# The Chemical Analysis of Propolis, Which are Produced in Western of Turkey

## Türkiye'nin Batısında Üretilen Propolislerin Kimyasal Analizi

Research Article

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**ABSTRACT**

Propolis or bee glue is a natural product that contains numerous fairly strong chemical compounds and it is important for people health. But propolis collecting area and collecting time are very important for the product quality. For this purpose, this study conducted in the region of Muğla city in western of Turkey and propolis features uncovered. 27 propolis samples were collected from nine areas of the Muğla city in western of Turkey where honeydew beekeeping is practiced extensively, from September to November. GC-MS chemical substance analyses of 27 propolis samples revealed many chemicals including alcohols, aromatic alcohols, linear aldehydes, flavanones, linear hydrocarbons, linear acid esters, aromatic acids, aromatic esters, aromatic acid esters, aliphatic carboxilic acids, aliphatic carboxilic acid esters, aliphatic esters and other chemical substances. Propolis concentration changed between 0.71% and 13%. according to the amount of propolis used.

**Key Words**
Propolis, GC-MS analysis, chemical compounds.

**ÖZET**

Propolis veya arı zamkı farklı kimyasal özellikte bileşikler ve mineral maddeler içeren oldukça kompleks bir yapıya sahip doğal bir üründür ve insan sağlığı için önemlidir. Fakat propolisin toplama alanı ve zamanı ürün kalitesi için oldukça önemlidir. Bu amaçla bu çalışmada Türkiye'nin batısında bulunan Muğla ilinde üretilen propolislerin özellikleri ortaya çıkarılmıştır. Çam balı arıcılığının yoğun olarak yapıldığı Muğla ilinin 9 noktasından Eylül ayından Kasım ayına kadar 27 propolis örneği toplanmıştır. 27 adet propolis örneğinin GC-MS ile kimyasal madde tayini sonucunda, alkoller, aromatik alkoller, düz zincirli aldehitler, flavanonlar, düz zinzirli hidrokarbonlar, aromatik hidrokarbonlar, düz zincirli asit esterleri, aromatik asitler, aromatik esterler, aromatik asit esterleri, alifatik karboksilik asitler, alifatik karboksilik asit esterleri, alifatik esterler ve diğer kimyasal maddeler tespit edilmiştir. Propolis derişimleri, kullanılan propolis miktarına bağlı olarak % 0.71 ile % 13 arasında değişmiştir

**Anahtar Kelimeler**
Propolis, GC-MS analizi, kimyasal bileşenler.

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## INTRODUCTION

Propolis or bee glue is a chemically complex resinous mixture collected by *Apis mellifera* bees from different parts of plants [1]. It is a resinous material prepared by honeybees (*Apis mellifera* L.) using beeswax and plant exudates. Bees generally use propolis as a construction material for sealing openings and cracks within the beehive [2].

Propolis is a sticky substance having colors from dark-brown to yellow with respect to its origin. It is a resinous and waxy substance collected from the buds and bark of trees by honeybees [3].

Propolis has become a popular ingredient in complementary healthcare, and the use of this natural material in pharmaceutical and food preparations is growing due to its wide range of therapeutic properties including; antimicrobial, anti-oxidant, anti-inflammatory, immunomodulatory and anticancer activities [4-6]. Some of the scientists show biological properties, including antibacterial effect against antibiotic-resistant human pathogenic bacteria [7-10] and canine pathogenic bacteria [11] antifungal activity against dermatophytes and yeasts [12,13], free radical scavenging and antimutagenic activities [9,14,15]. In the last few years, several *in vitro* and *in vivo* studies have also shown antitumoural activity of propolis from different geographic origin and of some of its isolated compounds on various tumour and non-tumour cells [16-21]. Briefly, this natural product can block specific oncogenic signalling pathways (e.g. β-catenin, c-myc, NF-κB and some intermediary of the PI3K/AKT pathway), which in turn leads to a decrease in cell proliferation and growth and can also act by decreasing the cancer stem cell population, increasing apoptosis, exerting antiangiogenic effects and modulating the tumour microenvironment, more specifically suppressing the invasion and migration [17]. Results obtained so far allow to confirm the various propolis biological properties as well as its safety, increasing the interest in the use of propolis as a functional food and nutraceutical that may provide a health benefit [22].

The chemical composition of propolis is known to be complex and variable between seasons and regions [23]. Numerous factors, such as the floristic composition of the area, location and time of collection impact on the chemical composition of propolis [24]. Propolis samples analysed from various parts of the world have been collectively reported to contain over 300 different chemical compounds, including polyphenols, esters of phenolic acids, flavonoids, sesquiterpenes, diterpenes, triterpenes, lignans, prenylated benzophenones, aldehydes, steroids and coumarins [25,26]. Phenolics (mostly flavonoids) constitute over 50% of the total weight of propolis [27].

Different types of propolis have been reported according to the geographical area of production, botanical source and chemical composition. Generally, propolis is composed of resin, wax, essential oils, pollen and other substances and it includes minerals and organic compounds like phenolic acids or their esters, flavonoids, terpenes, aromatic aldehydes and alcohols, fatty acids, stilbenes and β-steroids [28]. Nevertheless, the standardization of the chemical composition of propolis is difficult since it depends on the plant sources and on the geographical and climatic conditions of the site of collection [28, 29] and hence, metabolite profiling of propolis is a valuable tool to standardise as well as provide a chemical signature for a chemotype that may have superior health benefits [30].

In Turkey, Sorkun and Bozcuk [31] published the first report on propolis. Subsequently, a lot of studies related to propolis in Turkey were published [32-35]. Also Some Turkish studies on the anti-oxidant, antimicrobial and anti-inflammatory activities of propolis have been documented [8,36-39].

In this study we would like to find chemical compounds of propolis from western of Turkey. Especially Muğla is important place for beekeeping in our country and these studies informations will be important for the standardization of Turkish propolis.

**Table 1.** Propolis samples tested in the study.

| Sample no | Propolis sample location | Propolis amount (g) | Propolis amount in 1 ml (g) | % Propolis amount (w/v) |
|---|---|---|---|---|
| 1 | Marmaris | 19.1 | 0.06 | 6 |
| 2 | Ula | 3.2 | 0.04 | 4 |
| 3 | Fethiye | 45.7 | 0.072 | 7.2 |
| 4 | Milas | 105 | 0.06 | 6 |
| 5 | Marmaris | 27.1 | 0.053 | 5.3 |
| 6 | Datça | 4.6 | 0.13 | 13 |
| 7 | Fethiye | 26.2 | 0.105 | 10.5 |
| 8 | Köyceğiz | 1.5 | 0.05 | 5 |
| 9 | Datça | 20.4 | 0.0071 | 0.71 |
| 10 | Merkez | 2.8 | 0.06 | 6 |
| 11 | Ula | 14.1 | 0.068 | 6.8 |
| 12 | Bodrum | 9.5 | 0.0825 | 8.25 |
| 13 | Datça | 10.7 | 0.0525 | 5.25 |
| 14 | Datça | 7.3 | 0.03 | 3 |
| 15 | Fethiye | 30 | 0.077 | 7.7 |
| 16 | Fethiye | 12 | 0.058 | 5.8 |
| 17 | Merkez | 18.3 | 0.054 | 5.4 |
| 18 | Merkez | 5.8 | 0.048 | 4.8 |
| 19 | Merkez | 21.9 | 0.08 | 8 |
| 20 | Marmaris | 18.3 | 0.063 | 6.3 |
| 21 | Milas | 10 | 0.1 | 10 |
| 22 | Milas | 6.7 | 0.063 | 6.3 |
| 23 | Milas | 13.4 | 0.062 | 6.2 |
| 24 | Milas | 24.6 | 0.05 | 5 |
| 25 | Milas | 6.5 | 0.066 | 6.6 |
| 26 | Yatağan | 13.3 | 0.078 | 7.8 |
| 27 | Ula | 13.8 | 0.08 | 8 |

## MATERIALS AND METHODS

### Propolis Samples

227 propolis samples belonged to *A. mellifera* colonies were collected from nine areas of the Muğla city in western of Turkey, Bodrum, Datça, Fethiye, Köyceğiz, Marmaris, Merkez, Milas, Ula and Yatağan where honeydew beekeeping is practiced extensively, from September to November in the years of between 2004 and 2006. In this study, suitable apiaries were chosen from villages. It was important that the villages are separated with enough distance and there are enough vegetation differences, which also represent Muğla statistically The samples were collected using propolis traps and stored in the freezer until further processing.

**Preparation of Ethanol Extracts of Propolis (EEP)**

Propolis sample was hardened in a freezer and ground in a handy grinder. Then 100 g of the sample was dissolved in 300 ml of 96% ethanol. This mixture was incubated for 4 weeks at 30°C in a tightly closed bottle with periodically stirring. After incubation, supernatant was filtered twice with Whatman No. 4 then with No. 1 filter papers. The final filtered solution (concentrated EEP, Table 1) was diluted in 1:10 ratio (w/v) with 96% ethanol and this solution was called EEP. For GC-MS analysis, a portion of the EEP was evaporated to dryness. Then about 5 mg of residue was mixed with 75 μl of dry pyridine and 50 μl bis(trimethylsilyl)trifluoroacetamide(BSTFA), heated at 80°C for 20 min and then the final supernatant was analyzed by GC-MS [40,41].

**GC-M S (Gas Chromatography Coupled to Mass Spectrometry) Analysis**

A GC 6890N from Hewlett-Packard (Palo Alto, CA, USA) coupled with a mass detector (MS5973, Hewlett-Packard) was used for the analysis of the diluted EEP samples. Experimental conditions of the GC-MS system were as follows: a DB 5MS column (30 m x 0.25 mm and 0.25 μm of film thickness) was used and flow rate of mobile phase (He) was set at 0.7 mL/min. In the gas chromatography part, temperature was kept at 50°C for 1 min. After this period, the temperature was increased to 150°C with a 10°C/min heating ramp and then kept at 150°C for 2 min. Finally, temperature was increased to 280°C with a 20°C/min heating ramp and then kept at 280°C for 30 min [40,41].

## RESULTS AND DISCUSSION

In this study 27 propolis samples were collected from nine areas of the Muğla city in western of Turkey. Geographical regions and some other properties of the propolis samples are listed in Table 1.

1 μl of EEP extract was injected to the GC-MS system to screen the sample and identify the compounds present in each propolis sample. Compounds were identified by computer search using reference Wiley Library (HP commercial library) and mass spectra patterns.

GC-MS chemical substance analyses of 27 propolis samples revealed many chemicals including alcohols, aromatic alcohols, linear aldehydes, flavanones, linear hydrocarbons, linear acid esters, aromatic acids, aromatic esters, aromatic acid esters, aliphatic carboxilic acids, aliphatic carboxilic acid esters, aliphatic esters and other chemical substances (Table 2, Table 3).

Table 2 and Table 3 show the chemical compound results of the propolis samples.

Propolis samples dissolution rates were also different due to different compounds in ethanol that propolis samples are included. So EEP Propolis concentration changed between 0.71% and 13%. If the amount of hydrophilic compounds in propolis samples are more the rate of dissolution is higher. In other words, the high flavonoid content of propolis samples depends on propolis samples high dissolution (Uzel et. al., 2005). Similarly we found in our study generally high EEP concentrations and depends on it high flavanoid content. Uzel et al., (2005) also found in their studies 0.78%-13.40% EEP Propolis concentration in 4 Turkish propolis.

Flavanoids are important compounds because of their antioxidant effects. Flavanones are one of the most important groups of the flavonoids. We determined 4H-1-Benzopyran-4-one, 5-hydroxy-7-methoxy-2-phenyl, 4H-1-Benzopyran-4-one, 2,3-dihydro-5,7-dihydroxy-2-phenyl, 4H-1-Benzopyran-4-one,3,5,7-trihydroxy-2-phenyl, Chrysin and 4,5-Dihydroxy-7-methoxyflavanone as flavanones in the propolis samples. Chrysin and 4',5-dihydroxy-7methoxyflavanone (Sakuranetin) were previously found in propolis by Velikova et al., 2000. In our study the total amount of flavanones were found between 2.2%-31%. Güler et al., [42] has also determined the total flavanones amount in Turkish propolis between 4.72%-37.55%.

It has been reported that propolis has antimicrobial activity because of aromatic acid esters and flavanoids [39,43,44]. Additionally it has been showed that aromatic acids and flavanoids have antiviral activity. [45-49]. We found in our study 70% as the highest amount of total aromatic acid esters and some of them

**Table 2.** Chemical components of the EEP samples (%).

| Sample No | Alcohols | Aromatic Alcohols | Linear Aldehydes | Flavanones | Linear Hydrocarbons | Linear Acid Esters | Aromatic Acids | Aromatic Esters | Aromatic Acid Esters | Aliphatic Carboxylic Acids | Aliphatic Carboxylic Acid Esters | Aliphatic Esters | Ketones | Terpenes |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | - | 0.4 | - | - | 1.6 | 0.5 | 0.1 | - | 70 | 0.3 | 1.4 | - | - | - |
| 2 | - | - | - | 2.2 | 0.8 | 0.5 | 0.2 | - | 64 | 0.2 | 1.6 | - | - | - |
| 3 | - | 1.6 | - | 17 | 0.2 | 1.3 | 0.3 | 13 | 0.5 | - | 2.1 | - | 1.0 | - |
| 4 | - | 3.8 | - | 6.7 | 2.6 | 2 | - | 6.7 | - | - | 3.7 | - | - | 0.3 |
| 5 | - | 0.8 | - | 12 | - | 0.7 | - | - | 51 | - | 2.9 | - | - | - |
| 6 | - | 3.3 | - | 17 | - | 2.3 | - | 15 | - | - | 8.8 | - | - | - |
| 7 | 0.5 | 5 | - | 28 | - | 0.4 | - | - | 18 | - | 1.2 | - | 0.5 | - |
| 8 | - | 1.3 | - | - | 1.7 | 1.2 | - | - | 58 | - | 2.8 | 2.3 | - | 1.4 |
| 9 | 0.4 | 2 | 0.2 | 16 | - | 0.9 | 0.4 | 13 | 1.5 | - | 2.6 | - | - | - |
| 10 | - | - | - | - | 2.1 | 0.2 | - | 0.6 | 6.6 | - | 0.5 | - | - | - |
| 11 | - | 0.3 | - | 13 | - | 0.4 | - | - | 38 | - | 1.8 | - | - | - |
| 12 | 0.3 | 3.3 | - | 20 | 4.4 | 1.3 | 0.4 | 13 | - | - | 1.1 | - | - | 0.1 |
| 13 | 0.1 | 0.4 | - | 16 | 4.4 | 1.1 | 0.2 | 7.5 | 0.2 | - | 2.1 | - | 0.9 | 0.3 |
| 14 | 0.3 | 1.4 | - | 25 | 6.8 | 1.9 | - | 7 | 0.4 | - | 3.3 | - | 1 | - |
| 15 | 0.1 | 0.2 | - | 9 | 2.3 | 0.6 | 0.3 | - | 51 | - | 1.7 | - | - | 0.3 |
| 16 | - | 1.7 | 1.6 | 11 | 5.4 | 0.8 | 0.2 | - | 28 | - | 2.3 | - | - | 0.9 |
| 17 | 0.5 | 0.4 | - | 22 | 6.7 | 1.7 | 0.2 | 9.5 | - | - | 2.6 | - | 1 | 0.3 |
| 18 | - | 0.3 | - | 10 | 5.1 | 0.8 | - | - | 35 | 0.2 | 2.6 | 1 | - | - |
| 19 | 0.8 | 4.8 | 0.2 | 31 | 3.5 | 0.7 | - | 6.1 | - | - | 1.3 | - | - | - |
| 20 | 0.3 | 1.6 | - | 12 | 5.2 | 1.6 | - | - | 28 | - | 1.4 | - | 1.1 | - |
| 21 | - | 0.1 | - | 4.4 | - | 1.3 | - | 1.6 | 13 | - | 4.1 | 1.6 | - | 0.7 |
| 22 | - | 0.7 | - | 8.4 | 6.8 | 2.2 | - | 8.3 | - | - | 3.8 | - | 1.4 | 1.5 |
| 23 | 0.3 | 2.4 | - | 23 | 3.9 | 0.6 | - | 9.7 | 2.3 | - | 2.9 | - | - | - |
| 24 | - | 0.6 | - | 13 | 4.5 | 1.1 | - | 4.9 | - | - | 4.9 | - | - | 4.1 |
| 25 | - | 1 | - | 4.4 | 3.1 | 0.9 | - | 1.2 | 23 | - | 3.2 | 3.1 | - | 1.1 |
| 26 | - | 0.9 | - | 9.7 | 4.3 | 1.4 | - | 1.8 | 0.2 | - | 5.7 | 0.8 | - | 3 |
| 27 | 0.1 | 1.4 | 0.9 | 20 | 4.6 | 0.7 | - | 8.7 | 7.3 | - | 3.2 | 0.7 | - | 0.2 |

**Table 3.** GC-MS Results of Propolis Samples (%).

| | Sample No | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Compounds** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** |
| **Linear acid esters** | | | | | | | | | | | |
| Hexadecanoic acid,ethyl ester | 0.47 | 0.49 | 1.30 | 2.00 | 0.73 | 2.32 | 0.39 | 1.25 | 0.99 | 0.22 | 0.46 |
| **Aromatic acids** | | | | | | | | | | | |
| 4-Pentenoic acid,5-phenyl | - | - | - | - | - | - | - | - | 0.43 | - | - |
| Benzeneacetic acid | 0.14 | 0.22 | - | - | - | - | - | - | - | - | - |
| 4-Pentenoic acid, 5-phenyl- | - | - | 0.31 | - | - | - | - | - | - | - | - |
| **Total** | 0.14 | 0.22 | 0.31 | - | - | - | - | - | 0.43 | - | - |
| **Aromatic acid esters** | | | | | | | | | | | |
| Cinnamyl cinnamate | 62.84 | 51.8 | - | - | 46.61 | - | 17.1 | 51.23 | - | - | 32.1 |
| 1,2-Benzenedicarboxylic acid,diis ooctyl ester | - | - | - | - | - | - | - | 3.75 | - | 1.91 | - |
| 1,2-Benzenedicarboxylic acid,bis(8-methylnonyl)ester | - | 5.9 | - | - | - | - | - | 1.37 | - | 4.73 | - |
| 1,2-Benzenedicarboxylic acid, butyl(8-methylnonyl)ester | - | 0.42 | - | - | - | - | - | - | - | - | - |
| Benzyl cinnamate | - | - | - | - | - | - | 0.91 | - | - | - | 0.17 |
| **Total** | 62.84 | 58.1 | - | - | 46.6 | - | 18.0 | 56.35 | - | 6.64 | 32.2 |
| **Aliphatic carboxylic acids** | | | | | | | | | | | |
| 3-Butenoic acid | 0.39 | 0.24 | - | - | - | - | - | - | - | - | - |
| **Aliphatic carboxylic acid esters** | | | | | | | | | | | |
| Ethyl Oleate | 1.42 | 1.61 | 2.08 | 3.71 | 2.91 | 8.85 | 1.21 | 2.85 | 2.63 | 0.56 | 1.84 |
| **Aliphatic esters** | | | | | | | | | | | |
| Didecyl phthalate | - | - | - | - | - | - | - | 2.29 | - | - | - |
| **Ketones** | | | | | | | | | | | |

**Table 3.** GC-MS Results of Propolis Samples (%) (Continue).

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Nonadecanone | - | - | 1.02 | - | - | - | - | - | - | - | - |
| Cyclopentadecanone, 2 hydroxy- | - | - | - | - | - | - | 0.53 | - | - | - | - |
| **Total** | - | - | 1.02 | - | - | - | 0.53 | - | - | - | - |
| **Terpenes** | | | | | | | | | | | |
| Caryophyllene | - | - | - | 0.39 | - | - | - | 0.62 | - | - | - |
| Caryophyllene oxide | - | - | - | - | - | - | - | 0.79 | - | - | - |
| **Total** | - | - | - | 0.39 | - | - | - | 1.41 | - | - | - |
| | | | | | | **Sample No** | | | | | |
| **Compounds** | **12** | **13** | **14** | **15** | **16** | **17** | **18** | **19** | **20** | **21** | **22** |
| **Alcohols** | | | | | | | | | | | |
| 3-Buten-1-ol, 3-methyl- | 0.06 | 0.09 | 0.19 | 0.07 | - | 0.25 | - | 0.45 | 0.17 | - | - |
| 2-Buten-1-ol, 2-methyl- | 0.27 | - | 0.17 | - | - | 0.23 | - | 0.42 | 0.13 | - | - |
| **Total** | 0.33 | 0.09 | 0.36 | 0.07 | - | 0.48 | - | 0.87 | 0.3 | - | - |
| **Aromatic alcohols** | | | | | | | | | | | |
| Phenylethyl Alcohol | 1.47 | 0.43 | 0.54 | - | - | 0.39 | 0.13 | 0.89 | 0.56 | - | - |
| 2-Naphthalene-methanol | 1.36 | - | 0.90 | 0.19 | 0.75 | - | 0.17 | 3.54 | 0.48 | 0.12 | 0.71 |
| 1-Phenanthrenemethanol | - | - | - | - | 0.98 | - | - | - | - | - | - |
| Benzyl Alcohol | - | - | - | - | - | - | - | - | - | - | - |
| **Total** | 2.83 | 0.43 | 1.44 | 0.19 | 1.73 | 0.39 | 0.3 | 4.43 | 1.04 | 0.12 | 0.71 |
| **Linear Aldehydes** | | | | | | | | | | | |
| Octadecanal | - | - | - | - | 1.59 | - | - | - | 0.20 | - | - |
| **Flavone/Flavanone derivatives** | | | | | | | | | | | |
| 4H-1-Benzopyran-4-one, 5-hydroxy-7-methoxy-2-phenyl | 4.87 | 3.61 | 5.34 | 3.09 | 5.29 | 14.73 | 5.33 | 6.03 | 3.39 | - | 4.75 |

**Table 3.** GC-MS Results of Propolis Samples (%) (Continue).

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4H-1-Benzopyran-4-one, 2,3-dihydro-5,7-dihydroxy-2-phenyl | 8.00 | 7.43 | 9.65 | 4.56 | 6.02 | - | 4.13 | 13.52 | 4.63 | 4.42 | 3.68 |
| 4H-1-Benzopyran-4-one,3,5,7-trihydroxy-2-phenyl | 3.19 | 2.16 | 2.85 | - | - | 2.36 | 1.52 | 3.76 | 2.32 | - | - |
| Chrysin | 4.37 | 3.38 | 6.13 | 1.53 | - | 4.99 | - | 6.66 | 2.49 | - | - |
| 4,5-Dihydroxy-7-methoxyflavanone | - | - | 1.79 | - | - | - | - | 1.48 | - | - | - |
| ***Total*** | 20.43 | 16.5 | 25.76 | 9.18 | 11.3 | 22.08 | 10.98 | 31.45 | 12.83 | 4.42 | 8.43 |
| Linear hydrocarbons | | | | | | | | | | | |
| Heptacosane | - | - | - | - | - | - | - | - | - | - | - |
| Heptadecane | 0.79 | 0.98 | - | - | - | 1.00 | - | 0.98 | - | - | 0.73 |
| Heneicosane | - | - | - | - | - | - | - | - | - | - | - |
| Nonadecane | 3.63 | 1.80 | 6.82 | 1.75 | 4.36 | 2.80 | 3.84 | 2.24 | 4.58 | - | 5.11 |
| Docosane | - | 1.61 | - | 0.62 | 1.03 | 2.90 | 1.26 | 0.35 | 0.65 | - | 0.95 |
| **Total** | 4.42 | 4.39 | 6.82 | 2.37 | 5.39 | 6.7 | 5.1 | 3.57 | 5.23 | - | 6.79 |
| **Linear acid esters** | | | | | | | | | | | |
| Hexadecanoic acid, ethyl ester | 1.36 | 1.11 | 1.99 | 0.63 | 0.82 | 1.77 | 0.83 | 0.75 | 1.65 | 1.36 | 2.21 |
| **Aromatic acids** | | | | | | | | | | | |
| 4-Pentenoic acid,5-phenyl | 0.46 | 0.25 | - | - | - | 0.18 | - | - | - | - | - |
| Benzeneacetic acid | - | - | - | 0.29 | 0.18 | - | - | - | - | - | - |
| 4-Pentenoic acid, 5-phenyl- | - | - | - | - | - | - | - | - | - | - | - |
| **Total** | 0.46 | 0.25 | - | 0.29 | 0.18 | 0.18 | - | - | - | - | - |
| **Aromatic esters** | | | | | | | | | | | |
| 2-Propen-1-one | 13.25 | 7.55 | 7.04 | - | - | 9.53 | - | 6.13 | - | 1.61 | 8.36 |
| **Aromatic acid esters** | | | | | | | | | | | |

**Table 3.** GC-MS Results of Propolis Samples (%) (Continue).

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cinnamyl cinnamate | - | - | - | 37.0 | 24.4 | - | 18.56 | - | 27.53 | - | - |
| 1,2-Benzenedicarboxylic acid,diis ooctyl ester | - | - | - | - | - | - | 1.60 | - | - | 1.36 | - |
| 1,2-Benzenedicarboxylic acid,bis(8-methylnonyl)ester | - | - | - | - | - | - | 11.28 | - | - | 11.61 | - |
| 1,2-Benzenedicarboxylic acid, butyl(8-methylnonyl)ester | - | - | - | - | - | - | 0.81 | - | - | - | - |
| Benzyl cinnamate | - | - | - | - | 0.33 | - | - | - | 0.39 | - | - |
| **Total** | - | - | - | 37.0 | 24.7 | - | 32.25 | - | 27.9 | 12.97 | - |
| **Aliphatic carboxylic acids** | | | | | | | | | | | |
| 3-Butenoic acid | - | - | - | - | - | - | 0.23 | - | - | - | - |
| **Aliphatic carboxylic acid esters** | | | | | | | | | | | |
| Ethyl Oleate | 1.11 | 2.15 | 3.37 | 1.76 | 2.38 | 2.61 | 2.63 | 1.33 | 1.43 | 4.12 | 3.81 |
| **Aliphatic esters** | | | | | | | | | | | |
| Didecyl phthalate | - | - | - | - | - | - | 1.00 | - | - | 1.58 | - |
| **Ketones** | | | | | | | | | | | |
| 2-Nonadecanone | - | 0.99 | 1.05 | - | - | 1.09 | - | - | 1.13 | - | 1.40 |
| **Terpenes** | | | | | | | | | | | |
| Caryophyllene | 0.14 | 0.12 | - | 0.09 | 0.31 | 0.18 | - | - | - | 0.77 | 1.08 |
| Caryophyllene oxide | - | 0.17 | - | 0.28 | 0.64 | 0.20 | - | - | - | - | 0.42 |
| **Total** | 0.14 | 0.29 | - | 0.37 | 0.95 | 0.38 | - | - | - | 0.77 | 1.5 |

are Cinnamyl cinnamate, 1,2-Benzenedicarboxylic acid, diis ooctyl ester, 2-Benzenedicarboxylic acid, bis(8-methylnonyl)ester, 2-Benzenedicarboxylic acid, butyl (8-methylnonyl)ester and Benzyl cinnamate aromatic acid esters.

Linear hydrocarbons Heptacosane, Heptadecane, Heneicosane, Nonadecane, Docosane were found in propolis samples. The total amount of linear hydrocarbons were found between 0.2%-6.8%. Heneicosane was before determined by Greenaway et al., 1987 [50]; Seifert and Hasslinger, 1989 [51]; Garcia-Viguera et al., 1992 [52]; Marcucci et. al., 1993 [53]. Also Docosane was found by Bankova et al., (1998) [54] in propolis samples which belongs to Canarian Islands.

Aliphatic carboxylic acids and esters were found in this study. Especially Ethyl Oleate was found in all propolis samples. Ethyl oleate is a fatty acid ester formed by the condensation of oleic acid and ethanol. It is a colorless to light yellow liquid. Ethyl oleate is used as a solvent for pharmaceutical drug preparations involving lipophilic substances such as steroids. It also finds use as a lubricant and a plasticizer [55]. Ethyl oleate has been identified as a primer pheromone in honeybees [56]. This can be the answer why we found it all propolis samples.

Ketones are simple compounds that contain a carbonyl group (a carbon-oxygen double bond). Many ketones are known and many are of great importance in industry and in biology. Examples include many sugars (ketoses) and the industrial solvent acetone. It has been found in seven of the propolis samples between 0.5%-1.4%. 2-Nonadecanone and 2-Hydroxy-cyclopentadecanone were the ketones that we found in the research.

Terpenes are a large and diverse class of organic compounds, produced by a variety of plants, particularly conifers. They are the major components of resin, and of turpentine produced from resin. Terpenes and terpenoids are the primary constituents of the essential oils of many types of plants and flowers. Caryophyllene and Caryophyllene oxide were found in some propolis samples as terpenes between 0.1%-1.5%.

## CONCLUSIONS

In this study some propolis findings were found about in the western region of Turkey. Regional propolis data is very important for countries because of the international standard of the propolis. These informations can use preparation of the general propolis standard in the future.

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