The Quality of Cured Vanilla Beans

Flavor and sensory attributes and mouthfeel

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The rationale for curing mature vanilla beans is to transform the ripe, flavorless pod into the microbiologically stable, full flavored, chocolate brown product or extract of commerce. The traditional curing process as practiced globally is divided into four principal and sequential phases. The first of these phases prevents post-harvest vegetative growth, bean splitting, and initiates the enzymatic reactions responsible for the production of aroma and flavor. The green vanilla pods are soaked in hot water (blanching, scalding, killing) as practiced in Madagascar, Comoros, India, Indonesia and Uganda; placed in an oven, as in Mexico; or exposed to the sun, as employed in Papua New Guinea. The other stages are sweating (or fermentation), drying and finally conditioning. The biochemistry and chemistry of these different phases is not fully understood in detail and is discussed elsewhere.[1]

Quality Attributes of Cured Vanilla Beans

The principal elements in defining vanilla bean raw material quality are:

1. The genetic profile of the tissue
2. The nurture encompassing geographical origin of the raw material, location, soil, climatic and growing conditions
3. The maturity state of the tissue at harvest
4. The curing operation that generates the final product

The combination of the above elements contributes to the flavor of the final cured bean.

Vanilla beans originate from the seven major geographical locations of Madagascar, India, Uganda, Indonesia, Mexico, Papua New Guinea and Tahiti. In addition vanilla pods belong to the genus *Vanilla* with the commercially important species being *V. planifolia* Andrews, *V. pompona* Schiede and V. *tahitensis* Moore. The latter species differs from the other two by having a characteristically high content of anisic compounds. Cured V. *tahitensis* beans contain anisyl alcohol, aldehyde and acid and additionally anisyl ethyl and methyl ethers as well as anisyl anisate and the *trans*-cinnamate esters.[2]

The geographical origin encompasses the location, soil, climatic and growing conditions and as such these define the principal seven origins indicated above. Harvest maturity is a very important factor and frequently equates with the development of a particular trait, e.g. yellowing at the distal end of the vanilla pod and or splitting of the bean.[1]

The curing process itself can contribute significantly to the final flavor quality of the vanilla bean. Traditional methods as well as less conventional processes can affect the flavor outcome.

The combination of all of the above variables provides the complete flavor matrix in the cured vanilla bean. It is in the sequential hands of the grower, curer, extractor and the flavorist to exploit all the flavor opportunities of the vanilla bean.

For top quality gourmet vanilla beans the length and appearance (fleshy, flexible, dark brown/black in color and oily feel) are important. Moisture contents range from 15–25% for extraction grade and 25–38% for gourmet grade depending on origin, the nature of the curing process and the projected end use.[3, 4] The quality of cured extraction grade vanilla beans is determined primarily by the flavor of the extract.

The curing process converts 80–82% moisture containing product into a final processed bean with moisture content in the range 15–38%.[4] Water activities (a_w) of beans in the range from 38–25% moisture are quoted as 0.89–0.84.[5] Most bacteria are inhibited at a_w below 0.90 whilst for most molds the value is less than 0.80.[a] For most applications, however, final moisture levels in cured beans are around 15–25% and as such would not indicate a microbial hazard. Care must however be taken during

[a]*www.foodsafetysite.com/educarots/competencies/general/bacteria/bac5.html*

the earlier, high moisture stages of curing to prevent microbial growth. Flavor differences among beans from different origins are readily perceived.[b]

Bourbon beans have a very rich taste and smell, with oily skin and an abundance of tiny seeds. Bourbon beans from Madagascar and the Comoros are described as having robust, faintly phenolic, sweet, tobacco and balsamic notes, with vanillin overtones. Mexican beans have mild, smooth, creamy with slightly musty, vanillic and coumarinic character. Tahitian beans of the *V. tahitensis* type have a strongly anisic, fruity and floral character with notes associated with licorice. The skin is thick and very fibrous.

Flavor Attributes of Cured Vanilla Beans

Vanillin content is regarded as an important indicator of the final quality of cured vanilla beans as it is, in mass terms, by far the major aromatic phenol. Overall flavor impact is more important, however, since it is possible to have cured vanilla beans with high vanillin but inferior overall flavor. Sensory appreciation of cured vanilla flavor is recognized, but a clear sensory correspondence with key flavor chemical components is not currently available. In this context, knowledge is also lacking on the identities of the key phenolic and non-phenolic compounds that are present in cured vanilla beans; this despite the fact that in excess of 200 compounds have been reported in solvent extracts of cured pods of *V. planifolia.*[6]

As indicated above, vanillin is the most abundant aroma compound in cured beans (~2%), whilst other important constituents are *p*-hydroxybenzaldehyde (0.2%), *p*-hydroxybenzyl methyl ether (0.02%) and acetic acid (0.02%). The rest of the aroma compounds are present in amounts of less than 10 ppm.

The significant work of Perez-Silva et al. in the area of cured vanilla bean aroma was conducted on solvent extracts of cured Mexican *V. planifolia* G. Jackson ex Andrews beans.[7] Using gas chromatography odor assessment they identified a number of families of compounds that contributed significantly to the overall aroma of the cured bean. These included 13 phenolic compounds, two of which were esters, five aliphatic acids and six aliphatic aldehydes and alcohols—a total of 24 compounds in all. Interestingly three of the phenols detected in this study, 4-methylguaiacol, guaiacol and acetovanillone, at concentrations of 3.8 ppm, 9.3 ppm and 13.7 ppm, respectively, were considered in organoleptic terms to be as odor-potent as vanillin. This latter compound was present in the extracts between 1,400 and 5,000 times their concentrations. This confirmed the relative position of vanillin in the cured product flavor hierarchy. Dignum et al., using gas chromatography-olfactometry, reported that *p*-cresol, 2-phenylethanol, guaiacol and 4-creosol had a considerable impact on vanilla aroma.[6] Other reports suggested that the two stereoisomeric vitaspiranes contributed to cured vanilla aroma.[c]

[b]*www.vanilla.com/index.php/TROPICAL-FOODS/VANILLA/vanilla-beans.html*

[c]*www.bojensen.net/EssentialOilsEng/EssentialOils30/EssentialOils30.htm*

T-1 Aroma active compounds in cured Mexican vanilla bean extracts[7]

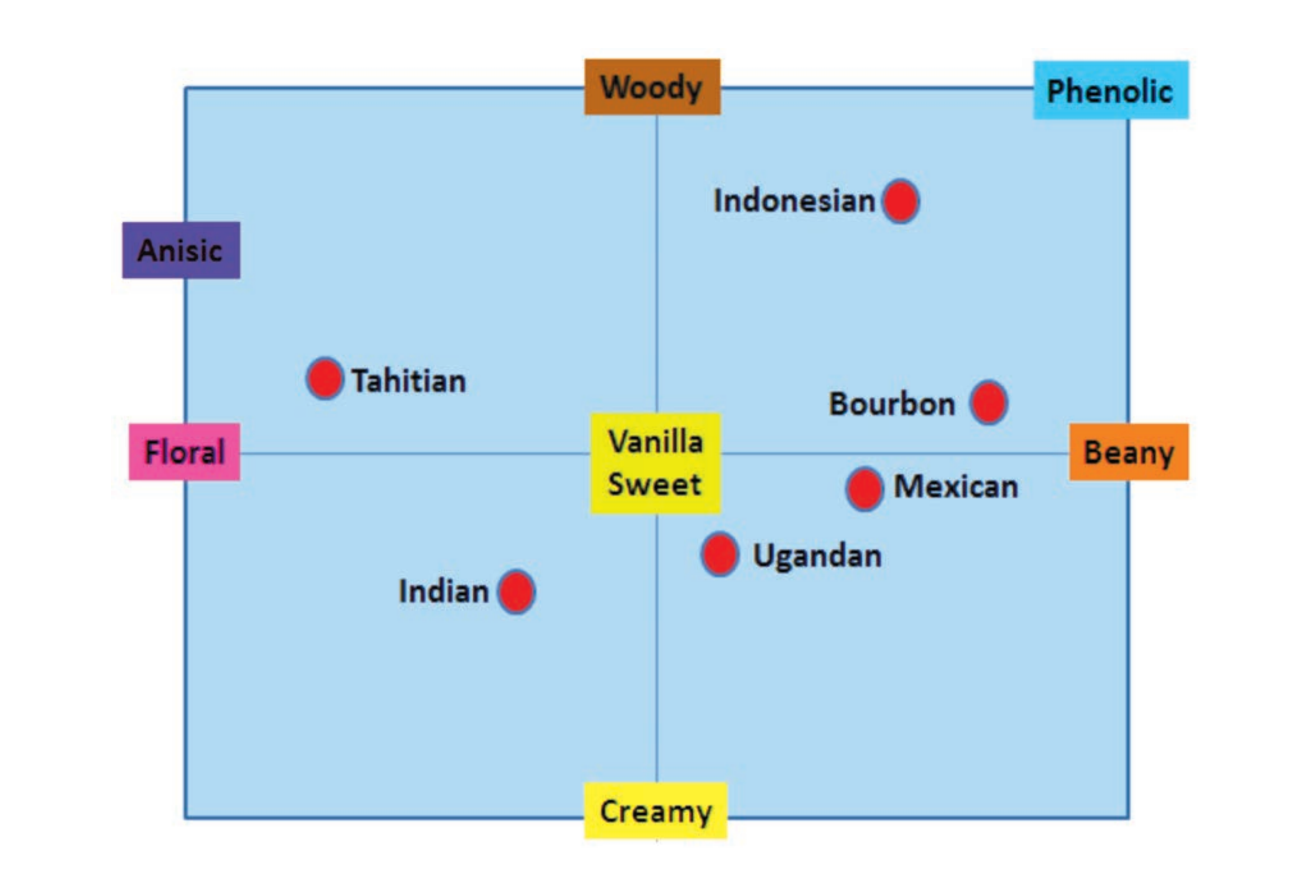
Compound (ppm)	Odor quality
Phenolics	
Guaiacol 9.3	Chemical, sweet spicy
4-Methyl guaiacol 3.8	Sweet, woody
4-Vinyl guaiacol 1.2	Chemical, phenolic
p-Cresol 2.6	Balsamic, woody, spicy
4-Vinyl phenol 1.8	Sweet, woody
Vanillin 19118.0	Vanilla, sweet
Acetovanillone 13.7	Vanilla, sweet, honey
Vanillyl alcohol 83.8	Vanillalike
p-Hydroxybenzaldehyde 873.0	Vanillalike, biscuit
p-Hydroxybenxyl alcohol 65.1	Vanillalike, sweet
Methyl salicylate < 1.0	Chalk
Methyl cinnamate 1.1	Sweet
Aliphatic acids	
Acetic acid 124.0	Sour, vinegar
Isobutyric acid 1.7	Buttery
Butyric acid < 1.0	Buttery, oily
Isovaleric acid 3.8	Buttery, oily
Valeric acid 1.5	Cheese
C4 Alcohols & Ketones	
2, 3-Butandiol 8.0	Floral, oily
3-Hydroxy-2-butanone 14.6	Buttery
Aldehydes	
2-Heptenal 2.1	Green, oily
(E)-2-Decenal 1.8	Herblike, floral
(E,Z)-2, 4-Decadienal 1.4	Herblike, fresh
(E,E)-2, 4-Decadienal 1.2	Fatty, wood

A combination of the 24 individual compounds reported above by Perez-Silva et al., at the levels found in the solvent extract of the Mexican beans, approximated closely the aroma of the original extract.[8] The aroma active compounds, their concentrations in ppm, and odor qualities in cured Mexican vanilla bean extracts are shown in **T-1**.

This type of information is very useful in the determination of the contribution of individual compounds and groups of like compounds, in terms of odor character, to cured vanilla pod aroma. Extension of this approach to other cured vanilla beans, especially Bourbon, would be very valuable. In this way it would be possible to link individual and groups of similarly formed compounds such as the phenols and the unsaturated aldehydes to the aroma character of the cured pods of different geographical origin(s) and/or process variables. It may be the case that the defining compounds, in terms of aroma of vanilla extracts of all origins may be a relatively small number perhaps as few as 30–35. These compounds present in the appropriate concentration could describe the aroma of vanilla extracts from any global origin.

A typical schematic sensory profile of global vanilla bean extracts

F-1



Sensory Attributes of Cured Vanilla Beans

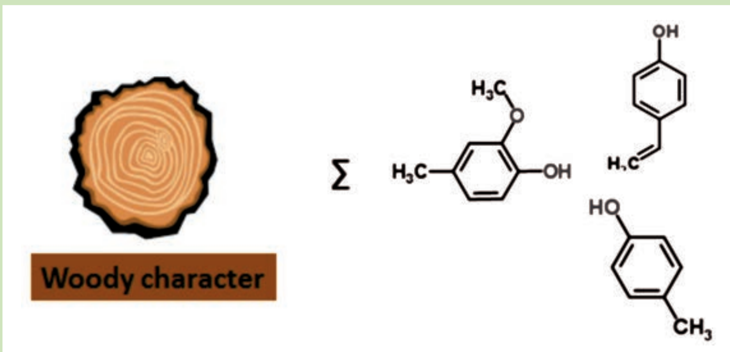
Sensory analysis of cured vanilla bean extracts has been conducted and a number of descriptors or attributes determined to cover the aroma characteristics of the total extract. A number of lexicons covering a wide range of vanilla extracts have been generated by sensory panels. [9]

Such attributes typically include the descriptors beany, spicy, balsamic, fruity, resinous, phenolic, smoky, woody, floral, creamy, sweet, perfumey, fatty and anisic, among others. Using sets of such descriptors it is possible to map extracts from the main geographical locations. This method clearly highlights particular directions, e.g. *V. tahitensis* from Papua New Guinea or Tahiti, as strongly anisic and floral, whilst Bourbon beans character is more in the beany and sweet direction (**F-1.**).

With a list of relevant sensory attributes for a particular origin of cured vanilla beans it then becomes feasible to begin to link these characteristics with associated descriptors and identified key aroma compounds or groups thereof. If we take cured Mexican vanilla beans as the example, we have both sensory attributes and identified key aroma compounds or groups of the same with known descriptors. Mexican vanilla extracts are described in sensory attribute terms such as vanillalike, sweet, creamy, oily, balsamic, beany, woody, smoked, fatty, spicy and phenolic.

Woody character in cured vanilla bean extracts

F-2



The Perez-Silva et al. data listed the key aroma compounds along with their odor character (**T-1**). The odor qualities of the phenolic family were vanillalike, sweet, spicy, woody, balsamic, phenolic and honey. The aliphatic acids were cheesy, buttery, oily and vinegarlike. The unsaturated aldehydes collectively were green, oily, fatty, woody, herblike, floral and fresh. Finally the ketones were floral, oily and buttery. The woody, phenolic and oily attributes are important sensory factors in Mexican vanilla flavor. Woody character is linked to the compounds 4-methylguaiacol, *p*-cresol and 4-vinylphenol. A representative "woody" flavor block would contain these three compounds in suitable ratio (**F-2**).

Phenolic character is associated with a number of compounds including 4-vinylguaiacol in vanilla bean extracts. Oily character is linked with butyric acid, isovaleric acid and 2-heptenal. Thus it begins to become possible to associate sensory attributes of cured beans to the odor qualities of identified "key" chemical compounds found in cured vanilla beans and extracts. Therefore a flavor block of a mixture in the correct ratio of 4-methylguaiacol, *p*-cresol and 4-vinylphenol could be used as a descriptor of "woody." In this way one can start to build up a list of key compounds *only found in cured beans*, which contribute to sensory attributes of, in this case, Mexican cured vanilla extract. To support this position in cured Mexican beans it is possible to draw up a list of sensory attributes linked to key chemicals found. An abbreviated form of such a list is shown in **T-2**. A collection of such blocks can lead to a match, based on flavor compounds, to the full aroma of a particular vanilla extract. Natural flavors could then be formulated to match the flavor of this vanilla extract.

T-2 shows clearly that the phenolic compounds contribute to six of the nine attributes listed**.** The buttery, fatty, oily, floral and herblike characters are derived mainly from the non-phenolic components.

Further extension of this thinking leads to a position where the manipulation of the level of individual collections of compounds, with similar sensory attributes and often similar biochemical origin, can potentially be achieved by modification of the conditions employed in the curing process. This can be exemplified by the group of phenols initially present as the β-D-glucosides in the ripe bean. A potential target for the phenolic glucosides during curing is to achieve their maximum conversion to the free phenols since this family is responsible for the sensory attributes of woody, phenolic, spicy, sweet, balsamic and vanillalike. Modification of the scalding and sweating phases of curing is known to influence the hydrolysis of these glucosides. The family of unsaturated aldehydes is very likely derived by biochemical and/or chemical oxidation of longer chain polyunsaturated lipids. Enhanced levels of these carbonyl compounds may be achieved by enhanced lipolysis and oxidative transformations of lipids facilitated by raising the oxidation level, such as saturating the atmosphere of the sweating reaction with molecular oxygen or inducing conditions for formation of reactive oxygen species. In this way it may be possible to direct the curing operation to specific targeted sensory attributes. An additional benefit of linking key chemical groups or blocks of compounds to sensory attributes is that armed with such tools it would be possible to dose vanilla extracts with specific flavor blocks and in a facile way evaluate the sensory consequences of such actions. Exercises of this kind could provide simple guidance for proposed future directions in curing modification. These options are outlined in **F-3**.

T-2 Attributes related to aroma compounds in cured Mexican vanilla bean extracts

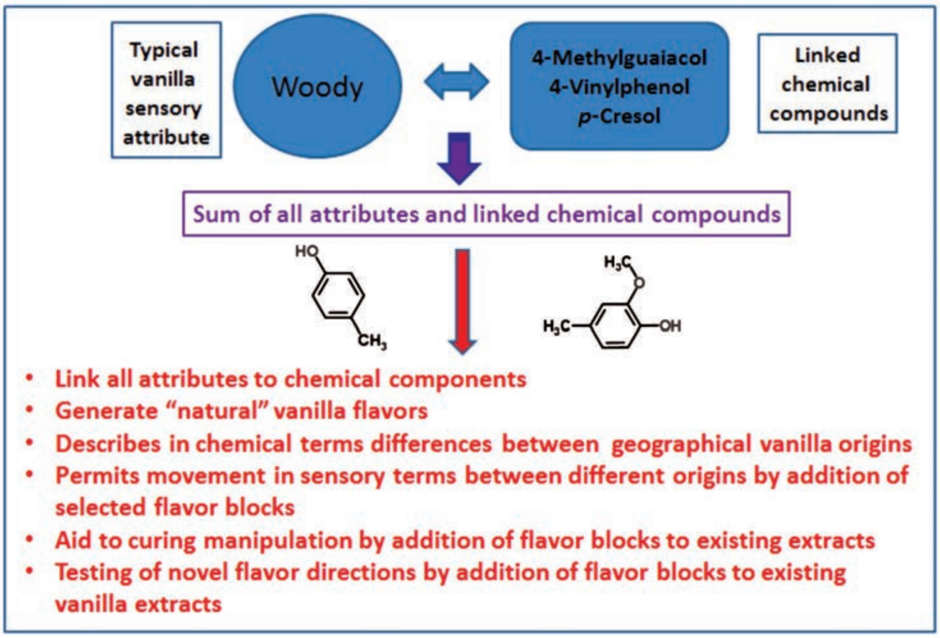
Attribute or odor quality	Compound(s)
Woody	4-Methylguaiacol *p*-Cresol 4-Vinylphenol
Vanilla, vanillalike	Vanillin Acetovanillone Vanillyl alcohol *p*-Hydroxybenzaldehyde *p*-Hydroxybenzyl alcohol
Sweet	4-Methylguaiacol 4-Vinylphenol Acetovanillone *p*-Hydroxybenzyl alcohol
Phenolic, chemical	4-Vinylguaiacol Guaiacol
Balsamic	*p*-Cresol
Spicy	Guaiacol *p*-Cresol
Buttery, fatty, oily	Isobutyric acid Butyric acid Isovaleric acid 2,3-Butandiol 2-Heptenal (E,E)-2,4-Decadienal
Floral	2,3-Butanediol (E)-2-Decenal
Herblike	(E)-2-Decenal (E, Z)-2,4-Decadienal

Other Compounds Contributing to the Flavor and Mouthfeel of Cured Vanilla Beans

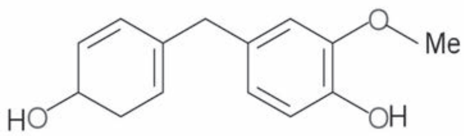
The understanding of the flavor and mouthfeel of cured vanilla beans was made both more complex and interesting by the isolation of a further family of non-volatile phenolic and non-phenolic compounds in green, ripe and cured vanilla beans. Schwarz and Hofmann identified a family of simple dimeric and other more complex coupled phenols that contributed to the mouthfeel of vanilla beans.[10] Seven of these compounds were isolated from extracts of traditionally cured Madagascan vanilla beans and had sensory characteristics described as velvety, mouth-coating. Six of these seven components have not previously been reported in the literature as velvety, mouth-coating tastants in vanilla.

The routes to the two identified *bis*-phenols, including the known divanillin, and the three methylene *bis*-phenols

Options for manipulation of vanilla aroma F-3

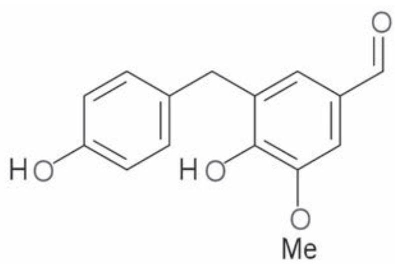


The three diphenyl-methane compounds found in cured vanilla beans, linked by methylene bridges F-4



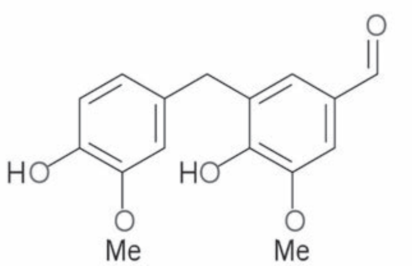
4-(-4-hydroxybenzyl)-2-methoxyphenol

Product #3 (I)



5-(-4-hydroxybenzyl)-vanillin

Product #4 (II)



4-hydroxy-3-(4-hydroxy-3-methoxybenzyl) -5-methoxy-benzaldehyde

Product #5 (III)

family of compounds in vanilla beans has not been fully established though most of the dimeric compounds can readily be linked structurally to known monomeric phenols that are present, or released from glucosides, during curing of the vanilla bean.[11] It is known from the literature that laccase, catechol oxidase (a polyphenoloxidase) and peroxidase are enzymes capable of oxidizing *o*-diphenols to semi-quinones and quinones. Additionally, laccase is capable of oxidizing *p*-diphenols. In the case of laccase and catechol oxidase the enzyme requires molecular oxygen, whilst for peroxidase hydrogen peroxide is the essential hydrogen acceptor.[12]

The phenol oxidation compounds described by Schwarz and Hofmann were almost exclusively absent from the ripe, green bean but appeared in the final cured product. It is likely that the *bis*-phenols described are derived by radical coupling at the 5-5' position between individual phenols.[13] It is well established that diphenol-linked compounds of this type can be produced from phenols by chemical oxidizing agents, or enzymatically via horseradish peroxidase/hydrogen peroxide.[14,15] The three diphenyl-methane compounds found in cured vanilla beans are as shown in **F-4**.

The origin of this family of compounds in cured vanilla beans has not been elucidated, though some methylene bridge linkages are known in lignin structure.[16] Methylene *bis*-phenols structurally similar to compounds 3 to 5 in **F-4** have been reported in nature. These include hibiscutaiwanin [IV] from the stem of *Hibiscus taiwanensi* and *bis*-(3, 5-dichloro-4-hydroxyphenyl)-methane [V] from fungal metabolism of 3, 5-dichloro-*p*-anisyl alcohol (**F-5**).[17,18]

The proposed mechanism of formation of *bis*-(3, 5-dichloro-4-hydroxypheny-methane [V] is via protonation of the benzylic hydroxyl group followed by elimination of water to form the stabilized benzylic carbocation. Attack by this electrophile on another molecule of the substituted 4-hydroxybenzyl alcohol produces the dimeric intermediate which loses formaldehyde to form the methylene bridged adduct [V]. In a similar way the three *bis*-diphenyl methanes from cured vanilla beans could be formed via the loss water as follows:

- Compound I could be formed by the reaction of *p*-hydroxybenzyl alcohol with the *para* position on the guaiacol ring with the elimination of water.
- Compound II could be formed by the reaction of *p*-hydroxybenzyl alcohol with the *ortho* position of the vanillin ring with the elimination of water.
- Compound III could be formed by the reaction of vanillyl alcohol with the *ortho* position of the vanillin ring with the elimination of water.

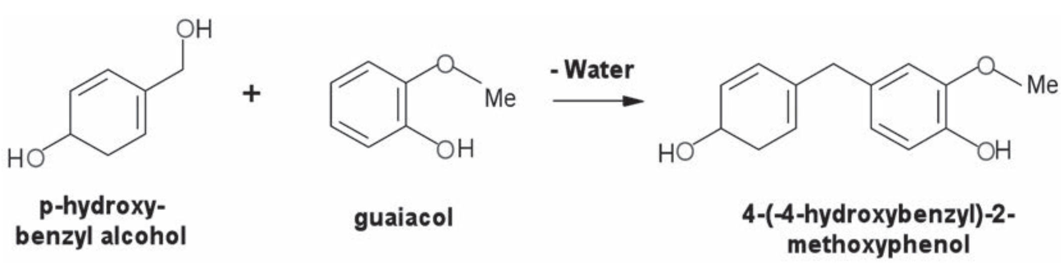
A potential reaction scheme for the formation of compound I, namely 4-(-4-hydroxybenzyl)-2-methoxyphenol, is shown in **F-6**.

An alternative mechanism, shown in **F-7**, involves the participation of formaldehyde. In this case compound I would be formed from reaction between phenol, formaldehyde and guaiacol with the elimination of water.[19, 20]

A series of model diphenyl methane dimers of the guaiacol type, and similar in structure to the vanilla compounds described above and representing the major types of lignin condensation reactions were also synthesized

Hibiscutaiwanin [IV] and *bis*-(3, 5-dichloro-4-hydroxyphenyl)-methane [V] **F-5**

Potential pathway for the synthesis of 4-(-4-hydroxybenzyl)-2-methoxyphenol **F-6**



by a variety of methods.[21] Thus there are precedents for molecules of these types associated with lignin containing tissues.

As previously indicated these methylene *bis*-phenols are absent in ripe vanilla beans and are only formed as the result of the curing process. As such these compounds are likely be present as part of another larger molecule or assembled during the curing process, possibly during the fermentation step and sunning stages of curing, when monomers such as vanillin, vanillyl alcohol, *p*-hydroxybenzyl alcohol and guaiacol are liberated. Thus the above family of compounds appears to be formed by the action of oxido-reductase enzymes during the curing process itself.

Screening of ripe green beans showed a number of uncharacterized precursor compounds that disappeared as the result of curing with the concomitant formation of (1-O-vanilloyl)-(6-O-feruloyl)-β-D-glucopyranoside (VI) (**F-8**).[10,22] The nature of these precursors has not yet been elucidated.

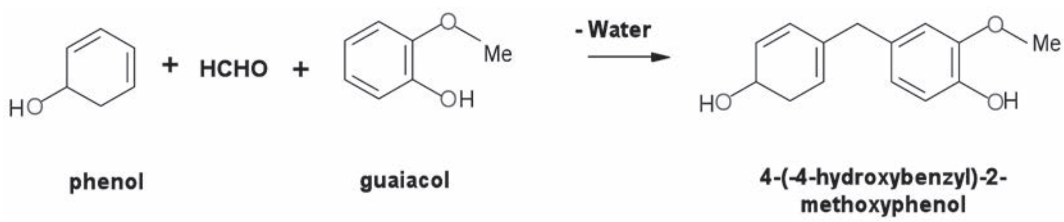
Candidate linkages in these precursors of (1-O-vanilloyl)-(6-O-feruloyl)-β-D-glucopyranoside could include esters or glucosides linked to the phenolic hydroxyl of the ferulate residue. The aldehyde group of the vanillin residue could also be involved via Schiff's base formation. Finally the glucose residue of compound VI could be linked to other sugar residues at the 2' or 3' position or to further ferulate units. (1-O-Vanilloyl)-(6-O-feruloyl)-β-D-glucopyranoside could be liberated from such precursors by known endogenous esterases and glucosidases. The biogenetic origin of this molecule is probably different than the route(s) to the *bis*-phenols and the methylene *bis*-phenols described above. Clearly however it bears similarity to glucovanillin.

Green vanilla beans contain, besides glucovanillin, other conjugated phenols readily extractable from the bean with methanol. Of these the two major compounds isolated were *bis*-[4-(β-D-glucopyranosyloxy)-benzyl]-2-isopropyltartrate (glucoside A) and *bis*-[4-(β-D-glucopyranosyloxy)-benzyl]-2-(2-butyl)-tartrate (glucoside B) (VII). Glucosides A and B belong to the loroglossin family of compounds reported in other members of the Orchidaceae (**F-9**).[23]

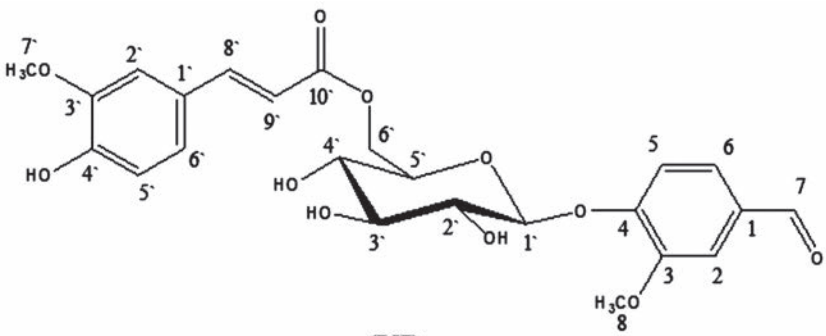
The role of glucosides A and B may be as precursors of *p*-hydroxy benzyl alcohol, vanillin and other related phenols, though this has not yet been confirmed.

Both ripe and cured vanilla beans contain in addition to the above glucosides A and B significant quantities of a family of novel lipid β-dicarbonyl compounds. These are long chain aliphatic compounds with a 2,4-dicarbonyl function and a *cis* double bond at the n-9 position. They represent ca. 28% of the neutral lipids, or 1.5%, in immature vanilla beans, and 10% of the neutral lipids, i.e. 0.9%, of the mature beans. In total, five β-dicarbonyl compounds have been identified including 16-pentacosene-2,4-dione, 18-heptacosene-2,4-dione, 20-nonacosene-2,4-dione, 22-hentriacontene-2,4-dione,

Potential formation of methylene *bis*-phenols from formaldehyde phenol and guaiacol **F-7**

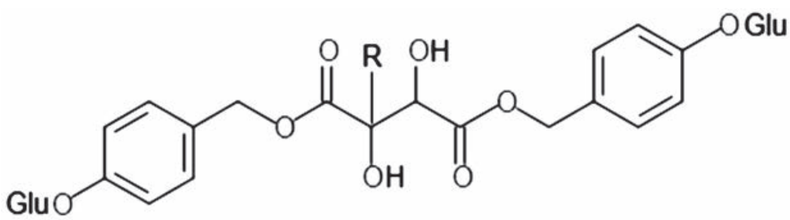


(1-O-Vanilloyl)-(6-O-feruloyl)-β-D-glucopyranoside (VI) **F-8**



(VI)

Glucosides A and B (VII) **F-9**



R = -CH(H3)2 (Glucoside A)

R = -CH(CH2CH3)(CH3) (Glucoside B)

(VII)

and 24-tritriacontene-2,4-dione.The major constituent 18-heptacosene-2,4-dione (nervonoylacetone), represented 74.5% of the β-dicarbonyl fraction.[24]

Green and cured vanilla beans also contain in the neutral lipid fraction, before saponification, a new product family in this genus namely long-chain γ-pyrone compounds with an aliphatic chain containing a *cis* double bond also at the n-9 position. These compounds represent 7–8% of the neutral lipids in mature beans. Three γ-pyrones have been identified, including 2-(10-nonadecenyl)-2,3-dihydro-6-methyl-4*H*-pyran-4-one, 2-(12-heneicosenyl)-2,3-dihydro-6-methyl-4*H*-pyran-4-one and 2-(14-tricosenyl)-2,3-dihydro-6-methyl-4*H*-pyran-4-one. The major constituent was 2-(14-tricosenyl)-2,3-dihydro-6-

methyl-4*H*-pyran-4-one, which represented 70.3% of the γ-pyrone fraction. This compound family has been found in *V. fragrans* and *V. tahitensis* beans but not found either in leaves or stems from the same genus or in *V. madagascariensis* beans.[25]

The biochemical role of the long-chain aliphatic β-dicarbonyl, γ-pyrones, and the glucosides A and B in the vanilla bean is not established. By nature of their structures, however, they may have a mouthfeel function in the final cured product and its solvent extracts.

Summary and Conclusions

A number of knowledge gaps in the understanding of the quality of cured vanilla beans remain, including:

- There is no complete list of the key aroma compound in the cured bean.
- Knowledge is lacking in the identity of the known key flavor compounds, with respect to how they are formed and lost during all stages of the curing process and by which routes.
- Knowledge is incomplete about phenyl glucosides and their relationship to separate compartmentation within the vanilla bean, the enzyme(s) responsible for their hydrolysis and interventions to facilitate high conversion of phenyl glucosides to the aglycone phenols.
- The knowledge base on flavor formation and loss is very limited, especially in the drying and conditioning stages of curing.
- There is limited information on the precursors of the final aroma compounds and their pathways to the same; these include all other non-phenolics such as the C4 compounds, the short chain acids and the unsaturated aldehydes.
- The phenolic tastants; what are their precursors, their catalysts and formation route(s), and what are their contributions to the overall flavor impact of cured vanilla beans?
- Do complex lipids and their breakdown products have a role to play in the flavor of the final product?
- Does the Maillard/Strecker and related reactions contribute to flavor development?
- Do polyunsaturated fatty acids and phenol couples contribute to non-phenolic flavor formation?
- What is the function of microorganisms in flavor development during the curing operation?
- We still have some way to go to establish close relationships between the compounds that contribute to vanilla aroma, taste and mouthfeel and the sensory attributes of the same.
- How do we control and direct the curing process to deliver tailored flavor profiles?

The answers to these and other questions will require further experiments with green vanilla beans, vanilla enzymes, analytical and sensory studies with vanilla extracts, as well as model studies with selected flavor blocks.

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