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A NEW COUMARIN FROM *PHYLLOSMA CAPENSIS*

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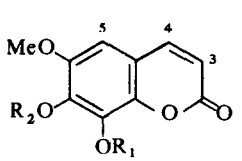
Key Word Index—*Phyllosma capensis*; Rutaceae; capensin; 8-hydroxy-6-methoxy-7-[(3-methyl-2-butenyl)oxy]-2H-1-benzopyran-2-one.

In the course of our work on the screening for anti-tumour activity of plants from the family Rutaceae, we have isolated and identified a new coumarin, capensin, from the petrol extract of *Phyllosma capensis*.

Capensin (1) analysed for $C_{15}H_{16}O_5$ (M^+ 276) and the structure was established as 8-hydroxy-6-methoxy-7-[(3-methyl-2-butenyl)oxy]-2H-1-benzopyran-2-one from both spectral and chemical evidence. The IR spectrum indicated an α-pyrone and a phenolic OH. Confirmation of the presence of the OH was obtained from the UV spectrum where the addition of alkali produced a bathochromic shift in the position of two of the absorption bands. The 100 MHz PMR spectrum of capensin enabled the identification of all 16 protons. The two doublets at δ 6.33 and 7.6 (J = 9.6 Hz) were assigned to H-3 and H-4 respectively. The one proton singlet at δ 6.50 was identified as H-5 since the chemical shift of H-4 indicated the probable absence of an O function at C-5 [1]. A 3 proton singlet at δ 3.9 and a one proton singlet at δ 6.11 (D_2O exchangeable) were attributable to OMe and OH substituents respectively. The doublet at δ 4.69 (2H, J = 7.4 Hz), the coupled triplet at δ 5.52 (1H) and the two non-equivalent Me resonances at δ 1.68 (3H) and 1.76 (3H) were consistent with a 3-methyl-2-butenyloxy substituent. The presence of the latter group was confirmed by the MS of capensin, where the low abundance (1.4%) of the M^+ and the intense fragments at *m/e* 208 (100%; fraxetin (2)) and *m/e* 69 (90%; $(CH_3)_2C{=}CH{-}CH_2$) are typical of an *O*-prenyl coumarin [2, 3].

The relative positions of the 3 substituents were established as follows: methylation of capensin with CH_2N_2 gave a product which was identified as puberulin (3), identical in all respect (UV, IR, PMR, MS, TLC, mmp) with an authentic sample [4].

Hydrogenation of capensin over Pd on a $BaSO_4$ catalyst gave a phenol, $C_{10}H_8O_5$, which was shown by mp, UV, IR, MS and PMR to be fraxetin (2).



1 R_1 = H; R_2 = $Me_2C{=}CHCH_2$
2 R_1 = R_2 = H
3 R_1 = Me; R_2 = $Me_2C{=}CHCH_2$

EXPERIMENTAL

P. capensis Bolus was collected in the Wupperthal district of the Cape Province. (Representative voucher specimen Williams 2125 in the Compton Herbarium, Kirstenbosch National Botanical Gardens, Cape Town).

Mps are uncorr. UV spectra were measured in MeOH and IR were recorded in KCl discs. PMR spectra in $CDCl_3$ and $(CD_3)_2SO$ were determined at 100 MHz using TMS as internal standard. MS were measured at 70 eV. TLC was carried out on Si gel using C_7H_{16}–EtOAc (7:3).

Extraction. Dried and ground stems, twigs and leaves (1.9 kg) were extracted in a Soxhlet apparatus with petrol (10 l., bp 60–80°) for 12 hr. On concentrating the extract to *ca* 1 l. and cooling, crystalline material, (5 g, 0.26%) was deposited. Crude capensin was decolourized with charcoal in hot C_6H_6 and recrystalized from C_6H_6–petrol (60–80°) to give colourless needles, mp 135–136°. (Found: C, 65.20; H, 5.65. Calc. for $C_{15}H_{16}O_5$: C, 65.22; H, 5.80%). UV λ_{max}^{MeOH} (ε): 312 (12450, 254 (5200), 232 sh (16400), 214 (36800) nm; λ_{max}^{NaOMe}: 334, 274, 214 nm; IR ν_{max}^{KCl}: 3260 (OH), 1710 (C=O), 1601, 1566 (C=C) cm^{-1}. PMR: δ 1.68 (3H, *s*), 1.76 (3H, *s*), 3.90 (3H, *s*), 4.69 (2H, *d*, J = 7 Hz), 5.52 (1H, *t*, J = 7 Hz), 6.11 (1H, *s*, disappears with D_2O), 6.33 (1H, *d*, J = 9.6 Hz), 6.5 (1H, *s*), 7.6 (1H, *d*, J = 9.6 Hz); MS *m/e* (rel. int.): 276 M^+ (1.4), 209 (33), 208 (100) (fraxetin), 207 (16), 193 (29), 190 (11), 180 (14), 123 (11), 69 (90) [$(CH_3)_2C{=}CH.CH_2^+$].

Methylation. An Et_2O soln of CH_2N_2 was slowly added to a cold, stirred soln of 1 (0.4 g) in $CHCl_3$ (10 ml). After removal of solvents, the residue was eluted from Al_2O_3 with $CHCl_3$ and crystallized from C_6H_6–petrol as colourless platelets (150 mg), mp 90–91° (lit. [4] 90–92°). The mp was not depressed when admixed with a sample of puberulin (3) and the UV, IR, PMR and MS were identical with those of 3.

Hydrogenation. A soln of 1 (0.5 g) in EtOH was hydrogenated over a Pd on $BaSO_4$ catalyst (5% Pd) [5] for 2 hr. The soln was filtered and the solvent removed to give a residue which crystallized from EtOH (charcoal) as colourless needles (243 mg) of 7,8-dihydroxy-6-methoxy-2H-1-benzopyran-2-one (fraxetin) (2), mp 226–227° (lit. [6] 228°). (Found: C, 57.61; H, 3.76; M^+ 208. Calc. for $C_{10}H_8O_5$: C, 57.69; H, 3.85%). UV λ_{max}^{MeOH} (ε): 340 (7810), 256 (4500), 230 sh (12920), 213 (27650) nm; λ_{max}^{NaOMe}: 400, 274, 216 nm; IR ν_{max}^{KCl}: 3420 (OH), 1700 (C=O), 1620, 1586 (C=C) cm^{-1}. PMR $(CD_3)_2SO$: δ 3.98 (3H, *s*), 6.27 (1H, *d*, J = 9.6 Hz), 6.85 (1H, *s*), 7.95 (1H, *d*, J = 9.6 Hz).

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A NEW CHALCONE GLYCOSIDE FROM *BAUHINIA PURPUREA*

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Key Word Index—*Bauhinia purpurea*; Caesalpinioideae; Leguminosae; butein 4′-*O*-β-arabino-*O*-β-D-galactoside.

Seeds of *Bauhinia purpurea* (identified by staff of the Botanical Survey of India, Allahabad) yielded a new chalcone glycoside, $C_{27}H_{34}O_{16}$, mp 265°. This gave the characteristic colour reactions of a chalcone and ion hydrolysis with 8% ethanolic H_2SO_4 for 12 hr gave butein [1, 2] and a disaccharide, the component sugars of which were found as galactose and arabinose. These sugars were confirmed by co-chromatography with authentic samples and by the preparation of their osazones. Galactose mp 164° (lit. 159°), phenylosazone mp 194° (lit. 196°), arabinose mp 156° (lit. 159°), osazone mp 160°, acetyl derivative mp 98° (lit. 96°) were identified.

The aglycone butein $C_{15}H_{12}O_5$, mp 213–214° was identified by its R_f 0.83, λ_{max}^{MeOH} 265 and 379 nm. It gave a shift of 60 nm on addition of NaOMe showing the presence of free hydroxyl group at position 4′. A bathochromic shift of 46 nm on addition of $AlCl_3$ showed the presence of a free hydroxyl group at 2′. The presence of an *ortho* dihydroxyl group at positions 3 and 4 was confirmed by the bathochromic shift of 36 nm with NaOAc–H_3BO_3. Periodate oxidation indicated that both sugars in the disaccharide had the pyranose configuration; 4 mol of periodate were consumed with the liberation of 1.8 mol of formic acid.

The attachment of the sugar moiety is at position 4′, since the aglycone gave a bathochromic shift of 60 nm with NaOMe while the glycoside did not. On methylation of the glycoside followed by hydrolysis with Kiliani's reagent (HCl–HOAc–H_2O, 35.5; 15:5), two methylated sugars were identified as 2,3,6-tri-*O*-methyl-D-galactose and 2,3,5,tri-*O*-methyl-L-arabinose. Both methylated sugars were confirmed by their R_G values relative to 2,3,4,6-tetramethyl-D-glucose (TMG). R_G found for 2,3,6-tri-*O*-methyl-D-galactose 0.70 (lit. 0.71) and for 2,3,5-tri-*O*-methyl-D-arabinose 0.95 (lit. 0.96) in *n*-BuOH–EtOH–H_2O (5:1:4). This indicates that C_1 of galactose is linked with aglycone at position 4′ and its C_4 is linked with arabinose at position C_1. The chloroform soluble-methylated aglycone, was identified as 2′,3,4,4′-tetra-*O*-methylbutein, which indicates that the sugar moiety is attached at position 4′ of the aglycone.

Arabinose was identified in the aqueous hydrolysate, obtained by the partial hydrolysis of the glycoside with formic acid in cyclohexanol [3] while galactose was not detected. This indicates that arabinose is linked at the terminal position of the disaccharide while galactose is linked with the aglycone.

Complete enzymic hydrolysis of glycoside with emulsin indicates that galactose is linked with arabinose as well as with aglycone by β-linkage. Thus the new glucoside is identified as butein 4′-*O*-β-L-arabinopyranosyl-*O*-β-D-galactoside.

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