1d (3.3 mg) and **1e** (15.4 mg) were obtained (identified by mp, mmp, TLC, UV and IR [6].

Wax alcohol esters of ferulic acid (Gel substances A and B). The froth obtained during liq.–liq. extraction was washed successively with Et_2O, 5% $NaHCO_3$ and H_2O and crystallized from MeOH to give gel substance A (10 mg). mp 95–105°. γ_{max}^{KBr} (cm^{-1}): 3430 *s*, 2920 *s*, 2850 *s*, 1710 *s*, 1630 *m*, 1600 *m*, 1585 *w*, 1510 *m*, 1465 *s*, 1435 *m*, 1380 *m*, 1310 *m*, 1270 *m*, 1170 *s*, 1120 *m*, 1030 *w*, 975 *w*, 845 *w*, 810 *w*, 720 *m*. λ_{max}^{MeOH} (nm): 296, 325. λ_{min}^{MeOH} (nm): 265. Gel substance B (mp 75–85°) isolated during recrystallization of **1c–1e** had the same UV and IR spectra as above. Saponification of the gel substance (*N* ethanolic NaOH, N_2, refluxing 2 hr) gave ferulic acid (identified by UV, PC and TLC) and 5 alcohols, which were acetylated (Ac_2O, C_6H_5N, room temp.), gas chromatographed on a 3% SE-30 column and 2 peaks were identified as behenyl and lignoceryl alcohols. The composition of wax alcohols in gel substance A were 5.47 (behenyl), 27.37 (lignoceryl), 36.23 (unknown (i)), 18.03 (unknown (ii)) and 12.88% (unknown (iii)) and in gel substance B, 24.54, 28.88, 21.66, 8.66 and 16.24%, respectively.

Examination of discoloured cross sections of E. deglupta. Discs (26 cm dia) from *E. deglupta* (11 yr old) which contained dark areas in the heartwood, were taken from the Keravat plantation in New Britain. One cross-section was divided into 7 parts: (a) sapwood and heartwood into (b) outermost and discoloured, (c) outer, (d) middle, (e) inner, (f) innermost, (g) innermost and discoloured. The amount of methanol soluble material and total ellagic acids [7] in these portions were respectively: (1) 1.2; 0.03; (2) 2.8, 0.18; (3) 1.4, 0.12; (4) 1.6, 0.12; (5) 1.3, 0.11; (6) 1.0, 0.09; (7) 0.7, 0.8%.

Acknowledgements—We thank the Department of Forests, Papua, New Guinea and Australian Paper Manufacturers Ltd., for supply logs of *E. deglupta* and *E. globulus* respectively and Dr. J. A. Lamberton and Dr. J. W. Rowe for samples of β-diketone and lignoceryl and behenyl alcohols.

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LIQCOUMARIN, A NOVEL COUMARIN FROM *GLYCYRRHIZA GLABRA*

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(*Received* 17 *February* 1976)

Key Word Index—*Glycyrrhiza glabra*; Leguminosae; liqcoumarin; 6-acetyl-5-hydroxy-4-methylcoumarin.

Plant. Glycyrrhiza glabra L.; *Source*: Dr. S. C. Sankhyadhar, experimental garden of Govt. Ayurvedic College, Jammu, (India). *Uses*: [1]. *Present work.* We earlier reported the occurrence of 2-methylisoflavones and other polyphenols from indigenous *Glycyrrhiza glabra* roots [2]. In the present communication we report a novel 4-methylcoumarin, liqcoumarin.

The solvent-free EtOH extract of air dried roots (1.5 kg) was repeatedly extracted with Et_2O. The Et_2O-soluble fraction was chromatographed over silica gel. Elution with C_6H_6–EtOAc in different proportions gave various compounds earlier reported [2]. The C_6H_6–EtOAc (9:1) eluate on preparative TLC purification using benzene gave liqcoumarin (35 mg), mp 165–6°, $C_{12}H_{10}O_4$ (M^+ 218, found C, 66.03, H, 4.55; required C, 66.05, H, 4.62%). It gave green colour with EtOH–$FeCl_3$, had UV fluoresence and had ν_{max}^{KBr}: 1720, 1650 cm^{-1}; λ_{max}^{MeOH} 255, 265, 310; +$AlCl_3$ 245, 285, 320; *MS* 218 (M^+ 100%), 203 (100%), 190 (98%), 175 (77%), 147 (60%), 119 (64%), 91 (98%), 77 (62%). *NMR* (δ $CDCl_3$, TMS as internal standard): 2.48 (3H, *d*, *J* 1 Hz, $-CH_3$), 2.95 (3H, *s*, –COMe), 6.15 (1H, *bs*), 6.80 (1H, *d*, *J* 10 Hz), 7.65 (1H, *d*, *J* 10 Hz) and 13,43 (1H, *s*, –OH). The spectral data showed it to be a coumarin with a chelated hydroxyl, a *C*-methyl and a *C*-acetyl substituents. The low field doublet at δ 7.65 could be either due to 4-proton of the coumarin or due to an aromatic proton adjacent to the *C*-acetyl unit and also ortho coupled with another proton (δ 6.80). The signal at δ 2.48 due to *C*-methyl shows allylic coupling (*J* 1 Hz) and hence the methyl group seems to be at C4. The signal at δ 7.65 is thus more likely due to an aromatic proton ortho-coupled with another proton (δ 6.80; *J* 10 Hz). Moreover, these signals have values which are lower than those of coumarin protons at C_3 and C_4 positions. *A priori*, liqcoumarin could be either a 6-acetyl-5-hydroxy-4-methylcoumarin or 7-acetyl-8-hydroxy-4-methylcoumarin. Liqcoumarin is assigned the structure of the former compound since it has been found to be identical with the synthetic sample obtained by condensing resacetophenone and ethyl acetoacetate in the presence of $AlCl_3$ in nitrobenzene [3], mp 164–5° (mp, mmp, TLC, superimposable IR and NMR).

Liqcoumarin seems to be of novel type and is presum-

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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(*Revised received* 5 *February* 1976)

Key Word Index—*Euonymus alatus* f. *ciliato-dentatus*; Celastraceae; kaempferol 3-rhamnosylxyloside.

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 Et_2O, 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 H_2O, 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–H_2O (6:1:2) and 0.39 in C_6H_6–HOAc–H_2O (125:72:3). In UV light, the glycoside was dark changing to yellow with NH_3 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 + NH_3: 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 $AlCl_3$ (band II, $\Delta\lambda$ +50), NaOEt (II, +53), fused NaOAc (I, +8) and NaOAc + H_3BO_3 (II, +2) were observed. Analysis of the compound (needles, mp 111–2°) acetylated with Ac_2O–pyridine gave: C, 55.92; H, 5.03. Calc. for $C_{42}H_{44}O_{22}$: C, 56.00; H, 4.92. The compound methylated with CH_2N_2 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–H_2O (4:1:5), and in UV light, yellow changing to intense bright yellow with NH_3 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 $CDCl_3$ indicated the presence of a *para*-substituted phenyl group [δ 8.17 (*d*, 2H) and δ 7.04 (*d*, 2H)], *meta*-related aromatic protons [δ6.57 (*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 [δ5.2 (broad *s*, 1H)]. The latter signal disappeared on deutration. 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 Me_2SO_4 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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