Journal of Natural Products
Vol. 49, No. 2, pp. 318-320, Mar-Apr 1986

CHEMISTRY OF MYZODENDRACEAE, I. MYZODENDRONE, A NEW PHENYLBUTANONE OF *MYZODENDRON PUNCTULATUM*

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Continuing our program of phyto chemical research in the southern region of Chile (1,2), we began the investigation of the Myzodendraceae, an important group of tree hemiparasites, with the study of *Myzodendron punctulatum* B. et S.

The members of the Myzodendraceae live preferentially on Fagaceae, specifically on *Nothofagus*, which is plentiful in the southern hemisphere. The *Nothofagus*, an important genus of trees, often suffer serious metabolic upset as a result of these hemiparasites, and this has a deleterious effect on the quality of the wood. Certain members of the *Nothofagus* genus are in great demand (e.g., for bridges and railroad ties) due to their outstanding resistance to inclement weather (3).

M. punctulatum was found as a parasite on *Nothofagus dombeyi* Mirb. (Blume), *Nothofagus antarctica* (Forst) Oerst, and *Nothofagus pumilio* (Poepp et Endl.) Krasser. A new phenolic glycoside, named myzodendrone, was isolated from *M. punctulatum* growing on *N. antarctica* and *N. pumilio* from Coyhaique. This glycoside has the molecular formula $C_{16}H_{22}O_8$ and has a short 1-keto-aliphatic chain. The phenolic portion of this compound was determined by ir absorptions at 3500, 1600, and 1520 cm^{-1} and by a uv max in MeOH at 278 nm, which was displaced bathochromically by addition of NaOMe. The keto group was confirmed by an ir absorption at 1700 cm^{-1}, a singlet at δ 2.2 in the ^1H nmr and, in the ms, a band at *m/z* 43 (77%) in comparison with *m/z* 180 (100%). The sugar portion was indicated by ^1H-nmr absorptions at δ 3.5-4.8 corresponding to seven protons and ions in the ms at *m/z* 180 and 162 (4). The identification of glucose as the sugar portion was confirmed by chromatographic comparison of the hydrolysis product of the natural compound with an authentic sample of glucose.

That the sugar portion was present as a β-glucoside was confirmed by comparison of the values of the ^{13}C-nmr spectrum: δ 62.5 (t, C-6), 71.4 (d, C-4), 74.9 (d, C-2), 77.6 (d, C-3), 78.3 (d, C-5), and 104.3 (d, C-1), with values reported in the literature (5,6). The aglycone $C_{10}H_{12}O_3$ gave a value of *m/z* 180 for the molecular ion in the ms. This aglycone was found to be the dihydroxy derivative of 4-phenylbutan-2-one. The loss of acetyl in the ms yielded the ion at *m/z* 137 (24%) $C_8H_9O_2^+$. From this ion, major ions were obtained at 123 (43%) $C_7H_7O_2^+$, 91 (13%), and 77 (7%).

The positions of the substituent groups on the benzene ring were determined from the ^1H-nmr spectrum of the acetylated derivative at 400 MHz in $CDCl_3$. The results were as follows: δ 6.84 (dd, 1H, J=8 Hz, J'=2 Hz, H-6), δ 6.9 (d, 1H, J=2 Hz, H-2), and δ 6.93 (d, 1H, J=8 Hz, H-5) (7). The methylene group adjacent to the phenyl group absorbed at δ 2.75 (t, J=7 Hz), whereas the methylene group adjacent to the carbonyl group absorbed at δ 2.85 (t, J=7 Hz). Thus, we conclude that the aglycone is 4-(3′, 4′-dihydroxyphenyl)-butan-2-one.

In addition, *M. punctulatum* growing on *N. antarctica* and *N. pumilio* contained the following compounds: β-sitosterol (1%), ursolic acid (2%), and oleanolic acid (8%). The following compounds were present in the *M. punctulatum* growing on *N. dombeyi*: β-sitosterol, ursolic acid, ursolic acid acetate, and

oleanolic acid. These products were identified (tlc, mp, mmp, ir) by comparison with known samples, especially their acetylated derivatives. The phenolic glycoside myzodendrone was not found in these specimens.

EXPERIMENTAL

PLANT MATERIAL.—Samples of *M. punctulatum* were deposited in the Herbarium of the Instituto de Botánica, Universidad Austral de Chile (Vald. 001630). The *M. punctulatum* hemiparasite of *N. pumilio*, obtained at San Antonio, Coyhaique (latitude 45°38′ south, longitude 72°02′ west), was dried and ground (1.5 kg); the *M. punctulatum* hemiparasite of *N. antarctica*, gathered at Antillanca (latitude 40°45′ south, longitude 72°12′ west, altitude 1000 m), was dried and ground (2 kg); the *M. punctulatum* of *N. antarctica* collected at San Antonio gave 4.8 kg of plant material; and the *M. punctulatum* of *N. dombeyi* obtained at Antillanca gave 2.25 kg (8).

EXTRACTION AND GENERAL EXPERIMENTAL.—The samples were extracted with 95% EtOH, and the ethanolic extracts were partitioned in C_6H_6, $CHCl_3$, EtOAc, and amyl alcohol. The uv spectra were obtained with a Shimadzu spectrophotometer. The ir spectra were determined on a Perkin-Elmer 700 spectrophotometer. ^1H nmr were recorded on a Varian EM-360 60 MHz spectrometer and a 400 MHz spectrometer using TMS as internal reference. ^{13}C nmr were determined on a Varian CFT-20 spectrometer; eims were taken on a Finnigan 400 mass spectrometer equipped with an Incos 2000 data system.

MYZODENDRONE [4-(3′,4′-DIHYDROXYPHENYL)-BUTAN-2-ONE-3′-*O*-GLUCOSIDE].—This product was isolated by means of silica gel column chromatography from the $CHCl_3$ and EtOAc fractions of *M. punctulatum* of *N. pumilio* (4.8 g, 0.32%) and *M. punctulatum* of *N. antarctica* (15 g, 0.31%) obtained in Coyhaique. This compound was not obtained from the other samples of *M. punctulatum*. It crystallized from EtOH-EtOAc (1:1) as a yellow-white solid, mp 120-123°; tlc Rf 0.6 silica gel, EtOAc-EtOH (4:1) and 0.44 silica gel, $CHCl_3$-MeOH (4:1). A tlc of this compound, when developed with a spray of 30% H_2SO_4, gave a characteristic blue color; uv λ max (MeOH) 222 nm (log ε 3.68), 278 nm (log ε 3.26); (MeONa); 240, 294 nm; ir (Nujol) ν max at 3500 (OH), 1700 (C=O), 1600 and 1520 (aromatic bands), 1260, 1220, 1120, and 1060 (OH bending, C-O stretching) cm^{-1} (9); ^1H nmr (60 MHz, CD_3OD) δ 2.1 (s, 3H, Me-CO), 2.9 (s, 4H, 2 CH_2), 3.4-4.0 and 5.0 (m, 7H, glucosyl-H), 6.9 (s, 2H, Ar-H), 7.1 (s, 1H, Ar-H); ^{13}C nmr (CD_3OD) δ 30.2 (q, Me), 30.2 (t, CH_2), 45.9 (t, CH_2), 62.5 (t, C-6 glucose), 71.4 (d, C-4), 74.9 (s, C-2), 77.6 (d, C-3), 78.3 (d, C-5), 104.3 (d, C-1), 117.0 (d, aromatic-C), 118.9 (d, ar-C), 119.0 (d, ar-C), 124.5 (s, ar-C), 134.2 (s, ar-C), 146.5 (s, ar-C), 165.6 (s, C=O) ppm; ms *m/z* (%) 342 (0.01 M^+), 259 (2), 219 (2), 181 (11), 180 (100), 165 (4), 162 (7), 137 (24), 123 (43), 110 (7), 91 (13), 77 (7), 69 (12), 57 (24), and 43 (77). Glucose was identified on the basis of cellulose tlc using several solvent systems (10).

Anal. calcd for $C_{12}H_{22}O_8$: C, 56.14; H, 6.43. Found: C, 56.28; H, 6.56.

ACETYLATION OF MYZODENDRONE.—The acetylated derivative was prepared by the usual treatment with Ac_2O in pyridine. Recrystallization from EtOAc resulted in white needles mp 108-110°; tlc Rf 0.67 silica gel $CHCl_3$-MeOH (9:1); uv λ max (MeOH) 270 nm (log ε 3.20), 276 nm (log ε 3.19); ir ν max (Nujol) 1760, 1740, 1700, 1600, 1520, 1260, 1220, 1120, 1060, and 1040 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 2.0-2.2 (m, 15H, 5 Me-COO), 2.3 (s, 3H, Me-CO), 2.8 (s, 4H), 3.6-4.4 (m, 4H), 5.3 (m, 3H), 6.9 (s, 2H), 7.1 (s, 1H); ^1H nmr (400 MHz, $CDCl_3$) δ 2.01 (s), 2.04 (s), 2.06 (s), 2.1 (s), 2.75 (t, J=7 Hz), 2.85 (t, J=7 Hz), 3.5 (m), 3.9 (m), 4.3 (dd, J=12 Hz, J'=2 Hz), 4.4 (dd, J=12 Hz, J'=5 Hz), 5.0 (d), 5.2 (m), 5.3 (m), 6.8 (dd, J=8 Hz, J'=2 Hz), 6.9 (d, J=2 Hz), 6.93 (d, H=8 Hz); ^{13}C nmr ($CDCl_3$) δ 20.6 (q), 29.3 (q), 30.1 (t), 44.8 (t), 61.9 (t), 69.3 (d), 70.7 (d), 72.7 (d), 98.6 (d), 115.8 (d), 122.9 (d), 123.1 (d), 138.3 (s), 140.2 (s), 148.1 (s), 169.0 (s), 169.4 (s), 170.1 (s), 170.5 (s), 174.9 (s) ppm; ms *m/z* (%) 331 (9), 180 (5), 169 (43), 137 (2), 127 (8), 123 (3), 109 (29), 97 (3), 81 (3), 43 (100).

ACKNOWLEDGMENTS

We are grateful to the Dirección de Investigación y Desarrollo de la Universidad Austral de Chile (Grant RS-80-15) for support of this work. The authors also wish to thank Dr. J. Bartulín of the Universidad de Concepción and Dr. F. Bolhmann of the Technical University of Berlin for cooperation in sending the spectral information.

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Received 8 July 1985