Ultrasonic Velocity Measurements in Some Liquid Triglycerides and Vegetable Oils

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A pulse echo technique was used to measure the ultrasonic velocity of nine vegetable oils (5–70 C, 1.25 MHz) and a number of liquid triglycerides and triglyceride/sunflower oil mixtures (70 C, 1.25 MHz). The velocities of the vegetable oils at 70 C were related to the velocities of their constituent components using two empirical equations; the first related the velocity of a triglyceride to its molecular formula, and the second related the velocity of an oil to the velocities of its triglyceride components.

Ultrasonics has been to investigate a number of the properties of fat/oil mixtures. These include solid fat content determinations (1–5), estimation of crystal compressibilities (5) and investigation of phase transitions (6). The technique also has been used to investigate the properties of many liquid oils. The ultrasonic velocity of a number of liquid triglycerides and fatty acid methyl esters has been empirically related to their chemical formulae (7–9). Empirical formulae also have been used to relate the ultrasonic velocity of vegetable oils to the velocities of their constituent components (9). The temperature dependence of the velocity of a number of animal and vegetable oils has been measured (1,5,9), and the technique has been used to detect adulteration in oils (10). In this work the variation of ultrasonic velocity with temperature for nine commercially available vegetable oils is measured, and the relationship between their triglyceride compositions and ultrasonic velocities at 70 C examined.

MATERIALS AND METHODS

Tristearin (SSS); tripalmitin (PPP); trilaurin (LLL); triolein (OOO); glycerol 1,3 dipalmitate-2-oleate (POP); glycerol 2,3 dipalmitate-1-oleate (OPP); glycerol 1,3 dipalmitate-2-stearate (PSP); glycerol 1-palmitate 2-oleate-3-stearate (POS), and glycerol 1,3 disterate-2-oleate (SOS) were supplied by Unilever Research Laboratories, Sharnbrook, England. The purity of the mono-acid saturated triglycerides was determined using high pressure liquid chromatography (HPLC) of the fatty acid methyl esters (FAME) and was better than 96%. Corn oil, grapeseed oil, groundnut oil, olive oil, palm oil, rapeseed oil, safflower oil, soybean oil and sunflower oil were purchased from Wm. Morrisons Supermarkets PLC, U.K.

Samples were prepared as follows. Triglycerides and/or vegetable oils were weighed into small glass cuvettes, heated to 80 C in a vacuum oven and mixed thoroughly before degassing at 650 mmHg for 30 min. Samples were then placed in a water bath thermostated at the appropriate temperature and the ultrasonic velocity measured. The cuvettes were specially manufactured for us by Chandos Intercontinental, Cheshire, England.

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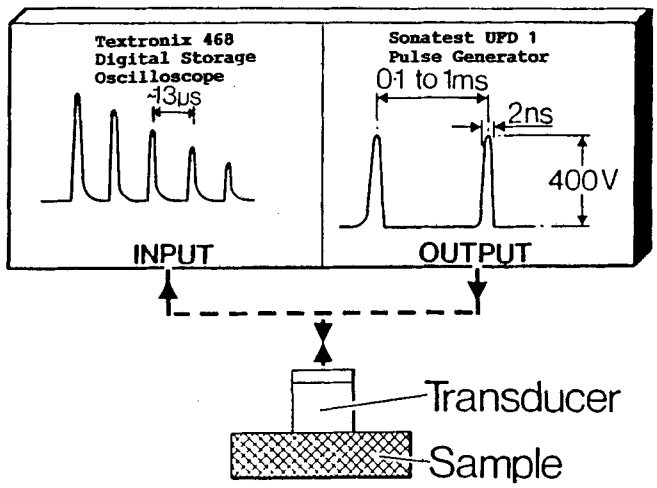

FIG. 1. Block diagram of pulse echo technique used to measure the ultrasonic velocities of the samples.

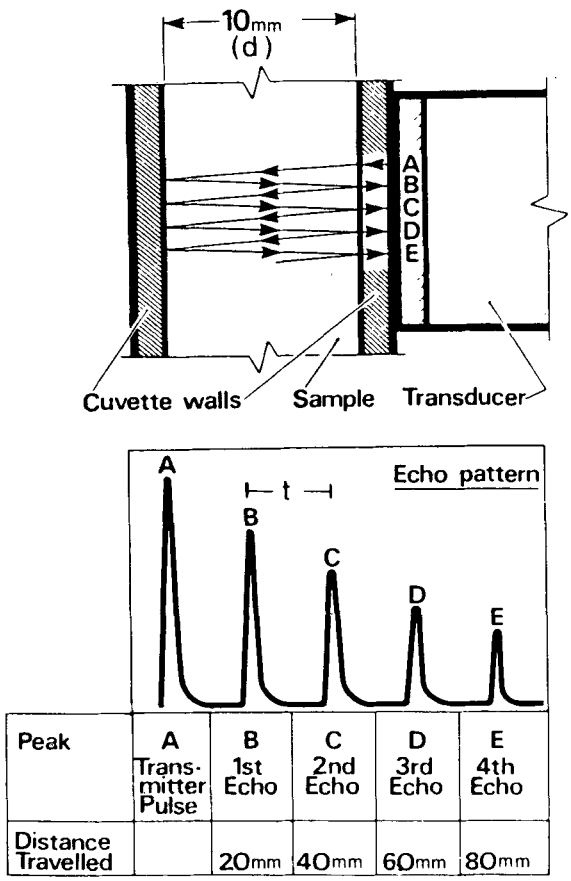

FIG. 2. An illustration of the relationship between the number of echoes and the distance travelled by a pulse through the sample.

TABLE 1

Variation of Ultrasonic Velocity with Temperature for Nine Vegetable Oils Presented in the Form of Regression Lines[a]

			Linear fit V = a + bT			Exponential fit v = a.exp(bT)		
Oils	T	n	a/ms^{-1} ± 1.0	b/ms^{-1}C^{-1} ± 0.02	r	a/ms^{-1} ± 0.2	b/C^{-1} ± 2 × 10^{-5}	r
Corn	20-70	36	1532.4	-3.23	-0.9997	1539.3	-0.00232	-0.9999
Grapeseed	20-70	36	1533.9	-3.24	-0.9997	1540.9	-0.00233	-0.9999
Groundnut	20-70	36	1528.9	-3.23	-0.9993	1535.8	-0.00233	-0.9995
Olive	20-70	36	1528.9	-3.28	-0.9995	1536.1	-0.00237	-0.9996
Palm	50-70	10	1515.0	-3.10	-1.0000	1529.2	-0.00234	-1.0000
Rapeseed	20-70	36	1532.9	-3.24	-0.9997	1539.8	-0.00234	-0.9999
Safflower	20-70	36	1534.4	-3.24	-0.9998	1541.3	-0.00232	-0.9999
Soybean	5-70	30	1536.2	-3.29	-0.9997	1539.6	-0.00232	-1.0000
Sunflower	5-70	30	1538.0	-3.28	-0.9997	1541.5	-0.00232	-1.0000

[a]Where v is the ultrasonic velocity (ms^{-1}), T is the temperature (C), r is the correlation coefficient and n is the number of data points.

They are 10 mm pathlength, 30 mm wide and 50 mm high, with walls 1.5 mm thick.

The ultrasonic group velocity was measured using a pulse echo technique similar to that described in an earlier paper (2) but with the following differences. A Balteau Sonatest (UFD 1) was used as pulse generator, a Tektronix 468 digital storage oscilloscope was used to display the signal and a single Sonatest 1.25 MHz piezoelectric transducer was used as both receiver and generator (Fig. 1).

Each pulse generated travels through the sample and is partially transmitted, partially reflected at the cuvette walls. A pulse therefore travels through the sample a number of times, and a series of echoes is observed on the oscilloscope (Fig. 2). By resolving successive peaks the time, t, for a pulse to travel twice the cuvette's length, d, can be determined. The velocity, v, through a sample, is then found from the simple relationship v = 2d/t. Using this technique the velocity can be measured to within 0.7 m/s (2). However, there are commercially available ultrasonic instruments, accurate to within 0.1 ms^{-1}, which may be adapted for this sort of measurement. These instruments are capable of rapid sampling rates, can be used either in-line or off-line and can be fully automated.

RESULTS AND DISCUSSION

The experimental measurements of ultrasonic velocity versus temperature for the nine vegetable oils are presented in Table 1 in the form of linear and exponential equations. The various constants and their standard errors were calculated using least squares regression analysis. Although the relationship between velocity and temperature is almost linear (Table 1), a better fit to the results was obtained when an exponential function was used. The average temperature coefficient of the velocity of all the oils was similar, being between 3.1 and 3.3 ms^{-1}; however, the actual velocity of the different oils varied significantly. In the following sections the relationship between the ultrasonic velocity of an oil and its composition, i.e., the type and amount of triglycerides present, is examined.

Type of triglyceride. Javanaud and Rahalker (9) have suggested that a simple empirical equation may be used to relate the ultrasonic velocity, v, of a triglyceride to its molecular formula:

$$v = V_o + nV_1 + mV_2 \quad [1]$$

Here V_o, V_1 and V_2 are constants, where V_1 corresponds to the increase in velocity per additional carbon atom in the triglyceride, V_2 corresponds to the increase in velocity per additional unsaturated bond, n is the total number of carbon atoms and m is the total number of unsaturated bonds in the triglyceride. This equation assumes that the ultrasonic velocity of triglyceride isomers is similar (e.g., POP is equivalent to OPP). Although isomers do generally have different velocities the difference is usually small (Table 2) (8). The values of the three constants at 70 C were calculated from measurements of the ultrasonic velocity of nine liquid triglycerides (Table 2) using multiple linear regression,

TABLE 2

Ultrasonic Velocities and Densities of a Number of Triglycerides at 70 C[a]

Oil	n	m	ϱ/gcm^{-3}	v/ms^{-1}
LLL	36	0	0.8871[b]	1262.7
PPP	48	0	0.8733[b]	1290.2
PSP	50	0	0.8723[c]	1292.3
SSS	54	0	0.8702[b]	1301.0
POP	50	1	0.8776[c]	1293.4
OPP	50	1	0.8776[c]	1294.8
POS	52	1	0.8765[c]	1297.3
SOS	54	1	0.8753[c]	1301.5
OOO	54	3	0.8857[b]	1303.5

[a]Where n is the total number of carbon atoms in the fatty acid chains and m is the number of double bonds.
[b]Values extracted from reference 14.
[c]Values calculated from [b] using the additive property, Molar volume V_m (= M.W./ϱ) (15), i.e., $V_{mPOS} = 1/3 * (V_{mPPP} + \Theta m_{OOO} + Vm_{SSS})$.

and were found to be V_o = 1187.1+/-3 ms^{-1}; V_1 = 2.12+/-0.07 ms^{-1} and V_2 = 0.7+/-0.4 ms^{-1}.

In this work only triglycerides containing mono-unsaturated fatty acids were examined. Gouw and Vlugter (8) have measured the velocity in triolein and trilinolein at 20 and 40 C and have found that the difference in velocity between them is about 10.4 ms^{-1} at both temperatures, corresponding to an increase in velocity per unsaturated bond of about 3.5 ms^{-1}. This value is significantly larger than the value of V_2 calculated from our results (0.7 ms^{-1}), and therefore we assume that the addition of an unsaturated bond to an unsaturated fatty acid chain leads to a greater increase in velocity than the addition of an unsaturated bond to a saturated fatty acid chain. Equation 1 must therefore be modified:

$$v = V_o + nV_1 + mV_2 + oV_3 \quad [2]$$

now V_2 is the increase in velocity due to the addition of an unsaturated bond to a saturated fatty acid chain, V_3 is the increase in velocity due to the addition of an unsaturated bond to an unsaturated fatty acid chain, m is the number of unsaturated fatty acid chains per triglyceride molecule and o is the total number of unsaturated bonds in the triglyceride, excluding the first on each unsaturated fatty acid chain. The value of V_3 at 70 C was calculated from the measurements of Gouw and Vlugter (8) at 20 and 40 C by assuming that the temperature coefficient of ultrasonic velocity of triolein and trilinolein are similar, and was found to be about 3.5 ms^{-1}.

Using these values of V_0, V_1, V_2, V_3 and Equation 2 it is possible to predict the ultrasonic velocity of a triglyceride at 70 C from a knowledge of its molecular formula. This may be useful if the velocity of a particular glyceride is not known or difficult to measure.

Amount of triglyceride. It has been suggested that an equation proposed by Wood (11) can be used to relate the ultrasonic velocity of many vegetable oils to the velocities and densities of their constituent triglycerides (9). In this section the suitability of this equation is examined by measuring the velocity through three binary triglyceride/sunflower oil mixtures of varying triglyceride content (0–100%) at 70 C (Fig. 3). Tristearin, tripalmitin and trilaurin in sunflower oil mixtures were used as examples.

The Wood equation can be written as follows:

$$v = \left[\left(\sum_{i=1}^{n} \phi_i / v_i^2 \rho_i\right)\left(\sum_{i=1}^{n} \phi_i \rho_i\right)\right]^{-1/2} \quad [3]$$

Where v is the velocity, ϱ is the density and ϕ is the volume fraction (which can simply be converted to a mass fraction). The subscript i represents the i^{th} component, and n is the number of components. This equation assumes that $\sum_{i=1}^{n} \phi_i = 1$, i.e., that the components form an ideal mixture.

For many oils the densities of the component phases are similar and the velocity through a mixture can be described by a simpler relationship (1):

$$v = \left[\sum_{i=1}^{n} \phi_i / v_i^2\right]^{-1/2} \quad [4]$$

which depends on velocity measurements only. The difference between the velocities calculated using this equation and those calculated using Equation 3 was always less than 0.2 m/s, even when the triglyceride mass fraction was used instead of the volume fraction. This equation may therefore prove a practical way of relating the velocity of an oil to the velocities of its constituent components because only ultrasonic measurements are required.

Figure 3 shows excellent agreement between the experimentally measured velocities and those predicted using Equation 4 for the three triglyceride/sunflower oil mixtures investigated. This equation may therefore prove useful for estimating the composition of binary oil mixtures if the velocities of the component phases are known, or for calculating the velocity of vegetable oils from their triglyceride composition once the velocities of the various triglycerides are known.

Relationship between ultrasonic velocity and oil composition. To determine whether Equations 2 and 4 are indeed suitable for relating the ultrasonic velocity of vegetable oils to their chemical composition, predicted values of velocity at 70 C were compared with experimental values (Table 3). The predicted values were calculated from typical triglyceride compositions of the

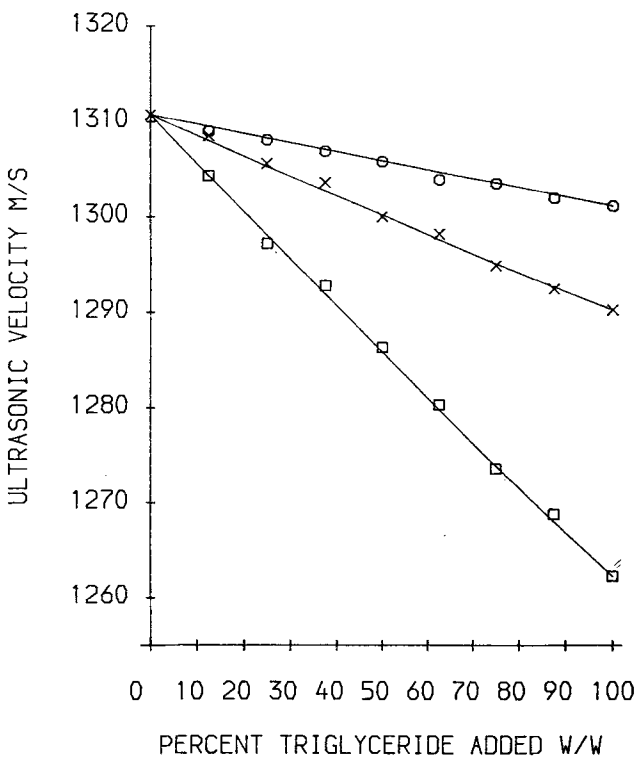

FIG. 3. Variation of ultrasonic velocity with triglyceride content in tristearin (○), tripalmitin (×) and trilaurin (□) in sunflower oil mixtures at 70 C and 1.25 MHz. The standard error of the mean of the velocity measurements was about 0.7 ms^{-1}.

TABLE 3

Comparison Between Predicted[a] and Experimentally Measured Ultrasonic Velocities of a Number of Vegetable Oils at 70 C

	Measured velocity/ms^{-1}	Calculated velocity[b]/ms^{-1}
Corn	1308.4	1308.2
Grapeseed	1309.3	1308.7[c]
Groundnut	1304.9	1305.9
Olive	1301.5	1302.4
Palm	1298.3	1297.2
Rapeseed	1307.6	1307.6
Safflower	1310.1	1310.4
Soybean	1308.7	1309.3
Sunflower	1310.7	1310.4

[a]Calculated using Equations 2 and 4 and literature values of the triglyceride compositions.
[b]Triglyceride composition from reference 12 unless otherwise stated.
[c]Triglyceride composition from reference 13.

oils found in the literature (12,13), using Equation 2 to calculate the velocity of the various triglycerides present and Equation 4 to calculate the velocities of the triglyceride mixtures. Table 3 shows that there is reasonable agreement between the predicted and experimental values of velocity for the various vegetable oils investigated. The discrepancies between the predicted and calculated values are probably because the actual fatty acid composition of the oils was not known and the fatty acid distribution of a given oil may vary significantly (9). Equations 2 and 4 would therefore appear to be a suitable means of relating the velocity of vegetable oils to their triglyceride composition.

The results suggest that the ultrasonic velocities of many vegetable oils can be related to their chemical composition using simple empirical formulae and that the composition of binary oil mixtures may be estimated if the velocities of the component phases are known. Ultrasonic velocity measurements may therefore prove a useful means of characterizing oils or of monitoring processes where there is a change in the degree of unsaturation or chain length of the fatty acids present or of processes which involve the separation of one oil component from another.

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