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THERMOXIDATIVE STABILITY OF A NEW SUNFLOWER SEED OIL WITH HIGH LEVELS OF OLEIC AND PALMITIC ACIDS

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Summary: High-oleic, high-palmitic liquid oil has been obtained from mutant sunflower seeds. The fatty acid and triacylglycerol compositions and the thermal stability of the new oil were determined and compared with those of conventional sunflower oil, high-oleic sunflower oil and palm olein. The new oil contained 31% palmitic acid, 58.3% oleic acid and 2% linoleic acid and, thus, unusually high contents of triacylglycerol molecular species with one and two saturated fatty acids at the *sn*-1,3 positions and oleic acid at the *sn*-2 position. Total purified triacylglycerols devoid of tocopherols were subjected to controlled thermoxidative treatment thus resembling the usual conditions for discontinuous frying. Total polar compounds and their distribution in oxidized triacylglycerol monomers and TAG polymers were determined after 10 h at 180°C. The triacylglycerols of the new oil showed enhanced thermal stability producing half the amount of total polar compounds as the conventional sunflower oil and less than two-thirds that of the high-oleic oil and the palm olein. The time course of polymerised triacylglycerols formation indicated that the high-oleic, high-palmitic oil produced much less polymers than the high oleic sunflower or the palm olein. According to this, the high-oleic, high-palmitic oil showed the highest stability index (13 h at 120°C, using the Rancimat method). The new oil is a promising alternative for high performance frying operations.

Introduction.

Vegetable fats and oils used for deep-frying and other applications of the food industry require high thermal stability. Palm oil, partially hydrogenated and high-oleic vegetable oils are used to fulfil this requirement. However, partially hydrogenated fats contain *trans* isomers of fatty acids that are considered nutritionally undesirable. Also, palm oil and partially hydrogenated fats contain higher levels of saturated fatty acids at position *sn*-2 of triacylglycerols (TAG) than do most vegetable oils, such as soybean and sunflower (Gunstone et al., 1994). The location of saturated fatty acids in the *sn*-2 position has been suggested to have negative biological effects and be involved in the atherogenic process (Braco, U., 1994; Renaud et al., 1995). High-oleic sunflower oil has been shown to be more resistant to oxidation and polymerisation under frying conditions at high temperatures than conventional sunflower oil (Dobarganes et al., 1993). Investigations on changes of specific TAG molecular species of conventional and high-oleic sunflower oils, and palm oil, during frying operations (Dobson et al., 1996), indicated that, although all species underwent degradation, linoleate-containing species oxidized more rapidly than those containing oleate. Linoleic acid was preferentially involved in the formation of dimeric fatty acyl residues and thus TAG polymers (Jorge et al., 1997).

Recently, new sunflower mutant lines were developed that contain high levels of palmitic acid in conventional and high oleic backgrounds (Osorio et al., 1995; Fernandez-Martinez et al., 1997). It is of great interest to study the properties of the oil of the high-oleic, high-palmitic (HOHPSO) sunflower mutant, which contains TAG molecular species with oleic acid at any position and palmitic acid at the *sn*-1,3 positions. In this paper, the fatty acid and TAG composition and thermoxidative stability of the oil of the new sunflower mutant was compared with those of conventional sunflower oil, high oleic sunflower oil with similar linoleic acid content and palm oleins with different levels of palmitic acid.

Experimental

Oil stability index were determined in the refined oils using a Rancimat apparatus following the standard AOCS Method (AOCS, 1994). The thermoxidative stability of purified TAG was determined according to the procedure of Barrera-Arellano et al., (1997). The evolution of polymerised TAG was followed during heating and a complete analysis of polar compounds, including total level and their distribution in oxidized TAG monomers and TAG polymers, was carried out at the end point (Dobarganes et al., 1988). For additional experimental details see Marquez-Ruiz et al., (1999).

Results and discussion

The fatty acid composition of total TAG, which are the main components of the oils, and the content of saturated (palmitic and stearic) fatty acids at the *sn*-2 position of TAG are shown in Table 1.

Table 1. Fatty acid composition of total TAG and content of saturated fatty acids at the *sn*-2 position of conventional (SO), high-oleic (HOSO) and high-palmitic, high-oleic (HOHPSO) sunflower oils and two palm oleins.

	Fatty acid composition (mol%)						
	Total triacylglycerols					*sn*-2 position	
Oil	16:0	16:1	18:0	18:1[a]	18:2	16:0	18:0
SO	6.4	--	5.0	36.5	52.0	0.8	0.6
HOSO	3.8	--	3.9	89.7	2.5	0.8	0.5
HOHPSO	31.0	6.6	2.1	58.3	2.0	1.2	0.2
Palm olein (1)	34.6	--	4.4	48.2	12.6	7.3	0.2
Palm olein (2)	39.5	--	4.5	42.3	12.2	9.0	0.2

[a] 18:1 n-9 and 18:1 n-7

The new HOHPSO sunflower oil contained 31% palmitic acid. The linoleic acid content (2%), was similar to that of HOSO but much lower than that of palm olein (aprox. 12.5%). In the three sunflower lines, despite the very different fatty acid composition, the saturated fatty acids were nearly absent from the *sn*-2 position. The new line only contained 1.4% of these acids at the *sn*-2 position while palm olein contained 7.5-9.2%. The calculated content of TAG molecular species is shown in Table 2. These data were calculated according to the 1,3-

random-2-random distribution model (Vander Wal, 1960) from the fatty acid composition in the *sn*-2 and *sn*-1,3 positions (for more details see Marquez-Ruiz et al., 1999). The TAG species of the different sunflower oils contained mainly unsaturated fatty acids at the *sn*-2 position, while those of palm olein contained positional isomers with 16:0 or 18:0 at this position (in parenthesis in the table).

Table 2. Major triacylglycerols molecular species (%) from the oils of sunflower lines HOHPSO and HOSO and palm oleins.

TAG species	HOHPSO	HOSO	Palm olein (1)	Palm olein (2)
PPP	---	---	1.6	2.9
POP (PPO)	20.1	---	17.8	24.6
POO (OPO)	34.2	9.5	26.0	23.3
OOO	14.7	72.9	10.3	5.9
POPo	9.4	---	---	---
POS (OPS)	2.7	---	5.1	5.7
PLO (LPO)	2.4	---	13.7	13.6
OOS	2.2	8.6	3.8	2.8
OLO	1.6	6.5	7.6	4.9
SLO	---	---	2.0	1.6
LLO	---	---	1.8	1.4

P, 16:0, 18:1 (n-9 and n-7); Po, 16:1, L, 18:2, S, 18:0.

Great differences were observed in the TAG composition of the oils. Whereas OOO was particularly abundant in HOSO (72.9%), the main species in HOHPSO were POO (34.2%) and POP (20.1%). In palm olein, due to its higher content of 16:0, particularly at position *sn*-2, the main species were POP + PPO (17.8-24.6%) and POO + OPO (23.3-26%). It is worthy to note that palm olein contained more species with 18:2, mainly PLO + LPO (13.6%) than HOHPSO. In conventional SO, the main TAG species are OLL, OOL and LLL (Marquez-Ruiz et al., 1999). The TAG composition strongly affects the technological applications of the oils. The lower the content of species with 18:2 and the higher the content of species with

16:0 the higher the thermal stability and the resistance to oxidation. On the other hand, the higher the content of species with 16:0, the higher the solid fat content.

The thermoxidative stability of the oils and purified TAG is shown in Table 3. At both 110°C and 120°C the refined oil of HOHPSO showed the highest stability. Purified TAG allowed to study the formation of polar compounds without the influence of natural antioxidants (tocopherols) and other minor compounds. According to these results, the TAG of HOHPSO were more resistant to oxidation and polymerisation than the others. The time course of formation of polymerised TAG was followed (Fig. 1). TAG from polyunsaturated oils such as soybean, rape and normal sunflower were easily polymerised, while olive, high oleic sunflower and palm olein, which are considered as stable oils, were less polymerised. Interestingly, the TAG of HOHPSO were by far the less altered and, thus, the more resistant to polymerisation.

Table 3. Quantitation of polar compounds in purified triacylglycerols (TAG), from sunflower oils and palm olein heated at 180°C for 10 h, and oil stability index (Rancimat) at 110°C and 120°C.

	TAG polar compounds (wt %)			Oil stability (Rancimat)	
Oil	Total	Ox-TAG monomer	TAG polymers	hours at 110°C	hours at 120°C
SO	24.6	9.7	14.9	n.d.	n.d.
HOSO	21.3	10.6	10.7	8.4	3.9
Palm olein (1)	17.8	8.3	9.5	20.0	9.5
HOHPSO	12.9	6.7	6.2	30.0	13.0

n.d., not determined

The results of this study indicated that, due to its unique TAG composition and high stability, the high-oleic, high-palmitic sunflower oil is a promising alternative for high performance frying operations.

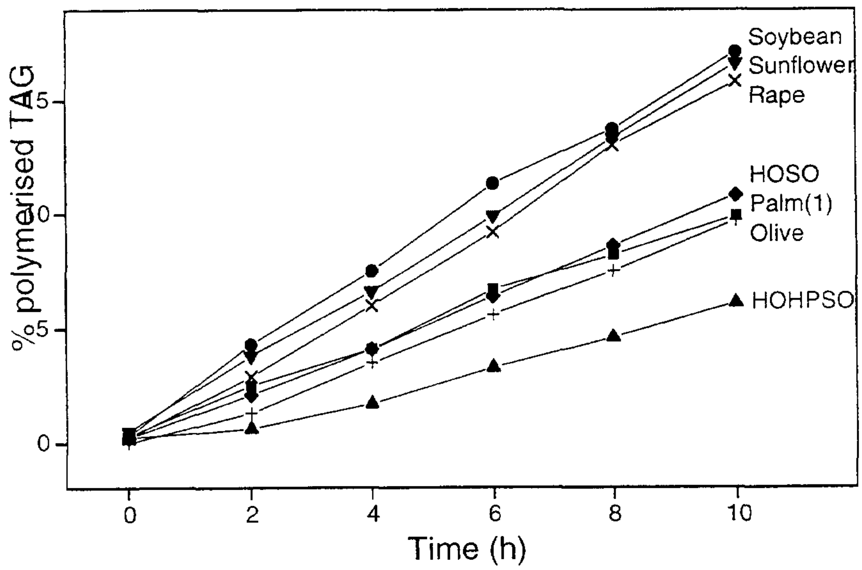

FIG. 1. Evolution of polymerised triacylglycerols formation in purified TAG from different types of oils heated at 180°C.

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