



ABSTRACT SUBMISSION FORM

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Fingerprinting of high quality cocoa by two-dimensional comprehensive gas chromatography - time-of-flight mass spectrometry and tandem ionization

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Summary: *Comprehensive two-dimensional gas chromatography (GC×GC) coupled with time of flight mass spectrometry (TOF-MS) is a powerful technique for detailed analysis (profiling and fingerprinting studies) of medium-to-high complexity mixtures of volatiles. In this study the characteristic volatiles fingerprints of “high quality” cocoa are investigated by advanced pattern recognition approaches on MS signals from tandem ionization (70 and 12 eV) detection.*

Keywords: *Theobroma cacao L.; combined untargeted and targeted fingerprinting; comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry and tandem ionization*

1 Introduction

Cocoa, produced from cocoa beans (*Theobroma cacao* L. Malvaceae family), is a crop of great economic relevance as raw ingredient for chocolate manufacturing. Cocoa and chocolate are consumed worldwide and their popularity is related to pleasant sensory properties, although, recent evidences of health benefits open new market perspectives and uses as functionalized food(s) [1, 2].

Theobroma cacao L. is a tree crop native to tropical forests of American continent. Recent studies on cocoa germoplasm [3], defined 10 major genetic clusters or groups, i.e. Marañon, Curaray, Criollo, Iquitos, Nanay, Contamana, Amelonado, Purõs, Nacional and Guiana. This new classification reflects accurately the genetic diversity available and overcomes the traditional in Criollo, Forastero or Trinitario.

Cocoa quality and economic value are related to its unique and complex flavour. The sensory profile (aroma, taste, mouth feeling, and texture) is a key-factor for premium quality products suited to consumer preferences. Flavours develop from complex

biochemical and chemical reactions occurring at post-harvesting and vary with genotype, geographical origin, farming practices, and technological processing [4]. Above all, post-harvest treatments and, in particular, fermentation [5] and roasting [6] are key steps in the formation of the characteristic cocoa aromas.

The present study investigates volatile organic compounds (VOCs) peculiar signatures from commercial grade, high-quality cocoa with novel pattern recognition strategies that combine untargeted and targeted fingerprinting on GC×GC-TOF-MS and tandem ionization (*UT fingerprinting*) [7]. Samples are from different origins and stages of processing. Advanced pattern recognition is tested to validate its effectiveness in highlighting the chemical information encrypted in VOCs signatures. Furthermore tandem ionization data (70 and 12 eV) are mined to explore different issues such as origin/process characteristics and sensory profile(s) quality.

2. Experimental

Samples: cocoa samples were selected by confectionery experts for their peculiar sensory characteristics. Origins: Mexico, Ecuador, Colombia and Sao Tomè (harvest 2015).

Four technological stages: raw, roasted, steamed and nibs after removal of shells. Processing was by hot-air roasting in a Bühler

AG apparatus (Uzwil, Switzerland) by Guido Gobino srl (Turin, Italy) in two batches.

Head Space Solid Phase Micro Extraction sampling: samples were frozen in liquid nitrogen and ground up to 300 µm (Grindomix GM200, Retsch, Haan, Germany); precisely

References

1. Andujar, Recio MC, Giner RM, Rios JR (2012) Cocoa Polyphenols and Their Potential Benefits for Human Health. *Oxid. Med. Cell. Longev.*
2. Ackar D, Lendik KV, Valek M, Subaric D, Milicevic B, Babic J, Nedic I (2013) Cocoa Polyphenols : Can We Consider Cocoa and Chocolate as Potential Functional Food ? *J. Chem.*
3. Motamayor JC, Lachenaud P, da Silva e Mota JW, Loor R, Kuhn DN, Brown JS, Schnell RJ (2008) Geographic and genetic population differentiation of the Amazonian chocolate tree (*Theobroma cacao* L). *PLoS One*. doi: 10.1371/journal.pone.0003311
4. Kongor EJ, Hinneh M, Van De Walle D, Afoakwa OE, Boeckx P, Dewettinck K (2016) Factors influencing quality variation in cocoa (*Theobroma cacao*) bean flavour profile — A review. *Food Res Int* 82:44–52.
5. De Melo Pereira GV, Soccol VT, Soccol CR (2016) Current state of research on cocoa and coffee fermentations. *Curr Opin Food Sci* 7:50–57.
6. Ramli N, Hassan O, Said M, Samsudin W, Idris NA (2006) Influence Of Roasting Conditions On Volatile Flavour Of Roasted Malaysian Cocoa Beans. *J Food Process Preserv* 30:280–298.
7. Magagna F, Valverde-Som L, Ruíz-Samblás C, Cuadros-Rodríguez L, Reichenbach SE, Bicchi C, Cordero C (2016) Combined Untargeted and Targeted fingerprinting with comprehensive two-dimensional chromatography for volatiles and ripening indicators in olive oil. *Anal Chim Acta*. doi: 10.1016/j.aca.2016.07.005
8. Reichenbach SE, Tian X, Tao Q, Stoll DR, Carr PW (2010) Comprehensive feature analysis for sample classification with comprehensive two-dimensional LC. 33:1365–1374. doi: 10.1002/jssc.200900859
9. Reichenbach SE, Tian X, Tao Q, Ledford EB, Wu Z, Fiehn O (2011) Informatics for cross-sample analysis with comprehensive two-dimensional gas chromatography and high-resolution mass spectrometry (GCxGC-HRMS). *Talanta* 83:1279–1288. doi: 10.1016/j.talanta.2010.09.057