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TWO NEW OXAZOLES FROM AMYRIS TEXANA P. WILSON

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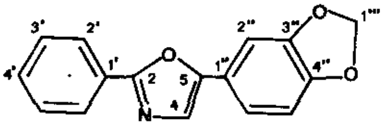
Abstract - From the roots of Amyris texana P. Wilson, two new oxazoles, texamine (1) and texaline (2) were isolated together with O-isopentenylhalfordinol (3). The structures of the new compounds were established by spectroscopic methods, including long-range HETCOR 2-D nmr.

Oxazole alkaloids are rare naturally-occurring compounds, and those found in flowering plants such as the genera Lolium,[1] Amyris,[2-4] Aeglopsis,[5] Aegle,[6-7] and Halfordia[8,9] are structurally simple substances bearing substituents at the 2 and 5 positions of the ring.

During our study of the chemical constituents of the roots of Amyris texana P. Wilson, we have isolated two new 2,5-diaryloxazoles, texamine (1) and texaline (2), together with O-isopentenylhalfordinol (3).



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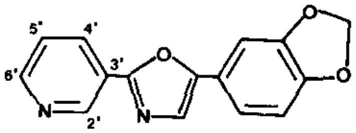

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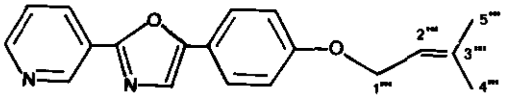

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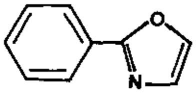

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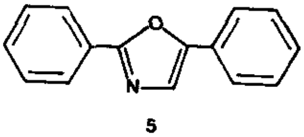

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Texanine (1) had mp 134-137°C, crystallized from ethyl acetate-hexane. Its elemental composition $C_{16}H_{11}NO_3$ was established by high-resolution mass measurement; M^+, m/z 265.0748, Δ-1.0 mmu. Ir (KBr), 1600, 1585, 1543, 1495, 1480, and 1445 (aromatic), 1240 and 928 cm^{-1} (ether). The uv (MeOH) spectrum gave maxima at 215, 253, and 324 nm (log ε 4.53, 4.39, and 4.63, respectively), characteristic of a 2,5-diaryloxazole.[10] The typical cleavages of 2,5-diaryloxazoles[11] were also observed in its ms, giving ions at m/z, 265 (100%) M^+, 251 (12%), 237 (19%) M^+-CO, 236 (6%) $|M^+-CO|-H$, 210 (9%) $|M^+-CO|-HCN$, 209 (10%) $|M^+-CO|-HCN|-H$, 180 (36%), 152 (62%), 121 (11%), 105 (21%), and 77 (33%).

The ^1H-nmr spectrum (200 MHz, $CDCl_3$) of texanine (1) exhibited signals at δ 5.96 (2H, s, O_2CH_2), 6.84 (1H, d, J = 8 Hz, H-5"), 7.13 (1H, d, J = 1.6 Hz, H-2"), 7.19 (1H, dd, J_1 = 8 Hz, J_2 = 1.6 Hz, H-6"), 7.27 (1H, s, H-4), 7.44 (3H, m, 2H-3' and H-4'), and 8.05 (2H, m, 2H-2').

Texaline (2), $C_{15}H_{10}N_2O_3$ (M^+, m/z 266.0699, Δ-0.8 mmu), had mp 171-174°C, crystallized from ethyl acetate-hexane. Ir (KBr), 1608, 1580, 1568, 1485 (br), 1445, and 1427 (aromatic), 1230 and 928 cm^{-1} (ether). The uv (MeOH) spectrum provided maxima at 202 (log ε 4.64), 221 (sh), 257 (4.24), and 331 nm (4.50), and a bathochromic shift to 264 and 348 nm was produced after acid addition.[3] Its ms presented ions at m/z, 266 (100%), M^+, 252 (12%), 238 (19%) M^+-CO, 211 (14%) $|M^+-CO|-HCN$, 210 (9%) $|M^+-CO|-HCN|-H$, 181 (27%), 153 (55%), 133 (25%), 121 (13%), 106 (12%), and 78 (17%).

The ^1H-nmr spectrum (200 MHz, $CDCl_3$) of texaline (2) gave signals at δ 6.00 (2H, s, O_2CH_2), 6.87 (1H, d, J = 8 Hz, H-5"), 7.14 (1H, d, J = 1.6 Hz, H-2"), 7.21 (1H, dd, J_1 = 8 Hz, J_2 = 1.6 Hz, H-6"), 7.32 (1H, s, H-4), 7.39 (1H, dd, J_1 = 7.9 Hz, J_2 = 4.9 Hz, H-5'), 8.31 (1H, dt, J_1 = 8.1 Hz, J_2 = 1.9 Hz, H-4'), 8.67 (1H, br d, J = 4.8 Hz, H-6'), and 9.30 (1H, br s, H-2').

The oxazole O-isopentenylhalfordinol (3), mp 118-119°C, was identified by comparison of its spectral data (ir, uv, ms, and ^1H-nmr) with those reported in the literature.[5,6] Unambiguous proof of the structures of texanine (1) and texaline (2) was provided by their BBD and DEPT ^{13}C-nmr spectra (Table 1), and the connectivities observed in long-range HETCOR 2-D nmr experiments (Table 2). The assignments given in Table 1 were also made taking into account the spectral data of 2,5-diphenyloxazole (5), 2-phenyloxazole (4),[12] and 3-methyl-2-buten-1-ol.[13]

Table 1. ^{13}C-Nmr chemical shifts and assignments for texanine (1), 2,5-diphenyloxazole (5), 2-phenyloxazole (4), texaline (2), and O-isopentenylhalfordinol (3).

C	1	5	4	2	3	C	1	5	4	2	3
2	160.8	161.3	162.2	158.4	159.6	2"	105.0	124.4		105.1	126.0
4	122.5	123.6	128.6	122.7	122.3	3"	148.4	129.0		148.4	115.4
5	151.3	151.4	139.1	152.2	152.4	4"	148.4	128.5		148.5	158.3
1'	127.7	127.6	127.7			5"	108.9			109.1	
2'	126.3	126.4	126.6	147.6	147.6	6"	118.4			118.4	
3'	128.9	129.1	129.0	124.0	124.0	1"'	101.5			101.7	65.1
4'	130.3	130.5	130.6	133.5	133.3	2"'					119.5
5'				123.8	123.7	3"'					138.6
6'				150.9	150.8	4"'					18.4
1"	122.4	128.2		121.9	120.5	5"'					25.9

Chemical shifts in ppm downfield from TMS. Solvent deuterochloroform.

Table 2. ^{13}C-^{1}H long-range connectivities in texanine (1) and texaline (2).

(1) C	δ	H	(2) C	δ	H
2	160.8	H-4	2	158.4	H-4
4	122.5	H-4	4	122.7	H-4
5	151.3	H-2", H-6"	5	152.2	H-4, H-2", H-6"
1'	127.7	H-3'	2'	147.6	---
2'	126.3	H-2', H-4'	3'	124.0	H-5'
3'	128.9	H-3'	4'	133.5	H-4'
4'	130.3	H-2'	5'	123.8	H-5'
1"	122.4	H-4, H-5"	6'	150.9	---
2"	105.0	H-2", H-6"	1"	121.9	H-5"
3"	148.4	H-2", H-5", H-6", H-1"	2"	105.1	H-6", H-2"
4"	148.4		3"	148.4	H-5", H-1"'
5"	108.9	H-5"	4"	148.5	H-5", H-1"'
6"	118.4	H-2", H-6"	5"	109.1	H-5"
1"'	101.5	H-1"'	6"	118.4	H-2", H-6"
			1"'	101.7	H-1"'

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