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MIXTECACIN, A PRENYLATED FLAVANONE AND OAXACACIN ITS CHALCONE FROM THE ROOTS OF *TEPHROSIA WOODII*

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Key Word Index—*Tephrosia woodii*; Leguminosae; prenylated flavanone; mixtecacin; chalcone; oaxacacin.

Abstract—From the roots of *Tephrosia woodii*, a new Mexican *Tephrosia* species, a new prenylated flavanone, oaxacacin, and its chalcone, mixtecacin, have been isolated and their structures elucidated from their chemical properties and spectral data.

INTRODUCTION

Recently, Tellez [1] found and identified *Tephrosia woodii* T., a new species, in the Mexican state of Oaxaca. *Tephrosia* species have been found to contain rotenoids and prenylated flavones [2], flavonols [3], isoflavones [4], flavanones [5] and chalcones [6]. The chemotaxonomical importance of flavonoid constituents in the genus has been pointed [7]. The results of the present chemical study of *T. woodii* follow the expected chemotaxonomical pattern for the genus.

RESULTS AND DISCUSSION

A hexane extract of the roots of *T. woodii* afforded, after 'flash' liquid chromatography, two flavonoids, mixtecacin (**1**) and oaxacacin (**2**). Elemental analysis and M^+ at *m/z* 336.1361 led to the molecular formula $C_{21}H_{20}O_4$ for **1**. It gave a negative ferric chloride test, a positive Shinoda test and a deep yellow color with ammonia vapor. The NMR spectrum of **1** showed the presence of one methoxyl group by a singlet at δ 3.89, a singlet at 7.45 integrating for five protons corresponding to a phenyl group, a large singlet at 1.45 assignable to a *gem*-dimethyl group and two doublets (J = 10 Hz) at 5.58 and 6.80 each integrating for one proton, corresponding vinylic protons, suggesting a 2,2-dimethylchromene residue. This was further supported by IR absorption at 1390 and 1375 cm^{-1} for a *gem*-dimethyl group. The C-2 and C-3 protons of the flavanone corresponding to the ABX system [8] appeared for C-2 as a double doublet at δ 5.29 (1H, J_{AX} = 12.7 Hz, J_{BX} = 3.3 Hz), while the C-3 protons, the AB part, appeared at 2.96 and 2.82 (J_{AB} = 17.5 Hz, J_{AX} = 12.7 Hz, J_{BX} = 3.3 Hz). The high value of J (12.7 Hz) for the coupling constant J_{AX} was indicative of an axial–axial coupling. Therefore, the C-2 hydrogen was axial and ring B was equatorial [9]. The high negative value of the optical rotation, $[\alpha]$ −67°, suggests that **1** is not an artifact of **2**, and it has a higher mp and optical rotation than the compound recently isolated from *T. praecans* [6]. The UV spectrum of **1**, before and after the addition of a few drops of the flavonoid diagnostic reagents [10, 11], supported the assigned flavanone structure. The mass spectrum agrees well with the expected cleavage pattern for **1** [11].

Oaxacacin (**2**) $C_{21}H_{20}O_4$, M^+ 336.1360, gave positive ferric chloride and Shinoda tests and a red color with sulfuric acid. The NMR spectrum, δ 7.59 (1H *br d*), 7.33 (1H, d) supported a chalcone structure with a 2,2-dimethylchromene residue [1.43 (6H), 5.47 (1H), 6.68 (1H)] and a methoxyl group [3.95 (3H)]. The UV spectrum was typical of a chalcone [10] and on addition of a few drops of aluminum chloride a bathochromic shift of 25 nm was observed. On the basis of all this information and the mass spectrum fragmentation pattern structure **2** was assigned.

EXPERIMENTAL

The roots of *Tephrosia woodii* T. were collected from plants growing in Putla, Oaxaca, Mexico, in April 1980. A voucher specimen has been deposited at the Herbarium of the National University of Mexico.

UV spectra were run in EtOH and IR spectra as KBr discs. ^{1}H NMR spectra were run at 90 and 400 MHz in $CDCl_3$ using TMS as int. standard. MS were obtained at 70 eV in a high resolution Fenn. Mps are uncorr. Elemental analysis were carried out by the Alfred Bernhardt Laboratories, Engelskirchen, West Germany.

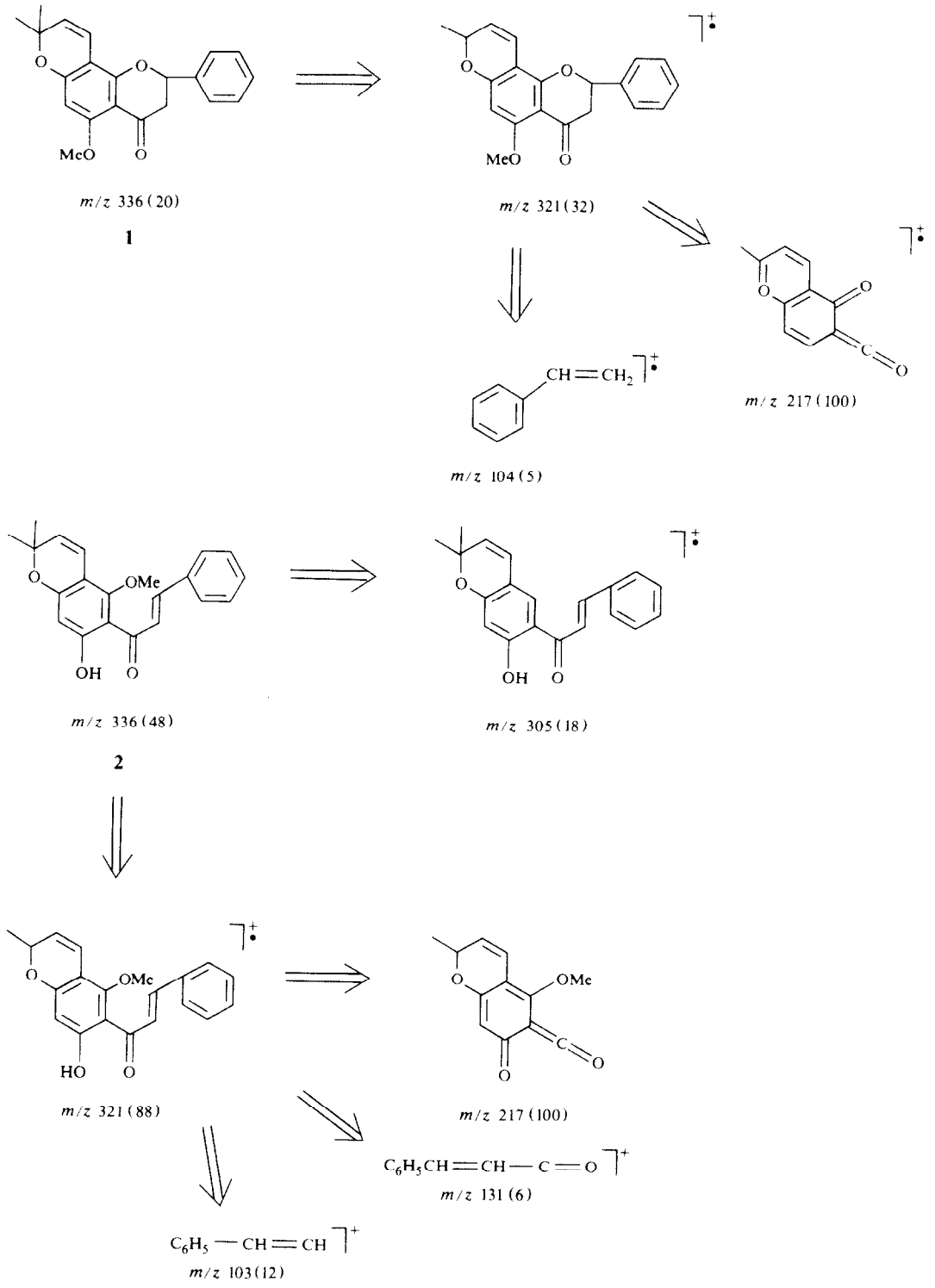
The air-dried roots (215 g) were extracted in a Soxhlet with hexane. Concn of the hexane extract yielded 11.4 g of an orange syrup. After refluxing with MeOH, filtration and concn of the MeOH soln yielded 10.35 g of an orange paste. 3 g portions of the paste were 'flash' liquid chromatographed on a Si gel column (Merck 60, 35–70 mesh) and eluted with hexane–Me_2CO (1:3) to give **1** as colorless needles (80 mg) and **2** as orange prisms (28 mg).

Mixtecacin (**1**). Colorless needles, mp 136–137°, UV λ_{max}^{MeOH} nm (ε): 230 (5075), 273 (9438). There were no changes after the addition of shift reagents [10].

$$[\alpha]_D^{22^\circ} = \frac{\begin{array}{ccccc} 589 & 578 & 546 & 436 & 365\ nm \\ -67 & -69.3 & -78.5 & -99.3 & \text{no lecture} \end{array}}{c\ 7.5} \text{ ($CHCl_3$;}$$

On KOH fusion, benzoic acid was obtained. IR ν_{max}^{KBr} cm^{-1}: 2890, 1665, (ArCO), 1625, 1595 (Ar), 1380, 1390 *gem*-Me_2, 1220 and 1060 (ArCO). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (5H, *s*), 6.80 (1H, *d*), 6.05 (1H, *s*), 5.58 (1H, *d*), 5.29 (1H, *dd*), 3.89 (3H, *s*), 2.96 (1H, *dd*), 2.82 (1H, *dd*), 1.45 (2H, 6H). MS *m/z* (%) 336.1361 (20), 321 (32, (Me), 217 (100), 104 (5), 77 (7).

Oaxacacin (**2**). Orange prisms, mp 107°, UV λ_{max}^{MeOH} nm(ε): 302



Scheme 1.

(36 691), 350 (40 219); with NaOAc 70 nm displacement. On KOH fusion, benzoic acid was obtained. IR ν_{max}^{KBr} cm^{-1}: 3600 (OH), 3030 (ArH), 1660 (ArCO), 1586 (Ar), 1575, 1380 and 1370 (*gem*-Me_2C). ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (1H, *d*, J = 9 Hz), 7.33 (1H, *d*, J = 9 Hz), 7.05 (5H, *d*), 6.68 (1H, *d*, J = 10 Hz), 5.93 (1H, *s*), 5.47 (1H, *d*, J = 10 Hz), 3.90 (3H, *s*), 1.43 (6H, *s*), 6.80 (1H, *d*, J = 9 Hz). MS *m/z* (%) 336.1360 (49), 321 (88), 305 (18) $[M-MeO]^+$, 217 (100), 160 (16), 131 (6) $[C_6H_5CH=CH-CO]^+$, 103 (12) $[C_6H_5CH=CH]^+$, 91 (11), 77(14).

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