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BISABOLONES AND OTHER CONSTITUENTS OF *MIKANIA SHUSHUNENSIS*

ALICIA B. GUTIERREZ and WERNER HERZ

Department of Chemistry, The Florida State University, Tallahassee, FL 32306, U.S.A.

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Key Word Index—*Mikania shushunensis*; Compositae; Eupatorieae; bisabolones; thymol derivative.

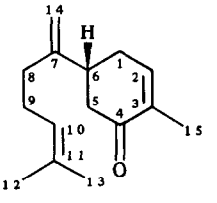
Abstract—Chemical investigation of the aerial parts of *Mikania shushunensis* furnished three new derivatives of cryptomerion as well as cryptomerion itself, a new thymol derivative, herniarin, 2,6-dimethoxyquinone, syringaldehyde and the corresponding alcohol.

INTRODUCTION

In continuation of our study of the chemistry of *Mikania* species [1], we have examined *M. shushunensis* Holmes & McDaniel, a newly described species from the province of Loreto, Peru [2]. Three new derivatives, **2a**, **3** and **4**, of cryptomerion (**1**) [3, 4] were isolated as well as (−)-cryptomerion itself, the new thymol derivative **5a**, herniarin (7-methoxycoumarin), 2,6-dimethoxyquinone, syringaldehyde and the corresponding benzyl alcohol.

RESULTS AND DISCUSSION

Structures of the new cryptomerion derivatives were deduced by comparing their ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) with those of cryptomerion and extensive decoupling; for comparison the previously reported ^{1}H NMR spectrum of **1** [5] is included in Table 1. For further characterization, **2a** was converted to a monoacetate **2b** while **3** resisted attempts at acetylation. The rotations of **2a, b**, **3** and **4** were all negative like those of (−)-cryptomerion itself and the CD curves were comparable, all substances exhibiting positive Cotton effects in the n, π^* and π, π^* region (see Experimental). This permits the conclusion that **2a, b**, **3** and **4** possess the same absolute configuration at C-6 as cryptomerion, i.e. 6*R* [4, 6]. Of further interest was the observation that in the ^{13}C NMR spectra of **3** and **4** (Table 2) many of the signals were duplicated. In the case of **3**, this could only be due to the existence of conformers in $CDCl_3$ solution not readily apparent from the ^{1}H NMR spectrum especially as the relative intensity of the signals changed with temperature; in the case of **4** this could likewise be ascribed to conformational equilibrium or alternatively to the presence of C-10 epimers. Compounds **2a** and **b** were hom-



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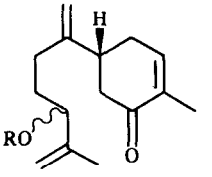

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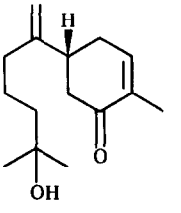
2b R = Ac



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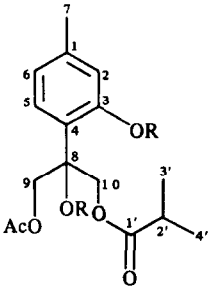

5a R = H
5b R = Ac

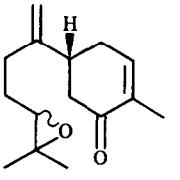

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Table 1. ^{1}H NMR spectra of compounds **1**, **2a**, **b**, **3** and **4** ($CDCl_3$, 270 MHz)

H	1	1*	2a	2b	3	4‡
1eq	2.47 *dddd* (18, 4.5, 4.5, 1.5)	1.86 *c*	2.46 *dddd*	2.46 *dddd*	2.47 *dddd*	2.50 *dddd*
1ax	2.23 *dddd* (18, 10.5, 2.5, 2.5)	1.86 *c*	2.26 *dddd*	2.23 *dddd*	2.27 *dddd*	2.24 *dddd*
2	6.76 *ddq* (5, 2.5, 1.5)	6.09 *m*	6.75 *ddq*	6.74 *ddq*	6.74 *ddq*	6.75 *ddq*
5eq	2.60 *ddd* (16, 4, 1.5)	2.54 *ddd* (15.5, 3.5, 1.5)	2.59 *ddd*	2.59 *ddd*	2.60 *ddd*	2.61, 2.59 *ddd*
5ax	2.35 *dd* (16, 13.5)	2.09 *dd* (15.5, 13)	2.35 *dd*	2.33 *dd*	2.35 *dd*	2.38, 2.36 *dd*
6	2,68 *br dddd* (13.5, 10, 4, 4)	2.35 *br dddd*	2.69 *br dddd*	2.66 *br dddd*	2.68 *br dddd*	2.70 *br dddd*
8	2.10 *c*	1.86 *c*	2.12 *br dt* (8, 7.5)	2.04 *br dt*	2.05 *br t* (6.5)	2.14, 2.10 *br dt* (6, 6)
9a	2.10 *c*	2.04*br t* (7)	1.71 (obsc.)	1.79 (obsc.)	2.05 *br t*	1.65, 1.60 *ddt* (6, 6, 2)
9b	2.10 *c*				1.49 (obsc.)	1.49, 1.43 *ddt* (10, 6, 5.5)
10a	5.10	5.12 *br tq* (7, 1.5)	4.07 *br t* (6.5)	5.17 *br t* (6.5)	obsc.	3.39 *dd* (10, 2)
10b	—	—	—	—	obsc.	—
12a	1.70 *br s*†	1.66 *br s*†	4.94 *q* (1)	4.95 *br s*	1.31 *s*†	1.21†
12b	—	—	4.85 *q* (1)	4.91 *br s*	—	—
13†	1.62 *br s*	1.52 *br s*	1.72 *br s*	1.72 *br s*	1.22 *s*	1.17 *s*
14a	4.86 *br s*	4.76 *br s*	4.86 *br s*	4.85 *br s*	4.85 *br s*	4.87 *br s*
14b	4.84 *br s*	4.66 *br s*	4.83 *br s*	4.85 *br s*	4.82 *br s*	4.85 *br s*
15†	1.80 *dt* (2.5, 1.5)	1.80 *br s*	1.78 *br s*	1.78 *br s*	1.78 *br s*	1.79 *br s*
OAc†	—	—	—	2.06 *s*	—	—

*Run in C_6D_6.
†Intensity three protons.
‡Mixture of two C-10 epimers or conformers.

Table 2. ^{13}C NMR spectra of compounds **1**, **2a**, **b**, **3** and **4** ($CDCl_3$, 67.89 MHz)

C	1	1*	2a	2b	3‡	4§
1	31.78 *t*	31.75 *t*	31.72 *t*†	31.70 *t*	31.75/31.58 *t*†	31.17 *t*
2	144.40 *d*†	143.11 *d*	144.54 *d*	144.24 *d*	144.43/144.29 *d*	144.85 *d*
3	150.86 *s*	151.14 *s*	150.68 *s*	150.07 *s*	150.81/149.59 *s*	150.74 *s*
4	198.64 *s*	197.71 *s*	199.73 *s*	199.38 *s*	199.62/199.41 *s*	199.99/199.93 *s*
5	43.56 *t*†	43.73 *t*†	43.47 *t*	43.52 *t*	43.54/43.37 *t*†	43.35/43.28 *t*
6	41.27 *d*	41.48 *d*	41.26 *d*	41.28 *d*	41.06/40.94 *d*†	41.03/41.23 *d*
7	135.47 *s*	135.53 *s*	135.47 *s*	135.56 *s*	135.46 *s*	135.26 *s*
8	34.33 *t*	34.49 *t*	30.13 *t*†	29.96 *t*†	34.76 *t*†	31.63/31.58 *t*
9	26.69 *t*	26.99 *t*†	33.29 *t*†	31.01 *t*†	22.70 *t*†	29.92/29.51 *t*†
10	123.75 *d*†	124.40 *d*	75.34 *d*†	76.84 *d*†	37.35 *t*	77.93 *d*
11	131.93 *s*	131.59 *s*	126.34 *s*	122.89 *s*	70.56/70.82 *s*	73.03 *s*
12	17.69 *q*†	17.69 *q*	111.15 *t*	113.03 *t*	29.30 *q*†	23.23 *q*
13	25.50 *q*†	25.71 *q*†	17.55 *q*†	18.05 *q*	29.83 *q*†	26.33 *q*†
14	109.18 *t*	109.16 *t*	109.27 *t*	109.55 *t*†	109.24/110.56 *t*†	109.29/109.18 *t*
15	15.58 *q*†	15.86 *q*†	15.53 *q*†	15.55 *q*	15.54 *q*†	15.46 *q*
–OAc	—	—	—	170.14 *s*	—	—
				21.09 *q*		

*Run in C_6D_6.
†Assignment by single frequency decoupling.
‡*Ca.* 7:3 ratio of two conformers, shifts for major constituent listed first.
§*Ca.* 2:1 ratio of two epimers or conformers; shifts for major constituent listed first.

Table 3. ^{1}H NMR spectra of compounds **5a**, **b** ($CDCl_3$, 270 MHz)

H	5a	5a*	5b
2	6.71 *br s*	6.84 *d* (1.5)	6.87 *br d* (1.5)
5	6,87 *d* (8)	6.77 *d* (8)	7.28 *d* (7.5)
6	6.65 *dd* (8, 1.5)	6.54 *dd* (8, 15)	7.06 *ddd* (8, 2, 1)
7‡	2.27 *br s*	2.19 *br s*	2.33*br s*
9a	4.48 *d* (11)	4.33 *d* (12)	4.85 *d* (11)
9b	4.43 *d* (11)	4.27 *d* (12)	4.71 *d* (11.5)
10	4.44 *s*	4.32 *s*	4.82 *d* (11), 4.77 *d* (11)
2′	2.56 *qq* (7, 7)	2.24 *qq* (7, 7)	2.52 *qq* (7)
3′‡	1.13 *d* (7)	0.95 *d* (7)	1.12 *d* (7)
4′‡		0.92 *d* (7)	1.12 *d* (7)
–OH	8.65 *br*†	8.78 *br s*	—
–OAc‡	2.07 *s*	1.53 *s*	2.36 *s*, 2.03 *s*, 1.99*s*

*Run in C_6D_6.
†Disappears on addition of D_2O.
‡Intensity three protons.

Table 4. ^{13}C NMR spectra of compounds **5a**, **b** ($CDCl_3$, 67.89 MHz)

C	5a	5b
1	140.16 *s*	140.01 *s*
2	118.71 *d*	124.89 *d*‡
3	156.63 *s*	147.89 *s*
4	118.97 *s*	125.99 *s*
5	126.34 *s*	126.90 *d*‡
6	120.54 *d*	127.58 *d*‡
7	20.67 *q**	21.26 *q**‡
8	78.52 *s*	80.91 *s*
9	67.35 *t*†	62.94 *t*†
10	67.47 *t*†	63.53 *t*†
1′	177.34 *s*	176.04 *s*
2′	33.96 *d*	33.96 *d*‡
3′	18.79 *q*	18.77 *q*‡
4′	18.79 *q*	18.82 *q*‡
–OAc	171.11 *s*	170.10 *s*, 170.10 *s*
	20.87*q**	170.10 *s*, 21.20 *q**‡
		20.82 *q*, 20.65 *q*

*†Assignments within the same column may be interchangeable.
‡Assignment by single frequency decoupling.

ogeneous by spectroscopic criteria but the absolute stereochemistry at C-10 remains unknown.

The structures of **5a** and its derived acetate were likewise deduced by comparison of their ^{1}H and ^{13}C NMR spectra (Tables 3 and 4) with those of similar compounds in the literature (for some examples see refs [7, 8]). Thymol derivatives of this type are relatively common in the Compositae and have previously been reported from the roots of *M. luetzelburgii* [9], *M. officinalis* [9], *M. purpurascens* [10], *M. goyazensis* [11] and *M. pohlii* [12] and from the aerial parts of *M. alvimii* [13].

While sesquiterpene dilactones of the mikanolide type appear to be characteristic secondary metabolites of the *Mikania scandens* complex [1, 14] and other *Mikania* species have furnished sesquiterpene lactones of a different type or specialize in the production of *ent*-labdanes and *ent*-kauranes [14], *M. shushunensis* so far appears to be *sui generis* in producing sesquiterpenes of the bisabolane class. Whether this possesses taxonomic significance must await the outcome of future studies of this large mainly tropical genus.

EXPERIMENTAL

Aerial parts of *M. shushunensis* Holmes & McDaniel (8.06 kg) collected by M. Rimachi in September 1980 on the trail to Rio Iquitos, carretera de Peña Negra *ca* 11 km from Quistros Cocha, Dpto. Iquitos, Maynas, Loreto, Peru and identified by Dr S. McDaniel (Vouchers MR. 5333 on deposit in herbaria of Institute of Botanical Exploration, Mississippi State, and Florida State University) were extracted with $CHCl_3$. Work-up in the usual fashion [15] gave 25 g of crude gum which was adsorbed on 35 g of silica gel (Merck, particle size 0.063–0.200 mm) and chromatographed over 250 g of the same adsorbent packed in *n*-hexane, 100 ml fractions being collected as follows: Frs 1,2 (hexane), 3–6 (hexane–Me_2CO 9:1), 7–10 (hexane–Me_2CO 4:1), 11–14 (hexane–Me_2CO 7:3), 15–18 (hexane–Me_2CO 3:2), 19–22 (hexane–Me_2CO 1:1), 23–28 (EtOH). Frs 1–12 (3.68 g) were combined and rechromatographed over silica gel. Elution with *n*-hexane–EtOAc (9:1) gave in fr. 39, 0.36 g of impure and in fr. 40, 41 1.78 g of pure (−)-cryptomerion [(−)(6*R*)-bisabol-2,7(14), 10-trien-4-one] (**1**) [3, 4].

Frs 13–17 of the original chromatogram on standing with Et_2O deposited solid material which on recrystallization from Et_2O–$CHCl_3$ afforded 1.08 g of herniarin, mp 114°, lit. mp 118° [16] IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3200, 1740, 1615, 1220; ^{1}H NMR ($CDCl_3$: δ6.24 *d* (9.5 Hz, H-3), 7.26 *d* (9.5 Hz, H-4), 7.35 *d* (8Hz, H-5), 6.85 *d* (8.2 Hz, H-6), 6.80 *s* (H-8), 3.88 *s* (−OMe); MS (EI) *m/z* (%). 176 (M^+, 100). The gummy material from the mother liquors of frs 13–17 was rechromatographed (silica gel, *n*-hexane and *n*-hexane–EtOAc mixtures, 200 ml fractions). Frs 12–15 from the rechromatogram (hexane–EtOAc 1:1) on standing deposited 0.235 g of herniarin; purification of the residue (1.5 g) by radial chromatography (4 mm and 1 mm, silica gel plates, CH_2Cl_2–Et_2O gradient, flow rate 8 ml/min and 3 ml/min respectively) followed by prep. TLC (CH_2Cl_2–Et_2O 9:2) furnished 44 mg of **5a**, 60 mg of **2**, 100 mg of a mixture of **2** and **3** and 180 mg of **3**.

Frs 18–22 of the original chromatogram on standing deposited a yellow solid which on recrystallization afforded 18 mg of

2,6-dimethoxybenzoquinone, mp 249–250°, identified by comparison with an authentic sample. Rechromatography of the mother liquors of frs 18–22 (silica gel, C_6H_6 and C_6H_6–Me_2CO mixtures, 10 ml fractions) gave an additional 20 mg of 2,6-dimethoxyquinone, 87 mg of 3,5-dimethoxy-4-hydroxybenzaldehyde (syringaldehyde), mp 107°, lit mp 111° [17], IR ν_{max}^{KBr} cm^{-1}: 3202, 1675, 1300, 1050; ^1H NMR ($CDCl_3$) δ9.8 *s* (–CHO), 7.16 *s* (H-2, 6), 6.03 *s* (–OH), 3.96 *s* (–OMe); MS (EI) *m/z* (rel. int.): 182 (100), and 215 mg of **4**.

Frs 23–26 of the original chromatogram on rechromatography (silica gel, C_6H_6 and C_6H_6–Me_2CO mixtures, 50 ml fractions) afforded from the fractions eluted with C_6H_6–Me_2CO (9:1) an additional 25 mg of 2,6-dimethoxybenzoquinone and from the fractions eluted with C_6H_6–Me_2CO (4:1) after prep. TLC (C_6H_6–Me_2CO 7:3, two developments) 15 mg of 3,5-dimethoxy-4-hydroxybenzyl alcohol; ^1H NMR: δ6.62 (H-2,6), 5.31 *s* (–OH), 4.61 *s* (–CH_2 O), 3.90 (–OMe), which on standing underwent air oxidation to syringaldehyde.

(−)-*Cryptomerion* (**1**). Colourless oil; $[\alpha]_D^{23}$ −40.21° ($CHCl_3$; *c* 1.89); CD curve (MeCN) $[\theta]_{317}$ +593, $[\theta]_{277}$ −1346 (sh), $[\theta]_{244}$ +5657°; $[\theta]_{230}$ 0 (last reading); IR ν_{max}^{KBr} (film) cm^{-1}: 1680, 1645, 1455, 910; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1666, 1430, 1200, 910; MS (EI) *m/z* (rel. int.): 218 $[M]^+$ (25), 203 (4.4), 175 (25.5), 161 (7.3), 149 (21), 148 (64.5), 135 (30), 122 (12), 121 (22.2), 109 (63), 69 (100), MS (CI) *m/z* (rel. int.): 219 (100), 201 (30), 175 (13.4), 148 (10.5), 135 (7), 109 (35); ^1H and ^{13}C NMR spectra in Tables 1 and 2.

(−)-(6R)-10-*Hydroxybisabol*-2,7(14),11-*trien*-4-*one* (**2a**). Colourless oil; $[\alpha]_D^{25}$ −16.19° ($CHCl_3$; *c* 0.49); CD curve (MeCN) $[\theta]_{317}$ +437, $[\theta]_{284}$ 197 (sh), $[\theta]_{269}$ 0, $[\theta]_{247}$ +2172, $[\theta]_{233}$ 0 (last reading); IR ν_{max}^{KBr} (film) cm^{-1}: 3430, 1665, 1450, 1230, 905; MS (EI, 15 eV) *m/z* (rel. int.): 234 $[M]^+$ (3.1), 217 (4.5), 216 (3.0), 209 (13), 164 (9), 148 (31.8), 135 (14.3), 125 (27.4), 111 (14), 110 (100), 109 (71), 85 (8.3), 71 (17.1); ^1H and ^{13}C NMR spectra in Tables 1 and 2.

Acetylation of **2a** (Ac_2O–pyridine) and prep. TLC furnished the acetate **2b**, $[\alpha]_D^{24}$ −22.70 ($CHCl_3$; *c* 0.28); CD curve (MeCN) $[\theta]_{317}$ +234, $[\theta]_{387}$ 0, $[\theta]_{246}$ 1037, $[\theta]_{236}$ 0 (last reading) IR ν_{max}^{KBr} (film) cm^{-1}: 1735, 1670, 1435, 1240, 910; MS (EI, 20 eV) *m/z* (rel. int.): 276 $[M]^+$ (4.3), 234 (26.0), 217 (19), 216 (95.8), 201 (33.9), 188 (41.4), 173 (61), 159 (41.4), 148 (85), 134 (43.3), 119 (14.7), 109 (100), 82 (13.3), 69 (4.4); ^1H and ^{13}C NMR spectra in Tables 1 and 2.

(−)-(6R)-11-*Hydroxybisabol*-2,7(14)-*dien*-4-*one* (**3**). Colourless oil; $[\alpha]_D^{24}$ −13.23° ($CHCl_3$; *c* 1.80); CD curve (MeCN) $[\theta]_{317}$ +258, $[\theta]_{284}$ +315 (sh), $[\theta]_{247}$ +2646, $[\theta]_{232}$ 0 (last reading); IR ν_{max}^{KBr} (film) cm^{-1}: 3450, 1735, 1665, 1450, 910; MS (EI, 25 eV) *m/z* (rel. int.): 236 $[M]^+$ (0.3), 219 (11.9), 218 (4.8), 174 (6.9), 163 (7.4), 161 (27.8), 149 (16.5), 135 (44.8), 110 (11), 109 (75), 104 (39.3), 93 (35.4), 82 (77), 69 (39), 59 (100); ^1H and ^{13}C NMR in Tables 1 and 2. Attempted acetylation resulted in recovery of starting material.

(−)-(6R)-10,11-*Epoxybisabol*-2,7(14)-*dien*-4-*one* (**4**). Colourless oil; $[\alpha]_D^{23}$ −18.86 ($CHCl_3$; *c* 2.11); CD curve (MeCN) $[\theta]_{310}$ +632, $[\theta]_{287}$ +816 (sh), $[\theta]_{247}$ +2550, $[\theta]_{236}$ 0 (last reading); IR ν_{max}^{KBr} (film) cm^{-1}: 1665, 1450, 1080, 910; MS (EI) *m/z* (rel. int.): 234 $[M]^+$ (5.7), 191 (1), 175 (6.7), 161 (17.0), 148 (47.7), 136 (15.4), 136 (100), 121 (22.7), 109 (67.9), 59 (58); MS (CI) *m/z* (rel. int.): 235 (100), 217 (27.3), 197 (18.3), 153 (26.9), 135 (27.7), 131 (15.6); ^1H and ^{13}C NMR in Tables 1 and 2.

9-*Acetoxy*-8-*hydroxy*-10-*isobutyryloxythymol* (**5a**). Colourless oil; MS (EI) *m/z* (rel. int.): 310 $[M]^+$ (54.9), 292 (18.2), 251 (7.5), 238 (10), 237 (68.8), 219 (5.3), 209 (100), 191 (5.8), 167 (44.8), 162 (27.9), 149 (27.3), 71 (49.5). MS (CI) *m/z* (rel. int.): 311 $[M+1]^+$ (1.7), 293 (30.3), 235 (23.7), 217 (100), 203 (32.7), 199 (45), 181 (29.7), 169 (76.4), 165 (89.5), 151 (32.1), 121 (43.7); ^1H and ^{13}C NMR spectra in Tables 3 and 4.

Acetylation (Ac_2O–pyridine) and chromatography (silica gel, CH_2Cl_2) furnished the diacetate **5b**, IR ν_{max}^{KBr} (film) cm^{-1}: 1760, 1740 (broad); MS (EI) *m/z* (rel. int.): 394 (0.8), 292 (11.3), 237 (10), 232 (6.7), 219 (23.4), 209 (16.7), 204 (31.3), 192 (8.9), 191 (34.4), 167 (19.5), 163 (16.2), 162 (90.1), 161 (8.4), 150 (25.3), 149 (100), 146 (12.3); 145 (73.5), 135 (30.5), 133 (11.3), 121 (14.9), 105 (21.4), 71 (35.9); MS (CI) *m/z* (rel. int.): 395 $[M+1]^+$ (0.6), 349 (20.5), 335 (100), 307 (21), 292 (33.8), 219 (11.0), 204 (17.4), 190 (12.7), 162 (23.9), 149 (24.6), 146 (12.4), 145 (65.7), 135 (6.2); ^1H and ^{13}C NMR spectra in Tables 3 and 4.

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Note added in proof: After acceptance of this article we discovered that compound **5a** had been isolated previously from *Arnica sachalinensis* [Willuhn, G., Junior, I. and Wendisch, D. (1986) *Planta Med.* 349] and *Calea nelsonii* [Martinez, M., Sanchez., V. H. and Joseph-Nathan, P. (1987) *Phytochemistry* **26**, 2577].