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HYDROCARBONS FROM THE ESSENTIAL OIL OF *CYMBOPOGON MARTINII*

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Key Word Index—*Cymbopogon martinii*; Gramineae; palmarosa; essential oil; monoterpenes; sesquiterpenes; *n*-alkanes.

Abstract—The composition of the hydrocarbon fraction of the essential oil from *Cymbopogon martinii*, which represents less than 5% of the oil, has been studied. Using well-established techniques, 11 monoterpenes (*ca* 46%), 28 sesquiterpenes (*ca* 52%) and 16 *n*-alkanes (*ca* 1.6%) have been identified. The major constituents are limonene, α-terpinene, myrcene, β-caryophyllene, α-humulene, β- and δ-selinenes. The study of the *n*-alkanes of *C. martinii* revealed the presence of all members of the homologous series C_{15}–C_{30}.

INTRODUCTION

The genus *Cymbopogon* is known for the presence, in many species, of economically important monoterpenes such as geraniol [1], citral [2, 3] and citronellal. *C. martinii* (Roxb.) W. Wats var. *martinii*, which is commonly named palmarosa, is a grass which gives by steam distillation from the freshly cut herb an essential oil rich in geraniol (60–80%) [4, 5]. Since only four monoterpenes [6], β-caryophyllene [6, 7] and α-humulene [7] have been reported in the hydrocarbon fraction of *C. martinii*, we have re-investigated this fraction.

RESULTS

The essential oil was obtained by steam distillation from the freshly cut herb in 0.48% yield. It was examined by routine temperature programmed GC and the main constituent was found to be geraniol (80.0%), the content of which agreed well with those in the literature [5–7]. The hydrocarbon fraction was obtained by column chromatographic fractionation and constituted 4.75% of the essential oil. Its constituents were identified by GC/MS using an electron-impact ionization technique and by R_I (Kovat's retention indices). The concentrations of the constituents in the essential oil were calculated from the GC peak areas. The various classes of hydrocarbons found in *C. martinii* essential oil identified in this work were monoterpenes (45.9%), sesquiterpenes (52.2%), *n*-alkanes (1.6%) and unknowns (0.4%).

Table 1 details the results obtained for the 11 monoterpenoid constituents (**1–11**) and the 29 sesquiterpene components (**12–40**) contained in the hydrocarbon fraction of *C. martinii*. The mass spectra of the components agreed with those in the literature [8–16]. Supportive evidence of the identity of these sesquiterpenes was obtained using R_I values, determined on a capillary column coated with Carbowax 20 M and compared with those in the literature [8–10, 13, 17–19].

Saturated hydrocarbons were identified on the basis of their mass spectra and by co-chromatography with authentic *n*-alkanes. The results revealed the presence of all saturated straight hydrocarbons in the series C_{15}–C_{30} (Table 2). Our GC analyses revealed some minor peaks between those representing the *n*-alkanes which might be due to branched, saturated hydrocarbons. However, they occurred in amounts too small to allow reliable determination.

DISCUSSION

Among the 11 monoterpenes identified in the hydrocarbon fraction of *C. martinii*, limonene is the major constituent (64.5%) and represents 14.1 mg/g of the essential oil. Myrcene, limonene, *cis*-β-ocimene and *trans*-β-ocimene have been identified in palmarosa oil produced in Brazil [6]. Most of these monoterpenes have been characterized in another species, *C. distans* [20], and high contents of limonene have also been observed in *C. flexuosus* var. *sikkimensis* and in *C. osmatonii* [21].

The sesquiterpene fraction of *C. martinii* contains β-caryophyllene (69.5%), selinenes (12.1%), α-humulene (6.8%), cadinenes (2.9%), γ-muurolene (2.2%), germacrenes (1.6%) and other sesquiterpenes in minor amounts. β-Caryophyllene is the main constituent of the hydrocarbon fraction of *C. martinii* (17.2 mg/g of the essential oil). β-Caryophyllene and α-humulene were isolated from *C. martinii* [7]. β-Selinene, β-elemene and germacrene D were isolated from the volatile oil of *C. nervatus* [22], and some of the other sesquiterpenes that we have characterized are included in the 13 sesquiterpenes identified in *C. distans* [20].

The *n*-alkane fraction consisted of a mixture of chain lengths varying from C_{15} to C_{30}. No significant dominance of odd- over even-numbered chains was observed since the former made up about 56% of the total *n*-alkane fraction. These results agree with the observations of Herbin and Robins [23], who have claimed that when *n*-alkanes form only a small percentage of the leaf cuticular

Table 1. Monoterpenes and sesquiterpenes identified in the hydrocarbon fraction of *C. martinii* essential oil

No.	Compound	Relative composition (%)
1	α-Pinene	4.4
2	β-Pinene	3.3
3	α-Phellandrene	2.2
4	Myrcene	6.9
5	α-Terpinene	14.6
6	Limonene	64.5
7	γ-Terpinene	0.5
8	*o*-Cymene	0.3
9	*m*-Cymene	0.4
10	*p*-Cymene	1.1
11	Terpinolene	1.8
12	β-Cubebene	0.24
13	β-Elemene	1.34
14	β-Caryophyllene	69.5
15	γ-Elemene	0.19
16	β-Helmiscapene	0.32
17	α-Humulene	6.82
18	β-Farnesene	0.06
19	γ-Muurolene	2.17
20	δ-Selinene	3.47
21	γ-Bisabolene	0.30
22	α-Amorphene	0.06
23	Germacrene D	0.13
24	β-Selinene	6.52
25	α-Selinene	2.11
26	Bicyclogermacrene	0.56
27	β-Bisabolene	0.06
28	$C_{15}H_{22}$	0.43
29	β-Curcumene	0.06
30	δ-Cadinene	1.31
31	γ-Cadinene	1.44
32	Cubenene	0.10
33	α-Farnesene	0.22
34	Selina-4,7-diene	0.19
35	α-Cadinene	0.19
36	α-Curcumene	0.06
37	Germacrene B	1.44
38	*cis*-Calamenene	0.19
39	*trans*-Calamenene	0.26
40	Calacorene	0.19

Table 2. Distribution of *n*-alkanes in the hydrocarbon fraction of *C. martinii* essential oil

No.	*n*-Alkane (*n* in C_nH_{n+2})	Relative composition (%)
41	15	5.0
42	16	9.8
43	17	4.4
44	18	8.7
45	19	4.4
46	20	10.2
47	21	3.8
48	22	7.1
49	23	7.7
50	24	6.6
51	25	5.5
52	26	4.4
53	27	8.2
54	28	6.5
55	29	5.0
56	30	2.7

wax, the dominance of odd over even carbon number chain lengths tends to disappear. Within the odd-numbered *n*-alkane population, *n*-heptacosane (C_{27}) dominated although in the even-numbered population, *n*-eicosane (C_{20}) was the dominant alkane. Herbin and Robins [24] have shown, in a study of leaf cuticular waxes from a large range of families in the Angiosperms, that *n*-nonacosane (C_{29}) and *n*-hentriacontane (C_{31}) are the most frequent major components among the predominating odd carbon number constituents, and that C_{28} and C_{30} are the most frequent major even-number constituents. The distillation procedure used to obtain the essential oils would not be expected to carry off all the *n*-alkanes and is a more drastic technique than the washing methods commonly used for the extraction of cuticular wax. Thus, the *n*-alkanes contained in *C. martinii* essential oil may represent only the lower M_r range of cuticular and internal (cell content) *n*-alkanes.

EXPERIMENTAL

Plant material. This was collected from the Mahajanga area of Madagascar. The freshly cut herb was used for extraction of the essential oil.

Isolation of hydrocarbons. A sample (0.4 g) of the essential oil (12 ml), obtained by steam distillation of the fresh plant material (2.5 kg), was fractionated by CC (40 cm × 0.8 cm i.d.) on silica gel (230–400 mesh, 30 g). Elution with *n*-pentane (120 ml) yielded 19 mg (4.75%) of hydrocarbons.

GC. The hydrocarbon fraction was analysed by routine temp. programmed GC (70–220° at 2°/min) with FID and a WCOT glass column (48 m × 0.2 mm i.d.) coated with Carbowax 20 M (0.15 μm phase thickness); inlet pressure of H_2 used as carrier gas, 0.4 bar.

GC/MS. GC/MS spectra were obtained under the following conditions: ionization energy, 70 eV; ion source, 220°; trap current, 60 μA; temp., 70–250° at 2°/min; GC column, 50 m × 0.2 mm; WCOT Carbowax 20 M fused silica column (0.15 μm phase thickness); carrier gas He, 30 ml/min; injection temp., 260°.

Identification of the constituents. The monoterpenes, sesquiterpenes and *n*-alkanes listed in Tables 1 and 2 were identified by comparison of their Kovat's retention indices with those for authentic samples and by comparison with reported mass spectra.

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