Tocopherols as a Quick Mean to Identify the Origin of Vegetable Oils

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ABSTRACT: The vast numbers of studies and research works have been carried out concerned with various methods to identify and detect the origin of vegetable oils. Although all have been approved and applied but due to time and economical constraints a quick and fast procedure is required. In this preliminary study tocopherols identification by High Pressure Liquid Chromatography might be considered as a method to be adopted. Commercial vegetable oils (sesame, olive, maize, canola, sunflower, soyabean) were sourced from the local industries and tocopherols contents were determined by the application of HPLC. The results indicated that the method might be considered as a reliable fast method however other methods namely determination of fatty acids and triglyceride profiles and sterol composition might be required for firm identification of oils that might have very similar tocopherol specifications and composition.

Keywords: Nonsaponifiable Matters, Tocopherols, Tocols, Vegetable Oils.

Introduction

The production of agricultural produce in particular vegetable oil seeds and seeds that produce protein concentrates have been increasing due to the increase in consumer demand. Oil seeds play an important role in agriculture product and large fields of fertile fields are dedicated to these crops. Since oils play a major role in agricultural produce and consequently affect the economy of countries, they might be susceptible to fraud and adulteration.

Originally Iodine, saponification values followed by fatty acid profiles were employed to identify the origin of the oils in question (Ghiassi Tarzi *et al.*, 2006). The method is quite reliable but takes a long time for methylation of fatty acid followed by the injection of the sample to an advanced gas chromatography equipped with a polar capillary column (quite expensive) and flame ionisation detector and realising that some oils namely olive and hazelnut oils have very similar fatty acid profiles.

Sterols have also been exercised and applied as a method to identify the origin of the oils. The method is quite successful but requires times for isolation of matter nonsaponifiable followed by fractionation of different classes of compounds on thin layer chromatography and isolation of sterols and finally injection to a GC equipped with semi nonpolar capillary column (quite expensive) and flame ionisation detector according to Itoh et al. (1973). Firm identification is made by comparing the Relative Retention Time to pure standards.

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Other fractions in the nonsaponifiable matter namely 4- methyl sterols and triterpene alcohols might also play important roles in the identification of the oils but due to various complications regarding these two fractions, the methods might not be recommended for the routine applications (Itoh *et al.*, 1973, 1974).

The nonsaponifiable matter by itself if fractionated on TLC professionally might identify the oil if pure standards of classes of compounds present in the nonsaponifiable matter is provided to some points according to Ghavami *et al.* (2008).

Therefore, the object of this research work is to identify the origin of the oil by a simple, quick and inexpensive method, therefore concentrating on tocols qualitative and quantitative identification.

Materials and Methods

- Materials

Crude soyabean, maize, sesame, canola, olive and sunflower seed oils were obtained from local vegetable oil refineries. All the chemicals consisting of solvents and others with analytical grades were purchased from Merck's Chemical Company. Fatty acid methyl esters, sterols and tocopherol standards were provided as a gift from a firm representing some chemical companies in Iran.

- Methods

Fatty acid methyl esters were prepared by interesterification procedure using sodium methoxide as an alkaline catalyst and finally injection to a gas chromatography apparatus equipped with CPSill 88 capillary column and flame ionisation detector according to Ghavami *et al.* (2008). Firm identifications were made by comparing the relative retention times of peaks and standards.

The nonsaponifiable matter of the oils were obtained by alcoholic potassium hydroxide saponification of the oils according to Ghavami *et al* (2008). The nonsaponifiable matter was fractionated into different classes of compounds on thin layer chromatography plates and sterols were isolated as described by Ghavami *et al.* (2008). The sterol fraction was injected to a GC apparatus equipped with SE54 capillary column and flame ionisation detector. Firm identifications were made by comparisons of relative retention times with standards.

Tocopherols were qualitatively and quantitatively determined by the application of the prepared sample to a High Pressure Liquid Chromatography as described by Ghavami *et al.* (2008).

Results and Discussion

Table1 presents tocopherol contents of crude oils investigated. The oils that have been chosen for this research work are the popular oils consumed by the majority of consumers. Some oils namely olive oil contains only alfa tocopherol in high concentration with traces of others. If gama and delta tocopherols are present at even low concentrations, that proves some kind of doubt concerned with adulteration. Soya bean oil has high concentrations of gama followed by delta tocopherols and low quantity of alfa tocopherol. The presence of these and taking into account the ratios of tocopherols one to another can prove the originality of soyabean oil. Sesame oil having high concentration of gama tocopherol with low or even trace concentrations of others, therefore the presence of this tocopherol can prove the originality of this oil. Sunflower seed oil and olive oil both have high concentrations of alfa and insignificant concentrations of other tocopherols. Even the fatty acid composition in the case of high oleic acid sunflower seed oil might not provide a firm identification.

Tables 2 and 3 present fatty acid and sterol compositions of the oils investigated. Therefore, in this case where sunflower seed oil of high linoleic acid is in the investigation, the fatty acid composition with sterol and tocopherol profiles can provide a firm identification of the originality. Considering canola and maize oils where gama tocopherol is the tocopherol predominant with lower quantities of others, fatty acid composition regarding the presence of linolenic acid in the case of canola and sterol profile with respect to the presence of brassicasterol in the case of canola provide a firm identification. Therefore, a combination of methods as mentioned earlier can provide a firm identification. A combination of methods might be time consuming and expensive. Therefore, tocopherol determination both qualitatively and quantitatively has proved to be considered as a firm method of determination for some oils in question such as olive oils.

Table1. Tocopherol contents of crude maize, sesame, olive, canola, soya bean and sunflower seed oils (ppm)

Oils	Maize	Sesame	Olive	Canola	Soya bean	Sunflower seed oil
α Tocopherol	168	Tr	450	272	80	580
β Tocopherol	Tr	Tr	Tr	Tr	Tr	Tr
γ Tocopherol	568	949	Tr	558	550	Tr
δ Tocopherol	73	Tr	Tr	32	300	Tr

Tr < 10 ppm

Table 2. Common fatty acid composition of crude maize, sesame, olive, canola, soya bean and sunflower seed oils (% of total fatty acid)

Oils	C _{16:0}	C _{16:1}	C _{18:0}	C _{18:1}	C _{18:2}	C _{18:3}
Maize	8.5	0.5	5.0	22.0	64.0	Tr
Sesame	10.0	0.5	6.0	39.5	43.5	0.4
Olive	8.0	0.5	4.5	77.0	10.0	Tr
Canola	3.5	0.5	2.5	67.0	20.5	6.0
Soya bean	10.5	1.0	3.5	25.0	52.0	8.0
Sunflower seed oil	6.5	0.5	5.0	21.5	66.5	Tr

Tr < 0.1 %

 Table 3. Common sterol composition of crude maize, sesame, olive, canola, soya bean and sunflower seed oils

 (% of total sterols)

Oils	Cholesterol	Brassicasterol	Campesterol	Stigmasterol	Apparent β-sitosterol
Maize	Tr	Tr	20.0	8.0	72.0
Sesame	Tr	Tr	18.0	12.0	70.0
Olive	Tr	Tr	3.5	1.5	95.0
Canola	Tr	12.0	31.0	1.0	56.0
Soyabean	Tr	Tr	21.0	19.0	60.0
Sunflower	Tr	Tr	12.0	11.0	78.0

 $Tr < 0.5 \ \%$

Apparent β -sitosterol consists of β -sitosterol, Δ^5 - avenasterol, Δ^7 – avenasterol and Δ^7 – stigmasterol and other minor sterols after β - sitosterol peak.

Conclusion

Many methods and procedures are available to identify the originality of an oil in question. However, the methods to apply are time consuming and costly. Therefore, tocopherol identification and quantification might be regarded as a preliminary and quick method to identify and filter the oil in question. However, some complications might originate in respect of some other oils where other means namely sterols, fatty acid compositions and triglyceride profile procedures might be applied.

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