

Linalool in green *Coffea arabica* by HS-SPME/GC-MS and HS/GC-IMS



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Introduction

Linalool is one of the key volatile compounds contributing to the aromatic profile of green coffee (1). Although typically present at low concentrations, it is associated with floral and citrus-like notes and may act as an important precursor or marker of coffee quality, varietal differences, and post-harvest processing effects. Linalool can also occur in glycosidically bound forms, where the volatile aglycone is linked to sugar moieties (2). These non-volatile precursors may contribute to the aroma potential of coffee, as linalool can be released during processing, roasting, or enzymatic/hydrolytic reactions, thereby influencing the final sensory profile of the beverage. In green coffee, this monoterpene is generally detected without any significant analytical issues in the headspace using SPME/GC-MS. However, the characterization of green coffee by HS/GC-IMS has evidenced the need for a strategy to detect linalool. In fact, the use of HS/GC-IMS has highlighted that in green coffee the ratio between free linalool and glycosidically bound linalool is very low and it is therefore necessary to invert this ratio in order to detect it without difficulty. In the present study, we address preliminary this topic by examining green *Coffea arabica* samples from three different geographical origins under both non-hydrolytic and hydrolytic conditions (2) by both HS-SPME/GC-MS and HS/GC-IMS.

Experimental

Samples of green wet-processed *C. arabica* from three different geographical origins (2 samples from Ethiopia, 1 sample from India and Colombia) were used. Linalool standard (Sigma-Aldrich, cat. n. W263508, ≥97%, FCC, FG, St. Louis, MO, USA) was used.

In the case of HS-SPME/GC-MS, the headspaces of ground samples (2 g; 2 g + 2 g of H₂O; 2 g + 2 g of H₂O + 1 g of citric acid) in 20 mL vials were adsorbed by a car/pdms 75 µm SPME fiber for 30 minutes at 60°C and then inserted into the injector of a GC/MS (GC7890 coupled with a 5977B MS, Agilent, Palo Alto) at 250°C for 10 minutes of desorption. GC was equipped with a HP5 UI column: 30 m x 0.250 mm I.D. x 0.25 µm film, (Agilent), temperature program was set at 40°C for 3 minutes, then heated at 5°C/min. to 150°C and 20°C/min. to 200°C, followed by the final temperature of 200°C hold for 2 minutes. MS signals were acquired in full scan and SIM mode simultaneously (selected ions 71, 93, 121 and 136).

In the case of HS/GC-IMS (FlavourSpec, G.A.S., Dortmund, Germany) same samples were analyzed under the following conditions: T IMS: 45°C; T GC: 40°C; GC column: MXT 5 column (15m x 0.53mm x 1 µm); T injection port: 80°C; T transfer line: 90°C - 45°C; T oven: 40°C; T stirrer: 60°C; T syringe: 80°C; Conditioning Time 20 min.

Results

HS-SPME/GC-MS analyses (Figure 1) easily detect free linalool in the headspace of green coffee samples under the two non-hydrolytic explored conditions (ground sample and ground sample after water addition) (Figure 2) and under the hydrolytic explored condition (ground sample after water and citric acid addition). In both Ethiopian and other green coffee samples, the linalool response markedly increased after hydrolysis compared with the non-hydrolytic conditions. This trend indicates that only a minor fraction of linalool is present in the free volatile form in the headspace, whereas most of it occurs as bound precursors that can be released upon hydrolysis. Overall, these findings suggest that free linalool accounts for only a small proportion of the total linalool potentially present in the examined green coffee samples.



Fig.1: GC/MS (GC7890 coupled with a 5977B MS, Agilent, Palo Alto)

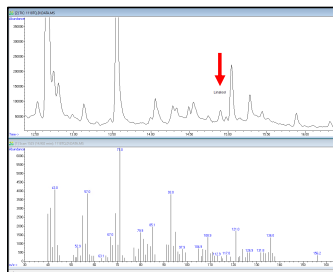


Fig. 2 HS-SPME-GC: *C. arabica* Ethiopia. Linalool in green ground coffee sample acquired in full scan

Surprisingly, as clearly shown in Figures 3, analyses by HS/GC-IMS (Figure 4) carried out on different green coffee samples don't show any signal related to linalool under non-hydrolytic conditions and only under hydrolytic conditions a well resolved linalool spot is evident.

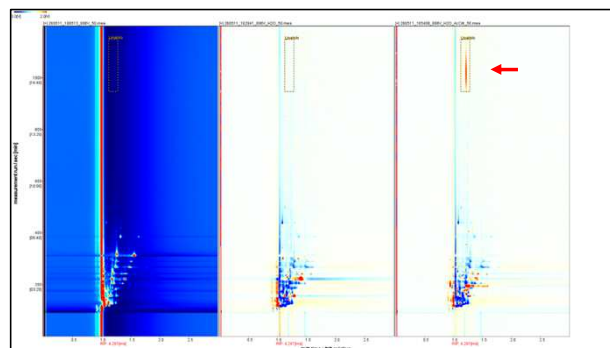


Fig. 3 HS/GC-IMS: *C. arabica* Ethiopia. Left 2 g ground sample; Middle 2 g + 2 g H₂O; Right 2 g + 2 g H₂O + 1 g citric acid.

The sensitivity of HS/GC-IMS appears insufficient to detect the low concentration of free linalool present in the headspace of green coffee. To define the linalool quantification range achievable by HS/GC-IMS, several aqueous linalool standard solutions in a wide range of concentrations were analysed. Based on these experimental data a LOD close to 0.315 µg has been determined. Across the investigated range (1–20 µg), the calibration response exhibits a non-linear behaviour, which is characteristic of IMS detection due to reactant ion depletion at higher mass loads. To account for this curvature, the calibration curve was fitted using a logarithmic regression model ($y = 0.5277 \ln(x) + 0.6097$), yielding a good coefficient of determination ($R^2 = 0.9781$). In Figure 5, for samples from India and Colombia under hydrolytic conditions the linalool content is under the LOD, whereas the 2 samples from Ethiopia shows a linalool content close to 0.4 µg in vial.



Fig.4: GC-IMS (FlavourSpec, G.A.S., Dortmund, Germany)

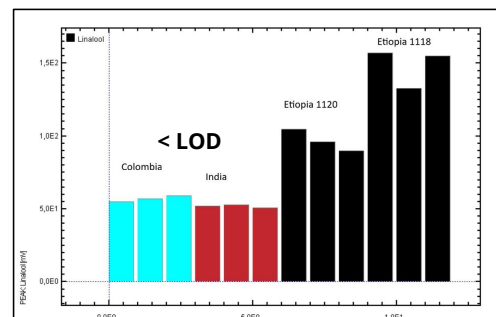


Fig. 5 HS/GC-IMS: Linalool in ground samples 2 g + 2 g H₂O + 1 g citric acid. Triplicate analyses

Conclusion

The present preliminary investigation has put in evidence that the low free linalool concentration in the headspace of green *C. arabica* is challenging to be detected by HS/GC-IMS. This observation may greatly assist in adopting the proper experimental conditions to perform linalool detection and quantification in green coffee. According to the obtained experimental data, the free linalool in the headspace of green coffee is below 0.315 µg and it represents a small fraction of the total linalool present in green coffee beans.

REFERENCES: [1] Flament, I., 2001. Coffee Flavour Chemistry. Wiley & Sons, New York., [2] De Rosso, M., Lonzarich, V., Navarini, L., Flamini, R., 2022, Current Research in Food Science, 5, 336-344

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