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ORIGINAL ARTICLE

A detailed study on chemical characterization of essential oil components of two *Plectranthus* species grown in Saudi Arabia

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P. arabicus;
Lamiaceae

Abstract The chemical composition of the essential oils of *Plectranthus cylindraceus* and *Plectranthus arabicus* grown in Saudi Arabia were analyzed using gas chromatography techniques (GC–MS, GC–FID, Co-GC, LRI determination, and database and literature searches) using two different stationary phase columns (polar and nonpolar). The analysis led to the characterization of a total of 157 different compounds from both oils. In the oil derived from *P. cylindraceus*, 79 compounds were identified, whereas 132 compounds were identified in the oil derived from *P. arabicus*; these compounds account for 95.2% and 98.4% of the total oil compositions, respectively. The major constituents of *P. cylindraceus* oil were patchouli alcohol (55.5 ± 0.01%), 1,8-cineole (6.0 ± 0.01%) and valerianol (3.8 ± 0.18%), whereas, the main compounds of the *P. arabicus* oil were 1,8-cineole (50.5 ± 1.37%), *β*-pinene (7.0 ± 0.08%), camphor (6.3 ± 0.19%) and *β*-myrcene (4.1 ± 0.10%). To the best of our knowledge, patchouli alcohol found in high concentration in the *P. cylindraceus* oil has never been reported from the genus *Plectranthus*. Moreover, this is the first phytochemical study of *P. arabicus*.

1. Introduction

Plectranthus L'Her. (Also famous with name spurflowers) is an important genus of ornamental flowering herbs and shrubs found in almost all habitats and altitudes. It belongs to the important family Lamiaceae (Originally known as Labiateae), a widely distributed plant group containing 236 genera and over 7000 species [1,2], among which many genera such as lavender (*Lavandula*), basil (*Ocimum*), thyme (*Thymus*), sage (*Salvia*), and mint (*Mentha*) are very famous for their commercial applications and various ethnobotanical uses [3]. Within this family, *Plectranthus* is included in the subfamily Nepetoideae of tribe Ocimeae, subtribe Plectranthinae and contains over 300 species, which are mainly found in countries having warm climatic conditions such as India, Saudi Arabia, Madagascar, Indonesia, Yemen, Australia, sub-Saharan Africa and

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Table 1 Chemical constituents of essential oils derived from *Plectranthus cylindraceus* and *P. arabicus* grown in Saudi Arabia.

No.	Compound*	LRI_{Lit}	LRI^{a}_{Exp}	LRI^{p}_{Exp}	PC (%)[c]	PA (%)[c]	Identification[b]
1	*trans*-2-Hexenal	846	852	1217	–	*t*	1, 2
2	*cis*-3-Hexen-1-ol	850	854	1389	–	0.1	1, 2, 3
3	*cis*-2-Hexen-1-ol	859	866	1411	–	*t*	1, 2
4	1-Hexanol	863	868	1359	–	*t*	1, 2
5	*trans*-2-Hexenyl formate	918	920	–	–	*t*	1, 2
6	Tricyclene	921	923	1004	–	*t*	1, 2
7	α-Thujene	924	928	1024	–	0.2	1, 2
8	**α-Pinene**	**932**	**935**	**1018**	**0.2**	**2.5 ± 0.09**	**1, 2, 3**
9	Camphene	946	950	1060	0.1	0.7	1, 2
10	α-Fenchene	945	–	1053	–	*t*	1, 2
11	Sabinene	969	975	1118	–	0.1	1, 2
12	**β-Pinene**	**974**	**978**	**1105**	**0.6**	**7.0 ± 0.08**	**1, 2, 3**
13	1-Octen-3-ol	974	980	1456	0.1	0.2	1, 2, 3
14	3-Octanone	979	988	1255	–	0.2	1, 2
15	**β-Myrcene**	**988**	**993**	**1164**	**0.3**	**4.1 ± 0.10**	**1, 2**
16	Dehydro-1,8-cineole	988	–	1191	–	*t*	1, 2
17	3-Octanol	988	997	1399	–	*t*	1, 2
18	α-Phellandrene	1002	1006	–	–	0.1	1, 2
19	*p*-Mentha-1(7),8-diene	1003	–	1167	–	*t*	1, 2
20	**α-Terpinene**	**1014**	**1018**	**1177**	–	**0.3**	**1, 2**
21	*p*-Cymene	1020	1027	1269	0.1	0.3	1, 2
22	**Limonene**	**1024**	**1031**	**1197**	**0.2**	**2.3 ± 0.23**	**1, 2, 3**
23	β-Phellandrene	1025	–	1203	–	*t*	1, 2
24	**1,8-Cineole**	**1026**	**1036**	**1213**	**6.0 ± 0.01**	**50.5 ± 1.37**	**1, 2, 3**
25	Benzeneacetaldehyde	1036	1046	–	–	0.1	1, 2
26	*trans*-β-Ocimene	1044	1050	1252	–	*t*	1, 2
27	γ-Terpinene	1054	1061	1245	0.1	0.7	1, 2
28	*cis*-Sabinene hydrate	1065	1069	1471	0.1	0.3	1, 2
29	*p*-Cymenene	1089	–	1437	–	*t*	1, 2
30	α-Terpinolene	1086	1090	1282	–	0.3	1, 2, 3
31	*trans*-Sabinene hydrate	1098	–	1555	0.1	0.2	1, 2
32	Linalool	1095	1101	1552	0.1	0.5	1, 2, 3
33	Nonanal	1100	1106	1395	–	*t*	1, 2, 3
34	α-Thujone	1101	1108	1423	0.2	0.9	1, 2
35	1-Octen-3-yl acetate	1110	1114	1381	–	*t*	1, 2
36	β-Thujone	1112	1119	1442	0.1	0.5	1, 2
37	*cis*-*p*-Mentha-2-en-1-ol	1118	1124	–	–	0.1	1, 2
38	*cis*-*p*-Mentha-2,8-dien-1-ol	1133	1138	–	–	*t*	1, 2
39	*trans*-*p*-Mentha-2-en-1-ol	1135	1143	1592	–	*t*	1, 2
40	**Camphor**	**1141**	**1148**	**1519**	**1.2 ± 0.01**	**6.3 ± 0.19**	**1, 2**
41	Camphene hydrate	1145	1152	–	–	*t*	1, 2
42	(2*E*,6*Z*)-Nonadienal	1150	1159	–	–	*t*	1, 2
43	Borneol	1165	1169	1709	–	0.2	1, 2
44	**δ-Terpineol**	**1162**	**1170**	**1679**	**0.3**	**1.5 ± 0.16**	**1, 2**
45	Ethylbenzoate	1169	1177	1667	–	*t*	1, 2
46	Terpinen-4-ol	1174	1180	1608	0.2	0.5	1, 2, 3
47	*p*-Cymene-8-ol	1179	1188	–	–	*t*	1, 2
48	**α-Terpineol**	**1186**	**1194**	**1704**	**0.9**	**4.1 ± 0.05**	**1, 2, 3**
49	Dihydrocarveol	1192	1198	–	–	*t*	1, 2
50	*cis*-Piperitol	1195	1203	1753	–	*t*	1, 2
51	*n*-Decanal	1201	1205	–	–	*t*	1, 2
52	*trans*-Piperitol	1207	1210	1714	–	*t*	1, 2
53	Shisofuran	1198	1219	1999	–	*t*	1, 2
54	(2*E*,4*E*)-Nonadienal	1210	1221	1694	–	0.1	1, 2
55	*trans*-Carveol	1215	1224	1842	–	*t*	1, 2
56	Nerol	1227	1229	1807	–	0.1	1, 2
57	Neral	1235	1244	–	–	*t*	1, 2
58	Methyl carvacrol	1241	1248	–	–	*t*	1, 2
59	Geraniol	1249	1256	1854	–	*t*	1, 2
60	Linalyl acetate	1254	1258	1559	–	0.1	1, 2
61	Geranial	1264	1273	1733	–	*t*	1, 2
62	*n*-Decanol	1266	1276	1755	–	*t*	1, 2
63	Neryl formate	1280	1287	–	–	*t*	1, 2

Table 1 (*continued*)

No.	Compound[*]	LRI_{Lit}	LRI^{a}_{Exp}	LRI^{p}_{Exp}	PC (%)[c]	PA (%)[c]	Identification[b]
64	Bornyl acetate	1284	1290	1585	0.1	0.2	1, 2
65	Thymol	1289	1293	2190	0.2	0.7	1, 2, 3
66	(2*E*,4*Z*)-Decadienal	1292	1297	–	–	*t*	1, 2
67	Carvacrol	1298	1303	2219	0.1	*t*	1, 2
68	(2*E*,4*E*)-Decadienal	1315	1321	1814	–	*t*	1, 2
69	Piperitenone	1340	1346	–	–	0.1	1, 2
70	α-Terpenyl acetate	1346	1353	1700	0.1	0.3	1, 2
71	α-Cubebene	1345	–	1459	–	*t*	1, 2
72	Carvacrol acetate	1370	1379	1881	–	*t*	1, 2
73	α-Copaene	1374	1382	1494	–	*t*	1, 2
74	Geranyl acetate	1379	1385	1751	–	*t*	1, 2
75	*β*-Patchoulene	1379	1389	1486	0.5	–	1, 2
76	*β*-Bourbonene	1387	1392	1522	–	*t*	1, 2
77	*β*-Elemene	1389	1397	–	0.2	–	1, 2
78	*cis*-Jasmone	1392	1401	1951	–	*t*	1, 2
79	α-Gurjunene	1409	1417	1532	0.2	*t*	1, 2
80	*cis*-α-Bergamotene	1411	1420	1569	–	0.1	1, 2
81	**β-Caryophyllene**	**1417**	**1428**	**1600**	**1.6 ± 0.03**	**3.7 ± 0.16**	**1, 2, 3**
82	*trans*-α-Bergamotene	1432	1436	1577	–	*t*	1, 2
83	**α-Guaiene**	**1437**	**1443**	**1594**	**1.7 ± 0.07**	*t*	**1, 2**
84	Aromadendrene	1439	1447	1610	–	0.2	1, 2
85	**Seychellene**	**1444**	**1451**	**1644**	**2.0 ± 0.22**	*t*	**1, 2**
86	**α-Humulene**	**1452**	**1462**	**1673**	**1.0 ± 0.05**	**2.1 ± 0.26**	**1, 2, 3**
87	α-Patchoulene	1454	1464	1639	0.9	–	1, 2
88	*allo*-Aromadendrene	1458	1465	1649	–	0.1	1, 2
89	*β*-Acoradiene	1469	1468	–	0.3	–	1, 2
90	9-*epi*-*E*-Caryophyllene	1464	1469	1643	–	0.1	1, 2
91	γ-Patchoulene	1502	1470	1660	0.3	–	1, 2
92	γ-Gurjunene	1475	1476	1667	0.1	–	1, 2
93	*E*-Cadina-1(6),4-diene	1475	1480	–	–	*t*	1, 2
94	γ-Muurolene	1478	1483	1692	0.1	0.1	1, 2
95	Germacrene-D	1484	1489	1712	0.1	0.1	1, 2
96	*β*-Selinene	1489	1494	1723	*t*	*t*	1, 2
97	*epi*-Cubebol	1493	–	1895	–	*t*	1, 2
98	γ-Amorphene	1495	–	1720	–	*t*	1, 2
99	α-Selinene	1498	1502	1728	0.2	0.2	1, 2
100	Bicyclogermacrene	1500	–	1737	–	0.1	1, 2
101	α-Muurolene	1500	1506	–	0.5	0.2	1, 2
102	*trans*-*β*-Guaiene	1502	–	1535	*t*	–	1, 2
103	**α-Bulnesene**	**1509**	**1512**	**1719**	**2.4 ± 0.01**	–	**1, 2**
104	γ-Cadinene	1513	1521	1762	0.1	*t*	1, 2
105	Cubebol	1514	–	1948	0.1	–	1, 2
106	7-*epi*-α-Selinene	1520	1526	1767	0.1	–	1, 2
107	δ-Cadinene	1522	1530	1761	0.1	0.1	1, 2
108	α-Cadinene	1537	1535	1774	0.1	–	1, 2
109	*cis*-Sesquisabinene hydrate	1542	1540	2078	0.1	–	1, 2
110	*cis*-Nerolidol	1531	1542	–	*t*	–	1, 2
111	α-Calacorene	1544	1550	1929	–	*t*	1, 2
112	Elemol	1548	1556	2087	0.1	–	1, 2
113	Germacrene-B	1559	1561	–	0.1	–	1, 2
114	Ledol	1602	1566	–	0.8	–	1, 2
115	*β*-Calacorene	1564	1567	1940	–	0.1	1, 2
116	Dodecanoic acid	1565	1571	–	–	*t*	1, 2
117	*cis*-3-Hexenyl benzoate	1565	1576	–	0.4	0.1	1, 2
118	Spathulenol	1577	1586	2131	0.1	0.1	1, 2
119	**Caryophyllene oxide**	**1582**	**1592**	**1990**	**2.3 ± 0.57**	**0.3**	**1, 2, 3**
120	Globulol	1590	1598	2084	0.2	–	1, 2
121	**Viridiflorol**	**1592**	**1601**	**2093**	**0.6**	**1.7 ± 0.11**	**1, 2**
122	Humulene epoxide II	1608	1619	2047	0.3	0.1	1, 2
123	1,10-Diepicubenol	1618	1623	2066	0.6	*t*	1, 2
124	1-*epi*-cubenol	1627	1626	–	0.6	–	1, 2
125	γ-Eudesmol	1630	1632	2173	0.9	*t*	1, 2
126	δ-Cadinol	–	1637	2166	0.3	–	1, 2

(*continued on next page*)

Table 1 (*continued*)

No.	Compound*	LRI_{Lit}	LRI^a_{Exp}	LRI^p_{Exp}	PC (%)[c]	PA (%)[c]	Identification[b]
127	*epoxyallo*-Aromadendrene	1639	1641	–	–	*t*	1, 2
128	*epi*-α-Muurolol	1640	1643	2179	0.4	–	1, 2
129	α-Muurolol	1644	1646	–	0.1	*t*	1, 2
130	τ-Cadinol	1638	1649	2181	0.1	*t*	1, 2
131	*β*-Eudesmol	1649	1653	2246	0.1	*t*	1, 2
132	α-Cadinol	1652	1663	2240	–	*t*	1, 2
133	**Valerianol**	**1656**	**1664**	**2217**	**3.8 ± 0.18**	–	**1, 2**
134	**Patchouli alcohol**	**1656**	**1671**	**2190**	**55.5 ± 0.01**	*t*	**1, 2**
135	*β*-Bisabolol	1674	1678	2146	–	0.1	1, 2
136	1-Tetradecanol	1671	1679	2151	0.8	–	1, 2
137	α-Bisabolol	1685	1694	–	0.6	*t*	1, 2, 3
138	*n*-Heptadecane	1700	1700	–	0.1	*t*	1, 2, 3
139	2-Pentadecanone	1697	1712	–	0.2	–	1, 2
140	Pentadecanal	–	1712		0.2	*t*	1, 2
141	(*Z*,*E*)-Farnesol	1722	1730	2365	0.1	–	1, 2
142	(*E*,*E*)-Farnesol	1742	1747	–	0.3	–	1, 2
143	Benzyl benzoate	1759	1756	2604	–	0.1	1, 2
144	Tetradecanoic acid	–	1772	–	0.1	*t*	1, 2
145	Aristolone	1762	1788	2278	0.2	–	1, 2
146	*n*-Octadecane	1800	1800	1800	–	*t*	1, 2, 3
147	Eudesm-7(11)-en-4-ol, acetate	1839	1849	–	–	*t*	1, 2
148	*n*-Nonadecane	1900	1900	1900	–	*t*	1, 2, 3
149	Methyl hexadecanoate	–	1924	2207	–	*t*	1, 2
150	**Manool**	**2056**	**2067**	**2669**	**0.7**	**2.1 ± 0.19**	**1, 2**
151	Methyl oleate	–	2097	2422	–	0.1	1, 2
152	Phytol	1942	2106	2622	–	*t*	1, 2
153	Octadecanoic acid	–	2177	–	0.2	*t*	1, 2
154	*trans*-Totarol	2314	2322	–	–	*t*	1, 2
155	3α-acetoxy manool	2359	2375	–	0.3	0.1	1, 2
156	*n*-Hexacosane	2600	2600	2600	–	*t*	1, 2, 3
157	*n*-Heptacosane	2700	2700	2700	–	*t*	1, 2, 3
Total identified					95.2	98.4	

LRI^a_{Exp} = Determined linear retention index against mixture of *n*-alkanes (C8-C31) on HP-5 MS column; LRI^p_{Exp} = Determined linear retention index against mixture of *n*-alkanes (C8-C31) on DB-wax column; PC = *P. cylindraceus*; PA = *P. arabicus*.

[*] Components are listed in their order of elution from HP-5MS column.

[c] Mean percentage calculated from flame ionization detector (FID) data and compounds higher than 1.0% are highlighted in boldface and their ±SD (n = 2) are mentioned; LRI_{Lit} = linear retention index from the literature (Adams, 2007).

[b] Identification by; 1 = linear retention index (LRI) identical to literatures (*cf*. exp. part); 2 = comparison of mass spectra (MS) with the library entries of mass spectra databases (*cf*. exp. part); 3 = co-injection/comparison with the LRI and mass spectra of standards; *t* = trace (<0.05%).

some Pacific Islands [3,4]. The genus is well known for its economic value as many plant species belonging to *Plectranthus* are rich in essential oils which have wide applications in cosmetics and pharmaceutical industries. These essential oils have also been reportedly used in traditional and modern medicines [3,5–8]. Moreover, in folk medicine *Plectranthus* species are frequently used for the treatment of several ailments such as respiratory conditions, muscular skeleton conditions, skin diseases, digestive problems, genito-urinary conditions, various infections and fever [3]. Furthermore, chemical investigations on *Plectranthus* species revealed that the genus is a rich source of diterpenoids [6,8,9] which have shown several important biological properties, such as antifungal [10], antibacterial [11–13], insecticidal [14], antiplasmodial [13] and antitumoral [12,13] activities. Phenolics [15–17], triterpenoids [18,19], flavonoids [20,21] and fatty acids [6,22] have also been reported from this genus.

In Saudi Arabia, the genus *Plectranthus* is represented by about 9 flowering aromatic species which grow naturally in several regions of Saudi Arabia [2,23]. Many plant species of this genus are often used in local traditional medical practices and in perfumery [3,6,24,25]. For instance, *P. asirensis* leaves are utilized by traditional healers as disinfectant for wound dressing, whereas, extracts obtained from *P. tenuiflorus* leaves are applied in the treatment of ear disorders. Moreover, it is also very famous for its use as ornamental plant in Saudi Arabia [6]. Although, *Plectranthus* species are known to have widespread applications in Saudi traditional medicine and many *Plectranthus* species are considered to be rich source of essential oils, but, chemical constituents of many plant species belonging to this genus are yet to be studied. Hence, as part of our interest in the characterization of chemical constituents of medicinal and aromatic plants growing in Saudi Arabia [26–28], we herein report a detailed chemical characterization of the volatile organic compounds of two unexplored species of *Plectranthus* (*P. cylindraceus* and *P. arabicus*) growing in Saudi Arabia.

P. cylindraceus Hochst. ex Benth (syn. *P. montanus* Benth.) is a bushy leafy herb with strong aromatic succulent foliage,

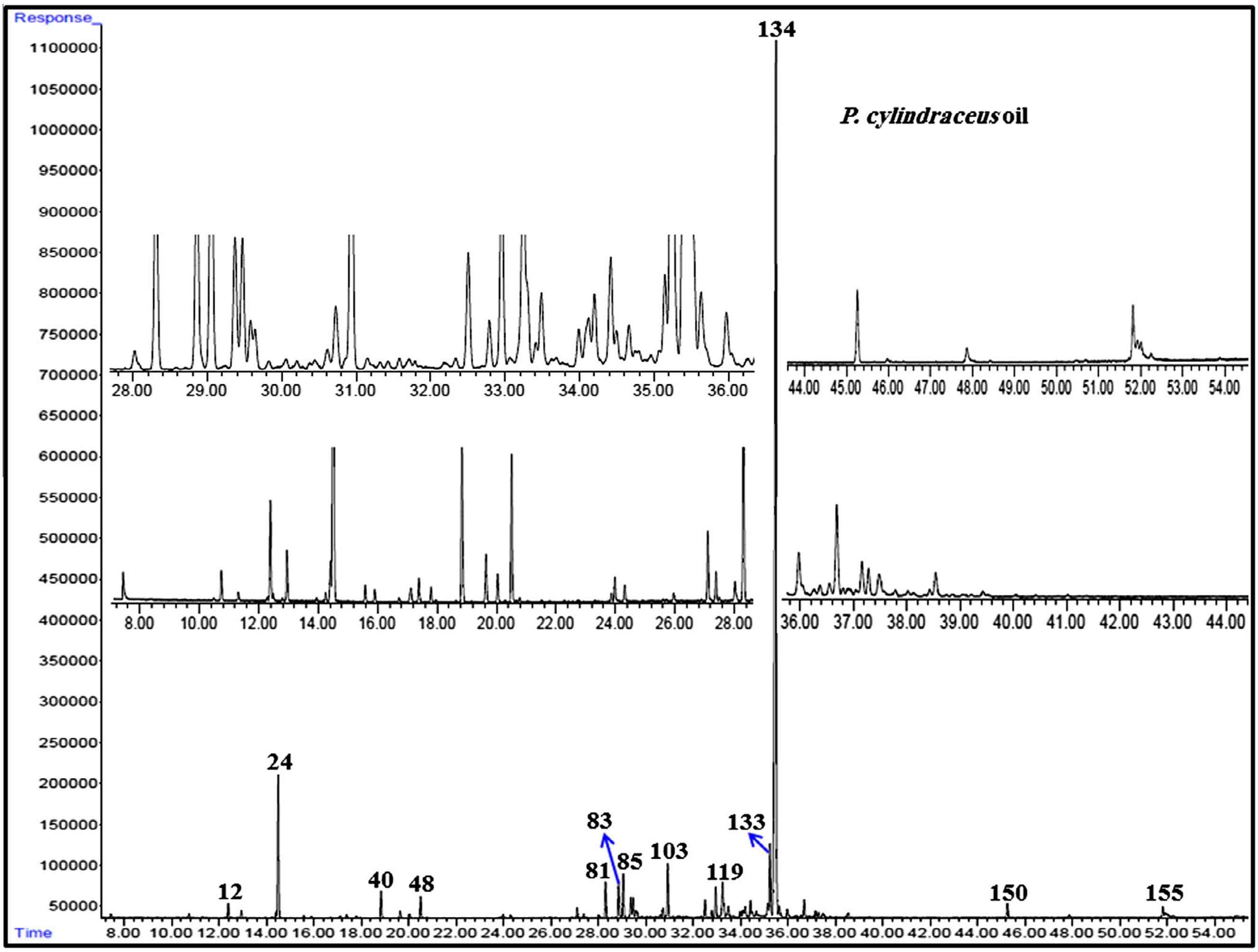

Figure 1 GC–FID chromatogram of aerial parts of essential oil of *P. cylindraceus* on HP-5MS column. Numbering of identified peaks is given according to the serial number of compounds in Table 1.

and about 3 mm long blue flowers [2]. It is abundantly found in various countries, such as Yemen, Oman, United Arab Emirates, and East African countries [29,30]. In Saudi Arabia, *P. cylindraceus* is widely distributed and goes under the local name of 'Kharoob' and traditionally used as deodorant, disinfectant and for the treatment of sore throat [2,23,31–33]. Phytochemical investigation of *P. cylindraceus* has been directed to the characterization of eudesmane type sesquiterpenoids and flavonoids [33]. Analysis of essential oils of *P. cylindraceus* from Oman, Ethiopia and Yemen have revealed that carvacrol, α-terpinolene, camphor, 1,8-cineol and thymol are the main constituents of the oil [29,30,32]. Moreover, *P. cylindraceus* oil has been described to display significant antimicrobial, nematicidal and antioxidant activities [29,30,32,34]. Thorough study of literature on *P. cylindraceus* revealed that, although there are some reports on phytochemical investigations of *P. cylindraceus* growing in different agro-climatic conditions of some countries, phytochemical investigation of *P. cylindraceus* growing in Saudi Arabia has never been carried out. This encouraged us to perform a comprehensive chemical characterization of essential oil constituents of *P. cylindraceus* growing in Saudi Arabia.

On the other hand, *P. arabicus* E.A. Bruce is a slightly aromatic bushy leafy herb with small fleshy dentate leaves and about 6 mm long bright deep blue flowers with a white hood. It is naturally distributed in different parts of Saudi Arabia [2]. Perusal of exhaustive literature searches on the genus *Pletcranthus* revealed that *P. arabicus* have never been studied before for its phytochemical investigation, which prompted us to carry out detailed characterization of its volatile phytomolecules.

2. Materials and methods

2.1. Plant material

Aerial parts of *P. cylindraceus* and *P. arabicus* were procured (during the blossoming stage of the plants) in the month of March 2012 from Taif and Jazan, respectively. The identity of the each plant species was established by a plant taxonomist (Herbarium Division, College of Science, King Saud University, Riyadh, KSA). Voucher specimens of both plant species are retained in our laboratory.

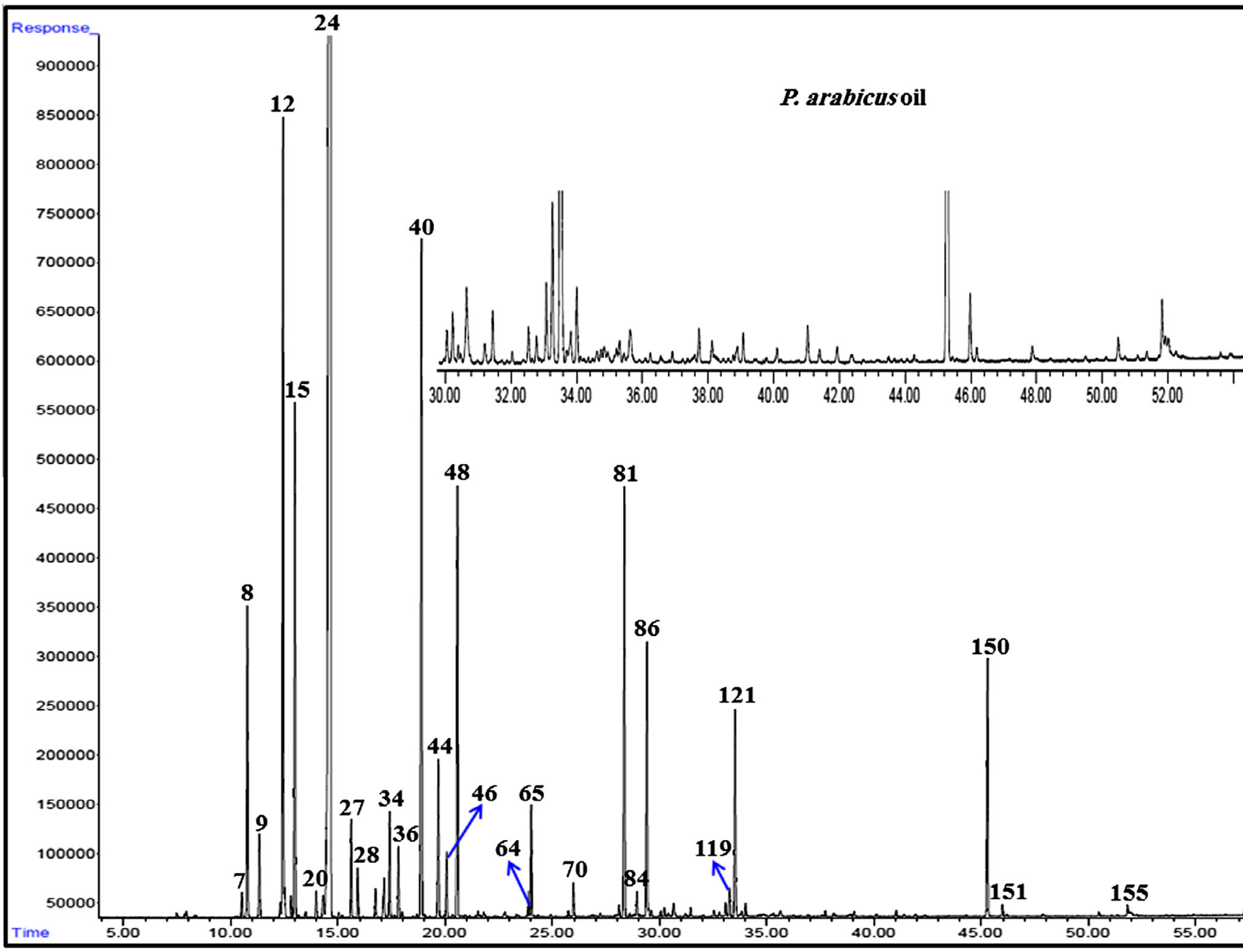

Figure 2 GC–FID chromatogram of aerial parts of essential oil of *P. arabicus* on HP-5MS column. Numbering of identified peaks is given according to the serial number of compounds in Table 1.

2.2. Isolation of essential oils

Freshly collected aerial parts of *P. cylindraceus* and *P. arabicus* were sliced into small pieces. The sliced parts of *P. cylindraceus* (250.0 g) and *P. arabicus* (250.0 g) were individually hydro-distilled in a Clevenger-type apparatus for 3 h as per the method described earlier [35] to give light yellow and colorless oils respectively. The volatile oils acquired after the distillations were dried using anhydrous sodium sulfate as dehydrating agent and put in storage at 4 °C till they were further used. The yield of the volatile oils obtained from the *P. cylindraceus* and *P. arabicus* were 0.8% and 1.1% (v/w), respectively, on the fresh weight basis.

2.3. Chemicals

Analytical-grade acetone (purchased from Sigma–Aldrich, Germany) was used for the dilution of oil samples. Pure essential oil constituents like for instance, linalool, *n*-octadecane, α-bisabolol, *n*-heptadecane, *β*-pinene, *n*-nonadecane, limonene, α-pinene, nonanal, thymol, and α-terpineol etc. as well as some essential oil fractions enriched with 1,8-cineole, α-humulene, *β*-caryophyllene, *p*-cymene, 1-octen-3-ol, terpenene-4-ol, *cis*-3-hexen-1-ol, caryophyllene oxide and α-terpinolene were available with us and were used for co-injection/comparison analysis.

2.4. Gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) analysis of volatile oils

The volatile oils were analyzed using a GC–MS and GC–FID equipped with two columns, one of which was polar (DB-Wax), and the other was nonpolar (HP-5MS). GC–MS was performed on an Agilent single-quadrupole mass spectrometer with an inert mass selective detector (MSD-5975C detector, Agilent Technologies, USA) coupled directly to an Agilent 7890A gas chromatograph which was equipped with a split–splitless injector, a quickswap assembly, an Agilent model 7693 autosampler and a HP-5MS fused silica capillary column (5% phenyl 95% dimethylpolysiloxane, 30 m × 0.25 mm i.d., film thickness 0.25 μm, Agilent Technologies, USA). Supplementary analyses were performed on a DB-Wax fused silica capillary column (polyethylene glycol, 30 m × 0.25 mm i.d., film thickness 0.25 μm, Agilent Technologies, USA). The HP-5MS column was operated using an injector temperature of 250 °C and the following oven temperature profile: an

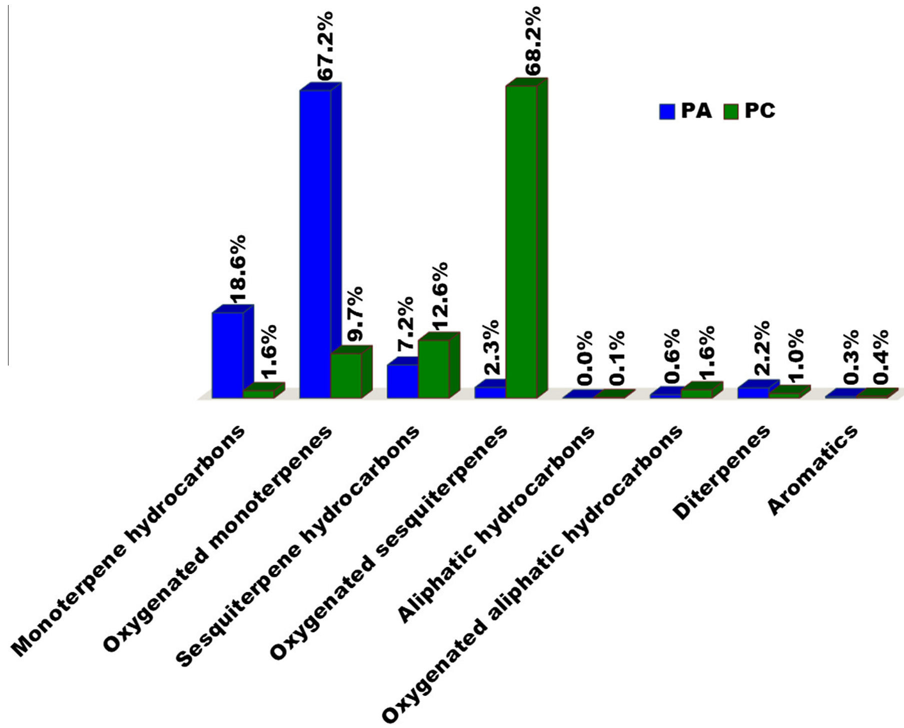

Figure 3 Chemical classes found in the oils of *P. cylindraceus* and *P. arabicus*.

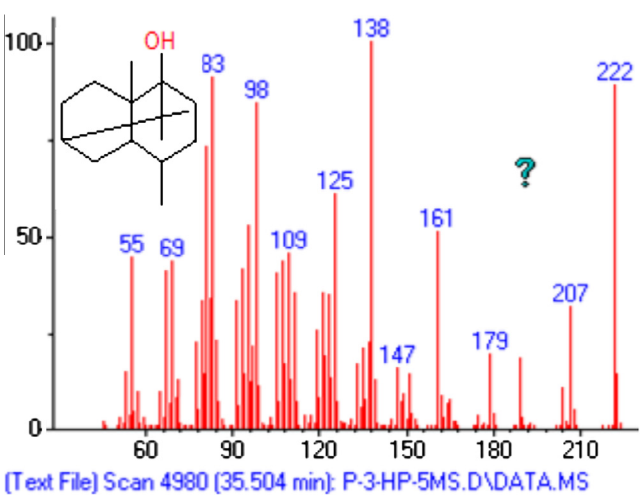

Figure 4 Chemical structure and EIMS fragmentation pattern of patchouli alcohol.

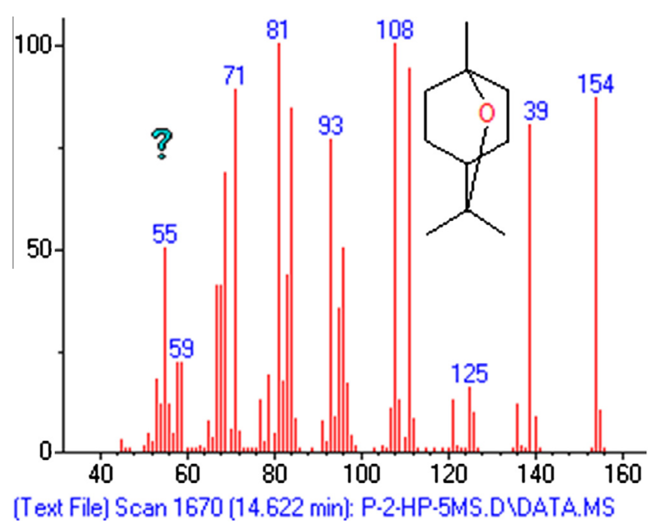

Figure 5 Chemical structure and EIMS fragmentation pattern of 1,8-cineole.

isothermal hold at 50 °C for 4 min, followed by a ramp of 4 °C/min to 220 °C, an isothermal hold for 2 min, a second ramp to 280 °C at 20 °C/min and finally an isothermal hold for 15 min. Conversely, the DB-Wax column was operated using an injector temperature of 250 °C and the following oven temperature profile: an isothermal hold at 40 °C for 4 min, followed by a ramp of 4 °C/min to 220 °C and an isothermal hold for 10 min.

Approximately 0.2 µl of each sample diluted in acetone (5% solution in acetone) was injected using the split injection mode; the split flow ratio was 10:1. The helium carrier gas was flowed at 1 ml/min. The GC–TIC profiles and mass spectra were obtained using the ChemStation data analysis software, version E-02.00.493 (Agilent). All mass spectra were acquired in the EI mode (scan range of m/z 45–600 and ionization energy of 70 eV). The temperatures of the electronic-impact ion source and the MS quadrupole were 230 °C and 150 °C, respectively. The MSD transfer line was maintained at 280 °C for both polar and nonpolar analysis. The GC analysis was performed on an Agilent GC-7890A dual-channel gas

Table 2 Major components of *P. cylindraceus* essential oils reported from various parts of the world.

Geographical regions	Major compounds (%)	Reference
Oman	Carvacrol (46.8), α-terpinolene (18.2), *p*-cymene (11.0), β-caryophyllene (5.7), β-selinene (2.2), myrcene (1.7).	[30]
Yemen	Thymol (68.5), α-terpinolene (5.3), β-selinene (4.7), β-caryophyllene (4.0), *p*-cymene (2.9), δ-cadinol (2.1).	[29]
Ethiopia	Camphor (40.93), 1,8-cineole (25.38), *p*-cymene (5.26), β-myrcene (2.90), α-terpinene (2.79), camphene (2.74).	[32]
Saudi Arabia	Patchouli alcohol (55.5), 1,8-cineole (6.0), caryophyllene oxide (2.3).	[Present study]

chromatograph (Agilent Technologies, USA) equipped with FID using both polar (DB-Wax) and nonpolar (HP-5MS) columns under the same conditions as described above. The detector temperature was maintained at 300 °C for both polar and nonpolar analyses. The relative composition of the oil components was calculated on the basis of the GC–FID peak areas measured using the HP-5MS column without using correction factor. Results are reported in Table 1 according to their elution order on the HP-5MS column.

2.5. Retention indices

A mixture of a continuous series of straight-chain hydrocarbons, C8–C31 (C8–C20, 04070, Sigma–Aldrich, USA and C20–C31, S23747, AccuStandard, USA) was injected into both polar (DB-Wax) and nonpolar (HP-5MS) columns under the same conditions previously described for the oil samples to obtain the linear retention indices (LRIs) (also referred to as linear temperature programmed retention indices (LTPRI)) of the oil constituents provided in Table 1. The LRIs were computed using van den Dool and Kratz's equation [36].

2.6. Identification of volatile components

GC–FID chromatogram of aerial parts essential oils of *P. cylindraceus* and *P. arabicus* with identified peaks of major components on HP-5MS column are shown in Figs. 1 and 2, respectively. The identification of different components was done by matching their mass spectra with the library entries of mass spectra databases (WILEY 9th edition, NIST-08 MS library version 2.0 f, and Adams and Flavor libraries) as well as by comparing their mass spectra and linear retention indices (LRI) with published data obtained using both polar and nonpolar columns [37–42] and the co-injection of authentic standards available in our laboratory.

3. Results and discussion

In this study, we present a detailed characterization of the chemical constituents of volatile oils isolated from two *Plectranthus* species (*P. cylindraceus* and *P. arabicus*) growing in Saudi Arabia. The hydro-distillation of fresh aerial parts of *P. cylindraceus* and *P. arabicus* in a traditional Clevenger-type tool produced colorless oils in yields of 0.8% and 1.1%, v/w, respectively, based on fresh weight. The phytochemical constituents of these oils were analyzed using gas chromatography–mass spectrometry (GC–MS) and gas chromatography–flame ionization detector (GC–FID) having two stationary phase columns (polar and nonpolar columns) which led to the identification of a total of 157 different compounds from both oils. In the oil derived from *P. cylindraceus*, 79 compounds were identified, whereas 132 compounds were identified in the oils derived from *P. arabicus*; these compounds account for 95.2% and 98.4% of the total oil compositions, respectively. The identified volatile constituents and their relative percentages are recorded in Table 1 according to their order of elution on the nonpolar column (HP-5MS).

From Fig. 3, it was evident that the *P. cylindraceus* oil was dominated by oxygenated sesquiterpenes (68.2%) followed by sesquiterpene hydrocarbons (12.6%) and oxygenated monoterpenes (9.7%). Monoterpene hydrocarbons (1.6%) and other classes of compounds such as oxygenated aliphatic hydrocarbons (1.6%), diterpenes (1.0%), aromatics (0.4%) and aliphatic hydrocarbons (0.1%) were present in minute concentration. In contrast, principle chemical class in *P. arabicus* oil was oxygenated monoterpenes (67.2%) followed by monoterpene hydrocarbons (18.6%) and sesquiterpene hydrocarbons (7.2%). Oxygenated sesquiterpenes (2.3%), diterpenes (2.2%), oxygenated aliphatic hydrocarbons (0.6%) and aromatics (0.3%) were present in lesser quantity.

The main components of volatile oil of *P. cylindraceus* were patchouli alcohol (55.5 ± 0.01%), 1,8-cineole (6.0 ± 0.01%) and valerianol (3.8 ± 0.18%), whereas, the main compounds of the *P. arabicus* oil were 1,8-cineole (50.5 ± 1.37%), β-pinene (7.0 ± 0.08%), camphor (6.3 ± 0.19%) and β-myrcene (4.1 ± 0.10%) and α-terpineol (4.1 ± 0.05%). The chemical structure and EIMS fragmentation pattern for the most prevalent compound, patchouli alcohol in *P. cylindraceus* oil and 1,8-cineole in *P. arabicus* oil is given in Figs. 4 and 5 respectively.

A comparison between *P. cylindraceus* and *P. arabicus* oils in terms of their chemical classes revealed that both oils differed significantly from one another since *P. cylindraceus* oil was dominated by sesquiterpenoids which account for 80.8% of the total oil composition, while, *P. arabicus* oil was found to contain monoterpenoids as the main class of compounds, accounting for 85.8% of the total oil composition. Furthermore, the two oils also showed notable differences with respect to relative concentrations of their individual constituents. For example, monoterpene hydrocarbons such as α-pinene, β-pinene, β-myrcene and limonene were about 11–14 folds more in *P. arabicus* oil than that in the *P. cylindraceus* oil. Similarly, oxygenated monoterpenes such as 1,8-cineole, camphor, α-terpineol and δ-terpineol were approximately 4–9 times more in *P. arabicus* oil, while, β-caryophyllene, α-humulene, viridiflorol and manool were 2–3 times greater in the oil of *P. arabicus* than that in the *P. cylindraceus* oil. Conversely, the oxygenated sesquiterpene, patchouli alcohol which was identified as the main component of *P. cylindraceus* oil was present only in trace amount in *P. arabicus* oil. On the other hand, valarianol, an oxygenated sesquiterpenoid, and α-bulnesene, a sesquiterpene hydrocarbon, present in appreciable amount in *P. cylindraceus* oil were not detected in *P. arabicus* oil, while caryophyllene oxide, another oxygenated

sesquiterpene was found to be approximately 8 folds more in *P. cylindraceus* oil than that in the oil of *P. arabicus*.

Previous reports on the volatile oil of *P. cylindraceus* from different regions of the world revealed that the composition of *P. cylindraceus* oil differed significantly with respect to their place of collections (Table 2). For example, Marwah et al. [30] reported carvacrol, α-terpinolene, *p*-cymene and *β*-caryophyllene as major components of the oil of *P. cylindraceus* grown in Oman. Asres et al. [32] reported camphor, 1,8-cineole and *p*-cymene as the principle constituents of *P. cylindraceus* oil grown in Ethiopia. Ali et al. [29] found thymol, α-terpinolene, *β*-selinene and *β*-caryophyllene as main components of *P. cylindraceus* oil from Yemen, whereas, in our present study patchouli alcohol, 1,8-cineole and caryophyllene oxide were determined as the main components of *P. cylindraceus* oil from Saudi Arabia.

It is noteworthy to mention here that patchouli alcohol, in our present study identified as the main component of *P. cylindraceus* oil has never been reported from the genus *Plectranthus*. Patchouli alcohol also known as patchoulol, is one of the most valued aroma compounds in flavor and fragrance industries. Because of its profound pleasant woody notes with long-lasting effect, it is widely used as a fragrance ingredient in perfumery, cosmetics, shampoos, soaps and non-cosmetic products like household cleaners and detergents [43]. It has also been reported to possesses various important biological activities including antimicrobial [44,45], anti-termite [46], antiviral [47,48] and antioxidant [48] activities. It is significant to mention that occurrence of patchouli alcohol in such a high proportion in the plant kingdom is very rare and only few plant species have been known to produce it in appreciable amount. Furthermore, although patchouli alcohol has been recently isolated from some plant species of the genus *Valeriana* [49], to the best of our knowledge, till date patchouli plant (*Pogostenum cablin* Benth.) has remained as the only source for commercial isolation of patchouli alcohol [50,51]. Thus, detection of patchouli alcohol in *P. cylindraceus* oil in such a great proportion (> 55%) through this study could be of immense importance and might provide an alternate source for commercial utilization of this plant for its isolation at industrial scale.

On the other hand, in this study phytochemical analysis of *P. arabicus* has been carried out for the first time. A detailed analysis of volatile oil of *P. arabicus* using GC–FID and GC–MS techniques revealed that most dominating compound of the *P. arabicus* oil is 1,8-cineole which accounts for more than 50.0% of the total oil composition. The high content of 1,8-cineole in the essential oil of *P. arabicus* is remarkable, as this compound has widespread medicinal and industrial applications. 1,8-cineole which is also famously known as eucalyptol, is an oxygenated monoterpene and has been reported to demonstrate various therapeutic properties, such as antioxidant, antispasmodic, antinociceptive, analgesic, insecticidal, hypotensive, bactericidal, increases cerebral blood flow, antiviral, herbicidal, antimicrobial and anticancer properties [52–55]. Furthermore, due to fresh camphor-like smell and pleasant spicy aroma with cooling taste of 1,8-cineole, it is extensively used as an important ingredient in flavorings, foods, fragrances, cosmetics and pharmaceutical industries. Moreover, it is also widely used in the treatment of various acute and chronic ailments, such as bronchitis, cough and colds, asthma, nasal infections, respiratory infections and sinusitis problems [52,56]. Notably, 1,8-cineole has various important medicinal and industrial applications, which has been detected in essential oil of *P. arabicus* in high percentage in this study. Therefore, this plant can be considered as a commercially important plant and can be propagated for cultivation in agricultural cropping system for its appropriate industrial exploitation.

4. Conclusion

The present study is the first detailed chemical characterization of the essential oil constituents of *P. cylindraceus* and *P. arabicus* growing in Saudi Arabia. This study revealed that oil composition of these two species differed significantly from one another. Essential oil composition of *P. cylindraceus* was dominated by sesquiterpenoids, whereas, *P. arabicus* oil contained monoterpenoids as the main class of compounds. Patchouli alcohol was characterized as most dominating compound of *P. cylindraceus* oil, whereas, in *P. arabicus* oil, 1,8-cineole was determined as most representative compound. Patchouli alcohol and 1,8-cineole, both compounds have widespread applications in perfumery, flavor and fragrance, cosmetics, soaps, detergent and pharmaceutical industries. Thus, presence of patchouli alcohol and 1,8-cineole in high quantity in *P. cylindraceus* and *P. arabicus* oils, respectively, is remarkable since they possess various significant medicinal and industrial applications. Furthermore, occurrence of patchouli alcohol in high proportion in the plant kingdom is very rare and to the best of our knowledge, till date patchouli plant (*P. cablin* Benth.) has remained as the only source for commercial isolation of patchouli alcohol. Thus, detection of patchouli alcohol in *P. cylindraceus* oil in such a great proportion (> 55%) might provide an alternate source for commercial utilization of this plant for the isolation of patchouli alcohol at industrial scale. However, further studies on seasonal and agro-climatic effects on compositions and yields of essential oil from various parts of these two plants growing in different regions of Saudi Arabia are required.

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