil of pipsisewa; spiceberry oil; teaberry oil

*French:* Salicylate de méthyle

*German:* Methyl Salicylat

*Portuguese:* Salicilato de metilo

*Spanish:* Salicilato de metilo

**Physical Data:**<sup>4,5</sup>

*Appearance:* Clear, colorless prismatic liquid

*Specific Gravity:* 1.180-1.185

*Melting Point:* -8.6°C

*Boiling Point:* 222-223°C at 760 Torr

*Refractive Index at 20°C:* 1.5240

*Flash Point, TCC:* >99°C (200°F)

*Odor Threshold:* 40 ppb

*Solubility:* Only sparingly soluble in water ~0.74% at 30°C, but soluble in ethanol, aliphatic and aromatic alcohols, esters, ketones, most essential oils, fixed oils, chlorinated solvents, DEP, propylene glycol and glycerine.

*Stability:* Very stable to air and when stored over long periods in opened drums in contact with air. Does not readily hydrolyze in the presence of moisture. However, methyl salicylate does display the normal instability innate to the salicylate group; a pink-red discoloration in contact with traces of iron salts. Do not store in unlined steel drums.

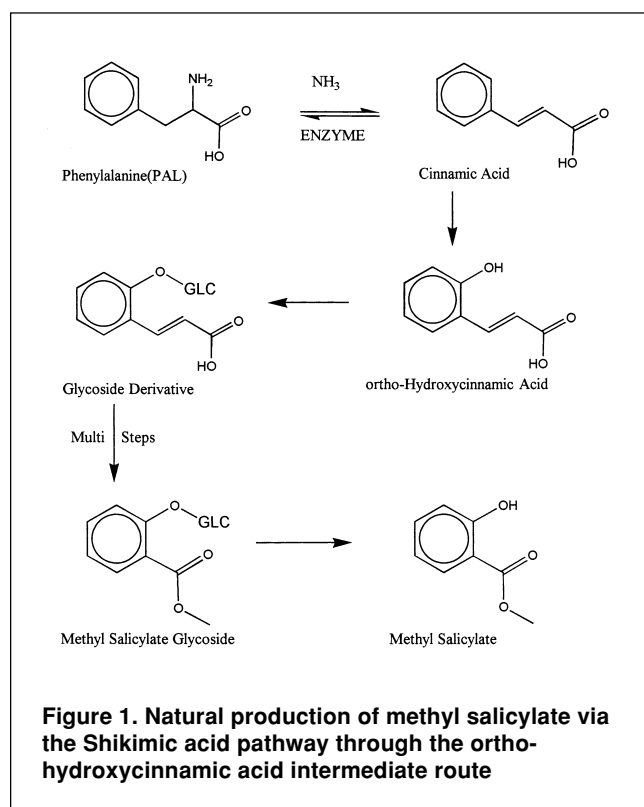
The European dislike for methyl salicylate is not a recent development. Writing in 1915, Mann states that the flavor of methyl salicylate is prized only in Great Britain and its former colonies, but is inappropriate to the German taste.<sup>6</sup> Other sources indicate this sentiment is shared by most other Europeans as well.

Arctander, who lived in the US but was a Dane by birth and upbringing, observed that the world is divided into two groups: regular users of wintergreen-flavored products and those who are not. Upon this basis, two descriptions arise. His description of the organoleptic nature of methyl salicylate is that of the European: a warm, sweet rooty-fruity odor with a pungent sweet fruity-rooty taste. The North American describes this product as having a warm, medicinal-minty-floral odor and a warm, sweet minty-herbal sassafas-like taste. Which description the reader finds most appropriate will depend on which Atlantic ocean shore his or her cradle rocked on.

### Natural Sources

Methyl salicylate is found in a fairly large number of plants in trace amounts, but seldom in the free state. It is usually tied up as a glucoside derivative, which releases the ester through enzymatic hydrolysis. In the plant kingdom, methyl salicylate arises via the Shikimic acid pathway<sup>7</sup> through the ortho-hydroxycinnamic acid intermediate route, as shown in Figure 1.

<sup>a</sup> Aspartame, Monsanto, St. Louis, MO



The first step in this process, the de-amination of phenylalanine (PAL), has proven to be reversible and is employed in the commercial production of at least one synthetic sweetener<sup>a</sup> to convert cinnamic acid to PAL. The exact details of the conversion of PAL to methyl salicylate are unknown, but the guess is that the multi-steps undergone take place as the glycoside derivative and not the free ester.

Methyl salicylate is found in the free state, usually in trace amounts, in the following plants:

<i>Acacia farnesiana</i> and <i>A. carvens</i> flowers	milkwort ( <i>Polygala sanguinea</i> )
alfalfa	parsley seed
apples	peppermint
birch bark and buds	<i>Pimenta dioica</i>
caraway seeds	raspberry
cherry	Otto of Rose
coriander seeds	tea
black currant leaf	tobacco leaf
Daphne odora	tomato leaf and stems
Dianthus caryophyllus	tuberose
Dillweed	wine (Sauvignon Blanc)
fig leaf absolute	wintergreen ( <i>Gaultheria procumbens</i> )
ginster ( <i>Spartium junceum</i> )	bitter wintergreen
grapes	( <i>Chimaphila umbellata</i> )
hyacinth flowers	berries and leaves
jasmin flowers	ylang-ylang
<i>Michelia champaca</i>	

It has never been reported in any animal flesh, fish or crustaceans or in citrus fruits.

The major commercial source of natural methyl salicylate is the oils obtained from the berries and leaves of *G. procumbens* (wintergreen) and the bark of various species of birch tree indigenous to North America. Although the ester is found free in both of these sources,<sup>8</sup> it is necessary to macerate the plant material in order to allow enzymatic hydrolysis to take place to maximize the yields of the ester. Ironically, the oil of sweet birch has a slightly higher methyl salicylate content (99.8%) than does oil of wintergreen (99.0%).

### History

The use of wintergreen plant and sweet birch for medicine and beverages was quickly learned from the local inhabitants when the Europeans arrived in North America. The North American wintergreen was in reality two plant species: the true wintergreen (*G. procumbens*) and bitter wintergreen (*Chimaphila umbellata*), both of which were and are referred to as wintergreen and were used to produce the oil bearing that name.

It appears that somewhere between 1812 and 1830, the commercial distillation of wintergreen and birch bark oils began in the US and Canada. The units employed for their production were "primitive in character, consisting of small whiskey stills or of wooden casks with copper bottoms."<sup>9</sup>

Most literature references credit the discovery of methyl salicylate as the major constituent in wintergreen oil to Cahours in 1844.<sup>10</sup> Yet, significant data credits the discovery of methyl salicylate to Procter, who analyzed wintergreen and sweet birch oil in 1842.<sup>11</sup> This discovery was not

scientifically earth-shaking; Procter reported that wintergreen oil contains 99% of this ester and sweet birch oil contains 99.8%. This type of concentration constituted a commercially pure chemical in 1900, and in some cases it still does even today.

Until 1874, the world's major commercial source of salicylic acid was these two oils, which were largely produced in North America. With the start of a commercial process for the production of salicylic acid from phenol in Germany in 1874, a reversal in roles occurred. Methyl salicylate could now be produced from wood alcohol (methanol) and salicylic acid. The ester was first synthesized on a commercial scale by Schimmel & Co. in Leipzig in 1886 and was initially marketed as "Natural oil of Wintergreen" (see sidebar).

Methyl salicylate proved a very easy ester to prepare and was soon being synthesized by the manufacturers of salicylic acid and sold on the open market against the flavor and fragrance industry's own production. By 1920, Dow Chemical and Monsanto were producing methyl salicylate in the US and selling it as "Artificial Oil of Wintergreen." A "natural" oil of wintergreen was still on the market in 1925. Parry characterized it as probably being a natural birch bark oil. Writing in that year, he observed that regarding natural wintergreen oil, "it is feared that in most cases it is, in fact, the distillate of *Betula lenta*, whatever the price may indicate. Both oils, however, consist almost entirely of the ester methyl salicylate (q.v.), so that there is a good deal of fraud in the article, the cheaper artificial ester being very frequently substituted for the more expensive natural oil." This practice continued well after 1960, as oil of wintergreen often was not labeled as an artificial product.

Methyl salicylate has been offered by most flavor and fragrance houses over the years, but produced by few. It has been less of a fragrance or flavor additive, than a chemical intermediate for the production of other salicylate esters or the active ingredient in analgesic balms. Its ease of production has made it a prime target for manufacturers of salicylic acid aiming to climb up the value added chain.

**From Natural to Synthetic**

It is interesting to look at the "state of the art" in the flavor and fragrance industry in the period of transition from natural ingredients to synthetics.

Prior to 1880, almost all formulas used extracts, infusions and essential oils. Between 1880 and 1900, a sudden surge of new aroma chemicals occurred and were incorporated into new formulas. These efforts were at first crude by today's standards, yet the technician had little to work with in the form of pure aroma chemicals. Formulas 1-2 present flavor and fragrance formulas developed in the period 1889-1890 using the new aroma chemical methyl salicylate. Note the continued reference to the natural product, although by 1890 most of the oil of wintergreen on the market was "made" in a factory in Germany.

**Suppliers and Capacity**

The production of methyl salicylate depends mainly upon a secure supply of salicylic acid and methanol. The chemistry is straight-forward and yields a product normally fitting the organoleptic needs of the flavor and fragrance industry. The equipment required to carry out the steps

**Formula 1. Handkerchief perfume (around 1890)<sup>12</sup>**

Parts	
Espirt de rose	1 pint
Essence of lavender	1/4 pint
Extract of neroli	1/2 pint
Extract of vanilla	1/4 pint
Extract of vitivert	1/4 pint
Extract of cassie	1/2 pint
Otto of Gaultheria	5 minims

**Formula 2. Orient cologne (around 1889)<sup>13</sup>**

Parts	
Oil of wintergreen	1/2 drachma
Oil of lemongrass	1/2 drachma
Oil of bergamot	3 drachmas
Oil of lavender	4 drachmas
Oil of cloves	1 drachma
Oil of cassia	1/2 drachma
Oil of sassafras	1/2 drachma
Oil of bitter almonds	20 drops
Oil of rosemary	1 drachma
Oil of geranium	1 drachma

**Table 1. Ingredients (relative parts) of artificial fruit essences (around 1890)<sup>14</sup>**

Ingredient	Apricot	Grape	Orange	Raspberry	Strawberry
Glycerin	4	10	10	4	2
Chloroform	1	2	2		
Nitrous ether (ethyl nitrate)*				1	1
Aldehyde (acetaldehyde)		2	2	1	
Acetate of ethyl			5	5	5
Formate of ethyl		2	1	1	1
Butyrate of ethyl	10		1	1	5
Valerianate of ethyl	5				
Benzoate of ethyl		1	1		
Oenanthate of ethyl (ethyl heptanoate)	1	10	1		
Salicylate of methyl	2	1	1	1	1
Sebacic acid				1	
Acetate of amyl			10		
Butyrate of amyl	1				2
Essence of orange			10	5	

\* Names in parentheses are translations of the ancient terms.

necessary for the esterification is plentiful and industrial capacity far exceeds demand. Thus, the production of this ester was quickly transferred from the flavor and fragrance industry, where it began in 1895, to the chemical industry by the 1920s. Today the major world producers of methyl salicylate are those shown in Table 2. Additional producers are located in China, Colombia, Poland, Russia, Romania and Taiwan.

### Pricing

Since the 1920s, methyl salicylate pricing has always reflected its production by bulk chemical producers: pricing has been depressed. The posted list price often has nothing to do with the actual selling price. Grades of material are most often meaningless because the label is the grade and the quality is usually excellent and fits all uses. However, the imports of low-quality Romanian ester in the late 1980s depressed prices in the US market. Average selling prices in the flavor and fragrance industry for methyl salicylate are given in Table 3.

### Imports

The North American market has seen imports of methyl salicylate at the level of 700,000-800,000 kg throughout the past decade. Prior to 1980, very little of this ester was imported because of the prohibitively high tariff rate in

place then. Since the oppressive duties of the ASP (American Selling Price) system (26.8% ad valorem) were removed in 1980, the duty on methyl salicylate has been reduced to 11.9% under Tariff Schedule of the United States Nr. 2918.23.20 and the imports of this product have correspondingly increased.

### Substitutes and Analogs

No other known organic chemical has the profile of methyl salicylate; hence, there are no substitutes. A general thesis in chemistry states that the first member of any series has unique properties that will be difficult to match with the other members of that series. This generalization is more than true with the organoleptics of methyl salicylate. The next higher homologue, ethyl salicylate, comes close, but misses. The remaining members of this ester series slowly diverge from the herbal-mint tone and acquire a pronounced floral note. See Figure 2 for a presentation of structure versus organoleptic profile of the salicylate series.

As one can imagine, every possible salicylate ester that could be made, has been made. More than 500 salicylates can be found in the chemical literature. Yet, little industry use is made of them because salicylate esters display a good deal of overlap in their odor profiles, making most of them redundant. When the molecular weight of a salicylate ester approaches 250 units or 16 carbon atoms, the ester's odor becomes too faint to be useful. Once the alcohol group exceeds C-10, the ester has no perceptible odor at room temperature.

The aromatic function in the form of benzyl alcohol produces benzyl salicylate with its balsamic-floral odor. Higher molecular weight aromatic alcohol esters of sali-

**Table 2. World producers of methyl salicylate in 1998**

Producer	Type
Arofine Chemical Ind., India	synthetic
K.V. Arochem Ltd., India	synthetic
Kalama Chemical, USA	synthetic
Nipa-Hardwicke, Inc., UK	synthetic
Quest, Mexico	synthetic
Rhone-Poulenc, USA, Brazil, France	synthetic
Robertet, France	natural

**Table 3. Average selling prices for methyl salicylate, 1960-1998**

Year	US\$/kg
1960	0.40
1965	0.45
1970	0.46
1975	0.91
1980	1.25
1986	1.79
1989	1.35
1995	1.50
1998	1.75

**Table 4. Common salicylate esters**

Ester	FEMA-GRAS Nr.
n-Amyl salicylate	-
Benzyl salicylate	2151
Bornyl salicylate	-
Butyl salicylate	3650
p-Cresyl salicylate	-
Cyclohexyl salicylate	-
Ethylhexyl salicylate	-
Ethyl salicylate	2458
cis-3-Hexenyl salicylate	-
trans-2-Hexenyl salicylate	-
Hexyl salicylate	-
isoAmyl salicylate	2084
iso-Butyl salicylate	2213
l-Menthyl salicylate	-
Methyl salicylate	2745
Phenethyl salicylate	2868
Phenyl salicylate	-
Prenyl salicylate	-
Propyl salicylate	-
ortho-Tolyl salicylate	3734

cyclic acid show little advantage over benzyl salicylate in fragrance formulations. For the odors of other aromatic and alkyl groups, consult Arctander works. Table 4 gives a list of the common salicylate esters sold commercially in the flavor and fragrance industry.

## Derivatives

There is not much one can do to modify a methyl group while retaining one carbon. Alkyl changes in the alcohol grouping were covered under the discussion of analogs.

Figure 3 explores modifications of the aromatic ring. An increase in the number of carbon atoms in the alcohol group and/or directly on the ring will result in a increase in floral character, such as with amyl para-methylsalicylate [1]. Modifying the aromatic ring by adding additional methoxyl groups or alkylating the phenol group will cause a drift away from the floral theme into the herbal-anise region; if done extensively, it will produce an oakmoss impression, as can be seen in methyl-3,6-dimethyl- $\beta$ -

resorcyolate [6]. This transition from herbal-floral to oakmoss with change in chemical structure is illustrated in Figure 3, via the use of selected salicylate esters.

## References

Address correspondence to George S. Clark, Cameron & Stuart Inc., 6304 Waterloo Drive, Easton, MD 21601 USA.

1. *The Givaudan Index*, 2nd Ed, New York: Givaudan Delawanna (1961) p 267
2. Methyl Salicylate Product Data Sheet, Rhone-Poulenc (1994)
3. J Dean, *Lange's Handbook of Chemistry*, 13th Ed, New York: McGraw-Hill (1985) pp 7-536 m774
4. J Leffingwell and D Leffingwell, GRAS flavor chemicals-detection thresholds, *Perfum Flavor* **16**(1) 1-19
5. B Harris, *The Complete Herbal*, New York: Bell Publishing (1985) pp 68, 148, 192
6. H Mann, *Die Schule des Modernen Parfümeurs*, Augsburg: Verlag für Chemische Industrie (1911) pp 72,128
7. R Croteau and F Karp, Origin of natural odorants, in *Perfumes: Art, Science and Technology*, P Müller and D Lamparsky, eds, London: Elsevier Applied Science (1993) p 112
8. N Kaneko et al, Aroma components in the bud oils of *Betula* species, *Proceedings of the 12th International Congress of Flavors, Fragrances and Essential Oils, Wien, Austria, Oct 4-8, 1992*, (1992) pp 54-61
9. E Parry, *Parry's Cyclopaedia of Perfumery*, London: J & A Churchill (1925) p 93
10. A Cahours, *Ann Chim* x 327-369 (1844)
11. F Powers and C Kleber, On the chemical composition of the oils of wintergreen and sweet birch, *Pharmaz Rundschau* **13** 228-232 (1895); see also Schimmel's Report (October 1895) p 50
12. C Piesse, *Piesse's Art of Perfumery*, 5th Ed, London: Piesse and Lubin (1891) p 236
13. J Begy, *Practical Handbook of Toilet Preparations*, New York: (1889) p 151
14. G Askinson, *Perfumes and Their Preparation*, 3rd Ed, New York: Norman W. Henley Publishing (1907) p 82

