

## TÜRK KEKİK YAĞLARININ GAZ KROMATOĞRAFİK ANALİZİ

### GAS CHROMATOGRAPHIC ANALYSIS ON TURKISH ORIGANUM OILS

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#### SUMMARY

Although in commerce frequently confused with, or mislabeled as thyme oil, origanum oil is in reality an entirely different plant species and in different regions. It has different chemical composition, containing 60 to 70 per cent of phenols, which consist mainly of carvacrol. Carvacrol remains liquid at room temperature but thymol crystallizes.

The Spanish oil, most important of all commercial thyme oils. It has 62 to 71 % phenol content. Also Turkish oil, Gaziantep region has 71 % and Bolu region has 68.5% phenol contents.

#### ÖZET

Ticari olarak genellikle kekik yağı olarak bilinen origanum oilin değişik bölgelerden ve farklı bitki cinslerinden elde edilen destilatları farklıdır, değişik bileşimlere sahiptirler. Esası carvacrol olmak üzere %60-70 arası fenol içerirler. Oda sıcaklığında carvacrolun sıvı olmasına karşın thymol kristalizedir.

İspanya kekik yağları ticari olarak en ön sırayı alır. %63-70 arası fenol içerirler. Türk kekik yağları, Gaziantep yöresi %71, Bolu yöresi %68.5 fenol içermektedirler.

#### INTRODUCTION

The plant is a perennial herbaceous shrub, commonly crown wild throughout the Mediterranean region (Spain, France, Italy, Morocco, Turkey), Eastern and Central Europe and North America (1,2).

Phenolic compounds are widely distributed in plants, but their functions are not yet known (3-5). Most of them are formed via the shikimic acid pathway, which leads also to amino acids (phenylalanine, tryptophan), growth substances (indole acetic acid) and secondary products such as lignins, coumarins, flavones and anthocyanins. In particular, the different amounts of thymol in the essential oil of origanum grown in different environments has been related to water supply (6).

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The herb is used whole or ground for seasoning foods, the essential oil is also used extensively in flavoring food and in perfumery and in pharmaceuticals (7-9).

Turkey has been exporting dried thyme plants at a variable amount. A summary of the annual export figures for thyme plants can be seen in Table I (9).

TABLE - I : The exported amounts of dried thyme plants

Year	Thyme plants(kg)	Cost (Dollar)
1978	23 000	34 000
1979	25 000	34 000
1980	10 000	17 000
1981	1 332 000	1 971 000
1982	1 593 000	2 744 000
1983	2 259 000	3 504 000
1984	2 647 796	2 977 626
1985	2 328 323	3 302 268
1986	2 453 125	4 192 990
1987	3 460 031	6 457 943

## EXPERIMENTAL

Plants were collected from July to September from Bolu and Gaziantep. Strip leaves and flowers from stalks by hand, only the essential oil containing parts of the plant was distilled. Essential oil extracted by steam distillation at atmospheric pressure and then separated from the aqueous phase with petroleum ether. The ethereal phase was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent removed in a rotary evaporator at low pressure and  $30^\circ\text{C}$ . The yield and some physicochemical properties of the oils are shown in Table II.

TABLE - II : The Yields and some physicochemical properties of the oils

	Bolu	Gaziantep
Yield ml/100 g material	1.45	0.65
Specific Gravity at $20^\circ\text{C}$	0.93145	0.92051
Optical Rotation at $20^\circ\text{C}$	$+ 0^\circ 40'$	$+ 0^\circ 52'$
Refractive Index at $20^\circ\text{C}$	1.4960	1.4915
Phenol Content	68.5 %	71.15 %
Solubility in 80% alcohol	2.85 vol	2.5 vol
Color	Yellow-reddish	Yellow

Gas chromatograph was carried out using a Varian 3700 apparatus equipped with a flame ionization dedector. The operation conditions for gas chromatography may bu summarized as fallows: Injector and dedector temperature 250°C; Carrier gas (N<sub>2</sub>) 30 ml/min, column %10 Carbowax 20 M an chromosorb W 100/120 mesh, 3 mm I.Dx3m. Temperature programme: 80°C (2 min) and then programmed to 240°C at 5°C/min and then held 240°C; integrator: Varian 4290.

The compounds were identified by the technique of peak enrichment.

The standard chemicals were purchased from Merck, Fluka and SCM Terpene Products.

The relative percentages of constituents found in the oils can be seen in Table III and chromatogram in Figure 1.

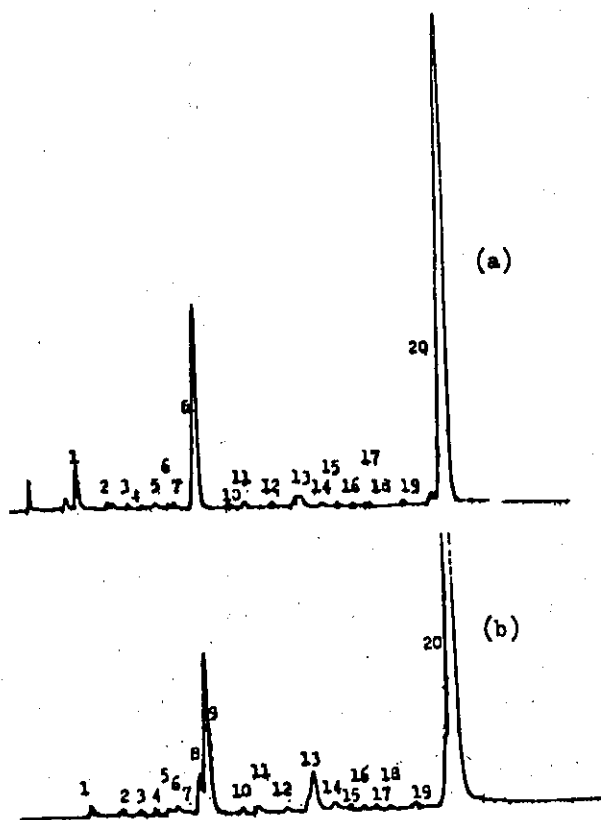


Figure-1: The chromatograms of orionum oil: a = Bolu ; b = Gaziantep.

TABLE III : Gas Chromatographic Analysis of The Turkish Thyme Oils

Compound	Relative percentage	
	Bolu	Gaziantep
1 Tricyclene	2.91	0.788
2 $\alpha$ - pinen	0.435	0.401
3 camphene	0.023	0.07
4 $\beta$ - pinen	0.005	0.061
5 myrceen	0.543	0.473
6 $\alpha$ -terpinen	0.053	0.798
7 limonen	--	0.289
8 $\gamma$ - terpinen	0.231	3.122
9 p - cymen	18.034	14.726
10 C <sub>9</sub> -aldehyde	0.132	0.124
11 linalool	0.571	0.718
12 pinocarvone	0.119	0.409
13 terpineol-4	0.938	4.972
14 $\beta$ - caryophyllene	0.368	1.158
15 pinocarveal	0.119	0.23
16 $\alpha$ - terpineol	0.029	0.111
17 borneol	0.084	0.174
18 geranly acetate	0.403	0.08
19 thymol	0.928	0.52
20 carvacrol	68.512	71.155

## RESULTS AND DISCUSSION

A good separation of origanum products has been obtained by Carbowax 20M column. The yield and physicochemical properties of the oils are shown Table II. The yield of oil from Bolu was higher than to Gaziantep. When we investigated the analysis results of these oils from GC Table III it could be seen that the compositions were different. In origanum oil of Bolu some increase was observed in the percentages of tricyclene,  $\alpha$  - pinen, myrceen, p - cymen, geranyl acetate, thymol while  $\beta$  - pinen,  $\alpha$  - terpinen,  $\gamma$  - terpinen, linalool, pinocarvone, terpineol-4,  $\beta$ -caryophyllene, pinocarveol,  $\alpha$  - terpineol, borneol and carvacrol decreased.

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