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High concrete and ester containing Jasmine species *(Jasminum malabaricum* Wight)

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Abstract
The present investigation was carried out to identify the compounds present in the head space volatiles of *Jasminum malabaricum* (IC560611). The Volatile compounds analysis of *J. malabaricum* flowers was carried out by solid phase micro extraction (SPME) and gas chromatography - mass spectrometry (GC-FID and GC-MS). A total of 109 volatile compounds accounting for 93.28% of the total volatiles present in the flowers. Of the various volatile compounds identified, terpenoids constituted major group accounted for 68.71% followed by esters representing 17.18%. Main constituents identified were 2-Methyl-2-bornene and Pentadecane (Hydrocarbons), β-Caryophyllene, α-Farnesene, trans-Ocimene and 3-methylene-p-menth-8-ene (Terpenoids), 2-Hexenyl propanoate and cis 3-Hexenyl tiglate (Esters), Linalool, Nerolidol and Cubenol (Oxygenated Terpenoids), 2-(5-Methyl-5-vinyltetrahydro-2-furanyl)-2-propanol and 1-Hexen-3-ol (Alcohols), cis-Jasmone and α-iso-Methyl ionone (Aldehydes and ketones), (2E)-5-Hydroxy-2-pentenenitrile and Indole (Nitrogenated Compounds). The result of this study revealed that the solid phase micro extraction (SPME) and gas chromatography - mass spectrometry (GC-FID and GC-MS) method is efficient, selective and rapid in the identification of the volatile compounds and composition variations.

Keywords: jasmine, *Jasminum malabaricum* Wight, high concrete

Introduction

Jasmine is an important traditional flower crop and belongs to the family *Oleaceae*. The genus *Jasminum* comprises of about 200 plant species (Bailey, 1958) [1]. It is the major traditional flower crop of southern parts and also grown in some of the northern parts of the Country. It is grown for different uses which includes traditionally for loose flowers, gardening purpose, making garlands and for the extraction of concrete and absolute and essential oils, used in high grade perfumery industry. Jasmine concrete and its absolute is an invaluable item in perfumery industry. It is regarded as unique, as it blends well with other floral extracts and which is highly valued throughout the world for its high grade perfumes. It is used in highly expensive perfumes and a considerable quantity of jasmine concrete has been produced in India for the last 20 years.

Jasmine concrete is produced in Morocco, France, Italy, Egypt, Guinea, the Comoro Islands, India, Lebanon, China, Taiwan and Japan. Global demand level for Jasmine concrete is around 500 tones per annum. Major global buyers are USA, UK, France, Japan, Russia and Holland. India is the second largest exporter of jasmine oil in the world accounting for over 40% of total world exports in jasmine oil. The world production of essential oils is growing at more than 10 per cent annually and at present it is estimated at about 1, 10,000 tonnes valued at over 11 billion US dollars.

Three species of jasmine viz. *J. sambac, J. auriculatum and J. grandiflorum* is cultivated in a commercial scale (Rimando, 2003; Green and Miller, 2009) [9]. *At present J. grandiflorum* and *J. sambac* are the two-species used for concrete extraction. The yield of the concrete from these varieties ranges from 0.2 to 0.3 %. *J. malabaricum*, which is hitherto unexplored for this purpose, has given rise to high concrete content of 0.375 to 0.45 %. The aroma of the product is unique, superior with subtle refreshing notes. GC-MS analysis of the product revealed that it contains more compounds with ester functional groups. These ester functional groups confer its unique fragrance qualities. The product obtained from *J. malabaricum* has unique features with high amount of ester components. This makes it a preferred product over the traditional one. The purpose of this study was to find out the feasibility of *J. malabaricum* species to the industrial use as a new potential jasmine species with high concrete recovery with high esters group.

Material and Methods

J. malabaricum germplasm (IC 560611) was collected from northern parts of Western Ghats and successfully domesticated at IIHR, Bengaluru, Karnataka (13° 58' N Latitude, 78° E Longitude and 890 m above mean sea level.

Flower material

Jasmine flower samples (grown in the open field) were obtained from the filed in IIHR, Bangalore. The volatile fragrance constituents were analyzed by headspace-solid phase micro extraction (HS-SPME) coupled to GC-MS.

SPME extraction of flower fragrance volatiles

Studies on the head space volatiles of flowers (fresh and dried flowers), were reported from direct sampling using SPME methods (Pawliszyn, 1997, Alain *et al* 2009, Li *et al.* 2008, Perraudin *et al.* 2006, Takeoka *et al.* 2008) [11, 10, 7, 12, 4] to avoid interferences from non-volatile matrix components. For this reason, headspace sampling for the extraction of volatiles was selected for this study. SPME types DVB/CAR/PDMS, 50/30 µm, highly crossed linked (Supelco), fibre was used for extraction of volatile compounds from flowers.

Extraction process for head space volatiles of Jasmine flower was followed as described earlier (Takeoka *et al.* 2008; Chaichana *et al.* 2009; Lee *et al.* 2010; Denga *et al.* 2004; Perraudin *et al.* 2006; Li *et al.* (2008) [4, 2, 6, 3, 12, 7]. In the two separate 50 mL vials, having screw caps with silicon rubber septum 15 g of flowers were transferred. A manual SPME holder and the commercial SPME fibre device (Supelco Inc. Bellefonte, PA, USA) coated with DVB/CAR/PDMS (50/30 µm, highly crossed linked) fiber was first conditioned by inserting it into the GC injector port at 260°C for2 h. For sampling, the conditioned fiber was inserted into the headspace of the flask for 3 hrs at 25 ±1 °C.

GC analysis

Subsequently, the SPME device was introduced in the injector port for gas chromatographic analysis and was remained in the inlet for 15 min. The GC-FID analysis was carried out using a Varian-3800 Gas Chromatograph, equipped with a FID detector. Nitrogen (1ml/min) was used as the carrier gas. The components were separated on VF-5, (factor Four) capillary column from Varian, USA, 30 m x 0, 25 mm i. e. 0, 25 µm film thickness. The injector temperature was set at 260 ºC and all injections were made in split mode (1:5). The detector and injector temperature was 270 ºC and 260 °C, and the temperature programmed for column was as follows: 50 °C for 2 min at an increment 3 °C /min to 200 °C, hold for 3 min, then 10 °C/min to 220 °C and maintaining the constant temperature for 8 min.

Capillary gas chromatography and mass spectrometry (GC/MS)

The system consisted of a Varian-3800 Gas Chromatograph coupled to a Varian-4000 Ion-Trap mass spectrometer. The ion trap, transfer line and ion source temperatures were 210 °C, 230 °C and 220 °C, respectively. A 30 m x 0.25 mm id 0, 25 mm film thickness) VF-5MS (Factor four) fused-silica capillary column from Varian, USA was used. Helium was used as carrier gas at a column head pressure of 20 psi. Narrow bore (0.75nim id.) injector port liners were used. The mass spectrometer was operated in the external electron ionization mode. The carrier gas was helium 1 ml/min; injector temperature, 260 °C; trap temperature 220 °C, ion source-heating at 230 °C, transfer line temperature 240 °C, EI-mode was 70 eV, with full scan-range 50-450 amu was used. Temperature pogramme for column was used same as described for GC-FID above. The total volatile production was estimated by the sum of all GC-FID peak areas in the chromatogram and individual compounds were quantified as relative percent area. Volatile compounds were identified by comparing the retention index which was determined by using homologous series of n-alkanes (C_5 to C_{32}) as standard (Kovats, 1965) [5] and comparing the spectra available with two spectral libraries using Wiley and NIST-2007.

Results and Discussion

GC/MS analysis resulted in the identification of major compounds *in Jasminum malabaricum* germplasm (IC 560611) such as 2-Methyl-2-bornene (0.692%) and Pentadecane (0.573%) in hydrocarbons, β-Caryophyllene (17.007%), α-Farnesene (11.304%), trans-Ocimene(9.695%) and 3-methylene-p-menth-8-ene (9.295%) in terpenoids, 2-Hexenyl propanoate (8.299%) and cis 3-Hexenyl tiglate (3.880%) (Esters), Linalool (2.065%), Nerolidol (2.065%) and Cubenol (1.068%) in oxygenated terpenoids, 2-(5-Methyl-5-vinyltetrahydro-2-furanyl)-2-propanol (0.247%) and 1-Hexen-3-ol(Alcohols) (0.111%) , cis-Jasmone (0.706%) and α-iso-Methyl iononein (0.596%) in aldehydes and ketones, (2E)-5-Hydroxy-2-pentenenitrile (0.852%) and Indole (1.212%) in nitrogenated compounds. Whereas, Ethyl salicylate (0.007%) of Esters, α-Sinensal (0.007%) and ζ.-Cadinol(0.011%) of Oxygenated Terpenoids, cadina-1,4-diene (0.008%), α-Guaiene(0.010%) and γ-Cadinene (0.008%) of terpenoids and lastly 2-Methyl-1-nonen-3-yne(0.010%) of hydrocarbons were present as minor compounds.

Associated characters

J. malabaricum germplasm (IC 560611) registered high concrete recovery (0.375%) with significantly higher percentage of terpenoids (62.59 %) and esters (17%) followed by oxygenated terpenoids, hydrocarbons, nitrogenated compounds, aldehydes and ketones and alcohol group of volatiles in flowers (Table 1).

The genotype of *J. grandiflorum*, CO-1 pitchi concrete consists of major volatile compounds namely Pentane,3-ethyl-2,2,2- dimethyl-; Pentane-2,2,3,4-tetramethyl-; 1- Pentanol,4-methyl-2-propyl-; Isobutyl vinylacetate; 2-Butanamine,3,3-dimethylfound as major compounds (Table 2, Fig 2). Whereas, 1-Heptatriacotanol; Ethyl isoallocholate; Tricyclo triacontane, 1, 7- diepoxy; Cholestan-3-01, 2-methylene- and E, E, Z-1, 3, 12-Nonadecatriene-5, 14-diol were present as minor compounds (Rachana *et al.*2017) [8].

Whereas in *J. malabaricum* main constituents identified were 2-Methyl-2-bornene and Pentadecane (Hydrocarbons), β-Caryophyllene, α- Farnesene, trans-Ocimene and 3-methylene-p-menth-8-ene (Terpenoids), 2-Hexenyl propanoate and cis 3-Hexenyl tiglate (Esters), Linalool, Nerolidol and Cubenol (Oxygenated Terpenoids), 2-(5-Methyl-5-vinyltetrahydro-2-furanyl)-2-propanol and 1-Hexen-3-ol (Alcohols), cis-Jasmone and α-iso-Methyl ionone (Aldehydes and ketones), (2E)-5-Hydroxy-2-pentenenitrile and Indole (Nitrogenated Compounds).

Conclusion

At present *J. sambac*, and *J. grandiflorum* are cultivated commercially for concrete extraction. The concrete recovery from *J. grandiflorum* 0.25-0.30 %. And from *J. sambac* is 0.15% - 0.18%. Any new species with high concrete recovery can boost the perfumery industry in India. Comparison with above two species which are under cultivation, *J. malabaricum* germplasm (IC 560611) is domesticated from wild at IIHR Bengaluru, is unique because of its high concrete recovery (0.375%). And the flowers emit fruit fragrance due to the presence of high esters group (17%), which makes it different from other Jasmine species.

New species with high concrete recovery can boost the perfumery industry. Therefore, *J. malabaricum* has a potential for commercial flower production and can be used in future breeding programmes.

Table 1: Volatile compounds composition in *J. malabaricum.*

Name of the Compounds	**K.I.***	***J. malabaricum (%)***
Hydrocarbons		
3-Methyl-1-cyclopentene	610	0.019
Toluene	762	0.043
Ethylbenzene	856	0.024
p-Xylene	861	0.223
3-Butyl-1-cyclopentene	935	-
1,3,5,5-tetramethyl-1,3-Cyclohexadiene	997	0.396
2-Methyl-1-nonen-3-yne	1002	0.010
1,2-Dimethyl-3-vinyl-1,4-cyclohexadiene	1018	0.107
2-Methyl-2-bornene	1021	0.692
1-Undecyne	1116	0.035
(-)-Aristolene	1403	0.422
1,5,9,13-Tetradecatetraene	1411	0.033
(+)-9-Aristolene	1450	0.107
4-Isopropyl-1,6-dimethyl-1,2,3,4,4a,7-hexahydronaphthalene	1528	0.037
Pentadecane	1505	0.573
Eicosane	2006	-
		2.721
Terpenoids		
Sabinene	971	0.155
α-Pinene	938	0.081
Dihydromyrcene	947	0.407
δ- 3-carene	1009	0.041
cis-Ocimene	1042	0.397
trans-Ocimene	1052	9.695
3-methylene-p-menth-8-ene	1105	9.295
1,3,8-para-Menthatriene	1118	1.623
Allo-Ocimene	1127	0.205
E,E-2,6-Dimethyl-1,3,5,7-octatetraene	1134	0.590
α-Cubebene	1345	0.073
Ylangene	1371	0.031
α-Copaene	1375	0.112
β-Elemene	1391	0.028
β-Cubebene	1393	0.042
α-Longipinene	1348	0.099
α-Gurjunene	1411	0.150
α-Cedrene	1415	0.202
β-Caryophyllene	1418	17.007
α-Guaiene	1425	0.010
α-Amorphene	1433	0.094
(+)-Aromadendrene	1439	0.050
α-Humulene	1459	5.814
α-Patchoulene	1464	0.083
Germacrene D	1464	0.231
(+)-Epi-bicyclosesquiphellandrene	1470	-
γ-Muurolene	1474	-
α-Curcumene	1476	0.170
α-Muurolene	1495	-
(Z,E)-α-Farnesene	1496	2.593
Valencene	1499	0.028
γ-Cadinene	1510	0.012
Germacrene B	1512	0.016
δ-Cadinene	1515	0.025
α-Farnesene	1522	11.304
(-)-β-Cadinene	1522	0.241
cadina-1,4-diene	1542	0.008
Bicyclogermacrene		0.720
trans-γ-bisabolene		0.872
		62.504

Oxygenated Terpenoids		
Linalool	1102	2.065
trans-3-carene-2-ol	1145	0.254
2-Pinen-10-ol	1192	0.146
Eugenol	1355	0.379
Nerolidol	1564	2.065
tau.-Cadinol	1614	0.011
Cubenol	1642	1.068
(-)-δ-Cadinol	1646	0.128
α-Sinensal	1752	0.007
		6.123
Alcohols		
1-Pentanol	766	0.027
1-Hexen-3-ol	768	0.111
Benzyl Alcohol	1021	0.092
2-(5-Methyl-5-vinyltetrahydro-2-furanyl)-2-propanol	1088	0.247
(E,Z)-3,6-Nonadien-1-ol	1178	0.076
1-phenyl-1,2-Ethanediol	1372	0.090
2-Hexyl-1-decanol	1802	0.000
11-Hexadecyn-1-ol	1885	0.048
		0.691
Esters		
2-Hexenyl propanoate	1111	8.299
Benzyl ethanoate	1168	0.150
Hexyl butanoate	1190	0.082
Methyl salicylate	1198	0.695
Hexyl 2-methylbutanoate	1237	0.897
Ethyl salicylate	1270	0.007
Sabinyl acetate	1298	0.156
(Z)-3-Hexenyl pentanoate	1308	0.082
Isobutyl benzoate	1322	0.140
cis 3-Hexenyl tiglate	1324	3.880
Hexyl tiglate	1351	0.627
Butyl benzoate	1352	0.288
Isoamyl benzoate	1422	0.472
cis-3-Hexenyl Benzoate	1570	0.545
Phenyl benzoate	1668	0.382
5-Hydroxypentyl benzoate	1708	0.463
Ethyl hexadecanoate	1975	0.015
		17.182
Aldehydes and ketones		
Pulegone	1176	0.099
cis-Jasmone	1394	0.706
α-iso-Methyl ionone	1518	0.596
7,11-hexadecadienal	1882	0.025
		1.426
Nitrogenated Compounds		
(E)-2-Butenedinitrile	924	0.121
(2E)-5-Hydroxy-2-pentenenitrile	1014	0.852
Indole	1295	1.212
Benzylisothiocyanate	1362	0.373
		2.558

*Kovat index

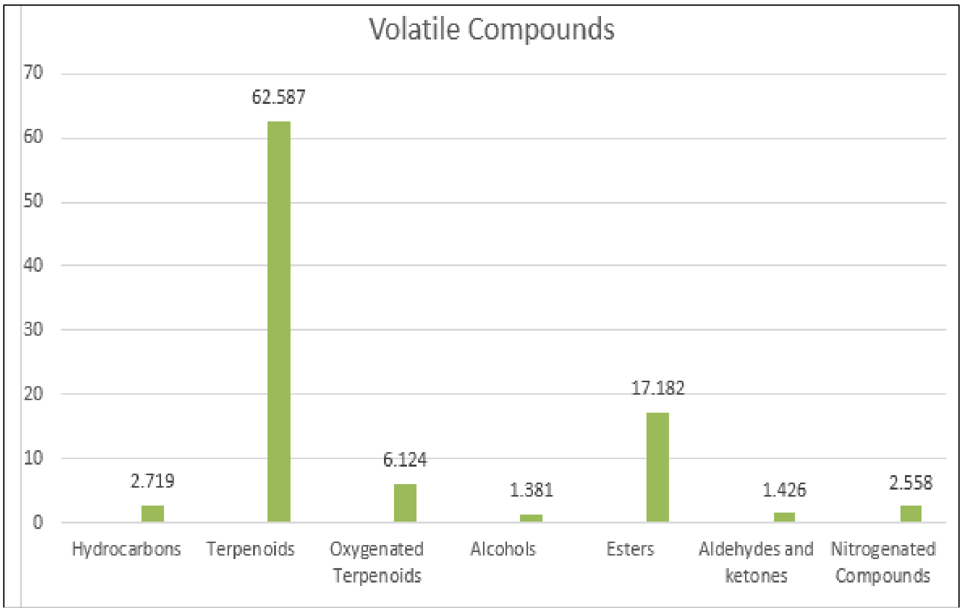
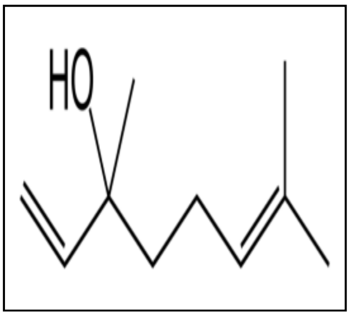
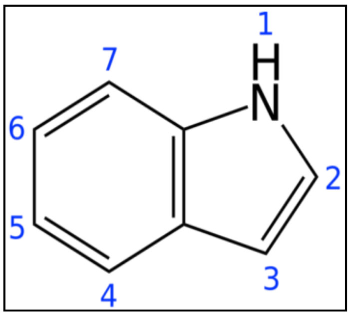


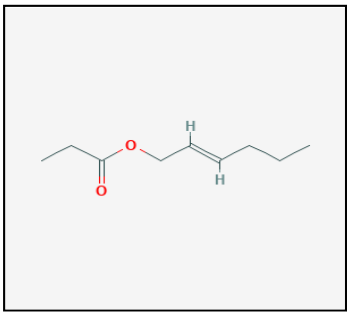
Fig 1: Contribution of major volatile compounds in *J. malabaricum* (IC 560611)



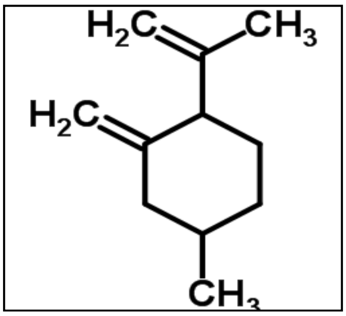
Linalool



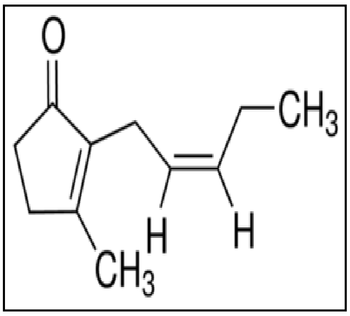
Indole



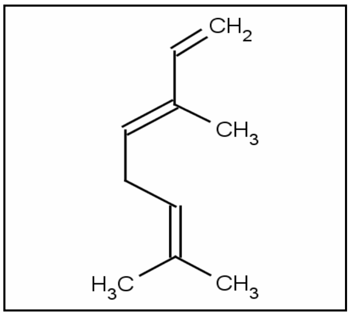
2-Hexenyl propanoate



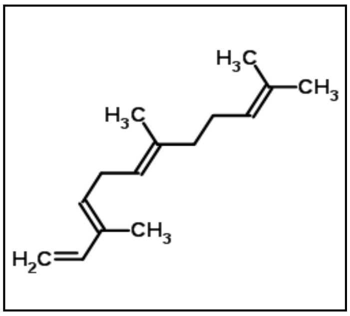
3-methylene-p-menth-8-ene



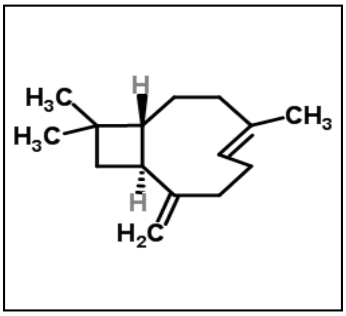
Cis-Jasmone



Trans-Ocimene



α-Farnesene



β-Caryophyllene

Fig 2: chemical structure of Volatile compounds of *J. malabaricum* (IC 560611)

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