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HERMOSILLOL, AN 8,3'-NEOLIGNAN FROM *KRAMERIA SONORAE**

XORGE A. DOMINGUEZ, CARLOS ROMBOLD†, JULIA VERDE STAR, HANS ACHENBACH‡ and JOHANN GROß‡

Departamento de Quimica, Instituto Tecnologico y de Estudios Superiores de Monterrey, Monterrey, NL 64849, Mexico; †CIDESON, Hermosillo, Sonora Mexico; ‡Institute of Pharmacy and Food Chemistry, Department of Pharmaceutical Chemistry, Universität Erlangen, D-8520 Erlangen, F.R.G.

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Key Word Index—*Krameria sonorae*; Krameriaceae; hermosillol; 8.3'-neolignan.

Abstract—The aerial parts of *Krameria sonorae* afforded seven known neolignans and nor-neolignans, and as a major component, a new 8,3'-neolignan which was named hermosillol.

INTRODUCTION

Krameria species occur in arid areas of tropic and subtropic America [2–4]. Plants of the genus *Krameria* were originally considered to be part of the Leguminosae but later were established as an individual botanical family [5]. In the course of our investigations on the non-polar constituents of *Krameria* species we have studied *K. sonorae* Britt. [3] plants collected in Northern Mexico.

RESULTS AND DISCUSSION

The aerial parts of *K. sonorae* afforded seven known compounds (1–7) [1, 6–9] and, as a major component, the new compound **8**.

The ^{1}H NMR spectrum of **8** contains signals which are attributable to two phenyl systems, one of which is *p*-hydroxy substituted, the other methoxy and propenyl substituted. In addition, it exhibits signals of an ABX_2-system at δ 5.01 (1H, *m*), 5.09 (1H, *m*) and 3.69 [2H, *s* (*br*)]. Irradiation at δ3.69 transforms both multiplets into doublets (J = 2.0 Hz) thus establishing the presence of partial structure **a**.

Location of the hydroxyl group at ring A is proved by the MS of **8** and its hydrogenation product **9**, which both show characteristic fragments at *m/z* 107 (after H/D-exchange: *m/z* 107 → 108) and, in the case of **9**, a base peak at *m/z* 177 (no shift on H/D-exchange).

Ring B according to the ^{1}H NMR data is 1,2,5-substituted. The positions of the individual substituents are given by (i) increment calculations using ^{13}C NMR data (see Table 1) and (ii) the effect caused by the OCH_3-substituent on the ^{13}C-resonance of C-8 in **9**. By comparison with the data published for aurein [10, 11] this shift was found to be $\Delta\delta_{C\text{-}8} = -7.5$ ppm.

Although neolignans with a 1,2-diphenyl-propane (= lancifolin type) skeleton are found in nature [12, 13], hermosillol (**8**) is the first compound of the hitherto unknown 1,2-diphenyl-2-propene type.

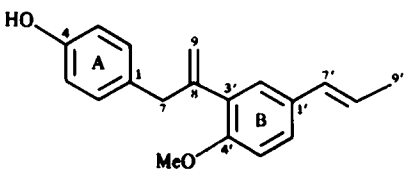
EXPERIMENTAL

Plant material. Plants were collected around Hermosillo, Sonora (Mexico) in November 1985; a voucher specimen is kept at our herbarium (Reg. No. 8032) in Monterrey.

Extraction and chromatography. Aerial parts (370 g) were extracted successively with hexane and MeOH to yield 2.2 g hexane extract and 16.0 g MeOH extract. The hexane extract was repeatedly chromatographed on silica gel (Macherey-Nagel 815338) using: cyclohexane–EtOAc, $CHCl_3$–MeOH and CH_2Cl_2 (at 7°). This yielded compounds **1–8**.

General procedures. TLC: Nano plates Sil-20 UV (Macherey-Nagel), solvent systems: S-1 = cyclohexane–EtOAc (17:1), S-2 = $CHCl_3$, detection by UV and anisaldehyde reagent [14] followed by heating; IR: $CHCl_3$; UV: MeOH, unless stated otherwise; ^{1}H NMR: 90 and 400 MHz, $CDCl_3$; ^{13}C NMR: 22.5 MHz, $CDCl_3$, int. reference TMS; MS: 70 eV.

Identifications of compounds **1** to **7** were based on comparisons with authentic substances obtained from *K. cystisoides* according to [1].



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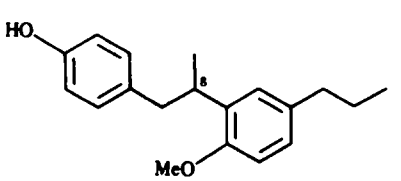

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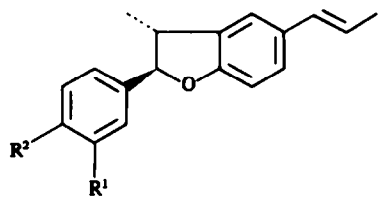
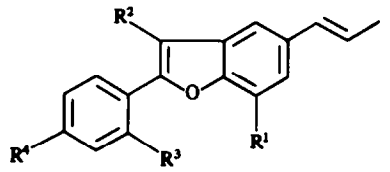
* Part 2 in the series 'Studies on Krameriaceae'. For part 1 see ref. [1].

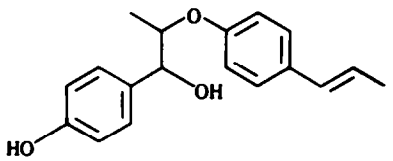


	R^1	R^2	
1	H	OH	(= conocarpan)
2	OMe		

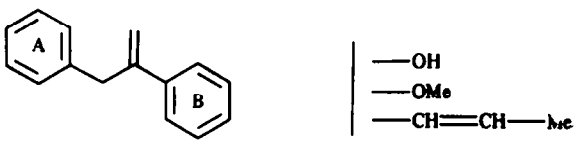
(Absolute configuration)



	R^1	R^2	R^3	R^4	
3	H	Me	H	OH	(= eupomatenoid 6)
4	OMe	Me	H	OH	(= eupomatenoid 13)
5	H	H	OH	OMe	(= ratanhiaphenol I)
6	H	H	OH	OH	



(Relative configuration) **7**



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Hermosillol (**8**) (4-[2-(2-Methoxy-5-(*E*)-propenyl)-phenyl]allylphenol. Oil (73 mg); TLC (S-1): R_f 0.28, violet with anisaldehyde; IR ν_{max} cm^{-1}: 3590 (OH), 2930, 2855, 2840, 1600; UV λ_{max} (log ε): 226(4.51), 262(4.49), 270(4.47, sh), 287(4.09, sh), 297(3.94); + NaOH: 220–262 (4.52, plateau), 272(4.47, sh), 295(4.38); ^{1}H NMR (400 MHz): δ1.83 (3H, *d* (*br*), J = 5 Hz, CH_3–9'), 3.69 (2H, *s* (*br*), CH_2-7), 3.82 (3H, *s*, MeO), 4.70 (1H, *s*, (*br*), OH), 5.01 (1H, *m*, H_A-9), 5.09 (1H, *m*, H_B-9), 6.06 (1H, *dq*, J_1 = 16, J_2 = 5 Hz, H-8'), 6.31 (1H, *d* (*br*), J = 16 Hz, H-7'), 6.71 (2H, AA'BB', J = 8.5 Hz, H-3, H-5), 6.78 (1H, *d*, J = 8.5 Hz, H-5'), 7.03 (2H, AA'BB', J = 8.5 Hz, H-2, H-6), 7.05 (1H, *s* (*br*), H-2'), 7.18 (1H, *dd*, J_1 = 8.5, J_2 = 2 Hz, H-6'); ^{13}C NMR: see Table 1; MS *m/z* (rel. int.): 280 (100) $[M]^+$, 145 (9), 132 (10), 131 (9), 129 (5), 128 (9), 117 (5), 115 (9), 107 (16), 91 (5), 77 (8), 43 (10).

Hydrogenation of **8**. 16.5 mg compound **8** were hydrogenated at 14° on PtO_2 in MeOH soln. CC (2 g silica gel; S-2) yielded 16.1 mg **9** as a colourless oil. TLC (S-1): R_f 0.41, violet with anisaldehyde; IR ν_{max} cm^{-1}: 3590 (OH), 2960, 2935, 2875, 2840, 1610, 1595; UV λ_{max} (log ε): 226 (4.23), 278 (3.65), 283 (3.60); + NaOH: 230 (4.19, sh), 244 (3.99, sh), 278 (3.65), 283 (3.67), 300 (3.35 s); ^{1}H NMR: δ0.92 (3H, *t* (*br*), J = 7.5 Hz, CH_3-9'), 1.15 (3H, *d*, J = 7.0 Hz, CH_3-9), 1.40–1.80 (2H, *m*, CH_2-8'), 2.52 (2H, *t* (*br*), J = 8 Hz, CH_2-7'), 2.70–3.00 (2H, *m*, CH_2-7), 3.19–3.58 (1H, *m*, H-8), 3.75 (3H, *s*, MeO), 4.71 (1H, *s* (*br*), OH), 6.62–6.77 (3H, *m*), 6.89–7.03 (4H, *m*); ^{13}C NMR: see Table 1; MS *m/z* (rel. int.): 284 (11) $[M]^+$, 178 (16), 177 (100), 133 (8), 107 (7).

Acetylation of **8**. 16.4 mg compound **8** were acetylated using Ac_2O–C_5H_5N. CC (3 g silica gel, S-1) yielded 16 mg of **10** as a colourless oil. TLC (S-1): R_f 0.39, violet with anisaldehyde; IR ν_{max} cm^{-1}: 2960, 2940, 2920, 2860, 2840, 1750, (C=O), 1630, 1600; UV λ_{max} (log ε): 220 (4.48), 262 (4.45), 295 (3.94 s); ^{1}H NMR: δ1.82 (3H, *d* (*br*), J = 5 Hz, CH_3-9'), 2.25 (3H, *s*), 3.75 (2H, *s* (*br*), CH_2-7), 3.80 (3H, *s*, MeO), 5.04 (1H, *m*, H_A-9), 5.10 (1H, *m*, H_B-9), 6.05 (1H, *dq*, J_1 = 16, J_2 = 5 Hz, H-8'), 6.31 (1H, *d* (*br*), J = 16 Hz, H-7'), 6.71–7.23 (7H); ^{13}C NMR: see Table 1; MS *m/z* (rel. int.): 322 (91) $[M]^+$, 281 (27), 280 (100), 173 (11), 148 (7), 145 (14), 132 (6), 131 (11), 129 (11), 128 (18), 115 (16), 107 (23), 91 (10), 77, (9), 43 (51).

Table 1. ^{13}C NMR data for hermosillol (**8**), tetrahydrohermosillol (**9**) and hermosillol acetate (**10**)

C	8	9	10
1	132.05[a]	135.13[a]	137.51
2	130.26	130.28	130.04
3	115.01	114.84	121.04
4	153.60	153.55	149.02[a]
5	115.01	114.84	121.04
6	130.26	130.28	130.04
7	41.82	42.76	42.11
8	148.56	34.37	148.05[a]
9	115.46	19.47	115.98
1'	130.32[b]	133.80[a]	130.36[b]
2'	130.65[b]	127.16[b]	130.77[b]
3'	125.70[c]	134.67[a]	125.89[c]
4'	155.59	155.17	155.72
5'	111.04	110.73	111.02
6'	127.66[c]	126.35[b]	127.68[c]
7'	131.98[a]	37.48	131.85
8'	123.56	24.75	123.64
9'	18.21	13.75	18.22
CH_3O	55.61	55.66	55.60
C=O			169.23
CH_3			21.01

a, *b* and *c* might be interchanged.

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