Flavor Characterization of Different Varieties of Vanilla Beans

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Despite the ubiquitous application of vanilla flavor in nonsavory foods, and despite the unprecedented number of studies by industry and academia, publications and information are scanty on the complete elucidation of the analytical and flavor chemistry of this unique spice. Most contemporary studies and advancement of its understanding are well-guarded proprietary information. The objective of the work described in this article is the aroma characterization of vanilla beans from different geographical locations with a view to developing a database of information to be used as an indication of geographical origin and bean quality.

Introduction

Vanilla, the most important and universally popular flavoring material and spice, is the fully grown fruit of an epiphytic orchid, *Vanilla planifolia* Andrews (syn. *Vanilla fragrance* Ames) or *Vanilla tahitensis* Moore. Harvested before it is fully ripe, then fermented and cured, the fruits are usually referred to as vanilla beans. The fragrance and flavor of vanilla are due to numerous compounds produced during the curing operation. Among these compounds, vanillin is the most abundant.

With vanilla, as is typical of natural agricultural products, the country of origin, agricultural practices, climatic factors, soil types, degree of ripeness at harvesting and method of curing play important roles in the quality and yield of flavor and aroma constituents.

The direct thermal desorption technique permits the analysis of solid samples without prior solvent extraction or other elaborate sample preparation. A concise and detailed description, mode of operation and different applications of this method have been published by Hartman et al.,^{1,2} and by Manura and Hartman.³

Direct thermal desorption has been demonstrated to be

highly sensitive, accurate, and reproducible. Quantitative measurements making use of various internal standard methods have yielded analytical precision in the range of 2.5% to 13%, depending on the specific analyte/matrix combination under investigation.¹

Experimental

Material: Six samples, designed Bourbon-A, Tahitian, Balinese-A, Java, Bourban-B and Balinese-B comprising four commercially important cultivars of vanilla beans, were obtained as gifts from David Michael Inc. (Philadelphia, Pennsylvania). Four other vanilla samples, designed Mexican, Tonga, Costa Rican and Jamaican, were gifts from Premier Vanilla Inc. (East Brunswick, New Jersey). 2,6-Dimethoxyphenol (internal standard) and vanillin standard were obtained from Aldrich Chemical Co. (Milwaukee, Wisconsin).

Tenax TA absorbent, 60-80 mesh was obtained from Alltech Associates, Inc. (Deerfield, Illinois). Chromosorb W-HP 60/80 mesh (used as chromatographic support) and silanized glass wool were from Sulpelco, Inc. (Belefonte, Pennsylvania).

Sample preparation: Silanized glass-lined stainlesssteel desorption tubes (3.0 mm i.d. x 10 cm) were packed with a 2 cm bed volume of Tenax-TA adsorbent between plugs of silanized glass wool. The tubes were conditioned by passing helium through them at a rate of 40 ml/min while heating from 50°C to 320°C at a rate of 10°C/min with a 1hour minimum hold at the upper limit.

Chromosorb W-HP was used as an aid during the sample milling operation, to prevent loss of flavor and caking up of resinous matter in the beans. The Chromosorb material was heat treated in a nonconvectional oven at 180°C for 8 hours to remove any volatiles present. Pooled homogenates of the vanilla bean samples were cut into 0.5 cm long bits and equal amounts (5 g) of cut beans and baked-out Chromosorb were milled (15-20 sec) by a temperature-controlled micro mill (Bel-Art Products, Pequannock, New Jersey) to obtain homogeneous samples. Prior to sample weighing and milling, the mill case and head were frozen in a bed of dry ice.

Prepared vanilla/Chromosorb homogeneous samples (10 mg) were then weighed into the desorption tubes above the Tenax adsorbent bed and plugged with silanized glass wool. The sample loaded desorption tube was spiked with 10 μ g of 2,6-dimethoxyphenol as the internal standard by injecting 1.0 μ l of a methanol stock solution (10 mg/ml) using a solvent flush technique to ensure quantitative delivery.

Direct thermal desorption-gas chromatography: The model TD-1 short path thermal desorption unit (Scientific Instrument Services, Inc., Ringoes, New Jersey) was placed directly on the injection port of the gas chromatograph for direct desorption of sample volatiles into the GC injection port and column. This short path of sample flow eliminates transfer lines which are easily contaminated by samples in previous desorption systems. The sample loaded desorption tube is then injected into the GC and thermally desorbed for 5 minutes at 220°C.

A Varian 3400 Gas Chromatograph was used. It was equipped with a capillary column (DB-1, 60 m x 0.32 mm i.d., 0.25 μm film thickness, J & W Scientific, Folsom, California). The injector and detector temperatures were 250°C and 325°C, respectively, with a split ratio of 1:100. The column was temperature programmed from -20°C (held for 5 minutes during the thermal desorption interval to achieve cryofocussing) to 40°C at a rate of 10°C/min, then to 280°C at 4°C/min and held for 30 minutes at the upper limit. Helium was used as a carrier gas with a flow rate of 1.0 ml/min.

The GC experiments utilized a flame ionization detector (FID) and chromatograms were recorded and processed

using a Varian 4290 integrator and a VG Multichrom chromatographic data system. Retention indices data were obtained by injecting a C_5 - C_{26} paraffin standard⁴ with the same analytical conditions as the samples.

DTD-GC-Mass spectrometry: DTD-GC-MS analyses were conducted with the same conditions as stated above for DTD-GC, but the end of the GC capillary column was inserted directly into the ion source of the mass spectrometer via a heated transfer line maintained at 280°C. The mass spectrometer was a Finnigan-MAT 8230 high-resolution double-focussing magnetic-sector instrument.

The mass spectrometer was operated in the electron ionization (EI) mode, scanning masses 35-350 once each second with a 0.8 second interscan time. The mass spectrometric data was acquired and processed using a Finnigan-MAT SS 300 data system. All mass spectra obtained were background-subtracted and library-searched against the National Institute of Standards and Technology (NIST) mass spectral reference collection.

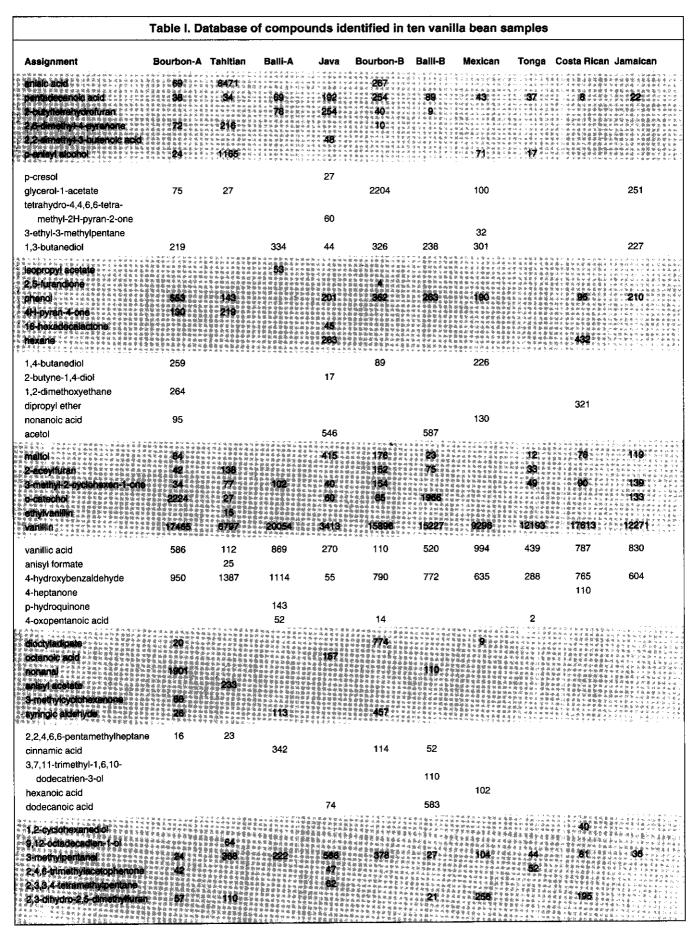
Development and operation of the database: The acquired data from the DTD-GC-MS of all ten bean samples were initially entered into Microsoft Excel on an Apple Macintosh SE. The Excel data was then exported to Foxbase (a Macintosh database package). A small program was written in the Foxbase language to sort all compounds for their Chemical Abstract (CAS) numbers, because this number is unique to individual compounds.

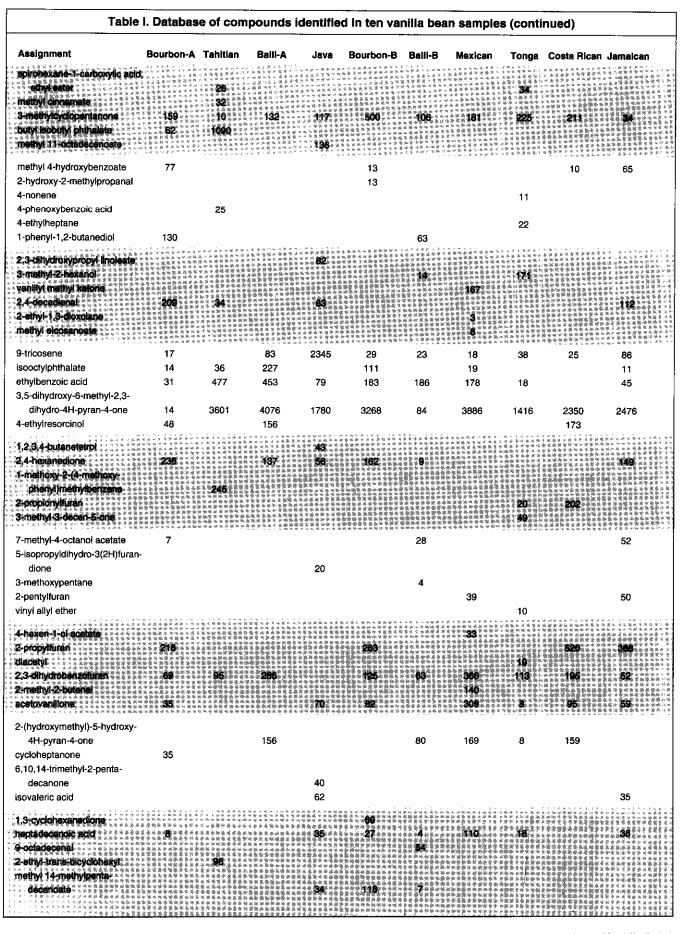
The next step was to populate the database with (+) and (-) for presence and absence of individual compounds, respectively. Then a program was written to print data from the database, and another was written to scrub the data and test the accuracy of CAS numbers. As a follow up, another program was written to apply individual concentration values to each bean type.

Results and Discussion

Bourbon-A, Bourbon-B, Bali-A, Bali-B, Mexican, Tonga and Jamaican beans all have a deep dark brown color with a shiny/oily appearance free of warts and blemishes. Bourbon-A, Bourbon-B, Bali-A, Bali-B and Mexican beans have a rich clean and delicate vanilla aroma. All samples have no apparent frosting of vanillin crystals. Tahitian beans were much darker with a noticeable flowery/perfumery note. The Java beans were much lighter in color, mostly "cuts" with some splits, with dry smoky/woody notes and a less characteristic vanilla aroma. The Costa Rican beans are generally close in color to Bourbon-A and Bourbon-B, but of less thickness and visual appeal.

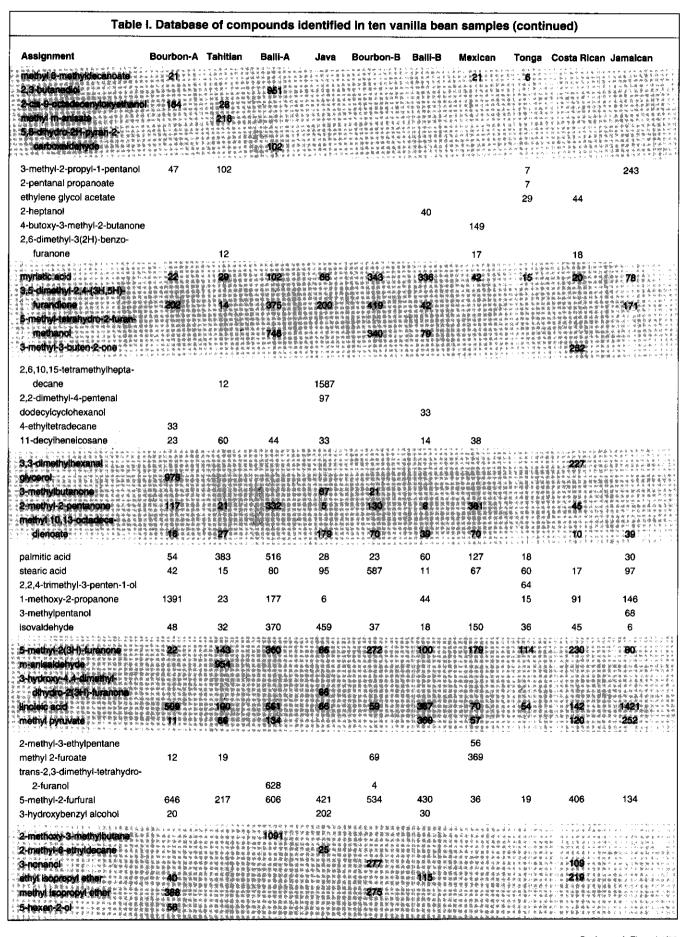
Ten different samples of vanilla beans from varied geographical origins were characterized. The identification and concentration of volatile compounds from various beans are listed in Table I. The identification was accomplished by searching the library database of the National Institute of Standards and Technology (NIST) mass spectral collection, or using published literature and data.⁵⁻⁷ The concentration values reported for the identified compounds in this study Vol. 18, March/April 1993





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are semi-quantitative. These semi-quantitative estimates are based on peak integration comparisons to that of the internal standard. No corrections were made to account for differences in individual detector response factors toward the internal standard in all these compounds, except for vanillin, anisyl alcohol, furfural, furfuryl alcohol, 4hydroxybenzaldehyde, anisic acid and vanillic acid.

The sugar content of vanilla beans is in the 7-20% range.⁸ Kleinert⁹ reported glucose and fructose as the main sugar constituents and sucrose is only present in small quantities. The identification of furanoids and pyranones such as 3,5-dimethyl-2,4 (3H,5H)-furandione, angelica lactone, 4H-pyran-4-one and 3,5-dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one in this study suggested that the dehydration and thermal degradation of sugars occurred in vanilla beans either during the bean fermentation process or some of them may have formed as a result of the desorption temperature employed in the direct thermal desorption analysis.

Acetic acid was found at very high concentrations in all the beans analyzed, ranging from a low of 270 ppm in the Tonga beans to a high of 1,515 ppm in the Tahitian beans. This is in agreement with 0.02% acetic acid reported by Klimes and Lamparsky.¹⁰

Bourbon-A: A total of 83 volatile compounds—including acids, alcohols, esters, aldehydes, ketones, heterocyclic compounds and aliphatic hydrocarbons—was identified from Bourbon-A vanilla beans. Most of the compounds identified (such as vanillin, vanillic acid, acetic acid, formic acid, furfural, furfuryl alcohol, 5-methyl-2-furfural, 5hydroxymethyl-2-furfural, *p*-anisyl alcohol, 4-hydroxybenzaldehyde, methyl 4-hydroxybenzoate, propyl 4hydroxybenzoate, syringic aldehyde and acetovanillone) are well-known contributors to the typical vanilla aroma.^{2,10-12} However, compounds such as 3-methylpentanal, 2-propylfuran, 2,5-dimethyl-2,3-dihydrofuran, 5-methyl-2(3H)-furanone, methyl 2-furoate and 4H-pyran-4-one have not previously been identified to the best of our knowledge.

Tahitian: Contrary to our findings for the Bourbon-type vanilla beans, in the beans of Tahitian origin only 67 compounds could be identified. Vanillin, *m*-anisaldehyde, 4-hydroxybenzaldehyde, *p*-anisyl alcohol, anisic acid, 4-hydroxybenzoic acid, vanillic acid and methyl *m*-anisate were found to be distinguishing character compounds for Tahitian beans in this study. This agrees with results of earlier investigators.^{8,9,13-21} On the other hand, acetic acid, 3-methyl-2-pentanone, 3-methylcyclopentanone, methyl pyruvate, anisyl acetate, acetylfuran, methyl furoate, 5-methyl-2(3H)-furanone, 3,5-dimethyl-2,4-(3H,5H)-furandione, 2,6-dimethyl-4H-pyran-4-one and 3,5-dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one are reported here for the first time as Tahitian vanilla volatiles.

Anisyl alcohol, anisaldehyde, piperonal, 4hydroxybenzaldehyde and anisic acid are well-known characteristic compounds in distinguishing Tahitian vanilla from other species and cultivars.^{13,14,16,20} The fact that these volatile compounds contribute so much to the aroma of Tahitian vanilla invalidates the suggestion by Purseglove et al.⁸ that the differences in volatile composition between vanilla bean species are quantitative rather than qualitative.

Piperonal (heliotropin) has been reported in Vanillin tahitensis both as a minor component⁹ and as a relatively abundant component.²¹ It is conspicuously absent in our investigation of the Tahitian bean, and this absence can only be attributed to the crop-to-crop and/or botanical variations typical of agricultural products. Another explanation for its absence in our study is the fact that we have essentially worked on the vanilla beans as they were received from commercial suppliers, while the studies in which piperonal has been found were done on the vanilla extracts. There is a substantial possibility that this compound was produced during the ethanolic extraction and aging of the vanilla extracts.

Bali-A: With respect to the Bali-A bean type, a total of 55 compounds was identified. These included acids, alcohols, esters, aldehydes, ketones, heterocyclic compounds and high-molecular-weight hydrocarbons. Reports on the flavor volatiles of Bali vanilla beans per se are nonexistent. Vanillin, furfural, furfuryl alcohol, 4-hydroxybenzaldehyde, cinnamic acid, 4-hydroxybenzoic acid and vanillic acid identified in the Bali-A samples are all well-recognized primary and secondary contributors to vanilla aroma.¹⁰

Java: A total of 71 compounds was reported in the Java beans. Except for the Tahitian beans, the Java beans are clearly different in visual appearance and volatile constituents. In Table I, we have reported 18 compounds unique to the Java bean profile. These include 2,2-dimethyl-3-butenoic acid, octanoic acid, 16-octadecalactone, *p*-cresol, 4,4,6,6tetramethyltetrahydro-2H-pyran-2-one, 3-methyl-4-ethyl-2,5-furandione and 3-hydroxy-4,4-dimethyldihydro-2(3H)furanone. These compounds have been reported as important contributors to wood smoke aroma.²² Their prevalence and occurrence in the Java bean is due to the use of wood smoke in autoclaves as in the Mexican method of bean curing.

In the present study, Java beans have shown the lowest concentration (ca. 0.34%) of vanillin in all the bean types examined. This is not surprising as Java beans have been reported to have the widest vanillin content variability. Purseglove et al.⁸ reported that these beans in fact have a reputation for a rather higher average vanillin content, but high and low values have also been reported by Hoover²³ and Martin et al.²⁴ The obvious explanation for this discrepancy is a far-reaching occurrence of the crop-to-crop variation widespread in agricultural products,²⁵ and the adequacy of the attention otherwise paid to the curing of these beans.

Bourbon-B: There exist only very subtle differences in the Bourbon-A beans as compared to the Bourbon-B vanilla beans. A total of 69 compounds was identified in the Bourbon-B bean type. The vanillin concentrations for these beans were 1.75% and 1.50% for Bourbon-A and Bourbon-B, respectively.

From information retrieved from the database generated in this study, seven compounds were found to be unique to the Bourbon-B vanilla beans. These seven are 2,5-furandione, 2-hydroxy-2-methylpropanal, 1,3cyclohexanedione, 13-methyl-oxacyclotetradecane-2,11dione, pyruvaldehyde, methyl acetate and 2-cyclohexyleicosane.

Bali-B: In the Bali-B type vanillins, 67 volatile compounds were reported, most of which occur in the other bean types discussed earlier. However eleven compounds were found to be unique to the Bali-B vanillin beans. These eleven included butanone, 3-methoxypentane, 2-heptanol, 9-octadecenal, allyl octadecanoate and tetrahydro-2-furfuryl acetate.

Mexican: Sixty-one compounds were identified in the Mexican beans. They had the major vanilla flavor compounds characteristic of good quality beans such as Bourbon and Bali beans. An obvious difference is the surprisingly low amount of vanillin (ca. 0.93%) which does not correspond with the average of 2.0% reported by Purseglove et al.⁸ and by Heath.²⁶

The aroma of the Mexican beans has been described as sharp, slightly pungent, sweet, spicy and tobacco-like.²⁶ Among compounds that have been found to be unique to the Mexican beans are hexanoic acid, vanillyl methyl ketone, methyl eicosanoate, 4-butoxy-3-methyl-2-butanone and methoxymethyl acetate.

Tonga: Nine of 55 compounds listed in Table I for Tonga beans are present only in these beans. They are 4-nonene, 4-ethylheptane, 3-methyl-3-decen-5-one, vinyl allyl ether, diacetyl, 2-propanal propanoate, 2,2,4-trimethyl-3-penten-1-ol, 2,6-dimethyl-4-ethyl-4-heptanol and 2-hydroxy-3-methyl-2-cyclopenten-1-one.

Costa Rican: Fifty-three compounds were identified in the Costa Rican beans. Most of the compounds listed have been found in the other beans, with the exception of dipropylether, 4-heptanone, 1,2-cyclohexanediol, 3-methyl-3-buten-2-one, 3,3-dimethylhexanal, methyl hexyl ether, eugenol and 1-acetyl-2-hydroxy-5-methylbenzene.

Jamaican: A total of 52 compounds was identified in the Jamaican beans out of which only 3-methylpentanol and 4-butoxy-1-butene were found to occur only in the Jamaican type bean. The vanillin content of approximately 1.2% is in agreement with an earlier report by Purseglove et al.⁸

Conclusion

The appealing characteristic vanilla flavor and aroma is made up of a wide variety of organic compounds, mostly aldehydes, ketones, acid, alcohols, esters, ethers, long-andshort-chain hydrocarbons, oils, waxes and resins.

In the highly competitive commercial environment which exists in the flavor industry in general and the vanilla trade

in particular, where selection for predetermined quality requirements in vanilla products is crucial, a database that would identify geographical source and indicate bean quality would be an expedient in flavor quality control and assurance.

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