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Supercritical CO_2 as a green solvent for the circular economy: Extraction of fatty acids from fruit pomace

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ABSTRACT

One of the empowering actions for the circular economy is deriving value from waste. In this context, recycling waste agro-food streams to make more sustainable chemical products through greener technologies promises to move away from the linear development model based on continuous growth and increasing resource throughput. We describe here the use of supercritical fluid extraction with carbon dioxide to extract fatty acids from waste pomace deriving from the preserves industry along with a comparison using hexane as solvent. The fatty acids extracted from the seeds and peels of raspberry, blueberry, wild strawberry, pomegranate, blackberry and blackcurrant using supercritical CO_2 as a greener solvent were purer and richer in essential fatty acids than the hexane ones. The wild strawberry pomace extraction with supercritical CO_2 is a representative example: selectivity towards fatty acids was 26 wt% (*vs.* 1.4 % with hexane) and the extracts contained, 145.8 mg mL^{-1} polyunsaturated, 64.0 mg mL^{-1} monounsaturated and 46.8 mg mL^{-1} saturated fatty acids (*vs.* 14.3 mg mL^{-1} total fatty acids with hexane).

1. Introduction

The recovery and reuse of waste streams from the agri-food sector is crucial in the value chain of this industry [1]. Several reasons should be considered in this respect. From the environmental standpoint, these streams most often need to be disposed of or are converted to low-value compounds (*e.g.* feed, fertilizers or off-grade fuels), while the implementation of new protocols to achieve high-value substances or materials from wastes implies lowering the environmental burden both directly (less waste) and indirectly (*e.g.* making new renewable products in place of petrochemical ones). From the economic standpoint, advantages and drivers of the upgrading of residual biomass include the reduction of waste (*i.e.* lower costs for landfilling, composting, incinerating or converting it to low-value feed or fertilizers) as well as the production of high-value products for the market. From a societal perspective, being able to extract value from waste represents a positive asset for the perception of any business willing to commit to this vision. The resulting products are therefore more likely to be accepted by health- and environmentally conscious consumers as "green", "sustainable", "renewable", "natural", *i.e.* as contributors to circular economy [2], and new employment opportunities [3]. One of the pillars of any strategy for waste upgrading is recycling which, as defined by the EU, encompasses any recovery operation for reprocessing waste into substances whether for the original or other purposes, excluding energy recovery [4,5]. In this context, the aim of the present work is to valorize seeds and peels (pomace) discarded from Rigoni di Asiago [6], one of the main Italian producers of fruit preserves, by recovering and reprocessing them into higher value products. During its fruit preserves production, Rigoni di Asiago generates about 80 tons of organic farming fruit waste (pomace) every year – in the present case deriving from blackberry, raspberry, blackcurrant, wild strawberry, pomegranate and blueberry processing. The low-temperature processing generates a residual high-quality biowaste in which all the natural properties of the fruit are particularly well preserved. Currently Rigoni di Asiago pays to discard this waste as compost, although it is known to be a natural source of precious biomolecules such as anthocyanins, flavonoids, phytosterols, tocopherols and fatty-acids (FAs) [7,8]. More specifically, the unique FAs composition, often in combination with high contents of lipid-soluble antioxidants, makes the berry pomaces a valuable raw materials for cosmetic formulations, nutraceuticals and functional

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ingredients of foods [9,10], and their recovery would therefore add value to the whole production chain. During the last few years, the cosmetic industry has become more interested in promising, sustainable, plant- and bio-based raw materials. Sustainability is, in fact, a major challenge that cosmetic manufacturers must take into account during the whole development process, starting from the selection of raw materials on to the manufacturing process and ending with a smart and easy to understand communication. It is also becoming a big marketing trend. These kinds of products must be guaranteed to meet specific quality standards, reproducibility, efficacy and above all a good or well- managed stability profile. Unifarco is an Italian-based company whose mission is to develop products with high scientific value. To reach this goal it develops cosmetics, food supplements and medical devices considering sustainability as an important aspect and in the same way one of the identifying characteristics of cosmetic products.

In the past two-decades, with respect to conventional technologies for the extraction of FAs (mainly cold pressing and extraction with organic solvents such as hexane), supercritical fluid extraction based on carbon dioxide (SFE-CO_2) has been identified as a privileged technique because, thanks to its low oxidative and thermal impact, it produces high quality oils that often do not require further refining, it preserves the original properties unaltered, and excludes contamination by residual liquid solvents [11,12]. For these reasons, SFE-CO_2 processing has become more and more relevant for the large-scale extraction of different types of matrices to produce lipids and other bioactive substances used in food, pharma, cosmetics and other high-value applications [13,14].

This paper comparatively investigates the efficiency of SFE-CO_2 and traditional liquid extractions to obtain unsaturated fatty acid-rich fractions from waste of the fruit processing industry.

2. Materials and methods

2.1. Equipment and chemicals

All chemicals and solvents were purchased from commercial sources and used without further purification. Ethanol (pharma-grade) and hexane were purchased from Sigma-Aldrich. The supercritical CO_2 extraction was performed in a laboratory apparatus consisting of a Jasco PU-2080-CO_2 Plus delivery Pump and a Jasco 2080 Plus Automatic Back Pressure Regulator used for the pressure control. The connecting stainless tubes and the different reactors were heated by a Chrompack CP-9003 oven. GC–MS analysis were conducted using a GC system Agilent 7820A coupled with a single quadrupole mass detector Agilent 5977B MSD equipped with a HP88 column (60 m x0.25 mm, 0.2 μm).

2.2. Sample preparation

Frozen seeds and peels of six different types of fruits (raspberry, blueberry, wild strawberry, pomegranate, blackberry and blackcurrant) were provided by Rigoni di Asiago (Asiago, Italy). Different pre-treatment techniques were tested on the frozen pomace prior to extraction: cryogenic crushing, simple air drying, and air drying preceded by rinsing with water. The latter pre-treatment was chosen as it yielded similar results to cryogenic crushing and allowed to obtain purer extracts respect to simple drying. Pre-treatment therefore involved weighing the frozen waste, followed by rinsing with milliQ water for 15 min and then air drying for 24 h. The initial water content of the pomace was determined by difference between initial and dry samples and is shown in Table 1.

Moreover, the residual water content was determined for each air-dried sample after heating in a vacuum-drying chamber (70 °C, 5 mbar, 24 h). Additional information on the composition in sugars, lipids and proteins of the biomass are reported in the SI (Table S1).

2.3. Soxhlet extraction

The Soxhlet (containing a cellulose thimble) was filled with 3 g of dry pomace and 150 mL of solvent (hexane); the solvent was refluxed for 24 h [15]. For the qualitative and quantitative characterisation of the extract, the solution was analysed by GC–MS, using methyl pentadecanoate (2 mg/mL) as internal standard. The solvent was then evaporated under reduced pressure to determine the extraction yield ($Y_{extract} = wt_{extract}/wt_{dry\ biomass}$ %).

2.4. Supercritical fluid extraction

The extraction experiments were conducted on an analytical-scale supercritical fluid extraction unit (internal volume of approximately 10 cm^3, plug diameter 3/8" and plug length 15 cm) using CO_2 as solvent. The extraction vessel was loaded with approximately 3 g of dry ground pomace and a constant flow rate of supercritical CO_2 (5.0 or 2.5 $cm^3\ min^{-1}$) at 300 bar, 70 °C for 5 h. The extracts were collected by venting into hexane at ambient temperature and pressure and were gravimetrically quantified ($Y_{extract} = wt_{extract}/wt_{dry\ biomass}$ %) at the end of each run (after hexane removal). For the qualitative and quantitative analysis of the extract were used GC–MS, using methyl pentadecanoate (2 mg/mL) as internal standard.

2.5. Chromatographic analysis of the extracts

Prior to GC–MS analysis, the FAs containing extracts were converted to the corresponding methyl esters (FAMEs) by dissolving the extracts (50 mg exactly weighted) in chloroform (5 mL) followed by addition of methanol (25 mL), of the internal standard (methyl pentadecanoate 0.5 mL of solution in chloroform 500 ug/mL) and of a catalytic quantity of sulfuric acid. The resulting solution was refluxed overnight. The FAMEs were extracted with a mixture of water and diethyl ether (10:2). The organic fraction was analyzed by GC–MS. Identification of fatty acid was obtained comparing the MS spectra and the retention index of compounds. Quantification was obtained using the methyl pentadecanoate as internal standard.

3. Results and discussion

We started by defining the experimental conditions for SFE-CO_2. Based on our previous recent experience [16], we decided to operate at the maximum pressure allowed by our system (300 bar) and at 70 °C in order to ensure a reasonably high CO_2 density (0.79 g/mL [17]) which was crucial for extraction, with a constant flow of 5 mL/min of CO_2. Under such conditions, control experiments with the wild strawberry pomace were used to determine the minimum extraction time for the highest yield of lipidic fractions varying the extraction time from 1 to 24 h. After 5 h the yield was substantially levelled off at 13.5 wt/wt% (Fig. 1). Prolonged experiments at 10 and 24 h had negligible, if any, effects.

Additional extractions were then carried out by decreasing both the temperature and the CO_2 flow. Albeit conditions of Fig. 1 (70 °C) are considered acceptable for the extraction of fatty acids, lower temperatures were investigated for the potential benefit on preserving heat sensitive compounds. However, experiments carried out at 50 and 40 °C (300 bar, 5 mL/min) brought about a decrease of the extract yield to 10.7 and 9.6 %, respectively, which corresponded to a drop in the extraction efficiency from 25 to 35 %. This result which appeared incoherent with the increase of the CO_2 density (0.87 and 0.91 g/mL at 50 °C and 40 °C, respectively), was probably due to the effect of the temperature on the vapor pressure of the extracted molecules (unsaturated fatty acids, FA: see later). In other words, the extraction yield was improved at 70 °C because the solute (FA) solubility was primarily affected by the increase of its vapor tension, rather than by the reduction of the CO_2 density. Similar behaviors have been documented in

Table 1
Initial water content in the different pomace samples (wt/wt%).

	Blackberry	Blackcurrant	Pomegranate	Wild strawberry	Blueberry	Raspberry
Initial Water (wt%)[a]	59.6	62.4	38.1	52.2	73.9	39.8
Pomace (wt%)	40.4	37.6	61.9	57.1	26.1	60.2
Residual water (wt%)[b]	8.2	2.6	7.2	2.4	5.2	8.7

[a] Determined by difference of weight between initial and air-dried samples.
[b] Determined after heating of each air-dried sample in a vacuum-drying chamber. Most of the mass loss (≥98 %) was water. The complement was plausibly due to a minor release of volatile organic compounds.

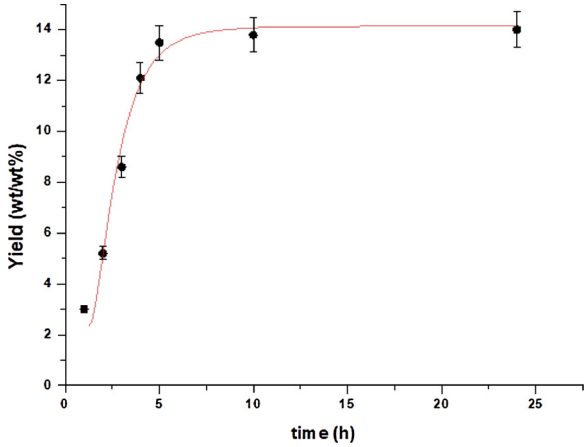

Fig. 1. SFE-CO_2 extraction yield (wt/wt%) of wild strawberry pomace as a function of time (300 bar, 70 °C, 5 mL/min).

the investigation of the solubility of apolar molecules in $scCO_2$ [18].

The temperature of 70 °C was therefore selected to continue the study and to implement the extraction of a sample of wild strawberry pomace by halving the CO_2 flow to 2.5 mL/min. At 300 bar, the extraction yield was 7.7 wt% which was almost one half the value (ca 14 wt%) achieved under the conditions of Fig. 1 (5 mL/min), suggesting a quasi-linear relationship between the yield and the CO_2 flow. Based on these results, we decided to carry on the experiments at the highest flow to allow for the obtainment of the maximum amount of extracted oil. Although the ratio of solvent to feed mass was apparently elevated (at 5 mL/min, it was approximately 500 mL CO_2/g dry pomace in 5 h) and potentially detrimental to the process economy, several other aspects should be assessed in this analysis. Among them: i) in case of commercial exploitation, the transfer from lab to commercial scale plants makes use of facilities for energy recovery operating under partial depressurization (with significant savings on compression cycles) and recycle of CO_2; [19]ii) if extracts are comprised of high added value compounds with market interest like the products investigated here, the incidence of CO_2-derived costs is limited compared to the commercial value of final compounds.

All the pomaces from the different berries were thereafter processed under the extraction conditions found for wild strawberry residues (70 °C, 300 bar, 5 mL/min CO_2, 5 h). All extracts obtained by SFE-CO_2 were then compared in terms of yield and FA content to the Soxhlet extracts using hexane as solvent (68 °C reflux, 24 h).

Albeit undesirable for its toxicity, flammability and cost, hexane is often chosen as a model non-polar solvent for conventional extractions. Moreover, its solvating properties are similar to CO_2 and its boiling point matches the extraction temperature used in this paper for SFE-CO_2. The results are reported in Table 2.

For each extract, the percentage of FAs in the oils – defined as the extraction selectivity towards FAs – was measured by GC using methyl pentadecanoate as the internal standard. The qualitative characterization of extracts was based on MS and on the Kovats retention index [20]

Table 2
SFE yields (wt/wt%) of the different pomaces with supercritical CO_2 and hexane as solvents.

Entry	Pomace	Solvent	Yield $_{extract\ (\%)}$ [c]	Total $_{fatty\text{-}acids}$ (%) [d]
1	Wild strawberry	$scCO_2$ [a]	13.5	26.0
2		hexane [b]	30.1	1.4
3	Blueberry	$scCO_2$ [a]	9.7	23.5
4		hexane [b]	29.5	0.7
5	Pomegranate	$scCO_2$ [a]	11.3	13.0
6		hexane [b]	20.3	0.3
7	Blackberry	$scCO_2$ [a]	6.6	29.5
8		hexane [b]	6.5	0.2
9	Raspberry	$scCO_2$ [a]	7.5	30.3
10		hexane [b]	5.8	0.02
11	Blackcurrant	$scCO_2$ [a]	4.6	16.5
12		hexane [b]	12.6	0.1

Extraction conditions: a) 3 g of pre-treated biomass, $scCO_2$ at 70 °C, 300 bar, 5 mL/min of CO_2, 5 h. b) 3 g of pre-treated biomass in Soxhlet, 150 mL of hexane, reflux, 24 h. c) Amount of compounds extracted by weight of sample (% wt/wt $_{biomass}$). d) Percentage of FAs in the extract as determined by GC–MS using methyl pentadecanoate as internal standard (% wt/wt $_{extract}$).

(equation 1 and Table 4) and compared with literature data [21] (wild strawberry [22], blueberry [23], pomegranate [24], blackberry [25], raspberry [22], blackcurrant [26]).

$$I_i = 100\left[n + \frac{\log(t_i) - \log(t_n)}{\log(t_{n+1}) - \log(t_n)}\right]$$

Equation 1: temperature programmed chromatography Kovats index equation, where I_i is the Kovats retention index of peak i, n is the carbon number of n-alkane peak heading peak i, t_i retention time of compound i in minutes, t_n is the retention time of the heading n-alkane and t_{n+1} is the retention time of the trailing n-alkane.

Visually, the SFE-CO_2 extracts were clear greenish oils, while the hexane extracts were clear almost colourless liquid samples. The extraction yields of the wild strawberry, blueberry, pomegranate and blackcurrant pomace obtained by using hexane as the solvent were generally higher than with SFE-CO_2, while the selectivity towards FAs was always better with SFE-CO2.

For the wild strawberry pomace, the extraction yield with hexane was 30.1 %, with 1.4 % FAs (Table 2, entry 2) against 13.5 % yield and 26.0 % FAs with SFE-CO_2 (13.5 % Table 2, entry 1). The oil from SFE-CO_2 was rich in essential FAs such as palmitic (2.1 %), stearic (1.7 %), oleic (6.4 %), linoleic (7.9 %) and α-linolenic (6.7 %) as shown in Table 3.

Blueberry pomace yielded 29.5 % of extract and 0.7 % selectivity with hexane (Table 2, entry 4) and 9.7 % yield and 23.5 % FA with SFE-CO_2 (Table 2, entry 3). Blueberry pomace SFE-CO_2 extract was very rich in palmitic acid (1.8 %), oleic acid (7.4 %), linoleic acid (8.4 %) and α-linolenic (5.4 %).

Pomegranate seeds and peels extracted with hexane afforded a 20.3 % yield with 0.3 % FAs (Table 2, entry 6), while the oils obtained with SFE-CO_2 were obtained in 11.3 % yield, with 13 % FAs (Table 2, entry 5). In this case also the extracts contained interesting FAs such as

Table 3
Yields of FAs in the extracts (mg/g, as FAMEs).

Pomace	Solvent	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	Σ SAFA	Σ MUFA	ΣPUFA	Total FAs
Wild strawberry	Hexane	0.9	–	0.5	1.8	–	0.2	–	–	4.6	6.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	1.6	6.4	6.3	14.3
	$scCO_2$	21.0	3.5	16.8	64.0	78.9	6.3	66.9	2.7	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	46.8	64.0	145.8	256.6
Blueberry	Hexane	0.5	–	–	–	2.6	–	2.5	–	–	–	–	–	–	–	–	–	–	1.1	–	–	–	–	–	–	–	0.5	1.1	5.1	6.7
	$scCO_2$	17.8	–	–	74.2	80.4	–	54.5	–	–	–	–	–	–	–	–	4.0	3.8	–	–	–	–	–	–	–	–	25.6	74.2	134.9	234.7
Pomegranate	Hexane	0.2	–	–	–	0.7	–	0.3	–	–	–	–	–	0.1	0.4	0.8	–	–	–	–	–	–	–	–	–	–	0.3	0.4	1.8	2.5
	$scCO_2$	4.8	–	3.1	6.9	–	–	–	–	–	–	7.7	103.0	–	–	–	–	–	–	–	0.2	0.7	–	–	–	–	110.9	6.9	7.7	125.5
Blackberry	Hexane	–	–	–	0.4	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.9	0.4	0.0	1.3
	$scCO_2$	18.2	–	–	66.3	166.7	–	30.3	–	–	–	–	–	–	–	–	–	–	–	13.2	–	–	–	–	–	–	31.4	66.3	197.0	294.7
Raspberry	Hexane	0.1	–	–	0.06	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	7.2	6.9	–	5.8	0.1	0.1	0.0	0.2
	$scCO_2$	14.3	–	6.9	61.2	191	–	–	5.5	–	–	–	4.1	–	–	–	–	–	–	0.07	–	–	–	–	0.4	–	0.6	0.0	0.0	0.6
Blackcurrant	Hexane	–	–	–	–	–	0.05	–	–	–	–	–	0.1	–	–	–	–	–	–	21.7	–	–	17.4	18.2	–	–	104.3	0.0	60.3	164.6
	$scCO_2$	22.0	–	–	–	51.2	7.1	–	6.2	–	9.1	–	11.7	–	–	–	–	–	–	–	–	–	–	–	–	–				

SAFA: saturated fatty acids, MUFA: monounsaturated fatty acids, PUFA: polyunsaturated fatty acids.

Table 4
GC retention time and Kovats indices of the FAs.

	Fatty-acid		Retention time (min)	Kovats index
1	Palmitic	C16:0	23.11	1908
2	Azelaic	C9dicarboxylic	26.46	1629
3	Stearic	C18:0	27.55	2133
4	Oleic	C18:1 (9Z)	28.65	2082
5	Linoleic	C18:2 (9Z, 12Z)	30.38	2139
6	Eicosanoic	C20:0	31.75	2311
7	α-Linolenic	C18:3 (ω3) (9Z, 12Z, 15Z)	32.28	2077
8	Behenic	C22:0	35.58	2531
9	9.12-Octadecenoic	C18:1 (9E)	31.622	2069
10	γ-Linolenic	C18:3 (6Z, 9Z, 12Z)	32.38	2077
11	Linolelaidic	C18:2 (9E, 12E)	30.41	2080
12	Tetracosanoic	C24:0	38.29	2732
13	Decanoic	C10:0	26.533	1578
14	*trans*-Vaccenic	C18:1 (11E)	29.821	2089
15	Arachidonic	C24:4 (5Z, 8Z, 11Z, 14Z)	39.448	7462
16	Pentadecanoic	C15:0	24.38	1877
17	Undecanoic	C11:0	27.57	1506
18	10-Octadecenoic	C18:1 (10Z)	29.843	2100
19	Octadecanoic	C18:0	27.58	2133
20	Nonadecanoic	C19:0	26.544	2266
21	Cyclopropan octanoic	C18-CH_2	33.494	1627
22	Hexacosanoic	C26:0	42.35	2962
23	Octacosanoic	C28:0	45.45	3115
24	Pentacosanoic	C25:0	46.27	2829
25	Octanoic	C8:0	24.29	1154

palmitic (0.5), oleic (0.7 %), linolelaidic (0.8 %) and tetracosanoic (10.3 %).

The blackcurrant pomace yielded 12.6 % of oil and 0.1 % FAs using hexane (Table 2, entry 12) and 3.6 % extract with 16.5 % of FAs with SFE-CO_2 (Table 2, entry 11). The SFE-CO_2 extract of blackcurrant waste was rich in different FAs such as palmitic (2.2 %), octadecanoic (2.2 %), linoleic (5.1 %) and octacosanoic (1.8 %).

The extraction yields for blackberry and raspberry waste was comparable for the two solvents, but the selectivity towards FAs was still higher with SFE-CO_2: 29.5 % FAs with SFE-CO_2 *versus* 0.2 % with hexane for blackberry (Table 2, entry 7, 8) and 30.3 % *versus* 0.02 % for raspberry (Table 2, entry 9, 10). Analytical data indicate that the blackberry waste SFE-CO_2extract is rich in linoleic acid (16.6 %), oleic acid (6.6 %), α-linolenic (3.0 %) and palmitic acid (1.8 %). The oil obtained from the extraction of raspberry seeds and peels has, instead, a FAs composition that contains linoleic acid (19.1 %), oleic acid (6.1 %), palmitic acid (1.4 %), esacosanoic acid (0.7 %), stearic acid (0.7 %) and more.

Although the SFE-CO_2 conditions were not strictly comparable to those of the conventional Soxhlet procedure, the higher yields of the extracts obtained using hexane as a solvent, were likely due to two factors. First, the longer extraction times with hexane compared to supercritical CO_2 (24 h *vs*. 5 h, respectively) that plausibly allowed progressive dissolution of less-soluble species. Second, the slightly higher polarity of hexane compared to supercritical CO_2 as measured by the empirical KamLet-Taft π* solvent polarity parameters. In fact, π* for supercritical CO_2 at 45 °C and 200 bars is reported to be π* = -0.20 [27]; extrapolation of the plot up to 300 bar indicates a value $-0.20 < \pi^* < -0.15$. The same parameter for hexane at 25 °C and atmospheric pressure is π* = -0.11 indicative of a slightly higher polarity compared to supercritical CO_2 [28].

The observed higher selectivity of SFE-CO_2 towards the FAs compared to hexane, was attributed to the combined effect of polarity and density of supercritical CO_2. As mentioned above, at 300 bar and 70 °C, the density of CO_2 is 0.79 g cm^{-3}, a value ca 20 % higher than that of hexane (0.62 g cm^{-3}, at 60 °C) [29]. Higher density along with lower

KamLet-Taft polarity favours the selective extraction of the more lipophilic compounds such as the FAs.

The SFE-CO_2 extracts generally had a high content of FAs and comprised a diversified range of saturated (SAFA), monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids. We identified 25 different acids, with each pomace yielding a different array. Table 3 highlights the total amounts of SAFAs, MUFAs and PUFAs for each pomace and each of the two extraction solvents. Alongside the fact that SFE-CO_2 extracts were always richer in FAs than the hexane ones, two other aspects emerged: the distribution of SAFAs, MUFAs and PUFAs extracted by SFE-CO_2 was different for each pomace: the FA mixtures obtained by SFE-CO_2 of wild strawberry, blueberry, blackberry and raspberry pomace possessed high contents of polyunsaturated fatty acids such as linoleic **5** and α-linolenic **7** acids and of the monounsaturated oleic acid **4**. On the other hand, pomegranate and blackcurrant SFE-CO_2 extracts were richer in the saturated palmitic **1**, tetracosanoic **12** and octadecanoic **19** fatty acids.

It should be noted here that the differences observed from the comparison of GC-chromatographic analyses of extracts in hexane and in scCO_2 (reported in the SI section), were not as such as to justify the greater yields obtained in hexane, for 4 out of the 6 samples of the berry residues explored in this work (cf entries 2, 4, 6 and 12 of Table 2). NMR analyses were then carried out to explore in greater detail the composition of the hexane extracts. Spectra are reported in the SI section for the case of wild strawberry. Compared to the sample in scCO_2, results were not conclusive. Though, the greater intensity of chemical shifts in the regions of vinyl protons and C—C double bonds, was consistent with a more abundant presence of unsaturated compounds. This aspect will be further inspected in future investigations.

The extraction experiments however, demonstrated the efficacy of the SFE-CO_2 for the selective achievement of FAs from different pomaces, suggesting the opportunity to use these secondary products of the food industry as a source of high value oils for the cosmetic and food supplement areas. There is in fact widespread interest for the use of unsaturated vegetable oils in cosmetic formulations [30] especially due to their anti-inflammatory and protective effects on skin [31]. Particularly, among PUFAs of Table 4, linoleic and linolenic acids which are not synthesized by the human body, play a fundamental role to preserve the barrier-function of the skin and the integrity of the *stratum corneum*. On the other hand, MUFAs and PUFAs such as oleic acid, α-linolenic acid, linoleic acid and γ-linolenic acid are frequent ingredients for the production of functional foods of food supplements due to their effects for the cardiovascular wellness, the regulatory activity of the cholesterol level in blood, the promotion of the cell's growth, and antioxidant properties.

4. Conclusions

In a circular economy context, it is mandatory to recover, reprocess, reuse and recycle as much as possible of all materials. We here demonstrate that agro-food waste pomaces obtained from the fruit preserves and juice industries represent an under-explored class of waste that are a source of valuable FAs, potentially of interest for cosmetic and nutraceutical applications. With a view on all-round sustainability, the processing of these wastes should also comply with the principles of green chemistry. Compared to mechanical pressing or solvent extraction, SFE-CO_2 FAs extraction eliminates solvent residues, operates under mild conditions and in the absence of oxygen; thus it can be considered valuable for the extraction of FAs from fruit pomaces with potential to improve the yields, to shorten the extraction times, and to obtain FAs that retain their unsaturated FAs content.

Indeed, this paper proves that SFE-CO_2 is not only successful for the upgrading of the investigated wastes but is also far more selective to obtain high-quality FAs compounds compared to conventional Soxhlet procedures based on toxic and dangerous hexane.

The affinity of supercritical CO_2 for lipophilic compounds leads to purer extracts, with a higher percentage of FAs compared to hexane (*i.e.* for wild strawberry 26.0 % of FA was obtained with supercritical CO_2 and 1.4 % using hexane), avoiding any solvent contamination of the products as well as additional process unit-operations.

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CRediT authorship contribution statement

Carlotta Campalani: Investigation, Writing - original draft, Writing - review & editing. **Emanuele Amadio:** Investigation. **Simone Zanini:** Investigation. **Stefano Dall'Acqua:** Validation, Funding acquisition. **Marina Panozzo:** Validation, Funding acquisition. **Sara Ferrari:** Validation, Funding acquisition. **Gabriele De Nadai:** Investigation. **Stefano Francescato:** Investigation, Funding acquisition. **Maurizio Selva:** Conceptualization, Validation, Writing - original draft, Writing - review & editing, Supervision, Funding acquisition. **Alvise Perosa:** Conceptualization, Validation, Writing - original draft, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jcou.2020.101259.

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