

A Profile: An Aroma Chemical

Vanillin

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Vanillin is the most universally appreciated aroma chemical. Its popularity transcends cultures, thus resulting in its ranking as the number one aroma chemical with respect to its consumption in tonnage. Even on a dollar value consideration, vanillin has few contenders for the top ranking in the world's list of aroma chemicals.

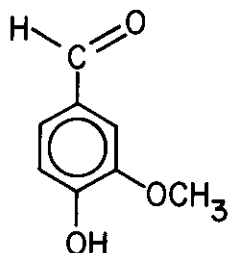
Vanillin's organoleptic impression is surprising in view of its chemical nature. It can be considered as a substituted benzaldehyde, yet it lacks an almond impression. When viewed as a substantial phenol, it displays none of the expected carbolic note. It is so

unique that it may be safe to say it represents an individual odor class—vanilla!

Vanillin N.F. is a synthetic product. Material available today is a highly pure, refined product, which possesses a pleasant, smooth, creamy-sweet aroma, that is best described by the seemingly redundant term *vanilla*.

In the past, grades of vanillin were available which carried off notes due to their production from eugenol or safrole. These grades have disappeared from the market today. Yet, this problem illustrates two facets of vanillin's nature—its very low threshold

Vanillin



Mwt 152

$C_8H_8O_3$

CAS 121-33-5

FEMA-GRAS 3107

Classification:

A monocyclic aromatic aldehyde-phenol containing a methoxy group, found in a number of natural products in low levels.

Additional Names:¹⁻⁴

The most common name, vanillin, is derived from the vanilla bean, which in turn received the name from the Spanish diminutive "vaina" (or vayna),

meaning a pod or sheath, describing the shape of the fruit. The following names are also found in the literature:

4-hydroxy-3-methoxy benzaldehyde

3-methoxy-4-hydroxybenzaldehyde

methyl protocatechuic aldehyde

vanillic aldehyde

French—Vanilline

German—Vanillin

Portugese—Vanilina

Spanish—Vainillina

Physical Data:

Appearance: white to off-white crystalline powder

Specific Gravity: 1.056

Melting Point: 80-81°C

Boiling Point: 285°C

Solubility: 1% in water at 20°C, soluble in ethanol, DEP, benzyl benzoate, aliphatic and aromatic esters, chlorinated solvents, acetic acid.

The U.S. Pharmacopeia lists specifications for vanillin in its National Formulary section as having a minimum of 97.0% purity.⁵

of odor recognition and its ability to pick up extraneous odors during production or storage.

There are many cases of vanillin being cross contaminated during shipment in sea-containers that also carried musk, indol, coumarin or menthol. Musk or indol with a slight vanillin note might be acceptable, but vanillin with a musk or indol note is a disaster.

The factories currently producing vanillin from either lignin or guaiacol are usually solely dedicated to its production, thus making contamination during manufacture unlikely. The problems arising today stem mainly from poor storage conditions.

The flavorist will find little problem using the commercial products available today with respect to organoleptic quality. However, vanillin is an aldehyde and thus capable of forming acetals and hemi-acetals. In flavor formulations using high concentrations of vanillin in conjunction with carriers such as propylene glycol, a GLC analysis often shows a reduced vanillin peak after storage of the compounded flavor and the presence of new peaks indicating acetal formation. In some cases, this had led to customer rejection of the lot. The simple addition of small amounts of water, approximately 0.5 percent, to the formula results in the reversal of the reaction and the reappearance of the vanillin peak with a similar reduction of the acetal peaks.

Less fortunate is the perfumer who must still contend with vanillin's chemical reactivity which limits its usage, i.e. discoloration in the presence of iron salts and formation of Schiff's bases with other ingredients containing amine functionalities.

Natural Sources

Vanillin is found in small amounts in many essential oils and extracts, but at such low concentration that they cannot serve as a source of natural vanillin. The major commercial source of natural vanillin is vanilla bean extract, which is used as such when natural vanillin is dictated.

Vanillin occurs in vanilla bean at about a two percent by weight level and vanilla beans are currently priced at around \$35.00/lb. After extraction and purification, natural vanillin would cost \$1,800/lb versus synthetic vanillin at \$7/lb.

Vanilla beans are the dried, fermented and then cured unripe fruit pods of a species of wild orchid, *Vanilla planifolia* Andr., which is indigenous to Mexico. Mexico has ceased production, and the current world sources of vanilla beans are Comore, Madagascar and Reunion (Bourbon type); and more recently, Indonesia and Java (Java type). The two classes of beans vary in secondary organoleptic impression due to varying trace amounts of other

aroma chemicals.

Vanilla beans possess the organoleptic impression of vanillin, enriched and rounded out by the following materials:⁶ Vanillic acid, vanillyl acetate, cinnamic acid, anisic acid, anisyl alcohol, anisyl aldehyde and a number of other minor esters which vary with the source of the bean.

Human consumption of natural vanillin is mainly via vanilla extract.⁷ The following products are reported to contain small to trace amounts of natural vanillin: Spanish anise oil, beer, benzoin, brandy, citronella Java, roasted coffee, clove bud oil, lily (*Lilium aurotim*), Peru balsam, strawberries, rum, and whiskey.

The presence of vanillin in such a wide sampling of materials indicates why the rule of thumb in the flavor and fragrance industries is—a trace of vanillin can't hurt.

History

Vanillin and vanilla were unknown to Europeans until Cortez discovered vanilla beans being used in the Aztec kingdom of Montezuma in 1520. Spain and then Mexico developed a lucrative monopoly in vanilla, which prompted many attempts to cultivate vanilla in similar climates throughout the world.

The plants grew, but no beans resulted until a French botanist, Charles Morren, discovered in 1836 that the flowers were not self-pollinating. Pollination occurred through the efforts of a tiny insect found in Mexico, but absent from the other geographic regions where vanilla bean production had been attempted.

In 1841, Edmond Albins discovered how to manually pollinate the flowers in Reunion. This opened up the areas of Reunion, Madagascar and Comore for the production of vanilla beans and shattered the Mexican monopoly.

The demand for vanilla beans grew and the popularity of chocolate products intensified demand for the product, making the production of synthetic vanillin a prime target for the organic chemist. This resulting demand can be illustrated with a few points. One is ice cream,⁸ where vanilla flavor commands a 20 percent market share in the US, followed by the runner-up, chocolate (a flavor which also uses vanillin) with a 9 percent market share. The third and fourth place contenders are strawberry and butter pecan with approximately 5 percent market shares each. Consumption of vanillin in the U.S. chocolate products industry is currently in excess of 1000 Mtons.

Other countries show similar consumption patterns with respect to ice cream; for instance Brazil, where vanilla has about the same market share as

the US, with strawberry in second place with about 20 percent of the market.⁹ The ability of vanilla to cover unpleasant odors and tastes makes it a prime choice for difficult projects.

During the second world war, the Japanese lacked oxygen mask equipment for their air force. This prevented their fighter pilots from pursuing American fighters and bombers in higher altitudes, because the oxygen depletion causes drowsiness and disorientation.

One solution was to provide caffeine tablets to their pilots to overcome the problem. However, the pills were so bitter, the pilots refused to use them. Vanillin was chosen as the best cover agent for the bitterness. Thus vanilla bean production was begun in Formosa to provide vanilla extract.¹⁰

By 1816, Bucholtz¹¹ had identified vanillin in vanilla beans, but it was not actually isolated until 1856 by Goble.¹² The structure of vanillin was determined by Tiemann and Haarmann in 1874.¹³

Haarmann developed a process to manufacture it from coniferin found in pine sap. This resulted in its first commercial production and the founding of the firm Haarmann and Reimer. However, the production of vanillin from coniferin proved impractical.

In 1876, Erlenmeyer reported the synthesis of

vanillin from eugenol and Reimer reported its preparation from guaiacol—the two main processes for its commercial production until the lignin-based process appeared in 1932.

Synthetic vanillin brought the price down to bearable levels and expanded its use beyond basic flavors. Fragrances showed increasing use of vanillin, as exemplified by Guerlain's introduction of Shalimar in 1925, with its heavy oriental vanillin notes.

The discovery that vanillin could be produced from lignin-based by-products found in sulfite waste liquor from the Kraft paper process led rapidly to commercial production of synthetic vanillin in the US (Monsanto) and Canada (Ontario Chemical) by 1937. The lignin-based process quickly dominated the field, although Rhone-Poulenc concentrated on its production from guaiacol.

By 1980, new technology developed in the pulp industry used chemo-thermal methods to process wood pulp without the generation of sulfite black liquor and all its recovery and environmental problems. If you have ever been down wind from a Kraft pulp and paper mill, your nose would give you a clue to some of those problems.

Changes in pulp and paper technology foreshadowed a questionable future for lignin-based vanillin. By 1986, Monsanto had sold its lignin-based synthetic vanillin operation, rated at 2000 Mton capacity, to Rhone-Poulenc. The following year, Ontario Paper Company shut down the world's largest lignin-based vanillin plant with a capacity of over 3000 MTons.

The resulting consolidation of production occurred as China ceased supplying large amounts of vanillin to the world market. As the disruptive pricing policies of China faded, the remaining major producers, Borregard, Rhone-Poulenc and ITT Rayonier could plan rational expansions of their capacity. In 1988, ITT announced plans to double their vanillin ex-lignin capacity to 1500 MTons by 1989 and Rhone-Poulenc announced plans for a new production facility for guaiacol and synthetic vanillin ex-guaiacol to be built at Baton Rouge, La. by 1990.

The processes for production of vanillin are coming full circle in slightly over 50 years, mainly due to environmental pressures. This renewed interest in vanillin has caused many firms to begin exploring the possibilities of its production using both modern chemical and bio-technologies.

World Consumption

Consumption in 1990 of natural and synthetic vanillin for flavors, fragrances and as a chemical intermediate for drugs and other derivatives is estimated by varying sources at between 7,000 to

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12,000 MTons. However, this author's estimates indicate 12,000 MTons is most realistic. Approximately 20 MT was in the form of natural vanillin as extract of vanilla beans while synthetic vanillin provided the remainder.

Worldwide usage with region figure estimates break down as follows (expressed as % of world consumption):

World Consumption	%
flavors	84
fragrances	3
chemical intermediates	13
Consumption by region	
North America	26.7
flavors	21.7
fragrances	.83
chemical intermediates	4.2
Europe (EEC Countries)	27.7
flavors	24.3
fragrances	.83
chemical intermediates	2.5
East Block (Including Soviet Union)	16.7
flavors	16.6
fragrances	<0.4
East Asia (Japan, China, Korea, etc.)	16.8
flavors	12.5
fragrances	<0.2
chemical intermediates	4.2
South Asia (Indonesia, Malaysia, India, etc.)	4.3
flavors	4.3
fragrances	<0.2
Latin America	4.3
flavors	4.3
fragrances	<0.4
Other (Africa, Oceania, Middle East)	1.7
flavors	1.67
fragrances	<.02
	Total 98.2%

(Total less than 100% due to rounding of % numbers.)

Pricing

Vanillin prices have shown considerable variation over the ten years from 1978 to 1988 (Figure 1), due to a number of factors. Average prices in 1976 were approximately \$4.25/lb and rose slowly to about \$5.80/lb by 1978. Supply and capacity were in excess of world demand.

China began shipping fair quantities to the world markets in 1978, which resulted in a steady price erosion at the same time the US dollar began rising versus other hard currencies. The nominal US tariff rate of 10.1 percent (TSUS 413.40) did little to effect US prices and almost 50 percent of US demand was met by imports from Canada, France and China.

Vanillin prices reached the levels of 1976 prices

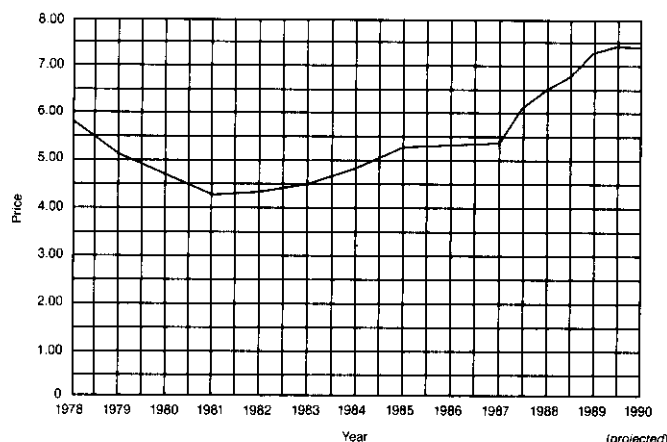


Figure 1. Synthetic Vanillin
Prices in U.S. \$/lb on the U.S. Market

by 1981, mainly due to Chinese imports. By 1983, prices began to firm as China withdrew from the world market and prices leveled in the \$5.25-5.40/lb area until 1987.

The shut down of Ontario Paper's production withdrew some excess capacity from the market. The bleak future for lignin-based vanillin affected other lignin-based producers, resulting in upward price pressure. Since 1987, prices have risen to the \$7.00-7.25 area. They are now projected to remain level as new capacity is brought on stream in 1990.

Supply

Current supply and demand (early 1990) are showing signs of being in tight balance. Spot shortages have not occurred to date because of careful inventory management by producers. Estimated demand in 1990 will be over 12,000 MTons with world production capacity gauged at about 13,000 MTons.

As various producers complete their expansion plans, growth and supply will again outpace that of demand. By the end of 1990, vanillin capacity will again be in excess of demand.

If world vanillin consumption grows at a one percent per annum rate, the capacity in place by the end of 1990 should be sufficient to supply market demand well into the next century, provided market changes do not force the shutdown of more lignin-based plants. However, flavor consumption is growing at rates of four to six percent in the developing countries and about three percent in the developed ones.

A worldwide growth rate of three percent or higher would be more realistic. Such a consumption increase, three percent per annum over the next 10 years, would require additional capacity by the year 2000 over that in place at the end of 1990 (16,000 MTons).

Vanillin Producers

Lignin-Based: The following producers supply vanillin from sulfite waste liquor. As newer chemo-thermal units replace the older pulp and paper units, the amount of vanillin from these sources will decline.

The other problem faced by these producers is the necessity of having the vanillin production unit close to the site generating the waste liquor. Approximately 1 MTon of waste liquor will produce 4.5kg of vanillin, making the shipment of waste liquor over any great distance uneconomical for the production of vanillin at current market prices.

Rhone-Poulenc U.S.A.—This older plant in Seattle, Washington was formerly owned by Monsanto and was sold to Rhone-Poulenc in 1986. Current capacity is rated at 2000 MTons/yr. with little prospect of increasing production volume.

ITT-Rayonier, Hoquiam, Washington—This facility is being expanded from 800 MTons/yr to 1500 MTons/yr. Further increases in capacity are deemed impractical.

Borregard, Norway—It is estimated that this producer of vanillin, operating under a license from Monsanto, has expanded its capacity from 1000 MTons to 1500 MTons/yr. It is doubtful if further increases in capacity are possible.

Others—The East Block has producers of lignin-based vanillin in Poland, Czechoslovakia and the Soviet Union. Their exact capacity is unknown, but is collectively estimated to be at least 200 MTons/yr.

Guaiacol-Based Producers: *Rhone-Poulenc*—The company is considered the traditional producer of vanillin from coal tar or petroleum-based feed stocks, using catechol as the starting material to generate guaiacol. Capacity is estimated as follows:

Lyon, France — 3000 MTons/yr

Baton Rouge, — Stated at several thousand
La, USA MTons, but estimated to be
capable of 3000 MTons with
minor bottlenecks removed.

Inoue, Japan—The company uses catechol as a starting material for the production of vanillin and ethyl vanillin. Capacity is estimated at 1000 Mtons/yr for vanillin production.

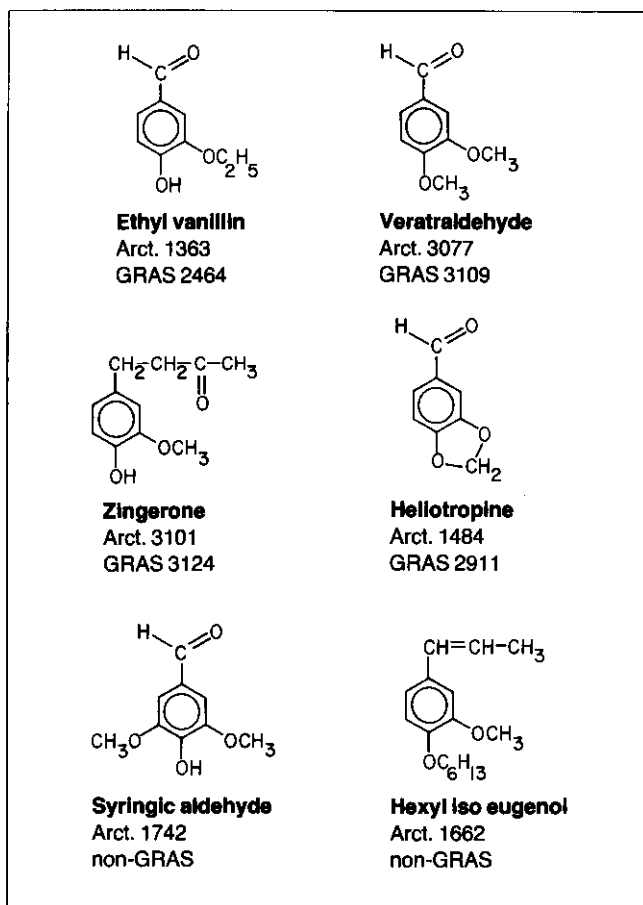
China—Although a recent report¹⁴ states China's production of vanillin is at approximately 1100 MTons/yr., it is estimated that China's current capacity is 2000 MTons/yr. Some of China's capacity is reported to be ex-lignin, but the majority of capacity is via guaiacol.

Substitutes

A number of structurally related cyclic-aromatic-phenolic aldehydes are available which can be sub-

Vanillin

stituted for vanillin in fragrances to create similar effects. In flavors, fewer substitutes are allowed; these are identified below by their accompanying FEMA GRAS numbers. The ARCT. numbers refer to Arctander's works.¹⁵



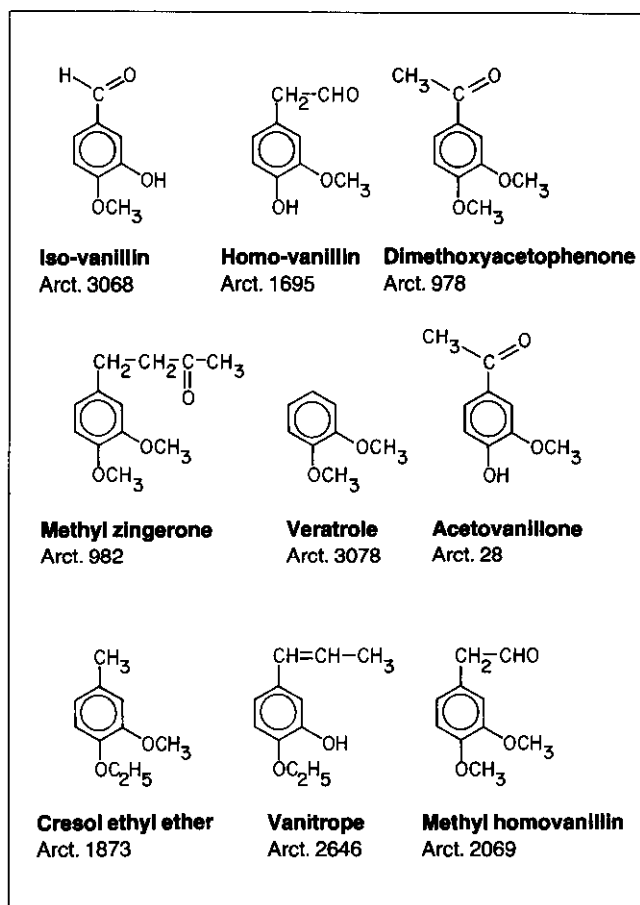
Analogs

The following materials have similar structures to vanillin and could be of interest to the perfumer as partial substitutes, for alternatives or twists in creative themes.

References

Address correspondence to George S. Clark, Commodity Services International, Inc., 114 North West St., Easton, MD 21601, USA

1. *The Merck Index*, 10th Ed, Rahway, NJ: Merck & Co, Inc, 1983, No. 9734
2. *The Givaudan Index*, 2nd Ed, New York, NY: Givaudan-Delawanna Inc, (1961) p 342
3. *Lange's Handbook of Chemistry*, 13th Ed, McGraw Hill Book Co (1985) 7-448, h279
4. F Rosengarten, *The Book of Spices*, New York, NY: Pyramid Books, (1973) p 427
5. *US Pharmacopeia*, USP XXI, The US Pharmacopeia Convention, Rockville, MD, p 1616



Derivatives

Vanillyl alcohol	FEMA-GRAS 3737
Vanillyl acetate	3108
Vanillylic acid	—
Vanillylidene acetone	3738
Vanillin propylene glycol acetal	—

Significant quantities of vanillin are used as an intermediate to produce the drugs L-dopa and methyl L-dopa as well as small quantities of other specialty chemicals.

6. P Calabretta & F Keppel, *The Chemistry of Vanilla*, VIIIth International Congress of Essential Oils, Cannes, France (1980) Paper 230
7. J Stoffberg, Consumption Ratio and Food Predominance of Flavoring Materials, *Perf & Flav*, 12 (4) 59 (1987)
8. A Levitt, *Dairy Foods*, 90 (1) 64 (January 1989)
9. D Hufenuessler, Industrias Reunidas Jaraqua SA, Santa Catharina, Brazil, private communication
10. T S Tsai, Formosa Perfume Co, Ltd, Taiwan, private communication
11. Buchholtz, *Repert Pharm* (1816)
12. Goble, *J Pharm* (3) 34 (1858)
13. Paul Z Bedoukian, *Perfumery and Flavoring Synthetics*, 3rd. Ed., Wheaton, IL: Allured Publishing Corp., (1985)
14. Z Qinghua, Steady Progress in China's Aromatics Industry, *Perf & Flav*, 14 (1) 42 (1989)
15. Steffen Arctander, *Perfume and Flavor Chemicals*, (1969)