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Flavonol glycosides from *Equisetum myriochaetum*

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1. Subject and source

Aerial parts of *Equisetum myriochaetum* Schlecht. et Cham. (Equisetaceae) were collected near Xochipala, Guerrero. The material was identified by M. Palacios-Rios, Inst. de Ecologia, Jalapa, Veracruz, and a voucher specimen is deposited at the herbarium of IMSS, Mexico-City (Voucher: IMSSM 11266).

2. Previous work

Pinocembrin, chrysin, β-sitosterol, β-D-glycosylsitosterol. β-D-glucose and fatty acids were mentioned as constituents of *E. myriochaetum* (Camacho et al., 1992).

3. Present study

Equisetum myriochaetum is traditionally used by the natives in Mexico to treat kidney diseases. Ethnopharmacological studies of the material from Guerrero state

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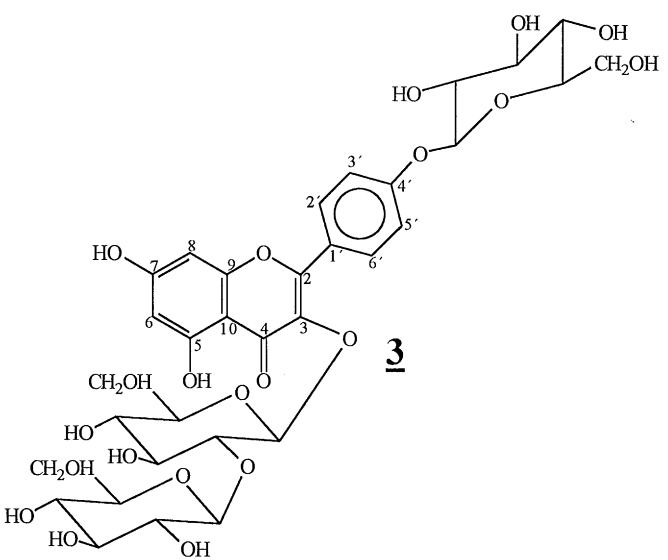
gave evidence for its use in treating diabetes type II (Andrade, 1995), while Mexican Indians use it as a herbal tea (Agua de Día). Separation of a purified extract (aqueous–aqueous separation) consisting of the water-soluble portion of the dried herbal material was carried out by CC on RP-silicagel (Polygoprep 60–30 C_{18}) with a water–acetonitrile–methanol eluent followed by prep. HPLC (SP 250/10 Nucleosil 120-7 C_{18}) to yield compounds **1**: kaempferol-3-O-sophoroside, **2**: kaempferol-3,7-di-O-β-glucoside, **3**: kaempferol-3-O-sophoroside-4′-O-β-glucoside, **4**: caffeoyl-methylate-4-β-glucopuranoside. Structural data of **1** and **2** correspond to those found in literature (Budzianowski, 1990; Markham et al., 1982). On account of varying amounts in plant extracts **4** is assumed to be an artifact. Kaempferol-3-O-sophoroside-4′-O-β-glucopyranoside (**3**) was first isolated from *Asplenium septentrionale* and confirmed by FAB-MS and ^{1}HNMR (Imperato, 1990). Here, the complete NMR data are reported which proved the β-linkage of the sugars at positions 3 and 4′ of the aglycone (MS: $[M]^+$: 286.0484 = $C_{15}H_{10}O_6$ (100); the Retro-Diels–Alder-cleavage with m/z 153.0192 ($C_7H_5O_4$ (6.64)) as well as 121.0306 ($C_7H_5O_2$ (20.2)) and the fragments m/z 257.0459 ($C_{14}H_9O_5$ (8.27)) and 229.0521 ($C_{13}H_9O_4$ (8.6)) gave evidence for an 3-OH-flavonol (kaempferol)). The NMR-signals showed three glucose molecules and appeared like a mixture of **1** and **2** leading to the conclusion that the sugar part in **3** has to be a sophorose as well as a β-glucose. The linkage of the sugars were found to be at C-3 and C-4′ on account of the lower C-3 (133 ppm), a higher C-7 (163.5 ppm) value and the highfield shift of C-4′ from 160 to 156 ppm. The corresponding shift values for kaempferol are 135.7 (C-3), 159.2 (C-4′) and 163.9 (C-7). Comparing HPLC-analysis showed that those isolated compounds can be found in the "Agua de Día", too.



3

3: ^{1}H NMR: δ 8.06 (2H, *d*, $J_{2'/6',3'/5'} = 8.7$ Hz, H-2′/H-6′), 6.91 (2H, *d*, $J_{3'/5',2'/6'} = 8.7$, H-3′/H-5′), 6.79 (1H, *d*, $J_{8,6} = 1.8$ Hz, H-8), 6.43 (1H, *d*, $J_{6,8} = 1.8$ Hz, H-6), 5.63 (1H, *d*, $J_{1'',2''} = 7.2$ Hz, H-1″), 5.03 (1H, *d*, $J_{1''',2'''} = 7.3$ Hz, H-1‴), 4.61 (1H, *d*, $J_{1''',2'''} = 7.8$ Hz, H-1‴), 3.71 (2H, *m*, H-6″$_\alpha$, H-6‴$_\alpha$), 3.58 (1H, *d*, $J_{6''\alpha,5''} = 10.8$ Hz, H-6‴$_\alpha$), 3.45 (3H, *m*, H-6″$_\beta$, H-6‴$_\beta$, H-6‴$_\beta$), 3.30 (3H, *d*, $J_{5''/'''/''',4''/'''/''''} = 8.9$ Hz, H-5″, H-5‴, H-5⁗), 3.25 (3H, *dd*, $J = 7.5$, $J = 5.9$ Hz, H-2″, H-2‴, H-2⁗), 3.16 (3H, *dd*, $J = 6.3$, $J = 5.1$ Hz, H-3″, H-3‴, H-3⁗), 3.10 (3H, *m*, H-4″, H-4‴, H-4⁗), 3.0 - 4.0 (all OH). ^{13}C NMR data: δ 178. 86 (*s*, C-4), 163.13 (*s*, C-7), 160.42 (*s*, C-5) 156.85 (*s*, *s*, C-4′, C-2), 156.43 (*s*, C-9), 133.65 (*s*, C-3), 131.62 (*d*, *d*, C-2′, C-6′), 121.23 (*s*, C-1′), 115.79 (*d*, *d*, C-3′, C-5′), 106.07 (*s*, C-10), 104.17 (*d*, C-1‴), 100.11 (*d*, C-1⁗), 99.79 (*d*, C-6), 98.43 (*d*, C-1″), 95.01 (*d*, C-8), 82.35 (*d*, C-2″), 77.77 (*d*, C-3″), 77.41 (*d*, C-3‴), 77.28 (*d*, C-3⁗), 76.87 (*d*, C-5″), 76.74 (*d*, C-5‴), 76.51 (*d*, C-5⁗), 74.21 (*d*, C-2‴), 73.38 (*d*, C-2⁗), 69.97 (*d*, *d*, C-4″, C-4‴), 69.84 (*d*, C-4⁗), 61.12 (*t*, C-6″), 60.98 (*t*, C-6‴), 60.85 (*t*, C-6⁗).

4. Chemotaxonomic justification

Our results show that previously investigated *Equisetum* species (Vert et al., 1993; Saleh and Abdallah, 1980) as well as the *E. myriochaetum* mentioned here contain structurally related flavonol glycosides (kaempferol derivatives) which can be used as chemotaxonomic markers. No evidence was found for the occurrance of either flavones or flavanones.

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