Divanillin

Novel Taste-Active Component of Fermented Vanilla Beans

The elucidation of the fate of vanillin during the traditional curing process

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The transition of the elegant blossom of the vanilla orchid into the green vanilla bean and the subsequent conversion of this into the traditionally cured brown vanilla bean have captivated generations of scientists. The flavor industry, in particular, is especially interested in understanding the formation of the typical vanilla flavor complex from the tasteless precursors that are present in the green bean, and much effort has gone into the analysis of the volatile components of the cured brown vanilla bean.[1]

Of specific interest to us was the elucidation of the fate of the vanillin during the traditional curing process, once it has been liberated via endogenous enzymatic hydrolysis of the corresponding glycoside, glucovanillin. It is known that physical losses occur during a number of the steps that are inherent to the traditional fermentation and drying process, and chemical losses occur via oxidative conversion into structurally related materials during the monthlong curing process.[2] Other chemical losses are due to its participation in the Maillard reaction, a process that gives the cured beans their typical dark brown color.[3]

At a glance …

Peroxidase efficiently catalyzes the dimerization of vanillin. The product, divanillin, can be detected in cured vanilla beans at the ppm level. Divanillin itself displays very interesting taste properties and positively influences creamy, fatty mouthfeel notes.

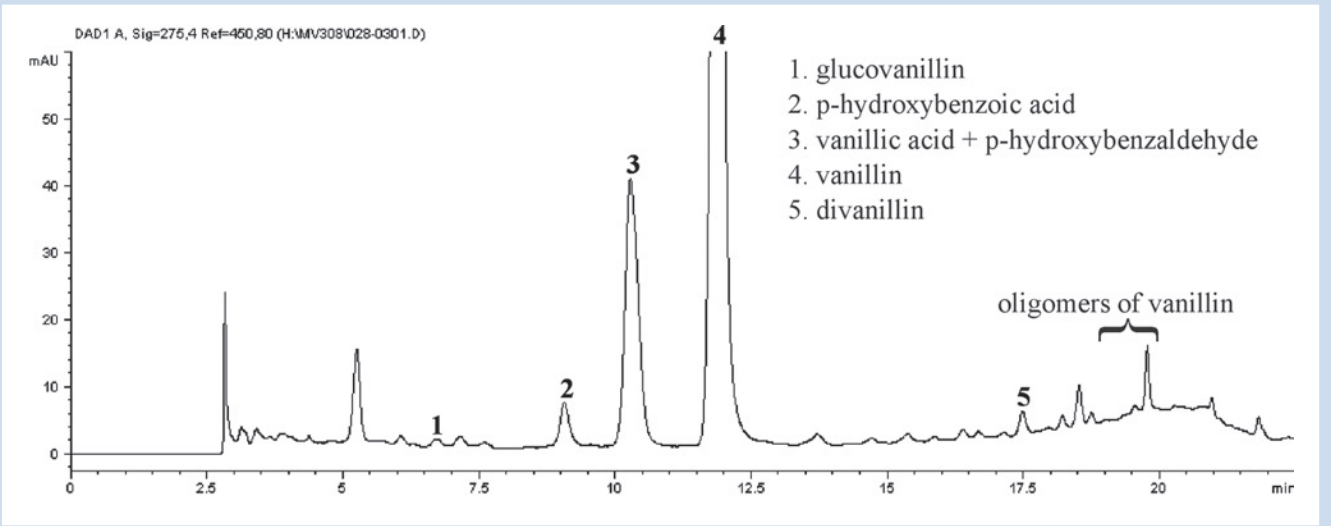
Results and Discussion

Specific interest in both the higher molecular weight and the more polar components that are present in traditionally fermented vanilla beans led us to perform HPLC analyses on various Symrise vanilla extracts under somewhat different conditions (F-1) compared to those normally used when the five key components — glucovanillin, vanillin, p-hydroxybenzaldehyde, vanillic acid and p-hydroxybenzoic acid — are routinely analyzed.

Analysis via GC/MS of those peaks that eluted after vanillin indicated the presence of oligomers of vanillin in these vanilla extracts. The peak eluting at approximately 17.5 min was unequivocally shown, via NMR after preparative, chromatographic isolation, to be divanillin. Other peaks that eluted after divanillin were identified as being higher oligomers of vanillin, but their exact chemical structures have not yet been elucidated.

Some commercially available vanilla extracts also were analyzed for the presence of divanillin, as were fermented beans obtained directly from Madagascar, Mexico and Tahiti. Certainly not all the samples that were investigated contained divanillin, and the highest

HPLC chromatogram of a Symrise vanilla extract manufactured from Madagascan beans (RP-18 nucleosil; water/acetic acid/methanol gradient; 1 mL per min; 40°C) **F-1**



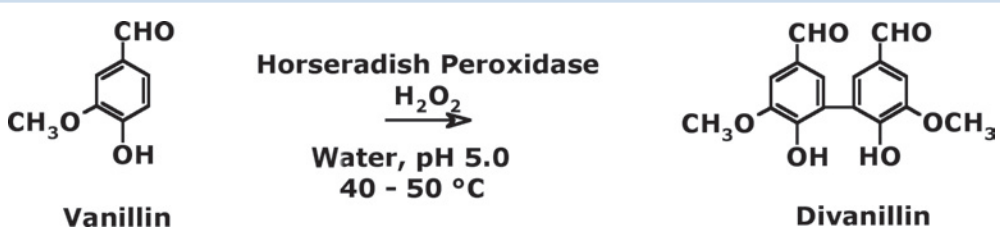
Divanillin content of some vanilla extracts **T-1**

Origin of beans	Solvent	Divanillin (ppm)	Comments
Madagascar	Ethanol / H_2O	170	internal, Symrise products
Mexico	Ethanol / H_2O	90	
Tahiti	Ethanol / H_2O	30	
Madagascar	Ethanol / H_2O	0	commercially available products
Madagascar	Ethanol / H_2O	170	
Madagascar	CO_2	0	

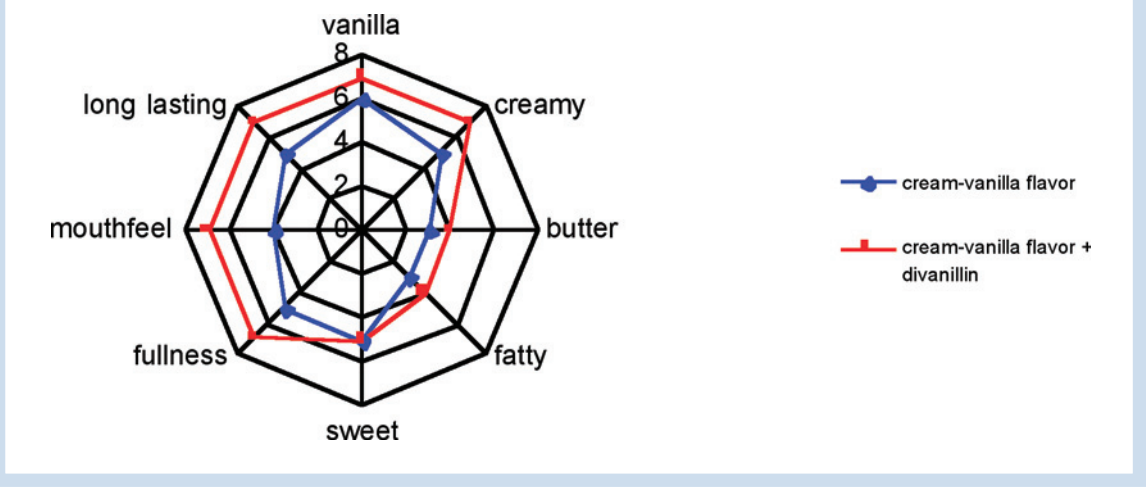
concentration determined was some 170 ppm (T-1). Numerous trials were performed to ensure that the divanillin was not an artifact formed during the extraction process and the analysis.

The dimer and higher oligomers of vanillin have not been previously reported as being naturally present in vanilla beans. We assume that divanillin is formed in the plant tissue during the curing process as a direct result of the action of peroxidase upon the vanillin that is present in the bean. This hypothesis seems plausible because it has been recently shown that peroxidase surprisingly survives the complex processing of the green beans in the field, and the enzyme is still active in the resulting fermented and cured product.[4] The in vitro dimerization reaction of vanillin (F-2) has been known for some years and

Dimerization of vanillin catalyzed by horseradish peroxidase **F-2**



Spider web diagram showing the effect of divanillin upon the sensory properties of a cream — vanilla flavor **F-3**



can be exploited to produce natural or nature identical divanillin on a preparative scale.[5,6]

The in-depth sensory evaluation of divanillin showed it to have very interesting and novel properties. At low concentrations in the region of 5-50 ppm, divanillin not only positively influences the creamy, fatty properties of the tested flavor, but also significantly improves the mouthfeel properties and fullness of the foodstuff containing the flavor (F-3). Typical applications for divanillin are in flavors designed for application in reduced-fat versions of products such as yogurt, ice cream, ultrahigh temperature-treated milk, instant desserts and the like.

Acknowledgments

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References

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