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Unconventional Source of Anise Volatile Oil

Mohamed E. Ibrahim[1], Makarem A. Mohamed[1], Hend E.Wahba[1], Salma A. El-Sawi[2]

[1]Department of Medicinal and Aromatic Plants Research, [2] Pharmacognosy Dept., National Research Centre, 33 El Bohouth St., Dokki, Giza, Egypt.

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S A El-Sawi
selsawi7@yahoo.com
+0201225709938

Abstract

Recycling agricultural waste plays a positive role in getting rid of the remnants of plants and reduces the proportion of environmental pollution, especially in agricultural areas, in addition to optimization of the economic situation in Egypt. This work intended to discuss the discovery of new and unconventional ways to produce essential oils. It amid to examine and evaluate anise oil extracted from new plant materials such as herb and waste (remnants of post-harvest) as new sources of anise essential oil. The chemical constituents of anise (*Pimpinella anisum*) oils were analyzed by means of GC and GC/MS. The results of anise oil analysis showed that, nineteen constituents representing 68.72% of the oil herb were identified, against twenty one (93.12 %) and nineteen constituents (84.88 %) for seed and waste oil, respectively. In all cases, the major component of essential oils is anethole <trans> which amounted to 52.17, 65.58 and 62.72 % in the oil extracted from herb, seeds and waste, respectively. All oils were rich in oxygenated monoterpenes (OM) compared with other terpene groups. The OM recorded (62.87%) in herb oil against 81.24 and 79.87 % in the oil of seeds and waste of anise, respectively. Significant compounds were detected in the oil of herb, seeds and waste of anise. From the compounds detected in the oils were, estragole, eugenyl acetate, germacrene D, anethole <cis-> and linalool. Some new compounds were identified in the Egyptian anise oil, such as butyrate, isopentyl N-butyrate, myrtenal, p-anisaldehyde, methyl eugenol, cuparene, nuciferol <E-> and eugenyl acetate .

1. Introduction

Essential oils have been used for medical purposes and as alternative medicine [1-4]. They have also been used widely in the production of perfumes and cosmetics, as well as an anti-fungal and antibacterial. Moreover, essential oil is an important economic source for the national economy of some countries, such as Egypt. Recycling agricultural wastes plays a positive role in getting rid of the remnants of plants and reducing the proportion of environmental pollution, especially in agricultural areas, in addition to optimization of the economic situation. Anise or aniseed (family Umbelliferae or Apiaceae) is an herbaceous flowering annual plant growing up to 3 ft or more tall [5]. It is cultivated in Egypt and the Middle East. Its flavors have parallels with some other spices, fennel [6]. Essential oil of anise can be isolated from the seeds by steam distillation. The essential oil yield is influenced by the growing conditions and extraction process [4]. The major component of the oil is anethole (80–90%), with minor constituents including, estragole, 4-anisaldehyde and pseudoisoeugenyl-2-methylbutyrate [7-9].
Anise is sweet and very aromatic, distinguished by its characteristic flavor [10]. The seeds, whole or ground, are used for preparation of tea. It has been used, specifically its essential oil, in the Egyptian folk medicine for many years [10].The main use of anise plant in traditional European herbal medicine was for its carminative effect. The seed waste is good against belching and upbraiding of the stomached [11]. Anise is also believed to treat menstrual cramps and colic [12].
This work intended to discuss the discovery of new and unconventional source for the production of essential oils. The objective of this work was to identify the chemical composition of the essential oil of Anise in

different stages of the plant (herb and waste) with potential commercial interest. The study of the anise plant as a source of flavoring compounds requires analysis not only seeds but also other parts of the plant. Also the most important objectives of this work is to address the effects of environmental pollution caused by the burning of agricultural waste after harvest

2. Materials and Methods

2.1. Plant materials

This experiment was conducted at Asuit region -Egypt during two successive seasons 2014-2015 and 2015-2016 to study the yield and chemical constituents of the essential oils produced from the green plants, the dry seeds and the waste of anise plant. The seeds were sown in the 15th of November during both seasons. All agricultural practices of anise cultivation were done. Samples of green herb were collected during the formation of the green anise seeds in March of each season. The dry seeds samples of anise plant were taken in May (mature seeds stage) and the dry waste (Straw) was taken after harvest.

2.2. Plant extraction

The essential oils of the dry plant materials were extracted by hydro-distillation for 3 hr. (by Clevenger apparatus)[13]. The essential oils were dehydrated over anhydrous sodium sulfate and subjected to GC/MS analysis.

2.3. Gas chromatography

GC analysis was performed using a Shimadzu GC- 9A gas chromatograph equipped with a DB5 fused silica column (30 m x 0.25 mm i.d., film thickness 0.25 μm). Oven temperature was held at 40°C for 5 min and then programmed until 250°C at a rate of 4°C/min. Injector and detector (FID) temperature were 260°C; helium was used as a carrier gas with a linear velocity of 32 cm/s.

2.4. Gas chromatography- mass spectrometry

GC-MS analyses were carried out on a Varian 3400 system equipped with a DB-5 fused silica column (30 m x 0.25 mm i.d.); Oven temperature was 40 to 240°C at a rate of 4°C/min, transfer line temperature 260°C, injector temperature 250°C, carrier gas helium with a linear velocity of 31.5 cm/s, split ratio 1/60, flow rate 1.1 ml/ min, Ionization energy 70 eV; scan time 1 s ; mass range 40-350 *m/z*..

2.5. Qualitative and quantitative analysis of essential oil

Identifications were made by library searches (Adams, 1995) [15] combining MS and retention data of authentic compounds by comparison of their GC retention indices (RI) with those of the literature or with those of standards available in our laboratories. The retention indices were determined in relation to a homologous series of n-alkanes (C8–C22) under the same operating conditions. Further identification was made by comparison of their mass spectra with those stored in NIST 98 and Wiley5 Libraries or with mass spectra from literature. Component relative concentrations were calculated based on GC peak areas without using correction factors.

3. Result and Discussion

3.1. Oil percentage

Table 1 showed that the seeds contained the highest percentage of oil followed by the waste with minor differences, while the oil percentage of the herb is about one half that of seed.

Table 1: Oil percentage of anise herb, seed and waste oil
(The mean of the two seasons)

Stage	%
Herb	0.53
Seeds	1.16
Waste	1.13

3.2. Anise herb oil

Data in Table 2 showed that nineteen constituents, representing 68.72% of the Egyptian anise herb essential oil, were identified. The major components of the essential oil are anethole <trans> (52.17), estragole (8.03%), eugenyl acetate (2.55%), germacrene D (2.11%), anethole <cis-> (1.06) and linalool (1.04%).

Essential oil of anise herb classified into five groups which are monoterpene hydrocarbons (MH), oxygenated monoterpenes (OM), sesquterpenes hydrocarbons (SH) , oxygenated sesquterpenes (OS) and various compounds (VC).

Table 2: Oil constituents of anise herb, seed and waste oils

Compound	Formula	KI	Herb	seeds	waste	Classification
			%	%	%	
Methyl butyrate	$C_5H_{10}O_2$	724	-	0.02	-	VC
Propyl butyrate	$C_7H_{14}O_2$	896	-	3.02	-	VC
α–Pinene	$C_{10}H_{16}$	939	0.04	0.06	0.04	MH
Sabinene	$C_{10}H_{16}$	976	0.04	0.04	0.05	MH
Myrecene	$C_{10}H_{16}$	991	0.03	0.03	0.02	MH
Limonene	$C_{10}H_{16}$	1031	0.12	0.95	-	MH
Benzyl alcohol	C_7H_8O	1032	0.03	-	-	VC
Isopentyl, N-butyrate	$C_9H_{18}O_2$	1060	0.26	3.73	2.19	VC
Terpinene <gamma->	$C_{10}H_{16}$	1062	0.06	0.04	0.02	MH
Linalool	$C_{10}H_{12}O$	1098	1.04	3.33	4.43	OM
Dihydro terpineol <cis.beta->	$C_{10}H_{20}O$	1136	-	-	0.01	VC
Myrtenal	$C_{10}H_{14}O$	1193	0.26	0.03	0.06	OM
Terpineol <alpha>	$C_{10}H_{18}O$	1189	-	0.01	-	OM
Myrtenol <cis>	$C_{10}H_{16}O$	1194	-	-	1.07	OM
Estragole	$C_{10}H_{12}O$	1195	8.03	10.81	11.02	OM
Cinnamaldehyde <Z->	C_9H_8O	1214	0.07	-	-	VC
p-Anisaldehyde	$C_8H_8O_2$	1252	-	0.12	-	VC
Anethole <cis>	$C_{10}H_{12}O$	1265	1.08	1.48	0.1	OM
Anethole <trans>	$C_{10}H_{12}O$	1283	52.17	65.58	62.72	OM
Methyl eugenol	$C_{11}H_{14}O_2$	1403	-	0.04	-	VC
Anisyl acetate <para->	$C_{10}H_{12}O_3$	1416	-	-	0.04	OM
Humulene <beta->	$C_{15}H_{24}$	1440	-	-	0.06	SH
Humulene <alpha->	$C_{15}H_{24}$	1454	-	-	0.04	SH
Ethyl cinnamate <E->	$C_{11}H_{12}O_2$	1462	-	-	0.14	VC
Germacrene D	$C_{15}H_{24}$	1480	0.08	0.03	0.08	SH
Cuparene	$C_{15}H_{24}$	1502	-	0.02	-	SH
Germacrene B	$C_{15}H_{24}$	1556	2.11	0.03	0.06	SH
Cadinene <delta>	$C_{15}H_{24}$	1524	0.03	-	-	SH
Eugenyl acetate	$C_{12}H_{14}O_3$	1525	2.55	3.42	2.30	VC
Santalol < Z, alpha-}	$C_{15}H_{24}O$	1678	0.03	-	-	OS
Coniferyl alcohol <E>	$C_{10}H_{12}O_3$	1729	0.69	-	-	VC
Nuciferol <E->	$C_{15}H_{22}O$	1758	-	0.33	-	OS
Total			68.72	93.12	84.45	

MH= Monoterpene hydrocarbons OM= Oxygenated monoterpenes
SH = Sesquterpenes hydrocarbons OS= Oxygenated sesquterpenes
VC= Various compounds

The (OM) was the highest percentage (62.87%) in the herb oil, followed by (VC) (3.31%) compared with the other chemical classes (MH) (0.29) and (OS) (0.03%). (OM) group included anethole <trans-> (52.17%), estragole (8.03%), anethole<cis-> (1.08%), linalool (1.04 %), isopentyl, N- butyrate (0.26 %), myrtenal (0.26 %) and benzyl alcohol (0.03 %).

Germacrene B was found as the main constituent of (SH) group which recorded 2.11% compared with germacrene D (0.08 %) and cadinene <delta-> (0.03%) in the same group. On the other hand santalol <Z, alpha-> was found in a low concentration (0.03) in the (OS) group. The (VC) included cinnamaldehyde <Z-> (0.07%), eugenyl acetate (2.55%) and coniferyl alcohol <E> (0.69%).

Table 3: Percentage of different chemical groups in anise herb, seed and waste oils

Group	Herb	Seeds	Waste
Monoterpene hydrocarbon	0.29	1.12	0.13
Oxygenated monoterpenes	62.87	81.24	79.44
Sesquterpenes hydrocarbons	2.22	0.08	0.24
Oxygenated sesquterpenes	0.03	0.33	0
Various compounds	3.31	10.35	4.64
Total	68.72	93.12	84.45

3.3. Anise seed essential oil

The main compounds of anise dry seed essential oil were trans-anethole (65.58%), estragole (10.81%), isopentyl N-butyrate (3.73%), eugenyl acetate (3,42%), linalool (3,33 %), propyl butyrate (3.03%) and anethole <cis-> (1.48%).The major group in the dry anise seed oil was also (OM). The total percentage of OM recorded (81.24%) against 1.12, 0.08, 0.33 and 10.33% for (MH), (SH), (OS) and (VC) group, respectively.

Similar results were reported by Khalid (2015) [16] and Milica *et al* (2015) [17] who stated that trans anethole was the main constituent of anise oil from Egypt and Serbia. Among the new constituents of anise seed oil identified in this work are methyl butyrate, propyl butyrate, isopentyl N-butyrate, myrtenal, p-anisaldehyde, methyl eugenol , cuparene , nuciferol <E-> and eugenyl acetate,

3.4, Anise waste essential oil

Nineteen constituents representing 84.88% of the Egyptian waste essential oil were identified. Anethole <trans> was found as the major constituent of anise waste oil which recorded 62.72% followed by estragole (11.02%), linalool (4.43%) , eugenyl acetate (2.3%), isopentyl N-butyrate (2.19%) and myrtenal <cis-> (1.07%). Essential oil of anise waste consists of four chemical groups. These groups were (MH), (OM), (SH) and (VC).

Data in Table 2 revealed the presence of eight components in (OM) group which recorded 79.87 %, against four, three and four compounds for (MH) (0.13%), (SH) (0.24%) and (VC) (4.64%) group, respectively. β–humulene (0.06%) and α–humulene (0.04%) were found as new compounds in the anise waste oil.

Comparing the oils of the herb, seeds and waste, it was found that, the main constituent was trans-anethole in the three oils. Its percentages were the highest in seeds oil followed by the waste oil. The least percentage was recorded in the herb oil. Some minor compounds found in seed oil as methyl butyrate, terpineol, p-anisaldehyde, methyl eugenol and nuciferol [E-] were absent in the other oils. Propyl butyrate which was found in reasonable amounts in seed oil was also absent in both, herb and waste oils, while limonene which found in moderate amounts in seed oil was absent in waste oil and found in much lower amounts in herb oil. On the other hand, five compounds were found in the herb oil and were absent in seed and waste oils namely benzyl alcohol, cinnamaldehyde <Z->, cadinene <delta>, santalol < Z, alpha-) and coniferyl alcohol <E>. The first four compounds were found in minor concentrations, while the waste oil contained four minor compounds; dihydro terpineol <cis, beta>, anisyl acetate (para), humulene (alpha-) and ethyl cinnamate and one compound at a higher concentration, myrtenol <cis->, not detected in herb and seed oils. The highest variation in group percentage was found in (VC) group followed by the (MH) group (Table3). The percentage of OM ranged from 62.78 % in herb oil to 81.24% in seed oil, while the waste group recorded 79.44% which is closer to that of the seed oil. Data in Table 2 revealed that except for limonene, anethole<cis-> and propyl butyrate, the composition of the waste oil resemble that of the seed oil. The composition of the waste oil was closer to that of the seed oil than that of the herb oil. This was also clear in the percentage of the main group (OM) and that of (SH) which means that waste oil resemble the seed oil to a great extent.

Conclusion

Optimization of the aromatic plant wastes by recycling the remnants of those plants after harvest for the purpose of reproducing new volatile oil from waste, as well as reducing environmental pollution after the burning of dry plant waste after harvest is a demand. The work was based on investigation and evaluation the anise oil extracted from the remains of dry plants after harvest of seed by identifying the chemical compositions and comparing it with the green herb oil at green seeds formation stages (Immature seeds), as well as from anise seed oil extracted from common source (dry mature seeds). In all cases there was a great similarity between components in oil extracted from the remains of dry plants after harvest with anise oil extracted either from dry seeds or from green herb at immature green seeds formation stage. The variation was only in the proportions of components with some additional new compounds. Anethole <trans> was found as the major constituents in all samples of anise plant. Taking in consideration that the yield of waste per unite cultivated area are greatly higher than that of seeds, it is clear that the extraction of oil from wastes is of great economic benefit especially that the composition of seed and waste oils are very close to each other.

Recommendation

We recommend strongly recycling aromatic agricultural waste after the harvest for two reasons:
First: Reduction of environmental pollution resulting from the burning of agricultural waste after harvest.
Second: Increase economic return by getting more of essential oil yield.

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