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AN ISOFLAVONE GLYCOSIDE FROM THE HEARTWOOD OF *PTEROCARPUS MARSUPIUM*

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Key Word Index—*Pterocarpus marsupium*: Leguminosae; 5,4′-dimethoxy-8-methylisoflavone 7-*O*-α-L-rhamnopyranoside.

Abstract—A new isoflavone, 5,4′-dimethoxy-8-methylisoflavone, has been identified from the heartwood of *Pterocarpus marsupium*.

Species of *Pterocarpus* are known to be rich in isoflavonoids and terpenoid derivatives [1]. From the ethyl acetate fraction of the ethanolic extract of the heartwood of *P. marsupium* a new isoflavone glycoside has been identified.

The compound had a molecular formula $C_{24}H_{26}O_9$, mp 185°, (*d*) gave the characteristic colour reactions of an isoflavone and was found to be glycosidic in nature. Its isoflavone nature was further confirmed by its UV and ^{1}H NMR spectra. Hydrolysis with 7% sulphuric acid gave rhamnose (co-chromatography with an authentic sample) and a yellow aglycone, $C_{18}H_{16}O_5$, mp 195°. The aglycone analysed for one hydroxyl (acetate and IR 3350 cm^{-1}), one *C*-methyl group (^{1}H NMR signal at δ 2.3 corresponding to three protons of CH–Me) and two methoxyl groups (Ziesel, IR ν_{max} cm^{-1} : 2865, 1185 and ^{1}H NMR signal at δ 3.8 corresponding to 6H of 2-OMe).

Spectral studies of the aglycone (UV λ_{max} nm: 260, 316(sh) indicated the presence of one free hydroxyl at position 7 (bathochromic shift of 12 nm of band II with fused sodium acetate and 8 and 10 nm shifts of band II and band I, respectively with sodium methoxide). In order to assign the positions of the methyl and methoxyl groups the aglycone was methylated with diazomethane and the resulting methyl ether subjected to alkali fission. One of the products was identified as the 2,4-dimethyl ether of 6-hydroxytoluene mp 60° (lit. 61°) [2]. Formation of this product confirms the position of one methyl group at position 8 and a methoxyl at both the 5- and 7-positions on the A ring. The other product formed was *p*-methoxyphenylacetic acid mp 83° (lit. 84°) and this clearly indicates the presence of one methoxyl group at the 4′-position of the B ring. The structure is further confirmed by 2′, 6′-proton signals at δ 7.4 and 3′, 5′-proton signals at δ 6.6 in the ^{1}H NMR spectrum. ^{1}H NMR also showed a singlet at δ 6.4 (C-6 proton of ring A) and confirmed that the 5-, 7- and 8-positions of ring A are substituted. A sharp signal at δ 7.8 corresponding to the C–2 proton of ring C which is specific for isoflavones, was also present in the ^{1}H NMR spectrum [3]. Thus the aglycone is 7-hydroxy-5,4′-dimethoxy-8-methylisoflavone. The attachment of the sugar molecule was confirmed from comparison of the UV spectra of the aglycone and glycoside. The aglycone gave a 12 nm bathochromic shift with sodium acetate whilst the glycoside gave no shift suggesting that the rhamnose is attached at the 7-position. Rhamnose is in the pyranose form since periodate oxidation gave 2 mol periodate per mol glycoside consumed and 1 mol formic acid was produced. The glycoside was hydrolysed by takadiastase but not by emulsin showing the presence of an α-linkage.

The isoflavone glycoside is thus 5,4′-dimethoxy-8-

methylisoflavone 7-*O*-α-L-rhamnopyranoside which has not been reported previously from any plant source.

EXPERIMENTAL

Isolation. The heartwood of *P. marsupium* was extracted with boiling EtOH and the concd extract (150 ml) fractionated into petrol, C_6H_6 and EtOAc soluble portions. The isoflavone glycoside was precipitated by petrol from the EtOAc fraction using fractional precipitation to remove impurities and its purity checked by PC and TLC.

Isoflavone glycoside. $C_{24}H_{26}O_9$ (Found: C, 62.15; H,5.92%; requires: C, 62.43%; H, 5.67%). UV λ_{max}^{MeOH} nm: 258, 318 (sh); +NaOAc 258, 317 (sh). ^{1}H NMR (90 MHz, $CDCl_3$): δ 2.4 (3H, *s* 8-Me), 3.7 (6H, *d*, *J* = 2.5, 8.5 Hz, 4′-OMe, 5-OMe), 7.5 (2H, *d*, *J* = 2.5, 8.5 Hz, 2′-H, 6′-H), 6.7 (2H, *d*,*J* = 2.5, 8.5 Hz, 3′-H, 5′-H), 6.5 (1H, *s*, 6-H), 7.8 (1H, *s*, 2-H), 0.93 (3H, *br s*, Me-Rha), 5.15 (*s*, H-1, Rha) and 3.10–5.10 *m* (5 sugar protons).

Aglycone. $C_{18}H_{16}O_5$ (Found: C, 69.15; H, 5.51% requires: C, 69.23: H, 5.12%). UVλ_{max}^{MeOH} nm: 260, 316(sh); +NaOAc 272 and 317 (sh); +NaOMe 268, 326 (sh). Acetate (pyridine-Ac_2O; 24 hr at room temp.) mp 192° (Found: C, 67.59; H, 5.45: acetyl 12.10%; requires: C, 67.79: H, 5.08; acetyl, 12.14%. ^{1}H NMR (90 MHz, $CDCl_3$): δ2.3 (3H, *s*, 8-Me), 3.8 (*d*, *J* = 2.5, 8.5 Hz 4′-OMe, 5-OMe), 7.4 (2H, *d*, *J* = 2.5, 8.5 Hz 2′-H, 6′-H), 6.6 (2H, *d*, *J* = 2.5, 8.5 Hz 3′-H, 5′-H), 6.4 (1H, *s*, 6-H), 7.8 (1H, *s*, 2-H).

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A REVISED STRUCTURE FOR ACETYLHELIOSUPINE

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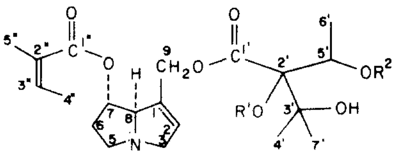
Key Word Index—*Cynoglossum officinale*; *Myosotis sylvatica*; Boraginaceae; hound's tongue; forget-me-not; pyrrolizidine alkaloids; acetylheliosupine.

Abstract—Acetylheliosupine, which has previously been isolated from *Cynoglossum officinale* and *Myosotis sylvatica*, is shown to be acetylated at the secondary hydroxyl group of heliosupine.

In 1970 Pedersen [1] described acetylheliosupine, a minor alkaloid of the hound's tongue, *Cynoglossum officinale* L. Structure **1** was proposed for this alkaloid, based largely on mass spectral evidence. Recently, Smith and Culvenor [2] reported that acetylheliosupine also occurs in the forget-me-not, *Myosotis sylvatica* Hoffm. We have also isolated acetyheliosupine from both of these species, but propose the revised structure **2** for this alkaloid.

Three lines of evidence support this conclusion. The ^{1}H NMR spectrum of acetylheliosupine shows a one-proton quartet at δ5.42, coupled only to a three-proton doublet at δ1.36. This suggests that the secondary alcohol at C-5′ is in fact the one acetylated, since the quartet for the corresponding methine occurs at δ4.19 heliosupine (**3**), the parent alcohol.

1 R′ = Ac, R² = H
2 R′ = H, R² = Ac
3 R′ = R² = H



The off-resonance decoupled ^{13}C NMR spectra for these two compounds support this structural assignment. The chemical shifts of the singlets for C-2′ and C-3′ differ little between acetylheliosupine and heliosupine, but the doublet for C-5′ exhibits a downfield shift of δ2.7 in acetylheliosupine relative to the parent alcohol. The magnitude of this shift demonstrates that the hydroxyl group on this carbon is the