Chemical Characterization of *V. pompona* Scheide, Part II

Vanilla pompona is resistant to climate change and diseases, and therefore is preferred for hybridization with *V. planifolia*. Its chemical characterization was carried out in a series of experiments, described in this second of four parts.

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Editor's note: *This article is the second in a series of four describing the chemical characterization of* Vanilla pompona*. GC-MS and DTD-GC-MS were carried out in Part I to determine its quality as a source of aromatic compounds. In addition, some results were disclosed. Here, additional results are presented and overall findings discussed. Part III will set up the GC-O/MS protocol used to further characterize the extract, while Part IV will conclude the results and describe how the chemical distribution of* V. pompona *impacts its odor profile.*

Alcohols

Twenty alcohols were identified in the *V. pompona* extract. The high level of anisyl alcohol coincides with levels reported in all previous studies using different analytical methods.[1, 4, 6, 21] Similarly, the high concentration of anisyl alcohol has been considered an identifying element of *V. tahitensis*.[4, 20]

Also present in this extract at 0.15% was the compound *tert*-amyl alcohol, which was found in Bourbon and Ugandan vanilla (*V. planifolia*) at very low levels by Zhang and Mueller,[13] utilizing the AMDIS deconvolution program. Another constituent, 3,4 dimethoxybenzyl alcohol (veratryl alcohol), present at a significant level of 0.52% in this extract, was found previously using DTD-GC-MS in cured beans of an unknown wild vanilla species from Peru.[6, 9]

Newly identified in this vanilla is the compound 2-methyl-3-buten-2-ol (0.01%), which is also naturally occurring in bilberry, cardamom, cherimoya, coffee, cranberry, mango, lemon, lavender oil, black currant and hops. Likewise, the compound *trans*-3-penten-2-ol (0.01%) has not previously been reported in vanilla—although its ketone counterpart, *trans*-3-penten-2-one, possibly produced by the oxidation of this alcohol, was reported by Klimes and Lamparsky[11] and Zhang and Mueller[13] in Bourbon vanilla species.

Esters

Eighteen esters were identified in the *V. pompona* extract. Among them, ten were long chain fatty acid esters. These were most likely produced as a result of the long chain fatty acids in plant material, and alcohols in extracts. The presence of the esters anisyl acetate at 1.22% and anisyl formate at 0.69% can be considered a fingerprint of this species, as in *V. tahitensis*, because these are absent or present only at trace concentrations in *V. planifolia*.[20] In addition, the compound *p*-anisaldehyde was present in the extract at 3.26%, as well as anisyl acetate and anisyl formate at 1.22% and 0.69%, respectively. These are also characteristic anisic compounds of the aroma of *V. tahitensis*.[20]

The presence of these characterizing aromatic compounds confirms that the volatile profile of *V. pompona* resembles *V. tahitensis* rather than *V. planifolia*, which agrees with previous observations. Here, amyl formate also is reported in vanilla for the first time, at a trace level of 0.001%. This is a naturally occurring component in strawberry, honey, prickly pear and tomato.

Heterocyclic Compounds

Eleven heterocyclic compounds were identified in this study. Furanoids and pyrans may have formed from the thermal degradation of sugars caused by the desorption temperature (250°C) used during GC analysis of the sample.[18, 19] The compounds 2-acetylpyrrole and lactone dihydroactinidiolide also were found; these had previously been reported by Klimes and Lamparsky[11] in *V. fragrans* of an unknown origin. Also identified in this extract was the compound 2-furfurol, which was previously reported in Madagascar *V. pompona*[6] and *V. planifolia*.[13] Ethyl pyrazine at 0.03% was found in this vanilla as well, reported here for the first time.

Carbonyls, Aldehydes and Ketones

Twelve aldehydes and 13 ketones were identified in this *V. pompona* extract. Among them, the compound 2-heptenal, found at 0.19%, was tentatively identified by Perez-Silva et al.[12] and confirmed as present in *V. planifolia* species by Toth.[14] The compounds *trans*-2-nonenal and *cis*-3-nonenal had not been previously identified in vanilla pods but they are naturally occurring in cucumber. Likewise, the compounds *trans*-2-octenal and 2-butenal, newly identified in this study, are natural occurring in cherry, apple, honey, guava, tomato, carrot, citrus fruits and other natural products.

The compounds piperonal (CAS# 120-57-0, CAS Name: 1,3-benzodioxole-5-carboxaldehyde) and coumarin (2H-1-benzopyran-2-one) were not found in this chemical characterization of *V. pompona* extract, under the conditions of this study. This confirms the results of Ehlers and Pfister,[22] from the analysis of vanillons.

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Ethers

Benzyl ethers, produced from phenyl aldehydes and alcohols, contribute to the overall character of vanilla flavor.[23] In this extract of *V. pompona*, only the ether *p*-methylanisole (*p*-cresyl methyl ether) was identified, and this has not previously been reported in vanilla. Comparatively, Lee[6] reported methyl hexyl ether as the sole ether present in *V. pompona* from Madagascar. These findings are in contrast with a greater abundance of ethers reported in the other two species; e.g., vanillyl methyl ether, vanillyl ethyl ether, *p*-hydroxybenzyl methyl ether and *p*-hydroxybenzyl ethyl ether were reported in cured beans of *V. planifolia*.[11, 23] The compounds *p*-cresyl isopropyl ether, anisyl ethyl ether and anisyl methyl ether have been reported in *V. tahitensis*.[24, 25]

Aliphatic Acids

A total of 13 fatty acids (FA) were found in this *V. pompona* extract. Among them, 10 were saturated fatty acids (SFA). Acetic acid is a typical constituent of cured beans of commercial vanilla and usually is the most abundant acid. However, in this study, the fatty acid fraction, i.e., caproic acid and pelargonic acid, was the most abundant. The fatty acid composition in cured beans of vanilla has been proposed as a key to discriminate among vanilla species and the curing method used.[20]

Volatiles Extracted by DTD-GC-MS

A total of eighty volatiles and semi volatiles were identified in the cured beans of *V. pompona* by DTD-GC-MS. The volatile profile is made up of the following nine chemical classes, by percentage of abundance: 17 acids at 38.51%; 14 heterocyclic compounds (mainly furans) at 34.81%; 10 hydrocarbons at 2.07%; 7 phenols at 9.0%; 7 alcohols at 5.32%; 7 carbonyl aldehydes at 4.93%; 7 carbonyl ketones at 3.39%; 3 acetals at 1.04%; and 8 esters at 0.88%.

T-3 shows the most abundant volatiles, expressed in g/100 g of cured beans of *V. pompona*, were: linoleic acid at 0.74%; hydroxy methyl furfural at 0.66%; 5-hydroxy-5,6-dihydromaltol at 0.43%; vanillin at 0.28%; palmitic acid at 0.20%; anisyl alcohol at 0.14%; acetic acid at 0.14%; and 2-furfural at 0.12%. The remainder of compounds were present at levels < 0.1 g/100 g cured beans.

Fifteen compounds reported in this study were previously found by Lee[6] in *V. pompona* from Madagascar. Among the remaining constituents, twelve have not previously been reported in vanilla; these are listed in **T-4**. Finally, neither piperonal nor coumarin were found in the cured beans of *V. pompona* under the conditions of this DTD-GC-MS study.

Aliphatic acids were the most abundant chemical class in the cured beans of *V. pompona*. Long chain fatty acids, high

T-3. Volatile compounds in cured beans of *V. pompona* as measured by GC column 0.32 mm x 60 m x 1 µm df

No.	Ret.Time	Compound Name	CAS #	Area %	~ppm
Chemical group: Acids; Area percentage = 38.51%					
1	25.04	linoleic acid	60-33-3	21.57	7,428
2	23.17	palmitic (hexadecanoic) acid	057-10-3	5.81	2,000
3	5.57	acetic acid	64-19-7	4.13	1,423
4	9.37	lactic acid	50-21-5	2.32	797
5	4.95	formic acid	64-18-6	1.94	668
6	18.97	isovanillic acid	645-08-9	1.09	374
7	10.93	acetic acid	064-19-7	0.57	196
8	17.11	p-anisic acid = 4-methoxybenzoic acid	100-09-4	0.39	135
9	10.51	caproic (hexanoic) acid	142-62-1	0.28	98
10	21.99	pentadecanoic acid	1002-84-2	0.1	36
11	20.92	myristic (tetradecanoic) acid	544-63-8	0.07	25
12	24.03	capric (decanoic) acid	334-48-5	0.07	24
13	19.77	homovanillic acid	306-08-1	0.05	18
14	18.61	lauric (dodecanoic) acid	143-07-7	0.05	17
15	13.33	benzoic acid	65-85-0	0.03	12
16	13.4	caprylic (octanoic) acid	124-07-2	0.03	9
17	16.08	valeric (pentanoic) acid	109-52-4	0.01	4
Chemical group: Heterocyclics, i.e, furans, pyrans; Area percentage = 34.81%					
18	14.78	5-(hydroxymethyl)-2-furfural	67-47-0	19.18	6,606
19	13.29	5-hydroxy-5,6-dihydromaltol	28564-83-2	12.68	4,368
20	14.36	2(5H)-furanone	497-23-4	0.9	311
21	13.6	3,4-dimethyl-2,5-furandione	766-39-2	0.5	173
22	10.17	2-hydroxyfuraneol = 2,4-dihydroxy-2,5-dimethyl-3(2H)-furanone	10230-62-3	0.47	162
23	13.79	5-hydroxymaltol	1073-96-7	0.27	93
24	9.1	2(5H)-furanone	497-23-4	0.21	71
25	11.93	5,6-dihydromaltol = 3-hydroxy-2-methyl-5,6-dihydropyran-4-one	38877-21-3	0.18	62
26	9.86	5-methyl-2-furfural= 5-methylfurfural	620-02-0	0.17	57
27	11.78	2,5-furandicarboxaldehyde	823-82-5	0.09	30

T-3. Volatile compounds in cured beans of *V. pompona* as measured by GC column 0.32 mm x 60 m x 1 µm df (Cont.)

No.	Ret.Time	Compound Name	CAS #	Area %	~ppm
28	15.44	5-acetyl-2-furfurol	55087-82-6	0.05	16
29	8.95	2-acetylfuran	1192-62-7	0.04	14
30	12.51	maltol = corps praline	118-71-8	0.04	14
31	33.24	3-pentyl-5-methyldihydro-2(3H)-furanone		0.03	11
Chemical group: Alcohols; Area percentage = 5.32%					
39	15.06	anisyl alcohol	105-13-5	4.14	1,427
40	8.18	3-furfurol	4412-91-3	0.48	164
41	30.84	stearyl alcohol	112-92-5	0.28	96
42	10.98	2-furfurol	98-00-0	0.22	76
43	12.19	1-butanol	71-36-3	0.07	23
44	7.2	2,3-butanediol II		0.04	15
45	11.07	benzyl alcohol	100-51-6	0.04	13
Chemical group: Carbonyls, aldehydes; Area percentage = 4.93%					
46	7.47	2-furfural	98-01-1	3.57	1,229
47	29.44	*cis*-9-octadecenal	56554-35-9	0.51	177
48	16.28	p-hydroxybenzaldehyde	123-08-0	0.32	109
49	14.5	p-anisaldehyde = 4-methoxybenzaldehyde	123-11-5	0.23	78
50	6.79	hexanal	66-25-1	0.18	64
51	15.4	E2,E4-decadienal	25152-84-5	0.11	38
52	9.73	benzaldehyde	100-52-7	0.01	4
Chemical group: Carbonyls, ketones; Area percentage = 3.39%					
53	31.7	*cis*-20-nonacosene-2,4-dione	305805-40-7	1.52	524
54	8.44	4-cyclopentene-1,3-dione	930-60-9	1.23	422
55	9.29	2-hydroxy-2-cyclopenten-1-one	10493-98-8	0.23	80
56	30.21	nonadecane-2,4-dione	16577-69-8	0.23	79
57	7.28	4-hexen-3-one	2497-21-4	0.12	42
58	17.8	apocynin = acetovanillone	498-02-2	0.05	17
59	15.44	2-acetyl-5-methylthiophene	13679-74-8	0.02	6
Chemical group: Hydrocarbons; Area percentage = 2.07%					
60	4.5	heptane	142-82-5	1.01	347
61	27.9	pentacosane	629-99-2	0.2	68
62	26.23	octadecane	593-45-3	0.19	64
63	30.47	squalene	111-02-4	0.16	56
64	29.46	tricosane	638-67-5	0.15	50
65	32.25	1-eicosene	567-04-0	0.14	48
66	30.93	tricosane	638-67-5	0.12	43
67	27.08	heneicosane	629-94-7	0.06	21
68	28.7	eicosane	112-95-8	0.04	13
69	20.03	cadalene	483-78-3	0.01	3
Chemical group: Other, i.e., acetals, unknown; Area percentage = 1.04%					
70	11.31	acetoin propyleneglycol acetal	94089-23-3	0.44	152
71	31.75	benzaldehyde dimethyl acetal	1125-88-8	0.39	136
72	22.76	vanillin 1,2-glyceryl acetal I	85377-00-0	0.07	25
Chemical group: Esters; Area percentage = 0.88% of abundance					
73	8.57	methyl pyruvate	600-22-6	0.36	123
74	6.68	methyl acrylate	96-33-3	0.2	68
75	30.45	anisyl palmitate		0.13	44
76	24.37	methyl linoleate	112-63-0	0.09	32
77	16.81	anisyl acetate	104-21-2	0.07	24
78	6.23	butyl formate	592-84-7	0.07	24
79	15.62	anisyl formate	122-91-8	0.06	21
80	25.33	anisyl salicylate	72845-81-9	0.03	12

T-4. Selected compounds newly identified as present in cured beans of *V. pompona*

Compound	Selected natural sources*
1,4-dimethoxybenzene	Cherimoya, menthe, papaya, tea
dimethoxy-methylbenzene (benzaldehyde dimethyl acetal)	Rhubarb
1-octadecanol	Acerola, apple, rice, cherimoya, gooseberry, guava, beef, cheese, milk and pork
2-acetyl-5-methylthiophene	Beef, coffee, krill and pork
butyl formate	Apple, cloudberry, cheese, strawberry and bread
methyl acrylate	Cashew, apple and pineapple
methyl pyruvate (methyl 2-oxopropionate)	Arctic bramble, honey and *Mangifera* species
1,2-benzenediol	Apple, barley, berry, cocoa, coffee and honey

molecular weight hydrocarbons, waxes, resins and tannins minimally contribute to the aroma of *V. pompona*, but serve as fixatives and help to control the release of volatiles.[18, 19]

Furan compounds, particularly hydroxymethylfurfural, were the second most abundant chemical class identified in cured *V. pompona* beans using DTD-GC-MS. These types of compounds also are generated by thermal degradation of the glucose due to the high thermal desorption temperature;[6, 18, 19] thermal degradation also produces a relatively high abundance of formic acid, acetic acid, furfurals and furfuryl alcohols.[26]

In terms of quantification, the percent of vanillin in the cured beans of this Mexican *V. pompona* using DTD-GC-MS analysis was 0.28% w/w, which is near the levels of commercial vanilla, i.e., between 0.3% and 3.4% w/w.[27, 28] However, this level of vanillin was lower than expected for this species, compared with previous results of 2.3% vanillin in *V. pompona* from Madagascar,[6] and levels of 2.33–5.71% reported in ripe fruits of Peruvian *V. pompona* by Maruenda et al.[1]

The 0.14% content of anisyl alcohol in these beans is in agreement with the level reported by Ehlers and Pfister[4] in *V. pompona* of unknown origin. Similarly, Maruenda et al. reported[1] high levels of anisyl alcohol, 1.05–7.13%, using nine-month-old fruits of Peruvian *V. pompona*. In contrast, under similar analytical conditions, the level of this compound reported by Lee[6] in *V. pompona* beans from Madagascar was a much lower 0.041%.

Important phenols such as *p*-hydroxybenzoic acid and vanillic acid, previously reported as present in *V. pompona*,[4] were not identified in this study. Vanillic acid, reported by Lee[6] at a level of 1,011 ppm, also was not found but two isomers were identified: 18 ppm of homovanillic acid, previously reported in vanilla, and 374 ppm of a newly reported compound: isovanillic acid (3-hydroxy-4-methoxybenzoic acid), for which no standard was available. The compound *p*-hydroxybenzaldehyde was found at a level of 0.01%, in contrast with the level of 0.35% reported in *V. pompona* from Madagascar.[6]

Despite *p*-anisaldehyde being the most abundant aldehyde found in the *V. pompona* extract, the level obtained using DTD-GC-MS in cured beans was very low: 0.0078% w/w. This level is lower than the 0.03% w/w obtained by Ehlers and Pfister using HPLC.[4] The compound *p*-anisaldehyde was not mentioned in the Peruvian uncured fruits studied by HPLC-DAD,[1] nor previous work using cured beans from Madagascar.[6] This difference in levels of *p*-anisaldehyde between the extract and cured beans is probably due to reactions of aromatic aglycones with alcohol organic solvents, which can lead to the formation of additional aromatic aldehydes in the extract; these do no occur in dry fruits.

Another characterizing compound, *p*-anisic acid, was present at level of 135 ppm in the cured beans. This level is higher than the 39 ppm reported by Lee in the Madagascar sample using DTD-GC-MS;[6] however, this is lower than the 400 ppm level reported by Ehlers and Pfister using HPLC.[4] It is well-known that the origin of the beans and the curing method play a role in the differences of volatile composition.

Two novel anisic compounds, anisyl palmitate and *p*-anisyl salicylate, were identified in *V. pompona* beans at levels of 44 ppm and 12 ppm, respectively. These were previously isolated from wild vanilla beans from a Peruvian rainforest using the same analytical method.[6, 29]

Differences in the concentrations of volatiles found in this study versus previous reports are not surprising. Similar differences are found among samples of different origins in commercial vanilla. The source of this variability is explained by the different origin of the beans; different farming practices; harvesting time; curing methods; and the varying sensitivities of the analytical methods used for studies.[26]

An additional cause of variation specific to this species was proposed by Maruenda et al.,[1] who found that *V. pompona* has a particular physiology in its formation of glycosides (aroma precursors). The glycosides in this species develop mostly at the late stages of ripening. This means 8-9 months of growth are required in order for its fruits to accumulate significant levels of aromatic glycosides, while the aroma precursors in the fruits of *V. planifolia* species build up progressively. In relation, a common and well-known practice in Mexico is to pick all the beans at the same time in December, without considering the heterogeneity of their ripeness.

Additional constituents of *V. pompona* were identified directly from cured beans using DTD-GC-MS, although they were not found using organic extraction. These include the phenolic compound 1,2 benzenediol, and high molecular weight wax compounds called β-diketones—i.e., 20-nonacosen-2,4-dione and the "tentative" compound nonadecane-2,4-dione. β-Diketones are common constituents of plant waxes and commonly found in commercial vanilla species.[6, 29]

Here, the compound 4-cyclopentene-1, 3-dione also was found in the extract by GC-MS and DTD-GC-MS, in both the beans and extracts, which concurs with the study by Lee[6] of *V. pompona* from Madagascar. Isovanillic acid

(3-hydroxy-4-methoxybenzoic acid) and 3-furfural (3-hydroxymethyl furfural) were found in vanilla beans for the first time, as well as other compounds, reported in Part I of this series.

The volatile profile of *V. pompona* obtained by liquid injection would be expected to differ from the volatile profile using direct analysis of the cured beans, as far as number of compounds and their chemical group distribution. Ethanol is a reactive solvent that modulates the vanilla flavor and produces an additional range of aromatic compounds as a result of reactions with the aglycones present in the cured pods. On the other hand, direct thermal desorption systems evaluate the volatiles produced by heating the beans directly, resulting in the desorption of a wider range of high boiling-point compounds and furanoids thermally degraded from the plant material.

Conclusions: Parts I and II

One hundred and twenty three volatile and semi volatile compounds were identified here in a *V. pompona* aqueous ethyl alcohol extract by means of liquid injection to GC-MS. Eighty volatiles were identified using DTD-GC-MS. Twenty six compounds were newly identified as present in this vanilla; however, these compounds are present in natural ingredients.

The volatile profiles of *V. pompona* by GC-MS and DTD-GC-MS were similar to cultivated *V. tahitensis* and *V. planifolia* species in terms of the identity and abundance of chemical classes, as well as number of compounds. In particular, this species presented the typical chemical distribution of natural vanilla beans, containing a high concentration of vanillin as well as anisyl alcohol followed by many compounds at trace concentrations.

The presence of high amounts of anysil alcohol indicate the overall profile of *V. pompona* more closely resembles the aroma of *V. tahitensis*, compared with the aroma compounds in *V. planifolia*, which is in agreement with previous observations. The relative abundance of anisic compounds and presence of two novel anisic compounds—i.e., anisyl palmitate and *p*-anisyl salicylate—is characterizing of the quality of this vanilla species. Coumarin or piperonal, ingredients regarded in the past as either naturally present or as adulterants in this species, were not found in this sample.

Finally, the expected range of eliciting aroma compounds that make commercial vanilla species so valued in the global market were also present in this vanilla, and the complexity and quality of its composition is comparable to the most recognized *V. tahitensis* and *V. planifolia* species. Therefore, *V. pompona* could be used as a novel source of aromatic compounds for use in fragrance applications.

Follow along in Part III of this series as the author uses gas chromatography-olfactometry (GC-O) analysis to investigate the extent to which each of these chemicals impacts the overall odor quality of *V. pompona*.

Editor's note: *References here are either a continuation from Part I or are numbered the same as they appeared in Part I.*

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