

Title: Uses of Vanilla in Perfumery:
Felix Buccellato President
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Many people have heard the phrase, "Plain Vanilla". The ubiquity of vanilla and vanilla flavored and fragranced products has created this common misconception!

A pair of astronomers from Johns Hopkins University, who previously believed that the color of the universe was green, announced that that was wrong. The real color is a pale beige, almost Vanilla White. Even astronomers think vanilla is white.1 (Discover Magazine, June 2003).

"White Vanilla", has often been referred to as "Plain Vanilla". There is nothing plain (or white) about vanilla. The vanilla beans start out as green and are dried to a dark chocolate brown.

How do we make the association that vanilla is white? It is most likely due to marketers of products like candles who think that vanilla should be white because vanilla ice cream is white. What may not be realized is that the dark brown vanilla flavor is added to the cold cream, sugar and other minor ingredients, kept frozen and in the dark. The product is now shielded from any light induced reactions which would normally cause the product to turn yellow, then brown. If we do that with a candle, it will also remain white.

Research: Earliest recorded use of vanilla,

Vanilla beans and their extracts were used by the ancient Aztec Totonaco Indians of Mexico. It was first recorded in 1520 by Bernal Diaz, one of Hernan Cortes officers. It was used to make a drink called chocolatl. It contained powdered cocoa beans, ground corn and flavored with tlilxochitl (ground black vanilla pods and honey).

As can be seen, vanilla was blended with chocolate and sweetened with honey to make a unique drink just like many of our "NEW" coffee emporiums of today.

I wonder why no one has tried to market this drink or concept. It certainly makes an interesting story and honey and chocolate are currently supposed to be good for you until we find otherwise again.

This probably made a very stimulating beverage that was used by the Aztec chiefs who drank as much as 50 cups per day. Not much different than our coffee consumption today? Starbucks Vanilla Mocha Frappuccino!

What is vanilla?

It is an extremely complex natural product containing more than 200 ingredients, (a number that grows every year). One of the major characterizing components is vanillin.

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The First Odor Threshold measurement on a Non-Human Primate (*Callitrichidae*) was done with a Computerized Olfactometer by D. Glasco, and colleagues Anthropological Institute, University Zurich. 2003?

He conducted 163 Trials resulting with 121 Correct responses at a level of 9.5×10^{-12}
Results from his testing is as follows:
Homo Sapiens = 11.8×10^{-14} M
Monkey *C. Pygmaica* 2.04×10^{-14} M = Mol

The nearly magical performance odor threshold for humans is 1.18×10^{-11}

This is approximately 100,000 parts per billion.

To put this in a perspective that can be more easily visualized, 1 part per million would be like looking for a Football in 6 football fields, 1 part per billion is like looking for a football in 6000 football fields.

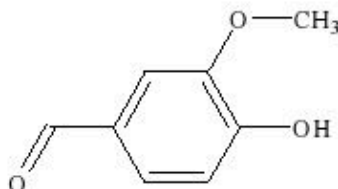
This number represents looking for a football in 600,000 football fields. All done with a sniff!
This is an incredibly low amount with a very low odor threshold. The fact that monkeys are five times more sensitive to vanillin than humans does not minimize the extraordinary detection level by Homo Sapiens.

The magic of vanilla or vanillin is that it is quite different in its effect on people. The odor is perceived as very pleasant, and it seems people cannot get quite enough of it. This may be due to its associated use with all things that contain sugar?

We have many products in the flavor and fragrance field with low odor thresholds. Vanillin differs in a very important way. Most ingredients with low odor thresholds like pyrazines, pyridines, thiols and various thiazoles, mercaptans and thiocsters possess a very pungent and negative odor at high concentrations. Vanillin can be smelled and appreciated at extremely high levels and never loses its appealing aroma. There are very few items that fall in this category.

Vanillin

$C_8H_8O_3$ FW: 152.15



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Vanillin

C

8

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3

FW: 152.15

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Vanillin became available as a synthetic ingredient in 1874 in a process developed by Ferdinand Tiemann and Wilhelm Harmann (Haarmann & Reimer) now Symrise in Holzminden Germany. (Tiemann - Reimer reaction)

We can see by the structure that this is vanillin. How do we know? The first clue is in the name: Vanillin. It is a multifunctional aromatic with extraordinary olfactory properties. Extremely diffusive and extremely long lasting. This is the magic of flavor and fragrances.

Of course, all Flavorists and Perfumers realize that not only are vanilla beans and all their extracts brown, but vanillin a major component, in a bit of twisted irony is a pale white crystal. It is however, highly color unstable and likes to turn everything that it is put into back to its original color brown! There are a few smart marketers, some of which we have coached, who put out a great vanilla fragrance in brown products.

The concept or belief that white is the color of vanilla has been a thorn in the side of the fragrance business ever since. Many products introduced through marketers have suffered with this misconception. While trying to tie in the image of vanilla with a marketed product, marketers want the "white" of vanilla to be the marketing impression. Vanilla does not want to be white, it wants to be brown!

Too many products have settled for a ghost of vanilla aroma or flavor in white color products which do not turn brown or speckle creating a mottled or spoiled image in a product. It is important to note that the product or flavor or fragrance is not spoiled, it is just the image that is spoiled. Be that as it may, image does count in the real world.

It is somewhat common knowledge of how vanilla is used in flavors but how is vanilla used in fragrances? Many of you may know that materials used and their formulas and information about them are considered to be trade secret information of the company that create them and perfumers.

Out of a database of 10,000 fragrances, 50 % of fragrances use vanilla in some amount. We will examine some of the types and how they are used.

Vanilla in its various forms use range from 10-20%

Other types include whipped cream, marshmallow, sugar cookies, coconut and baby powders or powder types. These all use vanilla in significant percentages and are part of the main character and theme.

Oriental Fragrances: - What are they? They are often a combination of vanilla, balsamic resins like olibanum (frankincense), balsam tolu, benzoin and musks which can be blended in an infinite number of ways. They have been described, (not always correctly) as Sweet, Spicy, Fruity, Animalic. The descriptor of sweet is a gustatory or taste description and does not directly apply to odor. In odor when the word "sweet" is used as an inability to attach the characterizing description like Apple sweet, or strawberry sweet or caramel sweet.

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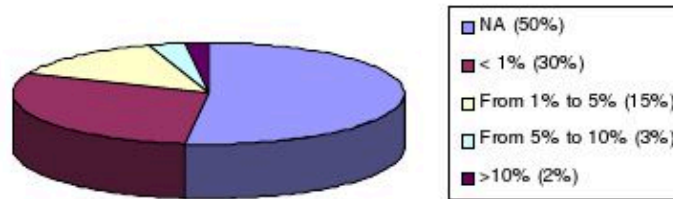
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What is sweet? It is a property of sugar(s) or other artificial sweeteners and is a property of a flavor. It certainly is not sugar in odor. Pure sugar has no real discernible odor. The sweet that many people refer to in odor generally comes from association of the aroma and sugar. The odor of vanilla or vanillin that is mixed with other characters is invariably described as "sweet" due to the association with the familiar sweetened and flavored products like ice cream and cakes.

Oriental often incorporate an accord referred to as amber. This is not the amber from wood products that you may be familiar with from Jurassic Park. It is a perfumery accord using Vanilla, Olibanum, Balsamic Resins, and citrus to varying degrees. They are often added as a complex or a foundation to an oriental fragrance.

One of the most famous fragrances that is based somewhat on vanilla is a beautiful oriental blend called Shalimar. It has a foundation of vanilla, benzoin, topped off with bergamot and citrus notes with traces of many modifiers. The signature however, is the beautiful and extremely long lasting and diffusive vanilla character.

PIE CHART - PERCENTAGE OF FRAGRANCES USING VANILLA NOTES



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NA (50%)

< 1% (30%)

From 1% to 5% (15%)

From 5% to 10% (3%)

>10% (2%)

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UUUUU

I have listed other examples Table I and Table II where Vanilla is a significant percentage and odor character.

Table I Women's Orientals

Name of Fragrance	By	Year	Materials used
Emeraude	Coty	1921	Vanilla, Florals, Musks
Shalimar	Guerlain	1925	Vanilla, Benzoin, Bergamot
Youth Dew	Lauder	1952	Vanilla, Balsams, Spices
Opium	St. Laurent	1977	Vanilla, Citrus, Spices
Obsession	Calvin Klein	1985	Vanilla, Patchouli, Resins, Citrus, Musks
Mademoiselle Coco	Chanel	2002	Vanilla, Oakmoss, Florals, Amber

Table II Mens Orientals

Name of Fragrance	By	Year	Materials used
Fougere Royal	Houbigant	1882	Vanilla, Oakmoss, Lavender
Canoe	Dana	1935	Vanilla, Oakmoss, Bergamot, Lavender
Brut	Faberge	1964	Vanilla, Oakmoss, Lavender, Patchouli
Paco Rabanne	Paco Rabanne	1973	Vanilla, Lavender, Oakmoss, Citrus
Obsession	Calvin Klein	1986	Vanilla, Patchouli, Citrus, Musk
Canoe II	New Dana	2001	Vanilla, Patchouli, Oakmoss, Musk

Nordstrom fragrance flyer September 23, 2003

Burberry Brit	2003	Icy Pear with base of amber & Vanilla Bean
Joy by Jean Patou	2003	Bergamot, roses, jasmine and Vanilla

New Vanilla Fragrances 2007

Lovely Sarah Jessica Parker	2005	Paper whites, Musk & Amber (contains Vanilla)
Princess by Vera Wang	2006	Water Lily, Apricot and Chiffon Vanilla
Midnight Fantasy Britney Spears	2007	Vanilla Amber Musk

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Obsession Calvin Klein 1985 Vanilla, Patchouli, Resins, Citrus, Musks
Mademoiselle Coco**

**Chanel 2002 Vanilla, Oakmoss, Florals, Amber
Table II Mens Orientals Name of Fragrance By Year
Materials used
Fougere Royal Houbigant 1882 Vanilla, Oakmoss, Lavender
Canoe Dana 1935 Vanilla, Oakmoss, Bergamot, Lavender
Brut Faberge 1964 Vanilla, Oakmoss, Lavender, Patchouli
Paco Rabanne Paco Rabanne 1973 Vanilla, Lavender, Oakmoss, Citrus
Obsession Calvin Klein 1986 Vanilla, Patchouli, Citrus, Musk
Canoe II New Dana 2001 Vanilla, Patchouli, Oakmoss, Musk
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Bean Joy by Jean Patou 2003 Bergamot, roses, jasmine and Vanilla
New Vanilla Fragrances 2007
Lovely Sarah Jessica 2005 Paper whites, Musk & Amber (contains Vanilla)
Parker Princess by Vera Wang 2006 Water Lily, Apricot and Chiffon
Vanilla Midnight Fantasy 2007 Vanilla Amber Musk
Britney Spears**

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If 50% of fragrances use vanilla or vanillin, or ethyl vanillin, which fragrances DO NOT use vanillin. The most glaring reason for non-use is stability and color requirements.

However there are several important fragrances that do not use vanilla because the accord or intended image is one that does not require any of the "sweet" character of vanillin. We have listed a few examples along with descriptions of their odor character.

Table III
Women's Fragrances without vanilla or vanilla components.

Fragrance	By	Year	Materials used
Muguet de Bois	Coty	1936	Bergamot, Citrus, Lily, Cyclamen
L'air du Temps	Ricci	1947	Bergamot, Rose, Lily, Muguet
Chanel 19	Chanel	1971	Bergamot, Rose, Woods, Muguet
Lauren	Cosmair	1978	Citrus, Ylang, Lily, Mandarin, Tropical fruits & flowers. mimosa, Orange Flower
Calyx	Prescriptives	1986	Lily, Mandarin, Tropical Fruits & Flowers

Mens Fragrances without vanilla or vanilla components

Fragrance	By	Year	Materials used
Imperiale	Guerlain	1850	Citrus, Bergamot, Mandarin, Lemon, Verbena, Cedarwood
Aqua Velva Ice Blue	Williams Hispania	1935	Bergamot, Lemon, Petitgrain, Lavender, Mint, Spices, Sage, Rose
Eau Sauvage	Dior	1966	Jasmin, Bergamot, Citrus, Herbal
Eau d'Hadrien	Annick Goutal Reintroduced	1980 1995	Citrus, Bergamot, Cypress
Eau de Cologne Extra Fine	L'Occitane	1990	Citrus, Bergamot, Petitgrain, Neroli, Woods
CK one	Calvin Klein	1994	Citrus, Jasmin, Woods

What are the problems with Vanilla? In a word, SOLUBILITY!

There are many mediums in which vanilla extract, an alcohol and water based DARK BROWN material is difficult or impossible to use. While the flavor industry has an exemption on shipments containing alcohol, the fragrance industry has no such exemption.

We are increasingly faced with customers who are unwilling to ship, receive, handle or pay for increased hazards due to flammability.

Vanilla Absolute is a very expensive and color problematic way to use vanilla and an expensive way to introduce vanillin and has lost all the top notes that are normally present in an alcoholic solution of vanilla.

Vanilla beans extracted into Propylene Glycol addresses the flammability issue but does little to reduce the solubility problems where a highly lipophilic system is needed. Color for many

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Calyx

Prescriptives 1986 Lily, Mandarin, Tropical Fruits & Flowers
Mens Fragrances without vanilla or vanilla components
Fragrance By Year Materials used
Imperiale

Guerlain 1850 Citrus, Bergamot, Mandarin, Lemon,

Verbena, Cedarwood
Aqua Velva Ice

Blue

Williams

1935 Bergamot, Lemon, Petitgrain, Hispania

Lavender, Mint, Spices, Sage, Rose

Eau Sauvage Dior 1966 Jasmin, Bergamot, Citrus, Herbal
Eau d'Hadrien

Annick Goutal

1980 Citrus, Bergamot, Cypress
Reintroduced

1995 Eau de Cologne

L'Occitane 1990 Citrus, Bergamot, Petitgrain, Neroli, Extra

Fine

Woods CK one Calvin Klein 1994

Citrus, Jasmin, Woods
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applications is often a requirement for many products like candles and any wax based or silicon based system. There are also air freshener devices and systems where any hydrophilic glycols or carriers are extremely undesirable. This is also true for certain lipophilic encapsulation procedures.

What can be done? Alternatives would be to extract vanilla beans with less polar materials. Alternatives might include types of esters or salicylates that are used in the flavor themselves or that can be used in the potential systems. The negative side of this is that Vanillin, a highly polar material will not be extracted in the same way as it would be in alcohol / water system. The resultant material will be application specific, not a real article of commerce or meant as a replacement for Vanilla extract of any kind. This would create an opportunity for vanilla to be used in new ways that do not currently exist. If vanillin is needed, it is always available to bolster the body without color problems.

Up to this point, the problem has been solved by using vanillin. I would be one of the few to espouse the view that Vanillin is NOT the same as Vanilla. I believe there is an opportunity to develop new types of extracts on Vanilla beans that would expand the use of vanilla as well as encourage growers to have a wider and expanding use of vanilla that may prove to stabilize an already volatile product.

The real beauty of vanilla lies in its extreme complexity. It is not due merely to vanillin or percentage content of vanillin. If this were true, we could replace vanilla with synthetic vanillin in a suitable solvent or diluent. There are a wide variety of functional groups and molecules that make vanilla such a wonderful material. While little attention has been paid to the sesquiterpene and hydrocarbon section of vanilla, it is this authors view that the sesquiterpene and unsaturated hydrocarbon section plays an extremely important part in the longevity and natural warm woody aroma that is intrinsic to a good quality vanilla.

What are the elements of Vanilla Bean Extract?

It is NOT solely the character of vanillin. While vanillin is certainly important, it is not the only character contributing component. Describing the character of vanillin is like trying to describe the character of orange. Orange is orange and vanillin is vanilla... Almost.

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ODOR ELEMENTS OF VANILLA

Vanilla	Fruity	Caramel/ Cooked	Woody	Spicy	Hydrocarbons
Vanillin	Ethyl Esters	Diacyl	Sesquiterpenes	Phenols	49
	Other esters	Hydroxy Ketones	Lactones	Substituted Phenols	10 Important
		Cyclic compounds			Including
		Lactones			Sesquiterpenes

CHEMICAL CLASSES ISOLATED FROM VANILLA EXTRACT [More than 300 components identified]

1	2	3	4	5	6	7	8	9	10	11	12	13
Alcohol	Aldehyde	Ketone	Acid	Ester	Lactone	Bases	Sulfur	Acetals	Ethers	Phenol	Furan	Epoxide
28	14	16	22	48	5	4	2	4	5	12	10	2
Includes sesqui terpene alcohol	Includes Vanillin	Butane dione	Few are key	Key Me Phen Acetate	Gamma Lactones	Me Nico tinate	Thio phene	From EtOH Rxn	Van Ethyl Ether EtOH Rxn	Very Key Ingred. p cresol	5 methyl furfural	Viti spirane

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ODOR ELEMENTS OF VANILLA

Vanilla Fruity Caramel / Cooked Woody Spicy Hydrocarbons Vanillin

Ethyl Esters Diacyl Sesquiterpenes Phenols 49 Other esters

Hydroxy Lactones Substituted Phenols 10 Important Ketones Cyclic compounds

Including Lactones Sesquiterpenes

CHEMICAL CLASSES ISOLATED FROM VANILLA EXTRACT [More than 300 components identified]

1 2 3 4 5 6 7 8 9 10 11 12 13 Alcohol

Aldehyde Ketone Acid Ester Lactone Bases Sulfur Acetals Ethers Phenol
Furan Epoxide 28 14 16 22 48 5 4 2 4 5 12 10 2 Includes

Includes**Butane**

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The problem of adulteration of vanilla with vanillin and a few other components has always plagued the vanilla market and the pricing. After 35 years of work and study of natural products I do not believe that we are yet able to do a better job than nature.

There is really nothing like the pure unadulterated vanilla extract or various folded and concentrated vanilla extracts available. It is always a shame to when users try to stretch the use and performance of vanilla with the adulteration of vanillin or mixtures to make an economic price point or performance point. When this happens, it affects the overall market by introducing unfair competitive pricing which can drive honest growers and manufacturers of vanilla extracts to their breaking points or at worst put them out of business permanently. The supply is then cut, the prices go up and the demand for good quality extracts goes down, thus creating a spiral downwards in supply and upwards in pricing of good quality material.

We have seen this happen in a variety of other natural products. The most striking examples are cinnamon bark oil, supplanted or replaced by cinnamic aldehyde or Bitter Almond oil replaced by Benzaldehyde. Our world would be much worse off without the quality of real vanillin in our daily lives.

Lastly, I hope the continued EU regulations don't prevent or eliminate use of natural products due to very weak contact allergens.

References:

1. Discover Magazine, June 2003.

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