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Alright Stop, Collaborate and Listen: Vanillin not Vanilla

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Abstract

In the modern lexicon, "vanilla" has the connotation of bland, generic, or ordinary. However, when vanilla flavoring and fragrance exploded onto the global stage in the mid-twentieth century due to advances in cultivation, it was rare and exotic. As soon as natural vanilla was introduced, supply could not keep pace with demand. However, during this same period, the chemical industry developed into a more modern, synthetic based industry, opening the door to a new era of easier to obtain and cheaper flavors and fragrances.¹ This working paper will provide an overview of the vanilla, and by consequence the vanillin, industry. Beginning with an introduction to vanilla, followed by a discussion of the advent of the synthetic vanilla flavoring, the paper will highlight the broader challenges within the natural and synthetic vanillin markets, including growing demand from U.S. consumers for "natural" products and the ability of the industry to meet such demands.

¹ Berenstein, "Flavor Added: The Sciences Of Flavor And The Industrialization Of Taste In America," xvii.

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Introduction

The ancient Aztecs of present-day Mexico were among the first civilizations to use the vanilla plant, *Vanilla Planifolia*, as a flavoring element to cut the bitterness of raw chocolate.² In 1519, the Spanish conquest of the Aztecs led to the introduction of the vanilla flower (and cacao) to Europe, but for centuries the imported plants did not offer up the sought after vanilla seeds.³ In 1836, Belgian horticulturist, Charles Morren, noted that the lack of seeds could be attributed to the dearth of natural pollinators—postulated to be a specific species of bee, the Melipona—in Europe. It wasn't until 1841 that Edmond Albius, an enslaved boy on the island of Réunion, developed a method for hand pollinating the vanilla flower to produce the desired seeds. This technique spread to Madagascar, which had better growing conditions for the vanilla plant than most of continental Europe, and eventually circled back to Mexico, where the technique accelerated vanilla seed (contained in the beans) production. Nearly all vanillin (the essential constituent in the vanilla seeds that elicits the desirable flavor) derived from the vanilla plant on the market today is produced via hand cultivation.⁴

Despite the exponential growth in harvesting of vanilla beans in the latter half of the nineteenth century, hand cultivation practices were time-consuming, and supply struggled to meet demand. At this time, production in the blossoming chemical industry focused more and more on chemical conversions and reactions.⁵ This era within the chemicals sector contributed to identifying flavor through the isolation and quantification of the molecular constituents that are the cornerstone of flavor and fragrance companies today.⁶ In 1851, "artificial essences" were showcased at the Great Exhibition of the Works of Industry of all Nations. August Hoffman of the Royal College of Chemistry noted that "pear oil" used to flavor lozenges that was part of the exhibit was simply amyl acetate, and that many of the other essential oils of other fruits on display (apple, pineapple, etc.) were attributable to compound ethers.⁷ Within a year of this discovery, artificial flavor essences were being sold commercially in the United States, and vanilla was part of the fragrant wave.⁸

A Brief History of Vanillin

After centuries of stagnation, the sudden boom in vanilla seed production in the mid-1800's stimulated the world's demand for vanilla. But as previously stated, even with the increase in vanilla seed production, supply could not meet demand. As cured vanilla beans yield only approximately two percent of extractable flavor, one kilogram (kg) of vanillin requires about 500 kg of vanilla pods from approximately 40,000 vanilla orchid flowers.⁹ However, in 1858, the application of modern scientific

² Cotton, "Vanillin - the Flavour of Vanilla Ice Cream," February 2008.

³ Sethi, "The Bittersweet Story of Vanilla," April 3, 2017.

⁴ Sethi, "The Bittersweet Story of Vanilla," April 3, 2017.

⁵ Berenstein, "Flavor Added: The Sciences Of Flavor And The Industrialization Of Taste In America," xvii.

⁶ Hofmann, , was a jurist at the Great Exhibition of the Works of Industry of All Nations. Berenstein, "Flavor Added: The Sciences Of Flavor And The Industrialization Of Taste In America," xix, 1–3.

⁷ Today known as esters, and classification for an organic functional group.

⁸ Berenstein, "Flavor Added: The Sciences Of Flavor And The Industrialization Of Taste In America," 1–3.

⁹ Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 40–41, 46–47; Bomgardner, "Following Many Routes to Naturally Derived Vanillin," February 10, 2014; Ciriminna et al., "Vanillin: The Case for Greener Production," May 2, 2019, 661–62.

processes and techniques allowed Theodore Gobley, a biochemist, to isolate and elucidate the chemical structure of vanillin. Vanillin, also referred to as methyl vanillin, is the key molecule found in the vanilla flower, specifically the beans within the pods, that gives off the vanilla fragrance and flavor (figure 1, left).¹⁰ Although vanillin is, predictably, found as a constituent in vanilla, this molecule is also found in variety of materials. Therefore, it is not surprising that less than 20 years after the vanillin molecule was classified, the first attempts to industrialize vanillin (i.e., isolated from a source other than the vanilla bean) began.¹¹ And the first factory to produce synthetic vanillin was Haarmann Vanillinfabrik, later Haarmann & Reimer, in 1875 in Germany.¹²



Figure 1 Chemical structure of methyl vanillin (left) and ethyl vanillin (right)

Note: Vanillin is imported under HTS-10 statistical reporting number 2912.41.0000 and ethyl vanillin enters under 2912.42.0000. For the purposes of this discussion, vanillin is considered as a market separate from that of ethyl vanillin.

The early days of industrial vanillin production were based on isolation of the molecule from coniferous trees. A more cost effective route of synthetic production developed using eugenol, the primary component of clove oil.¹³ Clove oil was the starting material of choice for synthetic vanillin production throughout the 1920s.¹⁴ In the mid 1930's, the United States began to synthesize vanillin from the lignin

¹⁰ Vanillin is a white crystalline powder that has low solubility at room temperature but is readily soluble in hot water, alcohol, and ether. IUPAC name is 4-hydroxy-3methoxybenzaldehyde. It is one of approximately 250 compounds that make up vanilla. Sethi, "The Bittersweet Story of Vanilla," April 3, 2017; Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 40.

¹¹ A synthesis developed by scientists Tiemann and Haarmann led to the founding of the company Haarmann and Reimer began producing vanillin. Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 41; Hocking, "Vanillin," September 1997, 1055–56; Symrise, "Our History - A Success Story - Symrise," accessed October 13, 2021.

¹² Koester, "Wilhelm Haarmann (1847 – 1931)," January 3, 2021.

¹³ Reimer helped Haarmann develop the eugenol based synthetic route. Tiemann helped reduce production costs

in 1891 by developing an iso-eugenol process. Koester, "Wilhelm Haarmann (1847 – 1931)," January 3, 2021. ¹⁴ Isoeugenol can be produced from eugenol. Hocking, "Vanillin," September 1997, 1056; USITC, *General Systems of Preferences*, September 2018, 181–85.

of waste sulfite from paper processing sites (i.e., paper mills), specifically the guaiacyl units.¹⁵ The processing of lignin became more efficient over the decades, so that by 1981, the Ontario Pulp and Paper company produced enough vanillin to supply 60 percent of the global market. Efforts to explore a variety of synthetic production pathways also led chemists to produce derivatives to enhance vanillin's desirable properties. This led to the production of ethyl vanillin, which has been used in vanilla flavoring since the 1930s (figure 1, right).¹⁶

The variety of sources for commercially produced vanillin, coupled with a growing flavor and fragrance industry, contributed to calls for regulation and the passage of the Pure Food and Drug Act in 1906. The legislation resulted in an official distinction between natural and artificial flavors.¹⁷ Since all flavoring agents, natural or artificial, are chemical compounds, denoting the difference between the two as chemical and non-chemical is not feasible. Today, the Food and Drug Administration (FDA) generally defines natural flavor as being isolated from naturals sources (i.e., plant or animal). By contrast, an artificial flavor is one that is not isolated from nature even if the flavor has the same chemical composition ("molecule") as its "non-chemical" counterpart.¹⁸ Despite there only being two types of flavoring designations (e.g., natural and artificial) there are three main categories of vanillin production, based on the source and the synthetic pathway used to the isolate the vanillin molecule: (1) natural, (2) chemical/synthetic, (3) biotechnological—also referred to as biosynthesis (figure 2).¹⁹ As figure 2 shows, "natural" vanillin can be derived not only from the vanilla plant but also from other natural sources such as corn, turmeric, and rice bran.²⁰ Despite its origin, 100 percent pure vanillin, whether natural or synthetic, will smell and taste the same since the isolated vanillin is structurally the same.²¹

¹⁵ A ligin is complex organic polymer that are deposited in the cell walls of many plants, contributes to rigidity and woodiness of plants. This commercialization was a joint venture from Salvo Chemical Corp. and Marathon Paper Mills Co. Today vanillin produced from lignin on a commercial scale is "chemically" derived. During the 1930's vanillin was also derived from coal tar. However as a result of studies reporting that consumption of flavors derived from "large" amount of coal can be carcinogenic, coal tar is not a widely used precursor in the U.S. Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 40; Hocking, "Vanillin," September 1997, 1057; Evolva, "Vanillin," accessed October 12, 2021.; Garfield, "Coal Is Used to Make a Surprising Everyday Ingredient in Food," May 8, 2016.

¹⁶ Ethyl vanillin is 2 to 4 times more flavorful than vanillin and does not occur in nature. Kennedy, "The Flavor Rundown: Natural vs. Artificial Flavors," September 21, 2015.

¹⁷ Vox Creative, "A Brief History of Making and Faking Flavor," accessed October 13, 2021.

¹⁸ Kennedy, "The Flavor Rundown: Natural vs. Artificial Flavors," September 21, 2015; Sethi, "The Bittersweet Story of Vanilla," April 3, 2017.

¹⁹ Arya et al., "Vanillin: A Review on the Therapeutic Prospects," September 2021, 417; Reineccius, "What Is the Difference between Artificial and Natural Flavors?," July 29, 2002.

²⁰ Industrial scale production of vanillin produced from lignin biosynthetically has been investigated but no commercially viable routes have been reported to date. Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 40–57.

²¹ All vanillin is structurally similar, and by consequence considered identical. But it should be noted that vanilla extract (imported under 1302.19.9140), is a mixture of different compounds (i.e., not just vanillin) and the vanillin used may not be 100 percent pure (eliciting different flavor profiles). The terminology that is applied to the different sources for vanilla extract are typically "pure" (natural) and "imitation" (synthetic). Sevier, "Is Real Vanilla Always Better," March 24, 2017.

Figure 2 The three pathways to isolate vanillin



Source: Compiled by USITC Staff.

Note: Both the source (substrate) and pathway to isolate the vanillin flavor need to meet "natural" standards. Simple extraction—sometimes referred to as soft chemistry—and bioconversions (e.g., fermentation) meet those qualifications so vanillin isolated via these routes meet natural standards. If a natural substrate is used, such as lignin sourced from a tree, but the vanillin is isolated using synthetic chemicals the isolated vanillin is considered artificial.

Vanillin Market Today

Although lignin was the primary source of synthetic vanillin for decades, by the 21st century, the primary source of synthetic vanillin was oil, specifically the guaiacol units derived from phenol.²² In 2019, one report estimates more than 85 percent (some say closer to 95 percent), of the global vanilla fragrance and flavor demand was met by petrol derived vanillin, and during this period at least five plants were producing vanillin from the guaiacol precursor.²³ The vanillin produced at these sites is sold to a variety of customers, ranging from flavor and fragrance companies to ice cream and chocolate manufacturers. As of 2020, the industry estimates that one percent or less of the global market demand is met by vanillin derived from natural vanilla beans.²⁴ Not surprisingly, synthetic vanillin commands a lower price on the market due to its wide availability. Synthetic vanillin can be priced as low as \$10 per kilo, while

²² Phenol is typically isolated as a white crystalline solid from coal tar. Structurally, phenol is a benzene ring bound to a hydroxy group. Fache, Boutevin, and Caillol, "Vanillin Production from Lignin and Its Use as a Renewable Chemical," January 4, 2016, 36.

²³ As of 2019 there were three plants in China (one a joint venture with an India-based company), one in France, and one in the U.S. Most of the remaining 15 percent of vanillin on the market is derived from lignin. Despite the dominance of synthetic vanilla, vanilla produced via natural extraction routes from the plant itself have not been completely displaced from the market and is largely sourced from Africa. Ciriminna et al., "Vanillin: The Case for Greener Production," May 2, 2019, 661; Green, "Solvay Increases Natural Vanillin Production," December 16, 2019. For information on U.S. imports of vanilla spice from Sub-Saharan Africa see USITC, *U.S. Trade and Investment with Sub-Saharan Africa*, March 2020, 86–87.

²⁴ Solvay, "Vanillin, Natural and on Trend," accessed September 30, 2021.

the price for vanillin produced from vanilla bean ranges from hundreds to even thousands of dollars per kilogram, depending on the harvest that year.²⁵

There are several companies, many multinational, that manufacture vanillin. Some examples are Camlin Fine Sciences Ltd. (CFS), Evolva, International Flavors and Fragrances (IFF), Solvay, and Symrise.²⁶ Vanillin is used by a variety of downstream industries ranging from food and fragrance to pharmaceuticals.²⁷ Although vanillin is produced in the United States, the United States is the largest importer of vanillin. U.S. imports for consumption of vanillin—which includes natural and synthetic—in 2019 (over 4,000 metric tons (MT)) represented 17 percent of the global vanillin market (figure 3).²⁸ Even in 2020, a time in which many supply chains suffered due to the ongoing COVID-19 pandemic, the United States imported over 3,000 MT (\$96 million) of vanillin—the number one source was China.²⁹ Despite less total trade of vanillin in 2020—U.S. domestic exports totaled almost \$800,000 (795 MT)—the value of vanillin trade grew over the preceding year. As a net importer the United States carried a significant trade deficit in vanillin by value, which totaled nearly \$95 million (2,600 MT), up 152 percent over 2019 (\$62 million, 3,350 MT).³⁰

²⁵ Bomgardner, "Following Many Routes to Naturally Derived Vanillin," February 10, 2014; Ciriminna et al., "Vanillin: The Case for Greener Production," May 2, 2019, 661–62; Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 41,46-47.

²⁶ In 2017 it was reported that CFS, a Chinese manufacturer, was the third largest vanillin producer globally. CFS supplies both vanillin and ethyl vanillin. Green, "Camil Fine Sciences Becomes," July 12, 2017.

²⁷ Arya et al., "Vanillin: A Review on the Therapeutic Prospects," September 2021, 416.

²⁸ The second largest importer in 2019 was India, which imported 2,000 MT—8 percent of global vanillin market.

²⁹ This is based only on the imports vanillin and estimates that the amount of vanillin on the market was 26,000 MT. Green, "Solvay Increases Natural Vanillin Production," December 16, 2019. IHS Markit, Global Trade Atlas database, HS 2912.41; USITC DataWeb/USDOC for HTSUS statistical reporting number 2912.41.0000. Also see Appendix A.

³⁰ Data reported for U.S. domestic exports by quantity are based on other countries individual imports of vanillin from the United States ("mirror data"). Global Trade Atlas database, HS 2912.41; USITC DataWeb/USDOC for HTSUS subheading 2912.41.





Due to the prevalence and accessibility of synthetic vanillin, the natural vanillin market was comparatively small and niche by the early 2000's. However, growing consumer demand for the natural products, including flavor and fragrances like vanillin, has pushed downstream users to want natural vanillin. Consequently, a number of flavor and fragrance companies have responded by developing and marketing vanillin produced via bioconversion of certain natural sources. Such microbial transformations of natural precursors are accepted as natural by both European and U.S. food legislators.³¹ Largely, companies have leaned towards using precursors (substrates) that hold Generally Recognized As Safe (GRAS) status.³² In the early 2000's, commercially scalable and viable biosynthetic routes for the production of natural vanilla were a small part of the industry, but the processes became more attractive due to concurrent years of poor vanilla bean harvests.³³ However, it was not until around 2009 that increased consumer demand for natural ingredients contributed to rapid growth and development in biosynthetic processes, such that some of the vanillin produced met natural standards and could be sold as such.³⁴ By 2015, several companies were marketing natural vanillin produced via biosynthesis pathways, including Evolva, De Monchy Aromatics, IFF, Mane, Solvay, and Symrise (figure 4).³⁵ Despite the increase, it is important to note that biosynthesized vanillin does not represent the

Source: USITC DataWeb/USDOC for HTSUS statistical reporting number 2912.41.0000. Underlying data is in Appendix A.

³¹ Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 42.

³² Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 42.

³³ Bomgardner, "Following Many Routes to Naturally Derived Vanillin," February 10, 2014; Ciriminna et al.,

[&]quot;Vanillin: The Case for Greener Production," May 2, 2019, 660–67.

³⁴ As noted in the previous section, vanillin derived from via biotechnical pathways are natural.

³⁵ These are just a representative examples of commercially established routes for the biosynthesis of vanillin by known producers, there are countless substrates and methods to isolate vanillin. Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 42; Braga, Guerreiro, and Belo, "Generation of Flavors and Fragrances Through Biotransformation and De Novo Synthesis," December 2018, 2218.

entire vanillin portfolio for any of these flavor and fragrance companies, although the biosynthesized vanillin market is expected to grow over the next several years.³⁶

Synthetic Pathway	Substrate	Relevant Chemical Structure in Substrate		
Extraction (natural)	Vanilla beans	HO		
Fermentation (bioconversion)	Ferulic acid (rice bran)	HO O O O O O O O O O HO		
Fermentation (soft chemistry or bioconversion)	Eugenol (clove)	HO		
Fermentation (bioconversion)	Curcumin (turmeric)			
Fermentation (<i>De novo</i> bioconversion)	Glucose (corn)			

Figure 4 Pathways used to produce natural vanillin via different substrates at commercial scale

Source: Adapted from Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 40–57. Note: Some biosynthetic pathways meet both EU and U.S. "natural" standards while others do not. *De novo* refers to the synthesis of substances from simple building block molecules (e.g., sugars, amino acids, etc.), which are subsequently metabolized to yield different and complex structures, which is why the vanillin structure is not immediately apparent when looking at the structure of glucose Bioconversions (also referred to as biotransformations) are single reactions that are catalyzed enzymatically to produce structurally similar molecules.

Conclusion

Vanillin is one of the oldest identifiable flavor and fragrance molecules, forming the foundation to the modern-day flavor and fragrance market. Changing customer preferences for natural products during the 21st century has driven an influx of innovation into this well-established industry—especially when coupled with the fact that vanilla bean harvests have been less reliable. However, despite a growing preference for natural vanillin, the vast majority of the market demand for vanillin is met by synthetic production routes, not biosynthetic, and most product is not natural. Synthetically produced vanillin will continue to represent the bulk of the market as long as it remains the most economically viable route.

³⁶ Gallage and Møller, "Vanillin–Bioconversion and Bioengineering," January 2015, 42; Symrise, "Creativity & Innovation – Scent - Symrise Vanilla," accessed October 13, 2021; Braga, Guerreiro, and Belo, "Generation of Flavors and Fragrances Through Biotransformation and De Novo Synthesis," December 2018, 2218; Luziatelli et al., "Maximizing the Efficiency of Vanillin Production by Biocatalyst Enhancement and Process Optimization," October 18, 2019, 279.

But sustained demand for cheaper, sustainable natural vanillin has allowed, and will continue to allow, the vanilla market to evolve.³⁷

³⁷ Kaur and Chakraborty, "Biotechnological and Molecular Approaches for Vanillin Production," February 2013, 1379.

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Appendix A U.S. Imports Data Tables

Country	2016	2017	2018	2019	2020	2021 (Jan–Aug)
China	31,192,858	28,582,692	38,751,626	34,855,130	47,475,028	39,773,974
Norway	4,205,888	4,301,931	7,346,227	8,492,970	22,225,360	13,780,676
Indonesia	4,587,901	5,434,353	7,778,206	11,060,834	11,906,174	9,554,708
France	1,032,956	2,119,870	4,217,895	6,661,823	8,186,025	6,313,178
India	49,268	568,783	1,139,508	1,896,074	2,545,208	1,388,664
Italy	-	-	448,523	260,794	1,405,120	952,837
Singapore	-	-	-	-	1,241,010	1,499,476
Germany	253,383	68,694	11,622	8,043	562,242	42,002
Canada	8,848	39,948	4,760	2,380	65,069	6,804
Dominican	52,624	85,841	88,106	22,809	15,495	2,425
Republic						
All Other	845,592	2,497,116	2,031,130	90,678	45,738	105,988
Total	42,229,318	43,699,228	61,817,603	63,351,535	95,672,469	73,420,732
			1			

 Table A.1 U.S. imports of vanillin 2016–2020, January–August 2021 (value, dollars); sorted full year

 2020

Source: USITC DataWeb/USDOC for HTSUS statistical reporting number 2912.41.0000.

Table A.2 U.S. imports of vanillin 2016–August 2021 ((quantity, metric tons)

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Country	2016	2017	2018	2019	2020	2021 (Jan–Aug)
China	2,563	2,168	2,719	2,652	2,249	1,744
Norway	339	336	568	644	620	385
Indonesia	444	570	734	838	218	198
France	13	57	52	112	194	158
India	5	60	113	161	103	85
Singapore	-	-	-	-	22	42
Germany	22	2	1	0	14	0
Italy	-	-	47	17	8	16
Canada	0	2	0	0	5	0
Israel	9	20	9	9	2	-
All Other	41	130	105	2	1	2
Total	3,436	3,345	4,348	4,434	3,437	2,630

Source: USITC DataWeb/USDOC for HTSUS statistical reporting number 2912.41.0000.

Table A.3 U.S. imports of	ethyl vanillin 2016–Augu	st 2021 (value, dollars)

		<u> </u>			
2016	2017	2018	2019	2020	2021 (Jan–Aug)
4,165,577	2,863,652	3,607,780	2,257,312	3,543,307	3,190,070
0	0	0	0	0	42,056
3,484,587	4,436,588	6,078,440	4,074,907	2,069,400	34,434
0	0	0	0	0	2,532
0	0	20,010	0	0	0
0	45,900	0	305,800	160,850	0
7,650,164	7,346,140	9,706,230	6,638,019	5,773,557	3,269,092
	4,165,577 0 3,484,587 0 0 0	4,165,577 2,863,652 0 0 3,484,587 4,436,588 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	4,165,577 2,863,652 3,607,780 0 0 0 3,484,587 4,436,588 6,078,440 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	4,165,577 2,863,652 3,607,780 2,257,312 0 0 0 0 0 3,484,587 4,436,588 6,078,440 4,074,907 0<	4,165,577 2,863,652 3,607,780 2,257,312 3,543,307 0

Source: USITC DataWeb/USDOC for HTSUS statistical reporting number 2912.42.0000.

Country	2016	2017	2018	2019	2020	2021 (Jan–Aug)
China	348	234	304	194	279	220
Norway	258	332	403	256	135	2
India	0	4	0	23	12	0
Ireland	0	0	1	0	0	0
Germany	0	0	0	0	0	0
Hong Kong	0	0	0	0	0	3
Total	606	569	708	473	426	225

Source: USITC DataWeb/USDOC for HTSUS statistical reporting number 2912.42.0000.