The Biflavonoid Pattern of Selaginella selaginoides
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From Selaginella selaginoides the following three biflavonoids were isolated: amentoflavone, hinokiflavone and robustaflavone. The compounds were identified by means of spectroscopic methods.

As part of our research on the biflavonoid pattern of Selaginellaceae growing in the Iberian Peninsula, the methanol extract of Selaginella selaginoides was analyzed by two dimensional TLC (López-Sáez, 1992). Only one spot was detected with the chromatographic behaviour of amentoflavone (1). We used column chromatography on silica gel and Sephadex LH 20 (Chakravarthy et al., 1981) for further separation and identification. Amentoflavone (1), hinokiflavone (2) and robustaflavone (3) were characterized. These compounds were identified by their spectroscopic data (1H NMR, 13C NMR, FAB-MS) (Chari et al., 1977; Chakravarthy et al., 1981; Markham et al., 1987; Shin and Kim, 1991) and by TLC with authentic standards.

The genus Selaginella is characterized by the presence of amentoflavone as the major biflavonoid (Geiger and Quinn, 1988). The hinokiflavone series has been reported from S. tamariscina (Miura and Kawano, 1967; Nakazawa, 1968; Okigawa et al., 1971), S. kraussiana and S. lepidophylla (Qasim et al., 1985). The isolation of robustaflavone (3) from S. selaginoides is the second report of this compound outside the seed plants, after its identification in S. lepidophylla (Qasim et al., 1985).

The biflavonoid pattern of Selaginella selaginoides is studied here for the first time.

Experimental

Plant material

Sporophytic material of Selaginella selaginoides (L.) PB. ex Schrank & C.F.P. Mart. was collected in Borleña, Santander (Spain), 4. 11.1991, leg. et det. J. A. López-Sáez. Voucher specimens are deposited in the Herbarium of the Department of Plant Biology, Faculty of Biology, Complutense University of Madrid (“MACB”, No. 42188 and 42189).

Extraction and isolation

185 g thoroughly cleaned air-dried plant material was ground and defatted with CHCl3. Afterwards the biflavonoids were exhaustively extracted by 80% aq. methanol. To eliminate chlorophylls the combined extracts were evaporated and the residue subjected to a four step Craig distribution between the upper and lower phases of DMF/H2O/Et2O (4:1:8). The combined lower phases were reduced in vacuo to a thin syrup (about 75 ml). This was chromatographed over silica gel column and eluted with C6H6-Me2CO mixture of increasing polarity. The compounds were eluted as follows: 2, 2+1, 1+3, 3. Further separation and purification was done by CC on Sephadex LH 20 with Me2CO: H2O:MeOH (2:1:1).

Yields: 65 mg of 1; 20 mg of 2; 45 mg of 3.
1H NMR spectroscopy: Bruker AM 400, 400 MHz, DMSO-d6, ambient temperature.
13C NMR spectroscopy: Bruker AM 400, 100 MHz, DMSO-d6, ambient temperature.
Mass spectra were recorded by FAB-technique (negative mode) on a Hewlett Packard 5970 (70 eV).

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