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Original Article

Carotenoid-derived aroma compounds detected and identified in brines and speciality sea salts (*fleur de sel*) produced in solar salterns from Saint-Armel (France)

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ABSTRACT

The flavor compounds of brines and *fleur de sel* collected in solar salterns from Saint-Armel (Brittany, France) were investigated by means of headspace-solid phase microextraction–gas chromatography–mass spectrometry (HS-SPME/GC–MS) analysis in order to find elements to link the salt product and its area of production. A total of 58 volatile compounds were identified with considerable number of apparently carotenoid-derived compounds, i.e. norisoprenoids. Some of these could be considered as tracers to characterize products from Saint-Armel salterns. Indeed, 4 common compounds were detected in the different samples: 3,3,5,5-tetramethyl-cyclohexan-1-one, 4-(2,6,6-trimethyl-cyclohex-1-en-1-yl)-but-3-en-2-ol (β-ionol), 5,5,8a-trimethyloctahydro-2*H*-chromen-2-one and 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-2(4*H*)-benzofuran-1-one (dihydroactinidiolide). At the same time, preliminary studies were conducted to gain knowledge about microorganisms present in solar salterns, such as halophilic microalgae like *Dunaliella salina*, bacteria, fungi or yeasts. Some of these living organisms produce carotenoids, the starting material of some volatiles, and could either be responsible through their metabolisms for the generation of flavor compounds detected. Color attribute C^* of the brine was closely positively correlated with the concentration of *D. salina* in the saline medium, linked to the concentration of viable and cultivable bacteria and highly correlated with the number of norisoprenoids detected.

1. Introduction

Salt (NaCl) has always been consumed by humans and is essential for the health of our cells (water transfer, muscular contraction, pH in stomach) (Kurlansky, 2002). Naturally present in fruits and vegetables (around 20% of daily contributions), added to precooked meals (around 50% of contribution) or directly added to home-made meals (around 30%), salt is consumed more than is advised (between 5 and 10 times more than the recommended 2 g/day) (He and MacGregor, 2003; Brown et al., 2009).

Academic literature is very scarce about the characteristics of salt products used in food. But it is known that salt overconsumption can contribute to the deterioration of health: increased blood pressure, obesity, cardiovascular diseases, and so on (Alderman, 2002; He and MacGregor, 2010). This is the reason why, in many parts of the world, workgroups associating scientists, administrations, agencies, economic actors, and association of consumers were set up to decrease by 20% the population consumption of salt in: (1) proposing implemented measures to respect a statistical distribution of NaCl consumption from 2 to 6 g/day; (2) identifying the salt food vectors; (3) proposing effective recommendations for lowering sodium chloride content in some food vectors; (4) carrying out simulations of salt supply in population; (5) thinking about means to limit consumption of salt (He and MacGregor, 2009).

After an analysis of the situation, these workgroups proposed a set of recommendations to decrease population consumption of salt.

Recommendations are: (1) salt content optimization in food products, that is to say, in food vectors (in particular, those facilitating the risk of excess) but vectors have to stay gustative,

Abbreviations: AU, arbitrary unit; CAR, carboxen; CFU, colony forming unit; CSW, concentrated sea water; DHA, dihydroactinidiolide; DVB, divinylbenzene; EU, European Union; GPS, global positioning system; h, hour; HS-SPME–GC–MS, headspace solid-phase microextraction–gas chromatography–mass spectrometry; LOD, limit of detection; LRIs, linear retention indices; min, minute; NaCl, salt or sodium chloride; ND, not detected; PCA, plate count agar; PDMS, polydimethylsiloxane; PGI, protected geographical indication; RAs, relatives amounts; STD, standard deviation; TSG, traditional speciality guaranteed; UV, ultraviolet.

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technological and safety acceptable and (2) consumers education and information by giving them responsibilities in the control and the management of their salt contribution.

Because of this situation, salt producers, in particular the smallest ones, have had to readjust their products to keep a place on the market. Thus, over the past few years, measures have been taken to diversify commercial offers of producers with standing salt products and products with a guarantee of know-how (i.e. speciality sea salt products) (Arfini, 1999).

Common salt, i.e. table salt, commonly employed in cooking, is cheaper than speciality sea salt obtained by evaporation of seawater in solar salterns. European producers (Michelin, 2009) intend to obtain protected geographical indication (PGI) or traditional speciality guaranteed (TSG) status in order to protect and value coarse salt, ground (fine) salt and *fleur de sel*, based on the quality policy for the products of European Union (EU) agriculture. The PGI associates a product with a region, to confirm its authentic origin whereas TSG highlights the traditional character, either in the composition or means of production.

The recent evolutions of globalization raise the question of the increase of standardization and delocalization of the production of some foods (Pecqueur, 2001). That is why, during food crises, in particular at the end of the nineties (mad cow, chicken diseases such as H1N1 or dioxin, and so on), certificates and labels played part of reassurance for the population (Tavoularis, 2008): quality control label and identification label of origin (e.g. Red Label) provided the consumers a greater legibility of the offer especially in Europe (Tavoularis, 2008; Arfini, 1999). In Europe, consumers are, for example, attracted by high price salt products that could be used in gourmet cooking. Moreover, empirical observation highlighted a concept of revenue linked with territorial qualities, that is to say, combining intrinsic quality of the product and its anchoring in a specific place with its history and its knowledge-to make (Pecqueur, 2001). This observation is worldwide known for all kind of food and the hand-collected products are usually linked, by producers, to an area of production, like olive oil or wine (Pecqueur, 2001; Arfini, 1999).

SPME is a powerful method for the characterization of aroma systems, readily used in quality control and food characterization (Cajka et al., 2009; Flamini, 2007). This is a fast, inexpensive and accurate method, which starts to be used for detection and characterization of volatile compounds from labeled food products with various qualities and/or geographic origins, e.g. honey (different flowers used in one honey) or olive oil (oil from Provence).

Flower of salt is a very specific salt, famous in some parts of Europe, such as in France where it is called *fleur de sel* or in Portugal where its name is *flor de sal*. Specific names are given in other countries and its quality for cooking is recognized worldwide. Its harvest is possible only 3 or 4 months in a year under very specific sun and wind conditions (e.g. between June and August in France). This is the first crystal formed at the surface of the salt pan. Manual harvest conditions of *fleur de sel*, raked like cream on the very top of ponds with specific tools, permits contact between crystals formed and microorganisms of brine. This characteristic allows to differentiate *fleur de sel* and the other types of sea salt. Indeed, for example, table salt obtained with coarse salt crushed, contains 97% of NaCl and iodine or fluor could be add in. Coarse salt, large crystals harvested on the ground of the condenser, contains 97% of NaCl. And grey salt, large salt crystals mixed with clay particles of salt pan during harvest, contains 94% NaCl. This last salt being the moistest and the less refined (Codex Alimentarius, 2006).

Average salt concentration (25% NaCl) and temperature (34 °C) in salt pan permits the formation of these different salts in the condensers (final basin of the salt pan cycle, also called crystallizer ponds) (Antón et al., 2000). But the *fleur de sel* is the only salt that stays always on the surface of the condensers before it is harvested. Moreover, each environment presents specific microorganisms. In solar salterns, halotolerant and halophilic microorganisms develop specific biological ways to control their osmotic pressure under high salinity (Margesin and Schinner, 2001; Jaenicke, 1998) or high light. Microbiology of saltern crystallizer ponds was re-evaluated quite recently in Spain, Israel and Australia. Molecular, 16S rRNA targeted methods were applied to hypersaline brines. Archea and bacteria coexist and among archea, *Haloquadratum walsbyi*, is very predominant (50% of total cell number). The second quantitatively important component of the biota is *Salinibacter ruber* (20–25% of the total prokaryote community) (Bardavid et al., 2008). Many other archea and bacteria (*Halobacterium*, *Halococcus*, and so on) were then described and many of them produce pigments, such as carotenoids (salinixanthin, β-carotene, spirilloxanthin, bacterioruberin, and so on).

As a result, in salt pan, derived compounds could appear from degradation of carotenoids, pigments known to allow safe life for halotolerant and halophilic species (e.g. UV protection) (Ye et al., 2008). Free in the salt pan after the death of microorganisms or resulting from microorganism metabolism, such carotenoid-derived aroma compounds could be found in the first formed crystals in the condenser, the *fleur de sel*.

Thus, our research team, by investigating the carotenoid-derived aroma compounds (so called norisoprenoids) on salt pan environment or *fleur de sel*, tries to amend PGI or TSG. Carotenoids are important precursors of a variety of compounds, e.g. C_{20}-retinoids or C_{13}-aroma (norisoprenoids). Carotenoid molecules and fragments of carotenoid molecules have important natural functions and actions, e.g. vitamin A or retinol which play a significant role in health and nutrition; others compounds contribute to the complex mixture that characterize a particular perfume or aroma. Carotenoid-derived aroma compounds have not only been detected in leaf products, such as tobacco, tea, and mate, but also in many essential oils, fruits (grapes, passionfruit, starfruit, quince, apple, nectarine), vegetables (tomato, melon), spices (saffron, red pepper), as well as additional sources such as wine, rum, coffee, oak wood, honey, seaweeds etc. (Winterhalter and Rouseff, 2002; Rodriguez-Bustamante et al., 2005).

The aim of this study is indeed to discuss the possibility to use such aroma compounds, formed by the degradation of carotenoids, biosynthesized by microorganisms, as markers for sea salt. The present work describes more specifically the results of the headspace GC–MS analysis of concentrated sea water and *fleur de sel* collected in solar salterns from Saint-Armel (Brittany, France, GPS coordinates: latitude 48°0′49.29″ north and longitude 1°35′34.55″ west). This old French salt marsh (existed since 1400) was chosen because of its preserved environment: (1) no pollution was detected in soil or in surrounding sea due to reduced human activities (no industries, boats, or cars; manual harvest); (2) clay and silt of the soil permit the conservation of fauna and flora; (3) environment and method of production permitted to have a natural product recognized by the Chefs all around the world for its gustative and gastronomic characteristics (Chenelle, 2010).

2. Materials and methods

2.1. Concentrated sea water (brine) and fleur de sel samples

Concentrated sea water (CSW or brine), raw *fleur de sel* ("flower" of salt collected at the surface of the salt pan, before landing and bleaching under sun drying) and marketed *fleur de sel* (*fleur de sel* after sun drying) from Saint-Armel (north west of France) have been studied.

Marketed *fleur de sel* was bought in a store. Samples of concentrated sea water and raw *fleur de sel* were collected during