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AN APIOSE-CONTAINING COUMARIN GLYCOSIDE FROM *GMELINA ARBOREA* ROOT*

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Key Word Index—*Gmelina arborea*; Verbenaceae; root; coumarin; β-apiofuranosyl-(1 → 6)-β-D-glucopyranosyl-umbelliferone

Abstract—Umbelliferone 7-apiosylglucoside has been characterised from the root of *Gmelina arborea*.

Isolation of a number of new lignans have been reported from *Gmelina arborea* [1–3]. We report from the same source the isolation of apiosylskimmin (**1**), a rare example of an apiose-containing product.

The new compound [**1**, $C_{20}H_{24}O_{12}$, mp 141–142°, $[\alpha]_D$ −38°; UV λ_{max}^{MeOH} nm (log ε): 220 (2.84), 297 (3.09), 328 (3.20); IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1690 (C=O), 1610 (aromatic), 1280, 1070] dissolved in conc. H_2SO_4 exhibiting bluish violet fluorescence and gave a positive Molisch test. These properties suggested that the new compound might be a coumarin glycoside.

The ^1H and ^{13}C NMR spectra of **1** are essentially similar to those of umbelliferone as aglycone with the carbohydrate moiety being a 6-linked β-glucoside and a terminal apioside. The chemical shifts located at δ6.25 (1H, *d*, *J* = 10 Hz), 7.65 (1H, *d*, *J* = 10 Hz), 7.55 (1H, *d*, *J* = 9 Hz), 6.98 (1H, *dd*, *J* = 9 and 2 Hz), 6.98 (1H, *d*, *J* = 2 Hz) are the umbelliferone protons and the 5.08 (1H, *d*, *J* = 5 Hz), 5.36 (1H, *br d*, *J* = 2 Hz), 4.84–4.86 (1H, *s*), 4.90–4.97 (1H, *s*), 4.58 (1H, *t*, *J* = 2.5 Hz), 4.4 (1H, *s*) 3.3–4.0 (9H, *m*) are due to sugar protons. Comparison of the ^{13}C NMR spectra (Table 1) with that of apiin [4] showed that C-7 (δ160.4) of umbelliferone is linked with C-1 (δ100.2) of glucose, further C-6 (δ67.9) of glucose is linked with C-1 (δ109.4) of terminal apiose.

The new compound (**1**) formed a hexa-acetate with Ac_2O–pyridine colourless micro-needles, mp 80°, $C_{32}H_{36}O_{18}$; UV λ_{max}^{MeOH} nm (log ε): 220 (3.84), 292 (3.69), 313 (3.80). Periodic oxidation of **1** consumed 1.5 moles of periodic acid indicating the occurrence of two *cis*-glycol systems. The ^1H NMR spectrum of the acetate confirmed the presence of six acetoxyls; δ1.99 (3H, *s*), 2.01 (3H, *s*), 2.02 (3H, *s*), 2.04 (3H, *s*), 2.1 (6H, *s*). The molecular ion was not found either in the mass spectrum of (**1**) or its acetate. However, the fragment ion at *m/z* 547 (7.1) [(hexose-pentose)Ac_6] was present in the later spectrum.

Partial hydrolysis of **1** using HCl–AcOH–H_2O (2.5:37.5:60) yielded the monoside, mp 210°. It was further hydrolysed with 2 N HCl and identified as umbelliferone (mmp 223°, IR and via its acetate) and glucose (descending paper chromatogram, BPW, 6:4:3, R_f 0.33). This established the monoside as being skimmin [5].

To establish the identity of the terminal sugar, **1** and authentic apiin were hydrolysed employing identical conditions (0.2 N HCl–dioxan, 1:1, 8 ml) and the residue was examined by descending paper chromatograms (Whatman No. 1 paper, *n*-BuOH–EtOH–H_2O, 52:32:6, benzidine–trichloroacetic acid as the spray reagent) [6] confirming the presence of glucose (R_f 0.31) and apiose (R_f 0.41). Thus **1** is a new apiofuranosyl-(1 → 6)-β-D-glucopyranosyl-(1.0.7)-umbelliferone and the first example of an apiose-containing coumarin.

EXPERIMENTAL

The roots (1 kg) were extracted with MeOH (3 l.) and the soln evaporated. The residue (22 g) was extracted with Me_2CO and the insoluble portion (10 g) was chromatographed on silica gel eluting with petrol (bp 40–60°), benzene and EtOAc successively collecting 250 ml fractions. The later EtOAc 25 fractions on evaporation yielded **1** (3 g) as colourless needles, mp 140–141° Found: C, 52.8, H, 3.9, $C_{20}H_{24}O_{12}$ requires C, 52.6; H, 3.5.

Table 1. ^{13}C NMR spectral data for **1**

Carbon	Chemical* shift	Carbon	Chemical shift
C-2	160.4	C-2′	73.6
C-3	113.6	C-3′	73.3
C-4	144.0	C-4′	70.1
C-5	129.7	C-5′	76.3
C-6	113.6	C-6′	67.9
C-7	160.4	C-1″	109.4
C-8	103.5	C-2″	76.3
C-9	155.2	C-3″	79.01
C-10	113.6	C-4″	73.6
C-1′	100.2	C-5″	63.5

*Off-resonance spectrum.

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Acetate: mp 80°; Found: C, 54.31; H, 5.15; $C_{32}H_{36}O_{18}$ requires C, 54.2; H, 5.15; ^1H NMR ($CDCl_3$): δ6.26 (1H, *d*, *J* = 10 Hz, H-3), 7.65 (1H, *d*, *J* = 10 Hz, H-4), 7.40 (1H, *d*, *J* = 9 Hz, H-5), 6.90 (1H, *dd*, *J* = 9 and 2 Hz, H-6), 6.90 (1H, *d*, *J* = 2 Hz, H-8), coumarin protons 5.2 (4H, *m*), 4.92 (1H, *s*), 4.64 (1H, *q*, *J* = 12, 6 Hz), 4.13 (2H, *d*, *J* = 1.8 Hz); sugar protons and acetoxyl chemical shifts given in the text.

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(+)-CALOCEDRIN, A LIGNAN DIHYDROANHYDRIDE FROM *CALOCEDRUS FORMOSANA*

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Key Word Index—*Calocedrus formosana*; Cupressaceae; calocedrin; lignan dihydroanhydride; hibalactone.

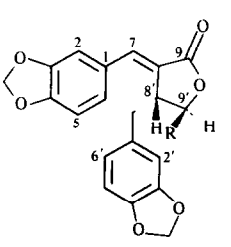
Abstract—A novel lignan dihydroanhydride, (+)-calocedrin, was isolated from the wood of *Calocedrus formosana*. Its structure was determined to be *trans*-α-(3,4-methylenedioxybenzylidene)-β-(3,4-methylenedioxybenzyl)-γ-hydroxybutanolide by spectroscopic methods. Reduction of (+)-calocedrin resulted in an optically inactive lignan lactone, (±)-hibalactone.

INTRODUCTION

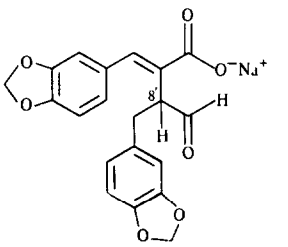
Calocedrus formosana, a member of the Cupressaceae, is an economically important tree indigenous to Taiwan [1]. Previous investigations [2, 3] on the heartwood have shown that it contains essential oil and a large quantity of terpenoid acids, such as shonanic, thujic and chaminic. Lignan components, such as hinokinin and hibalactone (savinin), have also been found.

RESULTS AND DISCUSSION

On continuing a study of the chemical constituents, the wood of *C. formosana* was collected in our campus and subjected to extraction with acetone. The combined extracts were concentrated and the residual contents separated on a silica gel column eluting with hexane–ethyl acetate gradients. After (−)-hibalactone **1** (R_f 0.30, hexane–acetone, 7:3) [4, 5], a novel lignan, namely (+)-calocedrin, was eluted (R_f 0.16). Calocedrin was recrystallized from ethanol, mp 187–188°, $[\alpha]_D^{25}$ +6° (*c* 0.9; acetone). The mass spectrum displayed the parent peak at *m/z* 368 and the base peak at *m/z* 135, ascribable to the 3,4-methylenedioxybenzyl fragment. The IR spectrum showed the presence of hydroxyl (3560 cm^{-1}), lactone (1745 cm^{-1}) and olefin (1640 cm^{-1}) groups. Analyses of



1 R = H
2 R = OH



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