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Studies on the Components of Essential Oil of *Zanthoxylum armatum* by GC-MS

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Abstract

The essential oil of *Zanthoxylum armatum* was extracted through hydro distillation and analyzed by GC-MS. Hydrocarbon fraction (17.35%) of the oil was much lower and oxygenated compounds comprised fairly high portion of essential oil (39.21%). Percentages of monoterpenes and sesquiterpenes found were 47.33% and 10.83% respectively. Oxygenated monoterpenes comprised major profile of chromatogram of essential oil of Zanthoxylum armatum *i.e.* 37.23% where as monoterpene hydrocarbons were 10.09%. Alcoholic percentage was much higher *i.e.* 26.76% and 15-hexadecanoloide (6.58%) the only cyclic ester was found in relatively high percentage.

Keywords: Essential Oil, *Zanthoxylum armatum*, Gas Chromatography-Mass Spectrometry (GC-MS)

1. Introduction

Family *Rutaceae* is a large botanical family [1] which comprises about one hundred and fifty genera [2] distributed in tropical and temperate region of the world [3-5]. From economic point, *Rutaceae* is an important family. *Zanthoxylum armatum* locally known as timber [6-9] is a wild species which is native to Laran Pass in Dir, Murree, Saidpur, Hazara, Kalapani, Jhelum and Swat valley. Hard thorny dense tree [10] of Timber is normally available on banks of Lilly streams and rivers.

The fruits and seeds are employed as an aromatic tonic in fever, dyspepsia, carminative, stomachic, anthelmintlc and expelling roundworms [11-13].The volatile oil is employed as an antidiarrehal, antiseptic, deodorant and anticataerhal [14-16]. The oil has a good tenacity and is appreciated for its fixative qualities. Almost all parts of the plant are aromatic and hence, supposed to possess essential oil. The essential oil composition can provide much more knowledge regarding the medicinal properties and active constituents of this plant [14].The pharmaceutical companies generally use *timur* fruit for making different types of toothpaste [17].

An examination of literature shows that a lot of work has been done on essential oils of family *Rutaceae* [18-20] but work on the essential oil of this species is very few [12,16,21].The present study deals with the chemical analysis of essential oil of wild collected timber seeds and is part of our screening programme of Pakistan wild aromatic flora.

2. Metarials and Method

2.1. Extraction of Essential Oil

The mature seeds of *Zanthoxylum armatum*, was collected from Balakot Mansehra (N.W.F.P Pakistan) and crushed for hydro distillation. The essential oil was extracted from distillate with diethyl ether: hexane mixture (1:3 v/v). Solvent mixture was removed by vacuum distillation.

2.2. Gas Chromatographic Analysis

Gas chromatographic analysis was carried out on Shimadzu GC-14A chromatograph equipped with flame ionization detector fitted with 25 m × 0.22 mm (id.) SE-30 capillary column at carrier gas flow rateof 2 ml/min with split ratio was 1:100 and sample size 0.2 µl. The column temperature was programmed at 70˚C for 4 min. with 4˚C/min rise to 220˚C while detector and injector temperature were maintained at 300˚C and 220˚C respectively. Percentage composition of individual components was calculated on the basis of peak area using Shimadzu C-R4A chromatopac electronic integrator.

2.3. Mass Spectrometry

Jeol model JMS-AX505H mass spectrometer combined with Hewlett Packard 5890 gas chromatograph was used for GC-MS analysis. The essential oil was injected on a 25 m × 0.22 mm BPS (5% phenyl-methyl silicone) capillary column using helium as a carrier gas with split ratio 1:100 and interface temperature 230˚C. Data acquisition and processing were performed by Jeol JMA DA 5000 system. Various components were identified by their retention time and peak enhancement with standard samples and MS library search.

3. Result and Discussion

The aim of present studies was to investigate composition of essential oil of *Zanthoxylum armatum* by GC-MS.

3.1. Composition of Essential Oil

Examination of essential oil of *Zanthoxylum armatum* by GC-MS revealed the presence of twenty-two components. Percentage of unidentified and identified fraction of oil was 34.554% and 68.364%. **Table 1** shows the list of compounds identified by GC-MS, and mass data of the components of essential oil of *Zanthoxylum armatum.*

GC-MS results showed that 3-borneol (9.718%), isobornylacetate (9.574%) and dihydro carveol (8.816%) are the components of highest percentage in the essential oil of *Zanthoxylum armatum*.In general citrus are mostly studied species of family Rutaceae [22,23] reported hydrocarbon as a major fraction of Essential oil of Sweet orange, lemon and grapefruit ranging from 83% - 95% and oxygenated components of these oils reported are in the range of 1.64% - 1.5%.

Table 1. Percentage Composition Of *zanthxylum armatum* Essential Oil.

Component	**Percentage**
α-pinene	0.685
α-terpinene	0.516
Sabinene	2.329
Δ^3-carene	0.698
β-pinene	1.889
α-phellendrene	0.661
terpinolene	2.148
α-terpinene	1.167
dihydro carveol	8.816
3-borneol	9.718
iso thujanol	3.596
terpinen-1-ol	0.697
iso pulegol	1.48
sabinene hydrate	0.903
iso fenchol	2.454
isobornyl acetate	9.574
trans-caryophyllene	3.074
humelene oxide	0.497
β-elemene	4.191
caryophyllene oxide	0.497
hexadecanoic acid	6.186
15-hexadecanolide	6.588

3.2. Comparison of Oil

The oxygenated components contribute to the flavor of oil. The alcohol, aldehyde and ether may contribute to the aroma of extracted oil [24]. In present studies, major fraction of the essential oil of *Zanthoxylum armatum* is oxygenated *i.e.* 39.21%, which is very far enough by the reported value, generally falls in the range of 1.6% - 3.0% [25,26]. Percentage of monoterpene hydrocarbons calculated from GC-MS (Nist library) results was (10.093%), oxygenated monoterpenes (37.238%), sesquiterpenes hy- drocarbon (7.265%) and oxygenated sesquiterpenes (3.571%) respectively. Decanal, octanal and nonal are the most commonly observing aldehydes in sweet orange and other species of citrus [19,27,28] reported aldehydic content of essential oil of sweet orange as octanal (0.2% - 2.8%) and decanal (0.1% - 0.7%). The aldehydic content of *Zanthoxylum armatum* analysed by GC-MS in present studies was much higher *i.e.* 6.588% than found in other species of *Rutaceae* family 16-hexadecanoloide was the only cyclic ester was found in the essential oil of *Zanthoxylum armatum.*

Major portion of oxygenated fraction of the oil was comprised by alcohols *i.e.* 26.761%. dihydro carveol, 3-borneol, iso-thujanol, terpinene-1-ol, iso-pulegol, and iso-fenchol were the alcohols which were observed in predominant percentages in the essential oil of *Zanthoxylum armatum* (**Table 2**).

Alcohols in oil are believed most important to flavor. It is also used as flavoring agents in the confectionery industry and in the manufacture of soft drinks, pharmaceutical and perfumery industries [29,30].due to the presence of oxygenated components the oil is recommended for flavoring agents in beverages and food

Table 2. Mass Data of Essential Oil of *Zanthoxylum armetum* by GC-MS.

Component	*Mass data*
α-pinene	(M^+, 25), 136 (25%), 121 (8%), 105 (9%), 93 (100%), 41 (10%)
α-terpinene	(M^+, 20), 121 (17%), 105 (12%), 93 (100%), 77(35%), 65 (10%), 51 (10%)
Sabinene	(M^+, 55), 121 (17%), 105 (10%), 93 (100%), 77 (12%) 51 (5%), 41(45%)
Δ^3-carene	(M^+, 22), 121 (20%), 93 (100%), 77 (25%), 51 (7%), 41 (27%)
β-pinene	(M^+, 10), 121 (12%), 105 (10%), 93 (100%), 79 (13%), 69 (35%), 53 (7%), 41 (25%)
α-phellendrene	(M^+, 45), 121 (3%), 105 (5%), 93 (100%), 91 (95%), 77 (45%), 65 (12%), 51 (10%), 41 (10%)
terpinolene	(M^+, 70), 121 (89%), 105 (35%), 93 (100%), 79 (55%), 67 (20%), 51 (28%), 41 (45%)
α-terpinene	(M^+, 48), 121 (100%), 105, (35%), 93 (72%), 77 (30%), 65 (5%), 41 (29%)
dihydro carveol	(M^+, 1%), 136 (50%), 81 (70%), 107 (45%), 93 (48%), 79 (25%), 67 (40%), 55 (20%), 41 (100%)
3-borneol	(M^+, 5), 137 (7%), 121 (17%), 95 (100%), 91 (25%), 81 (28%), 41 (15%)
iso thujanol	M^+, 136 (2%), 121 (25%), 95 (50%), 79 (45%), 67 (48%), 55 (50%), 43 (100%)
terpinen-1-ol	M^+, 136 (40%), 137 (51%), 121 (48%), 93 (55%), 81 (98%), 67 (30%), 55 (50%), 43 (100%)
iso pulegol	(M^+, 2), 121 (40%), 11 (7%), 95 (48%), 81 (55%), 67 (78%), 55 (50%), 41 (100%)
sabinene hydrate	(M^+, 2), 139 (7%), 121 (15%), 111 (18%), 93 (20%), 81 (22%), 71 (40%), 55 (30%), 43 (100%)
iso fenchol	(M^+, 1), 136 (10%), 121 (5%), 111 (8%), 81 (100%), 67 40%), 43 (45%)
isobornyl acetate	M^+, 154 (5%), 136 (40%), 121 (45%), 108 (9%), 95 (75%), 81 (20%), 67 (22%), 55 (15%), 43 (100%)
trans-caryophyllene	(M^+, 3), 189 (7%), 175 (4%), 161 (9%), 147 (15%), 133 (40%), 105 (45%), 91 (60%), 79 (48%), 69 (40%), 41 (100%)
humelene oxide	(M^+, 5), 161(3%), 138 (50%), 109 (55%), 96 (60%), 81 (40%), 67 (100%), 43 (85%)
β-elemene	(M^+, 2), 189 (5%), 175 (3%), 161 (20%), 133 (17%), 121 (22%), 105 (50%), 93 (70%), 79 (80%), 67 (100%), 41 (72%)
caryophyllene oxide	M^+, 187 (6%), 161 (8%), 149 (9%), 121 (25%), 107 (30%), 91 (60%), 79 (72%), 67 (45%), 41 (100%)
hexadecanoic acid	(M^+, 45), 239 (55%), 213 (45%), 185 (48%), 157 (46%), 129 (59%), 60 (100%), 41 (98%)
15-hexadecanolide	(M^+, 10), 236 (42%), 218 (20%), 192 (13%), 55 (100%), 39 (80%)

products. In the preparation of certain traditional dishes the use of timur as a flavoring agent or spice is very popular [17]. Alcoholic compounds found in *Zanthoxylum armatum* are variably found in the essential oils of sweet orange, lemon and grape fruit, but in low concentration as compared to the present studies. α-terpineol and terpinene-4-ol are known as degradation products of limonene in citrus essential oils [31].

4. Conclusions

In previous studies [12,14] limonene is present in *Zanthoxylum armatum but* in our study no limonene was found in the essential oil of *Zanthoxylum armatum*. The prominent monoterpene hydrocarbons are α-pinene (0.685%), sabinene (2.329%) and α-terpinolene (2.148%). [19,20] reported myricene, α-pinene and sabinene the monoterpene hydrocarbon with second highest percentage after limonene. Only two compounds identified as sesequiterpene *i.e.* trans-caryophyllene and β-elemene with 3.074% and 4.191% respectively.

5. References

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