Technical

Application of Infrared Spectroscopy in the Study of Polymorphism of Hydrogenated Canola Oil

AZZA NAGUIB MOSTAFA and **J.M. DEMAN**, Department of Food Science, University of Guelph, Guelph, Ont. N1G 2W1, Canada

ABSTRACT

Low temperature infrared spectroscopy was used to study the polymorphic transformations occurring in hydrogenated Canola oil. Hydrogenation of the oil was carried out under selective and nonselective conditions to an iodine value (IV) of 70 and 60, respectively. The four samples studied differed in their fatty acid composition, melting points and *trans* fatty acid content. For the first part of the study, the samples were cooled rapidly using liquid nitrogen to -100 C. All the samples initially crystallized in the α-form and further transformation to the β′-form was detected only in some samples. In the second part of the study, the melted samples were crystallized at 10 C. The resulting spectra showed either a pure β′-form or a mixture of β′ and β-forms.

INTRODUCTION

Several techniques have been used to study polymorphic transformations occurring in triglycerides, fats and fat products. Most common among these are X-ray analysis, differential scanning calorimetry, microscopy and infrared spectroscopy (1-7). Infrared spectroscopy has been used successfully by several researchers (8,9) to classify and study the three main polymorphic forms of triglycerides, namely α, β′ and β. It has been demonstrated that a doublet observed in the 720 cm^{-1} region of the infrared spectrum of triglycerides is related to the orthorhombic packing (β′-form) of the hydrocarbon chains, and a single band in the same region is indicative of the hexagonal (α-form) or triclinic (β-form) chain packing. This band is associated with the CH_2 rocking vibration of the molecules. The splitting of the band in this region of crystalline forms of molecules containing long hydrocarbon chains $(CH_2)_n$-CH_3 where $n \geq 3$, is attributed to interaction between neighboring chains in the orthorhombic sub-cell arrangement (10,11). From a practical standpoint, the different polymorphic forms in a fat affect the texture and hence the quality and acceptability of the final product.

This work is part of a broader study carried out on hydrogenated Canola oil (12) to determine the polymorphic transitions and the effect of hydrogenation conditions on their relative stability.

MATERIALS AND METHODS

Canola oil used in this study was commercially refined and obtained from CSP Food Ltd., Altona, Manitoba. Standard AOCS catalyst was used at a level of 0.2% by weight of oil. Hydrogenation was carried out in a Parr pressure hydrogenator, first under selective (200 C; 48 kPa hydrogen pressure) and then under nonselective (160 C; 303 kPa hydrogen pressure) conditions to produce Canola oil samples of IV 70 and 60. The samples were filtered while still warm and stored at 5 C in tightly capped containers. Physical properties of the samples, including dropping points, solid fat content, fatty acid composition and *trans* isomer content, have been reported in a previous publication (12). A Beckman model 4230 infrared spectrophotometer was used to record the spectra. A variable temperature unit (Beckman VLT-2) containing a cell fitted with silver chloride windows was used to hold the samples during scanning. A beam attenuator was placed in the reference beam. The spectra were run over the wavenumber range 1000-600 cm^{-1}.

For the first part of this study, the samples were prepared as follows: A drop of the melted fat was placed between the silver chloride windows of the cell. Teflon spacers of 0.025 mm thickness were used to ensure constant thickness of the sample. Immediately after mounting, the cell was chilled using liquid nitrogen and the unit was evacuated. The temperature was lowered to -100 C and maintained there for the duration of the scanning. The cell was then warmed carefully to allow the α-form to change to the β′-form. The sample was then cooled again to -100 C, and the spectrum was run. To obtain the β-form, the sample was warmed and left at room temperature for 24-48 hr; it was then scanned at -100 C. For the second part of the study, a drop of the melted fat was placed between the windows of the disassembled cell which was then kept in a dessicator at 10 C. Aluminum foil was used to cover the dessicator and protect the silver chloride windows from light damage. After 24 hr, the samples were scanned in the variable temperature chamber at -100 C.

RESULTS AND DISCUSSION

In the first part of the study, quenching the melted sample to -100 C resulted in spectra characteristic of α-form for all samples. This is represented in Figure 1A showing a single band at 720 cm^{-1}, which is attributed to the CH_2 main rocking mode of hexagonally packed chains (3). The sample was then warmed up in the cell, to allow the transition of the α to the β′-form. The scans obtained after lowering the temperature to -100 C were as follows: The sample selectively hydrogenated to IV 70 had a spectrum showing a doublet at 720 and 730 cm^{-1} (Fig. 1B), indicating orthorhombic chain packing (β′-form). The samples selectively hydrogenated to IV 60 and nonselectively hydrogenated to IV 70 had spectra characteristic of a mixture of β′ and β-forms with two sharp bands of unequal intensity at 718 and 728 cm^{-1} (Fig. 1C). The spectrum of the sample nonselectively hydrogenated to IV 60 was that of a pure β-form (Fig. 1D) with a sharp band at 720 cm^{-1}, indicative of the triclinic packing. There was also a strong band at 890 cm^{-1} which has been observed by other researchers (9) for triglycerides in the β-form. This band was associated with a methyl rocking vibration.

The results of the second part of the study are summarized in Table I. The sample selectively hydrogenated to IV 70 crystallized in the β-form. The three other samples crystallized in a mixture of β′ and β-forms evidenced by two bands of unequal intensities at 718 and 728 cm^{-1}. The sample that was selectively hydrogenated to IV 70 was found to be the only one that readily undergoes the transition from α to a pure β′-form. The stability of the β′-form of this sample had been confirmed by X-ray diffraction in earlier work (12). The results obtained indicate that the order of decreasing stability coincides with the order of decreasing *trans* fatty acids. Inherent differences in fats, namely degree

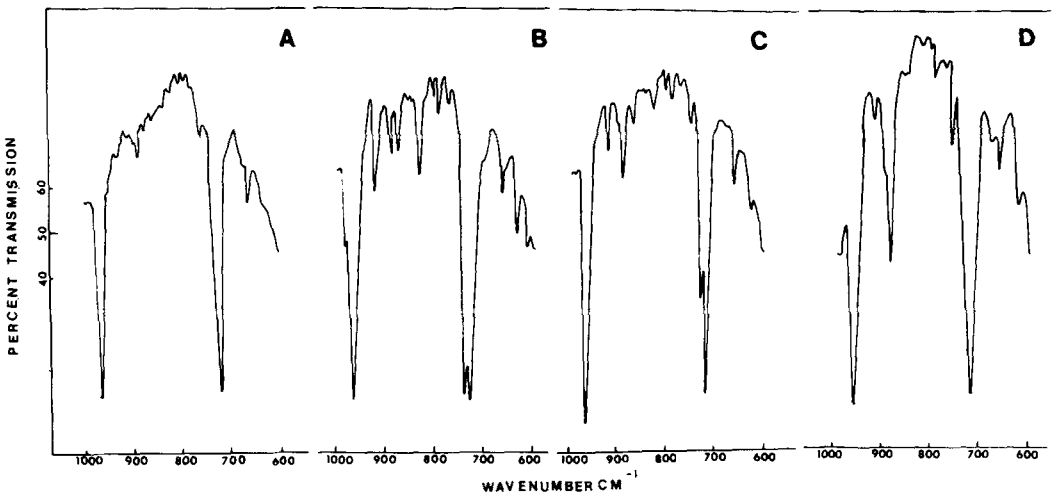

FIG. 1.A. Infrared scan ranging from 1000-600 cm^{-1} representing α-form of hydrogenated Canola oil. B. Infrared scan ranging from 1000-600 cm^{-1} representing β'-form of hydrogenated Canola oil. C. Infrared scan ranging from 1000-600 cm^{-1} representing a mixture of β' + β forms of hydrogenated Canola oil. D. Infrared scan ranging from 1000-600 cm^{-1} representing β-form of hydrogenated Canola oil.

TABLE I

Polymorphic Forms Present after Holding Samples at 10 C

Sample	CH_2 main rocking mode	Polymorphic form	*Trans* fatty acid (%)[a]
Selective IV 70	720 cm^{-1}; 730 cm^{-1} (equal intensity)	β'	51.5
Selective IV 60	718 cm^{-1}; 728 cm^{-1} (unequal intensity)	$\beta' + \beta$	44.0
Nonselective IV 70	718 cm^{-1}; 728 cm^{-1} (unequal intensity)	$\beta' + \beta$	38.5
Nonselective IV 60	718 cm^{-1}; 728 cm^{-1} (unequal intensity)	$\beta' + \beta$	32.6

[a]Reproduced from Reference 12.

of unsaturation and levels of *trans* fatty acids, can influence the stability of their various polymorphic forms and hence the texture of their final products.

An important observation made during this study was that, regardless of the temperature at which the transition from one polymorphic form to another occurs, the spectra have to be run at -100 C to obtain clear scans. In the case of fats, which are a complex mixture of several triglycerides, the identification of the different polymorphic forms can be misleading if the scans are run at the temperature of the transition. A possible explanation is that only at very low temperature are molecular rotations at a minimum allowing maximum interaction between neighboring molecules in each sub-cell. This interaction is the reason for either obtaining a singlet or doublets in the CH_2 rocking mode region of the infrared spectrum.

Low temperature infrared spectroscopy has proven to be useful in studying polymorphism of hydrogenated Canola oil and is complimentary to X-ray diffraction analysis.

ACKNOWLEDGMENT

Financial support was provided by the Natural Sciences and Engineering Research Council of Canada and the Ontario Ministry of Agriculture and Food.

REFERENCES

1. Lutton, E.S., JAOCS 27:276 (1950).
2. Malkin, T., Progress in the Chemistry of Fats and Other Lipids, Volume 2, p. 1-50, Pergamon Press, London (1954).
3. Chapman, D., The Structure of Lipids, John Wiley and Sons, New York (1956).
4. Larsson, K., Arkiv Kemi 23:35 (1964).
5. Riiner, U., Food Sci. Technol. 4:81 (1971).
6. Kawamura, K., JAOCS 57:1 (1980).
7. deMan, J.M., Food Microstructure 1:209 (1982).
8. Chapman, D., J. Chem. Soc. 2715 (1957).
9. deRuig, W.G., Appl. Spectroscopy 31:122 (1977).
10. Chapman, D., J. Chem. Soc. 55 (1956).
11. Chapman, D., Ibid. 2522 (1956).
12. Naguib-Mostafa, A., and J. deMan, JAOCS 62:756 (1985).

[Received February 1, 1985]