A Study of Dilatation and Acoustic Propagation in Solidifying Fats and Oils: II. Experimental

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ABSTRACT

Experimental evidence is presented to support the hypothesis that acoustic dilatation is linearly related to solid fat index dilation. This hypothesis is shown to be consistent with the measured temperature dependence of the dilation and ultrasonic velocity during solidification of palm oil, coconut oil, tristearin and a vegetable fat, all of which were diluted with triolein. The maximum solid content examined was 15%. The ultrasonic pulse echo method may provide a means of measuring the solid content of oils and of indicating the presence of phase transitions in the solid phase.

INTRODUCTION

In the preceeding paper, Povey (1) developed a theory relating the dilatation obtained in dilatometric assessment of the solid content in fats and oils to an acoustic dilatation. The purpose of this paper is to examine this theory in the light of experimental evidence obtained from a range of oils and fats. In order to simplify interpretation, all the oils and fats were diluted with triolein so that the properties of the liquid matrix were, more or less, known and in order to reduce the solid content. In the following text all equations referred to by number are found in Povey (1).

EXPERIMENT

A comprehensive explanation of the experimental details is presented in Hussin (2). The acoustic measurements were carried out simultaneously with the dilatometry, in a sample holder containing approximately the same amount of material as in the standard AOCS method (3) employed for the Solid Fat Index (SFI) measurements. The material in the dilatometric and acoustic sample holders was subjected to the same temperature/time profile. A standard pulse echo (4-5) technique was used for the acoustic velocity measurements.

Five MHz of probes compression were used that had been specially constructed to withstand immersion in hot oils up to 80 C; the time of flight of the acoustic pulse was computed from at least 4 echoes.

The acoustic apparatus is depicted in Figure 1. The acoustic cell, while holding approximately the same volume of material between the transducer and reflector as the dilatometer, differed from the dilatometer as material was allowed to flow from above the transducer into the cell while the material contracted. Thus the acoustic cell is a constant volume apparatus while the dilatometer is a constant mass apparatus. Because of the difficulty in obtaining uniform melting, and thus repeatable acoustic measurements of melting behavior, all our data is for melting after conditioning at 0 C.

Every data point in Figures 2 and 3 is the result of 5 replicate experiments and the standard deviation on the velocity measurements was always better than 1 m. The ultrasonic velocity was calibrated by filling the ultrasonic cell with distilled water and calibrating the oscilloscope time base using the data of Greenspan and Tschiegg (6-7) for the velocity of sound in pure water. This procedure had the additional merit of calibrating the transducer to reflector distance. Temperature was controlled in all experiments by using water baths, electronically controlled within ±.1 C. Density measurements were made at 40 C using standard density bottles and the dilatometric data was used to compute density at all other temperatures of interest.

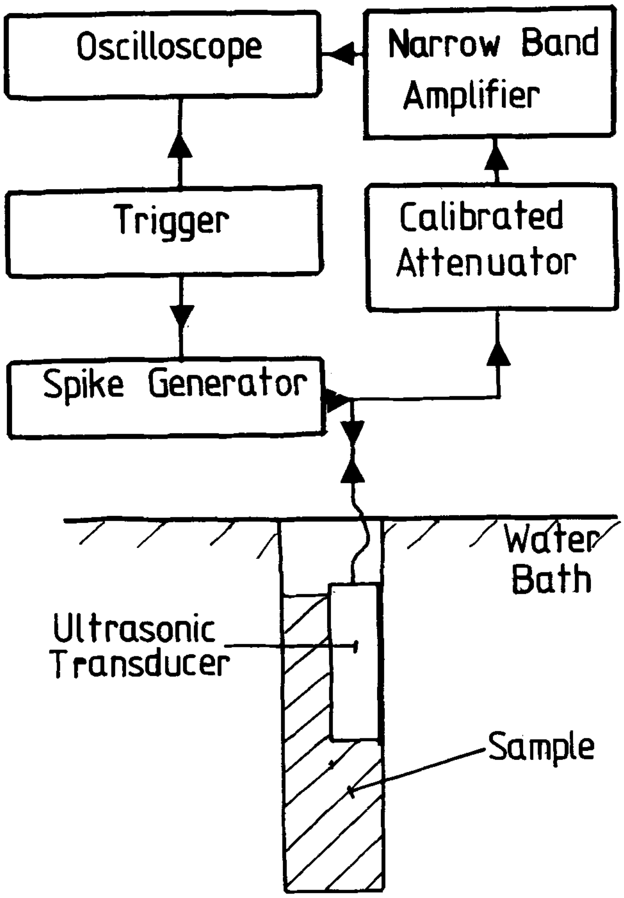

FIG. 1. Experimental apparatus for the measurement of the velocity of sound in solidifying fats and oils.

The palm oil, olive oil, soybean oil, coconut oil and Armour fat were all purchased as brand products. The tristearin and triolein were purchased from BDH Chemicals Ltd., U.K., as 99% pure. We assume that, since the solubility of tristearin in triolein, at the temperatures at which the solidified tristearin was measured, is so low that the percentage of tristearin actually represents the solid content. The Armour fat, coconut and palm oil and tristearin were all diluted with triolein in order to simplify the acoustic experimental arrangements and in order to reduce solid content. Percentages quoted are all weight percent of material in 100% of the mixture with triolein. The triolein dilutions further ensured that 3 different dilatations were obtained at any one temperature, the solid content remained below 15%, and the inclusion of vacuoles was minimized. In this way, the chances of accidental correlation with temperature is greatly reduced and the conditions for equation 12 are met.

In order to keep the data trends relatively clear in Figures 2 to 5, data has been omitted from the figures that

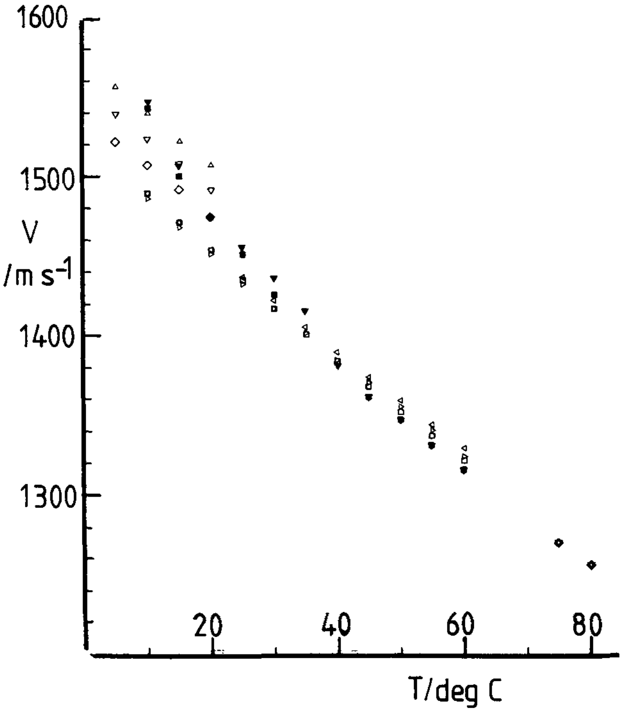

FIG. 2. Ultrasonic velocity (v*) plotted as a function of temperature for □ triolein, ◁ soybean and corn oil, ▷ olive oil, △ 15% tristearin, ▼10% tristearin, ◇ 5% tristearin, 67% Armour fat and ■ 67% palm oil.

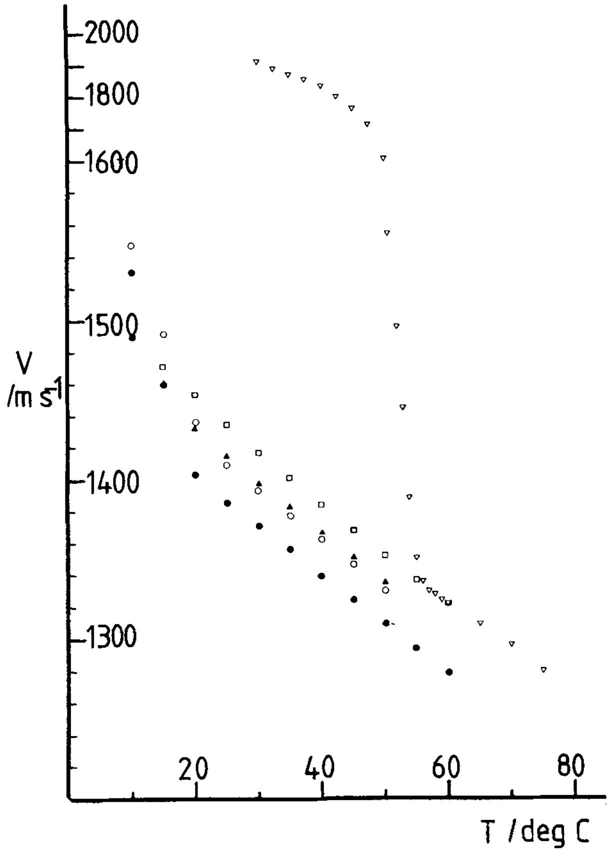

FIG. 3. Ultrasonic velocity (v*) plotted as a function of temperature for pure △ tristearin, □ triolein, ○ 50% coconut oil, ● 67% coconut oil and ▲ 33% coconut oil.

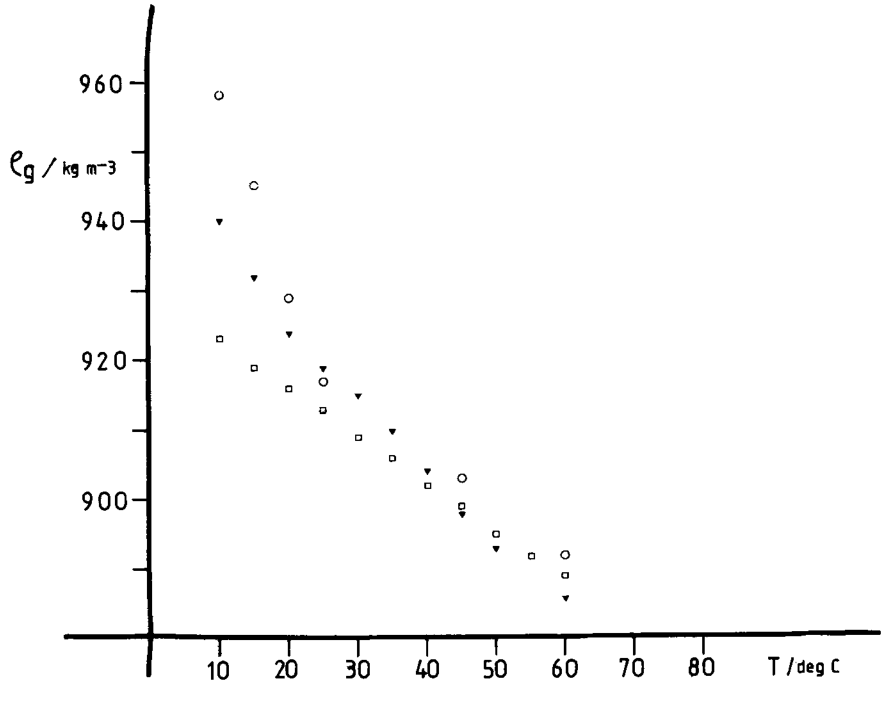

FIG. 4. Static density (ρ_g) plotted as a function of temperature for □ triolein, ○ 67% coconut oil and ▼67% Armour fat.

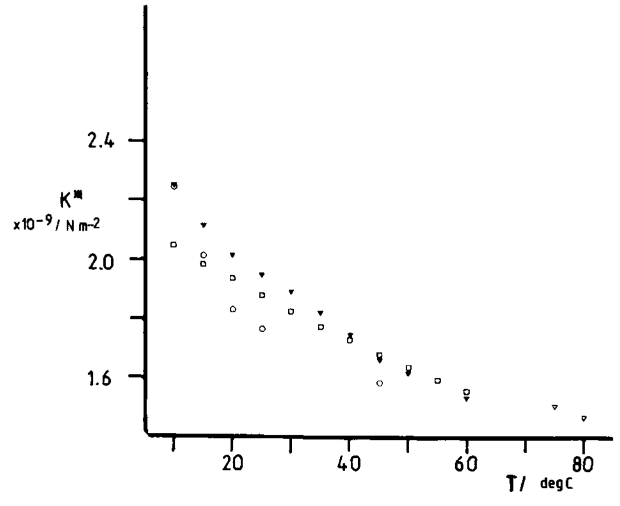

FIG. 5. Effective bulk modulus (K*) plotted as a function of temperature for □ triolein, ○ 67% coconut oil and ▾ 67% Armour fat.

have been included in the regression fits in Tables I and II. In particular, data for 50% and 33% Armour fat and palm oil, is omitted. Triolein is included since, apart from diluting Armour fat, palm oil, coconut oil and tristearin, it is very similar in acoustic and density behavior to olive, soybean and corn oil. 67% Armour fat represents the extreme behavior of all dilutions of Armour fat and 67% palm oil represents the extreme behavior of all dilutions of palm oil. Figure 6 contains all data points, except where the diagram would become so cluttered that the various points would become indistinguishable. All the data is contained in the regression fits of Table II.

Velocity vs temperature data are presented in Figures 2 and 3. For the sake of clarity, the least squares regression to the data is expressed in the form of equations in Table I. Data for 100% tristearin are included in Figure 3 for comparison purposes. Density data are presented in Figure 4 and a selection of compressibilities obtained from the velocity and the density data via equation 3 are plotted in Figure 5. The SFT dilatation is plotted against the acoustic dilatation in Figure 6 and only one regression line has been drawn for palm oil and Armour oil since their lines are indistinguishable. In the case of tristearin, the dilatation was not measured and is quoted as % tristearin in triolein taken as solid content. The dilatation measurements had a standard deviation that was less than 0.4 ml kg^{-1} for 5 replicates. The variation in the densities is given by the standard deviations for the dilatations. All the data presented in this paper has been reduced from data contained in Hussin (2).

TABLE II

Regression lines for SFI Dilatation Varying as a Function of Acoustic Dilatation in a Range of Solidifying Oils and a Fat.

	α	c	r	n
Tristearin diluted with triolein	4.75	−4.6	1.00	12
Coconut oil diluted with triolein	384	.88	.99	7
Palm oil diluted with triolein	477	2.4	.98	20
Armour fat diluted with triolein	478	1.8	.99	22

The linear fit is of the form $y = \alpha x + c$ where $y = D/m^3\ kg^{-1}$. $x = \Delta v/v^*$, r is the correlation coefficient and n is the number of data points. In the case of tristearin, $y = \epsilon$ and $x = \Delta v/v^*$.

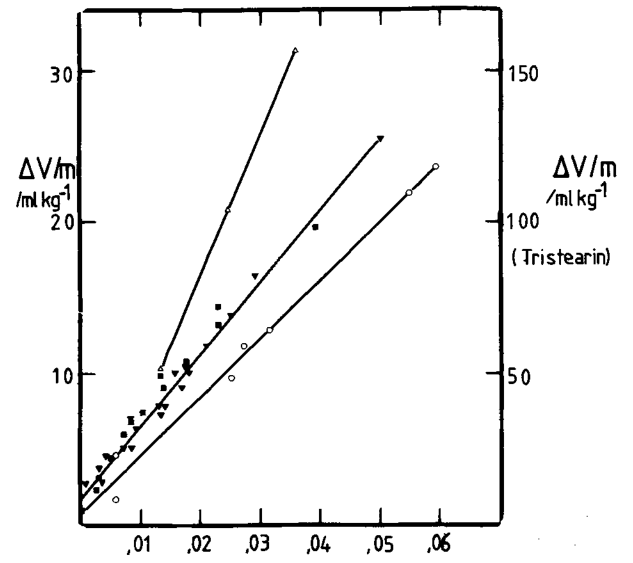

FIG. 6. SFI dilatation (D) plotted as a function of acoustic dilatation (Δv/v*) for ▼ 67%, 50% and 33% Armour fat; ○ 67%, 50% and 33% coconut oil and ■ 67%, 50% and 33% palm oil, ϵ versus Δv/v* is plotted for 15%, 10% and 5% tristearin.

TABLE I

Regression Lines for Ultrasonic Velocity Varied as a Function of Temperature for a Range of Liquid Oils and Fats. y = v/m s-1, x = T°C, r is the Correlation Coefficient and n is the Number of Data Points.

	Exponential fit y = a.exp(bx)				Linear fit y = a + bx			
Material	a	b	r	n	a	b	r	n
Triolein	1524	−.00239	.99991	11	1520	−3.356	.9993	11
Soybean oil	1521	−.00226	.99998	11	1518	−3.176	.9997	11
Corn oil	1523	−.00228	.99992	11	1520	−3.215	.9997	11
Olive oil	1519	−.00229	.99995	11	1515	−3.216	.9996	11
67% Armour fat	1512	−.00233	.925	3	1510	−3.1	.997	3
50% Armour fat	1513	−.00233	.93	3	1502	−3.1	.9990	3
33% Armour fat	1507	−.00225	.92	3	1496	−3.0	.9990	3
67% Coconut oil	1486	−.00231	1.00000	6	1481	−3.154	.99992	6
50% Coconut oil	1494	−.00232	1.00000	6	1488	−3.177	.99991	6
33% Coconut oil	1499	−.00232	1.00000	6	1494	−3.183	.99995	6
67% Palm oil	1511	−.00230	1.00000	4	1501	−3.08	.99991	4
50% Pal oil	1521	−.00242	1.00000	4	1510	−3.24	.9993	4
33% Palm oil	1507	−.00225	1.00000	4	1498	−3.02	.9997	4
Pure tristearin	1499	−.00209	1.00000	9	1486	−2.7	.997	9

DISCUSSION

The velocity and temperature data for liquid oils (Table I) agrees with Zacharias and Parnell (8) that the data is fitted well by a straight line. However, an even better fit is usually obtained with an exponential. Since the value of v in the solidifying region is obtained by an extrapolation of v in the wholly liquid region, the difference between linear and an exponential fit does make a significant difference to the values of $\Delta v/v^*$ in Figure 6. We have used the same expression, $v=v_0\exp(-0.0023T)$, for the extrapolation in all cases except that the value for v_0 has been obtained from Table I for each mixture. In Figures 2-5, the temperature dependence is similar in the liquid region for any of the physical parameters for all the mixtures. This similarity has an important bearing on whether equation k can be used to determine solid contents.

With regard to the assumptions employed to obtain equation 11, we note that in Figure 2, $\Delta v/v^*$ never exceeds 0.06 and that in Figure 4, $\Delta\rho_g/\rho_g$ never exceeds 0.07. Optical microscopy indicated that crystal sizes never exceeded 1.5 μm in diameter while acoustic wavelength was never less than 0.1 mm. Thus, the condition that wavelength should exceed inclusion diameter is satisfied. The only assumption not adhered to is that of sphericity. That the crystals formed during solidification were spherical is doubtful, mostly Type A spherulites were observed but we were unable to quantify or record their shape accurately. The tristearin consistently crystallized in the alpha phase with apparently spheroidal agglomerations of crystalites.

Turning to Figure 6, we see that equation 12 fits the data well with the parameter α as a constant that depends on the material. The parameters for the regression lines are shown in Table II.

We can estimate the ratio K/K′ from data presented in Figure 4, Figure 6 and Table II. In the case of tristearin, since ϵ is plotted against $\Delta v/v^*$, the slope α gives us, via equation 11 in Povey (1) and the value of R presented there, the value for K/K′ shown in Table III. This value compares well with the value computed of .58 in the first paper. For the remaining oils, α is given by equation (12) and both D_s and R have to be estimated before arriving at K/K′. D_s can be obtained from Table XVI of reference 9. We have used these values, presented in Table III, to obtain the density of the solid phase, ρ'. To do this, we have used the definition of melting dilatation given in reference 9. Referring to figure 9 of reference 9,

$$D_S = \frac{V_R - V_S}{\text{mass}}.$$

On the reasonable assumption that

$$\text{mass} = \rho V_R = \rho' V_S, \text{ then}$$

$$D_S = \frac{1}{\rho} - \frac{1}{\rho'} \text{ from which } \rho'$$

can be obtained when D_s and ρ are known. Note that the values for K/K′ obtained for all mixtures do not vary greatly.

Little evidence was found in our data that the coefficient α depends on dilution. If D_s depends on dilution, α may be expected to as well as they are connected through equation 12 in Povey (1). Evidence is presented in reference 9 for the dependence of D_s on dilution, but, since the variation to be expected is only 7% between a liquid oil and palm oil, for example, the variation in D_s may be too small to show up in our data.

CONCLUSIONS

Theoretical and experimental evidence is presented in favor of the hypothesis that a linear relationship exists between solid content and acoustic dilatation for small acoustic dilatations in solidifying fats and oils.

The compressibility ratio obtained from the slope of the plot of solid content line against acoustic dilatation for tristearin/triolein agrees reasonably well with the acoustically derived value obtained from measurements in pure tristearin and pure triolein. The value of the compressibility ratio for the other mixtures, obtained from dilatation vs acoustic dilatation data are of a similar magnitude. Overall, we would describe our results as encouraging.

The model predicts a dependence on the compressibility of both the solid and liquid phases and, since phase changes in the solid are usually accompanied by compressibility changes, we would expect the parameter κ to depend on the nature of the solid phase.

Finally, we suggest that the acoustic technique may form a useful adjunct to existing methods of solid fat measurement. The low cost of the apparatus compared with NMR equipment, the ability of the acoustic probe to be placed in the sample, the relative robustness of the probe and the accuracy with which acoustic velocity can be measured are recommendations for the method. An additional recommendation is that a rigorous theoretical relationship exists (equation 10) between the acoustic dilatation and the solid content.

TABLE III

The Ratio of Liquid to Solid Compressibilities, Computed from the Slopes of the Regression Lines in Figure 6 and Table II.

	$D_S{}^+$ ml kg^{-1}	ρ' kg m^{-3}	R	$\kappa-3R$	K/K′
Armour fat diluted with Triolein	–	–	–	.40*	.51*
Palm Oil diluted with Triolein	95	1000	.030	.40	.51
Coconut Oil diluted with Triolein	82	987	.026	.43	.50
Tristearin diluted with Triolein	–	856	–.016	.42	.63

+ reference 9 *Assuming the same value for D_S as for Palm oil.

Data employed in the computation of K/K′ is included in this table and all data are taken at 20 C.

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Thermal Isomerization of Jojoba Wax

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ABSTRACT

Jojoba wax was thermally isomerized over a range of temperatures. The equilibrium constant and the rates of *cis-trans* and *trans-cis* conversions were measured. Activation energy ($\sim$ 24 kcal/m) and enthalpy were calculated.

INTRODUCTION

The chemical homogeneity (1,2) and unique physical properties (3) of jojoba wax and its *trans* isomer, mentioned in some earlier works (4,5), motivated us to investigate the kinetics of its geometrical isomerization. The *cis* isomer has a higher heat of combustion, indicating lower thermal stability, and can be transformed into the *trans* form by heating to temperatures that supply enough energy to cause rotation about the double bond (6).

A large number of thermal isomerizations of simple olefins in the gas phase (7-12) and in the liquid phase (13-15) have been reported. The data from the early work can be divided into two classes: those with low frequency factors (A) and activation energies (E_a), and those with high (normal) frequency factors and activation energies. Surface effects and side reactions involving decomposition lead to apparent decreases in both A and E_a.

PROCEDURES

Materials

The crude jojoba wax used in this work was obtained in 1978 from the natural population of an Apache reservation in the U.S.A.

Gas chromatographic analyses, infrared spectra and NMR were performed. The material had an iodine value, refractive index, melting point, freezing point, ester number, acid number and saponification number identical to those given in reference 5. The crude jojoba wax (11) was mixed with 10 g of bleaching earth at 80 C for 15 min, and filtered.

Method

Gas chromatography. The gas chromatographic analyses were performed according to the method suggested by Miwa (1).

Infrared spectroscopy. IR analyses to determine the amount of isolated *trans* bonds were performed on a Perkin-Elmer model 357 spectrophotometer with a 0.2 mm KBr cell, according to AOCS method Cd-14-61 (1962) with brassidyl brassidate and erucyl erucate standards for calibration.

Heating. A micro carius furnace was used for thermal isomerizations.

Thin layer chromatography (TLC). Silica-gel coated glass plates were impregnated with a solution of 20% silver nitrate. The plates were dried in an oven for 3 hr at 110 C. The acids were converted to methyl esters by diazomethane and dropped on plates.

The developing solvent was petroleum ether (40-60 C) containing 5% ether. Spots were made visible by spraying an aqueous solution of 7.5% cuprous acetate and 0.5% potassium permanganate or by spraying with 50% sulphuric acid and heating to 250 C to char organic components. The latter procedure is not very effective with silver nitrate-impregnated plates, presumably because the nitric acid liberated causes overoxidation to carbon dioxide, leading to the loss of the charred spots. Silver(I) ions complex the *cis* double bond, thus the *cis* compound has a lower R_f value than the *trans* isomer, enabling differentiation between *cis* and *trans* forms (16).

Experimental

Thermal isomerization. Samples of bleached jojoba wax were isomerized in vacuum-sealed ampoules at temperatures between 250 C and 400 C (Table I). Heating for 192 hr at 300 C isomerized 53.3% *trans* jojoba wax to 37.6% with partial decomposition. Heating for 216 hr at 300 C in vacuum-sealed ampoules isomerized 65% brassidyl brassidate (containing 35% erucyl erucate) to 38%.

SYNTHESIS OF MODEL COMPOUNDS FOR THE DETERMINATION OF THE AMOUNT OF trans BONDS

Jojoba wax is a mixture of esters of varying compositions, and therefore its properties, such as melting range and molecular weight, are not constant, making analytical and spectroscopic calculations difficult.

Since C_{22} mono-13-unsaturated acids and alcohols are components (5) of this wax, we found it necessary to synthesize the pure *cis* and pure *trans* isomers of these esters as model compounds. The pure *cis* isomer is erucyl