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Odor-active compounds of Tahitian vanilla flavor

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ABSTRACT

Gas Chromatography–Olfactometry was performed on Tahitian vanilla extracts in order to highlight its flavor specificity. The results stressed that Tahitian vanilla flavor was very rich. 61 odorant zones were identified, 38 of them were attributed to an odor-active component. Among them, anisaldehyde and guaiacol were found to be the key flavor compounds of Tahitian vanilla. They were representative of the predominant "spicy-anise" and "phenolic" odor families. Moreover, three cultivars of Tahitian vanilla were characterized thanks to their GC–O profile, highlighting the diversity existing among Tahitian vanilla flavor, and providing prospects for valorizing them as well.

1. Introduction

Tahitian vanilla, formerly called *Vanilla tahitensis* and recently proposed being renamed *Vanilla ×tahitensis* because of its hybrid origin (Soto Arenas & Dressler, 2010), is esteemed throughout the world for its subtle flavor. Indeed, Tahitian vanilla exhibits a very typical flavor compared to other vanillas, mainly linked to strong anise and floral notes. This flavor is the result of the specific aroma composition of green beans combined with the ancestral Polynesian curing method. As a consequence, Tahitian vanilla flavor is unique in the global market and prized for luxury applications such as gastronomy and perfumery (Lepers-Andrzejewski, Brunschwig, Collard, & Dron, 2011).

Some characteristics of Tahitian vanilla that differentiate it from other vanillas have been extensively studied and seem to be well documented: i) morphological characteristics, ii) chemical characteristics iii) and more recently cytogenetic characteristics (Lepers-Andrzejewski et al., 2011). These studies specify the existence of around 14 cultivars in French Polynesia. Among them, Tahiti and Haapape morphotypes are the most cultivated in French Polynesia since ages because they exhibit interesting agronomic characteristics such as high productivity, relative indehiscence and good sensory properties such as high flavor content (Lepers-Andrzejewski et al., 2011). Moreover, another cultivar called Parahurahu is particularly interesting mostly not only because of its atypical anise-like and floral flavor but also because it shows an atypical pod morphology with a shape of bludgeon (Lepers-Andrzejewski et al., 2011).

The chemical composition of Tahitian vanilla has been extensively analyzed by HPLC and GC–MS so as more than 200 compounds have been identified in *V. ×tahitensis*, mainly volatiles and semi-volatiles including odor-active as well as non odor-active compounds. Among all the identified compounds in Tahitian vanilla, some of them are able to play a role in Tahitian vanilla flavor: aromatic carbonyl and aromatic ester compounds (Adedeji, Hartman, & Chi-Tang, 1993; Black, 2005; Da Costa & Pantini, 2006; De Rovira, 2007; Fayet, Tisse, Guérère, & Estienne, 1987; Hartman, 2003; Larcher, 1989; Rey, Carbonel, & Van Doorn, 1980; Scharrer, 2002; Sostaric, Boyce, & Spickett, 2000), aliphatic carbonyl compounds (Adedeji et al., 1993; Black, 2005; De Rovira, 2007; Hartman, 2003; Lechat-Vahirua & Bessiere, 1998) and monoterpens (Scharrer, 2002).

Actually, identifying key components responsible for organoleptic characteristics of Tahitian vanilla is an important issue i) to better describe this specific flavor, and ii) to better valorize it compared to other vanillas. Surprisingly, few studies (and even none in the case of *V. ×tahitensis*) have been undertaken to identify which compounds are really odor-active in vanilla flavor. To our knowledge, only two studies focused on odor-active compounds in vanilla, using GC–Olfactometry which is an analytical method aiming at targeting key compounds of a complex extract. A first study performed by Dignum, Van der Heijden, Kerler, & Verpoorte (2004) mentioned that four phenolic compounds, namely guaiacol, p-cresol, creosol and 2-phenylethanol

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had a high odor-impact in *V. planifolia* flavor, but without specifying neither the methodology used nor the descriptor associated to the compounds. A second study, more complete, was performed by Pérez-Silva et al. (2006) on *V. planifolia* flavor, stressing the complexity of its flavor, with the identification of 26 odorant zones.

The aim of the present study was to perform such GC–O analysis on Tahitian vanilla flavor for a better characterization.

2. Material and methods

The adopted methodology in this study included four steps:

i) first, in a preliminary GC–MS study, the selection of the most appropriate extract for GC–O analysis purpose
ii) then, the determination of the best method for Tahitian vanilla GC–O analysis between CHARM (Combined Hedonic of Aromatic Response Measurement) and OSME (Odour Specific Magnitude Estimation)
iii) the identification of impact character compounds in Tahitian vanilla flavor
iv) the comparison of flavor characteristics of three Tahitian vanilla cultivars: Haapape, Tahiti and Parahurahu.

2.1. Vanilla samples

Vanilla pods (500 g) of each cultivar of *V. ×tahitensis* (Haapape, Tahiti, and Parahurahu) were harvested at full maturity in the shadehouse of the "Etablissement Vanille de Tahiti", on the island of Raiatea (French Polynesia). The vanilla pods were then cured regarding the traditional Polynesian curing method in order to obtain around 50% moisture vanilla pods (Lepers-Andrzejewski et al., 2011). Vanilla samples were composed of 25 g of cured vanilla pods, used for extraction and analysis.

2.2. Obtaining extracts

A preliminary study was undertaken to select the most appropriate extract for GC–O analysis. In a previous GC–O study of *V. planifolia* carried out by Pérez-Silva et al. (2006), only solvent extracts were evaluated by GC–MS analysis. Among those solvent extracts, the pentane/ether extract was found to be the most representative of vanilla. Different organic extractions of one cultivar, namely Haapape, were therefore performed in this work: dichloromethane maceration giving organic and aqueous phases; ethanolic extraction, as well as a Simultaneous Distillation Extraction, which is commonly used in flavor analysis (Chaintreau, 2001).

The four different vanilla extracts were then analyzed by GC–MS to determine which method was the most suitable for further GC–O analysis. Once the SDE proved to be the most suitable method for Tahitian vanilla flavor analysis (see Section 3.1), only SDE was performed on Tahiti and Parahurahu samples. All the extracts were stored at low temperature (4 °C) prior to analysis.

2.2.1. Dichloromethane maceration

Vanilla pods (25 g of Haapape cultivar) were chopped and extracted with dichloromethane (150 g) and distilled water (400 g) under sonication for 1.5 h. The aqueous phase was reextracted three times for 10 min with dichloromethane (50 g). Organic phases were dried over anhydrous sodium sulfate and concentrated at 2 mL. Aqueous phases were extracted three times with diethylether (50 mL), dried over anhydrous sodium sulfate and concentrated at 2 mL.

2.2.2. Ethanolic extraction

Vanilla pods (25 g of Haapape cultivar) were chopped and extracted in a rotary evaporator at 60 °C with 60° ethanol (100 mL) for 8 h.

2.2.3. Simultaneous Distillation Extraction

Volatile vanilla compounds were extracted using a micro Simultaneous Distillation-Extraction (SDE) apparatus in the configuration suitable for heavier than-water solvent, a water bath, and a minichiller. Chopped vanilla pods (25 g of each cultivar Tahiti, Haapape and Parahurahu) were placed in a 100 mL round-bottom flask with 50 g of purified water linked to the appropriate arm of the SDE apparatus. A 5 mL vial containing 2 mL of dichloromethane was linked to the other arm of the SDE apparatus. The separation chamber was filled with 2 mL dichloromethane and with 2 mL of distilled water. The sample was heated at 100 °C and simultaneously extracted by dichloromethane heated in a water bath at 40 °C for 2 h. The condensation was assured by the circulation of ethanol at −10 °C. The organic extract was then dried over anhydrous sodium sulfate and concentrated at 2 mL.

2.3. Gas chromatography–olfactometry analysis (GC–O)

For the first time, GC–O analysis was performed on Tahitian vanilla flavor. Two GC–O analysis methods were evaluated on the selected Haapape SDE extract: CHARM analysis, which is a dilution method and OSME analysis, which is a direct intensity method.

Analyses by GC–O were conducted on a 6890 GC (Agilent Technologies, Massy, France) equipped with a FID detector, a sniffing port "Sniffer 9000" (Brechbühler Scientific Analytical Solutions, Grand-Lancy, Swiss), a HP-7683 Series Injector using a HP-1 (polymethylsiloxane, J & W Scientific) column (50 m × 0.32 mm × 0.52 μm).

The oven temperature was set as described hereinafter: from 40 °C to 130 °C at 2 °C/min, then from 130 °C to 250 °C at 4 °C/min and held at 250 °C for 50 min. Helium was used as the carrier gas at a constant flow rate of 1.5 mL/min. 1 μL of samples was injected in the splitless mode at 250 °C. The split ratio between sniffing port and FID was 3/1. The temperature of the FID and the sniffing port were 250 °C. Retention indices were determined by calculation within a range of alkanes used as standards, starting from C5 to C28.

Table 1
Distribution of descriptors used by the GC–O sniffers into the seven odor classes characterizing Tahitian vanilla flavor.

Odor classes		Odor descriptors
Phenolic		Smoky, phenolic, vanilla-bean like, burnt, almond, caramel, hazelnut, toasted, animal, leather
Spicy-anise		Anise-like, spicy, fresh, clove, cinnamon, almond
Floral		Floral, rose, fruity, honey
Aldehyde	Fatty	Fat, oily, wax, cooking fat, green, aldehyde, leather, olive
	Fruity	Orange, green, grass, geranium, melon, fat, floral, hay
	Chocolate	Chocolate, aldehyde
Butter		Butter, cheese, fruity, animal, unpleasant
Sulfury		Meat, burnt, bacon, cooked potato, cabbage-like
Earthy		Mushroom, metallic
Undefined		Plastic, ether, glue, gas, fresh, soap, hazelnut, cooked