Journal of Chromatography, 279 (1983) 145–150
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 111

CONSTITUENTS OF PLANTS GROWING IN QATAR

V. CONSTITUENTS OF THE VOLATILE OIL OF *CYMBOPOGON PARKERI*

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SUMMARY

Analysis of the volatile oil of *Cymbopogon parkeri* has been carried out by capillary gas chromatography–mass spectrometry. To facilitate identification, pre-fractionation of the oil by adsorption high-performance liquid chromatography was performed. Of the 55 compounds detected, 43 were identified. The major compounds are geraniol (33.55%), nerol (22.21%), geranyl acetate (8.9%), neryl acetate (3.78%), an unidentified sesquiterpene alcohol (4.82%) and farnesol (3.75%).

INTRODUCTION

Cymbopogon species are known to contain volatile oils that produce a number of economically important compounds, *e.g.*, citral, citronellal, citronellol, geraniol, piperitone and methyleugenol, highly valued as perfume chemicals and flavouring agents and in the pharmaceutical industry. In recent decades, several *Cymbopogon* species, and in particular their volatile oils, have been comprehensively studied[1–7]. Folk medicine records many applications of certain *Cymbopogon* species. The plants and/or their essential oils are used as carminative, stimulative, stomachic, diuretic and antirheumatic agents[8–10]. Moreover, the essential oils of certain *Cymbopogon* species show remarkable antibacterial and antifungal properties[3,11,12].

Cymbopogon parkeri Stapf. (local name Shabar[13]) is a perennial aromatic plant that is very common, particularly in central and northern Qatar, flourishing in spring and flowering from March to May. Nothing is known about the constituents of this plant. This paper describes a study of its volatile oil constituents.

0021-9673/83/$03.00

EXPERIMENTAL

Preparation of the oil

A 500-g amount of the fresh plant, collected in May, was subjected to steam distillation, yielding a yellowish essential oil (1.55%, calculated on the basis of anhydrous material).

Fractionation of the oil[14]

High-performance liquid chromatographic (HPLC) pre-separation of 10 mg of the essential oil was carried out on a silica column (25 cm × 0.46 cm I.D.) packed with 5-μm spherical silica ROSil (Alltech-Europe), which was installed in a Varian 5000 liquid chromatograph equipped with a Varichrom UV 50 detector, operated at 220 nm. Four main fractions originating from a gradient elution programme from 100% *n*-hexane to 100% tetrahydrofuran–methanol (20:80) at a flow-rate of 1 ml/min were collected.

Gas chromatographic analysis

Capillary gas chromatography (GC) was performed on a glass HTS SE-54 column (30 m × 0.3 mm I.D.; d_f 0.5 μm)[15], installed in a Carlo Erba 4160 chromatograph, equipped with a split and a cold on-column injector. The operating conditions were as follows: injection temperature, 30°C; column temperature, ballistically programmed to 50°C and then to 250°C at 3°C/min; flame-ionization detector at 280°C; carrier gas (hydrogen) flow-rate, 2 ml/min. Quantitation was carried out with a Varian CDS 111 integrator.

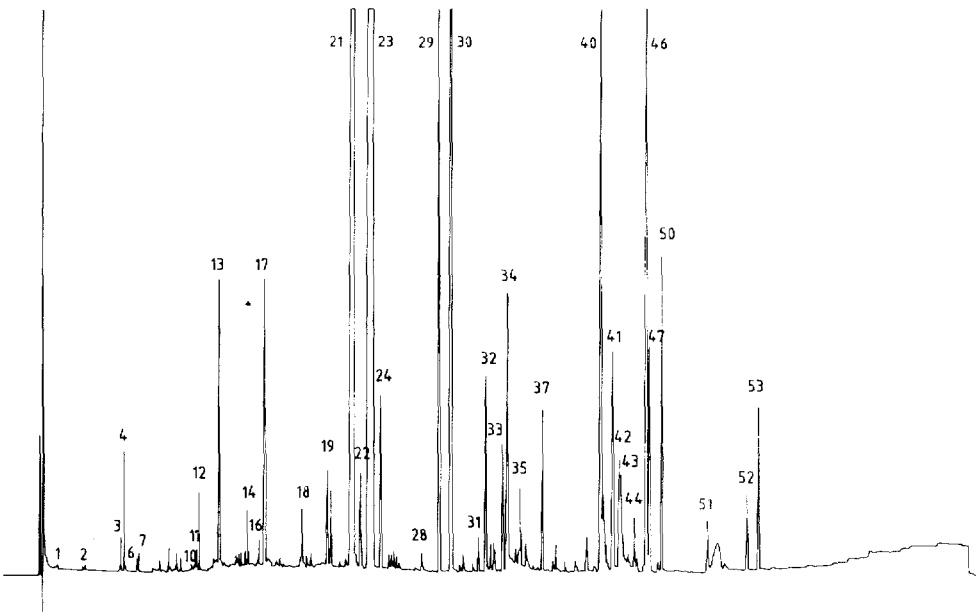

Fig. 1. Capillary gas chromatogram of the total essential oil of *Cymbopogon parkeri*.

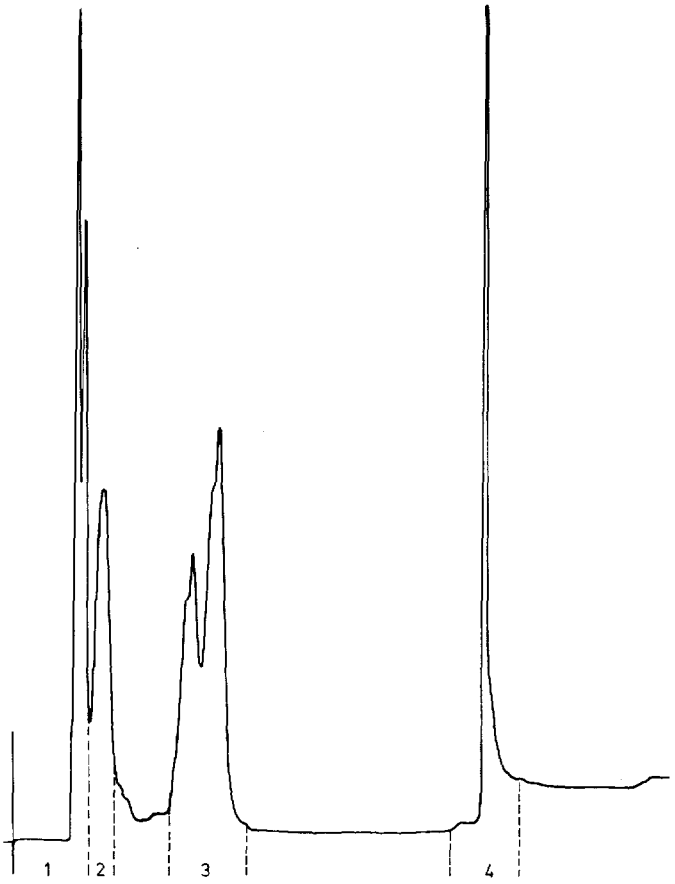

Fig. 2. HPLC trace of the total essential oil of *Cymbopogon parkeri*.

Gas chromatography–mass spectrometry (GC–MS)

For GC–MS a Finnigan 4000 system was used, equipped with a Data General Nova 3 computer. The same column and conditions as reported for the capillary GC analysis were used to obtain comparable results, except that helium was used as the carrier gas at a flow-rate of 2 ml/min. The column was directly connected to the ion source via 1-m HTS deactivated fused-silica tubing, connected to the glass column with a polyimide seal[16].

RESULTS AND DISCUSSION

Fig. 1 shows the capillary chromatogram of the total essential oil. Nerol (peak 21, 22.21%), geraniol (peak 23, 33.35%), neryl acetate (peak 29, 3,78%), geranyl acetate (peak 30, 8.91%), an unknown sesquiterpene alcohol (peak 40, 4.82%) and farnesol (peak 46, 3.75%) are the main constituents, totalling 67.12% of the oil.

The total essential oil was pre-fractionated by adsorption HPLC into four fractions. Each fraction was analysed by capillary GC–MS. The technique of com-

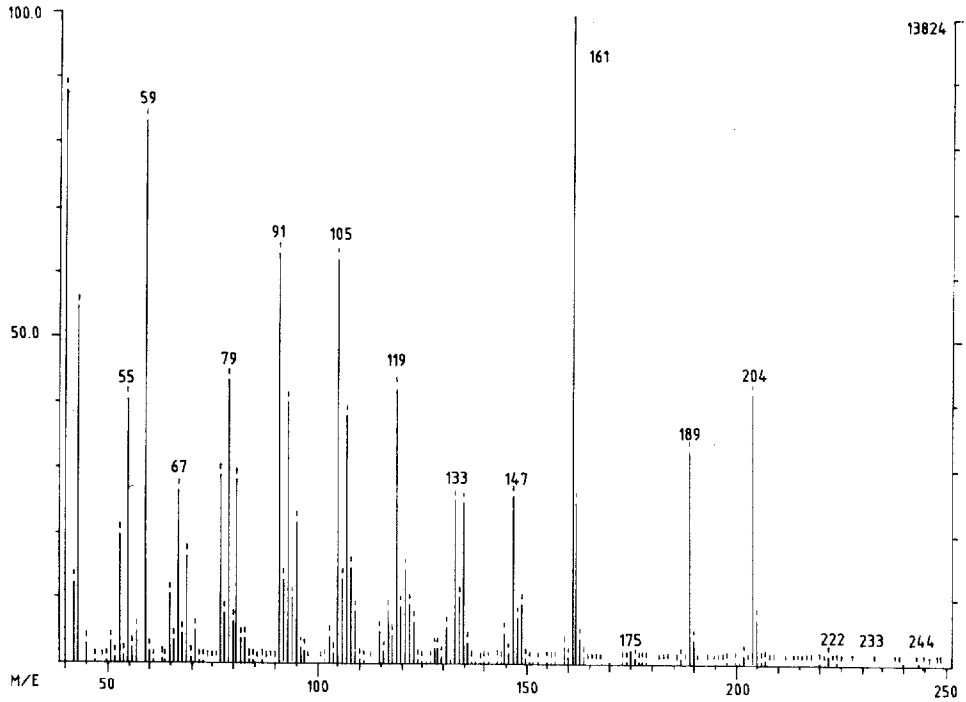

Fig. 3. Electron-impact mass spectrum of unidentified sesquiterpenoid accounting for 4.82% of the essential oil of *Cymbopogon parkeri*.

bined HPLC–capillary off-line offers several advantages for essential oil analysis: fast pre-separation of small sample amounts (10 mg), no loss of volatiles by evaporation of the mobile phase, because samples are injected as such by cold on-column injection, and reduction of artefacts or alterations of the oil. Fig. 2 shows the HPLC trace of the oil and the origin of the four fractions. The oil was separated into hydrocarbons and long-chain esters fraction (1), esters and ketones (2), aldehydes (3) and alcohols (4).

The first fraction contained the hydrocarbons and the long-chain fatty acid esters of nerol and geraniol (butanoate, hexanoate, octanoate). Twenty-three compounds were identified: limonene, α-terpinolene, undecane, β-gurjunene, geranyl hexanoate, neryl hexanoate, neryl octanoate and geranyl octanoate were the main constituents.

Fraction 2 consisted mainly of ketones and esters. Twelve compounds were identified. The principal components were neryl acetate, geranyl acetate, 12-methyl-4-tridecanone, 14-methyl-4-pentadecanone and trace amounts of neryl butanoate, neryl hexanoate, neryl octanoate and geranyl octanoate.

Fraction 3 was composed mainly of aldehydes. Six compounds were identified. Neral, geranial and farnesal were the main components of this fraction.

The last fraction (4) consisted mainly of alcohols and contained the most abundant components of the oil; ten compounds were identified. Nerol, geraniol, farnesol, guaiol, eudesmol and three unidentified sesquiterpene alcohols were present. The

TABLE I
COMPOUNDS IDENTIFIED IN THE ESSENTIAL OIL OF *CYMBOPOGON PARKERI*

*Compound**	*No.*	*Fraction No.***	*Content (%)*
Butyl acetate	1	1	
4-Hydroxy-4-methylpentanone	2	1	
Toluene	3	2	
Xylene	4	1	0.36
Nonane	5	1	
Car-3-ene	6	1	
Methylethylbenzene	7	1	
Diethylbenzene	8	1	
6-Methyl-5-hepten-2-one	9	3	
Myrcene	10	1	
p-Cymene	11	1	
Decane	12	1	0.27
Limonene	13	1	0.98
7-Methyl-4-octanone	14	2	0.28
α-terpinolene	15	1	
Undecane	16	1	
Linalool	17	4	1.46
Unknown (M.W. 152)	18	2	0.32
α-terpineol	19	4	0.45
Dodecane	20	1	
Nerol	21	4	22.21
Neral	22	3	0.6
Geraniol	23	4	33.55
Geranial	24	3	1.29
2,5-Dimethylhexan-3,4-dione	25	3	
9-Methyl-4-decanone	26	2	
Bornyl acetate	27	2	
10-Methyl-7-undecanone	28	2	
Neryl acetate	29	2	3.78
Geranyl acetate	30	2	8.91
Sesquiterpenoid (M.W. 220)	31	1	0.18
β-Gurjunene	32	1	0.91
Sesquiterpene (M.W. 204)	33	1	0.63
12-Methyltridecanone	34	2	1.67
Sesquiterpene alcohol (M.W. 222)	35		0.50
Sesquiterpenoid (M.W. 220)	36	1	
Neryl butanoate	37	2	0.69
Geranyl butanoate	38	2	
Geranyl valerate	39	2	
Sesquiterpene alcohol (M.W. 222)	40	4	4.82
Eudesmol (t)	41	4	1.43
14-Methylpentadecanone	42	2	0.61
Guaiol (t)	43	4	0.64
Sesquiterpene alcohol	44	4	
Sesquiterpene alcohol	45	4	0.36
Farnesol	46	4	3.75
Sesquiterpenoid (M.W. 220)	47	3	
Neryl hexanoate	48	1-2	0.92
Farnesal	49	3	
Geranyl hexanoate	50	1-2	1.09
Geranyl heptanoate	51		0.28
Neryl octanoate	52	1-2	0.36
Geranyl octanoate	53	1-2	0.77

* (t) = tentative.
** See Fig. 2.

electron-impact mass spectrum of the unknown sesquiterpene alcohol, yielding 4.82%, is shown in Fig. 3.

As a result of this investigation, 55 compounds were classified by their mass spectral pattern, 43 were identified and 2 were assigned tentative structures. Confirmation was obtained by comparing the retention times with literature data and, for some, with the retention data of the pure compounds.

The data are given in Table I, together with the percentages of the compounds accounting for more than 0.1%. Remarkable in this oil is the presence of the homologous series of the esters of nerol and geraniol, making the oil very interesting for perfumery purposes.

REFERENCES

1 A. K. Sinha and M. S. Mehra, *Indian Perfum.*, 22 (1977) 129–131.
2 T. Saeed, P. J. Sandra and M. J. E. Verzele, *Phytochemistry*, 17 (1978) 1433–1434.
3 C. S. Mathela and G. K. Sinha, *J. Indian Chem. Soc.*, 55 (1978) 621–622.
4 R. K. Thappa and K. L. Dhar, *Phytochemistry*, 18 (1979) 671–672.
5 M. L. S harma, G. S. Srivastava and A. Singh, *Indian Perfum.*, 24 (1980) 17–19.
6 D. B. Saxena and M. L. Maheshwari, *Indian Perfum.*, 24 (1980) 115–120.
7 C. S. Mathela and P. Joshi, *Phytochemistry*, 20 (1981) 2770–2771.
8 E. Quisumbing, *Medicinal Plants of the Philippines*, Bureau of Printing, Manilla, 1951, p. 85.
9 R. N. Chopra, S. L. Nayer and I. C. Chopra, *Glossary of Indian Medicinal Plants*, Council of Scientific and Industrial Research, New Delhi, 1956, p. 87.
10 F. M. Abdel-Moneim, Z. F. Ahmed, M. B. E. Fayez and H. Ghaleb, *Planta Med.*, 17 (1969) 209–212.
11 R. K. Garg and A. K. Sinha, *Indian J. Anim Res.*, 8 (1974) 27–29.
12 A. K. Singh, A. Dikshit, M. L. Sharma and S. N. Dixit, *Econ. Bot.*, 34 (1980) 186–190.
13 K. H. Batanouny, *Ecology and Flora of Qatar*, Centre for Scientific and Applied Research, Qatar University, Doha, Qatar, 1981, p. 183.
14 C. Bicchi, A. M. Rizk, H. I. Heiba, M. Mashaly and P. Sandra, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, submitted for publication.
15 M. Godefroot, M. Van Roelenbosch, M. Verstappe, P. Sandra and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 337.
16 P. Sandra, M. Schelfaut and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 81.