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RECOVERY OF FIXED AND VOLATILE OILS FROM LAURUS NOBILIS L.FRUIT AND LEAVES BY SOLVENT EXTRACTION METHOD

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ABSTRACT : *In this study, fixed oils of Laurus nobilis L. fruit were obtained by solvent extraction (Soxhlet method). Effects of solvent (hexane, petroleum ether, carbondisulfide and benzen) and particle size extraction yield were investigated. Fatty acids composition of the fixed oil was determined by using GC/MS method.*
Volatile oils isolated by hydrodistillation (Clevenger apparatus) from the dried leaves of Laurus nobilis L.. were analyzed by GC, and main components were identified.

KEYWORDS : *Laurus nobilis L., Extraction, Hydrodistillation.*

DEFNE MEYVE VE YAPRAKLARINDAN SABİT VE UÇUCU YAĞLARIN ÇÖZÜCÜ EKSTRAKSİYONU YÖNTEMİ İLE GERİ KAZANIMI

ÖZET : *Bu çalışmada defne meyvesinin sabit yağı çözücü ekstraksiyonuyla (Soxhelet metodu) elde edildi. Ekstraksiyon verimine çözücünün (hekzan, petrol eteri, carbon sülfür,benzen) ve partikül boyutunun etkisi araştırıldı. Sabit yağın yağ asitleri bileşimi ise gaz kromatografisi kütle spektrometresi kullanılarak belirlendi.*
Uçucu yağlar kurutulmuş defne yapraklarından su distilasyonuyla (clevenger cihazı) izole edildi ve başlıca bileşenleri gaz kromatografisi ile analiz edilerek belirlendi.

ANAHTAR KELİMELER : *Defne, Ekstraksiyon, Su distilasyonu.*

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I. INTRODUCTION

Laurus nobilis L. tree is either a shrub or small tree, usually growing to a height of from 20 to 30 feet. It is cultivated in many temperate warm parts of the world, particularly in southern Europe and around the shores of the Mediterranean Sea [1]. Dried or fresh leaves are commonly known as household culinary herb while the leaf oil is mostly used for flavors and fragrances [2-3-4]. Commercial production centres include areas such as Turkey, Algeria, France, Greece, Morocco, Portugal, Spain, Belgium, The Canary Islands, Mexico, Central America, and the Southern United States. Turkey is one of the main producers and suppliers of bay leaves [4].

Bay leaves are commonly used in soups, stews, sauce, pickles, sausages, and also an essential ingredient of the herb mixes. As a medicinal plant, bay leaves have been used as a cure for rheumatism, skin rashes and earaches. In addition, essential oil is used by the cosmetic industry. The oil content of bay leaves ranges from 1 to 3% on fresh-weight basis. The main constituent of the essential oil includes 1-8 cineole (45-50%), and pinene, sabinene, linalool, eugenol, eugenol acetate, methyleugenol, ternineol acetate, phellandrene, plus other esters and terponoids [4-5].

Fruits contain 26% fixed oil [6-7]. This oil is a green, granular, lard-like mixture, melting at 40°C, to a dark-green aromatic fluid, and consisting of a semi-solid fat. A variety of fatty matters are present, the glycerides of acetic, oleic, linoleic, stearic, palmitic, myristic, and lauric acids, with small amounts of free acetic acid [7].

The essential oils from aromatic plants are for the most part volatile and thus lend themselves to several methods of isolation such as hydrodistillation, water and steam distillation, direct steam distillation, solvent extraction and supercritical extraction.
The specific extraction method is dependent upon the plant material to be distilled and the desired end-product. Hydrodistillation method protects the oils so extracted to a certain degree since the surrounding water acts as a barrier to prevent it from overheating. The essential oils which impart the distinctive aromas are complex mixtures of organic constituents, some of which being less stable, may undergo chemical alterations when subjected to high temperatures. In this case, organic solvent extraction is required to ensure no decomposition or changes have occurred which would alter the aroma and fragrance of the end-product. Never methods of essential oil

extraction such as using supercritical CO_2 which yield very high quality oils are commercially used, but are less common and beyond the financial means of most processors. The recovery of nonvolatile essential oils are also obtained by solvent extraction although the process is more difficult and complex than the recovery of the volatiles. This process yields an aromatic resinous product known as an oleoresin, which is more concentrated than an essential oil and which has wide application in the food industry [8].

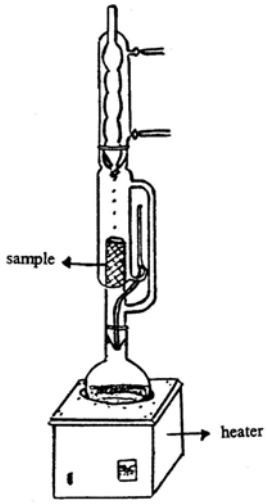
Several solvent extraction systems based on the Soxhlet device are on the market to allow fast and safe determination of total oils in food, soil. The Soxhlet method is the most commonly used example of a semi-continuous method applied to extraction of oils from foods. According to the Soxhlet's procedure, oil and fat from solid material are extracted by repeated washing with an organic solvent, usually hexane or petroleum ether, under reflux in a special glassware. Other organic solvents such as benzene, alcohol, chloroform are also used. Knoepfler et al used carbon tetrachloride, benzene, hexane, isopropyl alcohol and tetrachloroethylene to extract jojoba oil [9-10]. In a study, powdered leaves of *Laurus nobilis* L. were subjected to extraction by solvent extraction method and obtained fatty acids were identified by fractioning of the extractives by the gas chromatography technique [11].

In this study, fixed oils of *Laurus nobilis* L. fruit were obtained by solvent extraction (Soxhlet method) and the volatile oils of the leaves of *Laurus nobilis* L. were obtained by hydrodistillation (Clevenger apparatus).

II. EXPERIMENTAL STUDIES

Dried leaves and fruits of *Laurus nobilis* L. were purchased from İzmir. Fixed oils of *Laurus nobilis* L. fruit was extracted by soxhelet apparatus.

In this method the sample (Figure 1) is dried, ground into small particles and placed in a porous cellulose thimble. The thimble is placed in an extraction chamber, which is suspended above a flask containing the solvent and below a condenser. The flask is heated and the solvent evaporates and moves up into the condenser where it is converted into a liquid that trickles into the extraction chamber containing the sample. The extraction chamber is designed so that when the solvent surrounding the sample exceeds a certain level it overflows and trickles back down into the boiling flask. At the end of the extraction process the solvent in the flask is evaporated and the mass of the



remaining oil is measured. The percentage of oil in the initial sample can then be calculated.

Figure 1. Soxhelet apparatus

Sieve analysis was applied to ground fruits in order to investigate particle size distribution. They were separated as 0.224-0.425, 0.425-0.85 and 0.85-1.8mm particle size. 30 g of fruits and 200 ml of hexane was used.

To investigate effects of solvent hexane, petroleum ether, benzene and carbondisulfide used were as solvent. Extraction experiments were carried out duration of 1,3 and 6 hours. 30 g of fruits and 200 ml of solvent was used.

Fatty acids composition of the fixed oil was determined by using GC/MS method. The samples used in determination of fatty acids composition were prepared by using two different solvents such as petroleum ether and benzene.

GC/MS analysis was performed on a Shimadzu GC/MS-QP5050A system. CP sil 5CB column (25m.0.25mm i.d) was used with helium as the carrier gas. GC oven temperature was kept at 60^{o}C for 10 min and programmed to 260^{o}C at a rate of 5^{o}C/min, then kept constant at 260^{o}C for 40 min. Split ratio was adjusted as 50:1. MS were taken at 70 ev in El mode.

The volatile oils of *Laurus nobilis* L. leaves were obtained by hydrodistillation in Clevenger apparatus (Figure 2). In the manufacture of volatile oils using the method of water distillation, the sample is completely immersed in water and the still is brought to the boil. When the condensed sample cools down, the water and essential oil is separated and the oil decanted to be used as essential oil.

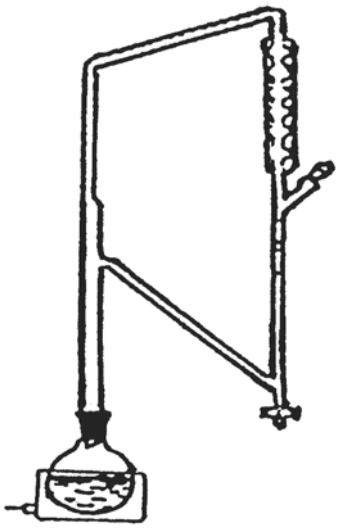


Figure 2. Clevenger apparatus

The compositions of isolated oils were determined qualitatively by GC. The volatile oils were analyzed on a Shimadzu GC-9A system. Thermon 600 T Column (50m, 0.25mm i.d.) was used with nitrogen as the carrier gas. GC oven temperature was kept at 70^{o}C for 10 min and programmed to 180^{o}C at a rate of 2^{o}C/min, then kept constant at 180^{o}C for 30 min. The injector temperature was 250^{o}C. Split ratio was adjusted as 60:1.

III. RESULTS AND DISCUSSION

The results obtained from sieve analysis are shown in Table 1. The proper particule size was selected as 0.425-0.85 mm.

Table 1. Extracted oil percentages of *Laurus nobilis* L. fruit in different particle sizes (solvent: hexane)

Particle size of Laurel fruit (mm)	Extracted oil %
0.224-0.425	32.12
0.425-0.85	23.92
0.85-1.8	22.61

There are two different mechanisms in extraction, namely, diffusion and wash out. Since most of the cells were broken in seeds with small particle size, wash out was occurs significantly. In this case, desired components could pass into the solution and purification process could be difficult [12]. Therefore the smallest particle size wasn't selected. It was considered that diffusion mechanism was effective in particle size was selected as 0.425-0.85 mm. In this case the produced fixed oil would be more pure. However, 0.85-1.8 mm particle size was used in the experiments carried out for proper solvent selection.

Table 2 shows the yield of different solvents used in this work. Solvents' properties and their cost [13] are also shown in Table 3.

Table 2. The yield of different solvents used in the extraction process for *Laurus nobilis* L. fruit (particle size: 0.85-1.8 mm)

Solvent	Yield oil %		
	1h	3h	6h
Hexane	16.52	18.61	22.01
Petroleum ether	17.10	22.55	24.20
Benzene	16.35	21.21	22.34
Carbondisulfide	16.42	19.65	21.15

Table 3. Properties of solvents used in the extraction process

Solvent	Structure	Cost of the Solvent (€/L)	Boiling point (^{o}C)
Hexane	C_6H_{14}	55.10	68.7
Petroleum ether	A mixture of hydrocarbon	25.50	30-60
Benzene	C_6H_6	46.00	80.1
Carbondisulfide	CS_2	50.90	46.0

Petroleum ether is the best solvent used in this research since its cost is relatively low and it extracted a high percentage of oil compared to the other solvents. Also petroleum ether has a low boiling point so it needs more little heat to vaporize in any distillation recovery process.

Fatty acids compositions were found as 34.8% and 44.2% and for saturated fatty acids and 62.4% and 55.8% for unsaturated fatty acids, respectively, when extraction was performed by using petroleum ether and benzene.

Table 4. Fatty acids composition determined by using petroleum ether and benzene

Compound	Percentage for petroleum ether	Percentage for benzene
Lauric acid	7.5	17.2
Myristic acid	0.4	–
Palmitic acid	25	27
Stearic acid	1.9	trace
Palmitoleic acid	0.7	–
Oleic acid	39.6	40.2
Linoleic acid	22.1	15.6
Aracidic acid	trace	–
Unknown	2.8	–
Saturated fatty acids	34.8	44.2
Unsaturated fatty acids	62.4	55.8

Tanrıverdi et all. found that fatty acids compositions of fixed oils of Silifke and Hatay fruits were 37.97%, 36,8% for saturated fatty acids, and 60.4%, 61.37% for unsaturated fatty acids, respectively, when fixed oils of Silifke and Hatay fruits were extracted by n-hexane-n-heptane mixture [14]. Baytop report that the acids compositions were 35.4% for saturated fatty acids and 64.6% for unsaturated fatty acids when extraction was performed by using petroleum ether [7].

As result, the solvent making the yield of fixed oil maximum must be chosen when the yield is important, and the other solvent making the desired component amount maximum must be chosen when this component is important.

The volatile oil yield obtained by hydrodistillation from *Laurus nobilis* L. leaves were found as 2.07%. The major components of the volatile oil were found 1-8 cineole (49.6%) (Table 5), α-pinene (6.4%), sabinene (5.6%), β-pinene (4.2%) and α-terpineol/borneol (10.4%) and totally ten components including these were found to constitute 85% of the oil. 1,8-cineole was found between 40-54% in different works by using different distillation condition [15-16-17-18].

Table 5. Volatile oils compositions of *Laurus nobilis* L. leaves

Compound	**Percentage**
α-pinene	6.4
β-pinene	4.2
sabinene	5.6
limonene	1.0
1,8-cineole	49.6
p-cymene	1.8
terpinene-4-ol	2.1
α-terpineol /borneol	10.4
metil eugenol	2.2
eugenol	1.5

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