^{1}H NMR (CDCl$_3$) δ1 57 (3H, *s*, Me-4), 2 75 (1H, *d*, *J* = 9 5 Hz, H-5), 3 81 (1H, *t*, *J* = 9 5, C-6), 5 55 (1H, *d*, *J* = 3 0 Hz, H-13), 6 20 (1H, *d*, *J* = 3 0 Hz, H-13), 6 70 (1H, *t*, *J* = 9 0 Hz, H-1) and 9 52 (1H, *s*, CHO), ^{13}C NMR (CDCl$_3$) Table 1, MS *m/z* 262 $[M]^+$ (< 1%) (Found C, 68 57, H, 7 02 $C_{15}H_{18}O_4$ (262) requires C, 68 68, H, 6 92)

Acetylation of melampomagnolide B (**2**) *to* **5** Compound **2** (60 mg) was stirred with 2 ml C_5H_5N–Ac_2O (1 1) for 24 hr Usual work-up provided **5** (69 mg) as colourless prisms from isopropyl ether, mp 143–144°, $[\alpha]_D$ −27° (CHCl$_3$, *c* 0 12), IR $\nu_{max}^{CHCl_3}$ cm^{-1} same pattern as for **2** with a band at 1727 (AcO), ^{1}H NMR (CDCl$_3$) same pattern as for **2** with a signal at δ2 05 (3H, *s*, AcO) and an AB system centred at δ4 52 (2H, *dd*, *J* = 12 5 Hz, –CH$_2$OAc), ^{13}C NMR (CDCl$_3$) Table 1, MS *m/z* 306 $[M]^+$ (< 1%) (Found C, 66 69, H, 7 27 $C_{17}H_{22}O_5$ (306) requires C, 66 65, H, 7 24%)

Oxidation of parthenolide (**4**) *to melampomagnolide B* (**2**) Compound **4** (248 mg), *tert*-BuOOH (0 50 ml of 70% soln in H$_2$O), SeO$_2$ (56 mg) were stirred in 10 ml of CH$_2$Cl$_2$ for 8 hr Flash chromatography [3] of the product on silica gel using EtOH–CHCl$_3$ (1 19) yielded 206 mg of **2** identical with the natural product (mp, mmp, IR and ^{1}H NMR), 7 mg of a product identical with **6** and 17 mg of unreacted **4**

Acknowledgements—The author would like to thank Mr M Hafez and Mr A Shehata, Department of Pharmacognosy, College of Pharmacy, King Saud University, for technical assistance

REFERENCES

1 El-Feraly, F S (1983) *Phytochemistry* **22**, 2239
2 Still, W C (1979) *J Am Chem Soc* **101**, 2493
3 Still, W C, Kahn, M and Mitra, A (1978) *J Org Chem* **43**, 2923
4 Haruna, M and Ito, K (1981) *J Chem Soc Chem Comm* 483
5 El-Feraly, F S and Chan, Y (1978) *J Pharm Sci* **67**, 347
6 El-Feraly, F S, Chan, Y, Capiton, G A, Doskotch, R W and Fairchild, E H (1979) *J Org Chem* **44**, 3952 and references therein
7 El-Feraly, F S, Benigni, D and McPhail, A (1983) *J Chem Soc Perkin Trans* 1, 355

Phytochemistry, Vol 23, No 10, pp 2374–2376, 1984
Printed in Great Britain

0031–9422/84 $3 00 + 0 00
© 1984 Pergamon Press Ltd

ESSENTIAL OILS OF SOME AMAZONIAN *MIKANIA* SPECIES

MIRIAM L DA SILVA, ARNALDO I R LUZ, MARIA G B ZOGHBI, LAMAR S RAMOS and JOSÉ G S MAIA

Departamento de Produtos Naturais, Instituto Nacional de Pesquisas da Amazônia, Conselho Nacional de Desenvolvimento Científico e Tecnológico, 69000, Manaus, Amazonas, Brazil

(*Revised received* 10 *February* 1984)

Key Word Index—*Mikania amara*, *M congesta*, *M banisteriae*, Compositae, essential oils, aliphatic alcohols, aldehydes and acids, monoterpenes, sesquiterpenes

Abstract—Terpenoid constituents were identified in the essential oils of *Mikania banisteriae* and *M congesta* *M amara* contains aliphatic alcohols, aldehydes and acids besides *p*-cymene and thymol

INTRODUCTION

Mikania banisteriae DC (called salsa branca) and *M congesta* DC grow wild in Peixe-Boi and Bujaru, State of Pará, while *M amara* Willd, known as 'cipó catinga', is distributed throughout Brazil and is esteemed for a number of medicinal properties, including use against fever, whooping cough and rheumatism [1] Flavonoids [2, 3], sesquiterpenoid lactones [4, 5], kaurenoid diterpenes [6] and triterpenoids [7, 8] have been reported from several species of *Mikania* Mono- and sesquiterpenes were identified in the essential oil of *M micrantha* [9] As part of an ongoing study of the essential oils of Amazonian plants, we have analysed the volatile components of *M amara*, *M banisteriae* and *M congesta* by GC/MS

RESULTS AND DISCUSSION

The essential oil of *M amara* exhibited a chemical composition quite different from that of *M banisteriae* and *M congesta* In these two latter species only mono- and sesquiterpenoids were found The monoterpene α-pinene (43 3%) is the major component in the oil of *M banisteriae* while limonene, β-cubebene, β-caryophyllene, germacrene B and an unidentified oxygenated sesquiterpene comprise 70% of the oil of *M congesta* The essential oil from *M amara* is dominated by the presence of dodecanal, 1-dodecanol and tetradecanal, in addition to a large number of other aliphatic alcohols, aldehydes and acids

Identification of most of the components was accomplished by comparison of both the mass spectrum and

Table 1 Constituents of the essential oils of *Mikania amara* (MG-59), *M banisteriae* (MG-25) and *M congesta* (MG-81)

Peak No	Compound	RR_t*	MG-59†	MG-25†	MG-81†
1	α-Pinene‡	0 416	—	43 25	2 14
2	Camphene‡	0 445	—	1 44	—
3	Sabinene‡	0 492	—	0 37	—
4	β-Pinene‡	0 495	—	0 58	2 08
5	Myrcene‡	0 525	—	1 58	0 18
6	α-Phellandrene‡	0 550	—	—	0 16
8	*p*-Cymene‡	0 588	0 18	1 41	0 92
9	Limonene‡	0 601	—	1 81	1 29
10	*Trans*-β-Ocimene‡	0 640	—	—	0 10
11	Benzyl-Formate	0 695	—	0 26	—
12	α-Terpinolene‡	0 718	—	0 37	—
13	Linalol‡	0 738	—	0 27	—
14	Nonanal‡	0 753	Trace	—	—
15	*Trans*-Pinocarveol	0 820	—	0 55	0 10
16	Borneol‡	0 880	—	0 97	—
17	4-Terpineol‡	0 903	—	0 37	—
18	α-Terpineol‡	0 930	—	1 54	—
19	Mirtenal	0 942	—	1 23	0 15
20	Decanal‡	0 961	Trace	—	—
21	Verbenone	0 968	—	0 44	—
22	*Trans*-Carveol	0 986	—	0 32	—
23	Decanol‡	1 091	Trace	—	—
24	Safrol‡	1 125	—	1 00	—
25	Thymol‡	1 134	1 10	—	—
26	Undecanal‡	1 164	1 50	—	—
27	δ-Elemene	1 219	—	—	0 22
28	α-Cubebene	1 243	—	1 36	0 76
29	Citronelyl acetate‡	1 250	—	0 86	—
30	1-Undecanol‡	1 287	2 40	—	—
31	α-Copaene	1 294	—	1 32	2 04
32	Geranyl acetate‡	1 309	—	0 80	—
33	β-Cubebene	1 323	—	2 79	19 50
34	Dodecanal	1 364	25 30	—	—
35	β-Caryophyllene‡	1 376	—	1 70	16 00
36	Germacrene B	1 405	—	—	12 86
37	α-Hummulene	1 436	—	0 31	3 16
38	Aromadendrene	1 450	—	0 57	1 68
39	1-Dodecanol	1 480	15 70	—	—
40	γ-Muurolene	1 482	—	—	0 74
41	Alloaromadendrene	1 520	—	1 58	0 84
42	Tridecanal	1 538	1 80	—	—
43	δ-Cadinene‡	1 560	—	4 10	1 25
44	Tridecanol	1 650	2 60	—	—
45	Dodecanoic acid	1 664	Trace	—	—
46	Tetradecanal	1 720	26 30	—	—
47	Guaiazulene‡	1 812	—	0 17	0 10
48	1-Tetradecanol	1 813	1 60	—	—
49	Pentadecanal	1 874	1 00	—	—
50	Tetradecanoic acid	1 961	1 77	—	—
51	Hexadecanal	2 032	3 70	—	—
52	1-Hexadecanol	2 120	Trace	—	—
53	Heptadecanal	2 717	Trace	—	—
54	Hexadecanoic acid	2 247	1 70	—	—
55	Octadecanal	2 319	0 40	—	—
56	1-Octadecanol	2 402	0 10	—	—

*R_t relative to Me pelargonate (IS)

† % Oil relative to quantitation report of the data system

‡Identity confirmed by MS and GC comparisons with authentic compounds

GC RR_ts with those of authentic standards Other identifications were made by comparison of mass spectra with those in the data system library and in the literature To analyse the oil from *M amara*, where standards were not available, but spectra resembled known components, identification was assigned according to a normal plot of carbon numbers vs R_t [10, 11]

EXPERIMENTAL

Plant material was collected in Ananindeua (*M amara*, MG-59), Peixe-Boi (*M banisteriae*, MG-25) and Bujaru (*M congesta*, MG-81), State of Pará, Brazil Voucher specimens (No 69,755, 69,739 and 72,093) are deposited in the Herbarium of Museu Emilio Goeldi, in Belém The samples were air dried, then subjected to steam distillation, according to usual techniques [12] The oils obtained were dried in the presence of anhydrous Na_2SO_4 and produced a yield of 0 1 % (MG-59), 0 1 % (MG-25) and 0 2 % (MG-81), respectively

The volatile oils were each analysed on a FID GC using a 30 m × 0 25 mm fused silica capillary column containing a 0 25 μm film of SE-54 H_2 was used as carrier gas, adjusted to a linear velocity of 33 cm/sec (measured at 150°), split flow was adjusted to give a 20 1 ratio and septum sweep was a constant 10 ml/min Splitless injection of 2 μl, of a 1 1000 *n*-hexane soln was followed by a delay of 30 sec before beginning purge Injection was done at 50° After 3 min initial delay, the temp was programmed at 6°/min at 230° GC/MS were obtained with a quadrupole instrument at 70 eV in the EI mode The GC was equipped with a Grob-type injector and He was used as carrier gas, with the same column and conditions as mentioned above except that the program was at 4°/min

Acknowledgements—This study was funded by the Banco de Amazônia S A (BASA) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) We thank Mrs Milton Lima and Milton Helio Lima, Departamento de Botânica, Museu Emílio Goeldi, Belém, for the collections, steam distillation and specimen identifications

REFERENCES

1 Pio Correa, M (1931) *Dicionário das Plantas Uteis do Brasil*, Vol 2, p 268, Imprensa Nacional, Rio de Janeiro

2 Muradian, J, Motidome, M, Ferreira, P C and Braz Filho, R (1977) *Rev Latinoam Quim* **8**, 88

3 Herz, W and Santhanam, P S (1969) *Tetrahedron Letters* **39**, 3419

4 Herz, W, Subramanian, P S, Santhanam, P S, Aota, K and Hall, A L (1970) *J Org Chem* **35**, 1453

5 Bohlmann, F, Natu Arvid, A and Mahanta, P (1978) *Phytochemistry* **17**, 483

6 Mathur, S B and Fermin, C H (1973) *Phytochemistry* **12**, 226

7 Herz, W, Santhanam, P S, Subramanian, P and Schmid, J J (1967) *Tetrahedron Letters* **32**, 3111

8 Kiang, A K (1965) *J Chem Soc* 6371

9 Nicollier, G and Thompson, A C (1981) *Phytochemistry* **20**, 2587

10 McNair, H M and Bonelli, E J (1969) *Basic Gas Chromatography* Varian Aerograph, California

11 Purnell, H (1962) *Gas Chromatography* Wiley, New York

12 Craveiro, A A, Matos, F J A and Alencar, J W (1976) *J Chem Ed* **53**, 652