Phytochemistry, Vol 24, No 5, p 1120, 1985
Printed in Great Britain

0031–9422/85 $3 00 + 0 00

FLAVONOIDS FROM THE FERNS *BLECHNUM REGNELLIANUM* AND *PITYROGRAMMA EBENEA*

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(*Revised received* 17 *September* 1984)

Key Word Index—*Blechnum regnellianum*, Blechnaceae, *Pityrogramma ebenea*, Hemiomtidaceae, Pteridophyta, *C*-methylated flavanone, methylenedioxydihydrochalcone

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Abstract—From the leaves of the fern *Pityrogramma ebenea* a new compound 2′,6′-dihydroxy-4,3′-dimethoxy-4′,5′-methylenedioxydihydrochalcone was characterized (2*S*)-5,7-Dihydroxy-4′-methoxy-6,8-dimethylflavanone was identified in another fern, *Blechnum regnellianum*

The two most widespread ferns of the mountainous region around 'Cachoeira das Andorinhas' were collected by the botanist José Badini from the Faculty of Pharmacy of the nearby town Ouro Preto, MG, Brazil, and identified by Dr David B Lellinger, Smithsonian Institution, Washington, D C, U S A, as *Blechnum regnellianum* (Kunze) C Chr and *Pityrogramma ebenea* (L) Proctor (common synonym *P tartarea* (Cav) Maxon) No previous reports on the chemical composition of the former species were found Extraction of its leaves with chloroform and fractionation of the extract gave (−)-matteucinol [(2*S*)-5,7-dihydroxy-4′-methoxy-6,8-dimethylflavanone] (**1**) originally obtained from the fern *Matteucia orientalis* Munesada [1] The structure of the compound became obvious upon inspection of its IR, UV, ^{1}H NMR and MS The identification was consubstantiated by comparison of its mp and $[\alpha]_D$ with published data [2] In contrast, several reports on *Pityrogramma tartarea* have appeared describing the isolation of flavones, chalcones and dihydrochalcones from the farinas of two varieties [3] Our specimen lacked a farinose indumentum and thus should belong to the chemically yet undescribed var *jamesonii* (Baker) Tyron [3] Extraction of the leaves with chloroform yielded the novel 2′,6′-dihydroxy-4,3′-dimethoxy-4,5′-methylenedioxydihydrochalcone (**2**)

The ^{1}H NMR spectrum of **2** with its AA′BB′ system of aromatic proton signals and its A_2B_2 system of aliphatic proton signals clearly agrees with the proposed structure The ^{13}C NMR peaks are indeed assignable to the twelve aromatic carbons, as well as to all other indicated functions Since both hydroxyl protons originate one sole ^{1}H NMR peak at low field (δ10 3), both hydroxyls must be equivalent and vicinal to the carbonyl (UV $AlCl_3$ shift) Only structure **2** is compatible with these data

EXPERIMENTAL

Isolation of the flavonoid constituents Vouchers of *Blechnum regnellianum* (No 26 286) and of *Pityrogramma ebenea* (No 25 237) were deposited at the Herbarium of Instituto de Ciências Exatas e Biológicas (formerly Herbarium of the Faculty of Pharmacy), Universidade Federal de Ouro Preto, Ouro Preto, MG, Brazil Dry fern leaves (100 g) were ground and extracted at room temp with $CHCl_3$ (3 hr) The $CHCl_3$ solns were extracted with aq NaOH (1 %) and the alkaline solns acidified and extracted with $CHCl_3$ The $CHCl_3$ solns were evaporated and the residues (31 mg ex *B regnellianum*, 273 mg ex *P ebenea*) were chromatographed on silica gel columns From the column with material from *B regnellianum* $CHCl_3$ eluted **1** (8 mg) From the column with material from *P ebenea* (C_6H_{14}–$CHCl_3$, 1 4) eluted a product which was purified on a column of Sephadex LH-20 swelled with $CHCl_3$ to give **2** (114 mg)

(2*S*)-*5,7-Dihydroxy-4′-methoxy-6,7-dimethylflavanone* (**1**), mp and lit [1] mp 172–174° (EtOH), $[\alpha]_D^{20°}$ and lit $[\alpha]_D^{20°}$ $-30°$ (*c* 1, Me_2CO) IR ν_{max}^{KBr} cm^{-1} 3400, 1640, 1610, 1545, 1515, 1455, 1440, 1385, 1250, 1178, 1030, 910, 834 UV λ_{max}^{MeOH} nm 231, 274, 285 sh, 298 (ε15 700, 4400, 8800, 11 500), $\lambda_{max}^{MeOH+NaOH}$ nm 230, 272, 288, 339 (ε13 900, 3600, 4100, 20 100), $\lambda_{max}^{AlCl_3}$ 231, 274, 286 sh, 310 (ε 13 200, 3450, 6600, 11 500) ^{1}H NMR (60 MHz, $CDCl_3$) δ7 52 and 7 01 (*J ca* 8 Hz, AA′BB′), 5 46 (*dd*, *J* = 12, 5 Hz, H-2), 3 83 (*s*, OMe), 3 1–2 8 (*m*, 2H-3), 2 07 (*s*, 2Me) MS *m/z* (rel int) 314 (32) $[M]^+$, 180 (93), 152 (100), 134 (58), 121 (33), 119 (19), 91 (28), 77 (19)

2′,6′-Dihydroxy-4,3′-dimethoxy-4′,5′-methylenedioxydihydrochalcone (**2**) Mp 143° (C_6H_6) IR ν_{max}^{KBr} cm^{-1} 3250, 1645, 1610, 1595, 1525, 1510, 1465, 1386, 1364, 1300, 1251, 1214, 1155, 1081, 1037, 968, 814 UV λ_{max}^{MeOH} nm 232, 288, 333 (ε 18 000, 24 000, 3500), $\lambda_{max}^{MeOH+NaOH}$ nm 237, 244 sh, 299, 366 (ε 25 000, 20 800, 22 800, 8800), $\lambda_{max}^{MeOH+AlCl_3}$ nm 244, 308, 369 (ε 16 000, 28 400, 3500) ^{1}H NMR (60 MHz, $CDCl_3$) δ10 3 (*br s*, 2OH), 6 91 and 6 73 (*J ca* 10 Hz, AA′BB′), 5 96 (*s*, O_2CH_2), 3 82 and 3 77 (2*s*, 2OMe), 3 38 and 2 91 (2 approx *t*, *J ca* 7 Hz, A_2B_2), ^{13}C NMR (20 MHz, $CDCl_3$) δ206 3 (C=O), 166 8 (C-2′,6′), 165 1 (C-3′,4′,5′), 159 0 (C-4), 134 6 (C-1), 130 1 (C-2,6), 114 6 (C-3,5), 105 7 (C-1′), 94 4 (O_2CH_2), 55 9 and 55 5 (2OMe), 46 7 (C-α), 30 4 (C-β) MS *m/z* (rel int) 303 (8) [M + 1], 302 (32) M, 168 (15), 167 (93), 135 (15), 134 (87), 122 (17), 121 (100)

Acknowledgements—Financial support by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and by Financiadora de Estudos e Projetos (FINEP) is gratefully acknowledged

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