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SEAWEED AS A NEW SOURCE OF FLAVONE, SCUTELLAREIN 4'-METHYL ETHER

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Abstract

Phycochemical investigation of a red alga *Osmundea pinnatifida* (Hudson) Stackhouse, collected from Karachi Coast of Pakistan, led to the isolation of a flavone, which was assigned as Scutellarein 4'-methyl ether. It was obtained from BuOH fraction of the alga and chemically elucidated by spectroscopic methods and 2D-NMR techniques. In the present study, occurrence of this compound is being reported for the first time as a metabolite in marine algae.

Introduction

Secondary metabolities are proposed to have evolved from the diversion of energy and nutrients from primary biosenthetic pathways (Fenical, 1982). More than 1000 chemical compounds with diverse structures and functions have been isolated from algae (Hay & Steiberg, 1991). Abundance of halogenated compounds are the most frequently reported metabolites from red algae (Fenical, 1975; Gribble, 1998; Faulkner, 2002). However on the basis of earlier reports, presence of flavonoids remained questionable in marine algae (Markham, 1988). Evidence of flavonoid has only once been reported from *Acanthophora spicifera* (Vahl) Børgesen (Wang *et al*., 1998; Zeng *et al*., 2001). No further investigation from seaweeds has been described in the literature. In the present study, Scutellarein 4'-methyl ether (5,6,7-trihydroxy-4'-methoxy flavone) is reported for the first time in algae, which was isolated from *Osmundea pinnatifida* Hudson (Stackhouse).

Materials and Methods

Plant material: The entire thalli of *Osmundea pinnatifida* (Hudson) Stackhouse [=*Laurencia pinnatifida* (Hudson) Lamouroux] (Rhodomelaceae, Ceramiales, Ceramophyceae, Rhodophycota; *fide* Shameel, 2008), were collected from the coast of Buleji, Karachi, (Pakistan) during September 2004. It was identified by Prof. Dr. Aliya Rehman, Department of Botany, University of Karachi, Pakistan and its voucher specimen has been deposited in the herbarium No.8.

Extraction and isolation: Freshly crushed parts of *O. pinnatifida* (10 kg) were extracted with EtOH. The ethanol extract of the alga was filtered and then evaporated under vacuum. The residue (126 g) was triturated with MeOH:H_2O (8:3) and successfully fractionated with *n*-Hexane, CH_2Cl_2, EtOAc and *n*-BuOH. The butanol extract (31 g) was fractionated by *CC* on Diaion HP-20 and eluted with the mixtures of H_2O-MeOH to obtain various sub-fractions F_1 to F_8. A sub-fraction eluted with H_2O-MeOH (100% H_2O, 10% MeOH, 20% MeOH- H_2O, 30% MeOH-H_2O, 50% MeOH-H_2O, 100% MeOH-H_2O) to afford various fractions. Fraction F_4-F_6 (8 g) were combined and subjected to polyamide column chromatography with MeOH/H_2O as eluting solvents in a gradient manner, final purification was carried out by using $CHCl_3$/MeOH/H_2O by polyamide

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column chromatography (8:2.8:0.2) as eluting solvents. This yielded a compound (15 mg) of Scutellarein 4'-methyl ether: Yellow powder, M.P. 272-274 °C; IR V_{max} ($CHCl_3$)cm-^{1}: 3418(OH), 2923(Ar CH), 1738(C=O); For ^{1}H-NMR and ^{13}C-NMR (300 MHz, DMSO) spectral data see Table 1; HR-EIMS *m/z* 300.27 $[M+H]^+$ (calcd. for $C_{16}H_{12}O_6$ 300.0634).

General experimental procedures: The melting point of the isolated compound was recorded on a YANACO apparatus, rotation was measured on a digital polarimeter JASCO DIP-360 in methanol. Infrared spectra were obtained on vector 22 Brukner spectrophotometer. High resolution mass spectrum HR-EIMS were recorded with a Jeol HX 110 mass spectrometer; in *m/*z (rel %). The ^{1}H-NMR,^{13}C-NMR, Cosy, HMBC spectra were obtained in Bruker AV-400 specrometer operating at MHz. The chemical shift values were reported in δ (ppm), referenced with respect to the residual solvent signal of CD_3OD, $CDCl_3$ and coupling constants (*J*) were measured in Hz. Column chromatography (CC) was performed using Diaion HP-20 (Mitsubishi Chem. Ind., Tokyo, Japan), polyamide-6 DF (Riedel-De Haen AG, Germany). Thin-layer chromatography (TLC) was performed on precoated silica gel plates (DC-Alugram 60 UV_{254} of E. Merck) by using Ceric sulphate spraying reagent.

Results and Discussion

On the basis of evidences (Table 1) and comparison with literature (Horie *et al*., 1998), the structure of compound was deduced to be 5,6,7-trihydroxy-4'-methoxy flavone, commonly known as Scutellarein 4'-methyl ether (Fig. 1) which was isolated for the first time from this genus.

The marine red algae of the genus *Osmundea* Stakhouse are widely distributed along the coast of tropical and sub-tropical areas around the world. From biological point of view *O*. *pinnatifida* was previously documented for its antimicrobial (Gonzalez, 2001), antifungal (Rizvi & Shameel, 2004), anti-leishmanial (Sabina *et al*., 2005, 2006a) and anti-oxidant (Sabina *et al* 2006b) activities. According to the literature survey Scutellarein 4'-methyl ether has been reported for its anti-allergic (Masaru *et al*., 1994), anti-cancer and anti-cytotoxic (Shan *et al*., 2006) activities *in vitro* and *in vivo*. In this context this research may enhance the evaluation of this flavonoid, which may lead to the useful adjunct for the treatment of multiple disease categories from marine resources.

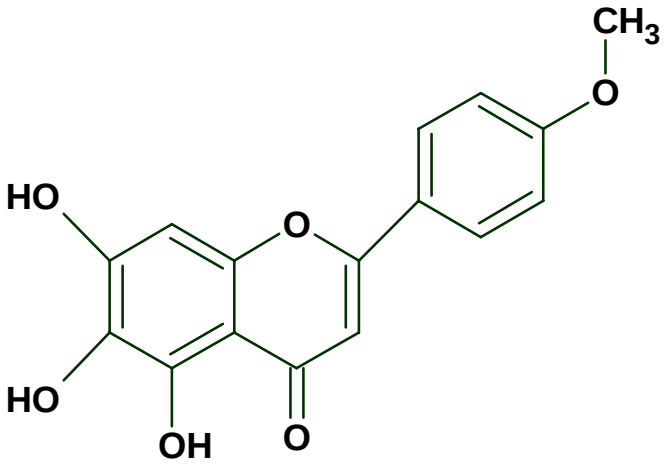

Fig. 1. Scutellarein 4'-methyl ether.

Table 1. ^{1}H-NMR (300 MHz, CD_3Cl, CD_3OD), ^{13}C-NMR (300 MHz, DMSO) for the compound isolated from *Osmundea pinnatifida*.

Position	^{1}H (δ = ppm)	^{13}C (δ = ppm)
1		181. 9
2		163
3	6. 69 (s, 1H)	102. 8
4		129. 1
5	-	147
6		153. 3
7	6. 50 (1H, s, C- 8H)	93. 8
9		149. 6
10		104. 0
1’		123
3’-5’	7.11-7.08 (2H, d, *J* = 7.096 Hz, C-3H, C- 5H)	114. 6
2’- 6’	7. 98-7. 96 (2H, d, *J* = 7.97 Hz, C-2H , C-6H)	127. 9
4’	3.88 s	55. 4

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