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DIHYDROCHALCONES FROM *LINDERA UMBELLATA*

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Key Word Index—*Lindera umbellata*; Lauraceae; 2′,6′-dihydroxy-4′-methoxydihydrochalcone; 2′,4′,6′-trihydroxydihydrochalcone.

Abstract—Two dihydrochalcones, 2′,6′-dihydroxy-4′-methoxydihydrochalcone and 2′,4′,6′-trihydroxydihydrochalcone have been isolated from leaves of *Lindera umbellata*.

INTRODUCTION

The deciduous small tree *Lindera umbellata* Thunb. (Japanese name Kuromoji) is widely distributed in the mountains of Japan. This plant gives an essential oil, called Kuromoji oil, and its wood has been used in the manufacture of toothpicks in Japan. Many workers [1–10] have studied the essential oil of Kuromoji. There are many terpenes [1–7], a chalcone [8], phytosterols [9], and an alkaloid [10] in this plant. This paper describes for the first time the isolation of dihydrochalcones from the genus *Lindera* and from the Lauraceae.

RESULTS AND DISCUSSION

From the ethyl acetate-soluble fraction of the methanol extract of *Lindera Umbellata* compounds **1** and **2** were separated by silica gel column chromatography. Compound **1** was isolated as a solid, mp 174–175°, having the molecular formula $C_{16}H_{16}O_4$, high resolution MS (Found *m/z* 272.1188, required 272.1048). It gave a red colour with ethanolic ferric chloride and exhibited UV absorption bands at λ_{max}^{EtOH} 211 (sh), 225, 284, and 323 (sh) nm (with log ε: 4.14, 4.15, 4.23 and 3.50) and IR bands at $\nu_{max}^{CHCl_3}$ 3580 cm^{-1} (OH) and 1630 cm^{-1} (CO) in chloroform solution. The ^1H NMR spectrum (in acetone-d_6) showed the presence of two methylene protons (δ2.97 and 3.42, 2 × 2H, 2 × *t*, *J* = 8 Hz, C-α, and C-β), a methoxyl group (δ3.78, 3H, *s*, OMe) and aromatic protons (δ6.00, 2H, *s*, C-3′ and C-5′, and δ7.26, 5H, *s*, ArH). Acetylation of **1** gave a diacetate (**3**), whose ^1H NMR spectrum exhibited signals of C-3′ and C-5′ protons shifted downfield in the comparison with those in the spectrum of **1**.

All these data suggest that **1** is 2′,6′-dihydroxy-4′-methoxydihydrochalcone. This identification has been confirmed by direct comparison (mmp, MS, ^1H NMR and IR data) with a synthetic sample, which was prepared along with the dimethyl ether (**4**) by treatment of **2** with excess diazomethane. The isolation of this dihydrochalcone (**1**) has previously been reported from *Populus balsamifera* [11] and *Pityrogramma chrysophylla* var. *marginata* [12].

The mass spectrum of **2** revealed a molecular ion at *m/z* 258 $[M]^+$ corresponding to $C_{15}H_{14}O_4$, and the ^1H NMR spectrum (in acetone-d_6) showed similar signals to those of **1** except for the presence of a methoxyl group. Therefore, **2** must be the known 2′,4′,6′-trihydroxydihydrochalcone, which was established by direct comparison (mmp, MS, ^1H NMR and IR spectra) with a synthetic sample. This dihydrochalcone (**2**) has been reported from *Helichrysum tenuifolium* [13], and shown to have antimicrobial activity [14].

EXPERIMENTAL

Mps are uncorr. ^1H NMR (100 MHz) spectra were determined in Me_2CO-d_6. Chemical shifts were shown in ppm (δ) with TMS as internal standard. MS (70 eV) and the high resolution spectrum were recorded using direct insertion. UV spectra were taken in 98% EtOH.

Extraction and isolation. The MeOH extract of fresh leaves (0.9 kg) of *Lindera umbellata* collected at Asuke, Aichi prefecture, Japan, in July 1983, was divided into the *n*-hexane and EtOAc-soluble fraction (7.2 g). The EtOAc-soluble fraction was subjected to chromatography over silica gel. Elution with $CHCl_3$ furnished 2′,6′-dihydroxy-4′-methoxydihydrochalcone (**1**, 101 mg) and 2′,4′,6′-trihydroxydihydrochalcone (**2**, 65 mg).

2′,6′-Dihydroxy-4′-methoxydihydrochalcone (**1**). Colourless plates, mp 174–175° (from CH_2Cl_2), lit. 175° [12]. MS *m/z*: 272 $[M]^+$ (100%), 255, 253, 177, 167. The diacetate (**3**) was a colourless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770, 1620. ^1H NMR ($CDCl_3$): δ2.12 (6H, *s*, 2 × Ac), 2.98 (4H, *t*, *J* = 5 Hz, C-α, C-β), 3.77 (3H, *s*, OMe), 6.54 (2H, *s*, C-3′, C-5′), 7.20 (5H, *s*, ArH). MS *m/z*: 356 $[M]^+$, 313, 296, 272, 255, 224, 209, 182, 167 (100%), 140.

The trihydroxydihydrochalcone (**2**) (100 mg), synthesized according to the method below, was treated with an excess of ethereal CH_2N_2 soln at room temp for 15 min to provide a mixture of monomethylated (13 mg) and dimethylated product (26 mg), separated by prep. TLC over silica gel.

Monomethyl ether (**1**). Colourless plates, mp 172–174° (from CH_2Cl_2). TLC (silica gel; $CHCl_3$–Me_2CO, 40:1), R_f 0.33). The spectra (IR, ^1H NMR, and MS) of this sample were superimposable on those of the naturally occurring dihydrochalcone (**1**) and the no depression of mmp was shown.

Dimethyl ether (**4**). Colourless prisms, mp 102–104° (from CH_2Cl_2), lit. 105–107° [12]. TLC (silica gel; $CHCl_3$–Me_2CO, 40:1, R_f 0.80); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550, 1620. ^1H NMR ($CDCl_3$): δ2.97 (2H, *t*, *J* = 8 Hz, C-β), 3.31 (2H, *t*, *J* = 8 Hz, C-α), 3.81 (6H, *s*, 2 × OMe), 5.91 (1H, *d*, *J* = 2 Hz, C-3′ or C-5′), 6.07 (1H, *d*, *J* = 2 Hz, C-3′ or C-5′), 7.22 (5H, *br s*, ArH). MS *m/z*: 286 $[M]^+$, 268, 255, 182, 181 (100%), 167, 155, 154.

2',4',6'-Trihydroxydihydrochalcone (**2**). Colourless prisms, mp 134–135°, lit. 138–139° [14]. UV λ_{max}^{EtOH} nm (log ε): 212 (4.14), 222 (4.12), 286 (4.20), 326 (sh) (3.57). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300, 1630. ^1H NMR (Me_2CO-d_6): δ2.96 (2H, *t*, J = 8 Hz, C-β), 3.40 (2H, *t*, J = 8 Hz, C-α), 4.24 (3H, *br s*, 3 × OH), 6.00 (2H, *s*, C-3', C-5'), 7.24 (5H, *s*, ArH). MS *m/z*: 258 $[M]^+$, 240, 241, 214, 153 (100%), 126, 123.

The nitrobenzene soln of phloroglucinol, $AlCl_3$ and dihydrocinnamoyl chloride, freshly prepared from dihydrocinnamic acid and PCl_5, was heated at 60° for 1 hr, to yield **2**, mp 138–139°, as product. The synthetic compound was identical with the natural compound (mmp, ^1H NMR, IR and MS spectra).

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SEXANGULARETIN 3-GLUCOSIDE-7-RHAMNOSIDE FROM *GOSSYPIUM HIRSUTUM*

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Key Word Index—*Gossypium hirsutum*; Malvaceae; cotton; 3,5,7,4'-tetrahydroxy-8-methoxyflavone 3-glucoside-7-rhamnoside; sexangularetin; herbacetin 8-methyl ether.

Abstract—A new diglycosylated flavonol was isolated from immature flower buds of the cotton plant *Gossypium hirsutum*. The structure was determined to be the 3-glucoside-7-rhamnoside of 3,5,7,4'-tetrahydroxy-8-methoxyflavone.

INTRODUCTION

In a study on host plant resistance against insects in cotton, *Gossypium hirsutum* L., many phenolic materials present in plant tissue consumed by lepidopterous larvae have been shown to be significant growth-inhibiting agents towards these pests [1]. Among the several flavonoid glycosides obtained from extracts of immature cotton flower buds (squares) was a diglycosylated derivative of herbacetin 8-methyl ether (sexangularetin), the aglycone of which had previously been obtained from *Sedum sexangulare* [2] in which it occurs as the 7-rhamnoside-3-rutinoside [3]. The 3-glucoside and the 3-rutinoside have been reported as occurring in *Sorbus aucuparis* and *Fagonia arabica*, respectively [4]. Spectroscopic and degradative methods show that the new glycoside is 3,5,7,4'-tetrahydroxy-8-methoxyflavone 3-glucoside-7-rhamnoside (**1**).

RESULTS AND DISCUSSION

The new glycoside (**1**) isolated in *ca* 0.15% yield by Sephadex LH-20 chromatography (methanol) of material adsorbing to Amberlite XAD-2 non-ionic macroreticular resin from aqueous solution gave rhamnose, glucose and 3,5,7,4'-tetrahydroxy-8-methoxyflavone (**2**) upon enzymic hydrolysis using naringinase. The identification of **2** was facilitated by comparison of its UV and ^1H NMR spectra (Tables 1 and 2) with reported values [2, 5], which were in close agreement. Especially significant is the position of the ^1H NMR singlet assigned to H-6 (δ 6.07) which is at higher field than that expected for a H-8 signal (δ 6.3–6.5) [6] thereby confirming oxygenation at positions 5, 7 and 8 of the A-ring. The observed acetate-induced shift in band II of the UV spectrum of **2** indicates a free 7-hydroxyl while the lack of a corresponding borate shift shows that no *ortho*-dihydroxy system is present. Therefore the