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Table 103.1 Predicted Dietary Exposure (mg/d) to Linalool and Linalyl Acetate via Consumption of Earl Grey Tea Prepared by Hot Water Infusion (3 min.) of a Tea Bag (2g) containing the Median and the 97.5th Percentile Amounts, respectively, Determined for 50 Earl Grey Teas Purchased in the EU

<table>
<thead>
<tr>
<th>Tea Consumption</th>
<th>Linalyl Acetate [mg/d]</th>
<th>Linalool [mg/d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ml/L] cups (at 200 mL)</td>
<td>median 97.5th perc.</td>
<td>median 97.5th perc.</td>
</tr>
<tr>
<td>mean 415 ~ 2</td>
<td>0.2 0.6</td>
<td>4.2 15.2</td>
</tr>
<tr>
<td>97.5th perc. 1286 ~ 6</td>
<td>0.5 1.8</td>
<td>13.2 47.1</td>
</tr>
</tbody>
</table>


samples with extreme outliers which might be of relevance for consumers exhibiting "product-loyalty."

Combining (i) the analytically determined median and 97.5th percentile values, (ii) the observed transfer rates of flavoring substances upon hot water infusion, and (iii) tea consumption data allows an estimation of the dietary exposure to flavoring substances via consumption of Earl Grey teas (Table 103.1).

The linalyl acetate example demonstrates that there may be structure-dependent differences in stability between flavoring substances resulting in varying degrees of degradation (e.g. formation of hydrolysis and rearrangement products) during processing. The rather simple procedure of a hot water infusion shows the need to consider correction factors when estimating actual dietary exposure to flavoring substances via processed foods.

REFERENCES


CHAPTER 104

Aroma-Active Compounds of Capsicum Chinense Var. Biquinho

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104.1 INTRODUCTION

Aroma and, consequently, the composition of volatiles are important quality parameters for peppers and bell peppers from the Capsicum genus [1,2]. The breeding program of cultivated and commercialized peppers in Brazil is made by Embrapa Vegetables (Brasília, Brazil).

Genus Capsicum comprises five species and Capsicumchinense is the one that usually has an extremely strong pungency and aroma [1,3]. The variety called Orange Biquinho, however, presents a strong aroma of pepper without the burning sensation. Its characteristic aroma combined with a sweet flavor and a mild pungency makes Orange Biquinho well appreciated in cooking as a flavoring agent and even as an appetizer. The aim of this work was to evaluate its volatile profile and determine the odor importance of these compounds, looking for markers that could help genetists in obtaining other strains able to add desirable aroma and flavor characteristics to food preparations.

104.2 MATERIALS AND METHODS

Samples of C. chinense var. Orange Biquinho were obtained from accesses of Embrapa’s Vegetable Germplasm Bank (Brasilia, DF, Brazil). The extraction of volatile compounds was made by solid phase microextraction (SPME). DVB/CAR/PDMS fibers were exposed to the headspace of 10g unground, sliced, and crushed mature samples for 45 min. at 65°C in a 40 mL amber glass vial. Gas chromatography-flame ionization detector (GC-FID) analyses were carried out using a Varian CP-3380 GC equipped with a CP-Sil 8 CB
(equivalent to DB-5) (30 m × 0.25 mm i.d. × 0.25 µm f.t.) column (Agilent, Santa Clara, CA, USA). The following instrumental conditions were used: injector at 230°C in splitless mode; He as carrier gas at 1.5 mL/min; oven temperature gradient 50–120°C at 5°C/min, and then to 180°C at 2°C/min.

A Shimadzu GC–2010 (Kyoto, Japan), equipped with a mass spectrometer detector Shimadzu QP–2010 (GC-MS), was used for the identification of volatile compounds. A DB-5 MS (J&W, 30 m × 0.25 mm i.d. × 0.25 µm f.t.) column was used for the separation. Temperature programming and split/splitless injector were the same as used in the GC-FID analyses. Compounds were identified by comparison of mass spectra with those provided by the NIST library, and comparison of retention indices (Kovats) and the elution order of compounds found in the literature [3,4].

A GC-olfactometry (GC-O) was used for the identification of active compounds. Three judges were selected through triangular tests, using different concentrations of a standard solution of ethyl pentanoate (a substance with a strong fruity aroma). The Osmo-olfactometry technique and software of time–intensity data collection (SCIDT) were used to report the quality and intensity of each perceived aroma in triplicates, using an unstructured scale (0 = no odor; 10 = maximum odor intensity). The same chromatographic conditions applied to the GC-FID and Gas chromatography–mass spectrometry (GC-MS) and each analysis was divided in half in order to avoid fatigue to the judges.

104.3 RESULTS AND DISCUSSION

GC-MS detected 62 peaks, out of which 41 (66.1% of peaks) were identified, accounting for 97.5% of the total chromatogram area. Esters (22), terpenes (7), hydrocarbons (6), alcohols (3), aldehydes (2), and ketones (1) were indentified. Alcohols represented 40.0% of the total chromatogram area. This fact can be explained due to the large amount of 3,3-dimethylcyclohexanone in the sample (39.4%), the major compound in C. chinense var. Biquinho and other peppers [1,3]. Compounds in significant quantities (relative area >2%) are pointed out in the chromatogram of Figure 104.1A.

Mono and sesquiterpenes represented 18.2% of the chromatogram relative area, mainly because of α-humulene (peak 43) and β-cubenene (peak 36). Non-identified compounds (n.i.) corresponded to one third of the detected peaks (21), but they represented only 2.5% of the total area.

Judges perceived 75 odor peaks, of which 14 were detected without the records from the instrumental detectors and were referred to as “not detected” (n.d.) and named with small letters. Aromagram (Figure 104.1B) was divided into regions according to the importance of odor compounds: The first region covers low odor importance compounds, corresponding to the range of odor intensity from zero to 3.75; the second region covers the moderate intensity compounds (values between 3.75 and 6.25); and the third region includes compounds with highest odor importance, comprising intensity values from 6.25 to 10. This last region showed 13 peaks: isohexanol (peak 3), p-xylene (peak 9), hexyl isobutanoate (peak 17), (Z)-3-hexenyl pentanoate (peak 24), heptylisobutanoate (peak 32), α-himachalene (peak 40), α-cardanol (peak 50), four n.i. compounds (peaks 10, 12, 53, 55), and two stimuli related to n.d. compounds (peaks “h” and “k”). Highest importance compounds accounted for only 5.7% of the GC-FID area.

With regard to odor description, four compounds were described with “pepper” or “spicy” notes: hexyl isobutanoate, (Z)-3-hexenyl pentanoate and n, i. peaks 10 and 12. Isohexanol, p-xylene, heptylisobutanoate, and peak 55 (n.i.) were reported in the class of “green” and “citrus” notes. Compounds α-cardanol and peak 53 (n.i.) were described with “floral”
notes, while α-himachalene as “woody,” peak “h” as “unpleasant,” and peak “k” as “toothpaste.” We also detected 30 peaks corresponding to moderate intensity compounds (19.3% of FID area), 7 of which were detected only by GC-O. Most of the compounds detected in this range (n = 10) were described as “pepper” and “spicy” like hexyl isobutanoate (peak 15), squalene (peak 48), and a.n.i. terpene (peak 44).

Most of the compounds (75%) identified in Orange Biquinho were detected in the low intensity range, including the major compound 3,3-dimethylcyclohexanol (“fried, onion”). In this range, a total of 29 peaks were detected and the majority was described by “pepper or spicy” (38%) and “floral” (31%) notes.

Upon comparing Orange Biquinho with other C. chinense peppers it is possible to see quantitative and qualitative differences. Despite presenting a profile that is characterized by large amounts of esters, as commonly observed for this species [1,3], the esters’ relative area in the chromatogram of Orange Biquinho was only 22.7%. Compounds like α-cardanol (0.74% of chromatogram area), detected in this work with a strong floral note, were not found in other C. chinense peppers [1,3]. Hexyl isopentanoate, with a characteristic aroma of pepper, is usually described as one of the main components in volatile species C. chinense, with more than 10% of chromatogram area [3], while in Orange Biquinho this ester represented only 3.45% of the area.

104.4 CONCLUSION

Orange Biquinho presented a significant amount of compounds described as “sweet” and “pepper-like” notes. With respect to compounds of high odor importance, α-cardanol, heptylisopentanoate, p-xylene, isohexanol, hexyl butanoate, (Z)-3-hexenyl pentanoate, and four non-identified compounds may be potential markers for the sweet and mild pepper flavor of Capsicum chinense var. Biquinho. A future effort must be carried out in order to identify these compounds. Considering the economic value of Capsicum peppers in Brazil, it is possible that in future genetic materials of other chili peppers may have crosses with aromatic peppers, such as the Orange Biquinho, which will improve their sensory characteristics, rendering them more attractive to consumers.

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REFERENCES