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RESEARCH ARTICLE

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Shedding light into the health-beneficial properties of *Corema album*—A vibrational spectroscopy study

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Abstract

Corema album (L.) D. Don is a wild maritime shrub endemic to the Iberian Peninsula, which contains bioactive compounds with promising chemoprotective activity. The present work reports the first study of the edible fruits of this potentially health-beneficial plant by complementary Raman and infrared techniques. Unique vibrational signatures were obtained for each part of the *Corema album* berries, revealing distinct chemical compositions for the skin (outer and inner) and the seeds, particularly regarding the content in phenolic derivatives, unsaturated fatty acids, and waxy polymers.

KEYWORDS

antioxidant, *Corema album* berries, FTIR spectroscopy, nutraceutical, Raman spectroscopy

1 | INTRODUCTION

The *Corema album* (L.) D. Don plant is a dioecious perennial maritime shrub endemic to the Atlantic coastal areas of the Iberian Peninsula that belongs to the *Ericaceae* family and is classified into two subspecies: *album* (from the Iberian Atlantic coast) and *azoricum* (found exclusively in the archipelago of Azores, Portugal).[1] It occurs in sand dunes and cliffs and can reach a maximum height of 1 m, with numerous branches, its fruits being small white berries that usually become pinkish and translucent upon over-ripening, storing for large periods or heating (due to an increase in anthocyanin content, Figure 1). These berries (white crowberries, Atlantic pearls or "camarinhas" in Portuguese), which grow during late spring and early summer, have a strong skin and usually three large seeds (pyrenes, ~0.5 mm long) within a thick endocarp and display a distinct fresh flavour and an acidic taste.[1–3] The fruits of *C. album* (L.) D. Don have been consumed in the Iberian Atlantic coast since the Islamic period (either fresh or in jams) and have been used in popular medicine as antipyretics and against pinworm infections.[2,4] In fact, they were found to contain flavonols, anthocyanins, and phenolic derivatives (mainly caffeic ester, benzoic, and chlorogenic acids),[3–6] which are responsible for a significant antioxidant capacity that confers them with interesting physiological properties, namely, as preventive agents against urinary infections,[7] cardiovascular and neurological disorders,[8–11] or cancer.[9,12,13] This antioxidant effect is suggested to be mediated by up-regulation of glutathione and cellular antioxidant enzymes, as well as by suppression of reactive oxygen species.[14,15] Therefore, although it is still not a commercial crop, this plant may be of

FIGURE 1 *Corema album* plants and berries (collected from Costa de Lavos, Coimbra district, Portugal), showing the different stages that can develop after harvesting

interest as a nutraceutical because it can exert a significant chemoprotective activity against oxidative-induced pathologies.

However, the application of berry-contained compounds as preventives, namely against carcinogenesis relies on a detailed knowledge of their structural and conformational preferences, in order to understand their mechanism of action at a molecular level aiming at achieving an optimum effect on biological matrices. This can be accomplished by the use of Raman and Fourier-transform infrared (FTIR) vibrational spectroscopy techniques that have been established as non-invasive tools of excellence for the characterisation of biospecimens with high sensitivity and selectivity.[16,17] Raman microspectroscopy, in particular, is a cutting-edge technique that enables an accurate and non-invasive profiling of biological samples of several types (e.g., plants, human cells, or tissues), virtually without interference from water, yielding unique chemical fingerprints.[18–21] Actually, the high sensitivity and subcellular spatial resolution of microRaman allows us to detect the smallest chemical variations and conformational rearrangements even in heterogeneous biological models such as leaves, fruits, or seeds. In turn, FTIR in attenuated total reflectance mode (FTIR–ATR) is particularly suitable for routine analysis because it is easily accessible, inexpensive, fast, and requires no sample preparation.[22]

Despite the interest of the *C. album* edible plant, the reported studies on its health-beneficial properties are very scarce, either on extracts or at the molecular level. In addition, no structural or chemical characterisation has been carried out to this date, namely through the application of spectroscopic techniques. The present work aims to fill this gap, by performing a thorough analysis of the *C. album* berries (skin and seeds) using the complementary FTIR and Raman techniques aiming at an accurate chemical profiling of these biospecimens at defined conditions: immediately after harvesting and upon storage at room temperature for different periods. To the best of the authors' knowledge, this is the first molecular analysis of the fruits from *C. album* using vibrational spectroscopy.

2 | EXPERIMENTAL

2.1 | Materials

Wild *C. album* berries (5 kg) were harvested by hand in early September 2018, randomly selected from 20 independent bushes, in the dunes of Costa de Lavos (Figueira da Foz) in the Centre region of Portugal (40°05′11.2″N 8°52′40.0″W). The berries (spherical, 0.3–0.5 g, with a diameter of ~5–8 mm) were collected in two different

degrees of maturation: white berries and pink berries, only the former being analysed in this work.

Commercial linoleic acid (LA; purity ≥99%) was purchased from Sigma-Aldrich Chemical S.A. (Sintra, Portugal). The samples were kept at −18°C until use, in order to avoid decomposition.

2.2 | Sample Preparation

Immediately after harvesting, the berries were transported to the laboratory in polyethylene containers. The berries were pooled and cleaned in order to remove damaged fruits and leaves and then stored at room temperature, protected from light and heat, until spectroscopic acquisition.

For each part of the plant, approximately four berries were analysed, immediately after harvesting. Three types of samples were prepared for spectroscopic analysis (by manual separation): outer skin (OSk), inner skin (ISk; near the endocarp), and seed (S; inner part, after opening the seed and removing the seed coat avoiding the external woody region).

2.3 | Raman and FTIR–ATR measurements

FTIR–ATR and Raman spectra were obtained for the *C. album* samples without any pretreatment procedures.

The Raman spectra were recorded in the 100–3750 cm^{-1} range, in a WITec confocal Raman microscope system alpha300 R, coupled to an ultra-high throughput spectrometer 300 VIS-NIR (300-mm focal length; 600 lines per millimetre blazed for 500-nm grating). The detection system was a thermoelectrically cooled charge-coupled device camera with Peltier cooling down to −55°C, chip with 1,650 × 200 pixels, front- illuminated with NIR/VIS AR coating, spectral resolution <0.8 cm^{-1}/pixel. The 532-nm line of a diode laser was used as the excitation radiation, yielding ~10 mW at the sample position. An objective Zeiss "Epiplan" 100× (NA 0.80; WD 1.3 mm) was used. Four spectra were collected per sample, with five accumulations and 10 s of exposure time.

The FTIR–ATR spectra were acquired in the mid-infrared interval (400–4,000 cm^{-1}) using a Bruker Optics Vertex 70 FTIR spectrometer purged by CO_2-free dry air and a Bruker Platinum ATR single reflection diamond accessory. A Ge on KBr substrate beamsplitter with a liquid nitrogen-cooled wide band mercury cadmium telluride detector was used. Each spectrum was the sum of 128 scans, at 2 cm^{-1} resolution, and the three-term Blackman–Harris apodisation function was applied. Under these conditions, the wavenumber accuracy was better than 1 cm^{-1}. The spectra were corrected for the frequency dependence of the penetration depth of the electric field in ATR (considering a mean reflection index of 1.0, as previously used for other phytochemical using the Opus 7.2 spectroscopy software).[23]

2.4 | Semi-quantitative Raman and FTIR–ATR analyses

A semi-quantitative Raman data analysis was performed using the procedure reported by Jamieson et al. (2018) for fatty acids (using a 532-nm laser)[24]. The experimental ratios currently obtained from the vibrational data were introduced into Equations (1) to (4), to yield an estimative of the values for the number of (C═C) bonds [n(C═C)]:

$$\frac{I_{1262}}{I_{1438}} = (0.613 \pm 0.02426)[n(C=C)] - (0.134 \pm 0.06354), \quad (1)$$

$$\frac{I_{1655}}{I_{1438}} = (28.15 \pm 2.244)\left[\frac{n(C=C)}{n(CH_2)}\right] - (0.4347 \pm 0.6263), \quad (2)$$

$$\frac{I_{3005}}{I_{2850}} = (1.249 \pm 0.0959)\left[\frac{n(H-C=)}{n(CH_2)}\right] - (0.03831 \pm 0.05348), \quad (3)$$

$$\frac{I_{2850}}{I_{2933}} = (0.1738 \pm 0.01968)\left[\frac{n(CH_2)}{n(CH_3)}\right] - (1 \pm 0.2285). \quad (4)$$

Semi-quantitative FTIR–ATR data were collected by mathematical treatment of the spectra, using area integration methods for the calculation of area ratios.[25–28] Detailed definitions and interpretations of semi-quantitative FTIR–ATR-derived ratios are given in Tables 1, S1 and S2, and in Figure S2.

3 | RESULTS and DISCUSSION

The Raman spectra of OSk and ISk and FTIR–ATR spectra of OSk, ISk, and S presently obtained for the white berries of *C. album* are represented in Figure 2. The corresponding wavenumbers and tentative assignments are comprised in Table 1. The results presently gathered evidence of a striking variation between the ISk (in contact with the endocarp) and the OSk, mainly unveiled through (a) the Raman signals below 1,000 cm^{-1}, ascribed to the external skin waxy constituents (e.g., amyrins),[29] and at 1,445 cm^{-1} mostly due to $\delta(CH_2/CH_3)$ from

TABLE 1 Raman and Fourier-transform infrared-attenuated total reflectance mode wavenumbers (cm^{-1}) and tentative assignments for *Corema album* white berries

OSk		ISk		S		
Raman	**FTIR–ATR**	**Raman**	**FTIR–ATR**	**Raman**	**FTIR–ATR**	**Tentative assignment**
160						Lattice modes
218						Lattice modes
280						Lattice modes
288						Lattice modes
320						Lattice modes
345						Lattice modes
356						Lattice modes
393						$\delta(CCC)_{ring}$ [40]
468						δ(CCC) triterpenoids
518sh		522				δ(COC) triterpenoids
535						δ(COC) triterpenoids
568	572	565				Triterpenoids
612						$\delta(CC)_{ring\ triterpenoids}$
		632				Fructose[41]
661	664					Triterpenoids
687	681	687				$\nu(CC)_{ring\ triterpenoids}$ [42]
	720					$\rho(CH_2)/\nu\ (CC)_{ring\ triterpenoids}$
732	731	733		725		
750		750				
	769					ν(CC)ring breathing stretches[29]
779	777					$\rho(CH_2)$ triterpenoids
802	808					Triterpenoids
822sh						Triterpenoids
833	830	828	833	840		$\gamma(C\text{-}H)_{\ aromatic\ (phenolic)}$
859		858				Triterpenoids/polysaccharide esters
				870		$\rho(CH_3) + \rho(CH_2) + \nu(C{-}C)$[39]
894	890					Triterpenoids
920	918	920				$\rho(CH_3)$ triterpenoids
954	952					$\rho(CH_3)$ triterpenoids
978	976	980		973		$\nu(CO)_{polysaccharides}$
1,014						$\nu(CC)_{ring}$
			1,032	1,032		$\nu(C{-}C)_{linear\ chains}$
1,037	$1{,}037_{br}$					$\nu(C{-}O{-}H)_{oleanolic\ acid}$ [29,43]
	1,047		1,055	1,032		$\nu(COC)_{glycosidic}$
1,069		1,066	1,078			ν(C—O)
1,092	1,090	1,090		1,074	1,081	$\nu_s(COC)_{glucosidic}$ [44,45] ν(C-C)[46]
1,107sh	1,105	1,123	1,111		1,104	$\nu_s(COC)_{glucosidic}$ [44,45]
1,138						ν(CC)
1,172	1,173	1,171	1,156		1,161	$\nu_a(COC)_{glucosidic}$

(Continues)

TABLE 1 (Continued)

OSk		ISk		S		
Raman	**FTIR–ATR**	**Raman**	**FTIR–ATR**	**Raman**	**FTIR–ATR**	**Tentative assignment**
1,208						
1,220	1,214vw					δ(CCH), $\delta_{i.p.}$(=CH)$_{cis\ lipids}$[44,47,48]
1,232						
	1,240		1,246		1,244	
	1,255		1,264	1,268	1,264$_{sh}$	δ(CH)$_{cis}$[46]
1,271	1,277 broad	1,270				Fructose/δ(OH)$_{polysaccharides;\ cutin}$
1,308		1,305		1,304		τ(CH$_2$)$_{aliph}$[39]
	1,317vw		1,317		1,317vvw	ν_{sym}(C—O)$_{ester}$[49]
			1,332			ν_{as}(C—H)[49]
1348vvw						δ(CH$_2$)
	1,358					ω(CH$_2$), τ(CH$_2$)
	1,367					
	1,377	1,375	1,373	1,375		
	1,389				1,402	ν(C—O)$_{phenols}$[49]
	1,417			1,423$_{sh}$	1,417	δ(CH$_2$)[39]
	1,434					δ(OH)[49]
1,445		1,444	1,444	1,445		δ(CH$_2$)/δ(CH$_3$) lipids and glucosidic
1,460sh	1,456sh	1,459			1,456	δ(CH$_2$)$_{FA}$[24]
	1,463					δ(CH$_2$)$_{cutin,\ waxes}$
	1,473					δ(CH$_2$)$_{cutin,\ waxes}$
	1,516vvw					ν(C=C)$_{aromatics,\ phenolics}$
					1,551	ν_{as}(COO$^-$) pectin
1,609		1,609				ν(C=C)$_{ring\ polyphenols}$
1,633		1,633		1,638$_{sh}$		ν(C=C)$_{ring/chain}$ *p*-coumaric ac/ν(C=C)$_{ooph}$[39]
	1,644		1,655			H_2O
					1,661	Pectin
1,662		1,662		1.659		ν(C=C)$_{FA}$
	1,688s					ν(C=O$^{\cdots}$ H)$_{acids}$; strong H bonded
1,717		1,717sh				ν(C=O)$_{esters/acid}$ lipids
1,737	1,737s	1,736	1,737	1,749	1,747	ν(C=O)$_{ester}$ lipids
2,725		2,726				ν(CH)$_{aliph.}$
				2,726		Overtone^2 δ(CH$_3$) δ(CH$_2$)[50–52]
2,855	2,849vs	2,854	2,853vvw	2,856	2,856w	ν_s(CH$_2$)
2,883sh	2,872vvw	2,884			2,873vvw	ν_s(CH$_3$)
2,903		2,903		2,903sh		ν_s(CH$_3$)
2,928	2,920vs	2,930	2,930vvw	2,934	2,929w	ν_a(CH$_2$)
	2,955sh		2,961		2,960	ν_a(CH$_3$)
				3,015	3,012	ν_s(=CH)$_{cis}$[39]
				3,068		FR(1,423 + 1,659)[39]

(Continues)

TABLE 1 (Continued)

OSk		ISk		S		
Raman	**FTIR–ATR**	**Raman**	**FTIR–ATR**	**Raman**	**FTIR–ATR**	**Tentative assignment**
				3,315	3,300sh	1638 + 1,659[39]
3,430	3,425	3,400	3,440	3,430	3,430	ν(O—H··· O) H_2O

Abbreviations: a, antisymmetric; FA, fatty acids; FR, Fermi resonance; FTIR–ATR, Fourier-transform infrared–attenuated total reflectance mode; ip, in plane; ISk, inner skin; ooph, out of phase; OSk, outer skin; S, seed; s, symmetric; ρ, rocking; τ, twisting; ν, stretching; ω, wagging; δ, bending.

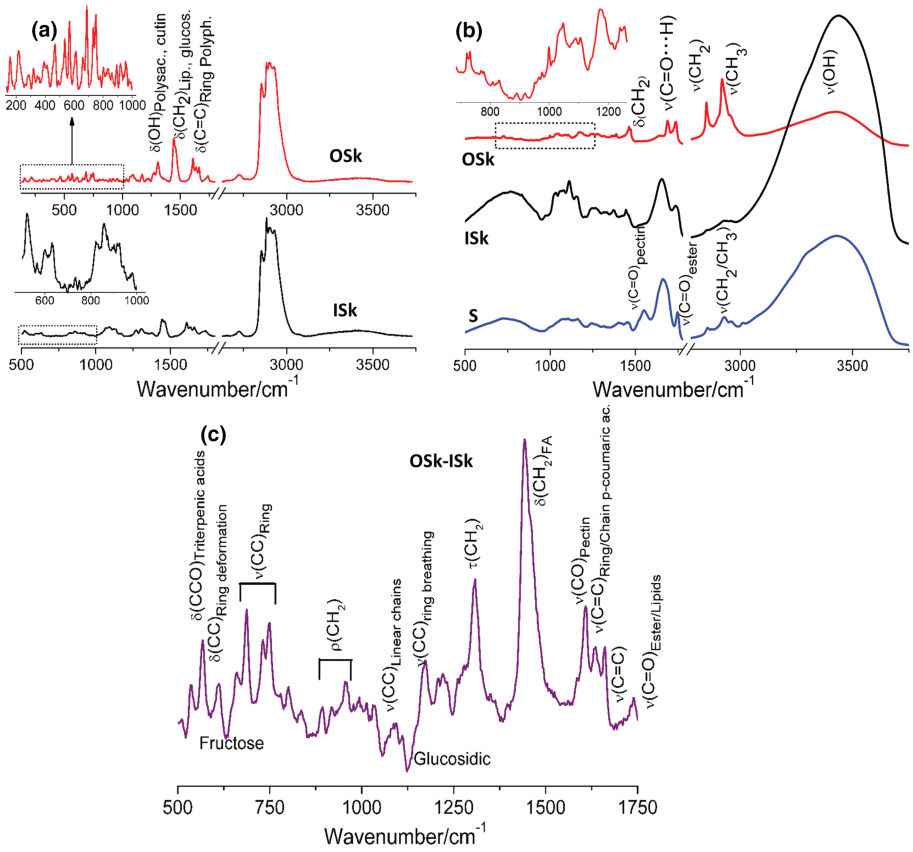

FIGURE 2 Raman (a) and FTIR–ATR (b) spectra of *Corema album* white berries—OSk, ISk and S. (c) Raman spectra of the outer skin after subtraction of the Raman profile from the inner skin. FTIR–ATR, Fourier-transform infrared-attenuated total reflectance mode; FA, fatty acids; ISk, inner skin; OSk, outer skin

phenolic acid derivatives (e.g., *p*-coumaric, caffeic, ferulic, and sinapic acids;[30–34] Figure 2a); (b) regarding both, the deformation [$\delta(CH_3)$ and $\delta(CH_2)$] at 1,450–1,470 cm^{-1} on the one hand and stretching modes [$\nu(CH_3)$ and $\nu(CH_2)$] of the polymeric waxy components at 2,849 and 2,920 cm^{-1} on the other hand is easy to notice that signals are intense in the OSk but virtually undetected in the ISk, especially the ones located at high wavenumber (Figure 2b); (c) the infrared signal at 1,688 cm^{-1}, due to protein components, detected only in the external skin of the berries; and (d) the carbonyl stretching mode (ester group) ν(C═O) band at ~1,740 cm^{-1}, which is mostly due to ester linkages within the polymeric compounds abundant in the outer cuticle. In addition, the characteristic ring stretching vibrations ν(CC) observed around 1,000 cm^{-1} for the ISk infrared spectrum display a marked intensity decrease in the external skin samples.

In order to evaluate the main differences between the Raman signals that belong to the external and internal skin of the berry, the Raman profile of the inner skin was subtracted from the one of the outer skin to clearly see the main signals in each part of the sample (Figure 2c). This procedure evidenced very noticeable differences, namely, in the features (a) between 530 and 1,300 cm^{-1}, ascribed to the triterpenoids from the cuticular wax,[29] predominant in the external skin; (b) at ~1,635 cm^{-1} from the phenolic constituents of the fruit,[35,36] which also prevail in the outer skin; (c) at

1,662 cm^{-1}, assigned to fatty acids found to be predominant in the outer skin (possibly exerting a protective role). The most striking distinctions between the internal and external regions of the berry skin are observed for the bands at 1,309 and at 1,445 cm^{-1} ascribed to the CH_2 torsional modes, $\tau(CH_2)$, and the $\delta(CH_2)$ and $\delta(CH_3)$ modes, respectively and are mainly due to the cuticular wax lipidic components (fatty acids, esters, and terpenes). This reflects a significant chemical variation among these parts of the fruit: the OSk expectedly containing a much higher amount of waxy components, mainly triterpenoids (e.g., amyrins, oleanolic, and ursolic acids) and cutin (an omega fatty acid polymer), which is in agreement with a previously reported Raman study on triterpenoids found in plant cuticles.[29] The cited study revealed typical bands for the components of this plant part that has a protecting role towards the surrounding environment (namely against water loss, pathogens, and herbivores). In fact, Yu and coworkers[29] found differences in the Raman spectra between cuticular membranes, with and without wax, that closely resemble those presently observed for the difference Raman spectrum between the outer and inner skin of the *C. album* berries—evidencing a discrimination predominantly based on the fatty acid polymers and terpenes of the external layer.[29] The main negative peaks are also remarkable: at 630 cm^{-1} assigned to fructose and at 1,123 cm^{-1} corresponding to glucosidic bonds. As expected, the main sugar components are present in the inner part of the skin, which is reflected in the negative peaks obtained after performing the spectral difference.

The *C. album* seeds also evidence significant spectral changes when compared with the skin, mainly relative to the outer skin. FTIR revealed a band at ~1,550 cm^{-1}, only detected in this region of the plant, as well as a signal at ~1,660 cm^{-1}, which is assigned to ν(C═O) from feruloyl-containing amidated forms of pectin,[37] a polysaccharide abundant in seeds. The remaining Raman profile (Figure 3; bottom) is similar to the one obtained for the inner skin, except for the doublet at 1,609 and 1,633 cm^{-1} that is characteristic of ferulic and *p*-coumaric acids—ν(C═C) from the phenyl ring and the propenoic chain.[35,38] These phenolic derivatives are absent in the seeds (Figure 2b; bottom and Figure 3; bottom), being only present in the fruit skin (both outer and inner parts).

The Raman spectrum of the *Corema* seeds displays a striking similarity with that of LA (Figure 3), except for the ester carbonyl group detected at 1,749 cm^{-1} for the seeds. In addition, the Raman profile of the seeds comprises two strikingly distinct signals compared with the spectra of OSk and ISk (Figure 2a): (a) at 1,660 cm^{-1}, assigned to ν(C═C) from unsaturated carbon chains, with a lower intensity in the skin revealing a higher degree of unsaturated cis fatty acids/esters; (b) at 3,013 cm^{-1}, ascribed to the symmetric stretching modes from cis double bonds from unsaturated carbon chains ($\nu_s[HC{=}CH]_{cis}$).[39] Both the $\nu_s(HC{=}CH)_{cis}$ and ν(C═C) bands are then reliable biomarkers of the unsaturation degree of this type of compounds (see further discussion).

4 | ON THE SIGNAL INTENSITY RATIOS

Taking into account the similarity between the vibrational profile of the present samples and fatty acids, a common data treatment may be applied,[24] through comparison of spectral ratios for the more representative

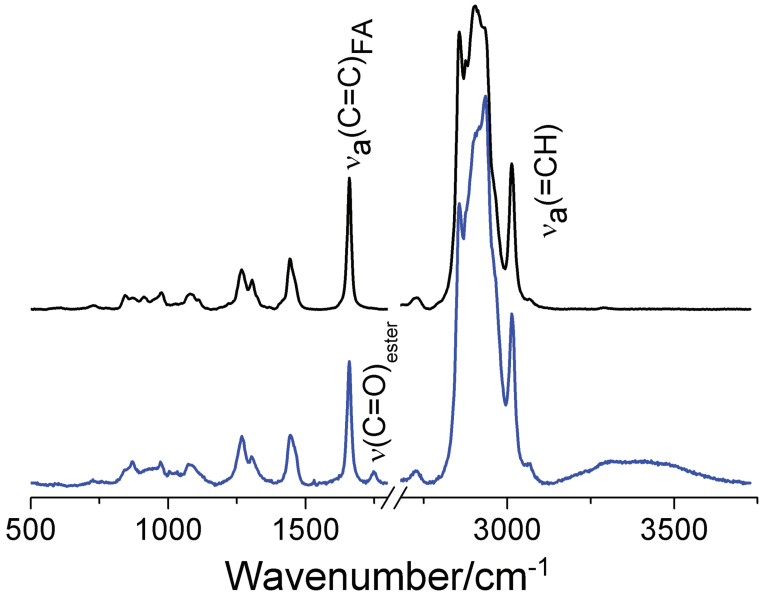

FIGURE 3 Raman spectra of linoleic acid (top) and *Corema album* seed (bottom)

bands, in order to gain an insight into the characteristics of the currently analysed samples. It should be clarified that in the present study, we are employing the results directly obtained from the seeds, which obviously contain other compounds apart from esters of fatty acids. Additionally, the data from Jamieson et al. (2018)[24] were obtained for fatty acids and not for esters, a fact that can lead to slight differences in the interpretation of the results.

4.1 | Raman data

Regarding the seeds of the white berries, it was possible to gather some information on the unsaturation degree and the chain length of their fatty acids (FA) esters: The presented data reveals an unsaturation degree close to two (Table 2). This result is consistent with the value previously obtained for LA[31] allowing us to conclude on the predominance of this FA in this part of the plant, probably in the ester form (according to the ν(C═O) Raman frequency presently measured at 1,749 cm^{-1}). The 2.53 ratio between I_{1660} and I_{1445}, assigned to $\nu(C{=}C)_{FA}$ and $\delta(CH_2)$, respectively, is also quite similar to the one corresponding to LA leading to a 0.11 ratio between the number of double bonds and CH_2 units, which compares well with the theoretical 0.17 value for LA. Regarding the I_{3013}/I_{2856} quotient, corresponding to $\nu_s(=CH)_{cis}$ and $\nu_s(CH_2)$, respectively, our interpretation is also similar to the one obtained for the LA (with a 0.07 difference). When compared with the theoretical value, the difference increases up to 0.1, which can be due to the mixture of different constituents present in the biological matrix of the *C. album* berries.

Finally, the 0.72 value for the quotient I_{2856}/I_{2935} evidences that the main chain within these compounds contains 10 CH_2 groups per CH_3 group. By comparison with the theoretical value of 12 previously reported for LA, it is possible to hypothesise that the average carbon chains in the *Corema* seeds are shorter. However, this should be taken with care, attending to the difficult assignment of the Raman bands between 2,850 and 2,960 cm^{-1} because contributions from other CH_2 and CH_3 groups are also present in this spectral range.

TABLE 2 Semi-quantitative intensity ratios derived from the Raman spectra of the seed of *Corema album* white berries as compared with linoleic acid

	Ratio (S)	Experimental value *Corema* (S)		Ratio (LA)	Experimental value (LA)	Exact value (LA)
I_{1268}/I_{1445}	0.97	n(C═C) = 1.8	I_{1268}/I_{1443}	0.79	n(C═C) = 1.5	n(C═C) = 2
I_{1660}/I_{1445}	2.53	$n(C{=}C)/n(CH_2) = 0.11$	I_{1660}/I_{1443}	2.59	$n(C{=}C)/n(CH_2) = 0.11$	$n(C{=}C)/n(CH_2) = 0.17$
I_{3013}/I_{2856}	0.61	$n(H{-}C{=})/n(CH_2) = 0.46$	I_{3013}/I_{2857}	0.53	$n(H{-}C{=})/n(CH_2) = 0.39$	$n(H{-}C{=})/n(CH_2) = 0.33$
I_{2856}/I_{2935}	0.72	$n(CH_2)/n(CH_3) = 9.9$	I_{2857}/I_{2932}	0.98	$n(CH_2)/n(CH_3) = 11.4$	$n(CH_2)/n(CH_3) = 12$

Abbreviations: LA, linoleic acid; S, seed.

TABLE 3 Semi-quantitative area ratios derived from the Fourier-transform infrared–attenuated total reflectance mode spectra of the seed and outer skin of *Corema album* white berries

Ratio	Assignment[a]	S	OSk	Interpretation[53,54]
$A_{2870–2960}/A_{2870–2960}$	$\nu CH_2/\nu CH_3$	1.69	0.37	Aliphatic chain length—higher values suggest longer and less branched chains
$A_{1500-1800}/A_{2800-3000}$	ox + νC═C/aliphatic stretching	2.51	0.79	Oxygenated group index—a higher index indicates more oxygenated groups compared to aliphatic chains
$A_{2800-3000}/A_{1600-1800}$	aliphatic stretching/νC═O	0.40	1.27	Lower values imply a higher C═O content, indicating the presence of ester linkages and other oxygen-bearing functional groups.

[a]oxygenated groups.

Abbreviations: OSk, outer skin; S, seed.

4.2 | FTIR–ATR data

The semi-quantitative area ratios derived from the FTIR–ATR spectra (Table 3) provided information regarding the main differences between two parts of the *C. album* berries: the S and the OSk. Upon spectral deconvolution to better individualise the peaks of interest (Tables S1, S2, and Figure S1), it was found that the seed components have longer and less branched aliphatic chains when compared with the OSk, as well as a higher number of oxygen-containing groups and ester links, possibly due to the higher content in pectin in this part of the plant.

5 | CONCLUSIONS

The *C. album* plants, extremely easy to wild grow, can become a new niche crop for application in novel food products (nutraceuticals) due to their high nutritional value and health-beneficial properties, namely as antioxidant cytoprotective agents. Therefore, a thorough evaluation of their chemical profile, identifying the parts of the plant with the highest amount of valuable components, is paramount for future practical applications. Accurate vibrational spectroscopic results are currently reported for *C. album* white berries, revealing a very high content in antioxidant polyphenols. Furthermore, the distinct vibrational signatures measured for each portion of the berries— OSk, ISk, and S—evidenced clear chemical differences: whereas the seeds are richer in unsaturated lipids, particularly cis fatty acids (mostly in the ester form), the skin comprises a higher amount of phenolic constituents. In addition, it was possible to distinguish between the external and internal surfaces of the skin, the outer cuticle showing predominant triterpenoids, cutin polymers (waxy protective components), and proteins and the inner skin (in contact with the endocarp) containing a larger amount of phenols.

The results presently reported confirm the capability of Raman microspectroscopy and FTIR (mainly in ATR mode) for providing unique and accurate information on the chemical composition of heterogeneous biological samples such as berries, being also able to deliver their spatial distribution within the epicuticular and intracuticular regions as well as in the seeds.

Further studies are envisaged on *C. album*, namely the analysis of its fruits at distinct maturation stages (white and pink berries) and under different conditions regarding the time after harvesting and the storage period and temperature. The data thus gathered will hopefully allow to better understand the health-beneficial properties of this plant, aiming at its inclusion in novel food products as a chemopreventive nutraceutical.

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