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CHEMICAL COMPOSITION OF ESSENTIAL OILS OF THE FLOWERS OF *CLERODENDRUM PHLOMIDIS* L.f. AND *PLUMERIA ALBA* L.

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ABSTRACT

Clerodendrum phlomidis L.f. (family Lamiaceae/Verbenaceae), a small tree or shrub of arid plains, is used to treat asthma, colds, coryza, cough, diabetes, gonorrhea, indigestion, inflammation, jaundice, measles, nervous disorders, piles, pox and rheumatism. *Plumeria alba* L. (family Apocynaceae), a deciduous, evergreen shrub, is utilized to cure blennorrhagia, herpes, syphilis, skin diseases, toothache and ulcers. The present study was carried out to analyse essential oils from the flowers of *C. phlomidis* and *P. alba*. The fresh flowers of each species were hydrodistilled individually to get the essential oils which were analyzed by GC and GC-MS techniques. The essential oil of *C. phlomidis* was characterized by high percentage of aliphatic (78.30%) and sesquiterpene (16.2%) constituents. In the essential oil fifty one compounds were characterized among which *n*-1-heptene (28.42%) was the prominent constituent followed by *cis*-1,2-dimethyl cyclopentane (8.01%), *cis*-1,3-dimethyl cyclopentane (7.55%), 3-ethyl *n*-pentane (6.01%) and 2,2-dimethyl *n*-hexane (4.90%). The essential oil of *P. alba* was characterized by high percentage of sesquiterpenes (89.14%) and monoterpenes (9.03%). In the essential oil twenty four compounds were identified among which ledol (38.66%) was the major component followed by globulol (20.69%), (-)-caryophyllene oxide (7.83%), *trans*-nerolidol (7.21%), spathulenol (6.39%), *trans*- caryophyllene (5.01%), lavandulol (3.41%) and trans-sabinene (2.62%).

KEYWORDS: *Clerodendrum phlomidis* L.f., *Plumeria alba* L., flowers, essential oils, isolation, chemical analysis.

INTRODUCTION

Clerodendrum phlomidis L.f., syn. *C. multiflorum* (Burm. f.) Kuntze non G. Don, *Volkameria multiflorum* Burm. f. (family Lamiaceae/Verbenaceae), commonly known as agnimantha, aarni and urni, is a small tree or shrub of arid plains, low hills and tropical deserts, distributed throughout the drier parts of India, Pakistan, Sri Lanka, Myanmar and south-eastern Asia. It is large shrub or small tree, up to 9 m in height; leaves are ovate, opposite, deltoid, hairy and wavy; flowers are in small rounded terminal panicle, white or pinkish and very fragrant. Its roots are branched, cylindrical, tough, yellowish-brown externally, with thin bark, easily peeled, outer surface rough due to exfoliation, wood light yellow, fracture hard; taste slightly astringent.[1] Its plant decoction is taken to relieve mental disorders. The plant juice is applied to kill ticks and lices of goats and fed to cattle against diarrhoea and dysentery. The stem bark with *Antidesma acidum* bark is ingested to cure jaundice. The roots are used as an analgesic, antiasthmatic, astringent, bitter tonic and to treat asthma, catarrhal affections, colds, coryza, cough, diabetes, glycosuria, gonorrhea, indigestion, inflammation, jaundice, measles, nervous disorders, piles, pox, rheumatism, scrotal enlargement and digestive, urinary and nervous disorders. The leaves are alterative, antiobesity and astringent, taken orally to relieve cholera, dropsy, dysentery, fevers, obesity, piles, rheumatism, stomachache, syphilis and to regain consciousness. A leaf paste is lapped to treat syphilis. Stem and leaf juices are mixed with an oil and dropped into the ear to calm down earache.[2-6]

The *C. phlomidis* plant contained pectolinaringenin, scutellarein, clerodin, clerodendrin, steroids, lup-20(29)-en-3-triacontanoate, chalcone-4,4'-alpha-D-diglucoside, 7-hydroxyflavone, 7-hydroxyflavanone-7-O-glucoside, flavonoid glycosides, tetratriacontanol, 24β-ethylcholesta-5,22E,25-triene-3β-ol, 2-[(2'R)-2'-hydroxytetracosanoylamino]-10-octadecene-1,3,4-triol and andrographolide.[5,7-9] The roots afforded naringin glucoside, 4,2',4'-trihydroxy-6'- methoxychalcone 4,4' -

D-diglucoside and a phenylethanoid glycoside (phlomidoside).[10,11] The flowers yielded 7-hydroxyflavone and 7-hydroxyflavanone.[10]

Plumeria alba L., syn. *Plumeria revolutifolia* Stokes (family Apocynaceae), known as champa, gulchin, white frangipani, is a native to Central America and the Caribbean and now naturalized in south-eastern Asia including India, Thailand, Indonesia and Vietnam. It is a deciduous, succulent, evergreen shrub, 2-8 m high with widely spaced thick succulent branches, narrow elongated, oblanceolate leaves, clustered near the tips of the branches, dark and leathery; flowers large, strongly perfumed, white having a small yellow center; fruit is an elongated dry follicle, seeds winged. A milky sap is exuded from the branches when they are bruised or punctured. The flowers are bitter and eaten as fritters. They are used as an ingredient in a complex pectoral syrup for relieving chest coughs and grippe. The heart of the wood is taken as a laxative and vermifuge. The root bark is alterative, depurative, detergent and purgative, causing thirst. It is prescribed to treat blennorrhagia, herpes and syphilis, externally as a lotion on syphilitic ulcers. The stem latex is caustic and applied to subside herpes, scabies, skin diseases, toothache and ulcers. The seeds are haemostatic, ingested to relieve bloody dysentery.[12-14]

The *P. alba* plant contained α- and β- amyrins, amyrin acetate, β-sitosterol, scopoletin, iriddoids, isoplumericin, plumieride, plumieride coumarate and its glucoside.[14] The major constituents of the leaf oil were linalool (13.2%), *n*-nonanal, phenyl acetaldehyde, neryl acetone and *n*-decanal. The flower oil was comprised mainly of limonene (9.1%), linalool, α-cedrene, caryophyllene oxide and α-farnesene.[15] The chemical components of cendana frangipani essential oils were classified as alcohols, terpenes, ketones, esters and acids.[16] The flowers afforded squalene, bis(2-ethylhexyl) phthalate and tricyclo- undecan-5-ol, kaempferol and its 4'-O-glucoside.[17,18] The flowers showed the presence of isoquinoline, pyridine, indole, vinca and resperine alkaloids.[19] The flower extracts of *Plumeria alba* and *P. rubra* responded positive tests of steroids, alkaloids, flavonoids, glycosides, tannins and carbohydrates.[20] The essential oil composition of herbal drugs is highly variable depending upon a variety of factors including their geographical origin, distillation procedures, post harvest treatment, processing, drying conditions and temperature. In the present communication, we report essential oil composition of the flowers of *Clerodendrum phlomidis* and *Plumeria alba*.

MATERIALS AND METHODS

Collection and authentification of plant materials

The fresh flowers of *C. phlomidis* were collected from the Herbal Garden of Jamia Hamdard, New Delhi. The flowers of *P. alba* were procured from the campus of Y. B. Chavan College of Pharmacy, Aurangabad (Maharashtra). The plant materials were identified by Dr. M.P. Sharma, taxonomist, Department of Botany, Jamia Hamdard, New Delhi, India. The specimen vouchers of these drugs are deposited in the herbariums of the Phytochemistry Research Laboratory, Jamia Hamdard, New Delhi and Y. B. Chavan College of Pharmacy, Aurangabad, respectively.

Isolation of the essential oil

The fresh flowers of *C. phlomidis* and *P. alba* (1 kg each) were hydrodistilled individually in a Clevenger type glass apparatus for 4 h. Each essential oil was collected, measured, dried over anhydrous sodium sulphate and stored at 4 ^{0}C in the dark. These oils were used for GC and GC-MS analysis. The yields of the essential oils obtained from the *C. phlomidis* flowers and *P. alba* flowers were 1.31% and 1.43%, respectively.

GC Analysis

The gas chromatographic analysis of each essential oil was carried out on a GC-2010 (Shimadzu) equipped with a flame ionization detector (FID) and ULBON HR-1 fused silica capillary column (60 m×0.25 mm×0.25 µm). The injector and detector (FID) temperatures were maintained at 250 and 270 ^{0}C, respectively. The carrier gas used was nitrogen at a flow rate of 1.21 ml/min with column pressure of 155.1 kPa. The sample (0.2 µl) was injected into the column with a split ratio of 80:1. Component separation was achieved following a linear temperature programmed from 60 to 230 ^{0}C at a rate of 3 ^{0}C/min and then held at 230 ^{0}C for 9 min, with a total run time of 55.14 min. Percentage of the constituents were calculated by electronic integration of FID peak areas.

GC-MS Analysis

The GC-MS analysis of these oils were carried out on a GC-MS-QP 2010 Plus (Shimadzu) fitted with a Column AB-Innowax (60 m×0.25 mm i.d., film thickness 0.25 µm). The carrier gas was nitrogen at a flow rate 1.21 ml/min. The oven column temperature was initially kept at 60 ^{0}C for 10 min and increased up to 230 ^{0}C at a rate of 4 ^{0}C/min, then held at 230 ^{0}C for 10 min, elevated up to 260 ^{0}C at a rate of 1 ^{0}C/min and then held at 260 ^{0}C for 10 min. The split flow was 101 ml/min. The split ratio was 1:80. The injector temperature was 240 ^{0}C and detector temperature was 280 ^{0}C. Injection volume was 0.3 µl. The ionization energy (voltage) was 70 eV and mass scan range (*m/z*) was 40-850 amu. The percentage composition of the oil was calculated automatically from the FID peak area without any correction.

Identification of compounds

The individual compounds were identified by comparing their Kovat's indices (KI) of the peaks on Innowax fused silica capillary column with literature values, matching against the standard library spectra, built up using pure substances and components of known essential oils. Further identification was carried out by comparison of fragmentation pattern of the mass spectra obtained by GC-MS analysis with those stored in the spectrometer database of NBS 54 K L, WILEY 8 libraries and

published literature.[21-24] Relative amounts of identical components were based on peak areas obtained without FID response factor correction.

RESULTS AND DISCUSSION

Clerodendrum phlomidis flowers essential oil

The chemical constituents of the essential oil were identified by analysis of GC and GC-MS. The chemical composition of the *Clerodendrum phlomidis* is summarized in Table 1 with their Kovat's indices and respective percentage. The essential oil was characterized by high percentage of aliphatic (78.30%) and sesquiterpene (16.2%) constituents. In the essential oil fifty one compounds were characterized among which *n*-1-heptene (28.42%) was the prominent constituent followed by *cis*-1,2-dimethyl cyclopentane (8.01%), *cis*-1,3-dimethyl cyclopentane (7.55%), 3-ethyl *n*-pentane (6.01%) and 2,2-dimethyl *n*-hexane (4.90%). The total number of aliphatic constituents was twenty three (78.30%) including nine alkanes (25.99%), one alkene (28.42%), four aliphatic alcohols (1.35%), three aliphatic aldehydes (1.36%), one aliphatic acid (2.37%) and five cyclic hydrocarbons (18.81%). Among thirteen monoterpenes (5.07%), there were three monoterpene hydrocarbons (0.53%), eight monoterpene alcohols (4.42%) and one monoterpene epoxide (0.12%). The major monoterpene was *trans*-verbenol (1.23%) and other monoterpenic components occurred in trace amounts less than 1.0%. There were fifteen sesquiterpenic constituents (16.2%) including nine sesquiterpene hydrocarbons (3.82%), three sesquiterpene alcohols (5.30%) and two sesquiterpene oxides (3.43%). The major sesquiterpenes were humulene oxide (2.92%), *α*-bisabolol (2.73%), *α*-cadinol (1.43%) and spathulenol (1.14%). There were one fatty acid, viz. oleic acid (2.37%) and two aromatic compounds, namely eugenol (1.34%) and dibutyl phthalate (3.65%). Besides these, bornyl formate, ascaridol acetate and citronellyl valerate were the ester constituents present in the essential oil. This is the first report of analysis of the essential oil of *C. phlomidis*.

Table 1: Chemical composition of essential oil of the flowers of *Clerodendrum phlomidis* L.

S. No.	Components	RI	Percentage
1.	*n*- Hexane	601	1.77
2.	2- Methyl *n*-hexane	667	3.09
3.	2,2-Dimethyl *n*-pentane	683	0.91
4.	*cis*-1,3-Dimethyl cyclopentane	685	7.55
5.	3-Ethyl *n*-pentane	687	6.01
6.	*n*-1-Heptene	688	28.42
7.	*cis*-1,2-Dimethyl cyclopentane	719	8.01
8.	2,2-Dimethyl *n*-hexane	722	4.90
9.	3,3-Dimethyl *n*-hexane	741	2.92
10.	2,3-Dimethyl *n*-hexane	760	3.93
11.	3,4-Dimethyl *n*-hexane	769	2.06
12.	3-Methyl n-heptane	774	0.40
13.	*cis*-1,2-Dimethyl cyclohexane	776	3.05
14.	*trans*-1,2-Dimethyl cyclohexane	822	0.08
15.	*n*-Propyl cyclopentane	827	0.12
16.	*n*-Oct-4-en-1-ol	964	0.20
17.	*n*-Oct-1-en-4-ol	978	0.17
18.	*α*-Terpinene	1001	0.13
19.	*p*-Cymene	1004	0.22
20.	*n*-Octanol	1070	0.45
21.	*trans*-Verbenol	1140	1.23
22.	*n*-Decanol	1180	0.53
23.	Borneol	1182	0.55
24.	*p*-Cymen-8-ol	1185	0.20
25.	Bornyl formate	1204	0.18
26.	(*E*)-*n*-Dec-2-en-1-al	1225	0.73
27.	*n*-Undecanal	1281	0.22
28.	Limonen-1,2- epoxode	1283	0.12
29.	Thymol	1290	0.11
30.	*p*-Cymen-7-ol	1292	0.34
31.	Carvacrol	1299	0.50
32.	(2*E*)(4*Z*)- *n*- Decadienal	1302	0.41
33.	Ipsdienol	1315	0.15
34.	*α*-Longipinene	1317	0.94
35.	*δ*- Elemene	1340	0.17

36.	Ascaridol acetate	1345	0.42
37.	Eugenol	1358	1.34
38.	*trans*-Caryophyllene	1403	0.35
39.	*β*- Gurjunene	1413	0.47
40.	*α*- Selinene	1473	0.37
41.	*γ*- Cadinene	1502	0.42
42.	*δ*- Cadinene	1504	0.46
43.	Germacrene-B	1522	0.25
44.	Caryophyllene oxide	1598	0.51
45.	Spathulenol	1602	1.14
46.	Citronellyl valerate	1608	0.39
47.	Humulene oxide	1625	2.92
48.	*α*-Bisabolol	1645	2.73
49.	*α*-Cadinol	1654	1.43
50.	Dibutyl phthalate	1938	3.65
51.	Oleic acid	2065	2.37

***Plumeria alba* flowers essential oil**

The chemical composition of the flowers essential oil of *Plumeria alba* is tabulated in Table 2 with their Kovat's indices and respective percentage. The essential oil was characterized by high percentage of sesquiterpenes (89.14%) and monoterpenes (9.03%). In the essential oil twenty four compounds were identified among which ledol (38.66%) was the predominant component followed by globulol (20.69%), (-)-caryophyllene oxide (7.83%), *trans*-nerolidol (7.21%), spathulenol (6.39%), *trans*-caryophyllene (5.01%), lavandulol (3.41%) and *trans*-sabinene (2.62%). Among the 13 sesquiterpenes (89.14%), the seven ones were the major constituents and *trans*-α-bergamotene, *cis*-α-farnesene, β-bisabolene, δ-cadinene and α-bisabolol were present in lesser than one percent amount. Among eight monoterpenes, there were three each monoterpene hydrocarbons (3.75%) and monoterpene alcohols (4.47%) and one each of monoterpenes were an aldehyde geranial (0.45%) and ester neryl acetate (0.36%). The prominent monoterpenes were lavandulol (3.41%) and *trans*-sabinene (2.62%). The remaining monoterpenic constituents occurred in less than 1%. Methyl eugenol was the only aromatic component present in the oil. In addition, there were one fatty acid, viz., hexadecanoic acid (0.29%) and two fatty esters characterized as methyl linoleate (0.21%) and methyl stearate (0.23%). The flowers essential oil of *Plumeria alba* grown in Nigeria was comprised mainly of limonene (9.1%), linalool (7.9%), α-cedrene (8.0%), caryophyllene oxide (7.9%) and (E, E)-α-farnesene (6.6%).[15]

Table 2: Chemical composition of essential oil of the flowers of *Plumeria alba*.

S. No.	Components	RI	Percentage
1	β-Pinene	974	0.21
2	Limonene	1024	0.92
3	*trans*-Sabinene	1045	2.62
4	Linalool	1101	0.81
5	Lavandulol	1153	3.41
6	Geraniol	1250	0.25
7	Geranial	1266	0.45
8	Neryl acetate	1371	0.36
9	*trans*-Cryophyllene	1404	5.01
10	Methyl eugenol	1418	0.33
11	*trans*-α-Bergamotene	1436	0.82
12	*cis*-β-Farnesene	1446	1.19
13	*cis*-α-Farnesene	1503	0.64
14	β-Bisabolene	1510	0.23
15	*trans*-Nerolidol	1541	7.21
16	(-)-Caryophyllene oxide	1548	7.83
17	Globulol	1572	20.69
18	Spathulenol	1576	6.39
19	Ledol	1580	38.66
20	δ-Cadinene	1647	0.26
21	α-Bisabolol	1688	0.21
22	Hexadecanoic acid	1957	0.29
23	Methyl linoleate	2089	0.21
24	Methyl stearate	2128	0.23

CONCLUSION

In the essential oil of *C. phlomidis* flowers fifty one compounds were characterized among which *n*-1-heptene (28.42%) was the prominent constituent followed by *cis*-1,2-dimethyl cyclopentane (8.0%), *cis*-1,3-dimethyl cyclopentane (7.55%), 3-ethyl *n*-pentane (6.01%) and 2,2-dimethyl *n*-hexane (4.90%). In the essential oil of *P. alba* flowers twenty four compounds were identified and ledol (38.66%), globulol (20.69%), (-)-caryophyllene oxide (7.83%), *trans*-nerolidol (7.21%), spathulenol (6.39%), *trans*- caryophyllene (5.01%), lavandulol (3.41%) and *trans*-sabinene (2.62%) were the major components.

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