Effect of surfactants on some physical properties of hydrogenated Canola oil

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Introduction

Selective breeding of rapeseed to produce an oil low in erucic acid and meal low in glucosinolate has resulted in a number of cultivars named Canola. The replacement of erucic acid has been achieved with a corresponding increase in 18 carbon fatty acids, and an oil with about 95% of 18 carbon fatty acids. The decrease in fatty acid diversity has caused an increased polymorphic instability. Margarines made from hydrogenated Canola oil may recrystallize in the beta form. During this recrystallization, large crystals are formed which adversely affect texture and spreadability and ultimately decrease consumer acceptance.

One of the ways in which this undesirable change can be prevented or at least slowed down is the use of certain fat soluble surfactants. A commonly used compound is sorbitan tristearate (Riiner, 1971; Kawamura, 1979). Recently, diglycerides have been suggested as suitable stabilizers (Hernqvist et al., 1981; Hernqvist and Anjou, 1983). Since little is known about the way in which these compounds affect the polymorphic behaviour of fats, this study was undertaken to gain a better insight into the mechanism of their action. Previous experiments (Lee and deMan, 1982) have shown that sorbitan tristearate, monostearate and monopalmitate are effective inhibitors of the polymorphic transformation to the beta phase.

Materials and methods

Canola oil was hydrogenated by two different methods. Selective hydrogenation was done at 200°C, 48.3 kPa of hydrogen pressure and with 0.2% AOCS standard nickel catalyst. The final fat showed an iodine value of 70 and a trans-isomer content of 55.1%. Non-selective hydrogenation was carried out at 160°C, 303.4 kPa of hydrogen pressure and catalyst concentration of 0.2%. The iodine value was 64 and the trans-isomer content was 39.9%. The two different hydrogenated fats will be identified by the symbols "Sel" and "NSel" respectively for the selectively and non-selectively hydrogenated

samples.

Six different surfactants were added to the fats at the 1% level (W/W). These were: sorbitan tristearate (STS); sorbitan monostearate (SMS); sorbitan monopalmitate (SMP); sorbitan trioleate (STO); sorbitan trilaurate (STL) and Admul Wol (AW). All sorbitan esters were obtained from Atkemix Inc. whereas Admul Wol was obtained from Food Specialties Comp. Ltd., Ajax, Ont.

Each sample was identified by a three or four letter code containing the first letter (S or N) describing the fat type followed by the two or three letter code representing the surfactant. Fats without surfactant addition were used as controls for all experiments.

Iodine value was determined in accordance with AOCS official method Cd 1-25 (1974).

Trans-isomer content was determined by infrared spectroscopy following AOCS official method Cd 14-61 using a Beckman infrared spectrophotometer, model 4230.

Melting point was obtained with the Mettler Dropping Point Apparatus using the procedures of Mertens and deMan (1972). The furnace was housed in a cold cabinet which allowed for rapid cooling of the hot furnace and also allowing starting temperatures to be 15-20°C below the actual dropping points of the samples.

Solid fat contents of all fat samples were measured by wide-line nuclear magnetic resonance. A Newport Quantity Analyzer Mark III and a sample temperature controller WR2 MKII was used. Tempering of the samples was done with a Praxis Model TU-900 tempering unit.

Two grams of melted fat were placed in a 6 ml cylindrical NMR tube. Olive oil was used as the reference oil. All tubes were kept in the tempering unit at 60°C for 30 minutes and each tube was then transferred to the analyzer and kept there for 5 minutes before a reading was taken. All tubes were moved from 60°C to 0°C for 15 minutes, tempered at 25°C for 30 minutes and returned to 0°C for 15 minutes. Following this pretreatment, NMR readings were taken at 0°C, 5°C, 10°C, 20°C, 25°C and 35°C. Solid fat content was calculated by the method proposed by Wettstrom (1971). Statistical analysis was performed using the Statistical Analysis System (SAS) of Barr and Goodnight (1972).

For determination of the sorbitan ester distribution, the crystallized fats were subjected to pressure filtration to isolate the liquid fraction (Vasic and deMan, 1966). Sorbitan was determined in the whole fat and in the liquid phase, using a modification of the method of Sahasrabudhe and Chadka (1969). The polar surfactants were separated from the triglycerides by

column chromatography on silica gel. The apolar fraction was eluted with benzene and discarded. The polar fraction was eluted with chloroform-methanol 2:1. After removal of the solvent, the material was saponified with 0.5N alcoholic KOH. After evaporation of the alcohol, the sorbitan was dissolved in pyridine containing tetradecane as internal standard. The mixture was silylated with hexamethyldisilazane and trimethylchlorosilane and analyzed by gas chromatography on a column of 3% OV17 stationary phase on Chromosorb G. The incorporation index was calculated as the ratio of sorbitan in the solid phase to that in the liquid phase.

Differential scanning calorimetry was performed using a DuPont model 990 thermal analyzer.

Results and discussion

It is well established that polymorphic transition to the beta phase may change certain physical properties of a fat and cause a noticeable increase in graininess. Surfactants which inhibit this change apparently block the transformation, but little is known about the mechanism of this action.

Addition of some of the surfactants was found to cause a decrease in dropping points. Dropping point values are listed in Table 1. The greatest decrease was found with sorbitan tristearate for both fats. This action is indicative of an interaction, possibly the formation of a eutectic mixture, with the highest melting portion of the fat.

The possible influence of surfactant addition on solid fat content was investigated. None of the surfactants investigated had a significant effect on solid fat content of either selectively or non-selectively hydrogenated fat. A solid fat curve for non-selectively hydrogenated fat before and after addition of sorbitan tristearate is given as an example in Figure 1.

The distribution of the sorbitan esters between the solid and the liquid phase of the fats was studied by separating the liquid phase by pressure filtration. Determination of sorbitan in the original fat and in the liquid fraction enabled the calculation of sorbitan in both phases. This analysis was carried out for all of the sorbitan esters in selectively hydrogenated Canola oil. Results are shown in Table 2. The sorbitan tristearate and monostearate were greatly enriched in the solid phase, whereas the monopalmitate was enriched to a lesser extent. The oleate and laurate esters were not preferentially incorporated into the solid phase.

Differential scanning calorimetry of the surfactants

indicated that the stearate and palmitate esters had sharp melting peaks at 56, 57 and 51 respectively. The laurate esters had a broader melting pattern at lower temperature (-5 to 12°C). The oleate ester also had a broad melting pattern at below 0° temperatures (-45 to -15°C). The Admul WOL did not show any solidification at all down to -50°C.

From these results it is now possible to conclude that effective action against the polymorphic transition to the beta phase is restricted to compounds which can cocrystallize with the solid portion of the hydrogenated Canola oil. These substances apparently incorporate into the crystal lattice. They should be similar in structure but sufficiently different so that they can interfere with the polymorphic transformation, presumably by creating irregularities in the crystal lattice.

Summary

The effect of the surface active agents, sorbitan tristearate, sorbitan monostearate, sorbitan monopalmitate, sorbitan trioleate, sorbitan trilaurate and Admul WOL, on the physical properties of hydrogenated Canola oil was investigated. Sorbitan tristearate caused a lowering in dropping point, as did the other surfactants but to a lesser degree. The surfactants had no effect on the solid fat content. Separation of the liquid phase and analysis of the sorbitan distribution indicated that the sorbitan stearates were incorporated preferentially into solid phase. The mechanism of action of the surfactants is discussed.

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Table 1. Dropping points of selectively and non-selectively hydrogenated Canola oil without and with addition of surfactants.

Sample	Dropping point
Sel	39.4[a]
SSTS	37.9
SSMS	38.2
SSMP	38.3
SSTO	38.2
SSTL	38.7
SAW	38.4
NSel	45.7[b]
NSTS	44.2
NSMS	44.4
NSMP	44.6
NSTO	44.9
NSTL	45.5
NAW	45.3

Table 2. Distribution of sorbitan between the solid and liquid phases of selectively hydrogenated Canola oil.

Sample	Sorbitan (mg/g) in solid fraction	Sorbitan (mg/g) in liquid fraction	Incorporation index
SSTS	3.68	0.85	4.45
SSMS	7.74	1.33	5.82
SSMP	5.56	3.34	1.66
SSTO	1.93	1.83	1.05
SSTL	2.37	2.63	0.86

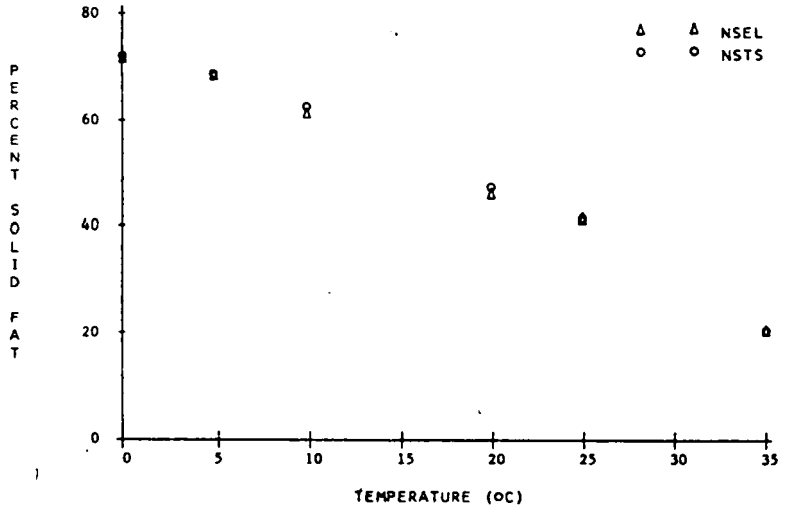

Fig. 1. Solid fat content of non-selectively hydrogenated Canola oil with and without 1% added sorbitan tristearate.