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A RESVERATROL DIMER FROM *PARTHENOCISSUS TRICUSPIDATA*

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Key Word Index—*Parthenocissus tricuspidata*; Vitaceae; resveratrol dimer; isoampelopsin F.

Abstract—From the stem wood of *Parthenocissus tricuspidata*, four stilbene derivatives were isolated. Three known structures were characterized as resveratrol, ε-viniferin and pallidol, and a new resveratrol dimer was confirmed to be a stereochemical isomer of ampelopsin F, isoampelopsin F, by spectroscopic analysis including 2D NMR.

INTRODUCTION

In our chemosystematic study of *Sophora* (Leguminosae), oligostilbenes were shown to be chemotaxonomic markers in two species (*S. leachiana* Peck. [1–4] and *S. davidii* (Franch.) Skeels [5–7]. Generally, resveratrol (3, 5, 4′-trihydroxystilbene) oligomers have been isolated from Dipterocarpaceae, Gnetaceae, Welwitschiaceae, Cyperaceae, Leguminsae, Umberiferae, and in particular from Vitaceae [8–18]. In relation to the stilbenoids in *Sophora*, our attention was drawn to oligostilbenoids in Vitaceaeous plants which are classified to 11 genera including about 700 species. As chemical constituents of *Parthenocissus tricuspidata* (Siebold et Zucc.) Planch. (Vitaceae), quercetin glycosides from leaves [19] and a new resveratrol dimer with a tetrahydrofuran ring, tricuspidatol A [20], from stem wood have been reported. We describe in the present paper another four stilbenoids including a new one in the stem wood of *P. tricuspidata*.

RESULTS AND DISCUSSION

Stem wood of *P. tricuspidata* was extracted successively with acetone and MeOH at room temperature. The acetone extract yielded three compounds which were identified as resveratrol, (±)ε-viniferin and (−)-pallidol, respectively, by analysis of the spectral data and by comparison with authentic samples, and an unknown compound (**1**).

Compound **1** positive Gibbs reaction (on TLC), gave a molecular ion at *m/z* 453 $[M-H]^-$ which corresponds to $C_{28}H_{22}O_6$. In the ^1H NMR spectrum, the presence of a set of *ortho*-coupled protons [δ 6.64, 6.99 (2H each, *d*, *J* = 8.5 Hz)], two sets of *meta*-coupled protons [δ 5.24, 6.04 (1H each, *d*, *J* = 2.0 Hz) and 6.14, 6.46 (1H each, *d*, *J* = 2.5 Hz)], four protons each in a double-doublet [δ 5.86 (*dd*, *J* = 2.4, 8.5 Hz), 6.39 (*dd*, *J* = 2.7, 8.5 Hz), 6.81 (*dd*, *J* = 2.7, 8.3 Hz) and 7.34 (*dd*, *J* = 5.8 Hz)], two methine protons [δ 3.62 and 4.07 (1H each *br s*)] and six phenolic hydroxyl groups [δ 6.60, 7.68, 7.86, 8.06, 8.07 and 8.10 (1H each, *s*] indicated that **1** was a resveratrol dimer. All the protonated carbons were assigned by CH COSY (Table 1). One of the *meta*-coupled protons (δ 5.24) was correlated with two carbons (δ 126.1 and 157.1), and the other was correlated with four carbons (δ 126.1, 144.7, 152.7 and 157.1) in the COLOC spectrum (Fig 1). This indicated that **1** had a 3,5-dioxo-1,2-disubstituted benzene ring which corresponded to a 3,5-dihydroxy-1,2-disubstituted benzyl moiety as the oxygenated carbons at δ 152.7 and 157.1 correlated to the hydroxyl groups at δ 7.86 and 7.68. Other *meta*-coupled protons at δ 6.46 and 6.14 were also attributed the 3,5-dihydroxy-1,2-disubstituted benzyl moiety after analysis of the correlations observed in the COLOC spectrum. The different chemical shifts of the four aromatic protons was attributed to the fact that the A1 ring unit was fixed in the structure. CH long range correlations between two methines (δ 3.43 and 4.54) and three benzene units (A1, A2 and B2) were observed. The methine proton (δ 3.62) was correlated with H-3 and H-5 on ring B1 in the HH long range COSY spectrum, and H-3 and H-5 caused an interaction in the phase sensitive NOESY (PSNOESY) spectrum, indicating that the proton was attributable to a benzyl methine and had a long range correlation in the COLOC spectrum through ^3J (Fig 1). Another methine (δ 4.07) was correlated to the carbon on rings

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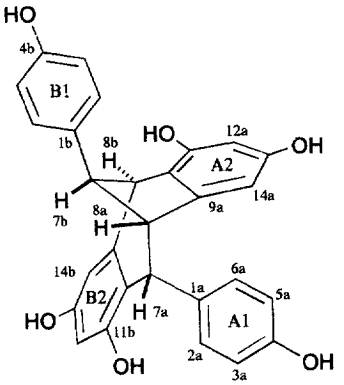

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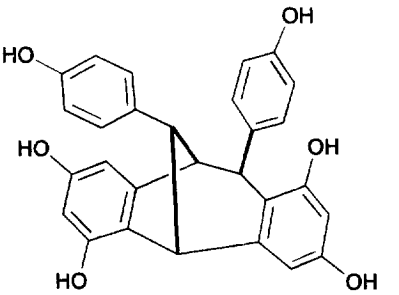

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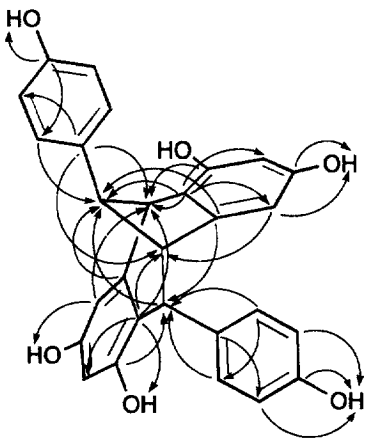

Fig. 1.

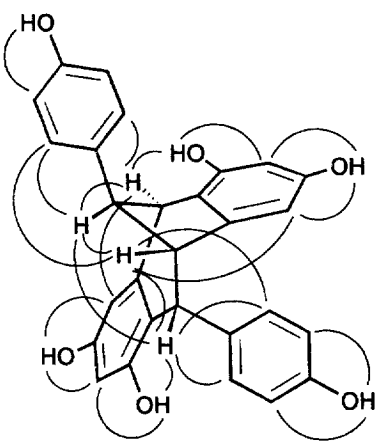

Fig. 2.

A2 and B2. In the PSNOEY spectrum, H-7a, H-8a and H-7b showed interactions, indicating that the protons were oriented in the *cis*-configuration. A NOE interaction was also observed between H-8b and H-14b. Consequently, the relative stereochemistry was concluded to be *rel*-(7a*R*, 8a*S*,7b*R*,8b*R*), and the plain structure was the same as that of amelopsin F (**2**), ([α]D +14°), isolated from *A. brevipedunculata* var. *hancei* [17]. All benzyl methine protons in ampelopsin F were observed as broad singlets in the ^{1}H NMR spectrum, while H-7a and 8a in **1** were doublets (J = 5.8 Hz). The specific rotation of **1**, [α]D −56.7°, was different from that of ampelopsin F. Therefore, **1** was one of the diastereomers of ampelopsin F, named isoampelopsin F.

EXPERIMENTAL

Plant material

Stem woods of *Parthenocissus tricuspidata* (Siebold et Zucc.) Planch. were collected in June 1995, at Ichinomiya City, Japan and the voucher specimens were deposited at the Herbarium of Gifu Pharmaceutical University.

Isolation of 1–4

The air-dried and ground stem woods of *P. tricuspidata* (950 g) were extracted with Me_2CO (3 × 3) and MeOH (3 × 3) at room temp., respectively. After concentration, the Me_2CO extract (17 g) was subjected to silica gel CC eluted a $CHCl_3$–MeOH gradient system and divided to 14 frs. Fr. 3 ($CHCl_3$–MeOH, 8:1) was further chromatographed on silica gel eluted with ($CHCl_3$–MeOH, 10:1) to give resveratrol (5 mg). Fr. 6 ($CHCl_3$–MeOH, 6:1) was also subjected to Sephadex LH20 CC (MeOH) to give seven fractions (Fr. 6-1–6-7). Fr. 6-5 was further purified by prep TLC ($CHCl_3$–MeOH, 8:1) to give (±)ε-viniferin (5 mg) and (−)-pallidol (8 mg), respectively. Fr. 4 was purified by vacuum liquid chromatography ($CHCl_3$–MeOH, 10:1) to give **1** (8 mg).

Compound 1 *(isoampelopsin F)*

A pale brownish solid. Negative ion FABMS *m/z*: 453 $[M-H]^-$; [α]D −56.7° (MeOH, c = 0.23); UV λ_{MeOH}^{max} 232, 279 nm; ^{1}H NMR (400 MHz, Me_2CO-d_6) δ: 3.43 (1H, *br d*, J = 5.8 Hz, H-8a), 3.62 (1H, *br s*,

H-7b), 4.07 (1H, *br s*, H-8b), 4.54 (1H, *d*, $J = 5.8$ Hz, H-7a), 5.24 (1H, *d*, $J = 2.0$H, H-14a), 5.86 (1H, *dd*, $J = 2.4$, 8.5 Hz, H-2a), 6.04 (1H, *d*, $J = 2.0$ Hz, H-12a), 6.14 (1H, *d*, $J = 2.5$ Hz, H-12b),6.39 (1H, *dd*, $J = 2.7$, 8.5 Hz, H-3a), 6.46 (1H, *d*, $J = 2.5$ Hz, H-14b), 6.60 (1H, *s*, C-11b-OH), 6.64 (2H, *d*, $J = 8.5$ Hz, H-3b, 5b), 6.81 (1H, *dd*, $J = 2.7$, 8.3 Hz, H-5a), 6.99 (2H, *d*, $J = 8.5$ Hz, H-2b, 6b), 7.68 (1H, *s*, C-13a-OH), 7.86 (1H, *s*, C-11a-OH), 8.06 (1H, *s*, C-13b-OH), 8.06 (1H, *s*, C-13b-OH), 8.07 (1H, *s*, C-4a-OH), 8.10 (1H, *s*, C-4b-OH); ^{13}C NMR (100 MHz, Me_2CO-d_6) δ: 46.3 (C-7a), 50.0 (C-8b) 56.6 (C-8a), 58.6 (C-7b), 101.8 (C-12a), 102.0 (C-12b), 106.0 (C-14b), 106.8 (C-14a), 114.3 (C-10b), 114.6 (C-3a), 115.2 (C-5a), 115.5 (C-3b, 5b), 126.1 (C-10a), 129.2 (C-2b, 6b), 129.9 (C-2a), 130.2 (C-6a), 134.7 (C-la), 135.3 (C-1b), 144.7 (C-9a), 147.2 (C-9b), 152.7 (C-11a), 156.1 (C-4a, 4b), 156.8 (C-13b), 157.1 (C-13a), 157.6 (C-11b).

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