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An evaluation of physicochemical parameters of some wild olive oil varieties in Syrian Coastal Territory

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ABSTRACT

In this study two wild cultivars of olive oil from Banyas and Masyaf in Syria were physically and chemically detected. Large areas of Syria mountainous and forestry territories are not properly exploited. Findings demonstrated the significant differences in terms of sensory attributes (color, taste) and chemical profile (chemical parameters acidity value, free fatty acid ratio, saponification number, ester value, peroxide value) of oils extracted from olives from Banyas and Masyaf. Fatty acid composition of these oils were analyzed using Gas- Chromatographic Technique. Gas chromatography analyses varied according to oil extracts of oil of different quantities ranged from 10.75 to 11.62% for wild olive and from 14.38 to 17.24 % for domesticated olive from Masyaf and Banyas, respectively. Furthermore, the Variety and number of structural fatty acids of oleaster cultivar oil accounted ranging from 7 to10 in Banyas wild olive oil and from 5 to7 in Masyaf wild olive oil. Besides, polyunsaturated fatty acids increased at expense of the saturated fatty acids in olive fruit collections sampled.

Keywords: Oleaster cultivar olive, Domesticated cultivar olive, Morphological characters, Physicochemical characters, GC technique.

1. Introduction

Olive tree was considered a sacred tree, a symbol of peace and spring of resources. It was affirmed that olive tree is native to Mediterranean region (Syria, Lebanon, Palestine) from where it spread to worldwide [1]. The range of olive farming is restricted to Mediterranean countries which are located between latitudes 25 north and 45 south [1]. Despite olive can grow in different corners of the world, it yields abundantly in places of Mediterranean or semi Mediterranean climates these places are considered optimal for olive farming [2].

In Syria, the olive sector is very important for the economy of the country. Many new olive orchards have been planted in recent years (about 57% of the olive trees in Syria are less than 20 years old) and Syria is now the fourth largest olive oil producing country in the world (http://www.rayanoliveoil.com).

Olive tree is of dicotyledonous perennial evergreen plants. It belongs to Oleacea family which comprises of 25 genera and 500 species of *Olea europea*. There are three sub species the most important of them is Euro-Mediterranean sativa known as cultivated olive tree which has large number of improved cultivars reproduce vegetatively or by grafting. A well-known species *Sylvestrisor oleaster* is also called Oleaster or wild olive which grows spontaneously in form of thorny shrubs with small size fruits such these shrubs are wide spread in Spain, Portugal, Moroccan countries, Sicily, Caucasian region and in Syria [3, 4]. Syria is part of the original habitat of olive and has a very rich germoplasm. There are more than seventy varieties of olive cultivated in the different areas of the country. However, only a few varieties have been extensively cultivated; in fact, five cultivars, Zaity, Sourani, Doebli, Khoderi and Kaissy, represent about 90% of the total olive trees cultivated in Syria. The others are local varieties that have a limited distribution.

To date, very few studies have evaluated the morphological, phenological, bio-agronomical and productive characteristics of Syrian olive varieties and very little has been done to assess the characteristics of their oils) and to characterize their genetic variability by using molecular markers More information about these aspects is needed in order to: identify the different cultivars and possible clones present in Syria; choose the best varieties for the establishment of new olive orchards; carry out programs for the genetic improvement of olive; develop procedures for certifying the genetic identity (variety) and sanitary state (absence of diseases and pests) of plants produced in nurseries, and other countries where olive is cultivated; characterize the quality of olive oils produced in Syria and determine if they meet the quality standards demanded by the international market [6, 7, 8].
Despite great success achieved in producing animal and plant oils of sunflower, soya bean, and turnip, olive oil still tops these products due to its edibility, nutritional value and sensory characters. It's extracted without any chemical treatment [9].

In the Mediterranean region, olive oil is the main source of fat of the diet mainly because of its use without refining which attribute it distinguishable characteristics such as: aroma, taste, color and nutritive properties than other vegetable oils. Moreover, its healthy, interesting nutritional and sensorial properties have been known for a long time. The sensory quality and health properties of virgin olive oil stem from a prominent and well-balanced chemical composition [10, 11]. On the other hand, the quality of oil is influenced by the time of storage [13].

The content of fatty acids of fatty acids is influenced by many factors according to some oil researches and listed as follows: cultivar 15%, maturity 3%, squeezing technique 20%, the way of collection 10%, period separating between collection and squeezing 20%. Also the content of some fatty acids such as Oleic and Linoleic acids is influenced by conditions of farming and climate [14, 15].

In fact, the high content of oleic acid in olive oil serves to slow down penetration of fatty acids into arterial walls Oils which are much higher in monounsaturated fatty acids and lower in saturated fatty acids are preferred because of the proven beneficial effect of on serum cholesterol levels. The biological properties of olive oil are also related to the presence of minor components such as antioxidant compounds, particularly [11, 16].
Keeping in the view the facts given above present study was undertaken with following aim and objectives:

i. To comparatively study the morphological characters of wild and local cultivars of olive from two different climate cities in Syria Banyas (coastal) and Masyaf (mountainous).
ii. To evaluate physicochemical properties of oil extracted from wild olive to be utilized in different sectors of economy and industry in comparison with domesticated(local)oil in the studied sampling regions

This research was carried out at labs of school of agriculture in Tishreen University during season of 2010-2011.

2. Material & Methods

2.1 Materials: Olive samples: fruits of olive of two cultivars domesticated (local) and wild obtained from Banyas- a coastal city and Masyaf –a mountainous city.

2.2 Chemicals and reagents: Hexane, Potassium hydroxide, Phenolphthalein, Ethanol, Toluene, Ether, Sodium hydroxide, Hydrochloride, Pyridine, Acetic acid and Methanol.

2.3 Instruments: Oven, Soxhlet, Incinator, Rotary evaporator, porcelain mortar, balance, desiccator, Erlenmeyers, funnels, Gas chromatography (Shimadzu 14B mode, equipped with glass column, spectrophotometer (Cintras mode)

2.4 Analytical methods:

A. Physicochemical analyses of olive fruit:
Up to hundred olive fruits of the studied samples were weighed, then moisture content, oil material percentage, and ash ratio were measured.

B. Physicochemical analyses of olive oil:
Comprise acidity, ratio of fatty acids, values of saponification, Esterification, peroxide in addition to elucidation of fatty acids which may be found in oil using GC [14, 17].

3. Results & Discussions

3.1 Wild olive tree properties

3.1.1olive fruit (drupe) characteristics

Fruit color: verifies according to olive cultivar .The color develops from yellowish white, violet spotted, brown and from then black at the stage of maturity which may take time depending on the variety so that when fruits are squeezed by hand the juice almost turns violet.

- **Shape of fruit:** Spherical to elongated spherical, symmetry was determined by the extent to which the two longitudinal halves match symmetric, slightly symmetric or a symmetric.
- **Size and weight of olive fruit:** generally medium in size and its weight ranged from 2-4g.
- **Maximum diameter of olive fruit:** a line extends from the apex towards base of olive fruit. The diameter of olive fruit sample reached 1cm.
- **Shape of fruit apex:** ovoid (semi-convex)
- **Shape of olive stone (kernel):** elliptical and asymmetric, the number of grooves ranged from 4-6.

3.1.2. Leaf shape:

Morphological features of wild olive leaves are distinguished from those of consumed olive cultivars

- **Shape:** Ovoid
- **Curvature:** Flat
- **Surface area:** Very narrow and about 3 cm^2
- **Color:** Dark green and sometimes yellowish spotted

3.1.3 General morphology of olive tree: Orthotropic, branching. The morphology and the growth of olive tree vary depending on olive cultivars.

3.2. The properties of olive fruit samples:

The properties of olive fruits and the extracted oil were evaluated analytically. Olive samples were collected from two types of wild olive trees from different regions (mountainous and coastal cities. Comparing those two cultivars with two local olive trees in same areas of sampling. Four trees of each cultivar were allocated (labeled) in Banyas and Masyaf orchards as experimental field of wild and local cultivars provided with safety conditions and protection means against lesions, insect or other infection as shown in Table 1.1 kg of sample was collected from each labeled tree at four sampling times; at the beginning and in the end of month

within two months (November-December, 2010-2011) explains the area and cultivars of studied olive fruits

Table 1: Explains the area and cultivars of studied olive fruits

Olive cultivar	Samping area
Sourani	Banyas (Al-anaza)
Oleaster	Banyas (Al-anaza)
Doebli	Masyaf (Der shmel)
Oleaster	Masyaf (Der shmel)

3.3 Physicochemical evaluation of olive samples:
3.3.1 Morphological characters of olive samples:

The samples of wild olive fruits that were obtained from Banyas orchards were small in size, weight ranged from 0.3-0.6 g per piece. Their color was yellowish green and the length ranged from 0.5-1.2 cm with diameters from 0.3-0.8 cm. While wild olive fruit taken from Masyaf orchards of medium size and with weight ranged from 1.2-2.2 g and colored in violet. Its length ranged from 0.8 -1.7 cm and with diameters ranged from 0.6-1.4 cm. Samples of domesticated (local) olive fruits were of Sourani cultivar. The shape of fruit was elongated and colored in pale green. While the shape of fruit of Doebli cultivar was spherical or even flattened and colored in dark green.

3.3.2 Average weight of olive samples:

Samples of 100 olive fruits were weighed in order to calculate the mean average weight of one piece of olive fruit. Random samples of olive fruits of different weights were taken and weighed accurately. From fixed number of olive fruits per sample of four collections. The average weight of one piece of fruit was calculated and the results were as shown in Table 2

Table 1: Explains the area and cultivars of studied olive fruits

Olive cultivar	Samping area
Sourani	Banyas (Al-anaza)
Oleaster	Banyas (Al-anaza)
Doebli	Masyaf (Der shmel)
Oleaster	Masyaf (Der shmel)

Table 2 shows the differences in size and weight of olive fruits whether of domesticated (cultivated) or of oleaster cultivars. It's obvious that the two cultivars collected from two areas are different in weight and –weight of oleaster olive fruits samples from Masyaf was two folds of their counterparts collected from Banyas Sourani olive fruits. It should be taken into consideration that weight is related to the yield of tree, rainfall, fruit cultivar, and kinds of cultivations.

3.3.3. Moisture content:

Flesh of olive fruits was gently mashed and placed in a previously weighed evaporating crucible. Moisture content was then determined by drying the flesh in an oven at 105 °C for 3-4 hrs until complete desiccation. The findings were as shown in Table 3.

Table 3: Moisture Content in Olive Fruits

Olive cultivar	Samping area	Mean average moisture content % of 4 collections (gm)
Sourani	Banyas	48.451
Oleaster	Banyas	39.103
Doebli	Masyaf	56.617
Oleaster	Masyaf	58.638

It's noticed from the finding that moisture content is higher in Masyaf olive fruits comparing to that from Banyas whether of domesticated or oleaster cultivars. Despite precipitation and humidity are higher in Banyas than other regions oleaster olive fruits from Banyas contain higher ratio of dry matter.

3.3.4 Oil content:

Oil and fatty acids were determined in olive fruit samples by Soxhlet extraction using hexane as an organic solvent. In the end of extraction the resulted miscela was filtered to remove tiny impurities. Then the filtrate was rotavapored to separate most of solvent and the resulted oil was weighed thereafter. The ratio of oil content was calculated from the following equation.

Oil content=oil weight /fruit weight x100

The indicated findings explains the average content of four collections as shown in Table 4.

Table 4: Mean average of oil content of 4 olive fruits collections

Olive cultivar	Sampling area	Mean average oil content
Sourani	Banyas	17.235
Oleaster	Banyas	11.618
Doebli	Masyaf	14.377
Oleaster	Masyaf	10.749

Findings in Table 4 and Figure 1 show that olive fruits from Banyas contain higher oil content than olive fruits from Masyaf whether Oleaster or Domesticated (local) cultivars.

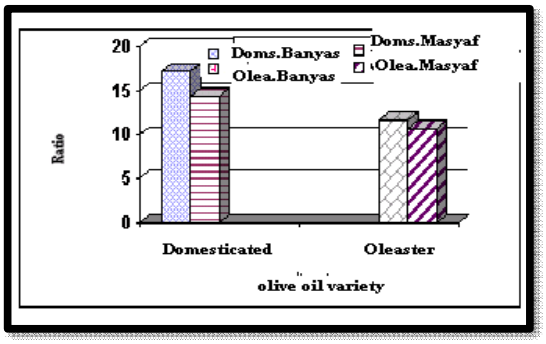

Fig 1: Oil ratio in olive fruit samples

3.3.5. Ash content:

Ash content in olive fruit samples was determined using drying method which is based on organic matter ashing to a constant weight in incinerator at temperature degrees range from 650-700 °C. Ash content was then calculated and the findings were as shown in Table 5.

Table 5: Ash content of olive fruits

Olive cultivar	Sampling area	ash content %
Sourani	Banyas	0.933
Oleaster	Banyas	1.137
Doebli	Masyaf	1.092
Oleaster	Masyaf	0.995

It's noticed from the findings shown in table 5 that Oleaster cultivar olives from Banyas contain higher ratio of minerals in comparison with other oils. Hence the effect of ash content on the quality of the extracted oil can be concluded.

3.4. Physicochemical specifications of the extracted olive oil

3.4.1. Sensory characters

Sensory characters (color and taste or palatability) for the extracted oil were detected and the findings were listed in Table 6.

Table 6: Sensory characters of the extracted oil

Olive cultivar	Sampling area	color	taste
Sourani	Banyas	green	light
Oleaster	Banyas	greenish yellow	light
Doebli	Masyaf	oily green	bitter
Oleaster	Masyaf	gold yellow	light

It's noticed from Table 6 that oil extracted from oleaster olive oil has color attributes differ from those Domesticated olive oil in terms of appearance and texture the resulted (extracted)oil is pure(clear) liquid free from residues. On the other hand odor and taste are similar in oil from both cultivars free from off favor and odor.

3.4.2. Identification of physicochemical indices of samples (in accordance with AOCS)

- **Acidity index and fatty acid percent**age: Standard method of identification of acidity was applied at room temperature using alcoholic potassium hydroxide where ethanol was used as solvent for fatty matter as well as phenolphthalein as an indicator. The fatty acid percentage expresses the number of fatty acids found in 100 grams of fatty material considering oil acid
- **saponification value**: was determined for oils, fats, and grease
- **Ester value**: was calculated for 1gram of oil sample by subtracting of acidity value from saponification number.
- **Peroxide value**: refers to the ability of peroxides to release Iodine by oxidizing iodine potassium.Findings were as shown in Table 7.

Table 7: Chemical parameters of olive oil samples

Olive cultivar	Sampling area	Acidity value	Free fatty acid ratio	Saponification number	Ester value	Peroxide value
Sourani	Banyas	0.176	0.4897	194	193.82	7.65
Oleaster	Banyas	0.3676	0.8391	202	201.73	8.34
Doebli	Masyaf	0.8581	2.236	186	185.14	7.80
Oleaster	Masyaf	0.3214	0.906	182	181.68	7.85

Findings in Table 7 reveal that olive oil extracted from Doebli cultivar from Masyaf showed high value of acidity in comparison with other types of olive oil especially from Domesticated cultivar from Banyas which showed low value noticing that oils from Oleaster cultivars from both Banyas and Masyaf had almost similar levels of free acidity value that was calculated based on oil fat acid ratio.

On the other hand findings related to saponification number. It's obvious that Oleaster cultivar olive oil had higher saponification number than other samples of extracted oil and in turn was attributed to the fact that this type of oil showed high percentage of fatty acid. While oils extracted from olive cultivars from Masyaf had saponification number less than that of two olive cultivar oils from Banyas.

This result was due to the fact that Banyas olive oils originated whether from domesticated or even oleaster cultivar had greater content of fatty acid content which was function with ester value.Banyas oleaster olive oil had peroxide value relatively higher than that of other studied oils which were similar in peroxide value.

3.5. GC Analysis of the extracted olive oil:

Here, GC analysis was used for quantitative and qualitative determination of fatty acids of triglycerides in the samples of the studied oils extracted from four collections of olives during two month (November and December 2011).

It's obvious from the findings in Table 8 and in GC chromatograms that Banyas oleaster olive oil contains 10 fatty acids while oleaster olive oil from Masyaf contains5fatty acids. Also domesticated olive oils from both cities contain 5fatty acids. As for the second and third collections, it's noticed that the number of fatty acid reached 9 in Banyas oleaster olive oil and 7 in that of the second collection from Masyaf .similarly to oil derived from the fourth collection of oleaster olive from Banyas. But they differ in the type of structural key fatty acids.

The number of Fatty acids of olive oil extracted from third and fourth collections of Masyaf oleaster olive declined to 5. It's obvious from comparing the findings that starting from the second collection, unsaturated fatty acids increased at expense of saturated fatty acids. These findings apply for Oleaster olive oil from both Banyas and Masyaf.

Table 8: Domesticated and oleaster cultivars olive oil structure of fatty acids obtained from Banyas and Masyaf

Number of FAs		1	2	3	4	5	6	7	8	9	10
Fatty acids / Olive oil variety		myristic C14:0	Palmatic C16:0	Palmoleic C16:1	Heptadicanoic C17:0	Heptanoic C17:1	Stearic C18: 0	Oleic C18: 1	Linoleic C18: 2	Linolenic C18: 3	Arachidic C20:0
1st collection	Oleaster-Banyas	0.185	12.174	0.573	0.209	0.217	4.122	70.173	10.977	0.462	0.908
	Oleaster -Masyaf		16.412	1.328			2.621	68.950	10.690		
	Domesticated -Banyas		13.575	0.745			3.937	70.246	11.498		
	Domesticated-Masyaf		12.764	0.626			2.816	69.155	14.639		
2nd collection	Oleaster -Banyas		12.373	0.816	0.172	0.206	3.895	69.215	11.969	0.476	0.878
	Oleaster-Masyaf		13.539	1.404			2.483	70.135	11.467	0.282	0.691
3rd collection	Oleaster -Banyas		12.452	0.789	0.183	0.238	4.212	66.887	13.662	0.533	0.979
	Oleaster-Masyaf		14.337	1.045			2.739	69.029	12.850		
4th collection	Oleaster -Banyas		11.786	0.559	0.179	0.190	4.212	71.076	11.998		
	Oleaster-		14.134	1.422			2.321	71.345	10.778		

As for the first collection of olive, the ratios of Fatty acid whether saturated or unsaturated in olive oil from oleaster and domesticated cultivars taken from both cities were closely similar. But saturated fatty acids were higher in oleaster olive oil from Masyaf, whereas unsaturated fatty acids were higher in oleaster olive oil from Banyas throughout the following collections of olive For this

reason, it's very important that oleaster olive fruit should be collected from the mid of November through the end of December because this procedure significantly leads to decline in saturated acids and rise in unsaturated poly fatty acids according to chromatograms of olive oils from Banyas and Masyaf as shown in Figures 2,3,4,5,6,7,8,9,10, and11.

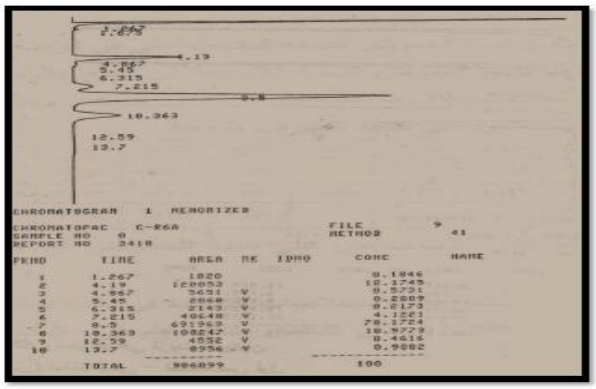

Figure 2Chromatogram of Banyas Oleaster olive oil (1st collection)

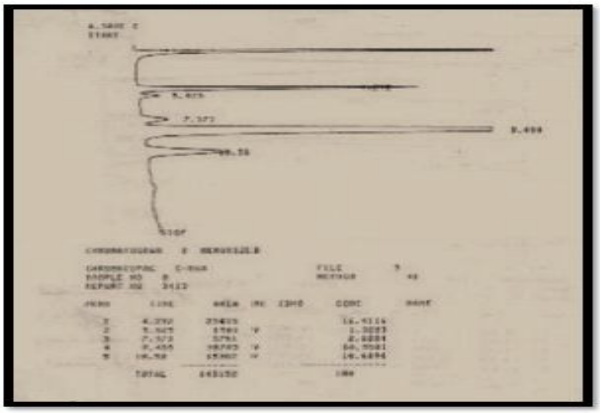

Figure 3 Chromatogram of Masyaf Oleaster olive oil (1st collection)

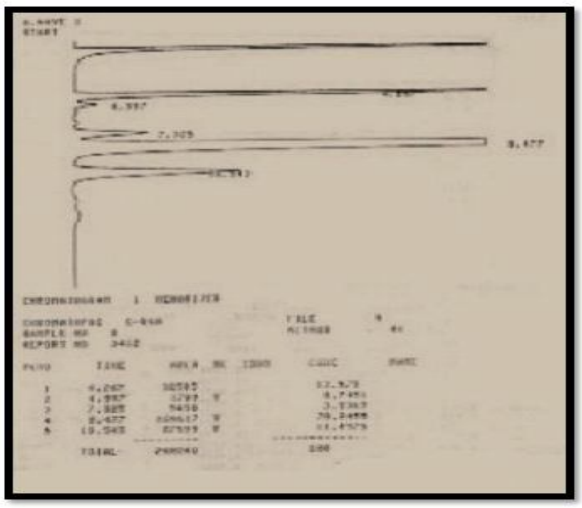

Figure 4 Chromatogram of Banyas Domesticated olive oil (1st collection)

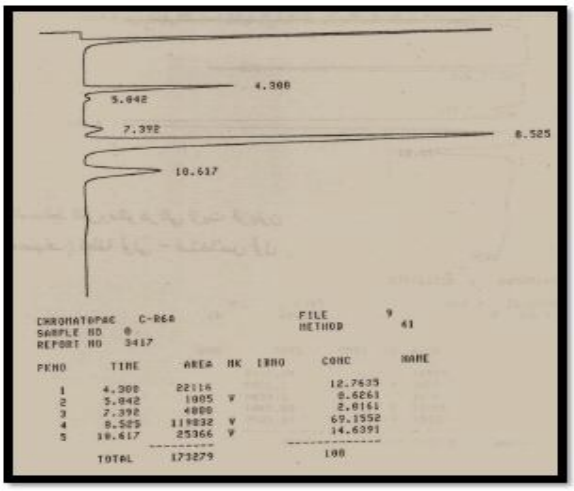

Figure 5 Chromatogram of Masyaf Domesticated olive oil (1st collection)

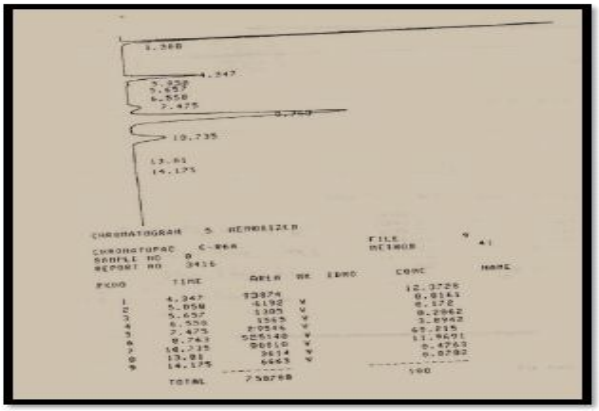

Figure 6 Chromatogram of Banyas Oleaster olive oil (2nd collection)

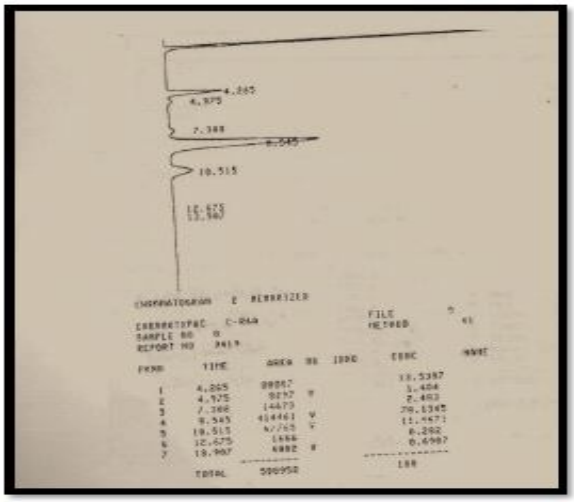

Figure 7 Chromatogram of Masyaf Oleaster olive oil (2nd collection)

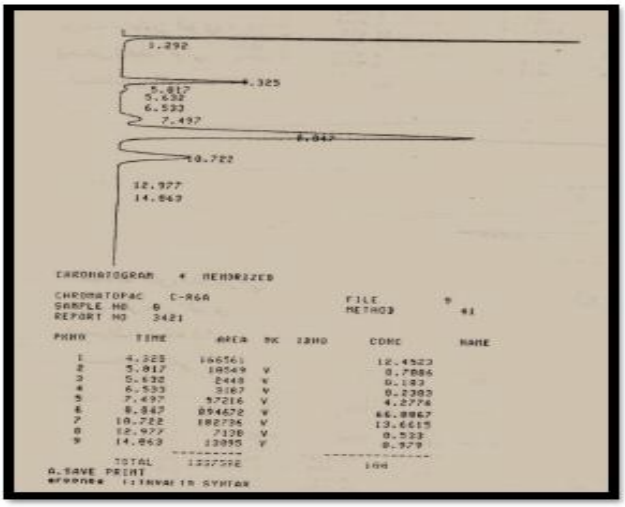

Figure 8 Chromatogram of Banyas Oleaster olive oil (3rd collection

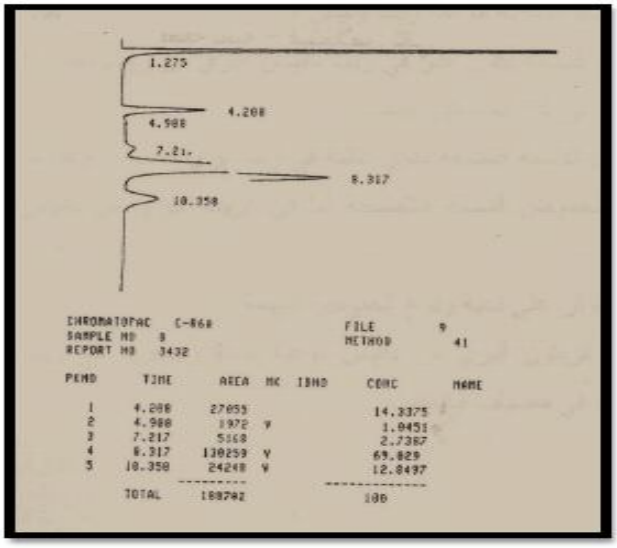

Figure 9 Chromatogram of Masyaf Oleaster olive oil (3rdcollection)

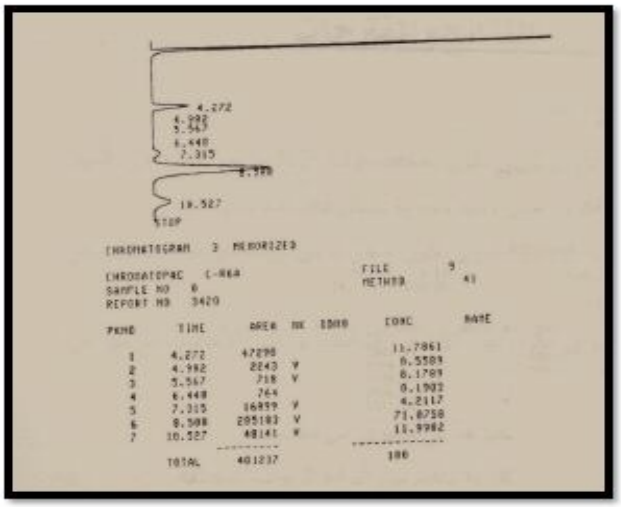

Figure 10 Chromatogram of Banyas Oleaster olive oil (4thcollection)

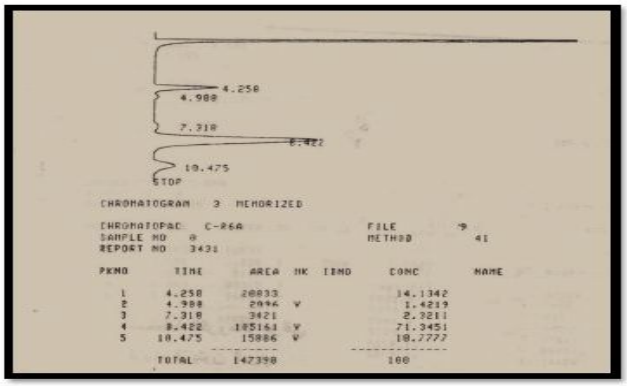

Figure 11 Chromatogram of Masyaf Oleaster olive oil (4th collection)

4. Conclusions

- Content of oil extracted from oleaster olive is relatively low (11-12%) in comparison with domesticated olive oil (15-18%).But economically is poor.
- The color of Sensory characters ranges from pale yellow for oleaster olive to oily green for domesticated olive oil.
- Free acidity, saponification number, peroxide value, are close for all studied cultivars except for values of oil from Banyas which are higher records.
- The number of fatty acid of in Banyas oleaster olive oil is higher than that of Masyaf oleaster olive and as than domesticated olive oil from both cities.
- Oleaster olive oil from Banyas is richer in unsaturated fatty acids. The ratio and type of fatty acid are influenced by the time olive collection.
- Oleaster olive oil from Banyas is of good quality which nearly matches domesticated olive and contrary to that fro Masyaf

5. Suggestions

- To further deepen the quantitative and qualitative study o oleaster olive of all cultivars and at all levels all over Syrian regions. This study should involve high qualities and specifications of olive oil and its composition of necessary fatty acids.
- To exploit varieties of oleaster olive in hybridization of local cultivars to obtain new varieties of olive resistant to climatic and agricultural changes. And to increase production or yield of olive fruits and extracted oil.

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