

ably acetate derived. There is only one other report on the natural occurrence of a 4-methylcoumarin, viz. 8-methoxy-4-methylcoumarin [4].

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KAEMPFEROL 3-RHAMNOSYLXYLOSIDE FROM *EUONYMUS ALATUS*

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Hydrolysed leaf-extract of *Euonymus alatus* (Thunb.) Sieb. f. *ciliato-dentatus* (Fr. et Sav.) Hiyama has been previously shown to contain leucocyanidin, leucodelphinidin, quercetin and kaempferol [1]. Fresh juvenile leaves (2 kg) were now refluxed with 80% EtOH. The extract was concentrated, washed with *n*-hexane and Et₂O, and extracted with EtOAc. This extract was evaporated to dryness and the residue was applied to a polyamide column [2]. After washing the column with H₂O, the eluates of 40% MeOH were collected, evaporated *in vacuo* to dryness and dissolved in MeOH. From this solution light yellow needles were obtained and recrystallized from MeOH. Yield 233.0 mg, mp 187°. PC *R_f* 0.71 in 15% HOAc, 0.61 in BuOH–HOAc–H₂O (6:1:2) and 0.39 in C₆H₆–HOAc–H₂O (125:72:3). In UV light, the glycoside was dark changing to yellow with NH₃ vapour. Complete acid hydrolysis gave kaempferol, xylose and rhamnose. Partial hydrolysis with N HCl by heating at 100° for 30 sec gave an intermediate (PC *R_f* 0.37 in 15% HOAc; UV: dark, UV + NH₃: lemon yellow), which was further degraded into kaempferol and xylose and identified as kaempferol 3-xyloside. UV max. (nm) of the glycoside in ethanol were 268 (band I) and 351 (II). Spectral shifts with AlCl₃ (band II, Δλ +50), NaOEt (II, +53), fused NaOAc (I, +8) and NaOAc + H₃BO₃ (II, +2) were observed. Analysis of the compound (needles, mp 111–2°) acetylated with Ac₂O–pyridine gave: C, 55.92; H, 5.03. Calc. for C₄₂H₄₄O₂₂: C, 56.00; H, 4.92. The compound methylated with CH₂N₂ was hydrolyzed with 2 M HCl for

30 min, and the aglycone was obtained as light yellow, long needles mp 134°. λ_{max} in EtOH: 259 (band I) and 358 (II). PC *R_f* 0.37 in 30% HOAc and 0.94 in BuOH–HOAc–H₂O (4:1:5), and in UV light, yellow changing to intense bright yellow with NH₃ vapour. This product was identified as kaempferol 5,7,4'-trimethyl ether by spectral and PC comparison with a synthetic specimen. The NMR spectrum in CDCl₃ indicated the presence of a *para*-substituted phenyl group [δ 8.17 (*d*, 2H) and δ 7.04 (*d*, 2H)], *meta*-related aromatic protons [δ 6.57 (*d*, 1H) and δ 6.38 (*d*, 1H), AB system, *J* 2.0 Hz], three methoxy groups [δ 3.98 (*s*, 3H), δ 3.91 (*s*, 3H) and δ 3.88 (*s*, 3H)], and a hydroxy group [δ 5.2 (broad *s*, 1H)]. The latter signal disappeared on deuteration. Thus the rhamnosylxylosyl residue in the new glycoside is linked to the 3-hydroxyl group of the aglycone kaempferol. Finally, methylation of the glycoside with Me₂SO₄ in NaOH aq. followed by acid hydrolysis gave 2,3,4-tri-*O*-methyl-L-rhamnose and 2,3-di-*O*-methyl-D-xylose identified by PC [3]. Hence the new glycoside is kaempferol 3-[*O*-α-L-rhamnosyl (1 → 4)-β-D-xyloside].

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