WHITEPAPER

BROOKS APPLIED LABS

Detection of Vanillin Adulteration Utilizing both Bulk Carbon Isotope Analysis and Compound Specific Isotope Analysis

Natural vanillin derived from vanilla beans is the second most expensive spice in the world (after saffron) and is widely used in the food and perfume industries. The synthetic version of vanillin is significantly cheaper and easier to produce, making natural vanillin a potential target for adulteration.

The stable carbon isotopic composition of vanillin, denoted as δ13C, differs between synthetic and natural vanillin, such that carbon isotope analysis can be used to distinguish between the two. The natural range of vanillin δ13C values is -14‰ to -22‰ VPDB while synthetic vanillin and natural vanillin not derived from vanilla beans has a δ13C range of -38‰ to -27‰ VPDB.

Method

Fifteen commercially available vanilla products and one pure vanillin standard (Thermo Scientific) where purchased. The products include 4 vanilla extracts, 5 pure ground vanilla bean samples, 3 samples of ground vanilla mixed with dextrose, 1 vanilla paste with seeds, and 2 multiple ingredient vanilla products, one of which included imitation vanilla.

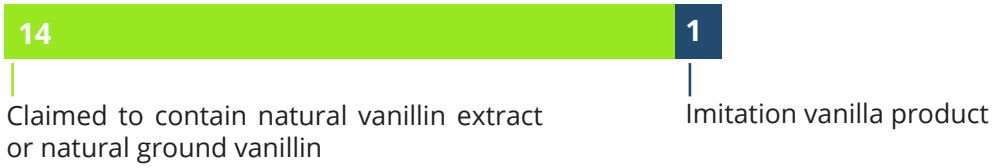
Vanillin was extracted from vanilla extract samples following the method of (Perinni et al., 2019). Three milliliters of sample were mixed with 3ml diether ether, the ether phase was collected, dried and reconstituted in ethanol. Three powder products were dissolved in a 3.5ml ethanol 6.5ml water mix and extracted by the same method, as was the vanilla paste sample. One of the ground vanilla powders was partially dissolved in the same ethanol-water mixture and vanillin was extracted from it.

Extracted vanillin dissolved in ethanol was analyzed using a Trace 1310 GC connected to a GC Isolink II coupled to a Delta V Plus Isotope Ratio Mass Spectrometer by a Conflo IV interface (GC-C-IRMS). Vanilla powders were also analyzed in bulk using an Elemental Analyzer coupled to a Delta XL Plus (EA-IRMS).

Results

Of the 15 samples analyzed in this study, 14 claimed to contain natural vanillin extracted from vanilla beans or natural ground vanillin. Our analysis indicates that 4 of these products did not contain natural vanilla-bean-derived vanillin. These include 3 identical powder products from a single manufacturer (but different LOT#) and one liquid product. All pure vanilla bean extracts and 4 of the 5 single-ingredient vanilla bean powders appeared authentic. One powder had a δ13C value slightly higher than the expected range (-11.0‰) which may indicate adulteration. The imitation vanilla product and the vanillin standard contained synthetic vanillin, as expected. The results are summarized in Table 1.

Claimed Authenticity



Analytical Findings

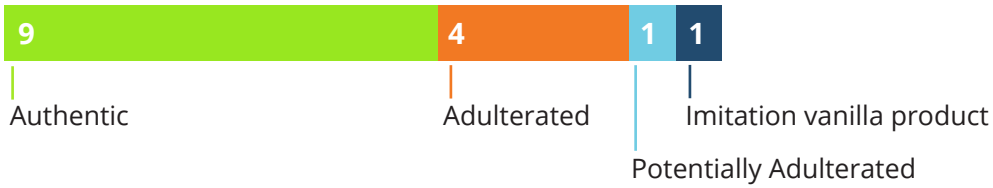


Table 1. Results of carbon Isotope analysis

Sample Information					Compound Specific GC-IRMS		Bulk Powder Measurement EA-IRMS
ID	Brand	Type	Country	Ingredients	$\delta^{13}C$ VPDB (‰)	SD	$\delta^{13}C$ VPDB (‰)
VN1	A	pure vanilla extract	-	vanilla bean extractives in water, alcohol (35%)	-17.73	0.25	-
VN2	B	pure vanilla extract	-	vanilla bean extractives in water and alcohol	-17.89	0.10	-
VN3	C	vanilla extract	Madagascar	water, organic alcohol, extractives of organic Madagascar vanilla beans	-17.93	0.11	-
VN4	D	pure ground vanilla	Madagascar	organic ground Madagascar vanilla beans	-18.37	0.22	-15.76
VN5	E	pure powder vanilla	Madagascar	dextrose, finest vanilla beans	-27.13	0.91	-26.37
VN6	E	pure Madagascar vanilla powder	Madagascar	tapioca dextrose and Madagascar vanilla bean extractives	-27.75	0.18	-26.3
VN7	F	pure Madagascar ground vanilla	Madagascar	organic Madagascar Bourbon vanilla beans	-	-	-16.04
VN8	G	vanilla bean powder	Madagascar	100% Madagascar vanilla bean powder	-	-	-11.01
VN9	H	vanilla bean powder	-	vanilla beans	-	-	-16.17
VN10	I	true vanilla bean powder	Madagascar	Whole vanilla bean powder	-	-	-18.78
VN11	K	imitation vanilla flavor	-	water, propylene glycol, vanillin, caramel color, 0.1% sodium benzoate, phosphoric acid, and ethyl vanillin	-28.64	0.07	-
VN12	K	baking vanilla with pure vanilla extract	-	water, sugar, glycerin, vanilla extract (water, alcohol, extractive of vanilla beans), alcohol, natural flavors, fruit juice (color)	-30.33	0.11	-
VN13	L	Vanilla extract	-	vanilla bean extractives in water, alcohol, corn syrup	-18.08	0.25	-
VN14	K	pure vanilla bean paste with seeds	-	organic pure vanilla extract (water, organic alcohol, organic vanilla bean extractives), organic sugar, water, organic vanilla bean seeds, Tragacanth gum	-18.40	0.11	-
VN15	E	pure powder vanilla	Madagascar	tapioca dextrose and finest vanilla bean extractives	-27.49	0.94	-26.15
VN STD	Thermo Scientific	Standard, solid	-	vanillin 99%	-29.42	0.11	-29.36

Samples highlighted in green appear to be authentic vanilla bean derived. Samples highlighted in orange appear to be either synthetic vanillin or natural vanillin which is not derived from vanilla beans. The sample highlighted in blue appears to exhibit potential adulteration.

Conclusions

This study demonstrates that carbon isotope analysis is an effective tool for vanilla authentication. Four commercially available products from two brands of the fifteen analyzed were mislabeled as authentic vanilla bean, highlighting the prevalence of adulteration. Using a simple extraction method and GC-C-IRMS vanillin was successfully isolated from solid and liquid samples, including samples with multiple ingredients, and analyzed, showing the versatility of the method.

References

Perini, M., Pianezze, S., Strojnik, L., & Camin, F. (2019). C and H stable isotope ratio analysis using solid-phase microextraction and gas chromatography-isotope ratio mass spectrometry for vanillin authentication. Journal of Chromatography A, 1595, 168-173.

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