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ESSENTIAL OIL OF *PSIADIA SALVIIFOLIA*

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Key Word Index—*Psiadia salviifolia;* Compositae; essential oil constituents; 7-methyl-3-methyleneocta-1,4-diene; calamenol.

Abstract—Utilizing GLC, IR, combined GC-MS, the following constituents were identified in the essential oil of *Psiadia salviifolia:* β-pinene, limonene, γ-terpinene, *p*-cymene, α-copaene, linalool, β-bourbonene, α-himachalene, γ-cadinene, δ-cadinene, γ-elemene, and a hydroxy derivative of calamenene. A new monoterpene hydrocarbon was also isolated which from MS and IR evidence was named as 7-methyl-3-methylene-octa-1,4-diene.

INTRODUCTION

Psiadia salviifolia Bak. (Compositae) is a shrub growing to a height of 5 m which is found in the central region of Madagascar. It has been reported that the aerial parts are used in local medicine as a specific for dysentery, for liver disorders and hypertension.[1–3] Apart from general screening tests,[1] no chemical work has been reported on the constituents of this plant or of any other members of the genus. In this paper are reported the results of a preliminary examination of the essential oil of *Psiadia salviifolia* leaves.

RESULTS AND DISCUSSION

By combined GC–MS, the oil was shown to consist of the following fractions: terpenes (15·0%), sesquiterpenes (69·4%), diterpenes (15·3%). Identification of some of the constituents was then accomplished utilizing MS, R_ts and IR. The results are summarized in Table 1.

Identification of Peak 2

A molecular ion at *m/e* 136 indicated a monoterpene hydrocarbon with 3 double bond equivalents. The MS did not agree with published spectra for acyclic, monocyclic or bicyclic structures.[4–7] The possibility of the spectrum being anomalous was discounted since other monoterpene constituents complied with published spectra. Thermal decomposition was also ruled out since characteristic fragments were absent.[4]

The base peak at *m/e* 91 suggested an acyclic structure not having a through-conjugated arrangement of the double-bonds.[4] At least 11 structures can be drawn complying with

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[1] PERNET, R. and MEYER, G. (1957) *Pharmacopée de Madagascar,* L'Institut de Recherche Scientifique, Tananarive.
[2] PERNET, R. (1959) *Mém. I.S.M. Tananarive* **IXB**, 239.
[3] STEINMETZ, E. F. (1962) *Q. J. Crude Drug Res.* **2**, 264.
[4] RYHAGE, R. and VON SYDOW, E. (1963) *Acta Chem. Scand.* **17**, 2025.
[5] THOMAS, A. F. and WILLHALM, B. (1964) *Helv. Chim. Acta* **47**, 475.
[6] HILL, H. C., REED, R. I. and ROBERT-LOPES, M. T. (1968) *J. Chem. Soc.* **C**, 93.
[7] VON BÜNAU, G., SCHADE, G. and GOLLNICK, K. (1969) *Z. Anal. Chem.* **244**, 7.

these requirements but only 7-methyl-3-methyleneocta-1,4-diene would be expected to lose a propyl fragment by the preferred β-cleavage. The other structures would not fragment in this way. Table 2 lists the metastable ions characteristic of acyclic structures which were found on the MS,[4–6] and Scheme 1 outlines a suggested fragmentation pattern for the above substance. An IR spectrum of this substance was obtained after trapping peak 2 in a AgCl microcell. The spectrum obtained confirmed the above deductions by indicating terminal $>C{=}CH_2$, conjugated double bonds and bending modes for $-CH_2$ and $-Me$ groups.

TABLE 1. CONSTITUENTS OF THE ESSENTIAL OIL OF *Psiadia salviifolia*

Peak No.	Class of compound of identification	Evidence	Percentage (w/w)
1	Hydroxymonoterpene	IR	1·74
2	7-Methyl-3-methyleneocta-1,4-diene	MS, IR	
3	β-Pinene	MS, IR	4·62
4	Limonene	MS, IR, R_t	2·11
5	γ-Terpinene	MS, IR	0·56
6	(a) *p*-Cymene	MS, IR, R_t	0·67
	(b) Hydroxyterpene	IR	
7–9	Sesquiterpene H/C	MS	4·73
10	α-Copaene	MS	1·28
11	(a) Linalool	IR, R_t	10·69
	(b) β-Bourbonene	MS	
12, 13	Sesquiterpene H/C	MS	3·45
14	Alloaromadendrene	MS	0·59
15, 16	Sesquiterpene H/C	MS	
17	α-Himachalene	MS	0·82
18	Sesquiterpene H/C	MS	3·99
19	γ-Cadinene	MS	3·84
20	δ-Cadinene	MS	12·44
21–23	Oxygenated sesquiterpenes	MS	
24	Calamenenol	MS	
25, 26	Oxygenated sesquiterpenes	MS	4·71
27	γ-Elemene	MS	2·67
28–31	Oxygenated sesquiterpenes	MS	25·57
32–38	Diterpenes	MS	11·76
			96·24
	Trace components		3·51
	Total		99·75

H/C—hydrocarbon; R_t—retention time.

Identification of Peak 24

The MS for this substance showed a molecular ion at *m/e* 220 with the next prominent peak at *m/e* 202; such a loss of M-18 is recognized as loss of water which occurs with alcohols.[8] Hence, the substance represented by peak 24 is a sesquiterpene alcohol.

Identification, however, is based on the spectrum for the sesquiterpene hydrocarbon, calamenene. Such an assumption is reasonable, since the MS of a sesquiterpene hydrocarbon and that of the corresponding alcohol can be very similar, e.g. β-elemene and

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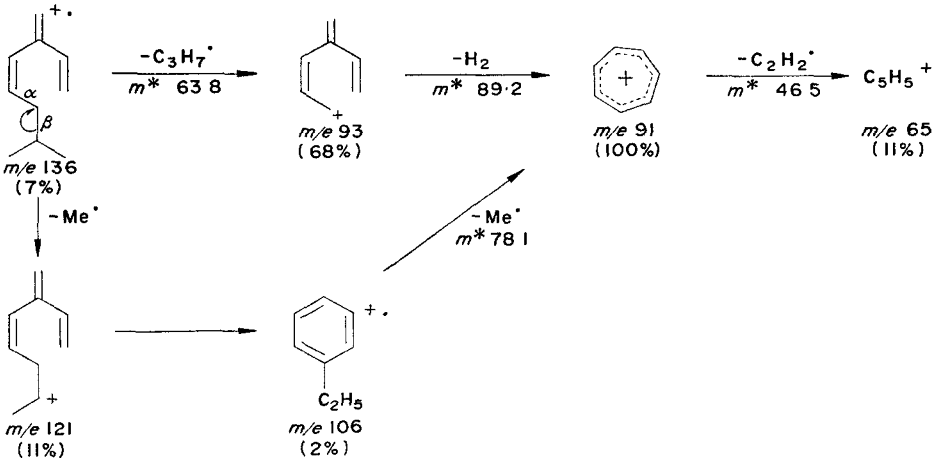
[8] BEYNON, J. H., SAUNDERS, R. A. and WILLIAMS, A. E. (1968) *The Mass Spectra of Organic Molecules*, p. 133, Elsevier, London.

elemol.[9] The metastable ions recorded for calamenene are all to be found on the trace for this peak; these are shown in Table 3.



SCHEME 1. SUGGESTED FRAGMENTATION OF 7-METHYL-3-METHYLENEOCTA-1,4-DIENE.

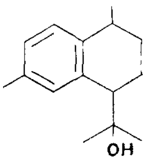
Variations in the relative abundances of the ions from the MS for calamenene published by Hayashi *et al.*[9] and the MS for peak 24 are apparent. However, the very large base peak

TABLE 2. METASTABLE IONS FOUND ON THE MS FOR PEAK 2

Metastable ion	Breakdown reaction
101·2	$105^+ \rightarrow 103^+ + 2$
89·2	$93^+ \rightarrow 91^+ + 2$
71·5	$121^+ \rightarrow 93^+ + 28$
63·8	$136^+ \rightarrow 93^+ + 43$
59·6	$105^+ \rightarrow 79^+ + 26$

TABLE 3. METASTABLE IONS FOUND ON THE MS FOR PEAK 24 AND ALSO RECORDED FOR CALAMENENE[9]

Metastable ion	Breakdown reaction
140·0	$144^+ \rightarrow 142^+ + 2$
130·4	$159^+ \rightarrow 144^+ + 15$
125·2	$202^+ \rightarrow 159^+ + 43$
107·9	$159^+ \rightarrow 131^+ + 28$
89·1	$159^+ \rightarrow 119^+ + 40$
69·6	$119^+ \rightarrow 91^+ + 28$



(I)

Calamenenol

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[9] HAYASHI, S., SÂTO, H., HAYASHI, N., OKUDE, T. and MAATSURA, T. (1967) *J. Sci. Hiroshima Univ. Ser. A-II* 31 (3), 217.

at m/e 159 in comparison with the abundance of the other ions indicates the basic structure of calamenene. It is proposed, therefore, that the substance represented by peak 24 is the alcohol of calamenene, and can be referred to as calamenenol. The position of the hydroxyl group has not been determined, but is most likely as in (I).

Such a substance would readily lose water and then give the fragmentation pattern of calamenene.

EXPERIMENTAL

Materials. Samples of the dried flowering tops were obtained from Dr. E. F. Steinmetz, Amsterdam.

Extraction of essential oil. The oil was obtained by simultaneous steam distillation and extraction in a Likens and Nickerson apparatus.[10]

GC. Pye series 104; glass column, 2·1 m × 5 mm; stationary phase, 10% Carbowax 20M on acid-washed Celite (B.D.H.) 60–85 mesh, HMDS treated; temp. programme, 70–220° at 5°/min, with an initial hold of 5 min and a final hold of 20 min; carrier gas (N_2) at 75 ml/min. Peak areas were obtained with a Kent Chromalog 2 electronic integrator coupled to a Pye wide-range amplifier.

GC–IR. Pye series 104; glass column 9·1 m × 9·5 mm; stationary phase, 25% Carbowax 20M on acid-washed Celite (B.D.H.) 60–85 mesh, HMDS treated; temp. programme, 70–220° at 5°/min; carrier gas (N_2) 150 ml/min; column effluent split in a ratio of 107.1. Peaks were trapped in AgCl microcells ('Extrocells' R.I.I.C.) having a path length of 0·025 mm.[11] Spectra were obtained on a Unicam SP200 IR spectrophotometer.

GC–MS. Perkin–Elmer Model 881; glass column 2·1 m × 2 mm; stationary phase, 15% Carbowax 20M on Chromosorb W; temp. programme, 70–210° at 2°/min, with an initial hold of 5 min; flow rate (He), 30 ml/min. The gas chromatograph was linked to an AEI MS902 mass spectrometer, capillary line temp., 220°; carrier gas separator, 220°; ion source temp , 220°; electron energy, 70 eV, trap current, 100 μA.

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[10] LIKENS, S. T. and NICKERSON, G. B. (1964) *Am. Soc. Brewing Chem. Proc.* 5–13.

[11] DANIELS, N. W. R. (1967) *Column* (W. G. Pye, Gas Chromatography Bulletin) 2(1), 2.