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PHENYLPROPANOIDS FROM *ARALIA BIPINNATA*

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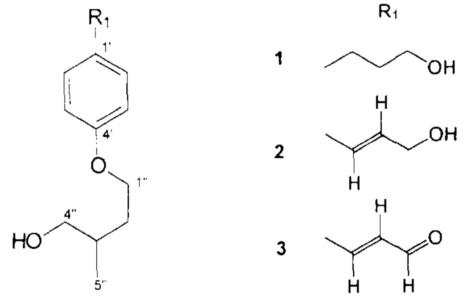
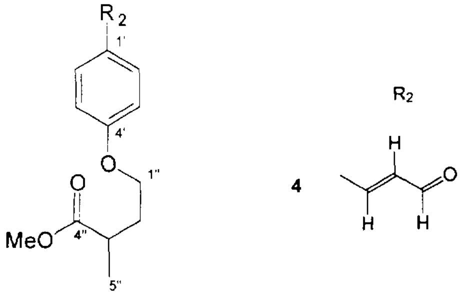
Key Word Index—*Aralia bipinnata*; Araliaceae; (−)-4′-(4″-hydroxy-3″-methylbutyloxy)-3-phenylpropenol; (+)-4′-(4″-hydroxy-3″-methylbutyloxy)-3-phenylpropenal; (+)-4′-(4″-methoxy-3″-methyl-4″-oxobutyloxy)-3-phenylpropenal; coumarins.

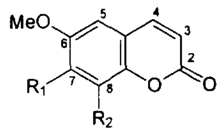
Abstract—Three new compounds, (−)-4′-(4″-hydroxy-3″-methylbutyloxy)-3-phenylpropenol, (+)-4′-(4″-hydroxy-3″-methylbutyloxy)-3-phenylpropenal and (+)-4′-(4″-methoxy-3″-methyl-4″-oxobutyloxy)-3-phenylpropenal were isolated, together with (−)-4′-(4″-hydroxy-3″-methylbutyloxy)-3-phenylpropanol, isofraxidin, scoparone and 6,7,8-trimethoxycoumarin, from the woody parts of *Aralia bipinnata*.

INTRODUCTION

Aralia bipinnata is a small diciduous tree that grows in deforested and sunny areas in Taiwan [1]. In previous work we reported the isolation of nine known compounds by silica gel column chromatography [2]. In this report, the constituents of the woody parts of *Aralia bipinnata* were separated by semi-preparative HPLC. We have isolated and identified three coumarins and four phenylpropanoids, three of which, (−)-4′-(4″-hydroxy-3″-methylbutyloxy)-3-phenylpropenol (**2**), (+)-4′-(4″-hydroxy-3″-methylbutyloxy)-3-phenylpropenal (**3**) and (+)-4′-(4″-methoxy-3″-methyl-4″-oxobutyloxy)-3-phenylpropenal (**4**) are new compounds.







	R1	R2
5	OMe	OMe
6	OH	OMe
7	OMe	H

RESULTS AND DISCUSSION

Compound **1** was fully characterized as (−)-4′-(4″-hydroxy-3″-methylbutyloxy)-3-phenylpropanol [3] by comparison of spectral properties (mass spectrum, UV, IR, ^{1}H NMR) with those of an authentic sample.

The UV and IR spectra of **2**–**4** indicated these compounds to be aromatic in nature. Their ^{1}H NMR spectra showed AB doublets with $J = 8.8$ Hz in the aromatic region suggesting the presence of a 1,4-disubstituted benzene ring. In the ^{1}H NMR spectrum of **2** and **3**, the presence of a (4″-hydroxy-3″-methylbutyloxy)phenyl moiety was confirmed by comparison with that of compound **1**.

The remaining signals in the ^{1}H NMR spectrum of **2**, consisted of two doublets and one double triplet suggesting the presence of a $-CH{=}CH{-}CH_2OH$ (*E*-form) side-chain. NOEs were observed between H-3′, 5′/H-1″

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Table 1. ^{1}H NMR data for compounds **24** (400 MHz, $CDCl_3$, TMS as int. standard, coupling constants (*J*) in Hz)

Proton	**2**	**3**	**4**
H-1	4.31, *d*, *J* = 5.8	9.65, *d*, *J* = 7.8	9.65, *d*, *J* = 7.8
H-2	6.25, *dt*, *J* = 15.6, 5.8	6.61, *dd*, *J* = 16.1, 7.8	6.60, *dd*, *J* = 15.6, 7.8
H-3	6.56, *d*, *J* = 15.6	7.41, *d*, *J* = 16.1	7.41, *d*, *J* = 15.6
H-2′,6′	7.33, *d*, *J* = 8.8	7.51, *d*, *J* = 8.8	7.50, *d*, *J* = 8.8
H-3′,5′	6.86, *d*, *J* = 8.8	6.93, *d*, *J* = 8.8	6.91, *d*, *J* = 8.8
H-1″	4.08, *m*	4.11, *m*	4.05, *m*
H-2″	1.72, 1.95, *m*	1.72, 1.95, *m*	1.91, 2.19, *m*
H-3″	1.92, *m*	1.92, *m*	2.74, *m*
H-4″	3.57, *d*, *J* = 5.4	3.65, *d*, *J* = 5.3	—
H-5″	1.01, *d*, *J* = 6.8	1.01, *d*, *J* = 6.8	1.25, *d*, *J* = 6.8
–OMe	–	–	3.69, *s*

and H-2′, 6′/H-3. The proposed gross structure was unambiguously confirmed by ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY experiments. From the above data, **2** was characterized as (−)-4′-(4″-hydroxy-3″-methylbutyloxy)-3-phenylpropenol.

The remaining signals in the ^{1}H NMR spectrum of **3**, consisted of two doublets and one double doublet suggesting the presence of a –CH=CH–CHO (*E*-form) side-chain; NOEs were observed between H-3′, 5′/H-1″ and H-2′, 6′/H-3. From the above data, **3** was characterized as (+)-4′-(4″-hydroxy-3″-methylbutyoxy)-3-phenylpropenal.

In the ^{1}H NMR spectrum of **4**, a singlet at δ3.69 (Me) coupled with a quartet at δ176.5 in the ^{13}C NMR and absorption in the IR spectrum at 1732 cm^{-1}, indicated the presence of a methoxy carbonyl moiety. Comparison of the ^{1}H NMR spectrum of **4** with that of **3** revealed that the signal assignable to H-3″ was shifted by + 0.82 ppm, suggesting the location of the methoxy carbonyl moiety on the C-3″ of **3**. NOEs were observed between H-3′, 5′/H-1″ and H-2′, 6′/H-3. From the above data, **4** was characterized as (+)-4-(4″-methoxy-3″-methyl-4″-oxobutyloxy)-3-phenylpropenal.

Compounds **5**–**7** were identified as 6,7,8-trimethoxycoumarin [4, 5], isofraxidin [6, 7] and scoparone [5], by comparison of spectral properties with those of authentic samples.

Table 2. ^{13}C NMR data for compounds **1**–**4** (100 MHz, $CDCl_3$, TMS as int. standard)

Carbon	**1**	**2**	**3**	**4**
C-1	61.9 *t*	63.6 *t*	193.6 *d*	193.6 *d*
C-2	34.2 *t*	126.3 *d*	126.5 *d*	126.5 *d*
C-3	29.6 *t*	130.7 *d*	152.6 *d*	152.6 *d*
C-1′	133.9 *s*	129.5 *s*	126.8 *s*	126.8 *s*
C-2′	129.2 *d*	127.6 *d*	130.3 *d*	130.3 *d*
C-3′	114.5 *d*	114.5 *d*	115.0 *d*	115.0 *d*
C-4′	156.8 *s*	158.4 *s*	161.5 *s*	161.4 *s*
C-5′	114.5 *d*	114.5 *d*	115.0 *d*	115.0 *d*
C-6′	129.2 *d*	127.6 *d*	130.3 *d*	130.3 *d*
C-1″	66.1 *t*	66.2 *t*	66.4 *t*	65.8 *t*
C-2″	32.8 *t*	32.7 *t*	32.6 *t*	32.8 *t*
C-3″	33.1 *d*	33.1 *d*	33.1 *d*	36.3 *d*
C-4″	67.7 *t*	67.8 *t*	67.9 *t*	176.5 *q*
C-5″	16.7 *q*	16.7 *q*	16.7 *q*	17.3 *s*
–OMe	—	—	—	51.7 *q*

EXPERIMENTAL

General. Mps: uncorr. NMR: 400 MHz, $CDCl_3$, TMS as int. standard. MS: 70 eV. IR: KBr. HPLC was performed on Si 60 (Waters, 6 μm, 7.8 × 300 nm) column using EtOAc–hexane and EtOAc–$CHCl_3$ as solvent systems and employing a RI detector.

Extraction and separation. Woody parts of *A. bipinnata* (3 kg) were extracted with MeOH (10 l × 3). The extracts were passed through a short column of activated charcoal. The filtrate was concd and the residue (31.5 g) coated on to silica gel (50 g) and subjected to chromatography on a silica gel (500 g) column by elution with gradients of EtOAc and hexane. Appropriate portions were combined to give six frs A–F in ascending order of polarity. Fr. B on HPLC (silica gel, EtOAc–hexane, 1:4) gave 17 mg of (**4**), as well as undefined material. Fr. D on HPLC (silica gel, EtOAc–hexane, 7:13) gave 8 mg of scoparone (**7**) and 35 mg of (**3**), as well as undefined material. Fr. E on HPLC (silica gel, EtOAc–$CHCl_3$, 3:2) gave 7 mg of 6,7,8-trimethoxycoumarin (**5**), 5 mg of isofraxidin (**6**), 60 mg of (−)-4′-(4″-hydroxy-3″-methylbutyloxy)-3-phenylpropanol (**1**) and 49 mg of (**2**), as well as undefined material. Known compounds were identified by comparison of spectral properties with those of authentic samples.

(−)-4′-(4″-*Hydroxy-3″-methylbutyloxy*)-3-*phenylpropanol* (**1**). $[\alpha]_D^{24}$ − 9.2° (MeOH; *c* 0.22). ^{13}C NMR: see Table 2.

(−)-4′-(4″-*Hydroxy-3″-methylbutyloxy*)-3-*phenylpropenol* (**2**). Solid. $[\alpha]_D^{24}$ − 5.1° (MeOH; *c* 0.21). UV λ_{max}^{MeOH} nm (log ε): 280 (3.79). IR ν_{max} cm^{-1}: 3385 (OH), 1612, 1512, 1464, 1246, 1174, 1016. HRMS *m/z*: 236. 1404 $[M]^+$ (calc. 236.1412, $C_{14}H_{20}O_3$). MS *m/z* (rel. int.): 236

$[M]^+$ (30), 150 (72), 107 (100), 94 (51), 77 (12). ^1H and ^{13}C NMR: see Tables 1 and 2.

(+)-4′-(4″-*Hydroxy*-3″-*methylbutyloxy*)-3-*phenylpropenal* (**3**). Solid. $[\alpha]_D^{24}$ 5.7° (MeOH; *c* 0.15). UV λ_{max}^{MeOH} nm (log ε): 318 (4.06). IR ν_{max} cm^{-1}: 3412 (OH), 1668, (CHO), 1601, 1512, 1471, 1251, 1174, 1016. HRMS *m/z*: 234.1263 $[M]^+$ (calc. 234.1256, $C_{14}H_{18}O_3$). MS *m/z* (rel. int.): 234 $[M]^+$ (28), 147 (95), 131 (81), 119 (100), 91 (17). ^1H and ^{13}C NMR: see Tables 1 and 2.

(+)-4′-(4″-*Methoxy*-3″-*methyl*-4″-*oxobutyloxy*)-3-*phenylpropenal* (**4**). Solid. $[\alpha]_D^{24}$ 29.4° (MeOH; *c* 0.07). UV λ_{max}^{MeOH} nm (log ε): 317 (4.01). IR ν_{max} cm^{-1}: 1732 (C(=O)O), 1674, (CHO), 1601, 1512, 1462, 1250, 1175. HRMS *m/z*: 262.1188 $[M]^+$ (calc. 262.1205, $C_{15}H_{18}O_4$). MS *m/z* (rel. int.): 262 $[M]^+$ (18), 213 (65), 147 (23), 115 (100). ^1H and ^{13}C NMR: see Tables 1 and 2.

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