WORLD JOURNAL OF PHARMACY AND PHARMACEUTICAL SCIENCES
SJIF Impact Factor 7.421
Volume 8, Issue 3, 50-59 Research Article ISSN 2278 – 4357

CHEMICAL COMPARISON STUDY OF THE VOLATILE OIL COMPONENTS IN ANISEEDS WHICH ARE SPREAD IN SYRIAN ENVIRONMENT

Dr. Anas Rajab*

Assistant Professor Faculty of Pharmacy, Syrian Private University (SPU).

Article Received on
25 December 2018,
Revised on 15 Jan. 2019,
Accepted on 05 Feb. 2019,
DOI: 10.20959/wjpps20193-13220

***Corresponding Author**
Dr. Anas Rajab
Assistant Professor Faculty of Pharmacy, Syrian Private University (SPU).

ABSTACT

Aniseed volatile oil was extracted from *Pimpinella Anisium* L. seed collected from (Aleppo, Damascus and Homs Countrysides) fields in Syria by hexane. Aniseed volatile oil component was identified qualitatively and quantitatively using gas chromatography GC and compared with standards. The components from different aniseed volatile oils were corresponded qualitatively. The aniseed volatile oil was chromatographed on column. Anethole and anisaldehyde were isolated and charachtarized using available spectra such: IR, UV, ^{1}H-NMR and MS, also the physical and chemical properities were determined.

KEYWORDS: Aniseed, gas chromatography, extraction, mobile phase, and isolated product.

1. INTRODUCTION

Anise is one of the oldest medicinal plants known to human, ancient egyptians interested to plant it. Anise was known to them as "Nikon" and it was mentioned in the therapeutic prescriptions by the greeks and Romans. It was described by greek philosopher Dioscorides natural scientist as a food flavour and it helps with the digestion of heavy meals.[1-3]

The cultivation of anise entered to the center of europe during the middle centuries, Britain tried to plant it but the weather did not suit their country's growth because it needs to a very warm summer season.[2]

The scientists have recently found aniseed in the graveyard the eastern desert of the pharaonic city of thebes, also they found the pharaonic scripts included several therapeutic prescriptions contained in their structures on the aniseed.[1]

Aniseed is used in combination with drugs to treat cough, sore throat, tonsillitis, and headache. It also facilitates childbirth and increases milk yield in nursing mothers. In addition, aniseed is good for healing abdominal cramps, removing bloating because it helps with digestion, and activates the immune system.[4-10,13]

It has been established in recent scientific researchs that aniseed has male hormone effect if taken in small amounts, but the effect is inhibited if taken in large amounts.[12,13]

The Aniseed volatile oil is used as flavor agent in foods and cosmetic industries.[12,15]

Aniseed volatile oil components are affected by the plant genetic factor, it is also affected by several physiological and environmental factors such as ripeness, climate, soil and storage conditions as well as the extraction method; and the difference in the composition of volatile oils is quantitative rather than qualitative.[7]

2. EXPERIMENTAL

2.1. Materials and instruments

2.1.1. Materials

- Aniseed was collected from (Aleppo, Homs and Damascus Countrysides) fields in Syria.
- Silica gel 60 (0.063-0.200mm) and silica gel 60 F254 (0.063-0.200mm), Merck (Germany).
- Hexane 99.7%, ethyl acetate 99.8%, toluen 99.9%, anethole 98%, anisaldehyde 98%, estragole 97% and linalool 97%, Merck (Germany).

2.1.2. Instruments

- UV-VIS Spectrophotometry, Jasco, model V-530, system software, made in Japan.
- FT-IR Spectrophotometry, Jasco, model FT/IR 460 Plus, system software, made in Japan.
- ^{1}H-NMR Spectrophotometry, Bruker, 400MHz, system software, made in Swiss.
- MS Spectrophotometry, Finnigan, modle 4000, made in Germany.
- GAS Chromatography, Shimadzu, model GC-9A (FID), made in Japan.
- Rotator Evaporator, Normschliff, model VV1, made in Germany.
- Balance, ±0.05mg, Sartorius, model ED224S, made in Germany.

2.2. Quantitative determination of main components from aniseed oil and comparing them with geography areas farming

The aniseed volatile oil was extracted from aniseed by hexane According to the following steps.[11,14]

1. The samples of aniseed have milled and soaked in hexane for seven days. The extraction process repeated three times.
2. Aniseed volatile oil were separated by distilling the resulting under normal pressure and then the solvent was evaporating using the rotary evaporator under low pressure at a temperature of 40° C.

The component of aniseed volatile oil was identified qualitatively and quantitatively using gas chromatography GC by comparison with standards, and the following conditions applied:

- Chromatographic column was carbowax 20 M, 2mm×2mm.
- Micro-sized injected 5 µL.
- Nitrogen carrier gas flow capacity of 0.5 ml / min.
- Degree Injector heat 200° C.
- The degree of the primitive temperature 90° C was maintained for a period of 4min.
- The final temperature 210° C was maintained for a period of 15min.
- Heating speed of 2 degrees per minute within the range 90°C to 210°C.

The percentage was calculated for anethole, anisaldehyde, linalol and estragole in the aniseed volatile oil using gas chromatographic technique (GC) that were compared with standard compounds. The areas of peaks was compared with the others that belong to standard compounds.

2.3. Separation of two main components from the aniseed volatile oil using column chromatography

Anethole and anisaldehyde were isolated from the aniseed volatile oil using chromatography column using following method.

The chromatography column was prepared with silica gel suspension in hexane, the contents packed in the column and solvent was separated, the stationary phase was carried with enough amount of aniseed volatile oil, when the mobile phase passed the anethole and anisaldehyde and various components were isolating (the mobile phase is toluene:

ethylacetate, 93:7), at a later stage the isolated components (anethole and anisaldehyde) purified using thin-layer chromatography (TLC).

Isolated anethole and anisaldehyde were characterized using available spectra: IR, UV, ^{1}H NMR and MS, and the physical and chemical prosperities were determined.

3. RESULTS AND DISCUSSION

3.1. Results of quantitative determination of essential components from aniseed oil and comparing them with geography areas farming

Anise oil was extracted from *Pimpinella Anisium* L. seeds collected from different areas (Aleppo, Homs and Damascus fields) in Syria and extracted using hexane. The percentage of total oil in the seeds was calculated, and then the physical and chemical properties were determined.

The aniseed volatile oil components was identified qualitatively and quantitatively using gas chromatography GC and compared with pure standards. The components from different aniseed volatile oil were corresponding qualitatively and different quantitative. The obtained results were summarized in the table (1).

Table 1: Percentages of the total oil and volatile oil and some volatile oil components in different geographical areas cultivated.

Percentages %	Aniseed of Aleppo Countryside	Aniseed of Homs Countryside	Aniseed of Damascus Countryside
Total Oil %	8.77	8.52	9.41
Volatile Oil %	4.83	4.42	5.54
Anethole %	86.99	84.74	89.11
Anisaldehyde %	0.564	0.487	0.576
Estragole %	2.971	2.683	3.280
Linalool %	0.0211	0.0064	0.0161

The table (2) shows the retention time for the standard mixture prepared.

Table 2: Retention time for the standard mixture prepared.

Standard Component	Retention time (min)
Linalool	4.46
Estragole	7.88
Anethole	11.15
Anisaldehyde	13.80

The figures (1), (1) and (3) are illustrate for comparative the percentages of the main components in aniseed volatile oil oil and change when the plant areas different.

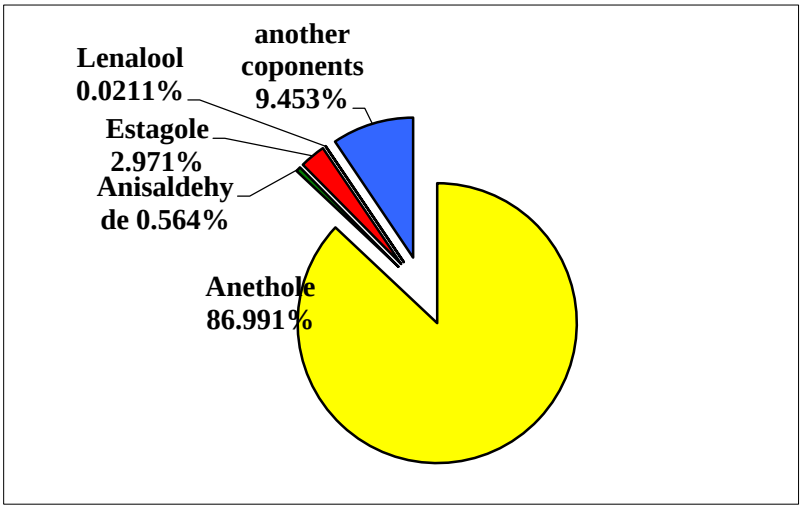


Figure 1: The percentages of main components in the aniseed volatile oil that collected from Aleppo countryside fields.

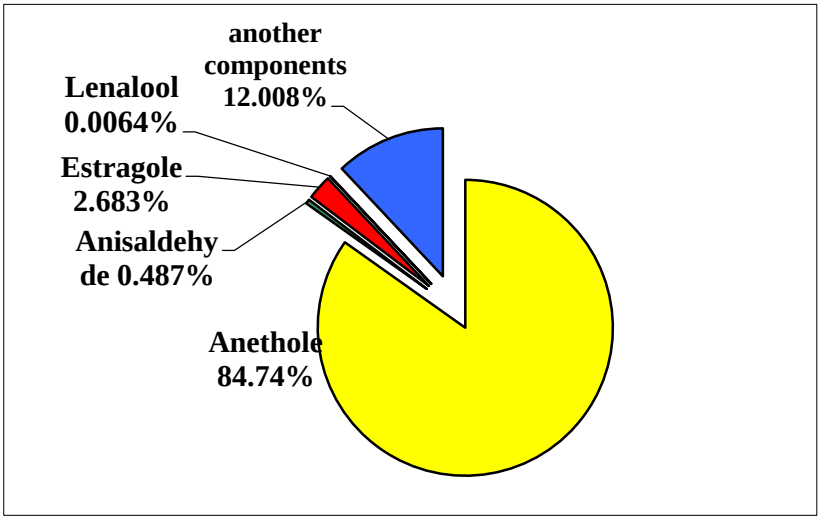


Figure 2: The percentages of main components in the aniseed volatile oil that collected from Homs countryside fields.

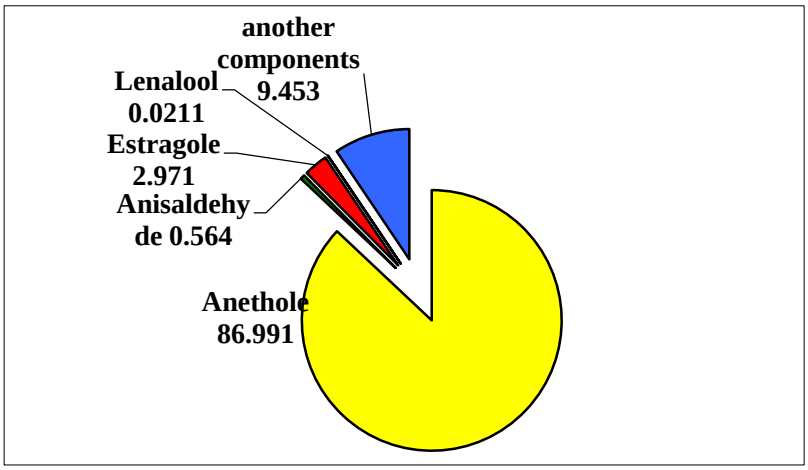


Figure (3): The percentages of main components in the aniseed volatile oil that collected from Damascus Countryside fields.

From the table (1) and figures (1), (2) and (3) we noted that the aniseed volatile oil contains the following major compounds:

1. The percentage of anethole was (84.74% - 89.11%) in the aniseed volatile oil, the biggest percentage was in aniseed collected from Damascus fields.
2. The percentage anisaldehyde was (0.487% - 0.576%) in the aniseed volatile oil, the biggest percentage in aniseed collected from Damascus fields.
3. The percentage estragole was (2.683% - 3.280%) in the aniseed volatile oil, the biggest percentage in aniseed collected from Damascus fields.
4. The percentage linalool was (0.0064% - 0.0211%) in the aniseed volatile oil, the biggest percentage in aniseed collected from Aleppo fields.

We Note from the previous study that the best studied of aniseed are those collected from Damascus fields compared with those collected from Aleppo and Homs fields. This is because several important factors, the most important climate factors.

It is known that the climate of Damascus is cold and snowy in winters, mild and wet in summers, while the climate of Aleppo is cool and rainy in winter, dry and hot summers, and the climate of Homs is very cold winter with formation of frost, hot and few humidity in summer, in addition to having high air currents over year coming from the Mediterranean Sea.

To compare these three climates that different weather which characterizes the climate of Damascus from the rest of other climates because it is the most appropriate climate for the

cultivation of anise and this increases the yield of production, also the quantity of the components are increasing in the seeds.

3.2. Charachterization of the Isolated Compounds

3.2.1. Charachterization of the first isolated product

The first isolated product was ascertained by using the spectroscopies studied (IR, UV, ^{1}H-NMR and MS) to prove their structures. In addition, physical and chemical constants were measured.

3.2.1.1. Determination of the physical constants for first isolated product

Melting point: 21.4^o C

Density at 25^{o}C: 0.9883

Boiling point under normal atmospheric pressure: 230^o C

Refractive index at 25^{o}C: 1.5620

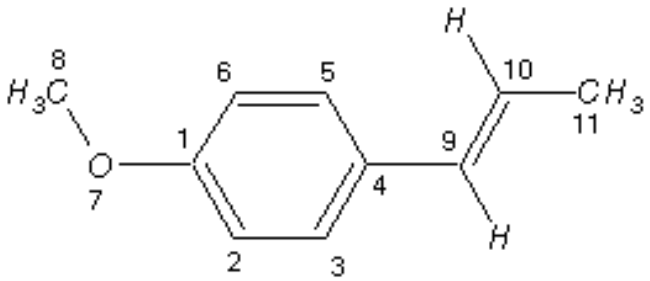
From the physical constants as an initially result, the first product should be Anethole.

3.2.1.2. Structural identification of the first isolated:

A maximum absorption was located at 208nm and 259nm in the UV absorption spectrum of the first isolated product. This result was compatible with the reference values for anethole.[11]

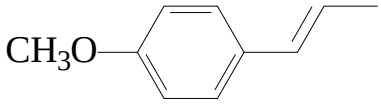
FT-IR spectrum for the first isolated product have the following absorption bands: C=C aromatic (1520 cm^{-1}) C=C vinylic (1620 cm^{-1}), and C-O (1250cm^{-1}).

^{1}H NMR spectrum for $CDCl_3$ solution of the first isolated product shows the following signals: H_2, H_6 (7.2ppm, m), H_3,H_5 (6.8ppm, m), H_9 (6.28-6.34 ppm, d) and H_{10} (5.98-6.33ppm, m).



MS spectrum of the first isolated product had approved its assumption structure. The peak at m/z = 181 resemble the molecular weight of the isolated product.

As a result, the first product is 1-(4-Methoxyphenyl)-1-propene (the anethole).



3.2.2. Charachterization of the second isolated product:

The second isolated product was ascertained by using the spectroscopies studied (IR , UV , ^{1}H NMR and MS) to prove their structures. Also, Physical and chemical constants were measured.

3.2.2.1. Determination of physical constants for second isolated product

Melting point : 0.1^{o} C

Density at 25^{o}C :1.120

Boiling point under normal atmospheric pressure: 248^{o} C

Refractive index at 25^{o}C:1.5764

From the physical constants as a initially result, the second product is anisaldehyde.

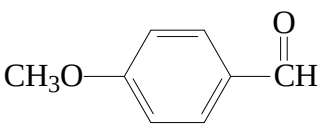
3.2.2.2. Structural identification of the second isolated

A maximum absorption was located at 204nm, 218nm and 275nm in the UV absorption spectrum of the first isolated product. This result was compatible with the reference values for Anisaldehyde.[11]

FT-IR spectrum for the second isolated product have the following absorption bands: C-H aliphatic (2880cm^{-1}), C-H aromatic (3080cm^{-1}), C=C aromatic (1500 cm^{-1} and 1600cm^{-1}) C=O (1250 cm^{-1}), C-H aldehyde (2700cm^{-1} and 2800cm^{-1}), and C=O aldehyde (1700cm^{-1}).

MS spectrum of the second isolated product had approved its assumption structure. The peak at m/z = 136 resemble the molecular weight of the isolated product.

As a result, the first product is 4-Methoxybenzaldehyde (The anisaldehyde).



4. CONCLUION

Anise oil was extracted from *Pimpinella anisium* L. seeds collected from (Aleppo, Homs, Damascus) fields in Syria by hexane. we calculated the percentage of total oil in the seeds and determined physical and chemical characteristics for it.

Aniseed volatile oil was extracted from the aniseed oils and its the percentage was about 50-60% w/w comparison with total oil.

The aniseed volatile oil components was identified qualitatively and quantitatively using gas chromatography GC by comparison with pure standards. The components from different aniseed volatile oil were corresponding qualitatively and different quantitative.

The aniseed volatile oil was chromatographed on column . Anethole and Anisaldehyde were isolated. The isolated compounds were studied using available spectroscopies: IR, UV, 1H NMR, MS, to prove their structures. Also, the physical and chemical data was measured.

REFERENCES

1. Salem M., "Medicinal herbs", Almarreek pub.; Reyad- KSA, 2012.
2. Labania M., "spices", Alsaboni pub.; Cairo, 2012.
3. The Arab Organization for Agricultural Development, " Medicinal, aromatic and poisonous plants", League of Arab States; Alkartoom, 2008.
4. Dhemosh A. S., " Medicinal plants and treatment methods (Part I)", Albatraa pub.; Amman, 1997.
5. Hakeem W.; Hasan Aga M. E.; Badawi S.; Alkadi E.; Darkalt A.; Alshater Z.; Ebrahem Th.; Karbesa M., 2012, "Atlas of medicinal and aromatic plants in the Arab world", the Arab Center for the Studies of Arid Zones and Dry lands; ACSAD; Damascus.
6. Hasan Aga M. E.; Alshamaa E.; Alnori M. S., "Drugs and Phytochemistry", Damascus University pub, 2012.
7. Huet R., "Les Huvilles essentielles d'agrumes Fruits", 1991; 46(5): 551576.
8. Choi H.S. , Sawamura M., Kondo Y., 2002, " Jornal of Food Science (Vol. 67)", Pages: 1713-1718.
9. Felix D.; Melle. J. P.; Routaun Boka, 1997, " Handbook of plant and fungal toxicants", New-York.

10. Gil M.I.; Ferreres F.; Barberan T., " Effect of post harvest storage and processing on the antioxidant constituents (flavonoide and vitamin C) of fresh-cut spinach" , J. Agric. Food chem, 1999; 47: 2213-2217.
11. Miething Holger; Seger Volkmar, " Separation of non-polar compounds by droplet counter-current chromatography", J.Chromatographia, 1989; 478(2): 433-7.
12. Wallis T. E., "Textbook of pharmacognosy", Delhi-India, 1991.
13. Trimen H.; Bentley R., "Medicinal plants. Allied Book center", Dehradun India, 1992.
14. Wagner H.; Bladt S. , 1996, "Plant drug analysis", spreinger – verlag, Berlin; Heidelberg
15. Choi H.S.; Sawamura M.; Kondo Y., Jornal of Food Science, 2002; 67(5): 1713-1718.