A tentative authentication of Parma dry cured ham using stable isotope ratio analyses

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Food characterization is important for the food industry. An increasing number of consumers are concerned about the origin of food products as an indicator of quality. Today many consumers demand high quality products with a clear regional identity.

In 1992 EU legislation came into force providing a system for the protection of regional foods, through the PGI (Protected Geographic Indication) and PDO (Protected Designation of Origin) labels (European Union Regulation (EEU) 2081/92).

The aims of this legislation were: to support diversity in agricultural production, to protect consumers by giving them information on the specific characteristic of the product and to protect product names against fraud and imitation. To achieve this goal, food authorities can rely on paper traceability, and/or physical and chemical analyses.

Parma dry cured ham (PDCH) is a typical Italian product monitored under the Protected Designation of Origin (PDO, Commission regulation (EC) No 1107/96). Its distinctive properties of aroma and taste are due to the long maturing process (12 months).

The aim of the research

To evaluate the usefulness of stable isotope ratio analyses by IRMS, volatile compounds by SPME/GCMS and fatty acids profile for characterizing PDCH samples in order to distinguish them from other types of dry cured ham without designation of origin. SPME was applied to study the volatile compounds in PDCH.

Material and method

Dry cured ham samples

Four Parma dry cured ham (PDCH) samples ripened for one year with protected designation of origin were taken from slices of dry-cured ham supplied by SSICA (Stazione Sperimentale Conserve Alimentari).

SPME extraction

Room temperature was selected as the extraction temperature, in order to prevent possible matrix alteration. At the end of the sample equilibration period (1 h), a conditioned (1.5 h at 280°C) 85 μm Carboxen™/polydimethylsiloxane (CAR/PDMS) StableFlex™ fiber (Supelco) was exposed to the headspace of the sample (8 g) for analyte extraction (3 h) by a CombiPAL system injector autosampler.

GC conditions

Analyses were performed with a Thermo Scientific TRACE GC Ultra equipped with a SolGel-WAX™ column (30 m x 0.25 mm x 0.25 μm), coupled to a quadrupole Thermo Scientific MS DSQ. Oven temperature program was: from 35°C, hold 8 min, to 60°C at 4°C/min, then from 60°C to 160°C at 6°C/min and finally from 160°C to 200°C at 20°C/min. Peak identification was based upon MS spectra in comparison with spectra and retention time of standards.

Fatty acid analysis

Total lipid extraction was carried out according to Bligh and Dyer. The preparation of fatty acid methyl esters was carried out through acid-catalysed trans-esterification with methanolic hydrogen chloride (5%) according to Christie. Fatty acid separation and identification were performed on a Thermo Scientific TRACE GC Ultra, fitted with a flame ionization detector (FID) and equipped with a BPX70 column (120 m x 0.25 mm x 0.2 μm). Fatty acids were identified relative to known internal standards.

Isotopic measurements, standards and equations

δ^{13}C and δ^{15}N values were measured by continuous flow (ConFlo III) elemental analysis isotope ratio.
Room temperature was selected as extraction temperature in order to prevent any artefact formation. The best results were obtained extracting 180 min with CAR/PDMS (85 μm thickness) fiber.

Volatile compounds and fatty acids
89 volatile compounds were identify and quantified in dry cured ham samples. The data was clustered in five series of compounds in order to evaluate the differences between PDCH and ham without designation of origin.

The results showed a good discrimination among PDCH and other typologies based on δ¹³C and δ¹⁵N.

Additionally we measured δ¹⁸O and δ²H and the values showed no overlapping and therefore a complete discrimination was achieved.

The explanation of these results is related to the geographical origin of the samples because oxygen and hydrogen have a strong influence on pedoclimatic conditions.

SPME development and sampling
Different SPME fiber coatings and extraction times were tested to study the volatile profile of dry cured ham samples in order to determine the most suitable condition for further analysis.

Results and discussion

Stable isotope ratio analyses
For isotopic discrimination of samples we analyzed the carbon and nitrogen isotopic ratios of muscle because it integrates isotopic values of food assimilated over a long period (in agreement with some feeding specifications on Parma dry cured ham PDO).

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The total amount of aldehydes detected in muscle showed significant differences between the two groups studied. Higher concentrations of hexanal were found in dry cured ham without designation
of origin. This fact can be related to the presence of higher concentrations of unsaturated fatty acids in the diet. Hexanal is formed by the oxidation of either esterified or free linoleic acid and play an important role in the ham flavour because of its low odour threshold.

A meaningful difference was observed in PUFA concentration between PDO and non-PDO samples. This fact can be explained by the use of some oil in animal feed formulation. It is important to highlight that the PDO scheme only admits the use of cereal.

Table 1. Volatile compounds extracted in PDHC samples and ham without denomination of origin (non-PDO) (ng/g).

**Conclusion**

IRMS proved to be a very effective and straightforward technique in combination with SPME-GC in the establishment of criteria to fight against common PDCH fraud.
References

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Information and support

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