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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 Ecología, Jalapa, Veracruz, and a voucher specimen is deposited at the herbarium of IMSS, Mexico-City (Voucher: IMSSM 11266).

### 2. Previous work

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

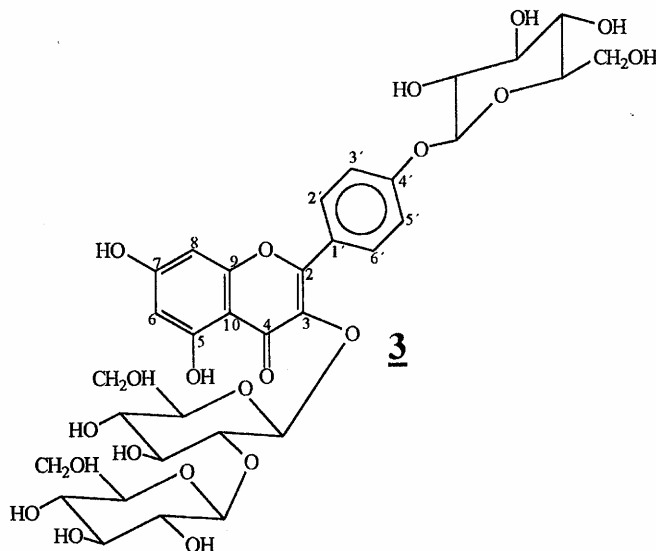
### 3. Present study

*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<sub>18</sub>) with a water–acetonitrile–methanol eluent followed by prep. HPLC (SP 250/10 Nucleosil 120–7 C<sub>18</sub>) to yield compounds **1**: kaempferol-3-O-sophorose, **2**: kaempferol-3,7-di-O-β-glucoside, **3**: kaempferol-3-O-sophorose-4'-O-β-glucoside, **4**: caffeoyl-methylate-4-β-glucopyranoside. 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-sophorose-4'-O-β-glucopyranoside (**3**) was first isolated from *Asplenium septentrionale* and confirmed by FAB-MS and <sup>1</sup>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]<sup>+</sup>: 286.0484 = C<sub>15</sub>H<sub>10</sub>O<sub>6</sub> (100); the Retro-Diels–Alder-cleavage with m/z 153.0192 (C<sub>7</sub>H<sub>5</sub>O<sub>4</sub> (6.64)) as well as 121.0306 (C<sub>7</sub>H<sub>5</sub>O<sub>2</sub> (20.2)) and the fragments m/z 257.0459 (C<sub>14</sub>H<sub>9</sub>O<sub>5</sub> (8.27)) and 229.0521 (C<sub>13</sub>H<sub>9</sub>O<sub>4</sub> (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:  $^1\text{H}$  NMR:  $\delta$  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 $''_a$ , H-6 $'''_a$ ), 3.58 (1H, *d*,  $J_{6''_a,5''}$  = 10.8 Hz, H-6 $''_a$ ), 3.45 (3H, *m*, H-6 $''_b$ , H-6 $'''_b$ , H-6 $''_b$ ), 3.30 (3H, *d*,  $J_{5''/1''',4''/1''''}$  = 8.9 Hz, 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).  $^{13}\text{C}$  NMR data:  $\delta$  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 occurrence of either flavones or flavanones.

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