OLIPO-WET OLIVE POMACE, A NEW RENEWABLE SOURCE FOR LEATHER RETANNING

CARMEN GAIDAU[1], MARIA STANCA[1,2*], DEMETRA SIMION[1], OLGA NICULESCU[1], COSMIN-ANDREI ALEXE[1], CONCEPCIO CASAS[3,4], ANNA BACARDIT[3], STOICA TONEA[5], GABRIELA PAUN[6]

[1]INCDTP - Leather and Footwear Research Institute Division, 93, Ion Minulescu St, 3, 031215, Bucharest, Romania

[2]Doctoral School of Faculty of Applied Chemistry and Materials Science, Department of Science and Engineering of Oxide Materials and Nanomaterials, University Politehnica of Bucharest, Romania, maria.stanca@icpi.ro

[3]Universitat de Lleida (UdL), A3 Leather Innovation Center Pla de la Massa, 8, 08700 Igualada, Spain

[4]Miret y Compañia S.A., 08700, concepcio.casas@udl.cat

[5]SC Taro Comimpex SRL, Int. Giurgiului, 28A, Jilava, Ilfov, 077120, Romania, tarocomimpex@yahoo.com

[6]National Institute for Research and Development of Biological Sciences, Center of Bioanalysis, 296 Splaiul Independentei, Bucharest 6, 060031, Romania, gpaunroman@gmail.com

The aim of OLIPO project is to find suitable extraction methods for an important waste of olive oil production, wet olive pomace, in view of reclaiming it as tanning and retanning material, alternative to petroleum origin materials. The total volume of wet olive pomace in Mediterranean countries where olive crops are traditional is about 80% of processed olives and is the result of a two-phase continuous extraction process. Wet olive pomace is rich in polyphenolic compounds, fats, tannins, non-tannins, possible to be extracted, concentrated, chemical processed in view of developing a new tanning product. The use of new renewable materials from oil industry as biobased tanning material for leather industry represents an important step in lowering carbon footprint of both sectors and complies with circular economy principles. The antioxidant and antimicrobial properties of olive oil pomace can be exploited in view of increasing the efficiency of the new product. The paper presents the characterisation of four kinds of wet olive pomace wastes, water and water-organic solvent extracts as tanning materials in order to select the methods for a new tanning material elaboration and testing on leathers in retanning processes.

Keywords: wet olive pomace, polyphenols, extraction methods.

INTRODUCTION

The olive oil industry and leather industry have in common the processing of valuable agriculture products with low yields (Araújo *et al.*, 2015; Ludvik and Buljan, 2000) and releasing of important biomass quantities with high potential to be recovered and recycled. Solid olive mill waste is mainly generated in two-phase extraction processes and it is rich in organic matters with phytotoxic potential for the environment. The reevaluation and the finding of efficient reclaiming solutions for wet olive pomace waste represents an actual requirement; moreover, Europe target for circular economy (European Commission, 2014) is very ambitious and proposes by 2025 to not landfill the biodegradable and recyclable waste. OLIPO project target is to find new synergies in olive oil industry waste processing in view of valuable tanning components recovery and ecological sound products implementation in leather industry. The olive oil is extracted only by mechanical methods (Souilem *et al.*, 2017) by fruits crushing and malaxation, followed by oil separation through pressure or centrifugation. Traditional discontinuous process uses the extraction of olive oil by pressure and generates pomace

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and olive milling wastewater (OMWW), meanwhile the modern processes in three and two phases use centrifugation and generate OMWW (Souilem *et al.*, 2017). Around 98% of phenolics are released in olive oil processing by-products (Araújo *et al.*, 2015) and represent a valuable component, able to replace synthesis preservatives with potential application in medical, food or cosmetic products. The composition of OMWW is very complex (Souilem *et al.*, 2017) and contains fat and oils, proteins, amino acids (glutamic acid, proline), sugars (glucose, mannitol, glucose, sucrose, galactose), cellulose, hemicelluloses, lignin, phosphorous, phenolic compounds, potassium, calcium and other metals (Pb, Cd, Fe, Zn, Mn, Mg, Na). The acidity of OMWW is between 4 and 6 and is due to the malic, citric, tartric, succinic or oxalic acids and the value depends on fruit variety, maturity time and storage conditions. The possibility to use OMWW in hide soaking and tanning processes showed similar performances in collagen crosslinking antioxidant and antibacterial as commercial vegetable tanning materials (Franceschi *et al.*, 2018). The olive mill solid waste in paste or cake form is composed from 50-56.8% moisture, 3.8-4.6% fats and oils, 3.4-2.8% proteins, 0.9-0.8% sugars, 17.3-14.5% cellulose, 6.6-7.9% hemicelluloses, 1.4-1.7% ash, 8.5-10.2% lignin, 0.4-0.5 N, 0.04-0.05% P_2O_3, 0.3-0.4% K_2O, 0.3-0.4% CaO and 25-29% C (Souilem *et al.*, 2017). Phenols represent the most valuable component of olive oil waste and the efficient use or extraction methods are not implemented at industrial level. The composition of phenol compounds can be classified as low molecular weight (tyrosol, hydroxyl tyrosol, oleuropein, apigenin, luteolin, p-coumaric acid, ferulic acid, syringic acid, protocatechuic acid etc.) and high molecular weight (tannins, anthocyanins, catechol-metaninic polymers etc.). The content of hydrolysable tannins and condensed tannins of extractable polyphenols from olive pomace was found to be 5.4% and 4.9%, respectively (Speroni *et al.*, 2019). The affinity of oleuropein (glycosylated seco-iridoid) or hydrolyzed oleuropein for collagen crosslinking was demonstrated on collagen films (Antunes *et al.*, 2008) or in leather processing with commercial products (wet-green® OBE tanning agent) originated from olive leaves. The aim of this paper is the characterization of wet olive pomace waste as biobased resource for tanning materials extraction and formulation.

EXPERIMENTAL

Materials and Methods

Wet Olive Pomace Waste

Four types of olive waste (Table 1) originated from 2-phase extraction process, by-products of the olive pomace (Arbequina, Palomar and Agro Igualada) and from 3-phase extraction process (Polpa d'oliva), in dry condition were received from different Spanish olive oil companies. In table 1 the aspect of 4 kinds of olive waste in dry state as they were received and after grinding with a coffee grinder are presented.

Table 1. Olive waste from 2- and 3-phase extraction processes of olive oil

			
Arbequina	Palomar	Agro Igualada	Polpa d'oliva

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Olive Pomace Waste Characterization

The characterization of olive solid waste was performed according to standardized methods for tanning materials: dry substance (SR EN ISO 4684:2006), ash (SR EN ISO 4047:2002), total nitrogen and protein content using 6.25 conversion factor (SR EN 5397: 1996), extractible substances (SR EN ISO 4048: 2018), total residuum, total soluble substances, non tannins, tannins (shaking method), insoluble substances, tanning power, binding power (SR 1883: 2008) and pH (STAS 86193/3: 1990). The total phenols were analyzed following Folin-Ciocalteu method (Singleton *et al.*, 1999). To obtain the phenols content 15 g of olive waste sample were magnetically stirred for 24 hours in 60 mL solution of 80% methanol. After stirring, the samples were ultrasounded for one hour and then filtered on Whatman paper. The UV-VIS spectra (JASCO V550) were recorded at λ =740 nm on a calibration curve made with gallic acid.

ATR-FTIR spectroscopy was performed on solid extracts in order to compare the chemical profile of different olive waste products and to understand the differences in their tanning properties by using a Jasco FT-IR 400 equipment from JASCO, Metertech.

Extraction Methods

The extraction methods were based on the variation of different conditions in aqueous and alcohol medium, at 55°C or by ultrasound (Elmo ultrasound bath, 280 W) and are presented in Table 2 for ground Polpa d'oliva.

Table 2. Extraction methods for olive waste

Sample	Extraction conditions
E1	water at pH= 2, 1: 40 (w/w), 1 h ultrasound.
E2	water at pH= 2, 1: 40 (w/w), 4 h at 55°C.
E3	water, 1: 40 (w/w), 1 h ultrasound.
E4	water, 1: 40 (w/w), 4 h at 55°C.
E5	water: ethanol = 1:1 (v/v), pH=2, 1:40 (w/w), 1h ultrasound.
E6	water: ethanol = 1:1 (v/v), pH= 2, 1:40 (w/w), 4h at 55°C.
E7	water: ethanol = 1:1 (v/v), 1:40 (w/w), 1h ultrasound.
E8	water: ethanol = 1:1 (v/v), 1:40 (w/w), 4h at 55°C.
E9	water: methanol=1:1(v/v), pH= 2, 1:40 (w/w), 1h ultrasound.
E10	water: methanol = 1:1 (v/v), pH= 2, 1:40 (w/w), 4h at 55°C.
E11	water: methanol = 1:1 (v/v), 1:40 (w/w), 1h ultrasound.
E12	water: methanol = 1:1 (v/v), 1:40 (w/w), 4h at 55°C.

RESULTS AND DISCUSSIONS

Olive Waste Characterization

The analyses of solid olive mill waste are presented in table 3 and show that the moisture is higher for Palomar (13.92%) as compared to Polpa d'oliva with 7.76% volatile matters, values which are lower than other solid olive waste with 19-27% moisture (Souilem *et al.*, 2017). The ash and protein contents are higher for Polpa d'oliva as compared to the other 3 olive wastes meanwhile the extractible substances are the highest in Arbequina waste. The pH variation is between 5.05 and 6.15, in the range of reported olive waste pH values (Souilem *et al.*, 2017). The tanning power has the values which are not in agreement with total phenol content (table 4), probably due to

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the low molecular phenol content of Polpa d'oliva waste and lower solubility. The tanning power was ranked as follows: Arbequina > Palomar > Agro Igualada > Polpa d'oliva. The binding power was not detectable due to the low concentration of the soluble substances in the analytical solution prepared directly from the solid wastes. From table 4 it can be seen that the phenols concentration extracted with methanol is highest in Polpa d'oliva and very similar in Arbequina and Palomar, all values being in the range of the stated values of 0.4-2.4 g GAE/100 g pomace for solid olive mill wastes (Demeche *et al.*, 2013).

The phenols content of analytical solutions and non tannin solutions shows that the Arbequina water extracted phenols have the highest affinity to hide powder as compared to the other extracts and confirms the potential low molecular weight phenol content of Polpa d'oliva waste.

Table 3. Physical-chemical characteristics of solid olive waste

Characteristics	Solid olive waste			
	Arbequina	Palomar	Agro Igualada	Polpa d'oliva
Dry substance, %,	89.31	86.08	90.24	92.24
Ash, %	2.65	1.74	2.40	6.18
Total nitrogen, %	0.76	0.70	1.17	2.23
Protein, %	4.75	4.38	7.31	13.93
Extractible substances %	14.48	10.90	11.71	7.92
Total residuum, %,	29.49	34.73	25.00	20.72
Total soluble substances, %	18.54	9.31	14.22	13.98
Non tannin, %	15.14	6.88	12.06	11.94
Tannin, %	3.40	2.43	2.16	1.77
Insoluble substance, %	10.95	25.42	10.78	8.51
pH (1:10), pH units	5.10	5.05	5.52	6.15
Tanning power, %	3.10	1.77	1.97	1.52
Binding power, %	nd	nd	nd	nd

Table 4. Total phenols in methanol (1), analytical water solution (2) extracts and in non tannins (3) of olive waste

Sample	Phenols, mg GAE/g olive waste		
	1	2	3
Arbequina	12.69	11.5	4.23
Palomar	12.57	7.50	3.56
Agro Igualada	6.74	9.62	8.31
Polpa d'oliva	19.02	13.96	4.38

The main components of olive waste (Fig.1) can be recognized from the main functional groups vibrations (Hamed *et al.*, 2005; Erdogan *et al.*, 2015): polyphenols, alcohols and carboxylic compounds (3258-3311.18 cm^{-1}), cellulose (2922.59-2925.48 cm^{-1} and 2853.15-2854.43 cm^{-1}), hemicelluloses in Agro Igualada and Arbequina (1740-1743 cm^{-1}), oleuropein (1022.05-1078 cm^{-1}), proteins (1631.48-1637.27 cm^{-1} and 1598 cm^{-1}), phenols (1371.14-1375.96 cm^{-1}) and ß-glycoside links (1151-1156.12 cm^{-1}).

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The absorption intensity at polyphenol wavelength was recorded for Arbequina waste product as the most intense, compared to the others, which is in agreement with tanning affinity.

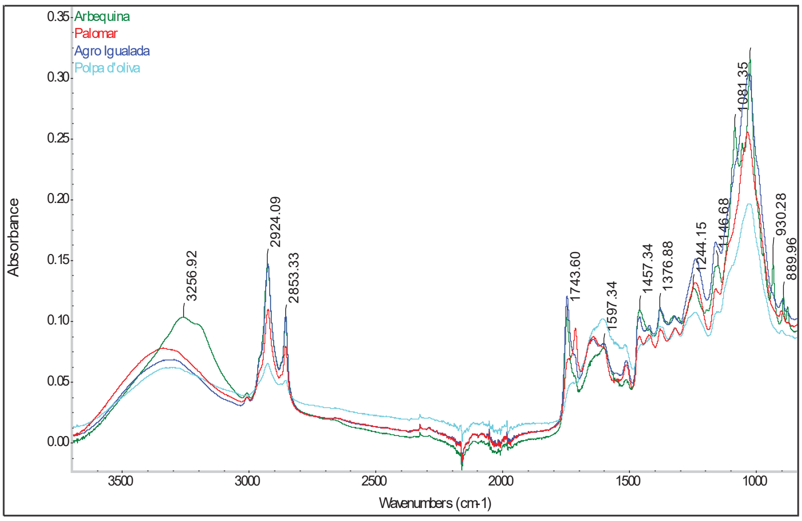

Figure 1. ATR-FTIR of solid olive waste: 1- Palomar, 2- Polpa d'oliva, 3- Agro Igualada, 4- Arbequina

Olive Waste Extracts Characterization

The total phenols of tested extracted methods performed on Polpa d'oliva waste (Table 2) are presented in Figure 2 and allowed to conclude that the extraction in aciduladed water and assisted by ultrasound was the most efficient (15.32 mg GAE/g pomace). Similar phenol concentrations, between 7.72-9.42 mg GAE/g pomace, were extracted in acidulated water or in water heated at 55°C for 4 hours, or in water by ultrasound for 1 hour (Figure 2).

Further research will be carried out for high molecular weight phenols identification (tannins, anthocyans, catechol-metaninic polymers etc. (Speroni *et al.*, 2019)) in correlation to extraction methods and tanning properties.

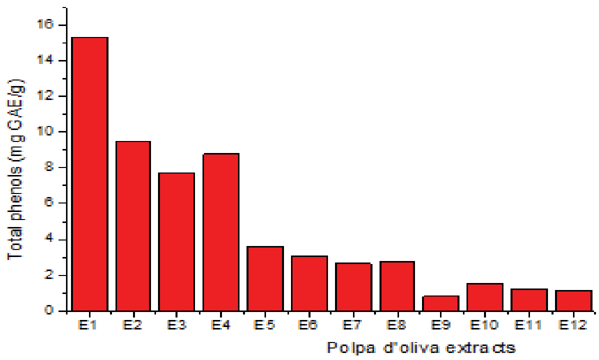

Figure 2. Total phenols content of Polpa d'oliva waste extracts

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CONCLUSIONS

OLIPO project aims are to find the suitable synergies for circular economy between olive oil and leather industries by exploiting the valuable polyphenol content of wet pomace wastes. Four solid olive pomace wastes were characterized from the tanning properties point of view. The experimental on extraction methods showed that the acidic conditions and ultrasound treatment are the most suitable for polyphenol solubilization. Further research will be focused on tanning and retanning experiments for a renewable product development.

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