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The interesterification-induced changes in olive and palm oil blends

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Refined olive oil and partially hydrogenated palm oil (PHPO) blends of varying proportions were subjected to both chemical and enzymatic interesterifications. The rearranged fats were investigated for their melting points, solid fat contents at selected temperatures, fatty acid compositions and *trans* isomer contents, as well as evaluations, by an expert sensory panel, of their spreadibility and appearance characteristics. The analytical results were compared with those of commercial Turkish margarines. The 30:70 olive oil-PHPO blend after enzymatic interesterification was found to have properties very similar to those of Turkish package margarines, with the additional advantage of possessing higher amounts of monounsaturated fatty acids. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

Interesterification modifies the physical propeties and crystallization behaviour of fats by altering the original specific triglyceride composition of the blend components. This fact has made its commercial use an alternative to hydrogenation for production of plastic fats to be used in margarine formulations.

Since the hydrogenation process also has the disadvantage of forming *trans* isomers (as well as losing essential fatty acids), interesterification of liquid oils with naturally saturated fats is now being explored to produce 'healthy' dietetic margarines with lower levels of *trans* isomers and higher levels of essential fatty acids. Moreover, in cases where the availability of unsaturated oils and highly saturated fats can be secured at lower prices, interesterification rather than hydrogenation may become the technology of economical choice for producing margarines.

Chemical interesterification has been thoroughly investigated for its effects on the properties of product obtained with many different blend components (List *et al.*, 1977; Lo and Handel, 1983; Gavrilidou and Boskou, 1991). Both positionally specific and non-specific lipases from differing sources have been exploited to investigate similar modifications on various blends of differing oil and fat components (Kalo *et al.*, 1986; Kurashige *et al.*, 1993; Mohamed *et al.*, 1995). From these studies, it was observed that the enzymatic interesterification studies with non-specific lipases have yielded fats similar to those obtainable with chemical interesterification; since these types of lipases show no specificity regarding the position of fatty acids in the glycerol molecule, the resulting triglycerides have randomly distributed fatty acids. The 1,3-specific lipases, on the other hand, catalyse reactions involving acyl exchange only at positions 1 and 3 of the glycerides. Thus, through studies using positionally specific lipases and by proper blending of selected liquid and hard fats, it has become apparent that 'tailor-made' fats having desired physical and nutritional properties which may be unattainable by conventional processes can now be attained. Chang and colleagues, study for production of a cocoa-butter substitute (1990) and Mohammed and colleagues, work (1995) with the use of olive oil as an alternative to milk in flavouring margarines are typical examples of such studies.

In the study reported here, indigenous olive oil with its highly desirable nutritional attributes was blended with partially hydrogenated palm oil (PHPO). Using both chemical and enzymatic esterification methods with the purpose of producing plastic fats similar in composition and properties to soft (tub) and package type margarines being produced in Turkey, the second aim was to investigate the effects of these processes on selected properties of blends with respective physico-chemical, chemical and sensory analyses.

MATERIALS AND METHODS

Materials

The fully refined olive oil and the commercial margarine samples used in this study were purchased from the

local market. The palm oil partially hydrogenated to a melting point of 46.3, which was selected to constitute the solid phase for its versatile polymorphic structure and ease of availability, was donated by Unilever Turkey. The 1,3 specific lipase (triacyl glycerol acyl hydrolase) enzyme preparation used was LIPOZYM IM60, produced by Novo Nordisk from *Rhizomucor miehei*, and immobilized on a macroporous anion-exchange resin.

The samples to be used in esterification trials were prepared by blending olive oil with the partially hydrogenated palm oil at weight ratios of 60:40, 50:50, 40:60, 30:70, and 20:80, respectively.

Methods

Technological procedures

The five blends prepared as above were initially subjected to enzymatic interesterification in a batch-type thermostat-controlled reactor at 70°C. For this purpose, a 30 g batch of each blend was incubated in the reactor for 5 min; then the immobilized enzyme LipozymIM60 was added at a ratio of 10% of the weight of blend. The mixture was stirred and kept in the reactor for 4 h. The reaction was terminated by removing the enzyme from the reaction mixture by filtration (Mohamed *et al.*, 1993). Later, the five blends were subjected to chemical interesterification by weighing 50 g of each into 500-ml rotary evaporator flasks and heating to 95°C under vacuum for a period of 60 min to remove any water present (Lo and Handel, 1983). After lowering the temperature to 80°C, 0.6% by weight of sodium methoxide catalyst was added to the blend, followed by a further 10 min of heating at 85°C, after which the reaction was terminated. The catalyst was removed by filtration under vacuum (Zeitoun *et al.*, 1993).

Analytical methodology

Melting points of samples were determined by closed capillary AOCS Official Method Cc1-25 (Anon, 1981). Solid fat contents were measured by pulsed nuclear magnetic resonance (p-NMR, Bruker Minispec PC/20 Series) according to the AOCS Official Method Cd16-81 (Anon, 1981) at 10, 20, 30 and 35°C, respectively.

Methyl esters of fatty acids formed with BF3-Methanol reagent according to AOAC Method 963.33 (Anon, 1990) were injected into a Hewlett Packard 6890 Series II Gas Chromatograph equipped with a flame ionization detector and HP Chemstation. A 2 mm×6.1 m stainless steel column packed with 15% OV-275 on Chromosorb PAW 100-200 mesh was used. The chromotograph was operated isothermally at 215°C, with a nitrogen carrier gas flow rate of 9.5 ml min^{-1}. The injection and detection temperatures were 250°C.

Quantification of *trans* fatty acids was conducted by the AOAC Official Method 985.21 (Anon, 1990) using gas chromatography.

The sensory analysis tests were carried out by a previously well-trained expert panel of eight fat specialists formed according to DLG Method (Anon, 1976). The grading numerical scale was established to be as follows: 1–2: unacceptable, 3–4: poor, 5–6: fair, 7–8: good, 9–10: excellent. For statistical evaluations, linear regression analysis was conducted on results of spreadibility gradings vs both melting points and solid fat content determinations (Soysal, 1992).

RESULTS AND DISCUSSION

The functional properties of margarines can be assessed with both sensory analyses of spreadibility and appearances and by determination of selected physicochemical properties like melting points and solid fat contents at a selected range of temperatures. Furthermore, the chemical composition of margarines is reflected best through the analyses of their fatty acid components. The results of these investigations on the sample blends are given below in respective tables and figures.

Physicochemical properties

The melting points and solid fat contents of non-interesterified and interesterified blends, together with those of two Turkish commercial margarines are given in Table 1. These findings are reflected graphically in Fig. 1.

The analytical findings clearly indicate that increasing the PHPO component resulted in corresponding increases in solid fat contents at 10, 20, 30 and 35°C. It is also apparent that the blends with lowest melting points were those that were enzymatically interesterified with Lipozym IM60. The melting points of blends chemically interesterified with sodium methoxide catalyst, too, were lower than those of non-interesterified blends.

A similar trend was observed in solid fat contents of respective blends: of the three sets of samples, they were lowest in enzymatically interesterified blends, intermediate for chemically interesterified ones and highest in non-interesterified ones, at the same corresponding temperature ranges. Zeitoun *et al.* (1993) had previously commented on this issue.

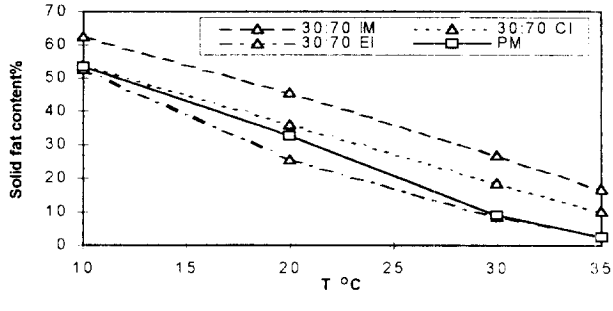

Fig. 1. Solid fat contents in relation to temperatures.

Table 1. Melting points and solid fat contents of olive oil, PHPO, initial mixture, chemically interesterified and enzymatically interesterified blends

Lipids	Melting point (°C)	Solid fat content (%) 10°C	20°C	30°C	35°C
Olive oil					
PHPO	46.3	85.6	74.1	48.9	33.8
60:40 IM	40.0	35.0	23.2	11.6	7.1
60:40 CI	31.4	27.5	14.1	4.8	2.3
60:40 EI	28.8	25.3	8.4	2.0	0.0
50:50 IM	41.1	43.5	29.6	15.8	9.4
50:50 CI	31.6	34.2	15.5	5.0	1.5
50:50 EI	29.7	34.4	12.1	3.8	0.6
40:60 IM	43.0	52.3	37.9	21.7	13.3
40:60 CI	37.8	45.7	25.3	10.2	4.7
40:60 EI	32.1	44.4	18.5	6.1	1.9
30:70 IM	44.1	62.5	45.5	26.8	17.0
30:70 CI	41.2	53.8	36.0	18.5	10.4
30:70 EI	31.8	52.5	25.6	8.6	2.9
20:80 IM	45.1	69.8	55.0	34.4	22.8
20:80 CI	42.8	62.5	45.3	25.6	15.9
20:80 EI	32.5	63.0	36.3	12.5	5.8
Soft (tub) margarine	33.0	15.9	10.2	4.5	1.4
Package margarine	34.5	53.5	32.4	9.3	2.8

PHPO, partially hydrogenated palm oil; IM, initial mixture; CI, chemically interesterified; EI, Enzymatic interesterified.

When compared with commercial Turkish soft margarines, the data on which is in close conformity with the data of De Man *et al.* (1991), the sample with the nearest melting point and solid fat content was found to be the enzymatically interesterified blend containing 30:70 olive oil:PHPO; however, none of the blends examined could achieve the very low solid fat content at 10°C of the soft tub margarines (15.9%).

On the other hand, the non-interesterified blends and even the chemically interesterified blends had relatively much higher solid fat contents at 35°C, when compared with both the commercial margarines and the enzymatically interesterified blends.

The solid fat contents, at the selected temperatures of the chemically interesterified blend of 40:60 olive oil and PHPO composition, were very similar to those obtained in a similar study, where Gavrilidou and Boskou (1991) had interesterified olive oil with tristearin. These decreases observed in overall melting points and solid fat contents at higher temperatures following the interesterification process have been shown to be due to respective decreases in the molar percentages of the original trisaturated triglycerides with the highest melting points and corresponding increases in the proportions of monounsaturated triglycerides (List *et al.*, 1977; Kalo *et al.*, 1986; Kurashige *et al.*, 1993).

Chemical properties

The results of analyses of fatty acid compositions and trans isomer contents are given in Table 2.

It was quite apparent that there were no significant differences observed in the overall fatty acid composition of blends after interesterifications. Similar observations were previously made by List *et al.* (1977) and by Lo and Handel (1983), following their own studies on interesterification.

Sensory properties and statistical analyses

The results of sensory analyses conducted by the expert panel of eight fat specialists grading the spreadability and appearances of initial and final products of interesterifications, together with those of commercial samples are tabulated in Table 3. It was observed that the enzymatically and chemically interesterified blends of 20:80 olive oil:PHPO composition had excellent spreadability and appearance grades. The respective grades of enzymatically interesterified blends of 30:70 and 40:60 olive oil:PHPO composition were also quite favourable and, when the additional fact that their *trans* fatty acid contents are also relatively lower is taken into consideration, it can be concluded that these last products can offer alternative formulations for commercial package margarines produced in Turkey.

Furthermore, when the results of sensory analyses of the expert panel were evaluated with regression analyses, positive correlations between the spreadability grades and respective melting points ($r = 0.218$ at $P < 0.05$) and between the spreadibility grades and respective solid fat contents ($r = 0.571$ at $P < 0.05$) were obtained; however, it was observed that the sensory assessments did not proportionately reflect the magnitude of the differences in melting points and solid fat contents.

Table 2. Fatty acid compositions of olive oil, PHPO, initial mixture, chemically and enzymatically interesterified blends (% as methyl esters)

Lipids	12:0	14:0	16:0	16:1	18:0	18:1 *trans*	18:1 *cis*	18:2 *trans*	18:2 *cis*	20:0	20:1	22:0	24:0
Olive oil		0.0	12.3	1.1	3.0	—	71.0	—	10.0	—	—	—	—
PHPO	1.2	1.2	37.8	0.3	11.4	23.0	22.3	1.2	0.7	0.4	0.1	0.2	—
60:40 IM	0.6	0.5	22.5	0.7	6.5	8.1	52.8	0.4	6.2	0.5	0.6	0.1	0.4
60:40 CI	0.4	0.5	22.3	0.7	6.4	7.5	53.5	0.5	6.3	0.5	0.6	0.1	0.4
60:40 EI	0.5	0.5	22.3	0.8	6.5	7.9	53.0	0.7	6.5	0.5	0.6	0.1	0.2
50:50 IM	0.6	0.6	24.8	0.7	7.1	10.4	48.3	0.6	5.3	0.5	0.6	0.4	0.1
50:50 CI	0.5	0.6	24.9	0.7	7.2	9.6	48.8	0.8	5.4	0.5	0.5	0.1	0.4
50:50 EI	0.6	0.6	24.5	0.7	7.2	10.2	48.7	0.8	5.4	0.4	0.5	0.1	0.2
40:60 IM	0.6	0.7	27.5	0.6	8.2	12.9	42.7	1.1	4.3	0.4	0.4	0.4	0.1
40:60 CI	0.7	0.7	27.6	0.6	8.1	12.8	42.4	1.1	4.5	0.5	0.5	0.5	0.1
40:60 EI	0.7	0.7	26.7	0.6	8.1	12.5	44.1	0.9	4.5	0.4	0.4	0.4	0.3
30:70 IM	0.9	0.9	29.8	0.5	8.8	17.6	35.4	1.5	3.5	0.4	0.3	0.3	0.1
30:70 CI	0.7	0.8	29.4	0.6	8.7	17.4	35.7	1.3	4.2	0.4	0.4	0.4	0.1
30:70 EI	0.9	0.8	29.0	0.6	8.8	17.4	37.0	1.0	3.6	0.4	0.2	0.1	0.1
20:80 IM	1.0	1.0	35.2	0.5	9.7	15.1	32.1	1.6	2.6	0.4	0.4	0.3	0.1
20:80 CI	0.7	0.8	34.8	0.4	9.7	14.6	32.9	1.4	3.7	0.4	0.3	0.4	0.1
20:80 EI	1.0	1.0	32.9	0.5	9.6	14.8	34.3	1.2	2.7	0.4	0.3	0.1	0.1
Soft margarine	1.6	1.2	11.3	—	8.2	3.5	21.5	—	52.6	—	—	—	—
Package margarine	0.9	0.6	19.9	—	5.5	22.8	34.6	1.2	14.3	—	0.2	—	—

Table 3. The results of sensory analyses

Lipids	Spreadability at 25°C	Appearance
60:40 IM	3	3
60:40 CI	4	4
60:40 EI	4	7
50:50 IM	4	4
50:50 CI	4	4
50:50 EI	5	7
40:60 IM	7	7
40:60 CI	7	7
40:60 EI	8	8
30:70 IM	7	7
30:70 CI	8	7
30:70 EI	9	8
20:80 IM	7	8
20:80 CI	9	9
20:80 EI	9	9
Soft (tub) margarine	10	10
Package margarine	7	10

CONCLUSION

The enzymatically interesterified sample blend with 30:70 olive oil:PHPO contents had comparable physicochemical and sensory properties with those of commercial Turkish package margarines, confirming its position as a valuable alternative to hydrogenation.

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