Environmental Research 220 (2023) 115207

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Sustainable recovery of phenolic antioxidants from real olive vegetation water with natural hydrophobic eutectic solvents and terpenoids

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ARTICLE INFO

Keywords:
Terpenoids
Eutectic solvents
Olive mill wastewater
Phenolic compounds
Liquid-liquid extraction
COSMO-RS

ABSTRACT

Olive oil production leads to the generation of olive mill wastewater (OMWW). Due to the presence of phenolic compounds, they are difficult to process, but they represent a source of high-added value chemicals since they have antioxidant and therapeutic properties. This work has studied the extraction of phenolic compounds from a type of OMWW, olive vegetation water, which presents these compounds in a more diluted dosage than in other studied to date, to revalue this waste stream. A real olive vegetation water from a Spanish olive oil producer was used, and liquid-liquid extraction was applied. Terpenoids and terpene-based hydrophobic eutectic solvents were systematically used to extract phenolic compounds following the concentrations of tyrosol, catechol, caffeic acid, and total phenolic content. By molecular simulation with the COSMO-RS method, 4 terpenoids, and 2 eutectic solvents were selected and compared with 2 conventional solvents. The Solvent/Feed ratio in the extraction of phenolic compounds was studied, showing that the solvents with the highest extraction results were geraniol, eucalyptol, and eutectic solvent menthol + camphor, which outperformed conventional solvents methyl isobutyl ketone and diisopropyl ether. Menthol + camphor gave total phenol extraction yields of 88.73% at a Solvent/Feed ratio in volume of 0.50, surpassing all solvents tested. A solvent reuse and regeneration process was applied by back-extraction of the 4 solvents: FTIR results showed the stability of the solvents while maintaining yields in the solvent reuse process. The phenolic compounds could be concentrated in the alkaline phase to factors up to 49.3 to the initial concentration in olive vegetation water. The alkaline phases were neutralized to obtain a precipitate with a caffeic acid content of up to 26 % wt%, and a tyrosol-rich supernatant with a concentration of up to 6.54 g/L. This work proposes a process using natural solvents to extract phenolic compounds from olive vegetation water.

1. Introduction

Olive oil production reached an estimated annual output of 3.1 million tons in 2019, 1.1 million of which are produced in Spain (Food and Agriculture Organization of the United Nations, 2022). Olive oil production generates waste, including olive oil wastewater (OMWW), which can reach 30 million cubic meters per year in Mediterranean countries (Meftah et al., 2019; Khdair and Abu-Rumman, 2020; Yangui et al., 2017). The production of these effluents poses a waste management problem since conventional systems cannot treat them due to their high toxicity to biological treatments (Mancuso et al., 2022; Klisović et al., 2021; Wang et al., 2021). It is mainly due to the presence of phenolic compounds, among which tyrosol, hydroxytyrosol, and to a lesser extent, other chemicals such as caffeic acid, *p*-coumaric, syringic, ferulic acid, or catechol, among others (Meftah et al., 2019; Rahmanian et al., 2014; de Marco et al., 2007). The presence of phenolic compounds in the OMWW presents an opportunity to revalorize these wastes by obtaining high-value-added products. Research has been conducted to obtain phenolic compounds (Esparza et al., 2020; Foti et al., 2021; Roig et al., 2006), as they show numerous therapeutic capacities of great interest, such as anti-inflammatory, antioxidant, antiaging, cardioprotective, and anticancer properties (Dai and Mumper, 2010; Hussain et al., 2016; Albuquerque et al., 2021; Leri et al., 2020; Brunetti et al., 2020). Moreover, they could be applied to other fields, such as

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https://doi.org/10.1016/j.envres.2022.115207
Received 15 November 2022; Received in revised form 25 December 2022; Accepted 31 December 2022

metal recovery for recycling printed circuit boards (Koul et al., 2022) or energy production (Klisović et al., 2021; Koul et al., 2022).

Due to the interest in recovering phenolic compounds while decontaminating olive wastewater, several different approaches for their recovery have been developed. Adsorption processes have been used to obtain phenolic compounds (Yangui et al., 2017; Frascari et al., 2016, 2019) or a specific chemical such as rutin (Şahin et al., 2022). Membrane processes have also been used (Ochando-Pulido et al., 2012; Cifuentes-Cabezas et al., 2021; Gebreyohannes et al., 2016). Extraction processes for the extraction of phenolic compounds have been developed in recent years (Panzella et al., 2020) using, among others, eutectic solvents (Ali Redha, 2021). Solvent extraction for recovering phenolic compounds from OMWW is the most employed technique due to its simplicity and convenience. However, there may be drawbacks when toxic solvents are used (Gómez-Caravaca et al., 2017).

The eutectic solvents are two or more chemicals with a depression of the melting point driven by hydrogen bonding interactions between the acceptor and the donor (Zainal-Abidin et al., 2017; Riveiro et al., 2020; Smink et al., 2020). The selection of the components of the mixture can tune their physicochemical properties. Eutectic solvents have been investigated given their advantageous characteristics of being easily prepared for their application in numerous research fields such as analytical chemistry (Santos et al., 2022), new materials development (Tomé et al., 2018; Wu et al., 2021), application as reaction media (Alonso et al., 2016; di Carmine et al., 2021), and processes of separation and extraction (Li and Row, 2016; Rodríguez-Llorente et al., 2020a; Jha et al., 2020; Haider et al., 2021; Lu et al., 2022). Using natural components in their formulation has also been considered to develop more sustainable processes by minimizing toxicity and price and enhancing biodegradability (Dai et al., 2013; Paiva et al., 2014; Liu et al., 2018; Phelps et al., 2018). Terpenes have gained popularity in forming hydrophobic eutectic solvents (van Osch et al., 2019; Schaeffer et al., 2018; Ribeiro et al., 2015; Bezold and Minceva, 2018; Verma et al., 2018; Martins et al., 2019; Rozas et al., 2021a, 2021b; Zamora et al., 2022; Liu et al., 2023; Li et al., 2022) due to the asymmetric polarity of several of them, leading to V-type eutectic solvents (Abranches and Coutinho, 2022; Abranches et al., 2019).

Terpenes and terpenoids are nature's most diverse plant-derived compounds (Zwenger Chhandak Basu et al., 2008). Using them would have advantages, including lower environmental impact, greater safety, and a renewable character compared to petroleum-derived solvents (Ribeiro et al., 2015; Boutekedjiret et al., 2014). Because of their hydrophobic nature, these solvents have been employed for the extraction of lipids, carotenoids, and phenolic compounds from food products (Li et al., 2022; Madji et al., 2019) and microalgae (Golmakani et al., 2014; Hamiche et al., 2018), volatile fatty acids (Rodríguez-Llorente et al., 2019), alcohols (Li et al., 2016a; Wan et al., 2016), pharmaceuticals (Rodríguez-Llorente et al., 2023; Gutiérrez-Sánchez et al., 2022a), pesticides (Gutiérrez-Sánchez et al., 2022b) and phenols (Li et al., 2016b; Rodríguez-Llorente et al., 2020b) from aqueous solutions. Improved results are obtained in some cases with pure terpenes rather than by forming eutectic solvents or by comparison with conventional solvents (Rodríguez-Llorente et al., 2020a). Although they can be competitive solvents, as they have high production and demand (Ribeiro et al., 2015), research on the extraction of organic compounds using pure terpenes and terpenoids is still scarce (Rodríguez-Llorente et al., 2020a).

In the application of the extraction for recovering phenolic compounds, the extraction from olive leaves (Durazzo et al., 2022), and winery wastewater (Cañadas et al., 2021a; Mikucka et al., 2022) have been studied. Extraction of tyrosol using ionic liquids (Larriba et al., 2016), phenolic acids with bio-based solvents (Cañadas et al., 2021b), and tyrosol with eutectic solvents formed by menthol + fatty acids (Buldo et al., 2019), all of them with synthetic solutions, have been studied in the extraction of phenolic compounds found in OMWW.

On the other hand, two types of wastewater can be distinguished in the production of olive oil: olive wash water and olive vegetation water. The latter combines olive fruit moisture with added process water (Cifuentes-Cabezas et al., 2021). Furthermore, depending on the centrifugation system, there are two-phase and three-phase systems. The two-phase system is the most widely used in Spain, at around 90%, and generates streams with a lower organic load than the three-phase centrifugation system (Ochando-Pulido et al., 2012; Cifuentes-Cabezas et al., 2021). The two-phase system, in which very little water is added (maximum 5% by weight), generates a wet pomace consisting of olive pulp (approx. 35%) and seed residues in the water released by the olive fruit and approximately 2.5% of processing water (Delisi et al., 2018). The extraction of concentrated streams generated with the three-phase system (Azzam and Hazaimeh, 2021) or the two-phase system with intermediate evaporation (Çelik et al., 2021) using ethyl acetate has been studied.

The novelty of this work lies in the extraction of antioxidants from real olive vegetation water at lower concentrations than those studied to date, thus valorizing this waste stream. In addition, green solvents as terpenes and eutectic solvents of natural origin are used for their extraction, being applied for the first time for the extraction of antioxidants from real olive vegetation water. Finally, the regeneration of these solvents and their concentration of antioxidants by back-extraction is studied.

The first objective of this work is the selection of the most promising solvents, terpenes and eutectic solvents, for the extraction of phenolic compounds. For this purpose, initially, a screening will be performed by molecular simulation using the COSMO-RS method. The second objective is to study the extraction conditions of phenolic compounds, using mild pressure and temperature conditions, applied to a real olive vegetation water. In particular, the extraction of tyrosol, catechol, and caffeic acid, as well as total phenols present in real olive vegetation water from a Spanish olive oil producer, will be studied. Finally, the development of solvent regeneration and the obtaining of the antioxidants will be carried out.

2. Methods and materials

2.1. Solvent screening with molecular simulation

Molecular simulation using the COSMO-RS method (Klamt, 1995; Klamt et al., 1998) was applied for the initial screening of solvents. This method has been widely employed for selecting solvents such as eutectic solvents (Abranches and Coutinho, 2022), as it allows further evaluation of properties such as extraction yields and activity coefficients. Turbomole 7.4 software with the COSMO continuous solvation method was used to optimize the geometries of the compounds with a BP86/TZVP computational level using the solvent effect. Optimization was performed by single-point calculation to obtain the minimum energy geometry, and the information was easily stored in a *.cosmo file. DFT-derived structures are shown in Table S1 of the Supplementary Material. The obtained COSMO files were input into COSMOtherm software (Eckert and Klamt, 2002), version 19.0.4. Calculations of the activity coefficients at infinite dilution (γ^{∞}) of three antioxidants (tyrosol, catechol, and caffeic acid) in solvents, 42 terpenes, 11 hydrophobic eutectic solvents, and five conventional solvents at a temperature of 298.2 K were performed. The computational level of theory BVP86/TZVP/DGA1 (Godbout et al., 1992) and the parameterization BP_TZVP_C30_1201 (Eckert and Klamt, 2012) were applied in predicting the activity coefficients. The particular case of eutectic solvents, formed by a binary mixture of compounds, was calculated as a mixture at the eutectic point molar composition of the hydrogen bond acceptor and donor compounds (Martins et al., 2019), as employed in previous works (Rodríguez-Llorente et al., 2019, 2020b, 2021).

2.2. Chemicals

Four terpenoids (eucalyptol, geraniol, lavandulol, and citronellol), two hydrophobic eutectic solvents (menthol + camphor and menthol + borneol), and two commercial solvents (methyl isobutyl ketone (MIBK) and diisopropyl ether (DIPE)) were chosen from the molecular simulation to perform experimental tests in vial. In addition, three antioxidants, catechol, tyrosol, and caffeic acid, were used to characterize olive vegetation water. The suppliers, purities, CAS numbers, structures, and physical properties of the chemicals used in this work are listed in Table S2 of the Supplementary Material. To prepare the hydrophobic eutectic solvents, hydrogen bond acceptor and hydrogen bond donor were gravimetrically added and stirred in a MultiMix BHM9E OVAN thermostatic bath at 323.2 K until a homogeneous liquid appeared. Eutectic solvents were prepared considering the eutectic point composition previously reported, with menthol mole fractions of 0.6 and 0.7 for the eutectic solvents menthol + camphor, and menthol + borneol, respectively (Martins et al., 2019). Moreover, the ultrapure water was obtained from a Purelab flex Elga Veolia water purification system.

2.3. Olive vegetation water characterization

Olive vegetation water from olive oil production was employed in this work obtained from the company Fejidosa Urdoliva in Mohedas de Granadilla, Cáceres, Spain. The olive vegetation water is obtained from the second vertical centrifugation of olive oil production. Before using olive vegetation water, it was filtered through a 0.2 μm filter.

A Hatch pH31 5014 T pHmeter, a Total Organic Carbon Analyzer Shimadzu Vcs4, and a Crison Basic 30 Pt1000 conductivity meter were used to characterize the olive vegetation water, and for COD analysis, a Macherey-Nagel PF-11 photometer with tube test LR COD Vario Lovivand®. Additionally, three antioxidants, tyrosol, catechol, and caffeic acid, were quantified by the HPLC method found in Table S3 of Supplementary Material as well as the total phenolic content.

An LC-MS analysis was performed to perform a qualitative analysis of other possible phenolic compounds in the olive vegetation water, with conditions found in Table S4 of Supplementary Material. The results of the peaks analyzed were compared with m/z found in the literature on possible phenolic compounds that might be present in olive vegetation water.

2.4. Liquid-liquid extraction of phenolic compounds from olive vegetation water

Extractions of antioxidants from olive vegetation water were performed using the eight selected solvents at different solvent-to-feed (S/F) ratios of 0.5, 1.0, 2.0, and 3.0. The feed and the solvents were stirred at 800 rpm in vials of 8 mL in a dry bath for 12 h at 303.2 ± 0.5 K and atmospheric pressure to ensure equilibrium. The separation of the phases was done for 12 h at 303.2 ± 0.5 K without stirring. Phase separation is then conducted with glass Pasteur pipettes to obtain the raffinates and the extracts. Raffinates were analyzed by HPLC, being the obtained deviation of the concentration after extraction with the proposed method of 1.5%.

Additionally, the total phenolic content (TC) was measured using Folin-Ciocalteús method (Folin and Ciocalteu, 1927; Singleton et al., 1999). For this measurement, 100 μL of the sample was added to 0.4 mL of ultrapure water, and 0.25 mL of Folin-Ciocalteús reagent (2 N) was added. The solution was stirred vigorously for 5 min 1 mL of 20% wt Na_2CO_3 was then added and stirred again. The samples rested for 2 h in darkness. After this, absorbance measurements at 760 nm were performed on a PerkinElmer Lambda 35 UV/Vis spectrometer with a 1 cm optical path length cell. The results are expressed in Gallic Acid Equivalence (GAE) in mg/L by comparison with the results obtained using gallic acid standards, as it is usually used as a reference (Wojdyłoa et al., 2007). The water content of the extracts was also analyzed by titration with Mettler Toledo DL 32 Karl Fisher Coulometer. The extraction yields of antioxidants and TP were calculated using the following equation:

$$Yld_i(\%) = \frac{C_{i,0}^{aq} - C_i^{aq}}{C_{i,0}^{aq}} 100 \quad (1)$$

where $(C_{i,0}^{aq})$ is the initial concentration of compound i in the aqueous feed and (C_i^{aq}) the concentration in the raffinate phase after the extraction.

2.5. Solvent reuse and regeneration

The solvents eucalyptol, geraniol and menthol + camphor, together with conventional MIBK, were selected from the vial experiments for the solvent reuse and solvent regeneration tests. In these assays described in Fig. 1, phenolic compounds were extracted from olive vegetation water at an S/F ratio of 2.0. Subsequently, the extracts were subjected to a back-extraction with 2 M NaOH (aqueous phase). In this way, it is possible to regenerate the solvents and concentrate the antioxidants in the alkaline phase in the form of phenolates, as already reported in previous work on the extraction of phenols and Bisphenol A (Rodríguez-Llorente et al., 2020b, 2021). The alkaline phase/extract ratio used was 1/100. After that step, the solvent was reused in a new extraction and subsequent regeneration stage with back-extraction up to 3 times. Extraction and back-extraction tests were performed in bottles immersed in a MultiMix BHM9E OVAN thermostatic bath at 303.2 K and with stirring of 800 rpm for 12 h. Subsequently, the phases were separated in separatory funnels for 12 h. The raffinates obtained in the extraction step were analyzed by HPLC with the method described above.

As for the alkaline phases obtained in the back-extraction, those obtained in the three regeneration stages were combined for each solvent separately. Aliquots of the resulting solutions were neutralized with 2 M HCl and diluted by a factor of 1/50. The resulting solutions were analyzed by the HPLC method described above.

Finally, 37% HCl was added to the alkaline solutions until a precipitate appeared (about 140–160 μL of HCl in 1 mL of the sample). This is because having concentrated the antioxidants during the back-extraction in the form of phenolates when lowering the pH again and forming the phenolic compounds; these can reach the solubility limit for some of them as caffeic acid (0.98 g/L at 298.2 K (Mota et al., 2008)), and separate them from other as tyrosol (106.9 g/L at 298.2 K (António et al., 2009)), catechol (461.3 g/L at 298.2 K (Cesari et al., 2017)). The precipitates were separated from the supernatant after centrifugation in Eppendorf tubes at 8000 rpm for 5 min in a Labnet Spectrafuge 24D. The solids obtained were separated and dried in a furnace at 378.2 K for 24 h.

An aliquot of the obtained solids was redissolved at a concentration of 50 mg/L in ultrapure water. They were reanalyzed in HPLC to observe the antioxidant content of the solid obtained.

2.6. ATR-FTIR analysis

To check the chemical stability of the solvents in the extraction processes, Attenuated Total Reflection with Fourier Transform Infrared (ATR-FTIR) measurements were performed. For this purpose, a Nicolet iS50 spectrometer with SpectraTech ATR Performer was used for measuring between 500 and 4000 cm^{-1}. The solvents MIBK, lavandulol, citronellol, and menthol + borneol were measured before and after being subjected to back-extraction with 2 M NaOH to check their chemical stability. The solvents eucalyptol, geraniol, and menthol + camphor were not analyzed after back-extraction because their chemical stability had already been tested in previous studies (Çelik et al., 2021).

Also, the pure solids of tyrosol, catechol, and caffeic acid were analyzed. In addition, the solids obtained in the precipitation by pH change of the alkaline phases of the solvent reuse process were analyzed by this technique.

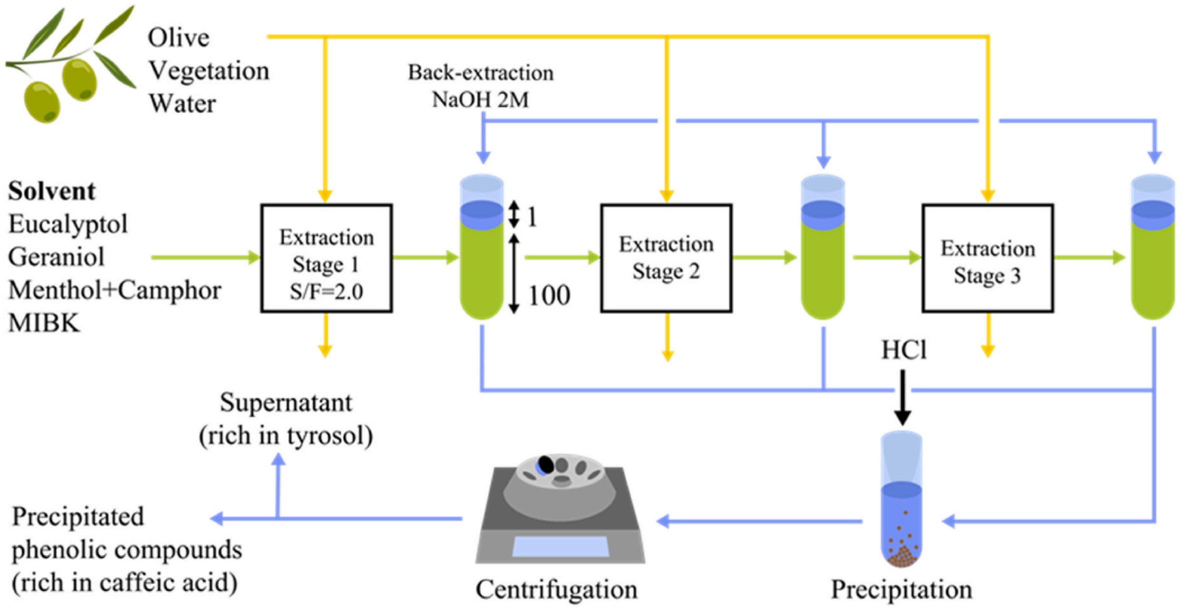

Fig. 1. Scheme of solvent reuse and back-extraction.

3. Results and discussion

3.1. Characterization of olive vegetation water

The results of the characterization of the olive vegetation water used in this work are shown in Table 1. The quantitative analysis of three phenolic compounds using HPLC-DAD shows the presence of a high amount of tyrosol compared to the other two antioxidants, catechol, and caffeic acid. This concentration value of these three antioxidants is below the range of TP found in olive mill wastewater 4–10 GAE g/L (Frascari et al., 2019; Azzam and Hazaimeh, 2021), while it is in the range of olive vegetation water for two-phase systems 100–400 GAE mg/L (Ochando-Pulido et al., 2012), as it is the effluent of the second centrifugation. The total phenols content is 356.4 GAE mg/L for the olive vegetation water. Therefore, this work seeks the extraction of antioxidants from diluted mixtures of olive vegetation water. In addition, the results show that most of the TOC would be in the form of phenolic compounds due to the values close to the TP.

Qualitative analysis of the vegetal water was also performed by LC-MS. Table 2 shows the main peaks identified and compared to possible phenolic compounds according to the literature. Tyrosol, catechol, and caffeic acid were detected, and retention times were checked by external standards. In addition, hydroxytyrosol was detected, which, together with tyrosol, is one of the most abundant compounds of olive vegetation water (Meftah et al., 2019; Rahmanian et al., 2014; de Marco et al., 2007). The difference between the three antioxidants, tyrosol, catechol, and caffeic acid to the TP would be 156 GAE mg/L, which according to the LC-MS analysis, would be the rest of the compounds found in Table 2, like hydroxytyrosol, hydroxytyrosol acetate, and phenolic acids.

Table 1
Characterization of the real olive vegetation water used in this work.

Parameters	Values
Tyrosol (mg/L)	156.50
Catechol (mg/L)	27.15
Caffeic acid (mg/L)	26.80
Total phenolic content, TP (GAE mg/L)	356.4
TOC (mg/L)	405
pH	4.15
Conductivity (μS/cm)	346
COD (mg/L)	954

3.2. Solvent screening by molecular simulation with COSMO-RS

Activity coefficient (γ_i) can be defined as the proportionality constant between a substance's activity and its mole fraction in a solution. It will have a value of 1 for ideal solutions, while the further it departs from unity, the greater the non-ideal behavior. They give information about solute-solvent interactions in terms of enthalpy as they characterize the behavior of a single solute molecule surrounded by the solvent (Kojima et al., 1997). Using γ^∞ allows the selection of solvents more affine to the solutes considering that entropy has both negligible or secondary role, as previously checked in equivalent systems (Rodríguez-Llorente et al., 2023). The lower the coefficient, the higher the affinity. They have also been used to select solvents to extract phenols and BPA from aqueous solutions (Rodríguez-Llorente et al., 2020b, 2021). The γ^∞ results for the three antioxidants are shown in Fig. 2 with terpenes, Fig. 3 with hydrophobic eutectic solvents, and Fig. 4 with conventional solvents.

The σ-profiles, showing a histogram of the polarized charge distribution p(σ), used for the molecular simulation calculations with COSMO*therm*, are shown in Figs. S1–10 of Supplementary Material. In these σ-profiles it can be distinguished the presence of different types of segments depending on polarized charge density (σ) values; ($\sigma > 0.008$ e Å^{-2}) correspond to hydrogen bond acceptor segments, intermediate σ values to non-polar sections, while ($\sigma < -0.008$ e Å^{-2}) to hydrogen bond donors (Casas et al., 2012). Analyzing the σ-profiles of antioxidants, they present both hydrogen bond acceptor and donor groups. However, the hydrogen bond donors are more prominent, reaching σ values lower than -0.02 e Å^{-2}. Therefore, solvents with strong hydrogen bond acceptor groups are expected to perform better than other solvents (Klamt et al., 2010; Zurob et al., 2020).

Regarding the results obtained with the terpenes in Fig. 2, a significant difference is observed between the terpenes without heteroatoms that obtain high results of γ^∞, such as pinane or pinene, and the terpenoids that do present oxygen in their structure, with lower values of activity coefficient. For most terpenoids, catechol and caffeic acid show a higher affinity and lower γ^∞ values, as opposed to tyrosol. However, there are some exceptions, observing the results for carvacrol and thymol, which show a higher affinity for tyrosol. This could be related to the phenolic nature of carvacrol and tyrosol, which favors π-interactions

Table 2
Compounds identified by LC-MS.

Rt (min)	Measured m/z	Theoretical m/z	Formula	Proposed Compound	Ref
1.0	315.1080	315.0721	$C_{13}H_{16}O_9$	Protocatechuic acid 4-O-glucoside	Hong et al. (2021)
1.5	153.0549	153.0553	$C_8H_{10}O_3$	Hydroxytyrosol	Quirantes-Piné et al. (2013)
2.5	151.0755	151.0401	$C_8H_8O_3$	Vanillin	Antolovich et al. (2004)
2.6	389.1072	389.1089	$C_{16}H_{22}O_{11}$	Oleoside/secologanoside	Quirantes-Piné et al. (2013)
2.6	137.0600	137.0608	$C_8H_{10}O_2$	Tyrosol	Antolovich et al. (2004)
3.0	325.0907	325.0718	$C_{18}H_{14}O_6$	Dimer of *m*/*p*-coumaric acid	Antolovich et al. (2004)
3.0	109.0274	109.0295	$C_6H_6O_2$	Catechol	Kiprop et al. (2013)
4.1	179.0334	179.0350	$C_9H_8O_4$	Caffeic acid	Hong et al. (2021)
4.6	403.1220	403.1246	$C_{17}H_{24}O_{11}$	Elenolic acid glucoside	Quirantes-Piné et al. (2013)
5.2	183.0644	183.0299	$C_8H_8O_5$	3-O-Methylgallic acid	Hong et al. (2021)
5.2	367.1370	367.1035	$C_{17}H_{20}O_9$	3-Feruloylquinic acid	Hong et al. (2021)
6.3	353.1218	353.0878	$C_{16}H_{18}O_9$	5-Caffeoylquinic acid	Antolovich et al. (2004)
9.7	197.0788	197.0455	$C_9H_{10}O_5$	Syringic acid	Antolovich et al. (2004)
13.2	195.0633	195.0663	$C_{10}H_{12}O_4$	Hydroxytyrosol acetate	Quirantes-Piné et al. (2013)

between the two molecules (Abranches et al., 2019). Also, both compounds, and to a greater extent thymol, hydrogen bond donor groups are present in their σ-profiles, the acceptor segments being in the minority.

Solvents that present the highest affinity for antioxidants are eucalyptol and verbenone. Analyzing their σ-profiles presented in Figs. S3 and S9 of Supplementary Material, they do not present hydrogen bond donor capacity. Still, they show strong hydrogen bond acceptor groups related to the free electrons of the ether of eucalyptol and the ketone group of verbenone. The rest of the terpenoids also present hydrogen bond donor groups, obtaining low γ^∞ of the three antioxidants with the terpenoids.

The results of the γ^∞ for the eutectic solvents are shown in Fig. 3. Results show that the eutectic solvents formed by thymol show little affinity for phenolic compounds. However, this is different for the eutectic solvents formed by menthol. As for carboxylic acids with menthol, the affinity for caffeic acid is increased by binding to menthol, but the opposite occurs when forming eutectic with thymol. Best values are obtained for menthol + borneol firstly and menthol + borneol secondly. These results are related to the fact that the solvents formulated with menthol have a higher capacity to accept hydrogen bonding, as reported by Martins et al. (2019). As well as the fact that camphor does not have the capacity to donate hydrogen bonds, as seen in the σ-profiles. It is worth noting the increase in the affinity of caffeic acid with menthol-based eutectic solvents, compared to pure menthol, from having the highest gamma values to the lowest among the antioxidants. However, when selecting the solvents, it must be taken into consideration that COSMO-RS simulations usually underestimate the affinity that can be achieved with a eutectic solvent (Rodríguez-Llorente et al., 2019, 2020b), subsequently obtaining higher values of experimental yields than expected.

The γ^∞ results with conventional solvents are shown in Fig. 4. Like terpenes, lower γ^∞ values are obtained for the phenolics caffeic acid and catechol and higher results with tyrosol. The presence of a heteroatom dramatically increases the affinity for phenolic compounds, as observed with the high γ^∞ results with toluene. This way, DIPE has the highest affinity for antioxidants, followed by MIBK. The selected conventional solvents also present hydrogen bond acceptor groups but no donor capacity, as seen in the σ-profiles of Fig. S10 of Supplementary Material. Ethyl acetate is commonly used as a solvent for extraction (Azzam and Hazaimeh, 2021; Çelik et al., 2021). However, MIBK and DIPE were selected because they were the solvents that COSMO-RS predicted would perform best.

The first solvent selected for the experimental studies is eucalyptol, which, together with verbenone, is the most promising terpene. Verbenone has not been chosen because the price of verbenone (40 $/kg (Alibaba Group, 2022)) is substantially higher than that of eucalyptol (8–10 $/kg (-Othmer, 2013)) while obtaining both very close γ^∞ results. Then, lavandulol was also selected since it is liquid at room temperature, unlike piperitone and thymol. Subsequently, to compare with other solvents that *a priori* would extract lower, geraniol and citronellol were used, also to check the screening capacity with molecular simulation. In addition, outstanding results were obtained in previous works in extracting phenols (Rodríguez-Llorente et al., 2020b).

Among the eutectic solvents, the selected solvents were the most promising ones; menthol + borneol and menthol + camphor were also chosen to analyze the influence of the selection of the hydrogen bond acceptor in the eutectic solvent. Finally, as for the conventional solvents, the ones that obtained the lowest γ^∞, DIPE, and MIBK, were selected.

3.3. Experimental phenolics extraction with terpenoids, eutectic, and conventional solvents

The results of the extraction yields for tyrosol are shown in Fig. 5. From the extraction yield values for terpenoids, it can be observed that the solvent that surpasses the rest at all S/F is geraniol, which reaches 91.10% yield at an S/F ratio of 3.0. Concerning the eutectic solvents, the highest yields are achieved with menthol + camphor. Moreover, the highest yields are obtained with respect to all other solvents at every S/F ratio, achieving an extraction yield value of 92.82% at an S/F ratio of 3.0. This highlights the great importance of the hydrogen bond acceptor in the formulation of the eutectic solvent (Tiecco et al., 2019). Regarding the conventional solvents, it is observed that MIBK obtains superior results, with similar values to those obtained with geraniol. DIPE is the solvent that, contrary to what was expected, gets the lowest yields, reaching only 45.57% at an S/F ratio of 3.0.

Catechol extraction yields are shown in Fig. 6. Among the terpenoids, there is also a correspondence with the molecular simulation, getting the best results with eucalyptol at every S/F ratio, reaching 97.71% of extraction yield at an S/F ratio of 3.0. Analogously to tyrosol results, among the eutectic solvents, higher extraction yields are achieved with menthol + camphor in catechol extraction. The results for the eutectic solvent were similar to those obtained with eucalyptol, with a maximum yield of 97.17%. Of the conventional solvents, MIBK again shows very high yields, slightly above those obtained with eucalyptol and menthol + camphor, while DIPE shows the lowest results of all the solvents.

The extraction yield results for caffeic acid are presented in Fig. 7. As for terpenoids, geraniol achieves the highest yields, with a maximum already at an S/F ratio of 1.0 of 98.87%. Regarding the eutectic solvents, the best results are obtained again with the eutectic solvent menthol + camphor rather than menthol + borneol. Geraniol and menthol + camphor outperform the results obtained with the conventional solvent MIBK.

Finally, Fig. 8 shows the results of total phenolic content (TP) extraction yields. Eucalyptol obtained the highest extraction yields among the terpenoids. Remarkably, geraniol gets lower yields of 78.92% at an S/F ratio of 3.0 versus 94.00% obtained with eucalyptol. The previous trend of higher yields of the three phenolics with geraniol than with eucalyptol is not followed. It implies a higher selectivity of geraniol

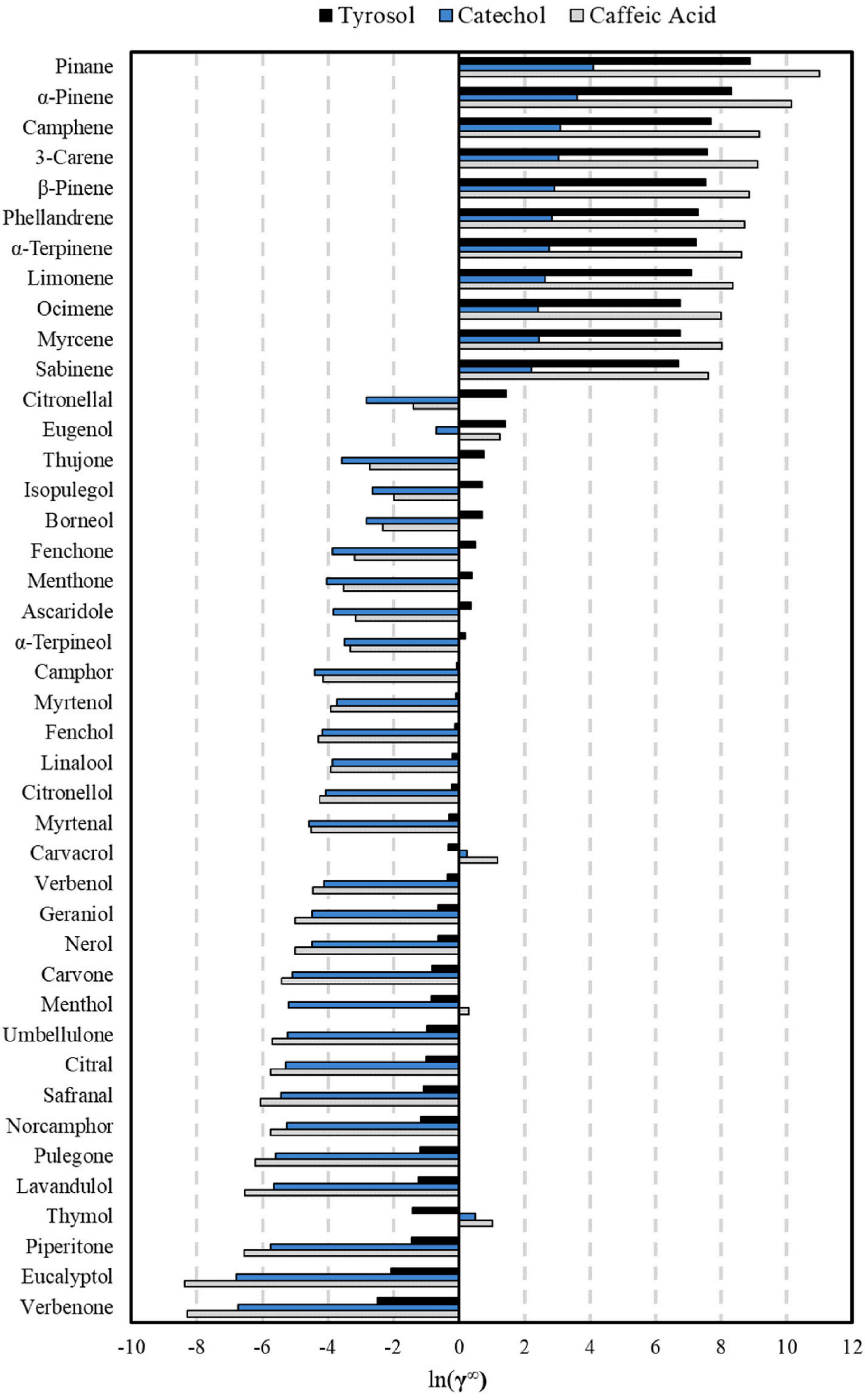

Fig. 2. Results of activity coefficients at infinite dilution (γ^{∞}) of phenolic compounds in the terpenoids at 303.2 K calculated with COSMO*therm*.

in the extraction of the three target phenolics versus TP. Conversely, eucalyptol has a higher TP extraction capacity but slightly lowers the individual yields of the three phenolics and selectivity.

For eutectic solvents, menthol + camphor presents high extraction capacity, reaching a maximum rapidly and having little influence of the S/F ratio on the TP extraction yield, increasing from 88.73 to 93.00%. However, in the individual analyses of the three antioxidants, there is an increase in the yields with the S/F ratios, so it must have a preference for these compounds in particular. Menthol + borneol, meanwhile, obtained results comparable to those obtained with menhtol + camphor (except at an S/F ratio of 0.5). In contrast, the extraction results were inferior in the individual extractions, so it must have a higher affinity for the rest of the antioxidants than the three target phenolics, as the TP yields show.

Regarding conventional solvents, very high extraction results of up to 96% were also obtained with MIBK. DIPE is very limited when working at low S/F, which may be related to the fact that DIPE saturates rapidly in the presence of phenols, as we have observed in previous work at higher phenol concentrations (Rodríguez-Llorente et al., 2020b). However, when increasing the S/F, a significant improvement in the

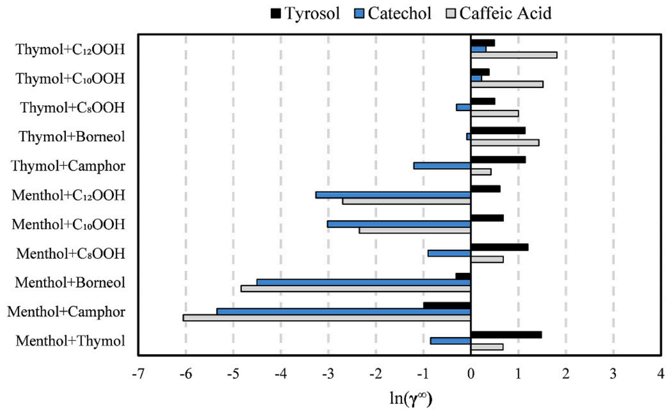

Fig. 3. Results of activity coefficients at infinite dilution (γ^∞) of phenolic compounds in the eutectic solvents at 303.2 K calculated with COSMO*therm*.

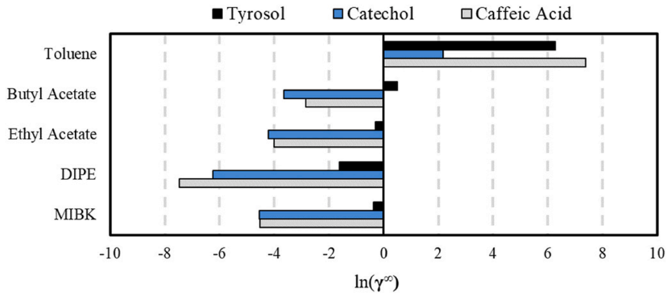

Fig. 4. Results of activity coefficients at infinite dilution (γ^∞) of phenolic compounds in the conventional at 303.2 K solvents calculated with COSMO*therm*.

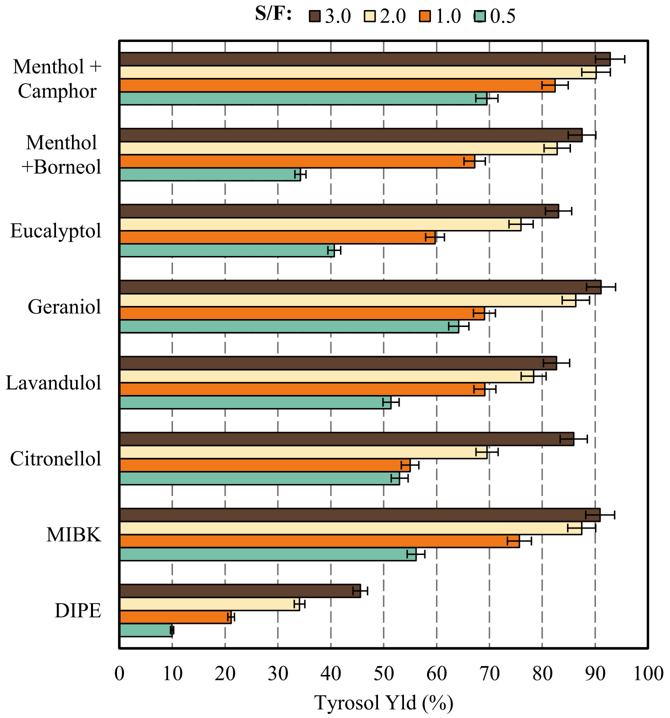

Fig. 5. Tyrosol extraction yields from real olive vegetation water at different S/F ratios at 303.2 K.

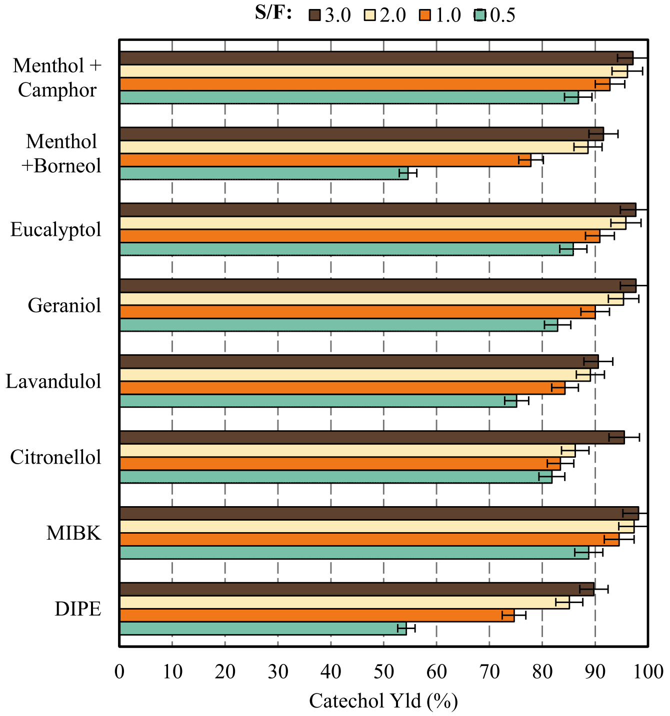

Fig. 6. Catechol extraction yields from real olive vegetation water at different S/F ratios at 303.2 K.

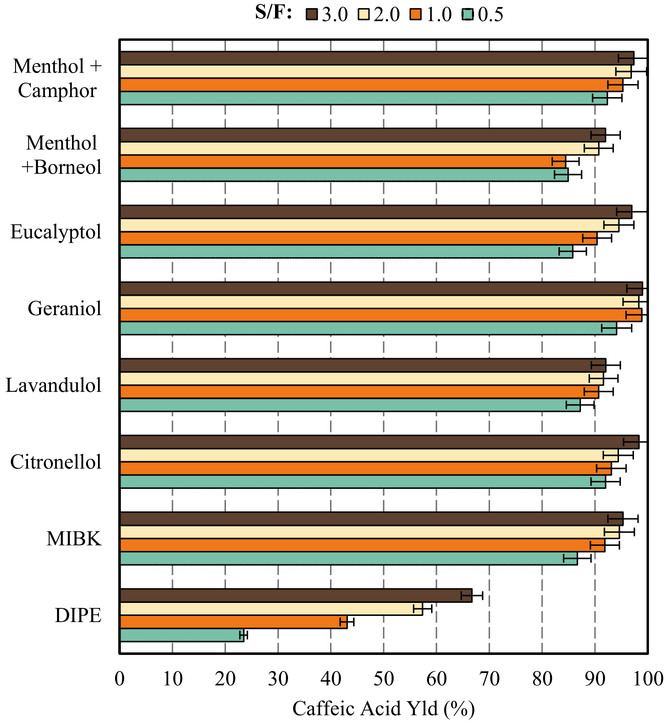

Fig. 7. Caffeic acid extraction yields from real olive vegetation water at different S/F ratios at 303.2 K.

extraction yields of TP is observed, reaching results better than those of the terpenoids, except eucalyptol. So, it is seen to have low selectivity to these three target phenolics and a higher capacity to extract the rest of the phenolic compounds.

Comparing all the extraction yields, the influence of the S/F ratio on the obtained yields is substantial, especially when the affinity of the

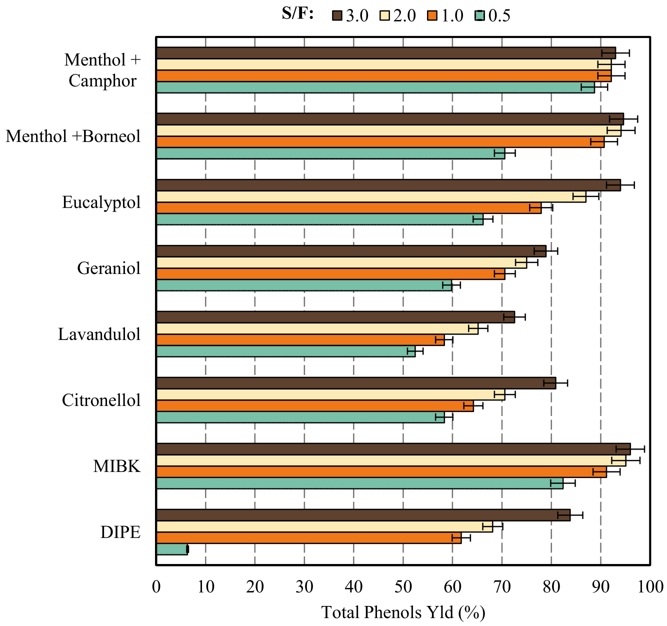

Fig. 8. Total phenolic content extraction yields from real olive vegetation water at different S/F ratios at 303.2 K.

solvents for the phenolic compounds is inferior. The most significant dependence is observed with DIPE, which is saturated when a low S/F ratio is used.

In conclusion, of the terpenoids, the highest results for the three target antioxidants were obtained for geraniol. In the extraction of caffeic acid and catechol, eucalyptol got similar results, although lower in the extraction of tyrosol. Eucalyptol, however, obtains higher TP results than all terpenoids. In this sense, eucalyptol has a higher TP extraction capacity than geraniol, but the latter is more selective in the extraction of the three antioxidants, especially tyrosol. As for menthol + camphor, it has the highest extraction yields among the natural solvents, both in values of the three antioxidants and in the extraction results of TP. MIBK obtained better results than DIPE, both in individual and TP yields. The yields obtained with MIBK are similar to those obtained with menthol + camphor and geraniol in the extractions of the three target antioxidants.

In the following, experimental results are compared with molecular predictions. First, the predictions of affinity order for phenolic compounds for the same solvent are fulfilled in the extraction yields. The only exceptions are found in lower extraction yields of caffeic acid, which should be higher than catechol with eucalyptol, which obtains slightly lower results (between 0.8 and 1.3% absolute difference in extraction yield), and DIPE, which obtains lower results (for the same S/F ratio yields lower than 23.06–31.6%).

Secondly, among the eutectic solvents, comparing them with each other, the molecular simulation predicts that the best would be menthol + camphor. The molecular simulation predicts the order of extraction of catechol with the terpenoids. However, there are discrepancies in the extraction of caffeic acid and tyrosol. The most notable is geraniol which outperforms eucalyptol in the extraction of both phenolic compounds. With conventional solvents, the most significant discrepancy was found with DIPE, which obtained much lower yields than expected. These results may be related to water-DIPE interactions that are not considered in the COSMO simulation.

Definitively, there is good agreement in the affinity for phenolic compounds compared to COSMO-RS predictions for the same solvent. There is less correspondence between the predictions instead if the solvents are compared with each other. This disagreement is related partly due to the low activity coefficients being compared. Moreover, COSMO-RS predictions can be biased due to the presence of water, which is not considered by the simulation, and the real matrix, since the presence of salts and organic matter can affect the extraction process.

The results obtained have been compared with those found in the literature on extracting phenolic compounds from OMWW in Table 3. The results obtained in this work show the improvement of extraction yields compared to the normally used solvent ethyl acetate.

The average values of water content in the different solvents employed are given in Table S5 of Supplementary Material. The results achieved show the high hydrophobicity of the selected solvents. Reduced water content values would imply higher phenolic/water selectivities. Concerning the eutectic solvents, the presence of water could provide benefits, such as improving the transport phenomena (Kivelä et al., 2022).

The solvents selected for solvent reuse and regeneration studies are geraniol, eucalyptol, menthol + camphor, and MIBK. The solvent prices for selected solvents would be geraniol 6–12 $/kg (-Othmer, 2013), eucalyptol 8–10 $/kg (-Othmer, 2013), menthol 10–20 $/kg (-Othmer, 2013), and camphor 5–10 $/kg (Icis Chemical Business, 2016). For MIBK, it would be 1–1.5 $/kg (Intratec Solutions, 2020). Despite the lower price of MIBK, solvent losses in the aqueous phase must also be considered. MIBK has a solubility in water of 1.57 % wt. (Góral and Wiśniewska-Gocłowska, 2008), whereas that of the terpenes is less than 0.09 % wt. for geraniol, 0.12 % wt. for eucalyptol, 0.07 % wt. for camphor, and 0.06 % wt. for menthol (Rodríguez-Llorente et al., 2021). Furthermore, terpenoids have the advantage of low toxicity, so their use as a solvent would imply lower solvent losses and less water pollution than MIBK, which would require subsequent treatment.

Due to the good results of the natural solvents, they have been applied in the studies of solvent reuse and regeneration cycles by back-extraction. However, the remaining natural solvents show promising results, and the chemical stability of these solvents was also evaluated when subjected to a back-extraction process with an alkaline medium.

3.4. *Cycles of solvent reuse and regeneration and obtention of phenolics compounds*

The next stage of the experimental work consists in regenerating the solvent by back-extraction using an alkali. In addition, by using a low alkali/solvent ratio, the phenolic compounds can be concentrated in the aqueous phase. Three regeneration stages were performed which is a usual number to study solvent reuse. However, it would be possible to perform future reuse cycles in order to know the service life of the solvents (Almustafa et al., 2020). The S/F ratio chosen was 2.0, to obtain high recoveries of antioxidants, without compromising their dilution in the solvent and reducing the concentration rate in the back-extraction.

3.4.1. *Chemical stability of solvents*

Before performing the back-extraction process, the stability of the solvents when subjected to the back-extraction process was verified. Some solvents used in this work, such as geraniol, eucalyptol, menthol + camphor, and DIPE, have already been stable in previous works (Rodríguez-Llorente et al., 2020b, 2021). However, the rest of the solvents have yet to be checked. Therefore, FTIR analyses of the solvents were performed before and after the back-extraction experiments. The main functional groups from the infrared spectra of all solvents are identified in Figs. S11–17 of Supplementary Material, performed using the infrared vibrational group identifying guidelines (Coates, 2006).

The results of the spectra for lavandulol, citronellol, menthol + borneol, and MIBK are given in Figs. S18–19 of Supplementary Material. Regarding the lavandulol and citronellol spectra, no differences are observed, thus proving the chemical stability of these solvents and verifying their hydrophobicity. On the other hand, the MIBK presents identical spectra, except for a slightly broad peak around 3500 cm^{-1} corresponding to the stretch of the OH due to the solubilization of part of the water in the solvent. No aldol reaction is observed for the ketone group. As for the menthol + borneol, presents the same peaks except for the appearance of a slight peak at 1636 cm^{-1} due to C═C. It is well

Table 3
Comparison of results with literature.

Solvent	S/F	Compound	C_0 (mg/L)	Yield (%)	Matrix	Ref
[N4441][Tf2N]	1	Tyrosol	1000	44.6	Synthetic	Larriba et al. (2016)
Ethyl Acetate	1	Tyrosol	1000	74.4	Synthetic	Larriba et al. (2016)
Ethyl Acetate	2	TP	>4300	≈60	Real	Azzam and Hazaimeh (2021)
Ethyl Acetate	1	TP	32,000	≈72	Real	Çelik et al. (2021)
MIBK	1	TP	356.4	91.18	Real	This Work
Menthol + camphor	1	TP	356.4	92.16	Real	This Work
Menthol + borneol	1	TP	356.4	90.69	Real	This Work

*TP in GAE.

known that the reactions of alcohols with alkali are highly disfavored, but it may be that dehydration of the alcohol is being formed, leading to a double bond, perhaps catalyzed with some impurity. An example is the Wagner-Meerwein rearrangement of borneol to form camphene (Birladeanu, 2000; Pelter and Harper, 1964).

Except for menthol + borneol, which shows a slight instability, it has been seen that these solvents are also stable in the back-extraction process, being able to be applied in this process of solvent reuse and regeneration cycles of the solvents.

3.4.2. Solvent reuse and regeneration. The concentration of phenolic compounds

The extraction yields at each solvent reuse extraction stage were obtained for the three antioxidants and TP. The results are shown in Fig. 9. With MIBK, the extraction yields do not decrease appreciably in the back-extraction process except for a slight reduction in the extraction yields of TP from 93.82% to 90.70% in stage 3. For the eutectic solvent menthol + camphor, there is a clear drop in the extraction yields of caffeic acid from 97.63% to 85.60%. Also, a slight decrease was observed with tyrosol and TP. Regarding geraniol, only a minor diminution is appreciated in the extraction of tyrosol from 88.88% to 84.84% in cycle 3. Finally, no reductions are observed in the extraction yields obtained with eucalyptol.

Therefore, catechol is an antioxidant that can be extracted and stripped with all solvents without lowering extraction yields. Among the natural solvents, menthol + camphor would show the best extraction results if not for the decrease in extraction yield of caffeic acid, which would be surpassed by geraniol. Eucalyptol would be the most suitable for the back-extraction process because it can be regenerated completely. To analyze these results, Table 4 shows the concentrations

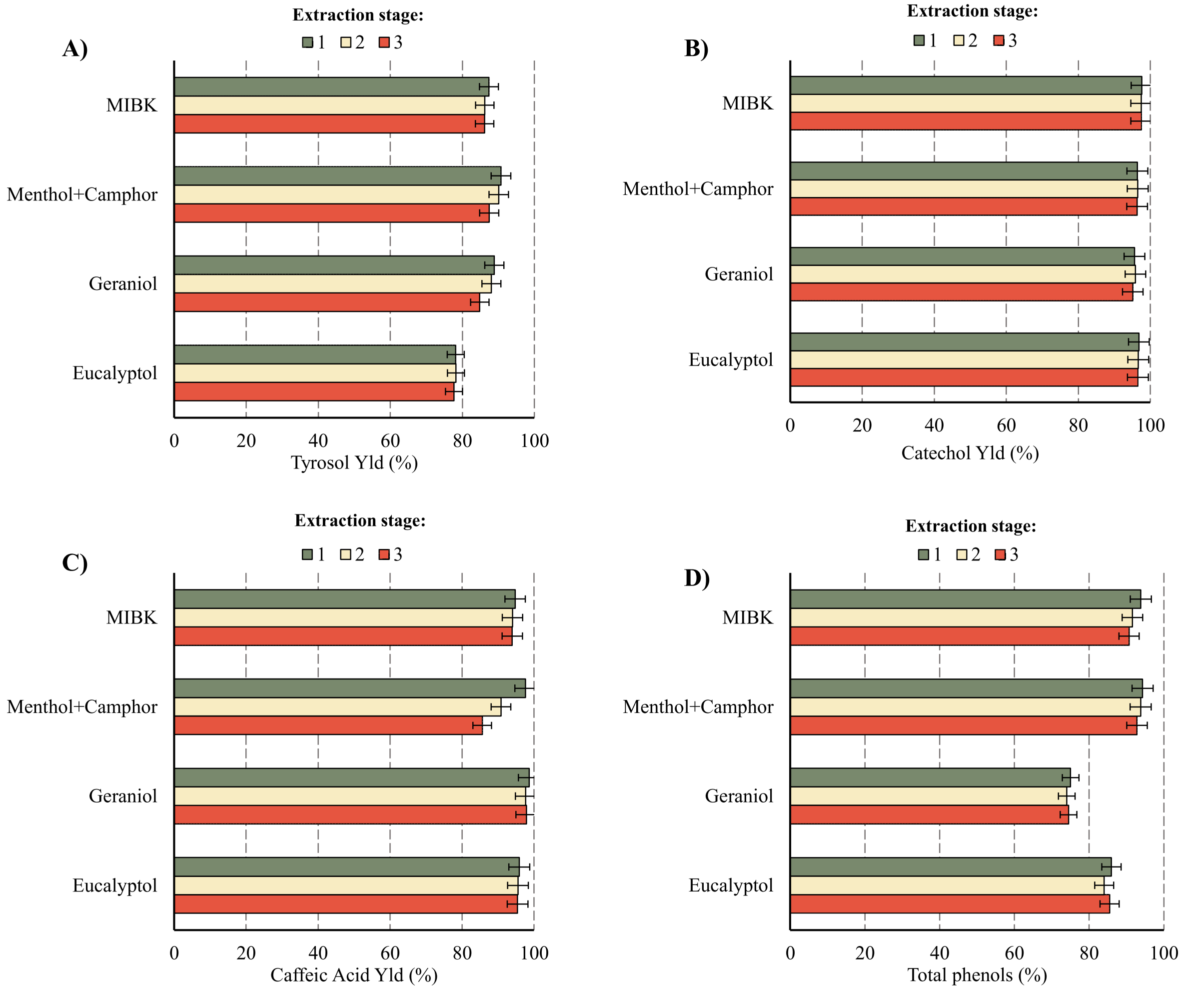

Fig. 9. Extraction yields (%) of tyrosol (A), catechol (B), caffeic acid (C), and TP (D) in each extraction stage using MIBK, menthol + camphor, geraniol, and eucalyptol at S/F ratio of 2.0 and 303.2 K.

Table 4
Concentration of phenolic compounds in the alkaline water phase after back-extraction and concentration factor of initial concentration (C/C_0) from olive vegetation water feed.

Solvent	Phenolic Compound	Conc (g/L)		C/C_0	
Eucalyptol	Tyrosol	7.52	±0.11	48.0	±1.44
	Catechol	1.16	±0.02	42.7	±1.28
	Caffeic acid	1.34	±0.02	49.3	±1.48
Geraniol	Tyrosol	5.21	±0.08	33.3	±1.00
	Catechol	0.93	±0.01	34.2	±1.03
	Caffeic acid	0.87	±0.01	31.9	±0.96
Menthol + Camphor	Tyrosol	6.85	±0.10	43.7	±1.31
	Catechol	0.80	±0.01	29.5	±0.88
	Caffeic acid	1.20	±0.02	44.1	±1.32
MIBK	Tyrosol	6.96	±0.10	44.5	±1.34
	Catechol	1.22	±0.02	45.0	±1.35
	Caffeic acid	1.06	±0.02	39.0	±1.17

of the antioxidants obtained in the alkaline phase and their concentration factor with respect to the initial concentration in the olive vegetation water.

The results with eucalyptol show that the highest concentration factor for the antioxidants is obtained with caffeic acid, with a factor of 49.3. Similar results were obtained with the eutectic solvent menthol + camphor, with the highest concentration factors for tyrosol and caffeic acid with respect to catechol. With the eutectic solvent, this is observed, although the highest extraction yields were obtained for catechol. This could be related first to the fact that tyrosol, the compound extracted with lower yields as well, is the one that is expected to be stripped more. Comparing caffeic acid instead with catechol, although they have similar extraction yields as caffeic acid presents the phenolic OH groups like catechol, the OH of the carboxylic acid can be deprotonated, generating more negative charges in the molecule and being more easily stripped. For MIBK, higher extractions were obtained with catechol, although very closely with tyrosol and to a lesser extent with caffeic acid. In this case, the yields with catechol were greater.

With different tendencies to the previous ones, geraniol obtained lower concentration factors in tyrosol and caffeic acid than the rest of the solvents, but above 30%. The lower tyrosol results are related to a reduction in the yields in Fig. 9A. Furthermore, there seems to be an accumulation of antioxidants in the geraniol, and a complete stripping of these cannot be performed. This is related to geraniol having the highest water content of natural solvents, which could increase the Na^+ concentrations and stabilize the charged molecules of the antioxidants, similar to the high concentration of chlorides in water in the solvents (Kivelä et al., 2022).

The results show that high extraction yields can be reached with the solvents used, which can be regenerated by back-extraction. In this case, even using a high concentration of NaOH in the alkaline medium, it was not necessary to add HCl to the solvents before reusing them in a new extraction, as is the case with the use of ionic liquids in tyrosol extraction (Larriba et al., 2016). Moreover, this method with 1/100 alkaline/solvent ratios allows a high concentration of the extracted antioxidants with factors up to 49.3 and all above 29.5 (since an S/F ratio of 2.0 was used in the extraction). Eucalyptol is the best-performing solvent in terms of antioxidant concentration, although it does not reach the highest extraction yields. However, higher stripping is achieved, which can be related to the solvent's lower water content (0.34 % wt).

3.4.3. *Separation of phenolics compounds*

When the phenolates in the concentrated alkaline solution are neutralized to obtain the phenolic compounds, precipitates of compounds that surpass the point of maximum solubility in the solution are obtained. This was the case with the final solutions of the extraction cycle using eucalyptol and menthol + camphor. The results of the infrared spectra are shown in Fig. 10. Additionally, the pure solids of tyrosol, catechol, and caffeic acid were analyzed, and the identification of the main functional groups can be found in Figs. S20–22 of Supplementary Material.

The FTIR results show the presence of the characteristic C═O stretch peak at 1720 cm^{-1}. This wavenumber is distinctive of carboxylic acids, as it can also be seen with a broad O–H stretch between 3600 and 3000 cm^{-1}. In addition, a peak at 1517 cm^{-1} would correspond to aromatic ring stretching. Related to the vibration of the aromatic ring is the C–H out-of-plane bend at 819 cm^{-1}, which is usually due to *para*-substitutions of the aromatic ring.

The presence of 26.0 and 21 % wt of caffeic acid was found for eucalyptol and menthol + camphor cycles, respectively. This is related to the solubility limit of caffeic acid was exceeded, which is 0.98 g/L at 298.2 K (Mota et al., 2008). The higher content of caffeic acid in the solids of the eucalyptol cycle, with respect to the menthol + camphor cycles, is related to a higher concentration in the alkaline phase of the acid. Also, analyzing the FTIR results, other phenolic acids with low solubility in water present in the olive vegetation water may have precipitated.

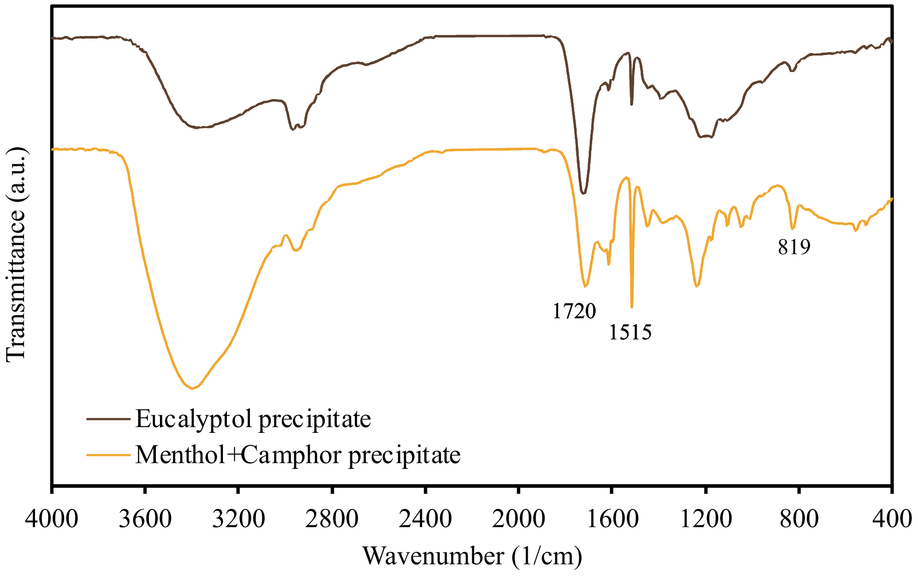

Fig. 10. ATR-FTIR spectra of precipitates from eucalyptol and menthol + camphor solvent cycles.

Thus, after neutralizing the alkaline phase, phenolic acids with low solubility in the aqueous phase could be separated from the aqueous phase, leaving mainly a concentrated stream of tyrosol since it has much higher solubility in water 106.9 g/L at 298.2 K (Godbout et al., 1992). The concentrations of tyrosol in the supernatant obtained with the eucalyptol cycle are 6.54 g/L, and with menthol + camphor 5.96 g/L. One approach to enhance the purity would be to reduce the solvent/alkaline phase ratio, obtaining a higher concentration of antioxidants in the supernatant and a precipitate. Finally, after obtaining concentrated streams of phenolic compounds, these could be separated using, for example, crystallization (Kontos et al., 2018). The work shows that it is possible to recover phenolic compounds from diluted streams of olive vegetation water and concentrate them. With more concentrated streams, high phenolics recovery results could be obtained, as well as higher solids precipitation during the alkaline phase's neutralization.

4. Conclusions

The presence of high-value-added phenolic compounds in olive vegetal water presents an opportunity to revalorize these residues, which can be recovered by liquid-liquid extraction. The COSMO-RS method has been combined with experimental essays to take advance of the predictability of the former and the *ad hoc* validation of the latter to narrow down most potential terpene and terpenoid-derived solvents, finding that geraniol, eucalyptol, and menthol + camphor obtained the best extraction yields, surpassing those obtained with MIBK, with extraction yields of 93.00% at a Solvent/Feed ratio in volume of 3.00. The solvent reuse and regeneration process show that the solvents are stable in back-extraction with an alkaline NaOH solution. Moreover, stripping phenolic compounds can be concentrated using a low alkaline solvent/solvent ratio. This way, it is possible to obtain concentrated solutions of phenolic compounds with factors up to 49.3 and all above 29.5 to the initial concentration in olive vegetation water. This stream, when neutralized, precipitates phenolic acids with low solubility in water, and it is possible to get a precipitate enriched in caffeic acid and a concentrated supernatant stream of tyrosol. Therefore, natural solvents and terpene-based eutectic solvents are an alternative to recover high value-added phenolic compounds from olive vegetation water, increasing biodegradability, safety, and reducing toxicity compared to conventional solvents.

Credit author statement

Diego Rodríguez-Llorente: Writing - Original Draft, Conceptualization, Methodology, Investigation; **Diego Martín-Gutiérrez:** Writing - Original Draft, Investigation; **Pablo Suárez-Rodríguez:** Writing - Original Draft, Investigation; **Pablo Navarro:** Writing - Review & Editing, Software; **Silvia Álvarez-Torrellas:** Writing - Review & Editing, Supervision; **Juan García:** Writing - Review & Editing, Supervision; **Marcos Larriba:** Writing - Review & Editing, Conceptualization, Methodology, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Juan Garcia and Marcos Larriba reports financial support was provided by Community of Madrid. Diego Rodriguez-Llorente reports financial support was provided by Spain Ministry of Science and Innovation. Diego Martin-Gutierrez and Pablo Suarez-Rodriguez reports financial support was provided by Government of Spain Ministry of Education and Vocational Training.

Data availability

No data was used for the research described in the article.

Acknowledgments

The authors thank Comunidad Autónoma de Madrid for the financial support of Projects P2018/EMT-4341 and PR65/19–22441. This work has been supported by the Madrid Government (Comunidad de Madrid, Spain) under the Multiannual Agreement with Complutense University in the line Program to Stimulate Research for Young Doctors in the context of the V PRICIT (Regional Programme of Research and Technological Innovation). Diego Rodríguez-Llorente thanks Ministerio de Ciencia, Innovación y Universidades, for awarding an FPU grant (FPU18/01536). Also, Diego Martín-Gutiérrez and Pablo Suárez-Rodríguez thank Ministerio de Educación y Formación Profesional for Collaboration Grants in University Departments. We thank Centro de Computación Científica de la Universidad Autónoma de Madrid for computational facilities, and the Spectroscopy and Correlation and Mass Spectrometry Centres of the Complutense University of Madrid for FTIR and HPLC-MS analysis. Finally, we thank Víctor Martín Domínguez and Fejidosa Urdoliva Company for supplying the olive vegetation water.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2022.115207.

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