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Valorization of the tomato pomace to obtain lycopene, carbohydrates-rich fraction and oil by applying a hydrolytic enzyme-based approach

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ABSTRACT

Tomato pomace (TP) was of interest as feedstock to extract the lycopene (lyc). This work aimed to design a process based on the use of enzymes to increase lyc extraction and at the same time to obtain additional products following a cascade approach. The pre-treatment with a mix of pectinase and cellulase doubled the lyc extraction recovery concerning the standard extraction. After the separation from the peel, the oil extract from the seeds was similar to edible oils but richer in bioactives. Indeed, the water solution (WP) in which the enzymes hydrolyzed the cell wall of the peel was significantly enriched on mono/oligosaccharides of industrial interest. The proposed approach gave more high value-added products and potential economic revenue from TP of the full scale tomato cannery industry of North Italy with respect to the current destination of the anaerobic digestion sector.

1. Introduction

Tomato pomace (TP) i.e., the residue from juice production, sauce, and similar tomato food production, which is made up of the peel, seeds, and traces of pulp residues was considered a remarkable resource to develop a biorefinery in terms of the amount available and bioactives content (Silva et al., 2019). The great interest was focused on the extraction of lycopene (lyc) the most powerful antioxidant carotenoid, which has a relevant market use in the food, nutraceutical, and cosmetic sectors (Barreiro and Barredo, 2018; Scaglia et al., 2020; Deng et al., 2021). The most common procedure to extract the lyc (standard extraction procedure-SEP) employed organic solvent such as hexane and the process was optimized by testing several experimental conditions (Silva et al., 2023). The SEP is economical and does not require innovative equipment, on the other hand, the use of solvent lowers the quality of the extract and was not considered satisfying in terms of sustainability. By 2012 several alternative methodologies had been proposed testing different solvents by introducing pre-treatment before the extraction (Silva et al., 2023).

Organic solvents that were less toxic (ethyl acetate, ethyl lactate, etc. …), vegetal oils, deep eutectic solvents, and CO_2 under supercritical conditions were tested; although with some differences the use of alternative solvents allowed significant recovery of the lyc in the most of the cases comparable with that of the SEP but rarely higher (Silva et al., 2023).

This result was easily explainable considering that all extractive processes are dependent not only on the affinity of the solvent for the solute but firstly on the possibility of the solvent reaching the molecules of interest that, in the case of the lyc, was obstacled by the presence of membrane arranged to form vesicles and by the cell wall (Deng et al., 2021).

The tomato peel, i.e. the fraction of TP with the highest lyc content, is described as a well-structured tissue made up of several cell layers and externally covered by a cutin coat (Cuccolini et al., 2013). Although the industrial process (heating and high-pressure treatments of the tomatoes) becomes the structure slacker, a reduction of permeability of the peel occurred by drying the biomass before SEP (Prothon et al., 2003; Szymanska-Chargot et al., 2017; Huang et al., 2018; Scaglia et al., 2020).

The water was directly involved in the structure of the gel-matrix and in the bounds among the cellulose microfibrils, thus its evaporation rearranged the original structure into a rigid network characterized by a

Abbreviations: tomato pomace, TP; lycopene, lyc; water phase, WP; standard extraction procedure, SEP; fast extraction procedure, FEP; exhausted TP, TP exh; pectinase, P; cellulase, C; galacturonic acid, GalA; galactose, Gal; glucose, Glu; peel, Pe.

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higher thickness due to the glow of the walls and further lesser the lyc recovery (Scaglia et al., 2020). The choice to use TP partially dehydrated (best residual moisture of 18 % dry matter –DM) or to add polar solvent (acetone or ethanol) to the apolar one to swell the cellulosic material, were strategies that facilitated the lyc extraction but, in any case, did not increase the yield of the extraction and highlighted that the wall is the main constraint to lyc recovery (Huang et al., 2018).

Taking into consideration this conclusion, an alternative approach considers the development of pre-treatment acting on the wall structure before the solvent extraction.

The analysis of the most recent scientific works (Silva et al., 2023) identifies the use of ultrasound, microwave-assisted extraction (MAE), and pulsed electric field (PEF) as examples of physical approaches able to break, erode, and micronize the wall structure, then a chemical approach tested the effect of the microemulsion as solvent (Amiri-Rigi et al., 2016). Destruction of the wall and the hydrolysis of the membrane present around the lyc were attempted by a biological approach (Choudhari and Ananthanarayan, 2007; Ranveer et al., 2013; Gu et al., 2020; Lavecchia and Zuorro, 2008).

Testing protease, cellulase, pectinase, and hemicellulase singularly on in the mix, the great yield of extraction was 1150 mg/100 g (Catalkaya and Kahveci, 2019) and the best improvement of the recovery concerning the SEP was of +30 folders using a mix of hydrolytic enzymes (Silva et al., 2023).

Despite the great interest in the development of more efficient extraction of lyc form residues, a recent bibliometric analysis (period: 1900–2022; studies included in the review = 204 selected from 626 reports applying quality criteria) (Silva et al., 2023) highlighted that most of the articles focused on the development of methods at laboratory scale aiming at optimisation and recovery of lyc. In addition, the possibility of developing a biorefinery based on Lyc extraction has rarely been attempted.

A fundamental aspect is the design of multi-production processes from the same biomass to meet the bioeconomy principles of full valorisation of the residues and zero waste generation.

In the case of TP-lyc-based production, recent studies have adopted supercritical fluids and ionic liquid as solvent to perform the lyc extraction (Allison and Simmons, 2017; Scaglia et al., 2020), which is then destined for biogas production. Morover, fermentation was tested as a core bioconversion to produce useful value-added products (Chakravarty and Mandavgane, 2023). The most profitable approaches were those that gave more production, in some cases using sequential processes by using residues as feedstock. In addition, scale-up and economic sustainability were improved by using technology already used in the industry, although for other purposes (e.g. supercritical extraction and fermentation) (Scaglia et al., 2020; Chakravarty and Mandavgane, 2023). In this work, the use of an enzyme-based approach is tested as an alternative core treatment for the development of a TP-lyc biorefinery. The prerequisites were the existence of commercial enzymes already used in the food industry, the moderate energy cost of the process and the improvement of the successive solvent extraction (FEP) in terms of duration.

Although not previously investigated, the water medium (WP) in which the enzymatic treatment was carried out is a potential source of molecules coming out from the cell (i.e. polyphenols) or derived from the wall deconstruction such as mono- oligosaccharides from cellulose, hemicellulose, and pectin (Görgüç et al., 2020).

The rich monosaccharide-oligosaccharides solutions are of interest in several industrial sectors and specific production has been developed for this purpose (Giuffrè and Capocasale, 2016; Durante et al., 2017; Bhatia et al., 2019; Cano et al., 2020). The choice of the feedstock and the setup of the technology modulate the characteristic of the product in terms of recovery, amount of oligosaccharides (cello-oligo-saccharides), pecto-oligosaccharides and xylo-oligosaccharides, amount of monosaccharides (galacturonic acid, glucose, ribose, xylose, etc.) thus the economic value and use (Bhatia et al., 2019; Cano et al., 2020). The lignocellulosic fractions originated from the food industry such as TP being of food grade quality, are suitable to obtain fractions destined for the food, nutraceutical, and pharmacological sectors and in some cases were characterized by bioactivity (Bhatia et al., 2019). The previous approach allowed to valorize of the peel fraction of the TP, on the other hand, the seeds were similar in amount and were rich in molecules with high added value and bioactivity. In particular, the seeds were a font of oil with yields that span from 12 to 15 % to 20–30 % *w*/w according to the method employed; its compositional characterization has highlighted the presence of around 80 % unsaturated fatty acids, of which linoleic acid is the most abundant, and of bioactive phytosterols like cycloartenol, sitosterol, and stigmasterol (Eller et al., 2010; Giuffrè and Capocasale, 2016).

In this work, the feasibility of the proposed approach was developed considering TP from a full-scale plant of Northern Italy. The enzymatic process was optimized and then the best technological solution was adopted as core technology to develop a multipurpose process.

2. Materials and methods

2.1. Materials

Two different tomato pomace (TP) were sampled at a full-scale tomato cannery (XII Morelli, FE, northern Italy) at different times (TP1 in July and TP2 in August) during the production season.

The moisture content of both TPs was measured by drying the biomass at 105 °C overnight (Scaglia et al., 2020). TP employed for the successive lyc extraction was partially dried in an oven at 50 °C to reach 18 % wet weight (w.w.) moisture content, which guaranteed adequate lyc extractability (Scaglia et al., 2020).

Based on the value of the moisture content of the TP (moisture = 77.6 ± 15 % w.w.), 1000 g w.w. of TP (224 g of DM and 776 g of water) were partially dried to reach the weight of 280 g (224 g of DM and 56 g of water) and the moisture successively checked to dry a portion of the biomass at 105 °C overnight. At the end of the process, the TP was stored in closed bags under vacuum conditions at 4 °C until analysis. Quali-quantitative lyc content of TP and peel were done by performing the extraction with ethyl acetate (>99.7 % v/v, 100 mL) (Sigma Aldrich, Milan, Italy) and the Soxhlet apparatus for 8 h. The procedure named standard extraction procedure (SEP) (Squillace et al., 2020) was carried out using 2 g of partially dried biomass. The lyc was characterized by using the HPLC instrument (Squillace et al., 2020) equipped with a C30 Develosil® rpaqueous column (5 μm, 250 × 4.6 mm). The eluents methyl tert-butyl ether (A) and methanol (B) were used with a gradient of 10 % for A in 0–35 min, then to 45 % in 35–45 min, and 60 % for A in 45–56 min, turning to 10 % A in 56–60 min, with a flow rate of 1.3 mL min^{-1}. The absorbance was recorded at 475 nm (Squillace et al., 2020).

2.2. Set up of lyc enzyme assisted extraction treatments

2.2.1. Treatment of TP with enzymes

In a preliminar experiment, 2.5 g of TP1, partially dehydrated, were milled to a size <2 mm using a conventional grinder (Cyclotec TM; Oy Cyclotec Ltd., Helsinki, Finland) and employed for the enzymes treatment as reported by Zuorro et al. (2011) with some modifications.

The TP1 was put in a flask (250 mL volume) in presence of commercial enzymes: 0.48 mL/g TP of pectinase from *Aspergillus aculeatus* (E6287, Sigma Aldrich) made by polygalacturonase –PGN- characterized by activity >5000 PGN Unit mL^{-1} + traces of hemicellulase (activity of 0.16 Unit mL^{-1}) and cellulase (activity of 0.7 Unit mL^{-1}) (named P), 0.42 mL/g TP cellulase from *Tricoderma reesi* (C2730, Sigma Aldrich) made by Beta endoglucanase –EG-characterized by activity >539 EG Unit mL^{-1}, (named C) and a mix of the two enzymes (1:1 vol: vol) (P + C treatment). The TP1+ enzymes were dissolved in acetate/acetate sodium buffer (158 mL) at pH = 5, pH = 4.5 and pH = 4.7, respectively for the P, C and P + C treatments. A control treatment, i.e.,

without enzymes, was carried out for all trials. All treatments were performed in triplicate.

The flasks were shaken (4g) at 30 °C for 30 h in an incubator. The kinetic processes were monitored by sampling 1.2 mL of water phase (WP) at 30, 45, 60, 120, 180, 240, 300, 360, 1440 and 1800 min to assess the chemical characteristics (see Sections 2.2.2, 2.2.3).

At the end of the process (t = 1800 min) The flasks were treated at 55 °C for 10 min, then the WP (120 mL) was immediately separated from the TP1 residues (named TP1 exhausted - TP1 exh) by centrifugation (7245g for 10 min, room temperature) and successively stored at −18 °C. Although complete inactivation of the enzymes occurred at 100 °C, the enzyme activity was slowed down by increasing the temperature and removing the substrate. This strategy was adopted to preserve the organic molecules of WP, since at high temperature the saccharides are subject to degradation or chemical modification (Eggleston and Vercellotti, 2000; Einhorn-Stoll et al., 2014).

The TP1 exh of all treatments (P, C, P + C, and control) was added to 40 mL of ethyl acetate and mixed for at least 10 s (fast extraction procedure-FEP). Then the ethyl acetate phase was separated from the TP1 exh and analysed for the lyc content.

2.2.2. *Quantification of WP monosaccharides*

A volume of 0.6 mL of WP sampled during the treatments was used for the determination of galacturonic acid (GalA), galactose (Gal), and glucose (Glu), selected as indicators of hydrolysis of pectin, hemicellulose, and cellulose respectively. The analyses were performed using a Shimadzu HPLC system (Shimadzu Corporation, Tokyo, Japan) with a Hi-Plex H Agilent column (300 × 7 mm, PL1170-6830) (Agilent Technologies, Santa Clara, CA, USA). The refractive index detector (RID) was held at 35 °C. The samples were run using an isocratic 4-mM sulfuric acid eluent at 0.4 mL min^{-1} at 60 °C for 40 min. Eluent was prepared using Milli-Q® water and 95 % sulfuric acid from Carlo Erba Reagents. Before analyses, samples were filtered through 0.2 μm centrifuge filters by centrifugation at 15115 g for 5 min at room temperature. LabSolutions 5.90 software package (Shimadzu Corporation, Tokyo, Japan) was used to calculate the concentration of the samples from a five-point standard calibration curve.

2.2.3. *Quantification of lyc extract in WP*

A volume of 0.6 mL of WP sampled during the treatment process was mixed with 1 mL of ethyl acetate and shaken for 10 s. After the phase separation, at least 0.5 mL of the ethyl acetate solution was collected for further lyc detection.

2.3. *Upgradation of the enzymatic pre-treatment process*

Based on the preliminary results, the P + C treatment was selected as the best in terms of lyc extraction and procedure duration. New experiments were therefore carried out using another sampled tomato pomace (TP2) as described in Section 2.2.1 and its peel fraction (named Pe2) separated by the seeds in water by exploiting their different densities. Both the samples were employed as feedstock to perform the P + C + FEP. To compare the performance of the P + C treatment for TP2 and Pe2, the same amount of dry matter biomass (2 g DM) was employed and the enzymes were dosed in accordance with the amount of peel present. At the end of the processes, the WP and the exhausted fractions were collected for chemical characterization. The TP2 and Pe2 before and after the treatment were characterized for their fiber and lyc content (Scaglia et al., 2020).

2.4. *Chemical characterization of WP*

The WP of all treatments was fully characterized for the organic carbon by using the chemical oxygen demand (COD) as indicator, N and acetic acid content; the total polyphenols content (TPC) and antiradical activity (AA) were also quantified by using the DPPH radical scavenging method and the Trolox (Prot. N. 238,813, Sigma Aldrich, Dermstadt, Germany) as reference (Abbasi-Parizad et al., 2022).

Moreover, WP at the end of the P + C pre-treatment was dried at 40 °C under vacuum and characterized by Fourier Transform InfraRed (FT-IR) spectroscopic technique. The spectrum was collected in total reflectance mode (ATR) with a Shimadzu IRAffinity-1S, equipped with a Miracle Pike ATR device (Shimadzu Italia srl, Milano, Italy); peak areas were determined using Shimadzu LabSolutions IR software. The investigated wavenumber range was of 4000–500 cm^{-1} and the resolution was of 2 cm^{-1}.

2.4.1. *Tomato seed oil extraction and characterization*

The seeds from TP2 were dried and ground to the powder size to guarantee a higher oil recovery (Squillace et al., 2020). The extraction of oil was carried out at lab scale using the Soxhlet apparatus with hexane as the solvent (Squillace et al., 2020). The yield of the oil was gravimetrically measured and was characterized for fatty acids, tocopherols, and phytosterols content. The tocopherols were quantified using an HPLC system (Agilent 1260 Infinity) equipped with a Phenomenex Kinetex XB C18 column (5 μm, 250 × 4.6 mm); by using the analytical method described by Chen and Bergman (2005): various tocopherols were identified using analytical standards.

For phytosterols analysis, 100 mg of oil was saponified in 2 M KOH/methanol at 60 °C for 45 min. The saponified solutions were extracted twice with 2 mL hexane and the combined resulting fractions were dried in a vacuum oven. Trimethylsilyl (TMS) derivatives were made by adding 100 μL pyridine and 100 μl N, O-bis (trimethylsilyl)-fluoroacetamide with 1 % trimethylchlorosilane to the saponified phytosterols, and the mixture was heated at 60 °C for 1 h in GC–MS glass vials (Eller et al., 2010). The compounds were separated using a polar capillary column Zebron ZB-SemiVolatiles (Zebron, Phenomenex, USA) of 30 m × 0.25 mm (ID) and a film thickness of 0.25 μm. The injection volume was 1 μL with a split ratio of 50:1. Carrier gas was helium at a flow rate of 1 mL min^{-1}. The temperature program was isothermal for 2 min at 250 °C, then the temperature was raised at a rate of 10 °C/min to 270 °C, kept at 270 °C for 20 min, raised at 10 °C/min to 280 °C and kept at 280 °C for 1 min. Injection temperature was 250 °C and the transfer line to the mass spectrometer was maintained at 290 °C. Chromatographic analysis was performed using an Agilent 5975C Series GC/MSD and FID as detector. Compounds were identified and quantified by comparison with the NIST library and by using 5-α-cholestane as an internal standard.

The TEAC (Trolox Equivalent Antioxidant Capacity) assay was conducted to assess the antioxidant capacity of oil by evaluating the 2,2-azinobis-3-ethyl-benzothiazoline-6-sulfonic acid ($ABTS^{+}$) radical cation decolorization reaction. ABTS+ was produced by mixing an aqueous solution of ABTS (7 mM) with potassium persulfate (2.45 mM, final concentration) and by letting the mixture react in the dark at room temperature for 12–16 h. An aliquot of oil was dissolved in 3.9 ml ABTS+ solution, and 1 ml of the resulting solution was read at $\lambda = 734$ nm both after 6 min and at the end reaction in the dark. The antioxidant capacity was expressed as trolox μmol which produces the same decolorization as 1 g of Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) used as standard. The spectrophotometric analysis was carried out with a UV/visible Varian Cary 60. Analyses were conducted in triplicate.

2.5. *Statistical analysis*

All statistical calculations were done using SPSS 25 (IBM, New York, NY, USA) except enzymatic kinetics, for which Graph-Pad Prism 10.0.2.232 (GraphPad Software LLC, San Diego, CA) was used.

3. Results and discussion

3.1. Effect of the enzyme pre-treatments on fiber hydrolysis and lyc recovery

All pre-treatments with the enzymes determined an increase in the concentrations of the monosaccharides (Fig. 1); the C was effective vs. Glu, whilst the P and the P + C vs. GalA, Gal, and Glu but with different results by following the Michaelis-Menten relationships.

The parameters of the kinetic (K_M and V_{MAX}) added information on the specificity for the substrate and velocity of the hydrolyses respectively. The best performance was obtained both in terms of monomer concentration and reduction of the time for the mix P + C. This result should have been explained as the consequence of the presence of two different cellulases characterized by completely different mechanisms of hydrolysis (high specificity and low velocity or high velocity and low specificity respectively) therefore their mix improved both those aspects reducing the time needed to get the same hydrolysis degree. The effect of the enzyme activity on the lyc content was moreover detected by measuring the concentration in the WP (Fig. 2), at the end of the processes the amount of extracts was similar but the P + C allowed to reach the plateau of the extraction very earlier than the other two (maximum lyc extract after 360 min for P + C and 1400 min for both P and C) (Fig. 2).

The lyc showed a trend very similar to those described for the standard extraction process (SEP) (Scaglia et al., 2020) that considered a different extractability based on its localization in the broken/intact cells and the outer/inner layers of the peel (Huang al., 2018; Scaglia et al., 2020). Aiming to better understand the relationships between lyc and fibers hydrolysis, the instantaneous concentration (i.e. cumulate concentration at time N + 1 - cumulate concentration at time N) of lyc and monosaccharides was calculated (Fig. 3). The kinetic of the lyc was very similar (both concentration and time) for all treatments, moreover, the time of the lyc-picks was the same of those of the monosaccharides, confirming the that the wall depolymerization improved the lyc extraction.

In addition, the P + C caused a bigger pick of lyc earlier that corresponded to most of the lyc extract (Fig. 3). Respect to the thing previously described, the lyc pick occurred later than those of monosaccharides that happened all at the same time probably the key factor that improved the subsequent lyc yield.

Lyc was insoluble in water and its concentration in the WP was explainable by the suspension phenomenon enhanced by the presence of organic colloidal such as proteins, pectin, etc. (Squillace et al., 2020). By using the standard extraction (SEP) as a reference (Fig. 3), the application of the pre-treatment plus the successive fast extraction with ethyl acetate gave higher lyc recovery only for the P + C (+194 % lyc of SEP) in agreement with the best performance reported in the literature (Choudhari and Ananthanarayan, 2007; Lenucci et al., 2015). The additive content of lyc obtained with the P + C + FEP was the *all-E* isomer i.e. the native lyc positioned in the deeper cell layers becomes achievable thanks to the P + C employment, at the same time degradation of the Z isomer occurred probably as a consequence of the long exposure to oxygen (Xianquan et al., 2005) (Fig. 4).

3.2. Optimisation of the size of biomass and choice of the best feedstock for lyc extraction and recovery

The seeds were not a font of lyc on the other hand their presence can affect the yield of extraction reducing the peel vs. enzyme physical interaction or for the presence of additional fibers i.e. substrate for the enzymes. To evaluate these aspects, the lyc recovery of TP2 was expressed on peel content basis and the data compared with that obtained treating the only peel fraction (Pe). The very similar data excluded a negative influence due to the seed presence. Similarly, no differences were found between the hydrolysis rate (i.e., fiber before – fiber after) of TP2 and Pe, indicating again that the seed did not have a negative effect but in any case, they were not valorized (Table 2).

3.3. Characterization of fractions from the multi-production process

3.3.1. Lycopene extract

The use of Pe2 gave a recovery of lyc of 3216 μg g^{-1} DM (i.e. 0.32 % DM) which was converted to powder after a drying step. Although the use of organic solvent has several drawbacks, ethyl acetate is considered "green" and its employment is allowed in the food industry (Joint FAO and WHO Expert Committee on Food Additives, 2006; Tobiszewski et al., 2017).

3.3.2. Chemical characterization of the WP fraction

The WP accounted for 90 mL/ g DM of Pe2; in addition to acid acetic/ Na acetate used as the buffer system, other organic molecules were found for a whole COD value of 9.9 g L^{-1}. From a qualitative point of view, the FT-IR spectrum (Fig. S1) showed a main area dominating at 2982 cm^{-1} (OH stretch) and at 1651 cm^{-1} (OH deformation) attributable to C—H stretching of carboxylic acids and NH_3 stretching band of free amino acids respectively attributable to the P and C or other proteins (Anjos et al., 2015). Moreover, in the region from 1651 cm^{-1} to 1080 cm^{-1} several narrow bands typical of sugars and organic acids were present (Wiercigroch et al., 2017). In particular, the peak at 951 cm^{-1} corresponds to the C—H bending of carbohydrates, the peak at 1254 cm^{-1} is indicative for C—O stretch in C–OH group as well as C—C stretch in the carbohydrate structure, the peak at 1385 cm^{-1} is attributable to O—H bending of the C–OH group and the broad peak at 1420 cm^{-1} is indicative of O—H bending of C–OH group and C—H bending of alkenes such as carotenoids (i.e. β-carotene). Furthermore, peaks detected at 1080 and 951 cm^{-1} are indicative of stretching vibrations (C—C) in carbohydrate structure (Kozłowicz et al., 2020).

The IR interpretation confirmed the lower content of cellulose and hemicellulose 44 % and − 73.3 % respectively (Table 1) in the biomass at the end of the process. The treatment affected the TP not only from a qualitative point of view but also in quantitative terms due to the partial solubilization of the carbohydrates. Considering qualitative and quantitative changes, the effectiveness of hydrolyses was estimated of 83.3 % and 67.3 % for the hemicellulose and cellulose respectively (Scaglia et al., 2020) to obtain monomers (Gal and Glu accounted for 42 % and 11 %) and oligomers (58 % and 89 %) of hydrolyzed hemicellulose and cellulose respectively.

The WP was characterized for the polyphenols too, molecules present in the cell of interest for their significant bioactivity (Abbasi-Parizad et al., 2022). Their concentration expressed as TPC agreed with those of previous works in which significant antiradical activity (AA) (Table 1) was observed.

3.3.3. Tomato oil characterization

The oil recovery was 34 % DM seed and corresponded to the 17 % DM of the starting TP2. The presence in terms of bioactives highlighted the possibility for the oil to be employed as an alternative to actual fractions known for the presence of unsaturated fatty acids, tocopherols, and phytosterols (Table 3). The high content of linoleic acid (53.92 % fatty acid) plus other unsaturated forms gave a total amount of unsaturated acids of 80.2 % fatty acids which is very similar to the amounts in sunflower and soybean oils commonly used in food, cosmetic, and nutraceutical sectors (Orsavova et al., 2015). Indeed, the quali-quantitative content of unsaturated fatty acids vs. saturated ones suggested an edible use in analogy with other fractions extracted from agro-industrial residues (Kumar et al., 2021).

The tocopherols were especially noted as being present in the γ-form in concentrations comparable to that obtained by *Hibiscus sabdariffa* pumpkin seed oil, to the best of our knowledge, one of the most tocopherol-rich edible oils (Stevenson et al., 2007; Ismail et al., 2008). Both the whole amount (4 mg g^{-1} oil) and the identification of the major

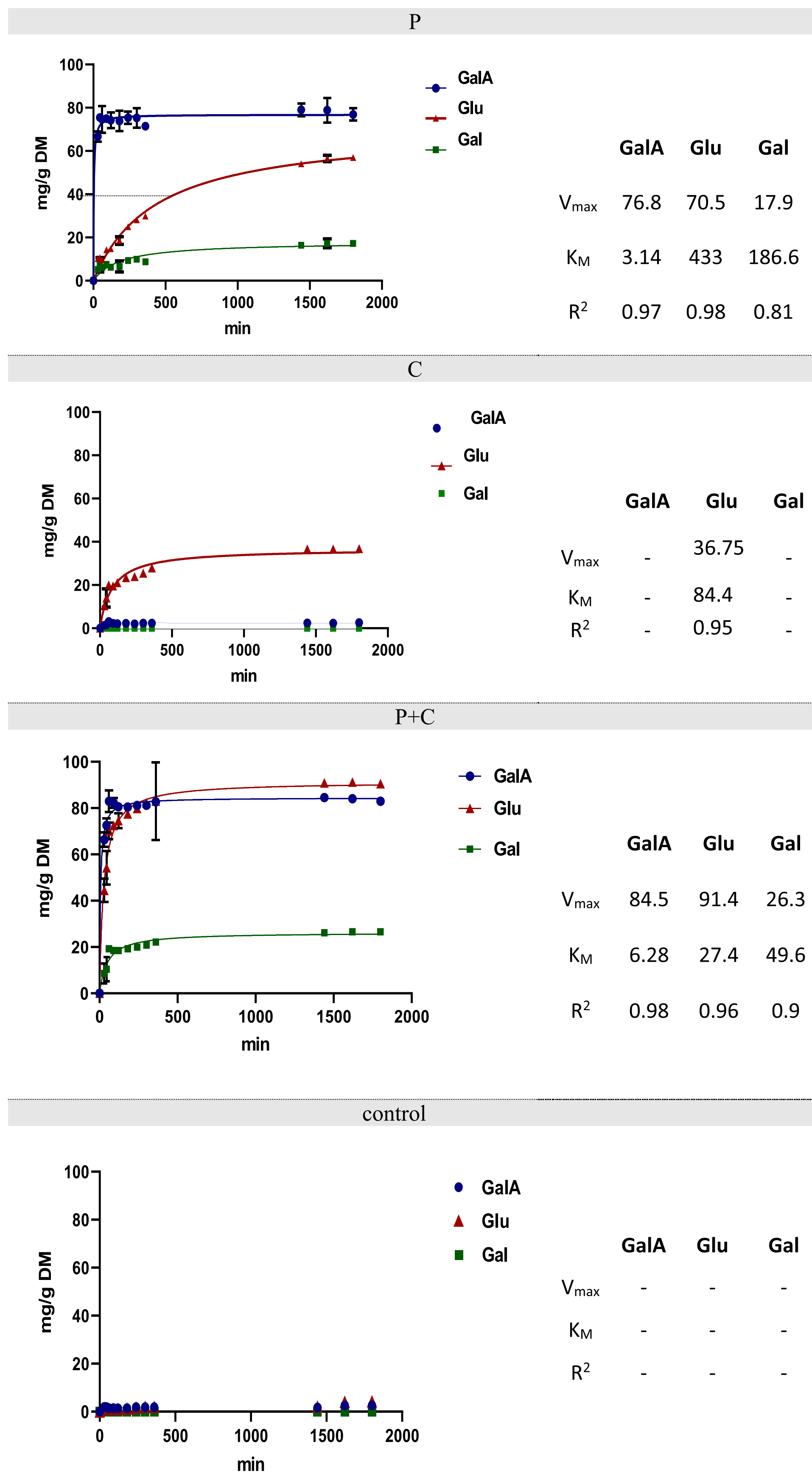

Fig. 1. Detection of the kinetic hydrolysis of the pectin, hemicellulose, and cellulose of the TP1 performed using the commercial solution of pectinase (pre-treatment P), cellulase (pre-treatment C), and the mix 1:1 v/v of the previous ones (pre-treatment P + C). By using the software GraphPad Prism the existence of significant Michaelis-Menten curves was checked and the parameters (K_M and V_{MAX}) were estimated.

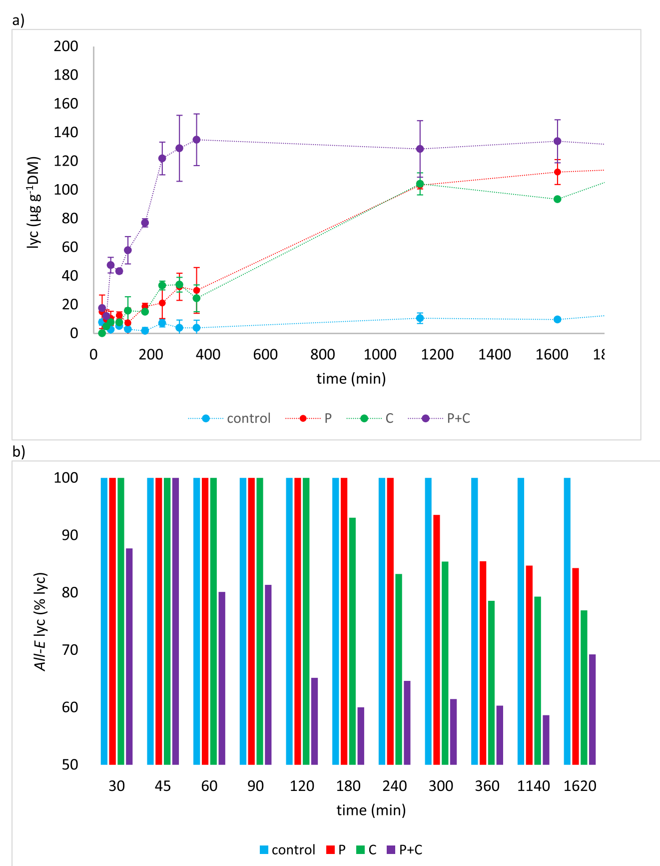

Fig. 2. a) The trend of the recovery of a) lycopene (lyc) and b) lycopene qualitative composition (*All-E* and Z isomers) during the pre-treatment with pectinase (P), cellulose (P + C) and their mix 1:1 (P + C) of the TP1. The data referred to the amount recovered in the water solution (WP) and successively extracted with ethyl acetate.

phytosterol forms in the β-sitosterol and stigmasterol (Zuorro et al., 2014; Kalogeropoulos et al., 2012) indicate that the oil is similar to ginseng, barley and rice seed oils (Beveridge et al., 2002; Lampi et al., 2004) which are employed for their capability to reduce cholesterol absorption (Racette et al., 2009).

The antioxidant activity of the oil was investigated resulting comparable with those of pure molecules such as tocopherols known to be powerful antioxidant molecules such as tocopherols (Beveridge et al., 2002; Melendez-Martínez, 2014).

3.4. *Proposal of the multi-production process and mass balance for a full scale tomato cannery plant*

To evaluate the feasibility of the approach considered, the data obtained have been applied to calculate potential yields at a full scale for northern Italy, one of the most abundant production regions for tomatoes destined for the cannery industry (Scaglia et al., 2020).

Considering an annual treatment of 600,000 t wet weight of tomatoes, a TP amount of 1800 t w.w. was expected in which the peel and seed contributed 67 % and 34 % w.w. respectively. In terms of dry matter, these data corresponded to 52 % and 48 % DM for peel and seed respectively (Scaglia et al., 2020). The current destination of most TP is the anaerobic digestion (AD) sector, well developed in the region as additional biomass to the feedstock of the plants made, above all, by silage maize. By using the biogas production potential of the silage maize (anaerobic biogassification potential – ABP = 250 Nm^3 ton^{-1} w.w.) as reference, the ABP of the TP was equal to the 29 % ABP silage maize. Short storability and low methane potential production affected the economic value of the TP for the AD sector therefore they are let for free or by paying for transportation (Scaglia et al., 2020).

This current approach partially met the rules of the bioeconomy that let to maximize the valorization of the residues in terms of number of the products and economical revenue (Stegmann et al., 2020). In comparison with the current management of TP, the application of the proposed production system potentially gives three products: lyc powder = 672 kg y^{-1}, WP = 18,801 m^3 y^{-1}, and tomato oil = 60,000 L y^{-1} instead of methane and digestate. The design of the process had a significant impact on the cost of production and the economic sustainability of the process. The lyc-rich powder from ethyl acetate extraction of tomato fruit is currently present in the market as a food and feed colouring agent and in the nutraceutical and cosmetic sectors with an economic value of 3000 Euro/kg (BCC Research, 2018).

The production cost of lyc extraction from TP was estimated at $ 1307/kg, corresponding to 60 % of the selling price (Yadav and Dhamole, 2023). In the case of pre-treatment, there was an increase in the cost of manufacturing due to instrumentation, reagents and energy (Silva et al., 2023). When the enzyme was used there was an increase in the cost of production up to $ 2544/kg, mainly due to the cost of the enzyme making the production economically unviable (Yadav and Dhamole, 2023). In this work, P and C were "low cost" enzymes (Giovannoni et al., 2020) and were already employed in the food industry (C was Celluclast® and P was Pectinex® Ultra Clear from Novozymes), therefore a limited increase in the cost of production of the lyc in relation to the SEP, especially in the perspective of doubling the recovery yield was expected.

The evaluation of enzymatic pre-treatment considers the use of free enzymes, i.e. free in the WP medium, which limits their recovery and reuse at the end of the process. An alternative approach is the immobilisation strategy, where the enzymes are chemically or physically bound to a support (Homamei et al., 2012). This technology, already applied in industry, allows a significant recovery and reuse of the enzyme to act on more production cycles, with a reduction in the cost of the process of up to 60 % (Sóti et al., 2018). Using the estimated cost of the free enzyme and the expected 60 % reduction, the calculated cost of the immobilised technology is $1107/kg, which is a production cost comparable to that of solvent extraction and therefore sustainable, respecting the market value of lyc.

A first attempt to estimate the economic convenience of the whole proposed platform was attempted considering the value of the additional fractions based on the economic value of the same or similar product on the market.

The WP is a cocktail of different molecules, but the main abundant fractions are the mono/oligosaccharides coming from the hydrolysis of hemicellulose and cellulose.

The derived hemicellulose fraction accounted for 555 mg L^{-1} of which only 31.7 % was recognized as Gal while the remaining amount could be made up by other monomers (mannose, glucose, xylose, glucuronic acid) or by oligomers coming from the galactoglucomannan-glucuronoxylan I and II sequences (Prakash et al., 2012). The composition, pureness degree, and potential bioactivity influence the value of hemicellulose derived fractions, estimated in the range of 22–50 USD $ kg^{-1} for use in the functional food and pharmaceutical sectors (Bhatia et al., 2019).

The cellulose-derived fraction was present in a higher concentration (1645 mg L^{-1} of WP) and was composed, above all, of cellobiose and higher cello-oligosaccharides (COS) plus 9 % of monomers, employable as feedstock of a C6 biorefinery platform (Farrán et al., 2015; Bhatia et al., 2019; Cano et al., 2020).

The tomato oil had a composition similar to that of the main edible oils, in particular sunflower oil. Although its main use is in the cosmetics and skin care sectors, a precautionary value estimation of 1432.32 USD m^{3-1} was made, considering the sunflower oil as reference (price = 1556.87 USD ton^{-1}, World Bank, https://www.theglobaleconomy.com/World/sunflower_oil_prices/, July 2022).

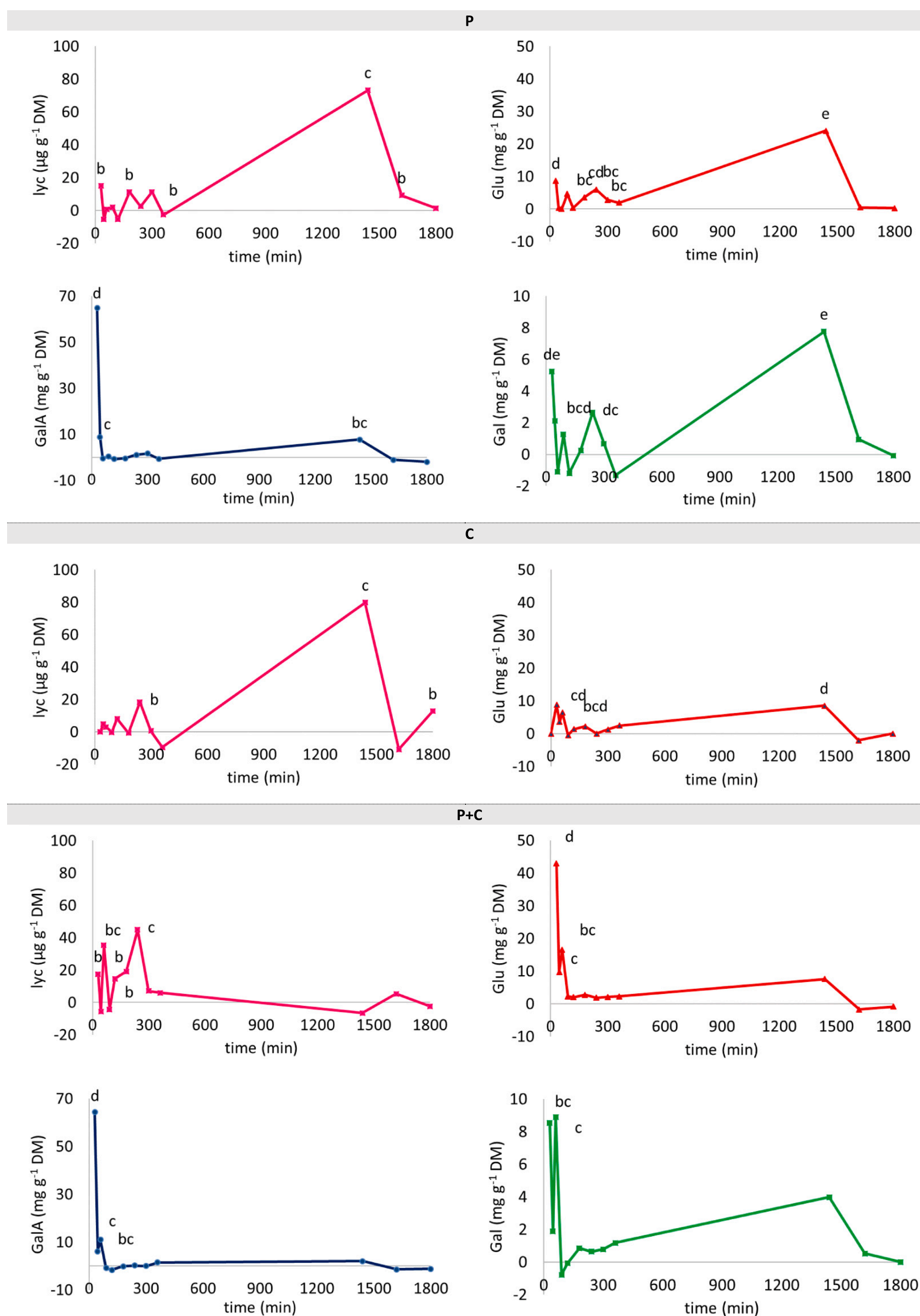

Fig. 3. Identification of the time of maximum extraction from TP1 of lycopene (lyc), galacturonic acid (GalA), glucose (Glu), and galactose (Gal) during the pretreatment with pectinase (P), cellulose (C), and their mix (P + C). The data were the average instantaneous concentration (i.e. cumulate concentration at time N + 1 - cumulate concentration at time N) of the data reported in Figs. 1 and 2. The values identified by different letters at different times of the kinetic were statistically different (ANOVA test, $p < 0.05$, post-test Duncan). Where the letter was absent it corresponded to a letter - a - omitted in the figure to improve the readability.

4. Conclusion

The food industry and in particular vegetal production generated a huge amount of residues characterized by high nutritional and bioactives content. To avoid the waste disposal discouraged by the EU waste hierarchy approach, the food producers gave the residues free to the energy producers for feed employment. This approach is considered the basic form of industrial symbiosis based on the self-organizing network of neighbour's activities. However, it limited the development of the multi-production process and did not consider the profitability of the process as the criterion of development.

In this paper, the tomato pomace that is the most profitable residue

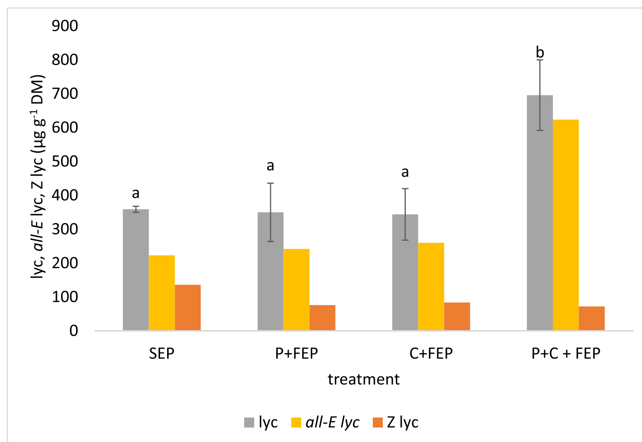

Fig. 4. Comparison of the lycopene (lyc), and isomers (*all-E* and Z) recoveries of the standard extraction procedure (SEP) and of the proposed processes (i.e. pre-treatment with pectinase -P-, cellulase -C- and their mix -P + C- followed by the fast extraction procedure - FEP). The lyc identified by different letters for the different processes were statistically different (ANOVA test, $p < 0.05$, post-test Duncan).

Table 2
Fiber composition of TP2 and Pe2 at the start and at the end of the process made by pectinase+cellulase pre-treatment+ fast extraction process (P + C + FEP).

	Soluble cell fraction	Hemicellulose	Cellulose	Lignin+cutin
	mg g^{-1} DM			
TP2	419±11[a]	96 ± 7	235 ± 31	250 ± 36
Pe2	340 ± 15	60 ± 16	220 ± 5	378 ± 36
TP2 exh	311 ± 37	55 ± 3	152 ± 5	483 ± 46
Pe2 exh	220 ± 62	16 ± 5	123 ± 9	641 ± 59

TP2: tomato pomace.
Pe2: peel fraction of the TP2.
TP2 exh: TP2 at the end of the made by pectinase+cellulase pre-treatment+ fast extraction process (P + C + + FEP).
Pe2 exh: Pe2 at the end of the made by pectinase+cellulase pre-treatment+ fast extraction process (P + C + + FEP).
[a] Data is average ± standard deviation.

of the tomato cannery industry, one of the most developed vegetal production around the world, was considered as valuable feedstock to develop a multi-production process addressed to high-added value production. To maximize the lyc extraction additional production of oil and carbohydrates rich fraction was considered while reducing residues. To conclude, the proposed approach had several advantages over that currently applied by the full scale plant producers, the validity of the proposal was strictly linked to the interest of the market for the products and on the feasibility to scale up the technology and can contribute to its widespread adoption and success.

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CRediT authorship contribution statement

Barbara Scaglia: Conceptualization, Writing – original draft, Data curation. **Pietro Squillace:** Investigation. **Parisa Abbasi-Parizad:** Investigation, Data curation. **Gabriella Papa:** Investigation. **Patrizia De Nisi:** Investigation. **Fulvia Tambone:** Investigation, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

Table 1
Lycopene recovery from the pectinase+cellulase pre-treatments (P + C) followed by the fast extraction procedure (FEP) with ethyl acetate (P + C + FEP) of TP2 and Pe2 and water phase (WP) compositions of the enzymatic pre-treatment.

Phase		Unit of measure	TP2	Pe2
P + C + FEP	lyc	µg g^{-1} DM	1568±308	3216 ± 86
	All-E	% lyc	89.1	82.8
WP	COD	g L^{-1}	10.5 ± 0.5	9.9 ± 1.5
	N	mg L^{-1}	215 ± 7	200 ± 28
	GalA		187 ± 1	176 ± 4
	Glu		146 ± 1	151 ± 0
	Gal		201 ± 1	233 ± 6
	Acetic acid		2315 ± 282	2115 ± 321
	TPC	mg GAE mL^{-1}	107 ± 15	76 ± 3.2
	AA	µmol $_{Trolox}$ mL^{-1}	161 ± 9	158 ± 2

TP2: tomato pomace number 2.
Pe2: peel fraction of the TP2.
P + C + FEP: pectinase+cellulase pre-treatments followed by fast extraction procedure with ethyl acetate.
lyc: lycopene.
All-E: E isomer of lyc.
WP: water phase of the enzymatic pre-treatment.
COD: chemical oxygen demand.
N: total nitrogen content.
GalA: galacturonic acid.
Glu: glucose.
Gal: galactose.
TPC: total polyphenols content.
GAE: gallic acid.
AA: antiradical activity.

Table 3
Characterization of tomato oil from the seed fraction of the TP2.

Category	Molecules	Unit of measure	Values[a]
Fatty acid	9, 12-cis octadecadienoic acid	% total fatty acids	53.92 ± 0.51
	9-Cis octadecenoic acid		18.66 ± 0.47
	Hexadecanoic acid		14.43 ± 0.61
	Octadecanoic acid		4.70 ± 0.28
	9-Trans octadecenoic acid		3.48 ± 0.2
	9, 12, 15-cis octadecatrienoic acid		2.55 ± 0.08
Tocopherol	γ-Tocopherol	mg/g_{oil}	1.66 ± 0.14
Phytosterol	β-Sitosterol		1.88 ± 0.01
	Cycloartenol		0.86 ± 0.06
	26-Nor-5-cholesten-3-β-ol-25-one		0.37 ± 0.02
	Lanost-8-en-3-ol		0.34 ± 0
	26-Nor-5-cholesten-3-β-ol-25-one		0.37 ± 0.02
	Cholesterol		0.16 ± 0.02
	Campesterol		0.14 ± 0.03
	Total		4
Antioxidant activity	TEAC	µmol$_{trolox}$/g_{oil}	8.17 ± 0.35

TEAC: Trolox Equivalent Antioxidant Capacity.
[a] Data is average ± standard deviation.

the work reported in this paper.

Data availability

Data will be made available on request.

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