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Feature

Current advances in sunflower oil and its applications

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Summary

The fatty acid and triacylglycerol composition of a vegetable oil determine its physical, chemical and nutritional properties. The applications of a specific oil depend mainly on its fatty acid composition and the way in which fatty acids are arranged in the glycerol backbone. Minor components, e. g. tocopherols, also modify oil properties such as thermo-oxidative resistance.

Sunflower seed commodity oils predominantly contain linoleic and oleic fatty acids with lower content of palmitic and stearic acids. High-oleic sunflower oil, which can be considered as a commodity oil, has oleic acid up to around 90%. Additionally, new sunflower varieties with different fatty acids and tocopherols compositions have been selected. Due to these modifications sunflower oils possess new properties and are better adapted for direct home consumption, for the food industry, and for non-food applications such as biolubricants and biodiesel production.

Introduction

Vegetable oils are mainly triacylglycerols which account for more than 95% of total oil. They also contain small quantities of diacylglycerols, phospholipids, tocopherols, free fatty acids, *etc*. Triacylglycerols consist of a glycerol molecule having three fatty acids esterified at the hydroxyl residues, one in the central position of the glycerol molecule *sn*-2 and the other two at the terminal positions *sn*-1 and *sn*-3. The most common fatty acids forming these triacylglycerols in sunflower oil are: saturated (palmitic and stearic) monounsaturated (oleic) and diunsaturated (linoleic).

The final use of each type of oil is defined by both physical and chemical characteristics depending on its fatty acids and triacylglycerol composition. For instance, the physical difference between oils (liquid) and fats (solid) is due to the amount of saturated fatty acids. The thermo-oxidative stability of vegetable oils depends mainly on the amount of polyunsaturated fatty acids they contain (oils with a high content of these unsaturated fatty acids are more unstable) as well as their content and type of tocopherols. Considerable research efforts in the plant lipids field are being put into the following aspects: (i) On the one hand, more stable sunflower oils have been obtained by increasing the content of monounsaturated (oleic acid) and decreasing the content in polyunsaturated fatty acids (linoleic acid). This kind of oil is also suitable for biolubricants. Vegetable oil stability can also be increased by modifying the tocopherol content. (ii) On the other hand, healthy substitutes for higher melting animal, tropical or hydrogenated fats – required by food industry – are being obtained by increasing their content in saturated mostly stearic fatty acids which does not modify the plasmatic cholesterol levels in humans.

Sunflower oils

Different sunflower lines with modification in the fatty acid composition of their oils have been obtained (Table 1). Since the selection of the high-oleic mutant by Prof. Soldatov several new fatty acid mutants have been obtained by ionization, radiation or chemical mutagenesis – none of which involve genetic modification. Among these are three independent high-palmitic lines with around 30% of palmitic acid in their oils, two of them in standard high-linoleic background and another in high-oleic background [1]. Additionally, some lines having high-stearic acid in high-linoleic background have been obtained; and lately high-stearic high-oleic lines have been developed by recombination [2]. In spite of their higher saturated acid content, these sunflower oils have a low content of saturated fatty acid in the middle position of the triacylglycerol [1], differentiating them from animal, palm and hydrogenated fats in this respect, and making them healthier than those oils [3].

Table 1. Fatty acid composition of several modified sunflower oils compared with the standard sunflower oil.

Sunflower line	Oil phenotype	Fatty acid composition (%)				
		16:0	16:1	18:0	18:1	18:2
Standard	HL	7		6	29	58
HA-OL9	HO	5		3	**90**	2
CAS-4	MS HL	6		**12**	28	53
CAS-3	HS HL	5		**26**	15	53
CAS-30	HS HL	6		**30**	10	50
CAS-15	HS HO	6		**24**	**62**	5
CAS-5	HP HL	**31**	5	3	12	48
CAS-12	HP HL	**32**	6	4	**54**	3

HL, high-linoleic; HO, high-oleic; HP, high-palmitic; HS, high-stearic; MS, medium-stearic.

Sunflower oil applications

Deep-frying, and other industrial processes for food preparation, require fats and oils with high thermo-oxidative stability. In these applications, due to easy storage and pouring, oils are better than fats. For margarine, spreads, confectionary and related products fats with a certain degree of plasticity (appropriate solid fat ratio) are required. For biolubricants production, oil liquid at temperatures below 0°C with a good thermo-oxidative stability is required. Biodiesel production only requires a minimal stability, and standard sunflower oils are as good as canola or other vegetable oils, but for this application most vegetable oils could be used.

By lowering the content of unsaturated fatty acids or modifying minor components, such as tocopherols, stability of oils could be enhanced, making them suitable for deep frying and biolubrican use. Increasing the saturated fatty acids content will increase the proportion of solid fat and, therefore, its melting temperature. With the exception of animal fats, palm oil fractions and lauric oils, natural fats hardly fulfill the requirements of many industrial processes. Nevertheless, the above-mentioned fats are considered unhealthy by many authors and the World Health Organization [4] because of their high content in palmitic, myristic and lauric fatty acids These were substituted by hydrogenated vegetable oils but, the hydrogenation process generates *trans* isomers of unsaturated fatty acids now considered to be nutritionally undesirable. In general, dietary recommendations encourage the intake of unsaturated fatty acids, such as oleic and linoleic, with stearic acid the preferred saturated one [4].

High temperature

Standard sunflower oil has good properties for low temperature and general food applications (salad dressings, emulsions, *etc*.), but for high temperature applications and deep frying, oils with a lower content of polyunsaturated fatty acids are required, and high-oleic oils are preferred. As already stated the oil properties at high temperature also depend on the tocopherols; oils with higher content of γ- and δ-tocopherols are more stable than oils with a and β-tocopherols. On the other hand, margarine and plastic fat production demands oils with higher content of saturated fatty acids such as palmitic or stearic acids, preferably stearic because of the unhealthy effect of palmitic acid.

To test oil stability, thermo-oxidative treatments are usually carried out at 180°C for 10 h monitoring the increasing formation of polar and polymer compounds over time. In this regard, as shown in Fig. 1A, vegetable oils could be classified in three groups: (i) standard oils with a high content of polymerised TAG, up to around 17% at 10 h treatment; (ii) high-oleic sunflower and palm olein oils with around 10% of polymerised TAG after the same treatment; and (iii) the high-palmitic high-oleic sunflower oil with only 6% of polymerised TAG at the same time. This indicates that oils with the higher content of oleic and palmitic acids are the best for high temperature applications. Rejection levels of 12% of polymers have been recommended in current regulations for discarding used frying fats for human consumption. As a result, commodity oils, soybean, canola and standard sunflower oils must be rejected after 8 h at 180°C, while high-oleic sunflower could still be used after 10 h and the high-palmitic high-oleic oil would be even further from rejection.

Tocopherols as good antioxidant molecules are one of the minor components of sunflower oil with α-tocopherol (vitamin E) being the largest in commodity sunflower oil. New sunflower lines with modified contents of tocopherols have been obtained (Table 2). These new lines have been obtained from germplasm

Table 2. Tocopherol composition of oils extracted from modified sunflower lines.

Oil Type	Tocopherol composition (%)			
	α-T	β-T	γ-T	δ-T
Standard α-T	95	4	1	0
Medium β-T	50	50	0	0
High β-T	75	25	0	0
High γ-T	5	0	95	0
High δ-T	5	0	30	65

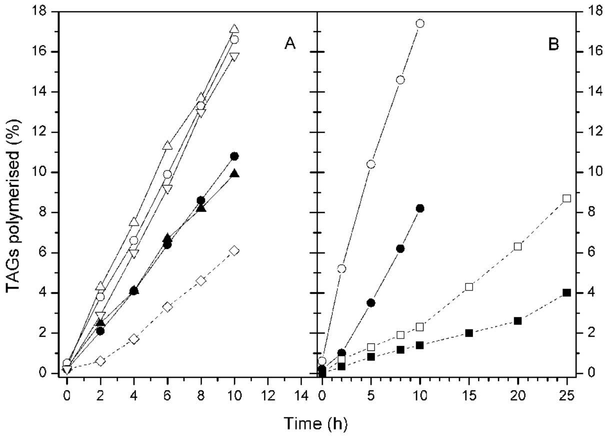

Figure 1. TAG polymerization at 180°C of vegetable oils. A. Soybean (△), canola (▽) and sunflower (○) are the standard commodity oils, palm (▲) is a commercial palm olein, high-oleic (●) and high-palmitic high-oleic (◇) sunflower oils are genetically modified sunflower oils. B. Standard sunflower oil (○), high-oleic (●), high-oleic high-palmitic oil containing a-tocopherol (□), and high-oleic high-palmitic oil containing γ-tocopherol (■).

of wild and cultivated sunflower. The tocopherols accumulated in these lines mainly depend on modifications on the genes that control the biosynthetic pathway. The oils containing γ-tocopherol and δ-tocopherol have the advantage of a higher oxidative stability but a reduced vitamin E content. As stated above, tocopherols could also modify the thermo-oxidative stability of the oils, and Fig. 1B shows the polymerised TAG at 180°C of genetically modified sunflower oils varying in their tocopherols [5]. Oils tested in this experiment were standard, high-oleic containing α-tocopherol, high-oleic high-palmitic containing α-tocopherol, and high-oleic high-palmitic containing γ-tocopherol. After 10 h at 180°C, standard and high oleic sunflower oils have 17.4% and 8.2% of polymerised TAG, respectively, while the high-palmitic high-oleic oils have only 2.3% and 1.4%. Furthermore, after 25 h of experiment the polymerised TAG in high-palmitic high-oleic oils were only 8.7% and 4% with less than 12% of total polymers and therefore still suitable for human consumption. These two high-palmitic high-oleic oils have very high oxidative stability; and the one with γ-tocopherol is the best showing always less than half of the polymerised TAG than the same oil with α-tocopherol – even after 25 h it was less polymerised than the standard sunflower after 2 h, making this oil extremely stable.

High-stearic high-oleic sunflower oils and also liquid fraction obtained from them by cold fractionation have good thermo-oxidative stabilities. These oils have a reduced content of polyunsaturated fatty acids, high content of oleic and some stearic acid. Experiments made to determine their oxidative stability have shown that the total amount of modified TAG in these oils after 10 h at 180°C is similar to the one observed in high-palmitic high-oleic oils with α-tocopherol.

For oils with high saturated content, which can be solid at relatively high temperatures, a new parameter must be defined, *i.e.* the cloud point or the temperature to which the liquid appears turbid. Oils with cloud point of above 0°C are difficult to transport and need special factory requirements. During transport and storage in winter the oil could become solid. Therefore, the preferred deep frying oils must have good oxidative stability and be liquid at least down to 0°C. The high-stearic high-oleic oils are very stable but they are solid at room temperature, and the high-palmitic oils are quite solid at temperatures between 0 and 10°C. However, high-oleic sunflower oil and olein fractions from high-stearic high-oleic sunflowers are probably the best oils for deep frying, particularly if they contain γ-tocopherol instead of α-tocopherol.

Confectionery fats

For the elaboration of some products the food industry needs solid or semisolid fats, whose traditional sources have been animal and some tropical fats, such as palm and lauric oils (palm kernel and coconut). Studies in human health have demonstrated that these fats are unhealthy due to their elevated contents of medium and long-chain saturated fatty acids (mainly myristic and palmitic acids). Their intake increases the plasma levels of low density lipoprotein (LDL)-cholesterol ("bad cholesterol"), which generates an increment in the risk of suffering cardiovascular diseases [4]. The effect of fats on the cholesterol levels depends on their fatty acid composition [6]. The relationship between plasma cholesterol levels and cardiovascular diseases is well-known. The ingested fatty acids modulate the lipoprotein levels (and therefore the type of cholesterol). In general, unsaturated fatty acids (oleic, linoleic, and linolenic acids) increase the high density lipoprotein (HDL) and diminish the LDL, for that reason they are considered healthy. On the other hand, saturated fatty acids (lauric, myristic and palmitic) increase both the LDL and the HDL and therefore the ratio LDL/HDL. But stearic acid – in spite of being saturated – does not have any effect on the cholesterol content [4]. The main reason for this is that stearic acid is transformed very quickly into oleic acid in the liver. In conclusion, it is possible to say that the ingestion of stearic, oleic or linoleic acid does not modify the profile of lipoproteins.

To solve the problem regarding the use of hydrogenated vegetable fat, animal fat or tropical fats, a research project was carried out with the aim of obtaining natural, semi-solid sunflower oils that could be used directly in the food industry for the production of margarine and similar products without the need for any chemical manipulation. New lines have been selected by classic methods, *i.e.* without the application of genetic engineering techniques, just the same as the high-oleic sunflower mutant. Sunflower lines having high-stearic acid content together with oleic or linoleic acids are a healthy alternative to these unhealthy fats. From a practical point of view, the comparison of the cloud points from standard (−8°C), high-oleic (−8°C) and high-stearic high-oleic (24°C) sunflower oils points to the last one as suitable for manufacture of margarine, spreads, bakery and other products were a plastic fat is needed.

The triacylglycerol composition of these new oils is different from those of the standard sunflower oil, making them appropriate for industry demands (Table 3; Fig. 2). High-stearic lines contain a considerable percentage of triacylglycerols with two saturated fatty acid molecules, EOE and POE (abbreviations as in Fig. 2, also see note with legend) being the most abundant species in high-stearic high-oleic oils, and ELE and PLE those in the lines with a high-linoleic background. These triacylglycerol species have mainly linoleic or oleic acids in the central position of the triacylglycerol, which makes them appropriate for the production of healthy margarines. With fats constituted by these types of triacylglycerol – keeping in mind the effect on cholesterol levels of these fatty acids besides the fact that they do not contain saturated acids in the central position of the triacylglycerol and following the recommendation of the World Health Organiation in its Technical Report Series 916: Diet, Nutrition and the Prevention of Chronic Diseases – it can be stated that a healthier margarine than existing ones can be manufactured from these oils.

Table 3. Triacylglycerol subclasses composition of standard sunflower (RHA-274), high-oleic (CAS-9), high-stearic high-linoleic (CAS-30), and high-stearic high-oleic (CAS-15) oils. SUS, disaturated triacylglycerols; SUU, monosaturated triacylglycerols; and UUU, triunsaturated triacylglycerols. S, saturated; U, unsaturated fatty acids.

TAG type	CAS-9	RHA-274	CAS-15	CAS-30
SUS	0.9	1.8	18.4	29.0
SUU	21.5	30.7	61.9	57.0
UUU	77.5	67.5	19.1	13.8

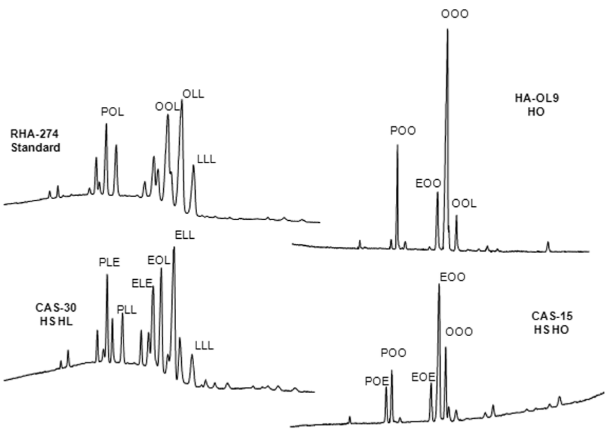

Figure 2. Triacylglycerols chromatograms of standard RHA-274, high-oleic HA-OL9, high-stearic CAS-3 and high-stearic high-oleic CAS-15 sunflower oils. P, palmitic; St, stearic; O, oleic; and L, linoleic fatty acids.

Non-food industrial uses

The price of sunflower oil usually prohibits its widespread use in industry, but several applications have been explored. That is the case of its use in the production of biodiesel and biolubricants. Biodiesel can be produced from any fat including sunflower oil through transesterification, but – as it has been commented – sunflower oil is priced at a premium to soybean and canola oils due to demand from the food processing industry making prohibitive its use as biodiesel.

Standard sunflower oil is rich in polyunsaturated fatty acids and therefore its thermal and oxidative stability is unsatisfactory for biolubricants. On the other hand, saturated triacylglycerols have poor low temperature properties. For these reasons, high-oleic sunflower oils provide acceptable oxidative stability, good low temperature properties, and good lubricating properties. The only consideration is that as base oil it is a good lubricant under mild conditions (*i.e.* lower temperature and lighter load) but under heavier loads, additives are necessary. Additionally, the use of sunflower oil as a pesticide carrier and in the production of paints, soaps and detergents, varnishes, agrichemicals, surfactants, adhesives, plastics, fabric softeners and coatings has been explored.

Conclusion

To sum up, these new sunflower oils with modified tocopherol and fatty acid composition developed as a feedback for the food industry requirements to offer healthier products, and the two commodity oils available nowadays (normal and high-oleic sunflower oils) can cover the requirements of the food industry without chemical manipulation with the aim of increasing the consumers' quality of life.

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