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Cocoa profiling from high quality cocoa samples at early stages of technological treatment by two-dimensional comprehensive gas chromatography – mass spectrometry

Federico Magagna1, Erica Liberti1, Stephen E. Reichenbach2, Qingping Tao1, Carlo Bicchi1 and Chiara Cordelloi3

1 Dipartimento di Scienze e Tecnologia del Farmaco, Università degli Studi di Torino, Via Pietro Giuria 9, I-10125 Torino, Italy
2 Computer Science and Engineering Department, University of Nebraska, 1400 R Street, Lincoln, NE, USA
3 GC Image LLC, Lincoln NE, USA

Aim and Scope
Cocoa derives from the cocoa tree (Theobroma Cacao L.) belonging to the Malvaceae family and it is the main ingredient in the production of chocolate. Cocoa is complex in origin, composition and nature, being also made up of simple and complex flavones. The sensory quality of cocoa (aroma, taste, texture) is undoubtedly a key factor in the production of a premium quality product and it can basically affect consumer preferences [5]. Focusing on aroma, about 500 terpenoids (alcohols, carbohydrates, acids, esters, and pyrazines) [2] have been identified and most of them are also abiotic volatiles. The peculiar cocoa flavor arises from complex biochemical and chemical reactions during the post-harvest processing of cocoa beans and, in particular, fermentation and roasting are considered the main steps in the formation of the characteristic cocoa aroma.

This study investigated the characteristic distribution of technologically informed and sensory active volatiles included in the unique profile of “high quality” selections of cocoa (Theobroma Cacao L.) from different origins.

In particular, it proposes an investigation strategy capable to fully exploit the potential of GC-GC-MS combination of SMES and automated fingerprinting approaches, in defining an informative chemical signature of cocoa volatile compounds [3-4] and explains how effective and automated data elaboration might improve food quality evaluation and authentication process.

1. Peak-region feature fingerprinting

Untargeted analysis was performed to extend the comparative process to the entire pattern of detected volatiles from the headspace of cocoa samples. The untargeted fingerprinting was based on the "peak-region feature" approach and implemented by Image Intelligence® in the GC image® software. This data elaboration method was made more informative by considering targeted 30 peaks, included in a targeted template. The strategy enables to preserve all information about known analytes within the fingerprinting. The fully automated procedure of peak-regions fingerprinting delineates a small 2D retention-times window (or region) per peak over the chromatographic plane and it approaches the "low-feature-to-one-analyte" selective topological of peak features methods, with all the advantages of regional features matching.

These advantages include unambiguous cross-detection/matching of trace peaks that may be detected in some samples but not in others and co-eluting analytes that may be resolved in some chromatograms but not in others.

2. Cocoa volatiles profiling/fingerprinting

The resulting 20 Peak volumes derived from GC-GC-MS analysis, referred to the 450 untargeted peak features (untargeted profiling) selected from the headspace of different cocoa samples, are visualized as Heat map in Figure 1. Columns follow the Linear Retention Indices (from left to right) ordered coherently with the polar a-polar column combination. Peak volumes were normalized by dividing by its standard deviation.

Experimental

Cocoa samples

Cocoa samples were collected from different origins (Mali, Ecuador, Venezuela, Colombia, Java, Sao Tomé) and from different technological stages (raw, roasted, steamed, kilned and massed). All samples were previously cleaned and free of foreign elements.

GC-GC-MS platform

Head Space Solid Phase Microextraction (HS-SPME) was run on a B&B GC-MS system (Shimadzu, Kyoto, Japan). The GC was a Super critical Fluid Chromatography (SFC) with mass selective detection (GC-DAD). 2 m, 0.25 mm i.d., 0.25 μm ID, DB-5 column. The oven temperature was programmed from 70°C (2 min) to 240°C. MS was operated in EI mode (70 eV).

Results and Discussion

3. Volatiles distribution across samples of different origin and technological stages

An untargeted multivariate approach (Principal Component Analysis – PCA) was adopted to map the natural formation of samples’ groups and subgroups and to localize informative chemicals responsible of samples differentiation – fingerprinting. The PCA was carried out on 1800 raw volatile target analytes for each of the different samples of cocoa from different origins and at five different technological stages (Figure 2), in total 105 GC-GC-MS runs (three analytical replicates for each sample).

Figure 4 (PCA scores plot) shows the influence of the processing stage on the sub-classification of the samples (Chontalpa samples). PCA carried out on Chontalpa data set shows a sub-classification of the stages raw, steamed, roasted, kilned and massed, with a clear separation between steamed and roasted samples.

Figure 3 (PCA loadings plot) shows how the chocolate volatiles are contributed to each stage of the cocoa processing, with steaming, roasting and kilning as the most important contributors to the overall discrimination.

Conclusions

The volatile fraction of cocoa of different geographical/origin/age and at different technological stages has been characterized by revealing its evolution along manufacturing processing. Furthermore, the current work, using high-resolution GC-GC-MS data mining enables an effective and objective chemical characterization of the product including data as an output. The results have shown how comprehensive and multiplex power of GC-GC-MS with automated data elaboration can be successfully in defining an informative chemical signature of cocoa volatile compounds, which sensory profile is fundamental for high quality foods and economic-value product.

Acknowledgments