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Characterization of macadamia and pecan oils and detection of mixtures with other edible seed oils by Raman spectroscopy

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SUMMARY: Authenticating fats and detecting their adulteration with substantially cheaper fats can pose major problems for producers of high-value oils for nutritional and cosmetic use. In this work, we used Raman spectroscopy to discriminate macadamia and pecan oils from other, cheaper vegetable oils including corn and sunflower oils. This technique additionally allows one to detect and assess the adulteration of macadamia oil with another vegetable oil.

KEYWORDS: *Adulteration of oils; Macadamia oil; Pecan oil; Raman spectroscopy*

RESUMEN: ***Caracterización de aceites de macadamia y de nuez pecanera y detección de mezclas con otros aceites de semillas comestibles por espectroscopía Raman***. La autentificación de grasas para detectar su adulteración con otras grasas más baratas es uno de los principales problemas a los que se enfrentan los productores de aceites de alto valor, ya sea para uso alimentario o para uso cosmético. En este trabajo se emplea la espectroscopia Raman, por un lado, para caracterizar los aceites de macadania y de nuez pecanera, de alto valor y diferenciarlos de otros más baratos, como los de maíz y de girasol, y por otro, para detectar mezclas del aceite de macadamia con estos aceites vegetales más baratos.

PALABRAS CLAVE: *Aceite de macadamia; Aceite de nuez pecanera; Adulteración de aceites; Espectroscopia Raman*

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1. INTRODUCTION

Fats and oils are essential ingredients of the human diet and have been widely consumed, whether directly or in processed foods, for centuries. The significance of fats and oils lies in their high energy and essential fatty acid contents; the latter are indispensable for the proper development of human tissues. Some vegetable oils contain additional substances with excellent properties for protecting human skin which have fostered their use in medical and aesthetic treatments throughout the world since ancient times.

Macadamia oil is among the most widely used in aromatherapy. This oil is obtained from the fruit of the macadamia tree, which originated in Australia and New Zealand and comprises nine species, the most important of which are *Macadamia integrifolia* and *Macadamia tetraphylla*. All nine species are edible and major sources of fats, proteins and vitamins.

Macadamia oil is edible and unique with regards to its composition of monounsaturated fatty acids; thus, it contains palmitoleic acid (C16:1 Δ^9) and asclepic acid (C18:1 Δ^{11}), which, together with its high content in oleic acid (C18:1 Δ^9), make it very healthy (Maguire, *et al.*, 2004). Macadamia oil has other industrial uses, particularly as a lubricant (Knothe, 2010). Also, its softening, soothing properties, its content in nutrients required to preserve skin in excellent conditions and its usefulness as a natural vehicle for essential oils, are highly appreciated for aromatherapy treatments.

Pecan nut oil is obtained from the fruit of the *Carya illinoinensis* tree, which originated in North America and subsequently expanded to large areas in the USA and Mexico. Like macadamia oil, pecan oil contains abundant unsaturated fatty acids (oleic and linoleic mainly); however, it is much less widely used for non-nutritional purposes than is macadamia oil.

A number of instrumental techniques have been used to discriminate between different types of vegetable oils or different samples of the same type. ^{1}H and ^{13}C nuclear magnetic resonance spectroscopies are especially suitable for this purpose (Guillén and Ruiz, 2003; Zamora, *et al.*, 2002; Shaw, *et al.*, 1997; Mannina, *et al.*, 2001). However, the use of Raman spectroscopy has grown dramatically in recent years, especially for the quantitative detection of the adulteration of extra virgin olive oil with other, cheaper edible oils (Zhang, *et al.*, 2011; El-Abassy, *et al.*, 2009; Baeten, *et al.*, 2005; Zou, *et al.*, 2009), its authentication (Korfi, *et al.*, 2011; Aparicio and Baeten, 1998) or even the determination of some chemical species such as antioxidants (Paiva-Martins, *et al.*, 2011) and free fatty acids (El-Abassy, *et al.*, 2009; Muik, *et al.*, 2003) present not only in olive oil, but also in other vegetable oils. In addition, Raman spectroscopy has been used to assess stability against oxidation in olive oil (Muik, *et al.*, 2007; Muik, *et al.*, 2005).

In this work, we used Raman spectroscopy for the first time to characterize macadamia and pecan nut oils with a view to their differentiation from other seed oils including corn and sunflower oils. This technique also allows the adulteration of macadamia or pecan oil with other, cheaper oils (e.g. corn, sunflower) to be detected.

2. MATERIALS AND METHODS

2.1. Reagents

All reagents used to establish the fatty acid profiles of the oils were commercially available products.

2.2. Oils samples

The macadamia, pecan, sunflower and corn oil were supplied by the Laboratorio Agroalimentario de la Junta de Andalucía (Córdoba, Spain). The four oils were from commercial origin and fully characterized in this laboratory. The macadamia and pecan oils were virgin oils. Sunflower and corn oil samples with volume percentages of 5, 10, 20, 30, 40 and 50% were blended into a sample of macadamia oil.

2.3. Determination of the fatty acid profile

The fatty acid analyses were carried out by methylation of the same prior and subsequent determination by gas chromatography with an FID detector on a Perkin Elmer Mod. Clarus-500, using a BPX70 capillary column (60 m×0.25 mm i. d.). Samples were prepared as follows: threaded tubes were weighed with 0.15 g of oil, previously purified, with an accuracy of 0.01 g and dissolved in 2 mL of hexane. Then 0.2 mL of methanolic 2N potassium hydroxide solution were added and stirred intensively for 1 minute. The mixture was left to decant the upper phase of hexane containing the fatty acid methyl esters for 30 min, and an aliquot of 1 ml was taken for injection into GC. The identification of fatty acid methyl esters was carried out by retention times and quantification was performed as % area. The uncertainty analysis method of fatty acids has been validated from different vegetable oils (certified reference materials). From these results we have obtained a relative uncertainty of 5% for all fatty acids (uncertainty calculated for a confidence interval of 98% and a coverage factor k=2).

2.4. Raman Analysis

The Raman spectra for the oil samples were acquired with a Renishaw Raman instrument (In Via Raman Microscope), equipped with a Leica DM2500 M microscope furnished with various lenses (5×, 20×, 50× and 100×), monochromators and filters, and a CCD. Spectra were obtained using a 20× magnification objective and by excitation with a green laser light (532 nm) over the wave number range 800–1800 cm^{-1} and 2800–3050 cm^{-1}. A total of 32 scans per spectrum were performed in order to improve the signal-to-noise ratio. The liquid samples were placed in the Raman microscope on a Petri dish. Each spectrum was automatically smoothed and baseline corrected using the functions of the spectrometer software Wire 3.3. The normalization of the spectra was performed using the PeakFit v4.11 software.

3. RESULTS

3.1. Fatty acid profile

Table 1 shows the results of the GC determination of the fatty acid profiles for four oil samples. Oleic acid was found to be the most abundant fatty acid in both macadamia and pecan oil. On the other

TABLE 1. Fatty acid composition of macadamia, pecan, corn and sunflower oils

Fatty acid	Macadamia	Pecan	Corn	Sunflower
Lauric	0.06	0	0	0
Myristic	0.64	0.04	0.03	0.07
Palmitic	8.38	6.35	10.84	6.16
Palmitoleic	18.28	0.09	0.15	0.11
Margaric	0.03	0.05	0.01	0.04
Margaroleic	0.01	0.05	0.04	0.02
Stearic	3.68	2.58	2.06	4.44
Oleic	56.76	62.86	30.85	23.87
Asclepic	3.72	0.00	0.00	0.00
Linoleic	2.78	26.40	54.31	64.77
Linolenic	0.27	1.19	0.93	0.07
Araquidic	2.91	0.15	0.45	0.31
Gadolenic	2.51	0.24	0.26	0.15

hand, linoleic acid was the major acid in corn and sunflower oils, which, however, contained substantial amounts of oleic acid. Macadamia oil had quite a high content in palmitoleic acid (over 18%); as noted earlier, this, together with the presence of asclepic acid, makes it very healthy. All oils had similar contents in linolenic and saturated fatty acids, with differences never exceeding 5% among oils.

3.2. Raman spectra

The Raman spectra for vegetable oils exhibit bands of use for authentication purposes in the regions 800–1800 and 2800–3050 cm^{-1} only (Baeten, *et al.*, 1998). All spectra obtained in this work were recorded in these two regions. The exact assignment of the Raman bands of different vegetable oils has taken some time. The signals for extra virgin olive oil, which is among the most widely studied with this technique, have been unequivocally established (El-Abassy, *et al.*, 2009; Baeten, *et al.,* 2009; Yang and Irudayaraj, 2001). Existing assignations can be used in conjunction with fatty acid profiles to elucidate the bands for other vegetable oils (*e.g.* corn and sunflower oils) (Zhang, *et al.*, 2011; Farhad, *et al.*, 2009; Sadighi-Jorabchi, *et al.*, 1990). In this work, we assigned the Raman bands for macadamia and pecan nut oils by comparison with those of corn and sunflower oils. Also, we assessed the potential of Raman spectroscopy for determining mixtures of these oils. To this end, we examined the previous two Raman regions separately.

First region: 2800–3050 cm^{-1}. Figure 1 shows the Raman spectra for the four studied oils in this region. All exhibited four well-defined bands below 3000 cm^{-1} and centered at about 2854, 2897, 2932 and 2968 cm^{-1}, respectively. These bands are typical of stretching vibrations of C–H bonds, ν_{C-H}, in methyl (CH_3) and methylene (CH_2) groups. These groups are the most abundant in the hydrocarbon chains of fatty acids present in vegetable oils. An additional signal, which appears at a shoulder, at about 2876 cm^{-1} was observed which was assigned to stretching vibrations in CH_2 groups bonded to an unsaturated carbon atom (–CH_2–CH=CH–) present in unsaturated fatty acids. The bonding of an unsaturated carbon atom to a CH_2 group shifts the absorption band for the C–H bond in the methylene group (Baranska, *et al.*, 1987). A sixth signal was observed above 3000 cm^{-1} due to stretching vibrations of the C–H bond of =C–H groups in fatty acid chains. According to Sadeghi-Jorabchi *et al.* (1990), the signal shifts to higher wave numbers with increasing numbers of double bonds; thus, it appears at *ca*. 3006 cm^{-1} in oleate chains and *ca*. 3013 cm^{-1} in linoleate chains. According to Li-Chan (1994) this signal can be used as a measurement of unsaturation in oil.

As stated above, the intensity of the band was related to the degree of unsaturation of the oil (DU). Thus, DU can be calculated from the combined proportions of mono-unsaturated acids plus two times the proportion of di-unsaturated acids plus three times the proportion of tri-unsaturated acids, both as determined by GC. A plot of DU as a function of the relative intensity of the Raman signal was a straight line with a high correlation coefficient (r^2>0.99). The wave number of the absorption band increased with an increasing proportion of poly-unsaturated acids. These results are shown in Table 2.

Second region: 800–1800 cm^{-1}. The Raman spectral region from 800 to 1800 cm^{-1} contained a number of absorption bands including those for stretching vibrations of C=O, C=C and C–C bonds, and others corresponding to various bending vibrations of C–H bonds. Figure 2 shows the spectra for the four studied oils in this region. As can be seen, all exhibited a small band at about 1748 cm^{-1} which was assigned to stretching vibrations of C=O bonds in glyceride esters. This relatively weak band was unaffected by the presence of unsaturated groups in the vicinity of the C=O groups, so it provided no information other than the presence of ester bonds. A very strong band was observed at 1657 cm^{-1} which was assigned to stretching vibrations of C=C bonds in the hydrocarbon chains of fatty acids. The exact position of the signal was found to depend on the *cis*-to-*trans* isomer ratio of each oil and its wave number is known to be about 5 cm^{-1} lower for *cis* isomers than for *trans* isomers (Bailey and Horvat, 1972). As confirmed by the GC analyses, the presence of *trans* isomers in our oils was negligible and, obviously, undetectable in the Raman spectra. The strength of this signal was again strongly correlated with the degree of unsaturation (r^2>0.98).

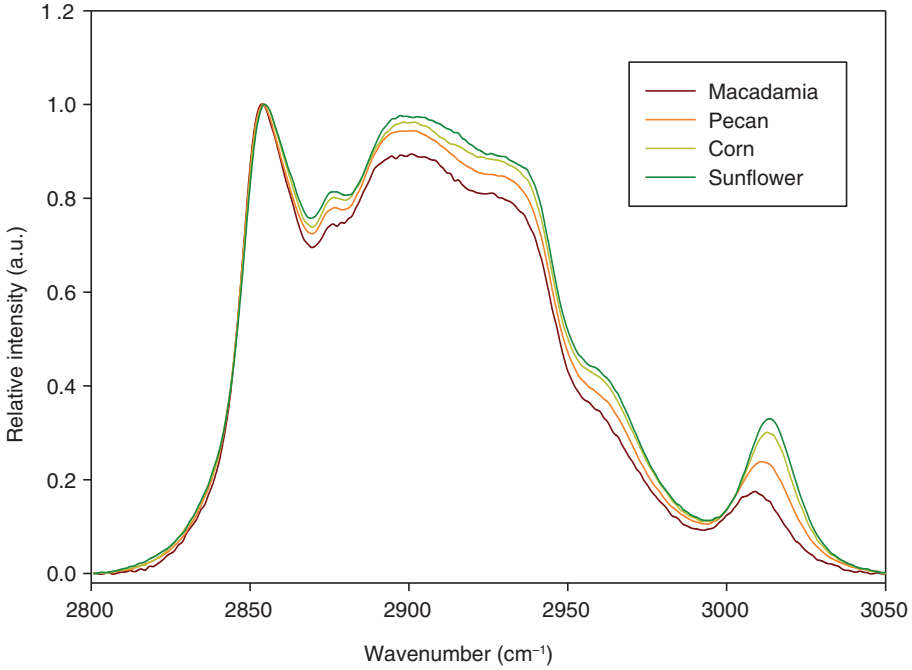

FIGURE 1. Raman spectra in the 2800–3050 cm^{-1} region for the studied oils.

A scissoring deformation band (ν_{CH_2}) for CH_2 groups in fatty acid chains was observed at about 1440 cm^{-1}. Despite its strength, this band provided no information of use towards discriminating among the oils. This was not the case with the zone from 1200 to 1400 cm^{-1}, which exhibited two strong bands assigned to in-phase methylene twisting motions and in-plane C=C–H deformation in an unconjugated *cis* double bond, centered at about 1303 and 1267 cm^{-1}, respectively. These bands can be used to determine the *cis*/*trans* ratio for oils and, in many cases, for their authentication. As for the band at 1440 cm^{-1}, at 1303 cm^{-1} it provided no useful information towards discriminating among the four oils. The band at 1267 cm^{-1} was due to a deformation vibration of C=C–H bonds, so it differed among the oils; thus, it exhibited the same sequence as the stretching vibrations of =C–H and C=C bonds.

TABLE 2. Degree of unsaturation (DU) and wavenumbers and intensity of the Raman bands for ν_{C-H} stretching vibrations of C=C–H bonds in the studied oils

Oil	Signal (cm^{-1})	Intensity (a.u.)	DU[a]
Macadamia	3009	0.109	87.65
Pecan	3011	0.167	119.61
Corn	3013	0.229	142.71
Sunflower	3013	0.258	153.90

[a]Degree of unsaturation.

Finally, the Raman zone from 800 to 1200 cm^{-1} was the one that provided the least discriminating information for our purpose. This zone contained the bands for the backbone vibrations of C–C bonds and stretching vibrations of C–O bonds.

3.3. Adulteration of macadamia oil with sunflower and corn oils

Based on the above-described results, Raman spectroscopy is a powerful tool for distinguishing vegetable oils in terms of degree of unsaturation. This led us to assess its potential for detecting the adulteration of a high-value oil such as macadamia with considerably cheaper oils such as sunflower or corn oil. This could in principle be accomplished by using the Raman spectral zones 2995–3050, 1600–1700 and 1200–1400 cm^{-1} to detect sunflower or corn oil added to macadamia oil. The three zones are in theory the most suitable for detecting adulteration since the correlation coefficients between band strength and degree of unsaturation are especially high (>0.99) in them. We used samples of macadamia oil containing 5, 10, 20, 30, 40 or 50% of sunflower or corn oil in order to have an adequate number of experimental determination points for establishing accurate correlations.

Raman spectra in the 2995–3050 cm^{-1} region are shown in Figures 3 and 4, for various mixtures of macadamia oil with sunflower and corn oil, in addition to those for the pure oil. This signal can be used

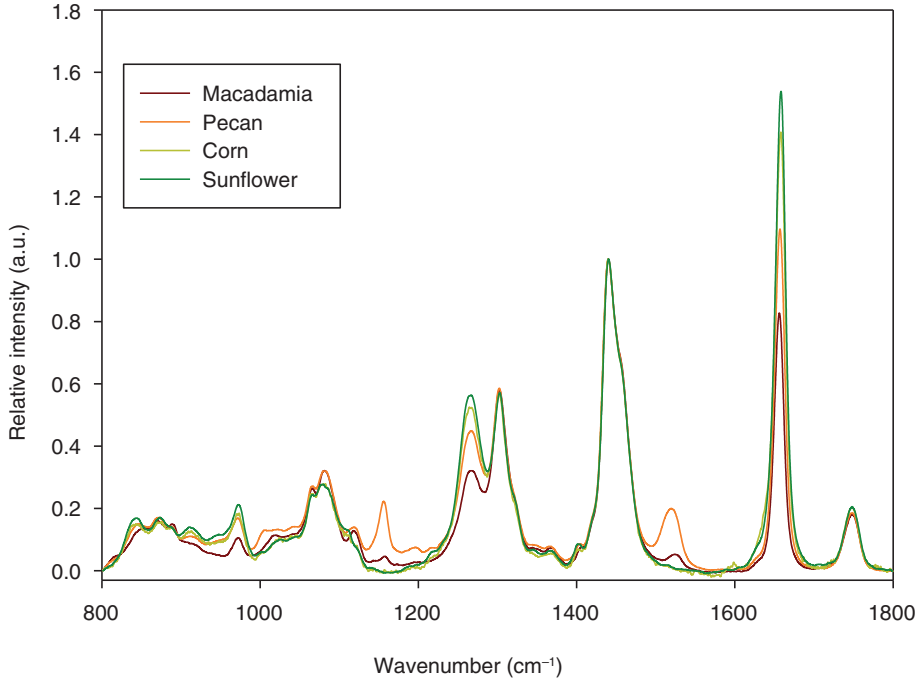

FIGURE 2. Raman spectra in the 800–1800 cm^{-1} region for the studied oils.

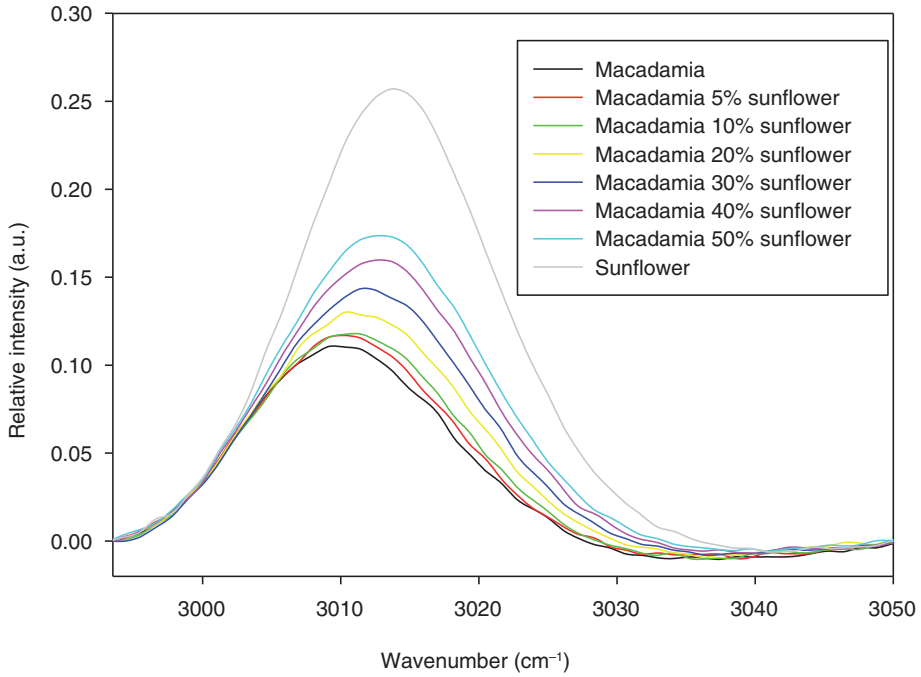

FIGURE 3. Raman spectra in 2990–3050 cm^{-1} region for macadamia oil adulterated with sunflower oil.

as a measurement of unsaturation in oil because it is assigned to the stretching vibrations of the C–H bonds of =C–H groups in fatty acid chains. In both cases, as can be seen from the figures, increasing the proportion of sunflower oil increased band strength through an increased degree of unsaturation in the oil mixture.

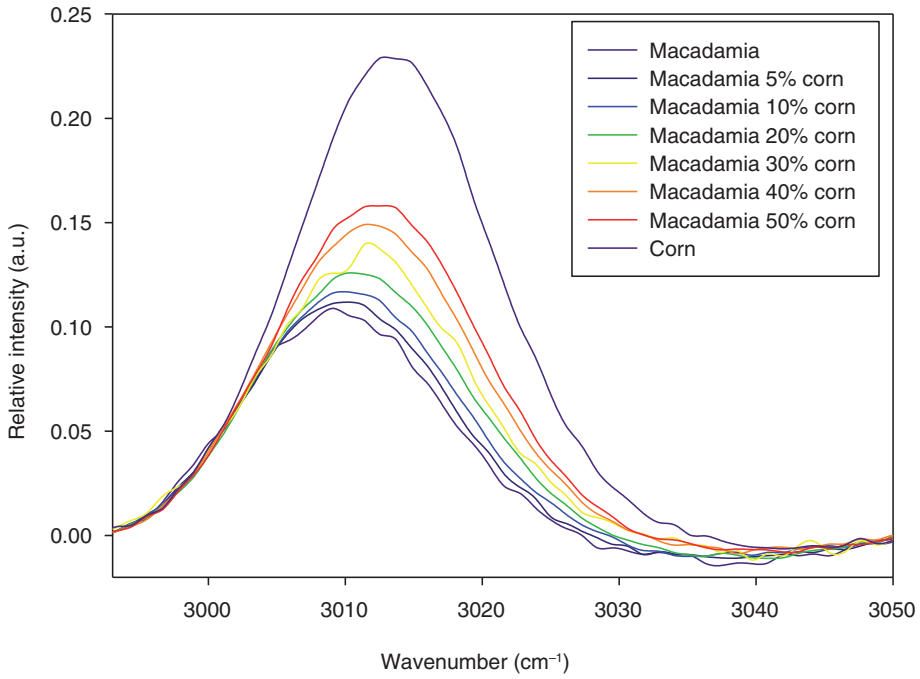

FIGURE 4. Raman spectra in 2990–3050 cm^{-1} region for macadamia oil adulterated with corn oil.

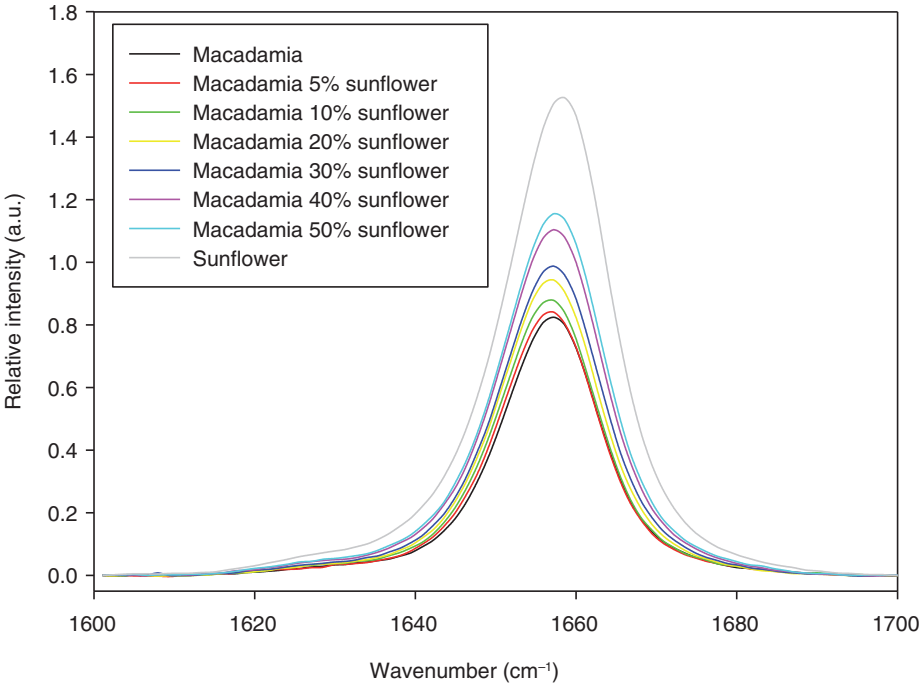

FIGURE 5. Raman spectra in the 1600–1700 cm^{-1} for macadamia oil adulterated with sunflower oil.

The plots of band strength against degree of unsaturation or proportion of seed oil added (not shown) exhibited excellent correlation (r^2>0.99).

Figures 5 and 6 show the Raman spectra in the 1600–1700 cm^{-1} region for various mixtures of macadamia oil with sunflower and corn oil, in addition

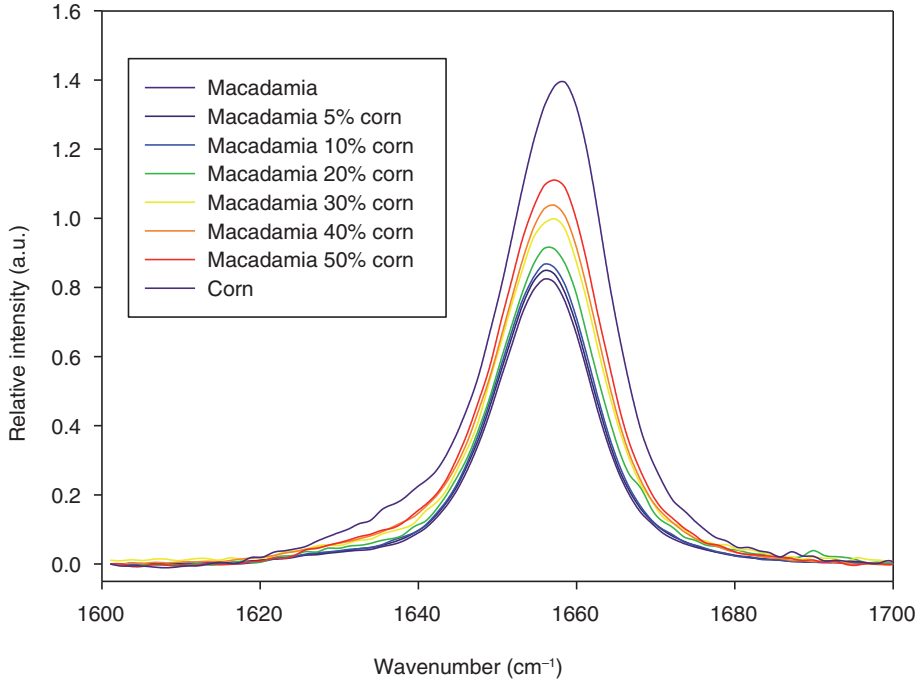

FIGURE 6. Raman spectra in the 1600–1700 cm^{-1} for macadamia oil adulterated with corn oil.

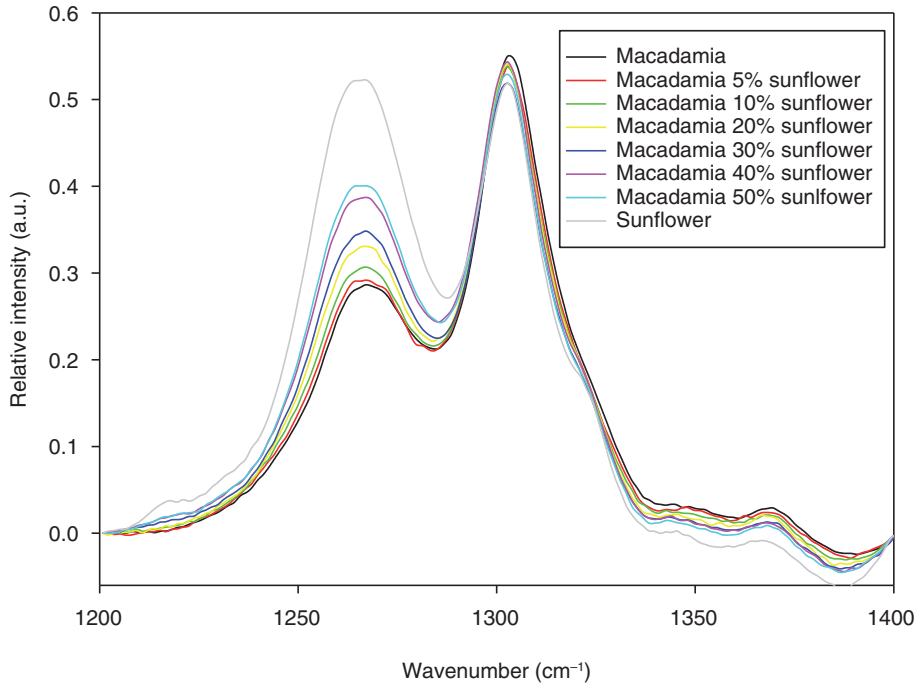

FIGURE 7. Raman spectra in the 1200–1400 cm^{-1} for macadamia oil adulterated with sunflower oil.

to those for the pure oils. As noted earlier, this zone exhibited a band assigned to the stretching vibrations of C=C bonds in unsaturated fatty acid chains. Again, in both cases, as can clearly be seen from the figures, increasing the proportion of corn oil (i.e. increasing the degree of unsaturation of the

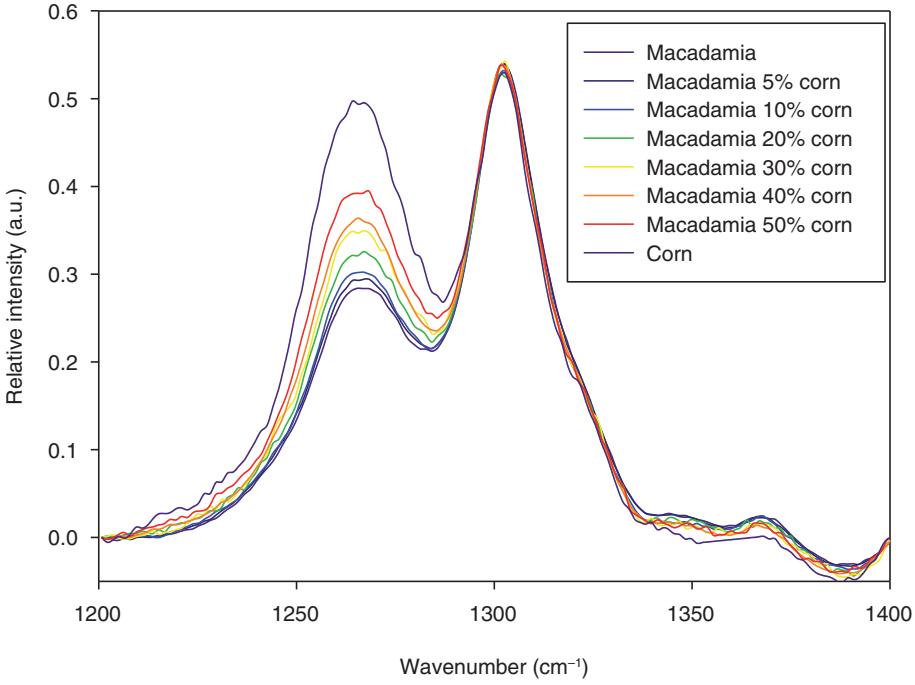

FIGURE 8. Raman spectra in the 1200–1400 cm^{-1} for macadamia oil adulterated with corn oil.

oil mixture) increased the strength of the absorption band. A plot (not shown) of band strength against degree of unsaturation or proportion of seed oil added exhibited excellent correlation (r^2>0.99).

The 1200–1400 cm^{-1} region exhibited two strong bands, one of which, at 1267 cm^{-1}, was assigned to in-plane bending of unconjugated *cis* C=C–CH bonds in unsaturated fatty acids. Figures 7 and 8 show the spectra for the mixtures of macadamia oil with sunflower and corn oil, respectively. Again, increasing the proportion of seed oil increased band strength through an increased degree of unsaturation in the oil mixture. A plot of band strength against the degree of unsaturation or proportion of seed oil exhibited excellent correlation (r^2>0.99) (not shown).

The results obtained in pecan oil adulteration with sunflower and corn oils are perfectly correlated with those described for macadamia oil, which are not shown.

Therefore, in our case, Raman spectroscopy affords the qualitative and quantitative detection of the adulteration of macadamia oil with sunflower or corn oil.

4. CONCLUSIONS

We demonstrated that Raman spectroscopy is a valuable and useful technique for determining the degree of unsaturation of a vegetable oil. Furthermore, in the case we studied, the technique can also detect adulteration of valuable oil, such as macadamia, with cheaper ones such as corn or sunflower. A generalization of these results requires further study, including a larger amount of macadamia oils. However, for any macadamia oil that can be acquired, its degree of unsaturation will always be considerably less than that of corn or sunflower oil, so that this methodology can be applied to determine the adulteration of macadamia oil with other cheaper oils.

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