

# Natural Vanilla in America and Flavor Chemistry

**DANISCO**

First you add knowledge...



Krishna Bala, Ph.D.

Danisco

# Ever Popular Vanilla

- Whether sweet or savory, simple or complex, vanilla complements and enhances a wide variety of products
- Crackers and Cookies
- Colas and candy
- Cakes and icing
- Syrups and sauces
- Ice cream and Irish cream
- Soy milk and flavored milk



# Vanilla is the Magic Bullet of Flavors

- Characterizing flavor – vanilla ice cream
- Flavor enhancer – frozen desert, baked goods, syrups, puddings
- Rounds out bitter notes – chocolates
- Increases fruitiness – strawberry and other fruit flavors by softening tartness
- Enhances the perception of sweetness in baked goods




# Vanilla Extract Standard

- Vanilla is the only Flavor in America that has a standard of Identity
- Code of federal regulations 169.175: Vanilla extract is the solution in aqueous ethyl alcohol of the sapid and odorous principles extractable from vanilla beans.

# Vanilla Beans Standard

- CFR 169.3 is very specific about the vanilla beans
- Vanilla beans mean the properly cured and dried fruit pods of *vanilla planifolia* Andrews and *vanilla tahitensis* Moore
- “Unit weight of vanilla beans” means 283.85 grams of moisture free vanilla beans

# Vanilla Extract

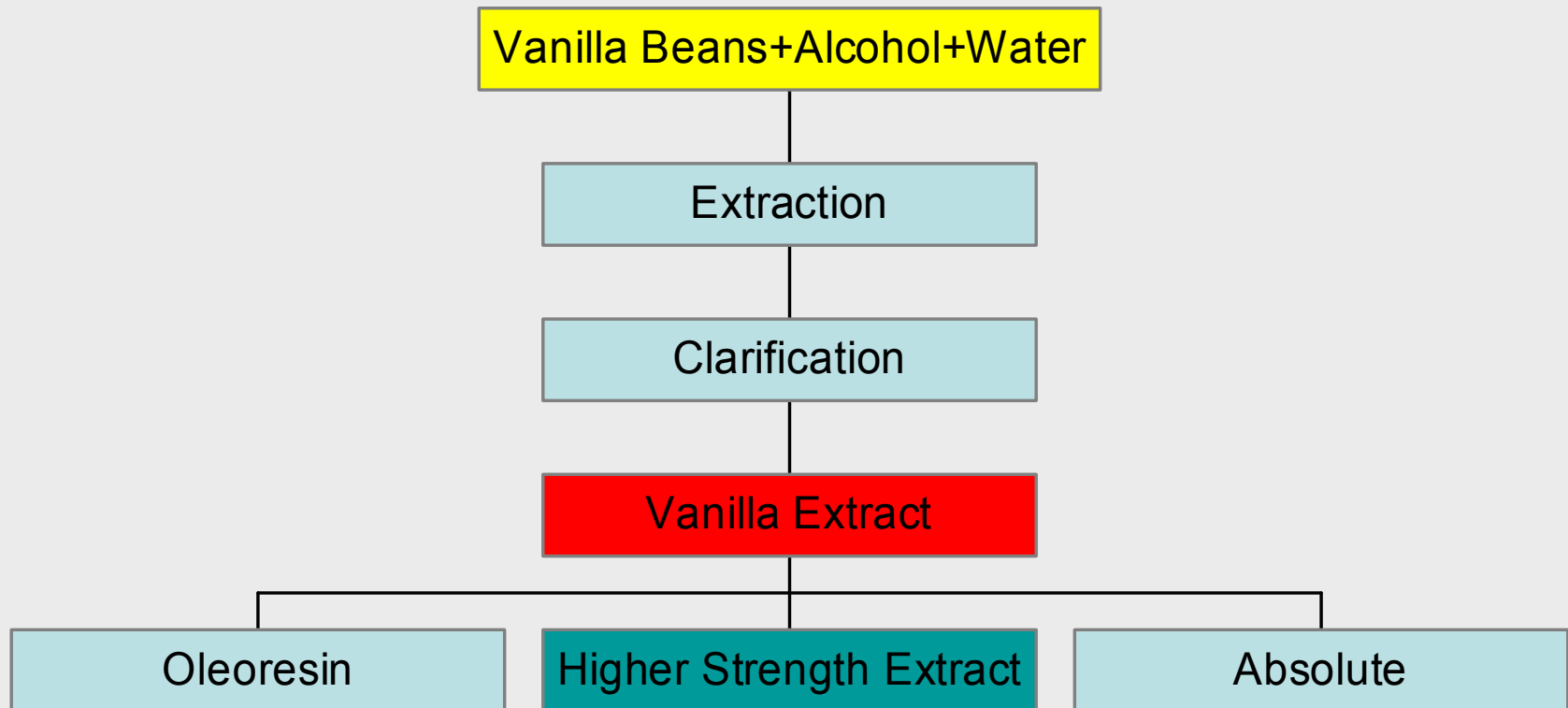


Vanilla extract is the solution in aqueous ethyl alcohol of the total sapid and odorous principles, extractable from vanilla beans. In vanilla extract the content of ethyl alcohol is not less 35 percent absolute by volume. Vanilla extract may contain one or more optional ingredients: Glycerin, Propylene Glycol, Sugar (as defined in 21 CFR 170.3 (41), Invert Sugar, Dextrose, Corn Syrup (including dry corn syrup)

# Fold Strength

- Fold is the number of units of vanilla constituent per gallon
- Single fold vanilla extract is made from 75 grams of moisture free vanilla beans per 1000 milliliters
- Three fold vanilla extract is made from 225 grams of moisture free vanilla beans per 1000 milliliters
- By removing the solvent, vanilla extracts can be concentrated to 10 fold, 20 fold etc.

# Vanilla Bean to Flavor



# Types of Vanillas

- Natural Vanilla Extract, Minimum 35% ethyl alcohol.
- Natural Vanilla Flavor, less than 35% alcohol, or no alcohol.
- Natural Vanilla Powder
- Natural Vanilla Vanillin Extract
- Natural Vanilla Vanillin Flavor
- Natural Vanilla Vanillin Powder
- Natural Concentrated Vanilla Extract 10 fold to 20 fold
- Natural Concentrated Vanilla Flavor 10 fold to 20 fold
- Natural & Artificial Vanilla Flavor
- Natural & Artificial Vanilla Powder
- Artificial Vanilla Flavor
- Artificial Vanilla Powder
- Nature Identical Vanilla Flavor
- Nature Identical Vanilla Powder
- Single Fold Organic Vanilla Extract
- Three Fold Organic Vanilla Extract
- 20 Fold Organic Vanilla Oleoresin
- “Natural flavor” : Natural vanilla and other natural flavor ingredients

# Does every one make the same?

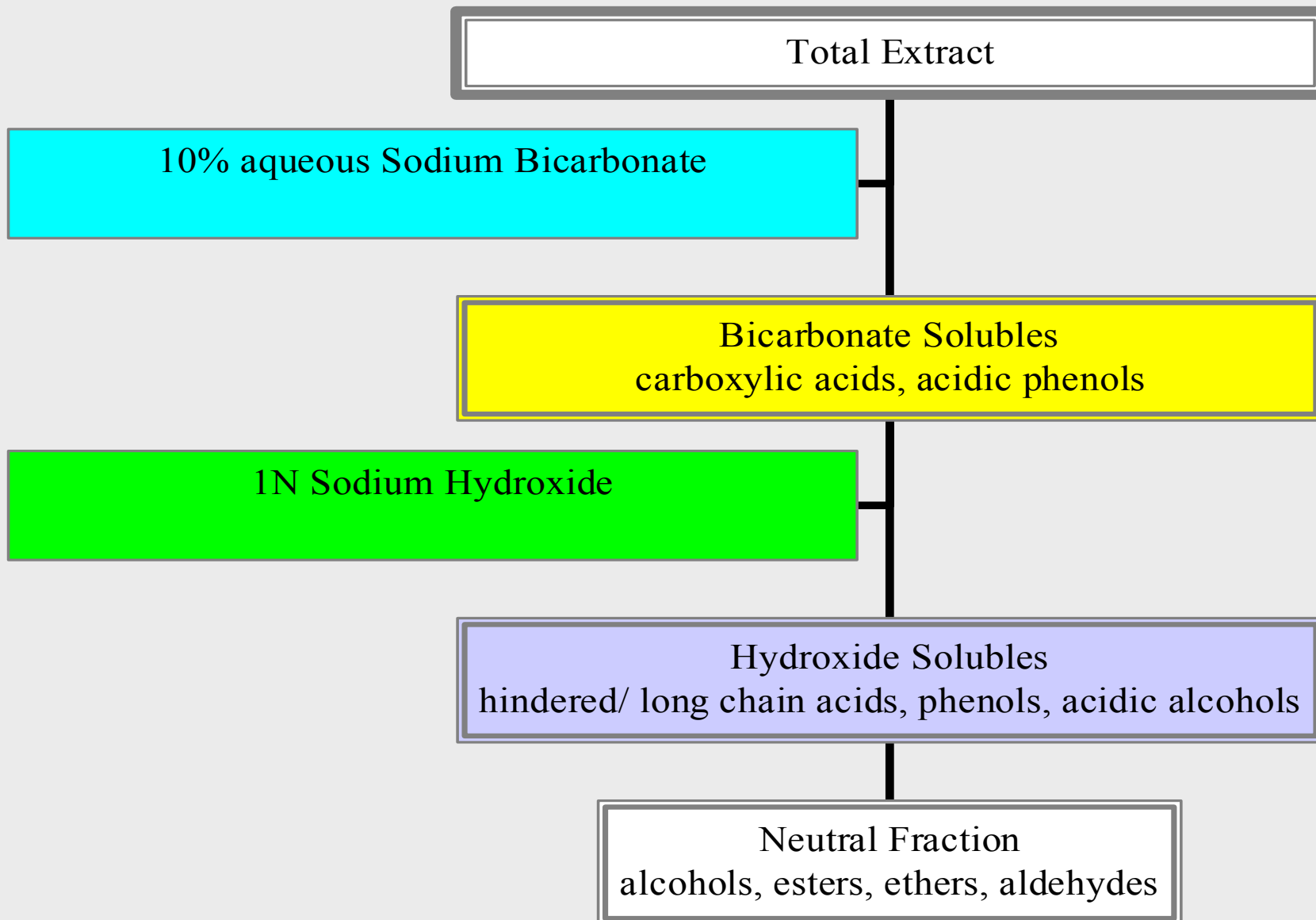
The ingredients used in making vanilla extracts are controlled by Food and Drug Administration, but not the processing conditions or the equipment. Flavor companies use different alcohol/water ratios, temperature, time and equipment to make their own unique vanilla extracts.

# Vanilla is Anything but Plain

- 250 flavor compounds make Vanilla, one of the most complex flavors
- Vanillin is the predominant flavor compound
- Other flavor compounds like Guaiacol & Anisic Aldehyde are also important since they are 100 to 10,000 times stronger than vanillin
- Danisco we identified 146 flavor compounds

# 3 Fold Natural Vanilla Extract

## Extraction Scheme



# GC-MS Conditions

- GC-MS: used for the identification and quantification of key compounds
- Hewlett Packard 5890 with GC-MS interface
- Column: J & W DB-5ms 30M X 0.25 mm 0.5 um film
- 50C initial, hold 5 minutes, 6C/minute to 230C hold 25 minutes
- Injector 250C, Transfer line 280C, 50:1 split ratio



- a) Total methylene chloride extract, b) Acid fraction soluble in bicarbonate Solution  
 c) Phenolic fraction soluble in NaOH  
 d) Neutral fraction

Compounds	Bourbon				Indonesian			
	a	b	c	d	a	b	c	d
2-methyl-2-butanol	0	0	0	0	0.03	0	0.04	0
2-methylbutyraldehyde	0	0	0	0	0.02	0	0	0
3-methyl-3-buten-2-one	0	0	0	1.18	0.09	0	1.18	1.93
3-penten-2-ol	0.04	0	0.22	2.85	0.44	0	0	3.47
valeraldehyde	0	0	0	0	0.04	0	0.07	0.16
acetal	0.26	0	0	2.17	3.35	0	0	11.49
4-methyl-2-pentanone	0	0	0	0	0.03	0	0	0
2-methyl-2-butenal	0	0	0	0	0	0	0.09	0
n-amyl alcohol	0	0	0	0	0.1	0	0.08	0.35
3-methyl-2-buten-1-ol	0	0	0.01	0	0	0	0.3	0
ethyl butyrate	0	0	0	0.58	0	0	0	0
hexanal	0.04	0	trace	0.68	0.36	0	0.24	1.39
ethyl lactate	0.1	0	0	0	0.21	0	0	0
furfural	0.32	0	0	5.08	0.11	0	0	0.32
2-methylpentanoic acid	0	0	0	0	0.07	0	0	0
n-butyraldehyde diethyl acetal	0.02	0	0	0.07	0	0	0	0
isobutyraldehyde diethyl acetal	0	0	0	0	0.04	0	0	0.09
n-hexanol	0	.	0	0	0.03	0	0	0.13
valeric acid	0	0	0	0	0.11	0.36	0.05	0
2-heptanone	0	0	trace	0	0.03	0	0.11	0
dihydro-2(3H)-furanone	0	0	0	0	0.07	0	0.09	0
isovaleraldehyde diethyl acetal	0.02	0	0	0.25	0.11	0	0	0.19

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 c) Phenolic fraction soluble in NaOH  
 d) Neutral fraction

Compounds	Bourbon				Indonesian			
	a	b	c	d	a	b	c	d
5-methylfurfural	0.04	0	0	0.23	0.06	0	0	0
caproic acid	0.03	0.26	0	0	2.71	40.4	0.46	0
benzaldehyde	0.14	0	0	0	0	0	0	0
1-octen-3-ol	0	0	0	0.24	0	0	0	0.47
valeraldehyde diethyl acetal	0	0	0	0.05	0.07	0	0	0.18
ethyl caproate	0.04	0	0	0.18	0.21	0	0	1.11
octanal	0	0	0.02	0.59	0.07	0	0.27	0.59
1H-pyrrole-2-carboxaldehyde	0.01	0	0	0	0.06	0	0	0.09
furfuryl alcohol	0.04	0	0	0	0.15	0	0	0
p-cymene	0	0	trace	0	0	0	0	0
d-limonene	0	0	0.04	0	0	0	0.04	0
benzyl alcohol	0.22	0	0	2.06	0.13	0	0.07	0.38
gamma-hexalactone	0	0	0	0	0.07	0	0	0
gamma-terpinene	0	0	0.01	0	0	0	0	0
heptanoic acid	0	0.03	0	0	0.29	3.45	0.1	0
1-octanol	0	0	0.03	0	0.06	0	0.23	0.78
p-cresol	0.15	0	0.04	0	0.09	0	0.15	0
hexanal diethyl acetal	0.06	0	0	0.79	0.32	0	0.35	0.94
valeraldehyde propylene glycol a	0	0	0	0	0.06	0	0	0.26
ethyl heptanoate	0	0	0	0.18	0	0	0	0

- 2001 a) Total methylene chloride extract, b) Acid fraction soluble in bicarbonate solution  
 c) Phenolic fraction soluble in NaOH  
 d) Neutral fraction

Compounds	a	b	c	d	a	b	c	d
guaiacol	2	0.02	0.28	0	1.87	1.36	0.84	0
linalool	0	0	0.03	0	0	0	0	0
4-methoxyphenol	0.04	0	0	0	0	0	0	0
trans-carveol	0.1	0	0	0	0	0	0	0
phenyl ethanol	0.1	0	0	0.78	0.05	0	0	0.16
veratrole	0	0	0	0	0.07	0	0	0.21
caprylic acid	0.27	0.18	0	0	0.47	5.85	0.28	0
3-ethyl phenol	0	0	0	0	0.05	0	0.06	0
diethyl succinate	0	0	0	0	0.26	0	0	0
ethyl benzoate	0	0	0	0	0.01	0	0	0
3-methyl-1H-pyrazole	0	0	0	0	0.11	0	0	0
1,4-dimethoxybenzene	0.36	0	0	0	0.3	0	0	0
2-octenoic acid	0	0	0	0	0	2.42	0	0
alpha-terpineol	0	0.01	0	0	0	0	0.1	0
methyl salicylate	0.15	0	0	0.29	0.02	0	0	0
4-methyl benzaldehyde	0	0	0	0	0.24	0	0	0
2,3-dihydrobenzofuran	0.87	0	0	0	0	0	0	0
5-(hydroxymethyl)furfural	0	0	0	0	0.11	0	0	0
3-ethyl-4-methyl-(1H)-pyrrole-2,5-	0.16	0	0	0	0.05	0	0	0
3,4-dimethoxytoluene	0	0	0	0	0.07	0	0	0.24
hydrocinnamyl alcohol	0.03	0	0	0.24	0	0	0	0.07

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 d) Neutral fraction

Compounds	Bourbon				Indonesian			
	a	b	c	d	a	b	c	d
hydrocinnamyl alcohol	0.03	0	0	0.24	0	0	0	0.07
3-methyl benzoic acid	0	0	0	0	0.16	0.58	0	0
phenylacetic acid	0	0	0	0	0	1.77	0.12	0
nonanoic acid	0.53	0.28	0	0	0.15	0	0	0.38
p-anisaldehyde	0.2	0	0	1.11	0	0	0	0
cinnamaldehyde	0.04	0	0	0.17	0	0	0	0
p-anisyl alcohol	0.86	0	0	5.78	0.12	0	0.02	0.42
4-methoxy-2-methyl phenol	0.59	0	0.01	0	0	0	0.06	0
2,3-dihydro-1H-inden-1-one	0	0	0	0	0	0	0	0
4-hydroxybenzyl methyl ether	0.02	0	0	0	0.1	0	0	0
1,2,3-trimethoxybenzene	0	0	0	0	0.17	0	0	0.57
cinnamyl alcohol	0.1	0	0	1.05	0	0	0	0
1,4-benzenediol	0	0	0.01	0	0	0	0	0
phenylpropanoic acid	0	0	0	0	0	0.31	0	0
decanoic acid	0	0.04	0	0	0	0	0.28	0
2,6-dimethoxyphenol	0.22	0	0	0	0.49	0.94	0	0
eugenol	0.05	0	0	0	0.54	0	0	1.4
gamma-nonalactone	0	0	0	0.62	0	0	0	0.35
4-ethoxy-2-methylphenol	22.75	trace	2.71	0	5.1	0	9.69	0
p-hydroxybenzaldehyde	0	2.46	0	0	2.14	2	0	0
methyl p-anisate	0	0	0	0.73	0	0	0	0

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 d) Neutral fraction

Compounds	Bourbon				Indonesian			
	a	b	c	d	a	b	c	d
<b>methyl cinnamate</b>	<b>0.87</b>	<b>0</b>	<b>0</b>	<b>7.94</b>	<b>0.13</b>	<b>0</b>	<b>0</b>	<b>0.2</b>
2-methoxy-1,4-benzenediol	0	0	0	0	0	0	0	0
eugenyl methyl ether	0	0	0	0	0.13	0	0	0.2
p-anisic acid	0	0	0	0	0	1.36	0	0
cinnamic acid	0	2.01	0	0	0.48	3.24	0	0
methyl 4-hydroxybenzoate	0	0	0	0	0.24	0	0	0
<b>vanillin</b>	<b>34.72</b>	<b>92.86</b>	<b>90.08</b>	<b>3.1</b>	<b>29.7</b>	<b>0</b>	<b>33.19</b>	<b>0.23</b>
vanillyl alcohol	0	0	0	0	0.33	0	0	0
3-methoxy-4-hydroxyphenyl acet	5.5	0	1.88	0	2.01	0	0.65	0
acetovanillone	1.31	0	0.51	0	0.73	0	0	0
isoeugenyl acetate	0	0	0	0	0.26	0	0	0
lauric acid	0	0.36	0	1.16	0	0	0	0
2-methyl-4,5-dimethoxyphenol	0	0	0	0	0.47	2.55	2.12	1.45
vanillic acid	0	0	0	0	0.98	0		0
5,6,7,7a-tetrahydro-2(4H)-benzof	0	0	0	1.27	0	1.44	0	0
2-methyl-1,1'-biphenyl	0	0	0	0	0.32	0	0	0.1
5,6-dihydro-7,12-dimethyl-benz[a	0	0	0	0	0.2	0	0	0
3-methyl phenol	0	0	0	0.89	0	0	0	0
4-methyldibenzofuran	0	0	0	0	0	0	0	0
<b>syringaldehyde</b>	<b>2.64</b>	<b>0.04</b>	<b>0.15</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>
1,1'-bis(p-tolyl)ethane	0	0	0	0	0.62	0	0	0
2,3,4-trimethoxyacetophenone	0	0	0	0	0.32	0	0	0
acetosyringone	0	0	0	0	0	0	0	0.38
myristic acid	0	0.05	0	0	0.65	0	0.06	0
2-methoxy-4-ethyl-6-methylphen	0	0	0	0	0.88	0.8	0.83	0.39
9H-fluoren-9-one	0	0	0	0	0	0	0	0
octacosane	0	0	0	0	0.15	0	0	0.44
1H-indole-3-carboxaldehyde	0.63	0	0	0.12	0	0	0	0.84
pentadecanoic acid	0	0	0	0	0.18	0	0	0
palmitic acid	0.77	0	0	0	0.66	0	0.35	0
ethyl palmitate	0.11	0	0	0.73	1.89	0.12	1.08	0

- a) Total methylene chloride extract, b) Acid fraction soluble in bicarbonate solution  
 c) Phenolic fraction soluble in NaOH  
 d) Neutral fraction


	Bourbon					Indonesian			
Compounds	a	b	c	d		a	b	c	d
ethyl palmitate	0.11	0	0	0.73		1.89	0.12	1.08	0
2-allyl-7-methylbenzo [b] thiophe	0	0	0	0		0.18	0.33	0	0
4,4'-methylenebisphenol	0.94	0	0.03	0		0	0	0	0
9,12-octadecadienoic acid (Z,Z) (	0.07	0	0	0		0.3	0	0	0
ethyl linoleate	0	0	0	0.77		5.52	0	3.01	0
2-methoxy-6-(3',5'-dimethoxy p	0	0	0	0		0.58	0.67	0	0
3,3'dimethoxy [1,1'-biphenyl]-4,4'	0.26	0	0	0		0	0	0	0
trans-1-(3-methyl-1-naphthyl)-2-(	1.3	0	0	0		0	0	0	3.73

# Flavor Compounds in Vanilla

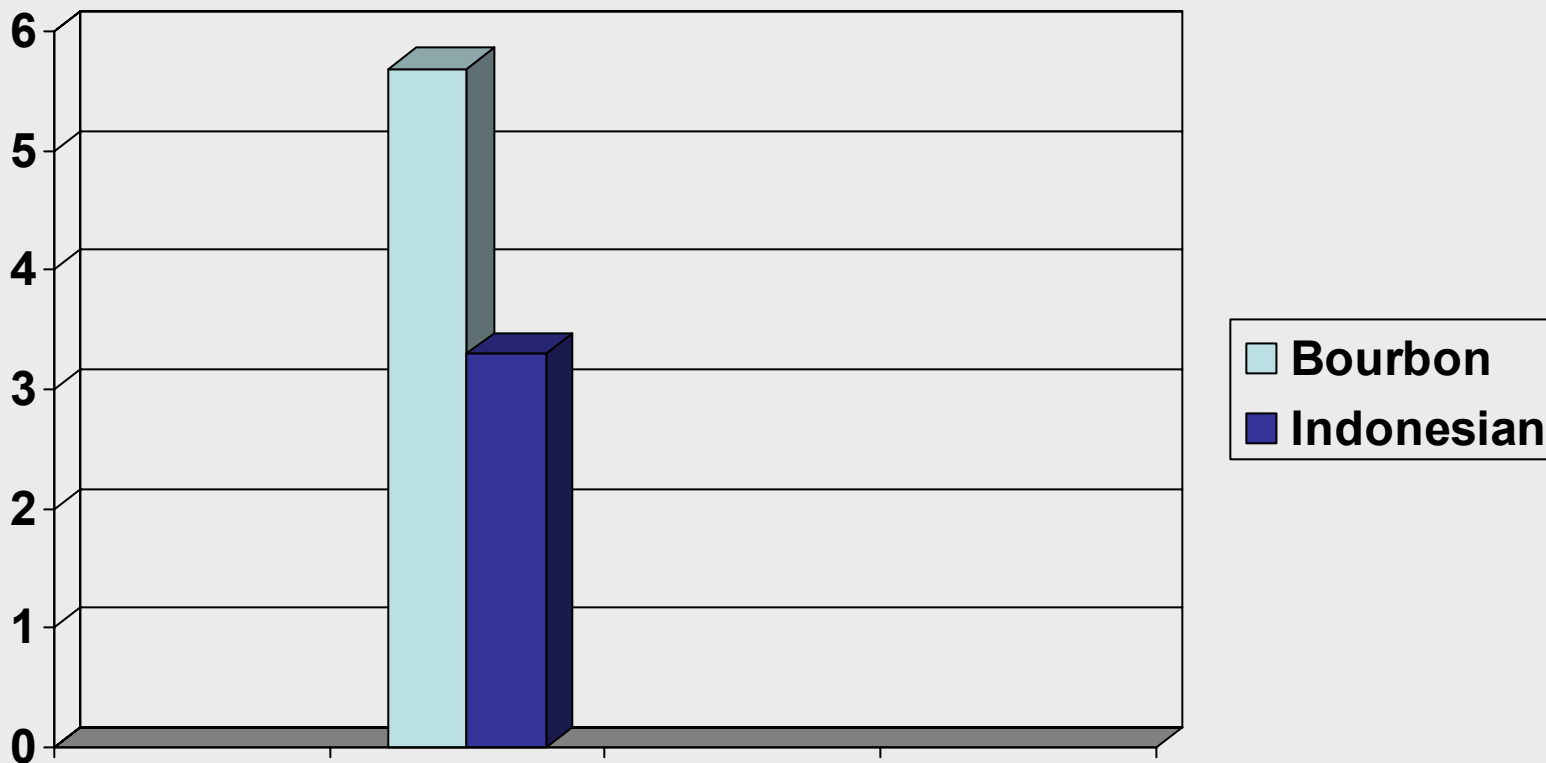
- Fruity-ethyl butyrate, benzaldehyde
- Floral-linalool, cinnamyl alcohol
- Green-hexanol, 2-heptanal
- Earthy-2-heptanone, gamma terpinene
- Vegetable-ethyl pyruvate
- Caramel-furfuryl alcohol, dihydro-2(3h)-furanone
- Honey-phenylacetic acid
- Rummy-ethyl propionate
- Spicy-eugenol, guaiacol
- Medicinal-cresol, trans-carveol
- Smoky/Phenolic-2,6 dimethoxyphenol, veratrole, guaiacol
- Fatty-decanoic acid, ethyl palmitate, gamma hexalactone
- Buttery-caproic acid, 2-methylpentanoic acid
- Vanilla-vanillin, syringaldehyde, guaiacol
- Rancid-isovaleric acid

- Three fold natural vanilla extracts
- Base: 4% sugar-water solution
- Dosage: 1.5 milliliters of vanilla extract/500 milliliters of sugar-water solution
- Panel: 14 trained judges
- Terms: Judges generated descriptors to describe the flavor
- Temperature: The solutions were evaluated at the room temperature

# Comparing and Relating Flavor Compounds to Taste

- 
- A horizontal teal bar spanning the width of the slide. On the left side, there are three small white icons: a square with a right-pointing arrow, a square with a left-pointing arrow, and a square with a right-pointing arrow.
- Differences in Indonesian vs. Bourbon vanilla extracts
  - Identifying major components responsible for taste
  - Noting the differences in the vanilla bean types

# Crème Soda Flavor Intensity Scores

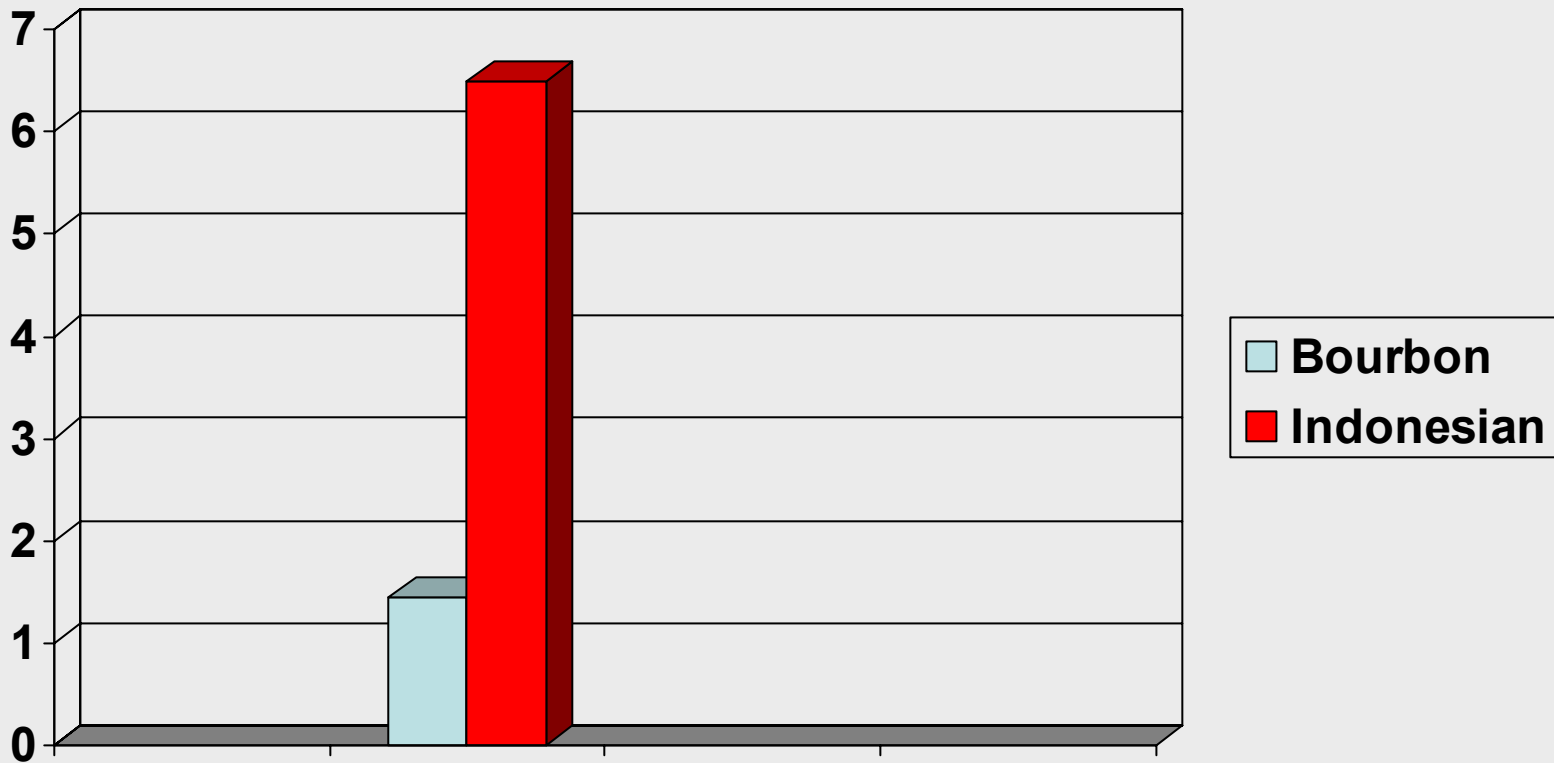


# Cream Soda Notes



		Bourbon	Indonesian
Benzaldehyde	a, c,e	0.14	0.00
Phenyl ethanol	a, c,e	0.1	0.05
Methyl salicylate	a, c,e	0.15	0.02
Hydrocinnamyl alcohol	a, c,e	0.03	0.00
p-anisyl alcohol	a, c,e	0.86	0.12
Methyl cinnamate	a,c,e	0.87	0.13
Vanillin	a,b,c,d,e	34.72	29.7
Acetovanillone	a,c,d,e	1.31	0.73

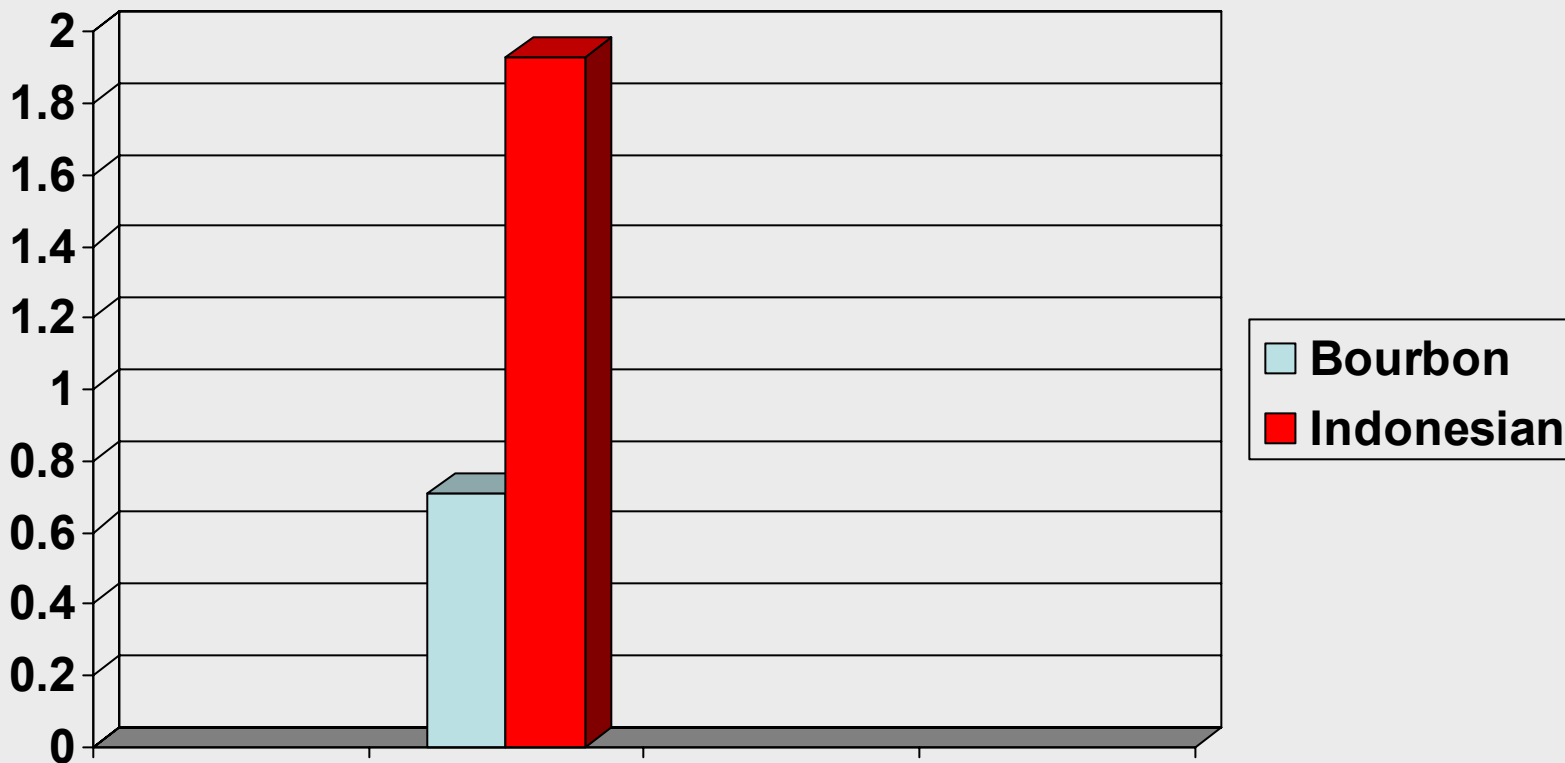
# Smokey Flavor Intensity Scores



# Smokey Notes

		Bourbon	Indonesian
3-methyl phenol	a	0.00	0.05
1,2,3-trmethoxybenzene	a,c,e	0.00	0.17
2,6-dimethoxyphenol	a,e	0.22	0.49
Eugenol	a,c,e	0.05	0.54
2-methyl-4-5-dimethoxyphenol	b	0.00	0.98
4-(2-propenyl)-2,6-dimethoxyphenol	a,c	0.00	0.32

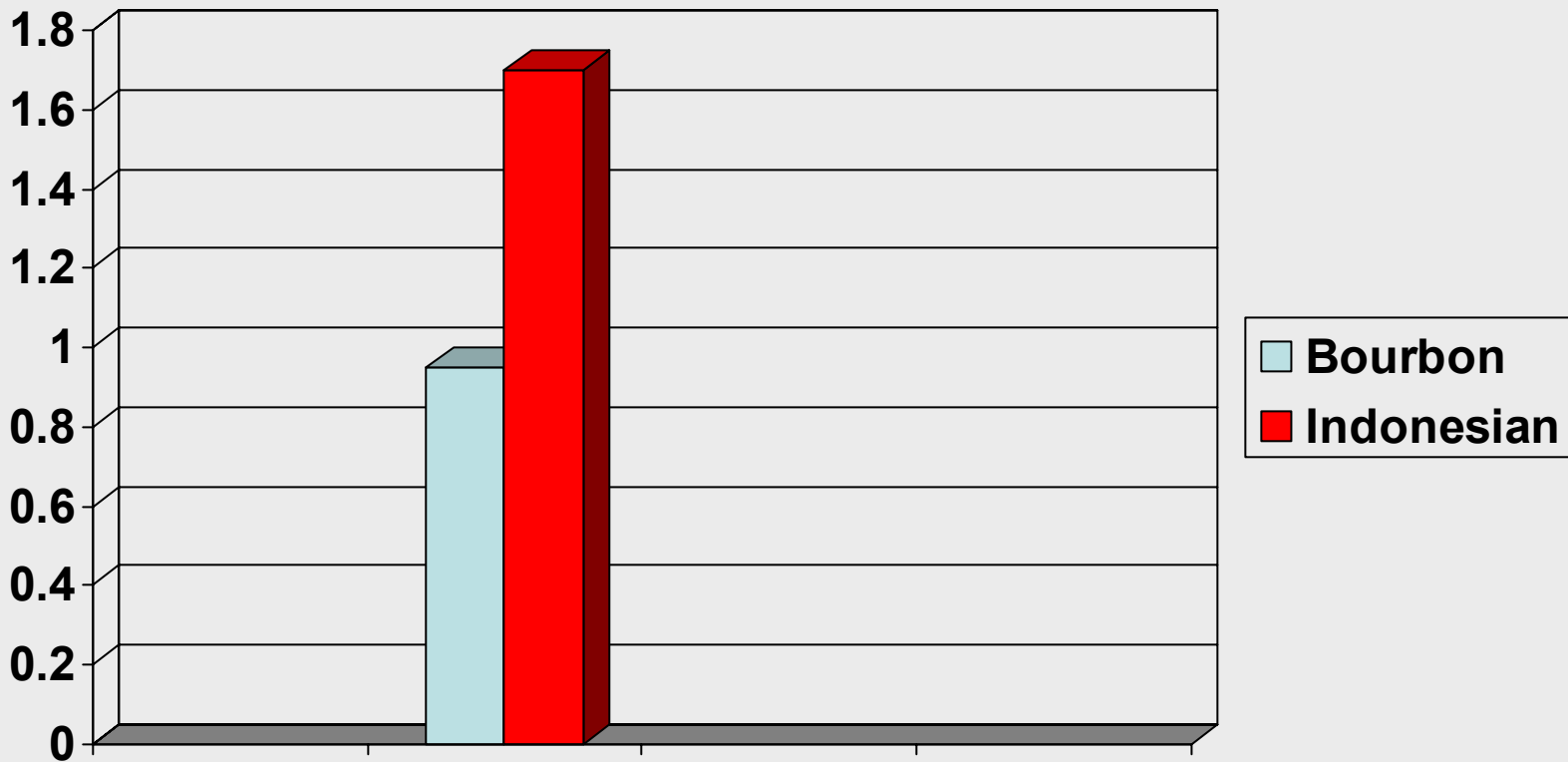
# Tobacco Aroma Intensity Scores



# Tobacco Notes

		Bourbon	Indonesian
Veratrole	a,c	0.00	0.17
3-methyl-H-pyrazole	a,c	0.00	0.11
Phenylacetic acid	a,b	0.00	0.16
Eugenyl methyl ether	a,c	0.00	0.13
Vanillyl alcohol	e	0.00	0.33

# Earthy Flavor Intensity Scores



# Earthy Notes

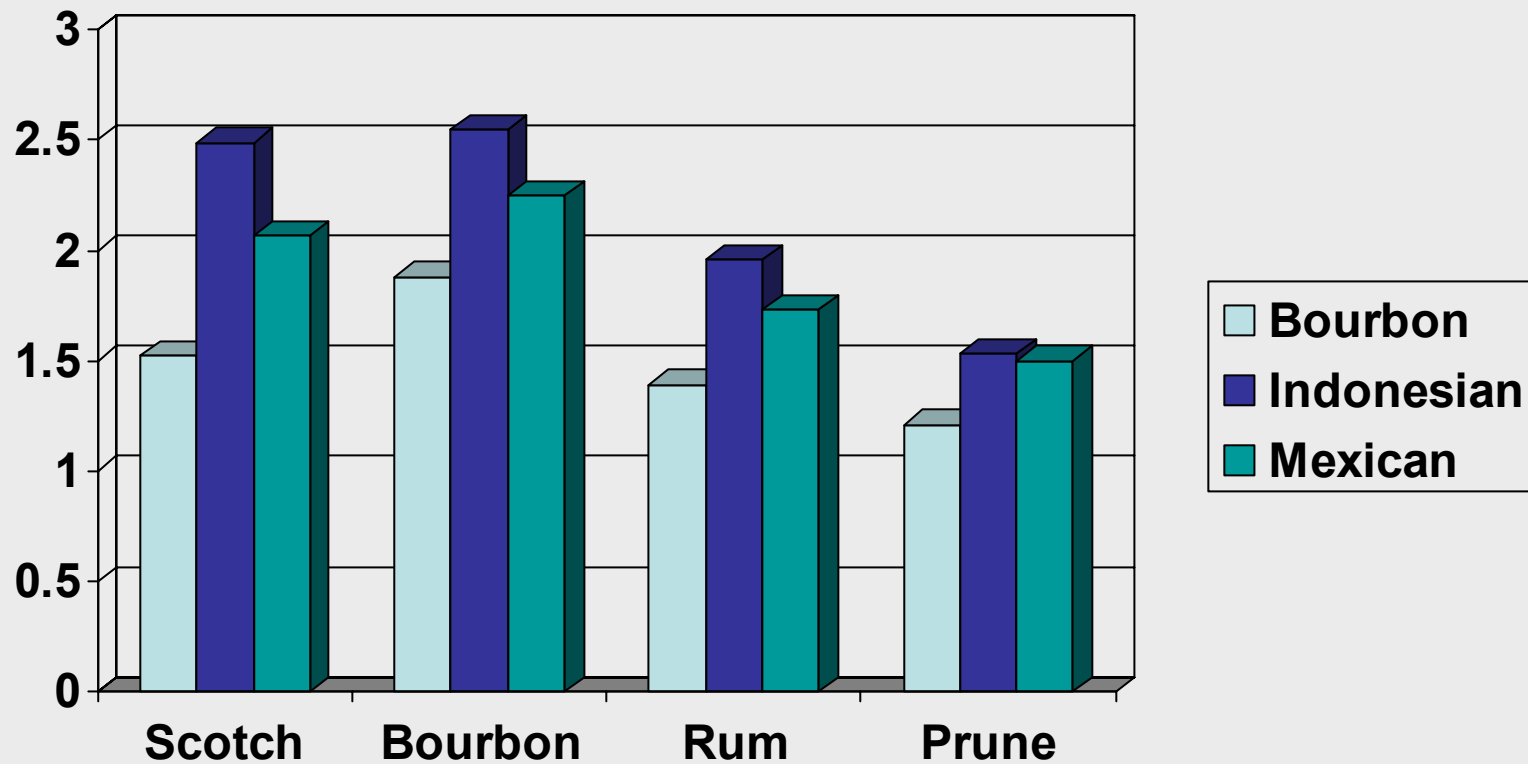


		Bourbon	Indonesian
2-hepanone	d	0.00	0.03
1H-pyrrole-2-carboxaldehyde	a,c	0.01	0.06
Furfural alcohol	a,c	0.04	0.15
1-octanol	d,e	0.00	0.06
5-(hydroxymethyl)fural	a,e	0.00	0.11

# Scotch, Bourbon, Rum and Prune Intensity Scores

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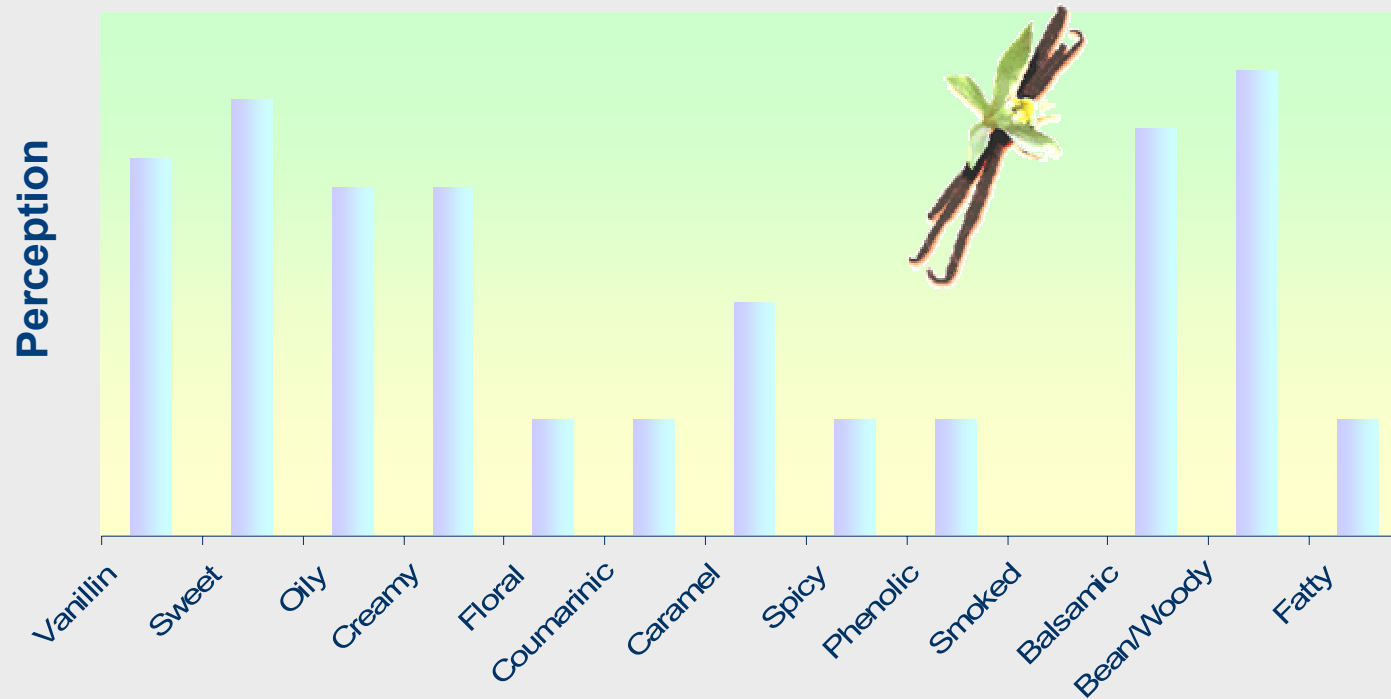
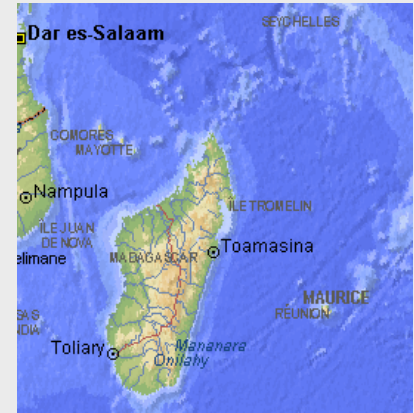


# Bourbon Vanilla

• **REGIONS OF CULTURE** : *Madagascar, Comoro Island, Réunion, Seychelles*

- **Major source of vanilla**

- Flavor characteristics : full, rich, smooth, sweet, almond, cream soda



# Indonesian Vanilla

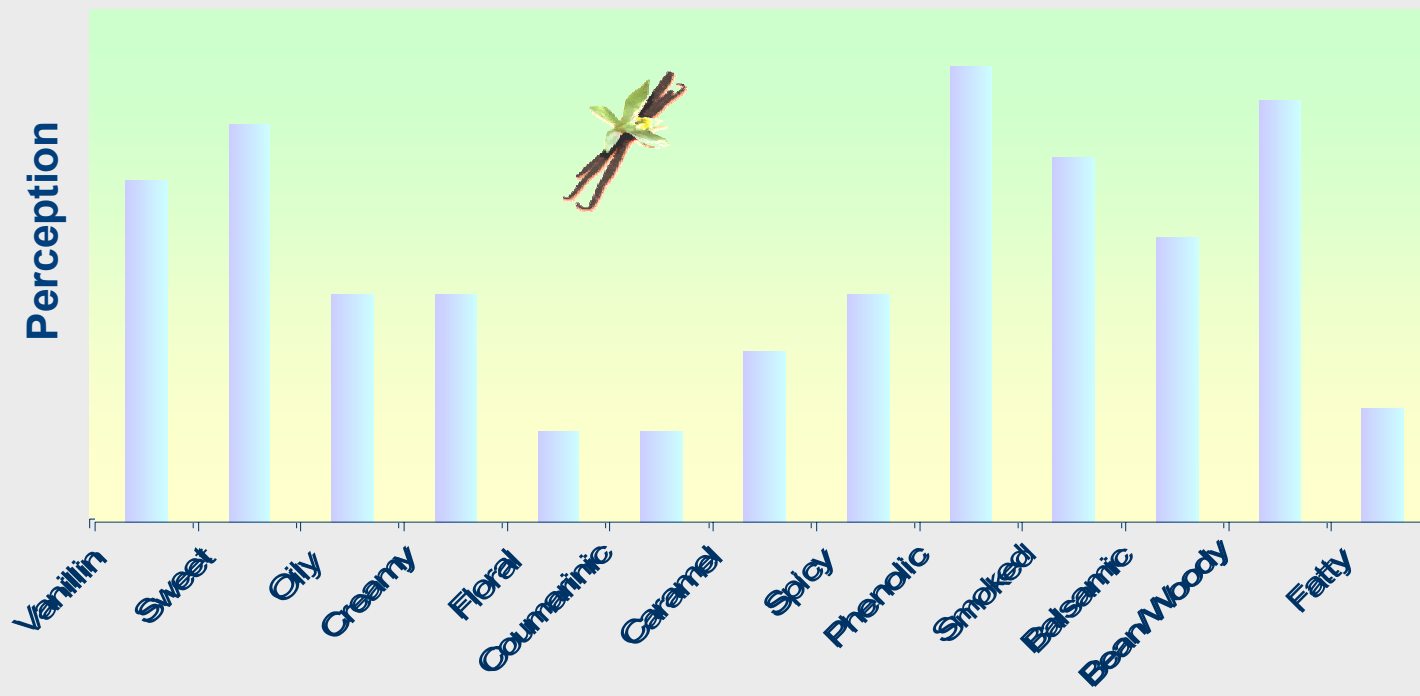
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## ❖ REGIONS OF CULTURE : *Bali, Java, Manado, Flores*

- Flavor characteristics : phenolic, rum raisin, woody, smoky & slightly sharp



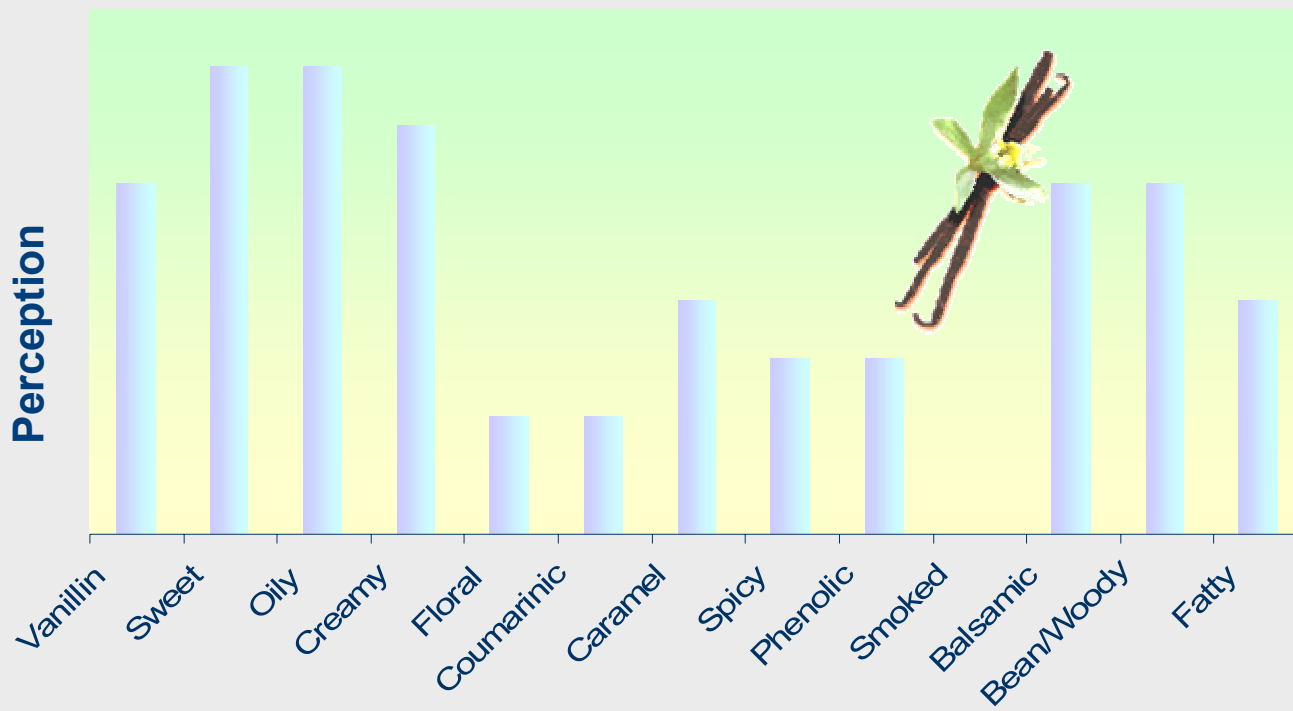
# Mexican Vanilla

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- **REGION OF CULTURE** : *Mexico*
- **Very limited production**
- Flavor characteristics : mild, smooth & creamy



# Tahitian Vanilla

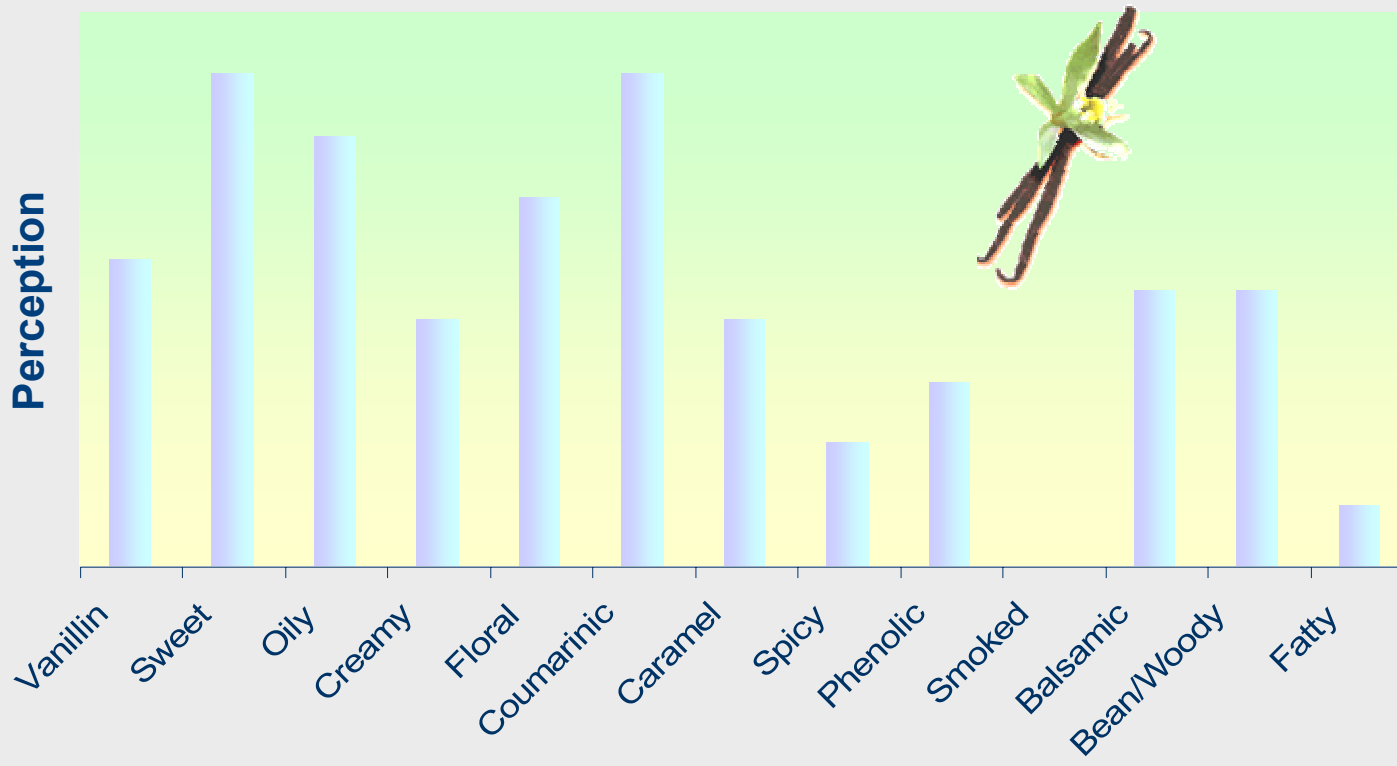
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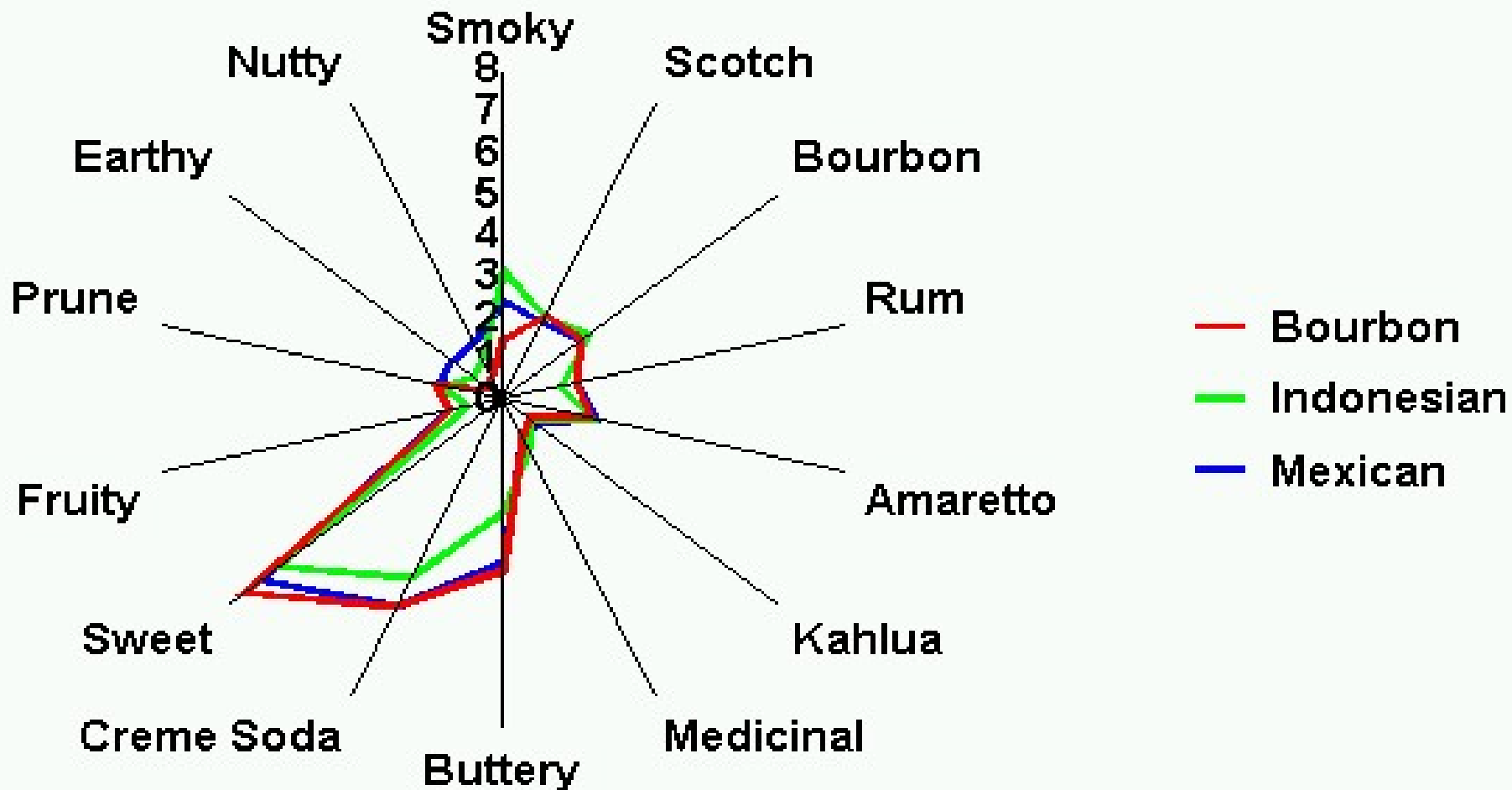
- **REGIONS OF CULTURE** : *Moorea, Tahiti*

- *Very limited production*
- Flavor characteristics : musky, aromatic due to anisyl derivatives



# Descriptive Analysis Data

## Product Analysis



# Summary

- Natural vanilla flavor is subtle and sophisticated
- Chemical analysis reveals the complex nature of the natural vanilla
- Chemical data indicate the vanilla varieties vary in their chemical concentrations
- The major component is Vanillin
- Vanillin is not Vanilla

# Summary

- There is a good correlation between the chemical data and sensory analysis
- Geographical location of vanilla cultivation has an effect on the sensory characteristics of the vanilla extracts
- Knowledge gained from the analytical data of the different vanilla extracts are useful in formulating natural vanilla type flavors