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DETECTION OF ADULTERATION OF VEGETABLE OILS WITH RAPESEED OIL BY GAS LIQUID CHROMATOGRAPHY

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Abstract

Gas liquid chromatography (GLC) was used for the detection of rapeseed oil added to olive oil, corn oil and cottonseed oil. The chromatograms of the unsaponifiable matter could be divided into two parts representing hydrocarbons and sterols. Squalene as hydrocarbon, brassicasterol, campesterol and B-sitosterol as sterols , also the ratio of TH/Ts were used for the detection of adulteration of olive oil with rapeseed oil. In fatty acid analysis, oleic acid, linoleic acid and the ratio of O/L, also linoleic to total unsaturated ratios were used as a safe criterion for eventual adulteration of corn oil and cottonseed oil with rapeseed oil.

INTRODUCTION

In Egypt, there is a great shortage in edible oils and large amounts are annually imported to cover such deficiency in the local market. Cottonseed oil, sunflower seed oil, corn oil and olive oil are the common vegetable oils used for cooking and frying, but recently , due to less supply than the demand , these oils have been replaced gradually by other vegetable oils of lower commercial price, such as rapeseed oil and Soybean oil.

Two general types of rapeseed oils are recognized, the traditional rapeseed oil of high erucic acid content (20-55%) and I erucic acid type (0-5%) Sonntage, 1979).

Adulteration of oils and fats is a continuing problem for law enforcement and

commercial quality control laboratories. The detection of adulteration of rapeseed oil of high erucic acid vegetable oils could be achieved by the fatty acids levels correspond to erucic acid contents. Several methods have been proposed the detection of adulteration of oils , such as the fatty acid codition (Imai *et al.,* 1974 and Rossell *et al.*, 1983) , by a comination of column chromatography and (GLC) Kapoulas and Passale Emmonuouilidou, 1981), by fractional crystallization and GLC (SVrettakous *et al.,* 1984) , by aid of sterols and / or hydrocarbon composition (Eisner and Firestone, 1963; Imai *et al.,* 1974), and by the determination of the specific exting cofficient in the ultraviolet (U.V.) (IOOC, 1984; Firestone *et al.,* 1985)

In this investigation , gas liquid chromatography was applied for the detection and identification of both unsaponifiable matter and fatty acids so as to detect the adulteration of olive, corn oil, and cottonseed oil with low erucic acid rapeseed oil.

MATERIALS AND METHODS

Olive oil was obtained from Vineyards Company (Gianaclis Alexanderia), while corn oil was obtained from Alexanderia Oil and soap company. Refined cottonseed oil was obtained from Cairo Oil and Soap Company, El - Ayate - Giza.

Rapeseed (Brassica napus) , west german variety AD - 201 GI, was kindly offerred by Agronomy Department , Faculty of Agriculture, Cairo University . This oil swas extracted by n- hexane.

The adulterated olive oils with rapeseed oil were prepared in the laboratory, the levels of rapeseed oil were 5,10,20 and 40% in the final oil samples. Similarly adultration of corn oil and cottonseed oil with rapeseed oil were prepared.

The unsaponifiable matter of pure and adulterated oils were deremind as described in A. O. A. C. (1980) The methyl esters of fatty acid samples were prepared as described by anon (1966) . Gas liquid chromatograph apparatus (Pye- Unicam model 104) was used for the identification of the fatty acid methyl esters and the unsapoinfiable compounds. The conditions used were identical to those reported by El - Agaimy *et al* . (1989).

RESULTS AND DISCUSSION

Detection of adulteration of olive oil with rapeseed oil :

The composition of the unsaponifiable portion of olive oil, rapeseed oil and admixture samples is shown in Table 1. The unsaponifiable fractions were separated by GLC into 10-22 compounds depending upon the oil origin. It is clear from these data that the unsaponifiable matter compsition differs widely among both olive and rapeseed oils . Olive oil is characterized by a higher percentage of hydrocabons (69.57%) compared to rapeseed oil which charac by a higher percentage of sterols (91.0%) . These results are confirmed by the findings of many investigators (Bas-

Table 1. Contents of unsapohifiable matter of olive oil , raspeseed oil and admixture samples.

Components	RRT*	Olive oil Repessed oil	100 0	95 5	90 10	60 40	0 100
C_{18}	0.45		0.10	-	-	-	-
C_{19}	0.47		0.09	-	-	-	-
C_{20}	0.49		0.20	0.10	-	-	-
C_{21}	0.51		0.05	0.05	1.80	1.90	4.30
C_{22}	0.55		4.10	3.90	3.30	2.50	-
C_{23}	0.61		0.03	-	0.90	2.40	3.80
C_{24}	0.63		0.95	0.90	0.70	0.70	0.20
C_{25}	0.67		0.20	0.20	0.10	-	-
C_{27}	0.71		0.20	0.20	0.10	0.10	0.20
C_{28}	0.75		0.60	0.60	-	0.20	-
C_{29}	0.78		1.30	1.30	1.2	-	-
Squalene	0.80		-	-	0.25	0.30	-
C_{31}	0.81		-	-	-	-	0.20
C_{32}	0.82		60.40	57.85	55.45	36.3	0.20
Tocopherol	0.84		0.40	0.45	-	0.60	0.10
Cholesterol	0.85		0.95	0.95	0.20	0.30	-
Jrassicasterol	0.87		0.12	0.10	-	-	-
Campesterol	0.99		0.20	0.20	0.10	-	-
Stigmasterol	0.91		0.20	0.60	1.30	5.60	12.50
B-sitosterol	0.94		0.20	1.35	3.35	11.85	28.20
$\blacktriangle^5$ - Avenasterol	0.97		0.60	0.50	0.30	0.10	-
$\blacktriangle^7$- Stigmasteral	1.00		26.00	27.50	28.2	35.90	20.30
$\blacktriangle^7$ - Avenasterol	1.03		-	0.30	0.10	-	-
	1.06		2.90	2.30	2.30	1.55	-
	1.10		0.21	0.20	1.50	–	-
TR			69.57	56.45	52.95	45.0	9.0
TS			30.43	33.55	37.05	55.0	91.0
TH/TS			2.29	1.98	1.70	0.82	0.10

tic *et al.*, Ackman and Sebedio, 1981, and Mohamed. 1989).

The unsaponifiable components of olive oil composed 69.57% hydrocarbons mainly squalene (60.4%), followed by another hydrocarbon compound of lower percentage , i. e. C22 (4.1%) As for sterol compounds of olive oil, B- Sitosterol represented 26.0% and ▲ 7 stigmasteral represent 2.9% . These results agree with those reported by Bastic *et al* .(1978) , Firestone *et al* . (1985) and Khalil et al. (1990) . For the unsaponifiable matter compounds of rapeseed oil it could be shown that C21and C 23 were the main hydrocarbons and amounted to 4.3% and 3.8% respectively , Results also showed that B-sitosterol was the major sterol, not only among sterol fraction but also in the unsaponifiable matter compounds of rapeseed oil , it represented 50.3% followed by campesterol and brassicasterol which amounted to 28.2% and 12.5% respectively, These results coinside with those reported by ABastic *et al.*(1978) and Mohamed (1989) who observed that B - sitiosterol repesented 36.1-52.3% while camp esterol and brassicaterol represented 27.0-2371.2% and 9.1- 11-7% rrespectively of the unsaponifiable matter in rapeseed oils.

Addition of different concentrations of rapeseed oil , i. e. 20,40% to the olive oil caused noticeable changes in the unsaponifiable fraction as seen in Table 1. The percentagee of squalene was found to decrease, to the contrary , B - sitiosterol percent increased gradually with increasing the level of rapeseed oil in olive oil . Also , this led to an increase of certain sterols , campsterol and brassicasterol. In olive oil , unsaponifiable fraction contained traces of these sterols , while unsaponifiable fraction of rapeseed oil contained 28.2% and 12.5% respectively. This might be helpful in detecting any addition of rapeseed oil , even at as low as 5% in the olive oil.

Total hydrocarbon / total sterols TH/TS ratio showed a gradual decrease with increasing rapeseed oil percentages added to olive oil . It was 2.29 for olive oil , and decreased to 1.98 , 1.70 , 1.33, 0.82 and 0.10 when the rapesed oil added at theleve of 5% , 10%, 20%, 40%, and 100% respectively. Therefore, it is useful to use this ratrio (TH/ TS) to detect the adulteration of olive oil with rapeseed oil , since it showed a great variation with the addition of rapeseed oil to olive oil at any level.

Detection of adulteration of corn oil with rapeseed oil :

From results in Table 2 , it was observed that the fatty acid composition of

corn oil showed 17.9% as total saturated fatty acids and 82.1% as total unsaturated fatty acids. Palmitic acid represent the major saturated fatty acid , which amounted to 14.9%. Among the unsaturatd acids, linoleic acid was the major fatty acid in corn oil which represented 47.45% followed by oleic acid (amounted to 34.2%) . Such results agree with those reported by Egan *et al* . (1981) and El - Agaimy *et al.* (1989) . As for the fatty acid composition of rapeseed oil , Table 2 showed that total saturated and total unsaturated fatty acids ,were 5.1% and 94.9% respectively. Palmitic acid represented also the major saturated acid (3.2%) . However unsaturated fatty acid were composed maninly of oleic i.e. 70.5% followed by linoleic 17.6 % , lionlenic 5.7% and erucic acid (1.1%) . Such results agree with those mentioned by Farag *et al.* (1986) . El - Khawas (1988) and Mohamed (1989).

Remarkable peculiarities were observed in oleic and lionle acid percentages in adulterated corn oils with rapeseed oil. Thus oleic/linoleic (O/L) acids ratio showed noticeable•changes when corn oil was mixed with any percent of rapeseed oil . Althoug this ratio was 0.72 for pure corn oil, it increased by 8.3%, 17.0% , 39.0% and 91.6%, (it increased to 0.78, 0.84, 1.00 and 1.38%) after addition of 5, 10,20 and 40% of rapeseed oil respectively.

Result in Table 2 indicated also that the ratio of linoleic acid to total unsaturated fatty acid (L/TU) showed another criterion which can be used for the detection of adulteration of corn oil with rapeseed oil , since it showed a continuous decrease with increasing rapeseed oil percentages in, corn oil , it was 0.58 and decreased to 0.56, 0.53, 0.49, 0.40 and 0.18 after addition of 5, 10, 20, 40 and 100% rapeseed oil.

Detection of adulteration of cotton seed oil with rapeseed oil :

The data of Table 3 show the fatty acid composition of cottonseed oil and adulterated samples with rapessed oil, results show that the fatty acids of cotton seed oil had 24.8% total saturated and 75.2% total unsaturated fatty acids. Palmitic acid reperesented the major saturated fatty acid (21.5%) , while linoleic acid was the major unsaturated fatty acids (52.5%) , followed by oleic acid (21.7%) . Such results are in agreement with Synouri - Vrettokous *et al.* (1984) and Mohamed (1989) . On the contrary rapeseed oil contained 70.5 % oleic acid and 17.6% linoleic acid, thus , changes in the O/L values could be used as reliable index for detecting the presence of rapeseed oil in cotton seed oil up to 5% since the value in pure cottonseed oil was 0.41 and increased by 14.6% , 29.3%, 65.8% and 153.6% (it in-

Table 2. The fatty acid composition of corn oil, rapessed oil and their mixture samples (%).

Corn oil 2	Resessed oil 2	C_{12}	C_{14}	C_{16}	$C_{16:1}$	C_{17}	C_{18}	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	C_{20}	$C_{22:1}$	Ts Tu Ts/Tu	O/L	L/Tu
100	0	0.15	0.80	14.9	0.45	-	2.05	34.20	47.65	-	-	-	17.90 82.10 0.22	0.72	0.58
95	5	0.15	0.80	14.4	0.45	-	2.00	35.80	66.10	0.25	-	0.05	17.33 87.65 0.71	0.78	0.56
90	10	0.12	0.70	13.22	0.33	0.30	1.80	37.40	44.70	0.70	0.10	0.11	16.74 83.26 0.20	0.84	0.33
80	20	010	0.60	12.60	0.33	0.40	1.60	41.1	41.18	1.30	0.27	0.20	15.57 48.43 0.18	1.00	0.49
60	40	0.05	0.55	10.30	0.20	0.45	1.00	68.6	34.10	2.80	0.50	0.45	12.83 87.15 0.15	1.38	0.40
0	100	-	0.20	3.20	-	0.45	-	70.50	17.60	3.7	1.25	1.10	5.1 94.9 0.05	4.00	0.18

Table 3. The fatty acid composition of cotton seed oil , rapessed oil and their mixture samples (%).

cotton seed oil 2	Rapessed oil 2	C_{12}	C_{14}	C_{16}	$C_{16:1}$	C_{17}	C_{18}	$C_{18:1}$	$C_{18:2}$	$C'_{18:3}$	C_{20}	$C_{22:1}$	Ts Tu Ts/Tu	O/L	L/Tu
100	0	0.50	0.30	20.50	0.50	-	2.30	21.7	92.30	0.30	-	-	24.8 75.2 0.33	0.41	0.70
95	5	0.50	0.30	20.50	0.50	-	2.33	24.14	30.90	0.76	0.03	-	23.65 76.35 0.31	0.41	0.67
90	10	0.40	0.30	19.60	0.40	0.10	2.70	26.60	49.07	1.30	0.13	0.10	22.65 77.55 0.29	0.33	0.63
80	20	0.40	0.23	17.05	0.40	0.13	7.00	31.30	46.00	1.33	0.23	0.20	20.55 79.49 0.26	0.61	0.38
60	40	0.20	0.20	14.10	0.20	0.20	1.30	40.90	39.20	2.60	0.60	0.30	16.60 83.40 0.20	1.04	0.47
0	100	-	0.20	3.70	-	0.43	-	70.50	17.60	3.70	1.25	1.10	5.10 9.9 0.05	4.00	0.81

creased to 0.47, 0.53, 0.68 and 1.04%) for 5,10,20 and 40% rapeseed oil samples respectively . Imai *et al.* (1974) reported that for adulterated cottonseed oils with high erucic rapeseed oil , erucic acid was remarkable as the evidence of adulteration and about 5% rapeseed oil in cottonseed oil could be detected.

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كشف غش الزيوت النباتيه بزيت اللفت باستخدام التحليل الكروماتوجرافي الغازي السائل GLC

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اجريت هذه الدراسه علي كل من زيت الزيتون – زيت الذرة– زيت بذره القطن وزيت اللفت المنخفض في حمض الايروسيك ١٪ وذلك لغرض كشف وجود زيت اللفت في الزيوت النباتيه المذكورة وقد استخدم التحليل الكروماتوجرافي الغازي السائل GLC لتحليل المواد الغير متصبنه والأحماض الدهنيه . وقد اتضح أن المواد غير المتصبنه يمكن تقسيمها الي جزئين وهما الهيدروكربونات والاستيرولات. ومن الهيدروكربونلتسات– الاسكوالين ومن الاستيرولات مركب البراسيكاستيرول – الكامبستيرول والبيتاستيوستيرول. وكذا نسبه مجموع الهيدروكربونات الي مجموعه الاستيرولات (TH/TS) أمكن استخدامها في كشف غش زيت الزيتوت بزيت اللفت وبتحليل الاحماض الدهنيه لوحظ أنه يمكن استخدام حامض الأوليك واللينوليك ونسبه حمض الاوليك الي حمض اللينوليك O/L وكذا حمض اللينوليك الي مجموعه الاحماض الدهينه الفير مشبعه كمقياس سليم لكشف غش زيت الذره وزيت بذره القطن بزيت اللفت.