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Olive mill wastewater microconstituents composition according to olive variety and extraction process

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all-trans-beta-carotene (PubChem CID: 5280489)
caffeic acid (PubChem CID: 689043)
gallic acid (PubChem CID: 370)
hydroxytyrosol (PubChem CID: 82755)
luteolin (PubChem CID: 5280445)
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ABSTRACT

Olive oil production yields a considerable amount of wastewater, a powerful pollutant that is currently discarded but could be considered as a potential source of valuable natural products due to its content in phenolic compounds and other natural antioxidants.

The aim of this work was to explore the variability in olive mill wastewater composition from Algerian olive oil mills considering extraction processes (traditional discontinuous press vs 3-phases centrifugal system) and olive varieties (Azerraj, Sigoise, Chemlal). Whereas pH, dry or organic matter content didn't vary, there was a significant difference in ash content according to extraction process and olive variety. Carotenoid content was 2.2-fold higher with 3-phases than with press systems whereas tocopherol content was not significantly different. Among the phenolic compounds quantified, tyrosol was usually the most abundant whereas oleuropein concentrations were highly variable. Differences in phenolic compound concentrations were more pronounced between olive varieties than between processes.

1. Introduction

Olive oil production is one of the most traditional agricultural industries with a great economic importance in most of the Mediterranean countries (Dermeche, Nadour, Larroche, Moulti-Mati, & Michaud, 2013). There are more than 800 million productive olive trees on the planet, occupying an area of 10 million hectares (Vossen, 2013). The Mediterranean region alone provides 98% of the total surface for olive tree cultivation and 97% of the world total olive oil production, which has been estimated at 2.74 million tons in the last six years (Vossen, 2013). Because of its excellent nutritional properties, the consumption of olive oil is increasing since 2005 and its production has grown by approximately 40% worldwide in the last decade (Dermeche et al., 2013).

The extraction of olive oil typically consists of three operational steps: (i) olive crushing, where fruit cells are broken down and the oil released; (ii) mixing, where the remaining paste is slowly mixed to increase the oil yield; and (iii) oil separation from the remaining

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wastes. This latter step could be conducted according to one of the following processes: (i) traditional discontinuous press process, (ii) 3-phases centrifugal or (iii) 2-phases centrifugal extraction system (Klen & Vodopivec, 2012).

Water is added in some of these steps to squeeze out most of the oil from the olive. The mix between olive vegetation water and this under-process added water is called olive mill wastewater (OMWW) (El-Abbassi, Kiai, & Hafidi, 2012). Among the three processes of olive oil production, pressure and 3-phases centrifugation systems generate huge amounts (up to 30 million m^3 per year) of OMWW (El-Abbassi et al., 2012). Even though less ecologically-friendly, these two processes are still largely in use, especially around the Mediterranean area where they induce the production of large OMWW volumes during a very short period of the year (November to February). These two elements (concentration in time and in location) combined to the OMWW content in salts, heavy metals or phenolic compounds play a major part in the negative ecologic footprint of olive oil production that is reinforced by insufficient OMWW specific treatment plants and by bad practices like their illegal dumping to the soil or in surrounding rivers (McNamara, Anastasiou, O'Flaherty, & Mitchell, 2008). This waste is one of the most harmful effluent produced by agro-food industries because of its high polluting load and high toxicity to the whole ecosystem (plants, bacteria, aquatic organisms and air) owing to its acidic pH and to its content in organic substances such as phenols (Dermeche et al., 2013; El-Abbassi et al., 2012). As an example of the extent of the environmental impact of OMWW, it should be noted that 10 million m^3 per year of this effluent are equivalent to the wastewater generated by about 20 million people (McNamara et al., 2008). Thus, OMWW treatment or valorization is a major environmental issue.

A great variety of processes have been investigated in the past to reduce OMWW toxicity or to facilitate their treatment, but research efforts turn nowadays toward other aspects. Indeed, OMWW could be considered as a source of bioactive compounds such as phenolics, tocopherols and carotenoids that can be extracted and applied as natural antioxidant for cosmetic, food and pharmaceutical industries (Dermeche et al., 2013).

Phenolic compounds found in OMWW exert potent biological activities. For example, hydroxytyrosol has been recognized by the European Food Safety Authority as a protector of blood lipids from oxidation. Its interest for diseases prevention has been shown in numerous studies performed in vitro or in animal models (Achmon & Fishman, 2015; Azaizeh et al., 2012). It has also been demonstrated that hydroxytyrosol exerts in vitro an antimicrobial activity against both Gram-positive and Gram-negative bacteria (Obied, Bedgood, Prenzler, & Robards, 2007). In addition, bioavailability studies have shown that oleuropein and hydroxytyrosol from olive can be absorbed efficiently in human (de Bock et al., 2013). This would encourage their addition in the diet (Azaizeh et al., 2012) and consequently their purification from OMWW that could be a rich and inexpensive source.

Olive oil is known to contain substantial amounts of carotenoids and vitamins E, which also play an important role in human health. They both have an antioxidant capacity with which they protect biological systems sensitive to oxidizing damage induced by free radicals. Furthermore, as precursors of vitamin A, carotenoids occupy at present an important place among food components of interest with respect to human health. As for vitamin E, it is known to promote immunity (Graulet, Martin, Agabriel, & Girard, 2013). However, the characterization of tocopherol and carotenoid contents in OMWW has never been performed.

For a long time, it has been reported that the low pH, the high organic load and the high salt concentrations are common characteristics of OMWW (Amaral et al., 2008). However, little is known on how OMWW composition is affected by the cultivar and the milling technology. According to Obied, Bedgood, Mailer, Prenzler, and Robards (2008), phenol content in OMWW is mainly a function of the olive cultivar. In contrast, Ben Sassi, Boularbah, Jaouad, Walker, and Boussaid (2006) demonstrated that OMWW from traditional process units had the highest concentrations of total phenols and total ash compared to OMWW from centrifugal process. El-Abbassi et al. (2012) showed that OMWW from traditional discontinuous press process had a higher phenolic content compared to that obtained from 3-phases centrifugal system. In this work, phenolic profiles also were affected by olive oil processing. On the contrary, Klen and Vodopivec (2012) stated that the process induced significant differences in phenol content, but no qualitative difference in phenol profiles.

The determination of the effects of such factors on OMWW's composition is expected to enhance the valuation at large scale as well as the development of sustainable OMWW management strategies.

Thus, the objective of the present study was to investigate the effect of oil extraction process (traditional discontinuous press vs. 3-phases centrifugal system) and olive variety on OMWW content and composition in minerals, organic matter, phenolic compounds, carotenoids and vitamin E.

2. Materials and methods

2.1. Chemicals

Zeaxanthin, lutein, β-cryptoxanthin, echinenone, 13Z-β-carotene and 9Z-β-carotene were purchased from Carotenature (Lupsingen, Switzerland). All-E-β-carotene, δ-tocopherol, γ-tocopherol and α-tocopherol were purchased from Sigma (Saint-Quentin-en-Yvelines, France). Gallic acid, caffeic acid, chlorogenic acid, 3,4-dihydroxyphenylacetic acid, 4-hydroxyphenylacetic acid, *p*-coumaric acid, ferulic acid, tyrosol, hydroxytyrosol, luteolin and luteolin-7-O-glucoside, apigenin, oleuropein were obtained from Extrasynthese (Genay, France).

All solvents used for standard and sample preparation and for chromatography (acetonitrile, dichloromethane, methanol, tetrahydrofuran (THF), ethyl alcohol, ethyl acetate, *n*-hexane, diethyl ether, acetone) and 99% formic acid were purchased from VWR (Fontenay-sous-Bois, France). All solvents were of HPLC grade and ultrapure water was prepared using a milli-Q system (Millipore Corp., Bedford, MA, USA).

2.2. Experimental design and OMWW sampling in oil mills

OMWW samples were collected from 15 olive oil mills located in four areas of the north-eastern Algeria (Batna, Constantine, Guelma and Skikda) during the milling campaign 2011–2012. Prior to sampling, a survey was conducted on the general characteristics of the oil mills (location, process used for olive oil production, staff size, average production at the plant...). The questionnaire, tested on 50 olive oil mills comprised 20 issues under 3 headings: (i) general characteristics of olive mill; (ii) characterization of the process at the day of sampling, olive varieties and maturity, storage mode and duration, salt addition, leaf removal, washing, treatment (volume and temperature of the added water), production yield (OMWW delivery), and environmental conditions (general tendency of the climate during the season before olive harvest); (iii) general questions: this section was designed to collect information about the awareness and sensitivity of the producers about the problems of OMWW and their management.

Thirty-five OMWW samples were collected at the beginning of the olive harvest season (October to December 2011). OMWW samples corresponded to olive oil production from 4 pure