Characterization of Edible Oils and Lard by Fourier Transform Infrared Spectroscopy. Relationships Between Composition and Frequency of Concrete Bands in the Fingerprint Region

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ABSTRACT: Fourteen samples of edible oils and lard have been studied by means of Fourier transform infrared spectroscopy. The spectra were recorded from a film of pure oil or lard between two discs of KBr. The bands of the spectra were assigned to different functional group vibrations. The frequencies of some bands have constant values, independent of the nature of the sample. However, frequencies of other bands, some of them in the fingerprint region, depend greatly on the sample composition. Equations obtained from frequency of these bands and composition data are valuable to predict the proportions of saturated, monounsaturated and polyunsaturated acyl groups in oils and lard.

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KEY WORDS: Acyl groups, characterization, edible oils, fingerprint region, Fourier transform infrared spectroscopy, frequency, lard, monounsaturated, polyunsaturated, saturated.

Midinfrared spectroscopy has scarcely been used for food studies in the past, basically because the dispersive technique is not fast and because of its poor quantitative capabilities. With the introduction of the Fourier transform technique in infrared spectroscopy, this is changing in many fields (1,2), including foods (3–5).

Midinfrared spectroscopy has scarcely been used for the study of fats and oils. However, even with the dispersive technique, determination of the degree of unsaturation of fats and oils from the intensity of concrete infrared spectroscopic bands has been known for a long time (6–10). The selected data for this determination come only from the C-H, and some times also from the C=C, stretching region of the spectra. Also the determination of *trans* unsaturated fatty acids by means of infrared spectroscopy has been widely used in the fats and oils industry, and the method has been standardized by AOCS (11) and IUPAC (12). The method is based on quantitation of the intensity of the band at 967 cm^{-1}, due to isolated *trans* double bonds. The same methodology has been applied to Fourier transform infrared spectroscopy with the advantages that this technique offers (13).

Recently, methods have been developed for determination of iodine value and saponification number (14), free fatty acids (15), peroxide value (16), and *cis-trans* content (17) of edible oils from Fourier transform infrared spectra. In some of these studies, only a concrete region of the spectra is taken into account: for instance, in the determination of free fatty acids, the band at 1711 cm^{-1} is used, while peroxide value can be determined from the region between 3750 and 3150 cm^{-1}. However, for determination of other indices, such as iodine value or saponification number, the regions used are wider and are readily selected by means of chemometric software, which is generally based on partial least squares. The partial least squares method, apart from the traditional regions for C=O, C-H, *cis, trans*, also uses the lipid fingerprint region, because it also contains pertinent information that, when included, accounts for a major portion of the variation not accounted for in the conventional wavelength approach. However, in these studies, the relation of the spectrum bands to the corresponding predicted indices is not explained.

Studies for authentication of vegetable oils, butters, and margarines from Fourier transform infrared spectra by principal component analysis and discriminant analysis have also been carried out (18–20). These multivariate statistical methods, applied to infrared data, classify vegetable oils according to plant species and are able to detect adulteration with a high degree of accuracy. However, these studies have not shown what information of the spectrum is relevant in each situation.

Some authors who use dispersive spectrometers have obtained similar infrared spectra from different vegetable oils (21). Conversely, others (19,22) affirm that subtle dissimilarities between spectra exist because the spectrum of each oil contains a great wealth and variety of information about the composition of the sample, although no explanation of the observed differences has been made. That is to say, to the best of our knowledge, studies regarding the differences in the spectra of various kinds of edible oils and fats for the purpose

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of extracting valuable information have not been made (23). For this reason, we have recorded the spectra of different oils with well-established compositions by the Fourier transform technique and characterized them. The study pays attention not only to the presence or absence of some bands but also to the values of their frequencies. Classification of oils based on frequency data of concrete bands has been tested, and relationships between frequencies of some bands and compositions of the samples have been studied. These relations could be used to know the proportion of the main components of the oils, and within certain limits, to detect adulteration in a simple fashion; the study also may be useful for monitoring studies of oxidation processes by Fourier transform infrared spectroscopy.

EXPERIMENTAL PROCEDURES

Samples. Fourteen lipid-rich commercial products were obtained from local supermarkets. All are commonly used in the Spanish diet, except sesame oil. The sample collection included: two samples of extra-virgin olive oil, designated A and B; three samples of olive oil made of a mixture of refined and virgin olive oil, named C, D, and E; one sample of virgin sesame oil, F; three samples of refined sunflower oil, G, H, and I; two samples of refined corn seed oil, J and K; a mixture of sunflower and corn oils, L; one sample of seed oil of unknown vegetable origin, designated as M; and finally one solid sample of lard, named N.

Fourier transform infrared spectra. The infrared spectra were recorded with a Fourier transform infrared spectrometer, Nicolet Magna-IR Spectrometer 550 (Nicolet Instrument Corporation, Madison, WI), interfaced to a 486 personal computer operating under Windows-based Nicolet Omnic software (version 2.1). The instrument was purged with a Balston dryer (Balston, Lexington, MA) to minimize water vapor and CO_2 interferences.

Spectral acquisition. A film of a small amount of each sample (approximately 2 μL for liquids) was deposited between two discs of KBr, avoiding the presence of air, as in previous studies (1,4,5). Multiple spectra (between three and four) were collected from each sample over different periods of time. All spectra were recorded from 4000 to 500 cm^{-1}.

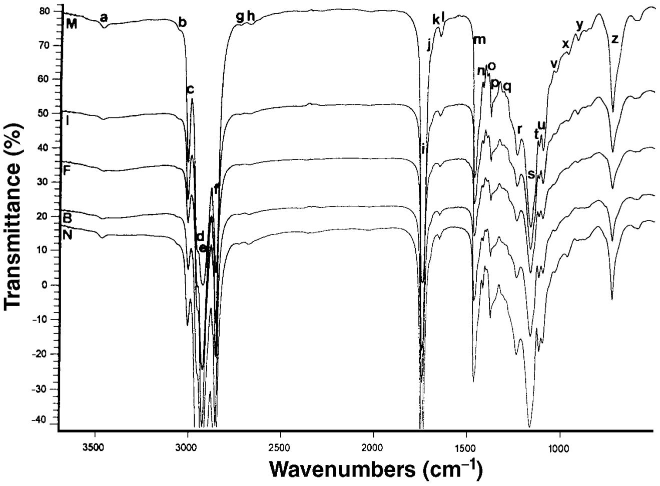

FIG. 1. Fourier transform infrared spectra of lard, N, and of some sample oils: extra virgin olive, B; sesame, F; sunflower, I; and unknown seed, M.

For each spectrum, 32 interferograms were co-added before Fourier transformation and zero-filled to give a data point spacing of approximately 1.9 cm^{-1} in the frequency domain.

Study of the spectra. The frequency of each band was obtained automatically by using the "find peaks" command of the instrument software.

RESULTS AND DISCUSSION

The edible oils and the lard are constituted basically of fatty triglyceride esters with different substitution patterns, lengths and degrees of saturation of the chains and of other minor components; Table 1 shows the fatty acid compositions of some of these samples, as given by the producers. Observation of the spectra of these samples allows one to make a first classification by groups because all spectra of olive oils on the one hand, and all spectra of sunflower and corn oils on the other, show the same features to the eye. For this reason, in Figure 1 only the spectra of lard, N, of extra-virgin olive oil, B, of sesame oil, F, of sunflower oil, I, and of unknown seed

TABLE 1
Composition of the Samples as Given by the Producers

	A	B	C	D	E	F	G
Monounsaturated acyl groups (%)	—	71	79	—	79	—	27
Saturated acyl groups (%)	—	14	13	—	13	—	13
Polyunsaturated acyl groups (%)	—	14	8	—	8	—	60
Maximal acidity (°)	0.7	0.4	0.4	1	1	—	0.2
Vitamin E (mg)	—	—	20	—	20	—	60
	H	I	J	K	L	M	N
Monounsaturated acyl groups (%)	—	—	30	27	24	—	47.5
Saturated acyl groups (%)	—	—	13	13	12	—	40.5
Polyunsaturated acyl groups (%)	—	—	57	59	64	—	10
Maximum acidity (°)	0.2	0.2	0.15	0.15	0.2	0.2	—
Vitamin E (mg)	—	—	30	30	—	—	—

oil, M, are given.

All spectra show a small band, **a**, near to 3468 cm^{-1}, which is associated with the overtone of the glyceride ester carbonyl absorption. In oxidized oils, a band of hydroperoxides is detected at approximately 3444 cm^{-1} (15). Stretching of the OH group of intermolecular-bonded water in butter and margarines absorbs at 3450 cm^{-1} (18).

A shoulder, **b**, near 3025 cm^{-1}, and a band, **c**, at approximately 3006 cm^{-1}, are observed in all spectra. These are due to the stretching vibration of the *trans* and the *cis* olefinic double bonds, respectively. The interference of both bands is minimal; however, the intensity of the *trans* band is low, owing to the scarce presence of *trans* isomers in edible oils and lard.

The methyl asymmetrical stretching vibration causes a shoulder, **d**, at 2953 cm^{-1}, and the symmetrical vibration band is not observed. Both the methylene asymmetrical stretching band, **e**, at approximately 2924 cm^{-1}, and the methylene symmetrical stretching band, **f**, near 2853 cm^{-1}, are obviously present in all samples.

Two weak bands, **g** and **h**, probably due to Fermi resonance of the carbonyl group, are observed at 2730 and 2677 cm^{-1}. The C=O group of triglycerides shows a stretching vibration band, **i**, at approximately 1746 cm^{-1}; a small shoulder, **j**, at 1711 cm^{-1}, is assigned to free fatty acids.

In all samples, two small bands, **k** and **l**, can be detected, at 1654 and at 1648 cm^{-1}. However, the intensity of the latter is very small or negligible in some samples, as can be observed in Figure 1. The C=C stretching mode of unconjugated olefins usually shows moderate to weak absorption at 1667–1640 cm^{-1}. Disubstituted *trans*-olefins absorb near 1670 cm^{-1}, but the band may be extremely weak or absent; disubstituted *cis*-olefins absorb near 1650 cm^{-1}, and the absorption of this band is stronger than that of *trans*-olefins (24). For this reason, these bands can be attributed to C=C stretching vibration of disubstituted *cis* C=C of acyl groups of oleic and linoleic acids. In samples of butter and margarine, absorptions at 1650 cm^{-1} (25) and 1640 cm^{-1} (18) are attributed to deformation bands of OH bonds of water.

The bands between 1400 and 1000 cm^{-1} are the most difficult to assign. However, in this region, the differences to the eye in Figure 1 are also the most significant. At approximately 1465 cm^{-1}, all spectra show the scissoring band, **m**, of the bending vibration of the methylene group. A band, **n**, at 1418 cm^{-1} is observed in all samples; this can be attributed to rocking vibrations of CH bonds of *cis*-disubstituted olefins. In all samples, near 1400 cm^{-1} a small band, **o**, is observed, which is difficult to assign; also a band, **p**, at 1377 cm^{-1} could be due to symmetrical bending vibration of methyl groups. Only the spectra of some samples show a band, **q**, at 1319 cm^{-1}, which is also difficult to assign; the other samples show a small shoulder at this frequency. In general, twisting and wagging vibrations of the CH_2 groups are observed in the zone between 1350 and 1150 cm^{-1}, and these bands are generally appreciably weaker than those resulting from methylene scissoring.

The following group of bands, **r**, **s**, **t**, and **u**, at approximately 1238, 1163, 1118, and 1097 cm^{-1}, respectively, and a shoulder, **v**, at 1033 cm^{-1}, are observed in all samples, and some of them could be assigned to the stretching vibrations of the C-O group in esters (24). This vibration consists of two asymmetric coupled vibrations C-C(=O)-O and O-C-C, the former being more important. Some authors assign the band at 1238 cm^{-1} to bending vibration out-of-plane of the methylene group (18).

In the region between 1000 and 800 cm^{-1}, there appear in some samples two small bands, **x** and **y**, at approximately 968 and 914 cm^{-1}; in others, they are small shoulders or are even absent. Band **x** is due to bending vibration out-of-plane of *trans* disubstituted olefinic groups; and band **y** has been associated by some authors (17) with bending vibration of *cis* disubstituted olefinic groups, even though olive oil spectra do not show this band.

Finally, at approximately 723 cm^{-1}, a band, **z**, results from the overlapping of the methylene rocking vibration and the out-of-plane bending vibration of *cis*-disubstituted olefins (24,26).

In the spectra obtained of the various samples, not all bands are present in all spectra, nor are their frequencies exactly the same. Table 2 shows the average frequencies that correspond to each band obtained from different spectra of the same oil sample, together with standard deviations (three or four spectra were recorded to obtain the average frequency data and the standard deviations). These data were obtained over different periods of time. A high reproducibility of the frequency data of most of the bands can be observed. Except for the frequency of bands **a** and **h**, the frequencies of the others show only small variations.

The frequencies of bands **a** and **h** show values in each sample that are independent of the nature of the oil. The frequencies of bands **g**, **i**, **k**, **m**, **n**, and **p** have almost the same values in all samples. However, the values of the frequencies of bands **c**, **e**, **f**, **o**, **r**, **s**, **t**, **u**, **x**, and **z** allow classification of the samples by groups. All olive oils, extra-virgin or refined, show similar values of the frequencies of these bands; another group, formed by sunflower and corn oils, also shows similar values, although it is possible to find subtle differences; and finally, sesame, unknown seed oil, and lard constitute three well-differentiated groups.

On the one hand, the values of the frequencies of bands **c** and u in the several groups of oils mentioned above increase in the order: olive (samples A–E), lard (N), sesame (F), unknown seed (M), corn and sunflower (samples G–L); the contrary is true for the value of the frequency of band **o**. This shows that these data are related to the proportion of monounsaturated and polyunsaturated acyl groups in the sample. Oils with the highest proportion of monounsaturated acyl groups show the smallest values for the frequencies of bands **c** and **u** and the highest value for the frequency of band **o**; and the opposite is true for the proportion of polyunsaturated acyl groups in the sample. Experimental data for the frequency of band **c** of triolein, trilinolein, and trilinolenin confirm these

TABLE 2
Average Frequencies in cm^{-1} of the Several Bands, Obtained from Three or Four Spectra of the Different Samples, Together with Standard Deviations

Band	A	B	C	D	E	F	G
a	3468.53 ± 0.73	3468.73 ± 0.52	3469.18 ± 0.41	3467.93 ± 0.62	3469.82 ± 0.93	3468.64 ± 1.41	3468.61 ± 0.49
c	3005.05 ± 0.00	3004.78 ± 0.02	3004.88 ± 0.00	3004.93 ± 0.02	3005.04 ± 0.02	3007.88 ± 0.00	3008.55 ± 0.00
e	2924.74 ± 0.05	2924.74 ± 0.05	2924.78 ± 0.02	2924.79 ± 0.02	2924.76 ± 0.02	2925.21 ± 0.05	2925.59 ± 0.05
f	2853.95 ± 0.00	2853.96 ± 0.02	2853.97 ± 0.02	2853.98 ± 0.02	2853.96 ± 0.00	2854.18 ± 0.02	2854.42 ± 0.00
g	2730.72 ± 0.03	2730.79 ± 0.08	2730.78 ± 0.03	2730.83 ± 0.12	2730.79 ± 0.05	2730.76 ± 0.02	2730.71 ± 0.05
h	2678.00 ± 0.89	2678.62 ± 0.68	2679.07 ± 0.37	2681.10 ± 1.26	2678.70 ± 0.84	2677.80 ± 0.96	2678.09 ± 0.82
i	1746.52 ± 0.04	1746.58 ± 0.07	1746.56 ± 0.06	1746.48 ± 0.06	1746.53 ± 0.07	1746.37 ± 0.04	1746.38 ± 0.04
k	1654.75 ± 0.01	1654.77 ± 0.11	1654.78 ± 0.11	1654.84 ± 0.11	1654.78 ± 0.12	1654.59 ± 0.41	1654.83 ± 0.17
m	1465.02 ± 0.01	1464.98 ± 0.03	1464.96 ± 0.05	1465.05 ± 0.07	1464.98 ± 0.06	1465.06 ± 0.03	1464.94 ± 0.04
n	1417.93 ± 0.14	1417.86 ± 0.12	1417.84 ± 0.04	1418.19 ± 0.29	1417.81 ± 0.09	1418.34 ± 0.34	1418.25 ± 0.09
o	1402.35 ± 0.05	1402.55 ± 0.04	1402.50 ± 0.01	1402.42 ± 0.06	1402.42 ± 0.07	1398.79 ± 0.43	1397.53 ± 0.03
p	1377.48 ± 0.01	1377.47 ± 0.02	1377.46 ± 0.02	1377.51 ± 0.02	1377.47 ± 0.01	1377.51 ± 0.01	1377.52 ± 0.04
r	1238.63 ± 0.03	1238.65 ± 0.04	1238.61 ± 0.08	1238.71 ± 0.07	1238.45 ± 0.04	1239.10 ± 0.05	1238.31 ± 0.07
s	1163.50 ± 0.08	1163.46 ± 0.01	1163.52 ± 0.02	1163.50 ± 0.06	1163.47 ± 0.13	1163.40 ± 0.10	1163.26 ± 0.03
t	1118.76 ± 0.02	1118.82 ± 0.03	1118.85 ± 0.01	1118.77 ± 0.03	1118.75 ± 0.06	1119.56 ± 0.08	1120.52 ± 0.02
u	1096.85 ± 0.02	1096.67 ± 0.02	1096.70 ± 0.03	1096.63 ± 0.06	1096.80 ± 0.11	1098.50 ± 0.07	1099.19 ± 0.03
z	722.82 ± 0.06	722.86 ± 0.01	722.85 ± 0.01	722.84 ± 0.02	722.83 ± 0.01	722.95 ± 0.01	723.14 ± 0.06

Band	H	I	J	K	L	M	N
a	3469.15 ± 0.03	3468.32 ± 0.37	3468.99 ± 0.29	3468.76 ± 0.49	3468.63 ± 0.79	3469.10 ± 0.22	3467.87 ± 0.08
c	3008.63 ± 0.00	3008.47 ± 0.02	3008.52 ± 0.00	3008.53 ± 0.00	3008.54 ± 0.00	3008.24 ± 0.00	3006.57 ± 0.00
e	2925.63 ± 0.00	2925.56 ± 0.03	2925.53 ± 0.03	2925.55 ± 0.03	2925.57 ± 0.06	2925.37 ± 0.04	2923.52 ± 0.03
f	2854.45 ± 0.02	2854.38 ± 0.02	2854.37 ± 0.02	2854.38 ± 0.00	2854.41 ± 0.02	2854.29 ± 0.03	2852.41 ± 0.10
g	2730.65 ± 0.04	2730.74 ± 0.00	2730.73 ± 0.00	2730.69 ± 0.04	2730.65 ± 0.02	2730.65 ± 0.07	2730.94 ± 0.07
h	2677.10 ± 0.76	2678.79 ± 0.98	2677.82 ± 0.80	2676.90 ± 1.55	2676.87 ± 1.94	2678.63 ± 0.04	2676.39 ± 0.46
i	1746.44 ± 0.06	1746.34 ± 0.01	1746.38 ± 0.07	1746.38 ± 0.07	1746.41 ± 0.11	1746.51 ± 0.10	1745.18 ± 0.47
k	1654.10 ± 0.06	1654.87 ± 0.09	1654.94 ± 0.03	1654.83 ± 0.11	1654.81 ± 0.11	1654.86 ± 0.04	1654.93 ± 0.04
m	1464.92 ± 0.0	1464.97 ± 0.02	1464.94 ± 0.05	1464.95 ± 0.05	1464.95 ± 0.03	1464.84 ± 0.03	1464.55 ± 0.16
n	1418.18 ± 0.05	1418.29 ± 0.15	1418.31 ± 0.08	1418.38 ± 0.14	1418.13 ± 0.07	1418.06 ± 0.04	1417.98 ± 0.08
o	1397.46 ± 0.03	1397.64 ± 0.04	1397.51 ± 0.04	1397.50 ± 0.04	1397.57 ± 0.08	1398.02 ± 0.03	1399.70 ± 0.38
p	1377.53 ± 0.02	1377.55 ± 0.01	1377.50 ± 0.02	1377.52 ± 0.01	1377.52 ± 0.02	1377.48 ± 0.02	1377.68 ± 0.03
r	1238.29 ± 0.02	1238.33 ± 0.01	1238.28 ± 0.07	1238.23 ± 0.07	1238.34 ± 0.07	1238.41 ± 0.03	1239.04 ± 0.02
s	1163.28 ± 0.02	1163.28 ± 0.02	1163.31 ± 0.03	1163.31 ± 0.05	1163.24 ± 0.10	1163.34 ± 0.04	1170.10 ± 0.14
t	1120.66 ± 0.01	1120.35 ± 0.04	1120.26 ± 0.01	1120.25 ± 0.01	1120.45 ± 0.09	1120.12 ± 0.02	1113.52 ± 0.02
u	1099.29 ± 0.04	1099.07 ± 0.02	1099.14 ± 0.03	1099.15 ± 0.06	1099.18 ± 0.04	1098.79 ± 0.04	1098.14 ± 0.96
z	723.20 ± 0.01	723.14 ± 0.03	723.12 ± 0.02	723.11 ± 0.03	723.14 ± 0.01	723.08 ± 0.02	720.28 ± 0.06

results (17).

For these reasons, the percentage of monounsaturated acyl groups (*%M*) and of polyunsaturated acyl groups (*%P*), given by producers in Table 1, and from frequency data in Table 2, fit linear equations with high correlation coefficients. Table 3 shows the coefficients of the several equations [frequency = a + *b %M* (Equations 1, 3, 5), or frequency = *a* + *b %P* (Equations 2, 4, 6)], together with the number of data and correlation coefficients. Some of these equations have predictive value to know the frequency of the bands **c**, **o**, and **u** for an edible oil of known composition; and vice versa, from the frequency of the cited bands it is possible to predict satisfactorily the proportion of monounsaturated or polyunsaturated acyl groups in the oil subject of study. Coefficient *a* of these equations gives the frequency value of bands **c**, **o**, and **u** of a hypothetical oil constituted by only monounsaturated or polyunsaturated acyl groups. In addition, these relationships indicate that the proportion of these functional groups affects not only the band near 3006 cm^{-1}, which is related to the CH bond of *cis* olefinic groups, but also bands of the fingerprint region, near 1400 and 1097 cm^{-1}, without a previous concrete assignation.

TABLE 3
Coefficients of Equations, Frequency = *a* + *b* %*M* (%*P* or %*S*), Together with Their Correlation Coefficients[a]

Equation no.	Band	Percentage	*a*	*b*(10^{-2})	*n*	*R*
1	**c**	*M*	3010.40	−7.24	8	0.9853
2	**c**	*P*	3004.85	+6.10	8	0.9492
3	**o**	*M*	1394.90	+9.90	8	0.9910
4	**o**	*P*	1402.61	−8.43	8	0.9223
5	**u**	*M*	1100.46	−4.87	8	0.9908
6	**u**	*P*	1096.68	+4.13	8	0.9176
7	**e**	*S*	2926.04	−6.28	8	0.8504
8	**f**	*S*	2855.07	−6.59	8	0.9565
9	**t**	*S*	1122.65	−22.65	8	0.9510
10	**z**	*S*	724.30	−9.93	8	0.9924
11	**r**	*S*	1238.11	+2.33	8	0.8408
12	**s**	*S*	1160.20	+24.44	8	0.9989

[a] %*M*, percentage of monounsaturated acyl groups; %*P*, percentage of polyunsaturated acyl groups; %*S*, percentage of saturated acyl groups.

Taking the two best equations in Table 3 (Equations 3 and

TABLE 4
Predicted Composition of the Samples by Using Different Equations[a]

Band	Equation used	%	A	B	C	D	E	F	G
u	5	*M*	74.1	77.8	77.2	78.6	75.1	40.2	26.1
o	3	*M*	75.2	77.3	76.8	76.0	76.0	39.3	26.6
s	12	*S*	13.5	13.3	13.6	13.5	13.4	13.1	12.5
z	10	*S*	14.9	14.5	14.6	14.7	14.8	13.6	11.7
u, **s**	5,12	*P*	12.4	8.8	9.2	7.8	11.5	46.7	61.4
Band	Equation used	%	H	I	J	K	L	M	N
u	5	*M*	24.0	28.5	27.1	26.9	26.3	34.3	47.6
o	3	*M*	25.9	27.7	26.4	26.3	27.0	31.5	48.5
s	12	*S*	12.6	12.6	12.7	12.7	12.4	12.8	40.5
z	10	*S*	11.1	11.7	11.9	12.0	11.7	12.3	40.5
u, **s**	5,12	*P*	63.4	58.9	60.2	60.4	61.3	52.9	11.8

[a] See Table 3 for abbreviations.

5), the proportion of monounsaturated acyl groups in the samples is predicted. These data are given in Table 4. For olive oils (samples A–E), a high proportion of monounsaturated groups is predicted and similar to the data given by producers. The highest deviation between producers and calculated data is found in sample B. For sesame oil (F), a proportion of approximately 40% monounsaturated acyl groups is predicted, in good agreement with data from the literature [39.4 (22) and 42% (27)]. Data obtained for corn and sunflower oils (samples G–L) are in good agreement with the composition given by producers. And finally, the difference between experimental and calculated proportions of monounsaturated acyl groups in lard (N) is also small.

On the other hand, the values of the frequencies of bands **e**, **f**, **t,** and **z** in the several groups of oils mentioned above increase in the order: lard (N), olive (samples A–E), sesame (F), unknown seed (M), corn and sunflower (G–L). This fact, taking into account the data in Table 1, could indicate that the frequency of these bands is related to the proportion of saturated (*%S*) acyl groups in the sample. Oils with the highest proportion of saturated acyl groups show the smallest values for the frequencies of bands **e**, **f**, **t**, and **z**. And the frequency of bands **r** and **s** increases as the proportion of saturated acyl groups increases. However, because all these bands include CH_2 groups, not only of the saturated acyl group but also of mono- and polyunsaturated acyl groups, the relation with composition is not as simple as above.

Table 3 gives the coefficients of the equations frequency = $a + b\ \%S$, obtained from frequencies of bands **e**, **f**, **t**, **z**, **r**, and **s**. By using the two best equations in Table 3, Equations 10 and 12, data for the proportion of saturated acyl groups have been predicted and given in Table 4, which shows that predicted values are close to the experimental data.

Because the proportion of saturated and monounsaturated acyl groups in each sample can be satisfactorily predicted, the proportion of polyunsaturated acyl groups can be calculated by difference. Table 4 gives the proportion of polyunsaturated acyl groups from data coming from Equations 5 and 12. These results are also close to experimental values given by producers and in the literature; the proportion of polyunsaturated acyl groups in concrete sesame oils, given by other authors, is 44.5 (27) and 42% (22).

Finally, band **x** is only present visibly in lard, corn and sunflower samples, and its frequency is related to the proportion of *trans* olefinic groups coming from mono- or polyunsaturated groups. In lard, this band appears at 965 cm^{-1}, and in corn and sunflower oils at approximately 967 cm^{-1}, showing that in lard the *trans* CH olefinic group is basically due to monounsaturated acyl groups, and in the other oils, this band is due to polyunsaturated acyl groups. This assumption is ratified by the frequency of band **x** of trielaidin at 966.3 cm^{-1} and of trilinelaidin at 967.8 cm^{-1} (17).

In conclusion, the frequency of absorption of concrete bands in the fingerprint region, such as **o**, **u**, **s** and **z**, allows one to make up groups of edible oils and lard with similar proportions of their main components. In addition, the frequency of these bands gives direct information about the proportion of saturated and *cis* monounsaturated fatty acyl groups in the sample. The proportion of polyunsaturated acyl groups can be obtained by difference. This information is obtained directly from the Fourier transform infrared spectra of films of pure oil or lard, and to the best of our knowledge, this is the first time that the frequencies of some bands of edible oils have been found to be related to the composition of the oil, which is useful for predictive purposes.

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