An Aroma Chemical Profile

Geraniol

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

Geraniol is one of the most organoleptically complicated aroma chemicals found on the market today and shows its complex nature by the number of geraniol grades offered (Table I). The product we refer to as "geraniol" is in reality a mixture of two cis-trans isomers properly named geraniol (trans) and nerol (cis).

Geraniol was found originally in geranium oil and thus was named "geraniol," while its isomer, nerol, was found in neroli oil. Thus, the organoleptic tone of each grade of geraniol offered on the market is colored by its cis-trans ratio.

In addition to its total "geraniols" content, the product is also colored by its production process and resulting impurities. A further market complication is the existence of both synthetic geraniol and natural geraniol from at least three sources. Rhodinol is a further complication because it is a mixture of geraniol-nerol and citronellol, plus minor quantities of other items.

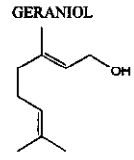
Geraniol is the allylic isomer of linalool. Linalool's bland universal-floral organoleptic profile has allowed it to become one of the work horses of the flavor and fragrance industry, so much so that one estimate[3] suggests that linalool is used in more than 90% of the fine fragrances offered to the market each year.

Geraniol plays a unique role because its odor is more pronounced and unusual than that of linalool. Geraniol is clearly an outstanding rose material. Even though the fragrance of roses is the most popular flower theme, the organoleptic profile of geraniol limits its use relative to that of linalool. Geraniol finds use in only 43% of the fine fragrances found on the market. Prices of the two alcohols are at similar levels, so usage volumes are determined by the innate properties of the two aroma chemicals.

Natural Sources

Geraniol is widely distributed throughout nature in the plant kingdom and is thought to arise via the biosynthetic route shown in Figure 1. This suggested route involves the

Geraniol



$C_{10}H_{18}O$
Mwt 154
CAS 106-24-1
FEMA-GRAS 2507

Harmonized Tariff No.: 2905.19
Classification: Acyclic, unsaturated, monoterpenoid primary allylic alcohol found widely in nature as a constituent of essential oils
Additional Names: 2-trans-3,7-dimethyl-2,6-octadien-1-ol*; Meranol (BBA); Gerallol (Givaudan); rhodeanol; rhodinol; roseneone; roseol; reuniol

French: Géraniol
German: Geraniol
Portuguese: Geraniol
Spanish: Geraniol

Physical Data:[1,2]
Appearance: clear, colorless, mobile liquid
Specific Gravity 20-25°C: 0.877
Refractive Index at 20°C: 1.477
Boiling Point at 760 Torr: 246-247°C
Flash Point TCC: >200°F or 93.3°C
Solubility: Only very slightly soluble in water, soluble in 70% ethanol, V/V 1 in 2. Soluble in most organic solvents, chlorinated solvents and in edible and essential oils.

* The early chemical literature usually based the cis-trans terminology on the relative placement of the group under consideration (here the CH_2OH) versus the adjacent methyl group. The more modern rule adopted by *Chemical Abstracts* in 1954 uses the relative placement of the two largest groups to determine the cis-trans relationship. Hence, geraniol is referred to as a cis isomer in the works of Gildemeister, Guenther and Simonsen, and as a trans isomer in the works of Arctander, Bauer and Garbe; and Bedoukian and Fenaroli.

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addition of dimethylallyl pyrophosphate to isopentenyl pyrophosphate to yield the geraniol pyrophosphate, which in turn produces geraniol.

Commercial sources of natural geraniol and (usually) nerol are shown in Table II. Because geraniol has so many "hiding places"—outnumbered only by linalool's—Table II is only a partial list. The essential oils of geranium, Palmarosa and citronella have been used as a source of geraniol and other aromatic materials for more than 100 years, while the essential oils from Jamrosa and Dhanrosa are recent developments by plant researchers in India.[5]

Geraniol has also been identified as a constituent in the following plant-derived materials, food stuffs and essential oils:

acacia oil
apple juice
beer
Bellary leaf oil
blueberries
cardamom oil
cinnamon oil
coriander oil
Daucus carota (2%)
davana oil
genet
ginger oil (5%)
grapes
grapefruit juice
lemon oil
lemon balm oil
lemon juice
lemongrass oil
lily of the valley
Litsea cubeba oil
marjoram oil
Monarda fistulosa (90-94%)
nutmeg
myrtle oil
neroli oil
osmanthus
orange oil
orange juice
orange flower water
orris root
raspberry
raspberry leaf
rose oils (0.3-43%)
Ottar of Rose
Bulgarian rose oil (14%)
Skimmia laureola oil (8%)
snakewood root
strawberry
strawberry leaf
Tagetes oil
teas, both black and green
tomato leaf
wine, both red and white

Table I. Grades of geraniol-nerol available in 1997

Grade	Geraniol (%)	Nerol (%)	Firm
Geraniol 500	60	40	BBA
Geraniol 600	60	40	BBA
Geraniol 902	91	9	BBA
Geraniol 980	98		BBA
Geraniol 5020	50	20	BBA
Geraniol 7030	70	30	BBA
Geraniol 8020	80	20	BBA
Geraniol Absolute	50-70	5 max	IFF
Geraniol Extra	70 min	12 max	IFF
Geraniol Coeur Natural	50-70	5 max	IFF
Geraniol Coeur Synthetic	50-70	5-20	IFF
Geraniol 60	60	39 max	Millennium
Geraniol 80	80	19 max	Millennium
Geraniol 90	90	9 max	Millennium
Geraniol BJ	70-72	29 max	Millennium
Geraniol Ex Palmarosa	90 min		IFF
Geraniol Extra, FCC			Ungerer
Geraniol Fine, FCC	98	2 max	Millennium
Geraniol NC	97 min	18 max	IFF
Geraniol N supra	94 min		H&R-Florasynth
Geraniol Prime	60-62	39 max	Millennium
Geraniol RG	50-70	25-45	IFF
Geraniol S			Ungerer
Nerol 50	50 max	50 min	Millennium
Nerol 70	29 max	70 min	Millennium
Nerol 80 (BJ)	19 max	80 min	Millennium
Nerol 900		93	BBA
Nerol 800		81	BBA
Nerol BG	10-30	70-90	IFF
Nerol Coeur	40-50	47-57	IFF
Nerol G	40-70	20-50	IFF
Nerol N supra			H&R-Florasynth
Nerol OM	40-70	20-50	IFF
Nerol Regular	56-62	38-42	IFF
Nerolex	3	95	Millennium

Table II. Commercial sources of natural geraniol (1997)

Oil	Geranial content (%)	World production of oil (Mtons-estimated)
citronella (*Cymbopogon winterianus*)	20-35	5,000
geranium (*Pelargonium graveolens*)	14-80	150
Jamrosa (*Cymbopogon jwarancusa*)	80-85	100
Palmarosa (*Cymbopogon martini*)	75-86	80
Dhanrosa (*Cymbopogon flexuosus*)	79-85	10

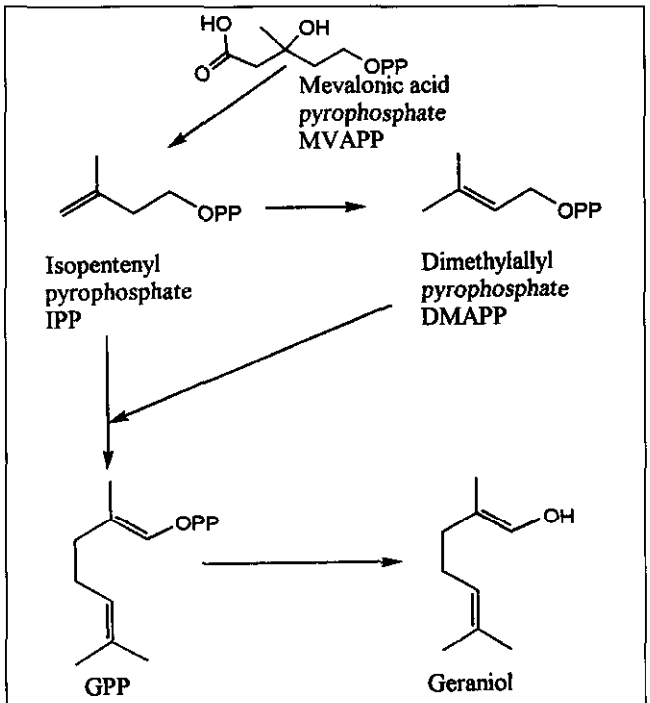


Figure 1. Proposed biosynthetic route to geraniol[4]

Consumption

Table III shows the estimated human consumption of geraniol from all sources in 1997. Table IV shows the global breakdown for geraniol consumption in 1997 by end use.

Table III. Human consumption of geraniol from all sources in 1997 (global estimate in Kgs)

Use	Consumption
food stuffs	100,000
citrus beverages	3,000
added flavors	10,000
Total	113,000

Table IV. Global breakdown of flavor and fragrance consumption of geraniol by end use in 1997 (Kgs)

synthetic F&F grade	1,550,000
natural F&F grade	300,000
intermediate for esters	320,000
intermediate for other aroma chemicals	9,500,000
F&F industry total	11,670,000

History

Rose oil and geranium oil: Geraniol is closely linked to the odor of roses. Its development as an aroma chemical has reflected the market needs for rose fragrances over the past 150 years.

Rose oil and rose water distillation were first developed in India more than 5,000 years ago. References to the production of rose oil from *Rosa damascena* Mill. are found in India as far back as the 1400s AD.[6] A romantic tale places rose oil later, during the reign of Emperor Jahangir (1605-1625) in India. His Empress, Noor Jehan, noticed insoluble drops of oil floating in her rose water bath and had the material collected.

The Moslems made contact with India through trade and took the secret of rose oil home. They prized rose water and rose oil. The Moslem Turks encouraged the growing and distillation of damask roses in the Kazanluk Valley of Bulgaria. By the early 1700s, both rose oil and rose water from this region were an item of commerce in Europe.

Rose oil was difficult to obtain. It was also expensive, because it takes 5,000 kg of rose petals to produce 1 kg of rose oil. Therefore, the French and German flavor and fragrance industries were always on the lookout for a cheaper substitute.

In 1819, a rose-like oil was noted from the distillation of the leaves of the geranium plant (*Pelargonium* sp.), which contains 75% geraniol.[7] Approximately 700–1,300 kg of leaves yield 1 kg of geranium oil. By 1847, plantations for the production of geranium oil were in place in Algeria and France, and by 1880 on the island of Reunion.

Geranium oil was originally referred to as rose geranium, along with Ottar of Rose and rose water, in the fragrance literature of the 1880s.[8] Geranium oil had become a lower-cost replacement for true rose oil, largely due to its geraniol content.

Geraniol from Palmarosa oil: Geraniol was discovered in 1871 by Jacobsen[9] in Turkish geranium or Rosha/Rusa grass oil (Palmarosa oil), where it occurs as a geraniol-nerol mixture in 80-95% concentrations.[10] Jacobsen isolated the pure geraniol from the oil by its calcium chloride addition complex. As luck would have it, the accompanying alcohols found in the Palmarosa oil—nerol and linalool—will not form a calcium chloride addition complex, so the geraniol was isolated as a pure substance.

In 1894, Heine and Haarmann & Reimer were producing geraniol from Palmarosa oil and nerol from neroli oil. Schimmel in Germany produced a grade of geraniol (1 kg) distilled with rose petals (500 kg) to impart a stronger rose oil note.[12,13] Soon rose oil was the item to use in fine fragrance, but geranium oil was *the* ingredient for soap. As demand grew and supplies of geranium oil could not keep up with demand, new sources of geraniol were sought out. Chemistry had not yet provided a synthetic route for this alcohol.

By 1900, Palmarosa oil was furnishing a high-grade geraniol that was offered by Delaire, Firmenich, Schimmel,

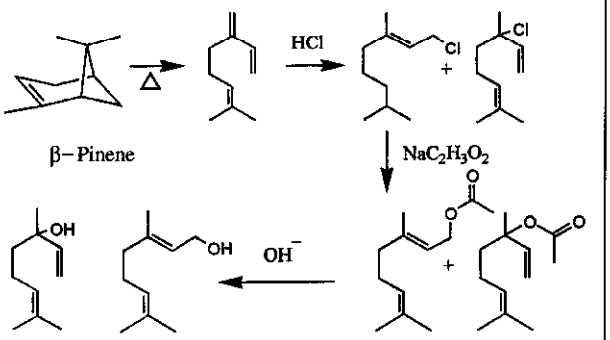


Figure 2. Bush Boake Allen route to geraniol-nerol

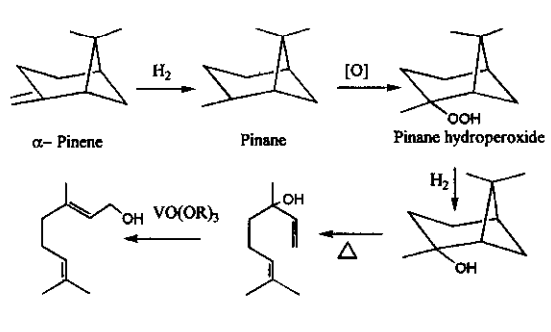


Figure 3. Current Millennium route to geraniol-nerol

Polak & Schwarz, Roure-Bertrand Fils and others. Palmarosa-isolated geraniol allowed the reconstruction of synthetic geranium oil by Haarmann & Reimer.[12]

Geraniol from citronella and β-pinene: Citronella oil was the next source to be found, but the geraniol obtained was considered inferior to that obtained from geranium or Palmarosa oils. In 1890, Dodge & Olcott became the first U.S. firm to produce geraniol from citronella oil. From 1900 to 1963 the world's main source of geraniol was its isolation from Palmarosa or citronella oils.

In the 1940s, the Glidden Company (now Millennium) of Jacksonville, Florida, developed a route to synthetic geraniol starting with β-pinene. It took more than ten years to perfect the chemistry of the β-pinene system[14] and another ten to fine-tune it.

Commercial volumes of synthetic geraniol, linalool and citral began flowing from the Glidden Company's new aroma-chemical plant in Jacksonville in late 1959. Soon after, a business relationship with Firmenich developed, involving the sales, quality control and organoleptic aspects of the new process. By 1966, Union Camp had developed a β-pinene-based process and constructed a plant, also in Jacksonville. Bush Boake Allen (BBA) developed the β-pinene route shown in Figure 2 and built pinene-based aroma chemical production facilities in the 1960s at Widnes and Rainham in the U.K. During the 1970s and 1980s, these geraniol plants were expanded to more than three times their original capacity.

Geraniol from α-pinene: In the early 1980s, the Glidden Company commercialized technology to convert α-pinene into linalool and then into geraniol. This α-pinene route, shown in Figure 3, is the route by which Glidden (Millennium) has produced its geraniol since the early 1980s.

Today, Millennium and BBA/Union Camp command 90% of the world's synthetic geraniol-nerol market.

Pricing

Over the past 20 years, geraniol prices have been very stable, rising with the economy. They have registered no surprises. In part, this is due to the fact that when synthetic geraniol was introduced to the market, the price of natural geraniol was already at a fairly high level, relatively speaking, compared to that of synthetic linalool from which synthetic geraniol is now produced (Figure 3). The average prices for geraniol (flavor and fragrance grade) are listed in Table V.

Derivatives

The following geraniol derivatives are normally offered

Table V. Average prices of flavor and fragrance grade geraniol 1950-1997 ($US/Kg)

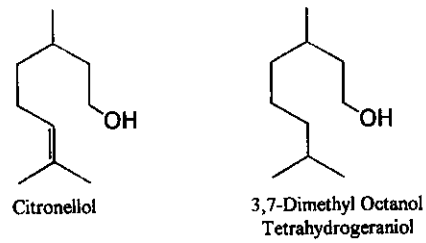
Year	Price
1956	6.20
1966	2.90
1976	5.60
1986	12.70
1996	14.30
1997	14.80

for use in the flavor and fragrance industry:

citral
geranic acid
geranyl acetone
geranyl anthranilate
geranyl crotonate
geranyl ethyl ether
geranyl isobutyrate
geranyl phenyl acetate
geranyl valerate
citronellol and derivatives
geranonitrile
geranyl acetate
geranyl benzoate
geranyl cyclopentanone
geranyl formate
geranyl isovalerate
geranyl propionate
tetrahydrogeraniol
geranoxy acetaldehyde
geranyl acetoacetate
geranyl butyrate
geranyl decanoate
geranyl hexanoate
geranyl linalool
geranyl tiglate

Table VI. Estimated world consumption of geraniol derivatives for 1997 (Kgs)

geranyl acetate	650,000
geranyl benzoate	22,000
geranyl butyrate	17,000
geranyl isobutyrate	25,000
geranyl formate	120,000
geranyl nitrile	1,500,000
geranyl propionate	300,000
geranyl tiglate	30,000



Citronellol — 3,7-Dimethyl Octanol Tetrahydrogeraniol

Figure 4. Two substitutes for flavor- and fragrance-grade geraniol

Table VI presents the estimated world consumption of some of these derivatives.

The following geraniol-based specialties are offered by only one or two houses in the trade:

geranyl acetoacetate (Bell)
geranyl ethyl ether (IFF)
geranyl methyl tiglate (Fairmount)
geranyl undecyclamate (Fruitarom)
geranyl caprylate (octanoate) (Bedoukian)
geranyl geraniol (Kuraray)
geranyl oxy-acetaldehyde (Bedoukian)

Substitutes

Figure 4 shows two substances whose organoleptic profiles allow them to substitute for geraniol in flavors or fragrances.

Producers of Synthetic Geraniol

In the world market, there really are only two major manufacturers of synthetic geraniol. A minor producer in the Peoples Republic of China might be included if one wishes to stretch the point.

Millennium: Millennium is clearly the leading producer of synthetic fragrance-grade geraniol-nerol. It has 60% of the world market. Millennium's current capacity is estimated at 10,000 metric tons (Mtons) per year for geraniol production, with their current product mix. Because geraniol is generated from linalool (Figure 3), the geraniol capacity could be increased by reducing linalool production. Millennium currently supplies about 2,900 Mtons of various grades of geraniol to the world market and is the main supplier of pure flavor- and fragrance-grade geraniol-nerol.

BBA: Bush Boake Allen is the second major world producer of synthetic geraniol-nerol, with an estimated production capacity of 8,000 Mtons/year and a sales level of about 3,000 Mtons/year. In BBA's process (Figure 2), which is similar to the original Millennium (Glidden) process, geraniol acetate is generated from β-pinene, via myrcene, to geranyl-neryl acetate. The ester must be saponified to obtain the alcohol. The bulk of the world's technical grades of geraniol-nerol are produced by this method.

Others: Other suppliers of synthetic geraniol purchase crude grades of geraniol from one or both of the two major producers and upgrade the product to their own specifications.

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