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NEOLIGNANS, *NOR*-NEOLIGNANS AND OTHER COMPOUNDS FROM ROOTS OF *KRAMERIA GRAYI**

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Key Word Index—*Krameria grayi*; Krameriaceae; roots; neolignans; *nor*-neolignans; 2-(4-methoxyphenyl)-5-((*E*)-1-propenyl)benzofuran.

Abstract—From the roots of *Krameria grayi*, a new *nor*-neolignan was isolated, besides 14 known lignan-type and three cycloartane-type compounds.

INTRODUCTION

Recently we reported on the constituents isolated from a hexane extract of the aerial parts of the Mexican *Krameria grayi* [2]. We have now started a phytochemical investigation of the roots of this species, which are used by Shoshoni Indians to prepare a wash against eye infections [3].

RESULTS AND DISCUSSION

Chromatographic separation of a dichloromethane extract of the roots from *K. grayi* yielded the hitherto unknown *nor*-neolignan **1** and the known constituents **2**–**18** [4–10]. The structures were determined by spectroscopic methods and/or by comparison with authentic substances.

The ^{1}H NMR spectrum of **1** exhibited a close similarity to that of **3** [4]. However, the singlet for the methyl substituent at C-3 was missing and an additional doublet (1H, J = 1 Hz) at δ7.10 revealed that **1** was the corresponding *nor*-neolignan with a hydrogen at C-3 [5]. Consequently, **1** was prepared by methylation of **19**, which has recently been isolated from *K. ixina* [4].

Compound **15** was isolated from *K. lanceolata* for the first time and a low $[\alpha]_D$ value had been registered [7]. However, the substance from *K. grayi* was found to be a racemate by ^{1}H NMR studies with the chiral shift reagent Eu(TFC)$_3$ [11], which revealed a significant doubling of the signal pattern for one of the protons at C-7. Since **15** contains the structural features of a benzyl alcohol, the racemate might occur due to facile proton-catalysed epimerization at the alcohol group.

Considering the isolated constituents, it seems of chemotaxonomic interest that ratanhiaphenol I (**5**) now has been isolated from *K. grayi* also, thus showing that **5** obviously represents a chemotaxonomic marker for plants of the Krameriaceae family. This *nor*-neolignan has always been isolated as a major constituent from all the *Krameria* species examined up to now [1, 4–8, 12–14], but, according to our knowledge, **5** has not yet been detected in any other plant family.

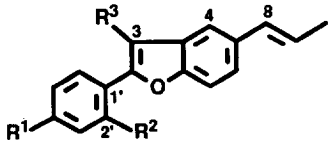
Compounds **2**, **9** and **14** are also major components of the root extract of *K. grayi*, while the other compounds have to be regarded minor or very minor constituents.

EXPERIMENTAL

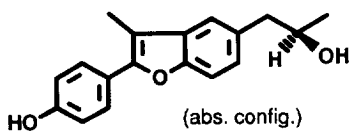
General. TLC was performed on silica gel with detection by UV or anisaldehyde [15] followed by heating. IR spectra were recorded in $CHCl_3$ solns. UV spectra were measured in MeOH. ^{1}H NMR spectra were recorded in Me_2CO-d_6 and $CDCl_3$, respectively; int. standard TMS. Eu(TFC)$_3$ was used for shift measurements of **15** [11]. MS were run at 70 eV using a direct inlet system. Identification of **2**–**16** was based on comparison with authentic substances [1, 4–8]. Compounds **17** and **18** were identified from their physicochemical properties [9, 10].

Plant material. Roots of *K. grayi* Rose & Painter were collected in November 1990 in San Joaquin de los Azufres, Mina, N. L. (Mexico). Identification was made by Prof. Humberto Sánchez V. and a voucher specimen is

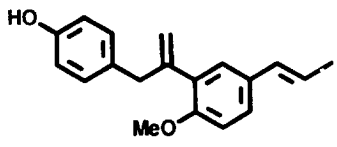
*Part 10 in the series "Studies on Krameriaceae". For Part 9 see ref. [1].



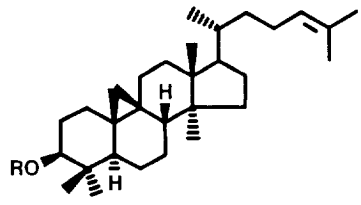
	R^1	R^2	R^3	Ref.
1	OMe	H	H	
2	OH	H	Me	[5]
3	OMe	H	Me	[4]
4	OH	OH	H	[5]
5	OMe	OH	H	[5]
6	OMe	OMe	H	[6]
19	OH	H	H	[4]



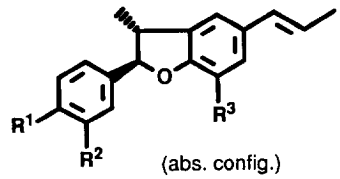
13 [1]



14 [14]

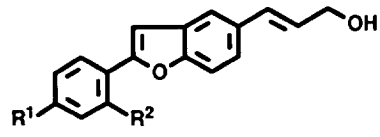


	R	Ref.
16	OH	[8]
17	Feruloyl	[9]

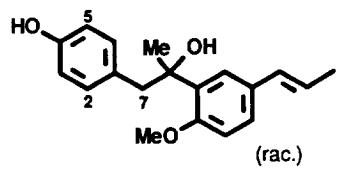


(abs. config.)

	R^1	R^2	R^3	Ref.
7	OMe	H	H	[4]
8	OH	H	OMe	[5]
9	OH	OMe	H	[5]
10	OH	OMe	OMe	[5]

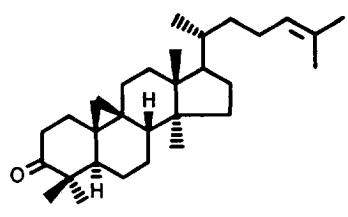


	R^1	R^2	Ref.
11	OMe	OH	[1]
12	OH	OMe	[1]



(rac.)

15 [7]



18 [10]

kept at the ITESM herbarium (Reg. ITESM No. 8746) in Monterrey, N. L. (Mexico).

Extraction and chromatography. Dried roots (222 g) were extracted exhaustively with CH_2Cl_2 to yield 3.8 g extract, which was first passed over Fractogel TSK HW-40 (s) (Merck) using MeOH–$CHCl_3$ (7:3). Frs were repeatedly chromatographed on silica gel using $CHCl_3$–MeOH and cyclohexane–EtOAc mixts and on Fractogel PVA 500 (Merck) using MeOH–$CHCl_3$ (7:3).

2-(4-*Methoxyphenyl*)-5-((E)-1-*propenyl*)*benzofuran* (**1**). Amorphous (1 mg). TLC: R_f 0.42 (cyclohexane–EtOAc, 4:1); anisaldehyde reagent: grey. IR ν_{max} cm^{-1}: 2916, 1615, 1508. UV λ_{max} nm (log ε): 224 (4.26), 256 (4.33), 272 (sh, 4.27), 291 (4.31), 304 (4.29), 318 (4.22), 325 (sh, 4.19), 333 (sh, 4.10). ^{1}H NMR (Me_2CO-d_6): δ1.87 (3H, *dd*, $J_1 = 6$, $J_2 = 1.5$ Hz, Me-10), 3.85 (3H, *s*, OMe), 6.26 (1H, *dq*, $J_1 = 16$, $J_2 = 6$ Hz, H-9), 6.52 (1H, *dm*, $J = 16$ Hz, H-8), 7.06 (2H, AA′ BB′-system, H-3′, H-5′), 7.10 (1H, *d*, $J = 1$ Hz, H-3), 7.33 (1H, *dd*, $J_1 = 8$, $J_2 = 1.5$ Hz, H-6), 7.45 (1H, *br d*, $J = 8$ Hz, H-7), 7.56 (1H, *d*, $J = 1.5$ Hz, H-4), 7.86 (2H, AA′ BB′-system, H-2′, H-6′). MS *m/z* (rel. int.): 264.1151 (100, $[M]^+$, calcd for $C_{18}H_{16}O_2$: 264.1150), 249 (32), 235 (7), 178 (8), 165 (8) 135 (10).

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