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Synthesis of Amurensin H, a New Resveratrol Dimer from the Roots of *Vitis Amurensis*

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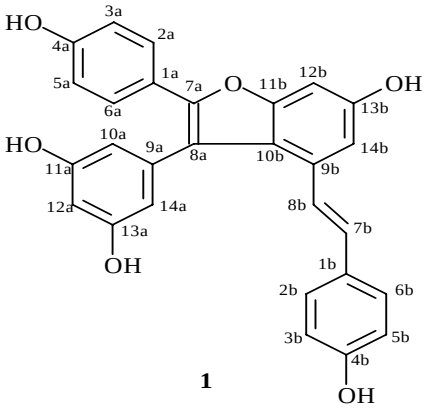
Abstract: Amurensin H**(1)** is a new resveratrol dimer isolated from the roots of *Vitis amurensis* Rupr. Its structure was determined by spectroscopic methods. It was synthesized from resveratrol with an oxidative coupling reaction as a key step.

Keywords: Synthesis, amurensin H, *Vitis amurensis*, resveratrol, oxidative coupling reaction.

Besides oligostilbenes we reported before[1], a new minor resveratrol dimer having a benzofuran moiety, amurensin H**(1)**, was isolated from the roots of *Vitis amurensis* Rupr. We have synthesized amurensin H in order to afford more samples for bioactivity test. In this paper, we report the structural determination and synthesis of amurensin H from resveratrol.



1

Amurensin H**(1)** was obtained as pale yellow amorphous powder, exhibiting strong blue fluorescence under UV-254 light. Its molecular formula of $C_{28}H_{20}O_6$ was given by HREI-MS *m/z* 452.1246 $[M]^+$ ($C_{28}H_{20}O_6$ requires 452.1260). Along with its ^1H and ^{13}C-NMR (**Table 1**), **1** seems to be a resveratrol dimer. The ^1H-NMR spectrum exhibited signals for two 4-hydroxybenzene groups at δ 7.43 (2H, d, J=8.7Hz) and 6.74

(2H, d, J=8.7Hz), δ 7.01 (2H, d, J=8.7Hz) and 6.69 (2H, d, J=8.7Hz); one 3,5-dihydroxy-benzene group at δ 6.43 (2H, d, J=2.1Hz) and 6.53 (1H, t, J=2.1Hz); two meta-coupled protons at δ 7.07 (1H, d, J=2.1Hz) and 6.85 (1H, d, J=2.1Hz); two *trans* olefinic protons at δ 6.98 (1H, d, J=16.8Hz) and 6.89 (1H, d, J=16.8Hz). Comparing the ^{1}H and ^{13}C-NMR data of **1** with those of ε-viniferin[2], it was found that they had similar patterns except that ε-viniferin showed more signals for two aliphatic protons of a dihydrobenzofuran moiety than **1** in ^{1}H-NMR spectrum and **1** had two more quaternary carbons at δ 149.9 and 117.0 than ε-viniferin in ^{13}C-NMR spectrum. Therefore we concluded that **1** should be a didehydro-ε-viniferin and has the structure as shown in the illustration, which was further confirmed by HMBC spectrum (**Figure 1**).

Figure 1. C-H long-range correlations in HMBC spectrum of **1**

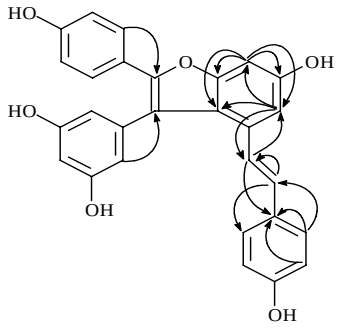


Table 1. ^{1}H and ^{13}C NMR spectral data for **1** [§]

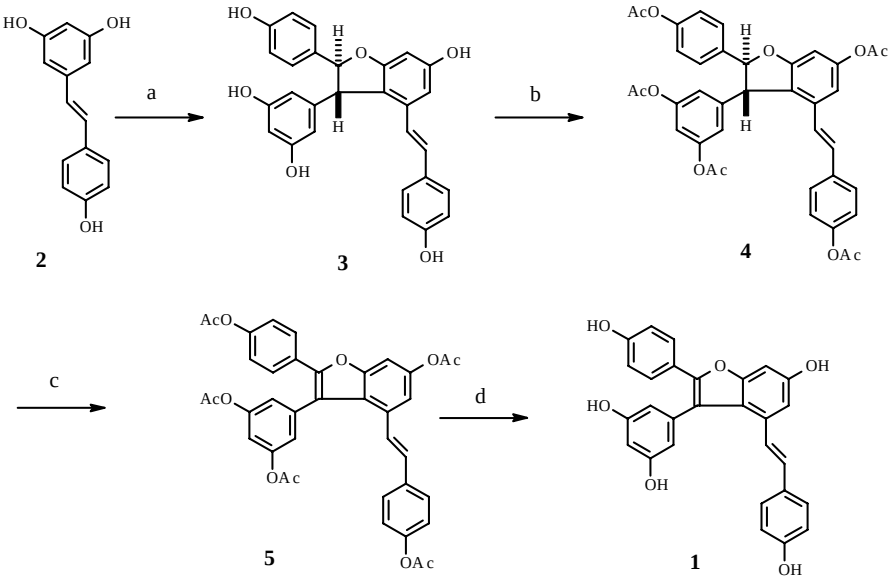
No.	^{1}H	^{13}C	No.	^{1}H	^{13}C
1a		123.3	2(6)b	7.01 d (8.7)	128.6
2(6)a	7.43 d (8.7)	128.2	3(5)b	6.69 d (8.7)	116.1
3(5)a	6.74 d (8.7)	116.0	4b		157.9
4a		158.1	7b	6.89 d (16.8)	129.0
7a		149.9	8b	6.98 d (16.8)	122.7
8a		117.0	9b		132.8
9a		138.0	10b		122.0
10(14)a	6.43 d (2.1)	109.7	11b		155.8
11(13)a		160.3	12b	6.85 d (2.1)	97.2
12a	6.53 t (2.1)	102.9	13b		156.4
1b		130.0	14b	7.07 d (2.1)	107.3

[§] All assignments were confirmed by ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, NOESY and HMBC spectra measured in CD_3COCD_3 at 300 and 75 MHz for ^{1}H and ^{13}C-NMR respectively.

In order to get more samples for bioactivity test, **1** was synthesized from resveratrol (**scheme 1**). Resveratrol was dimerized with $FeCl_3$ in methanol to give ε-viniferin **3** at room temperature; **3** was acetylated with acetic anhydride and pyridine to give **4** which was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[3] to afford **5**, and **5** was treated with K_2CO_3 in methanol to give **1** which was unambiguously identical with

natural amurensin H in all respects.

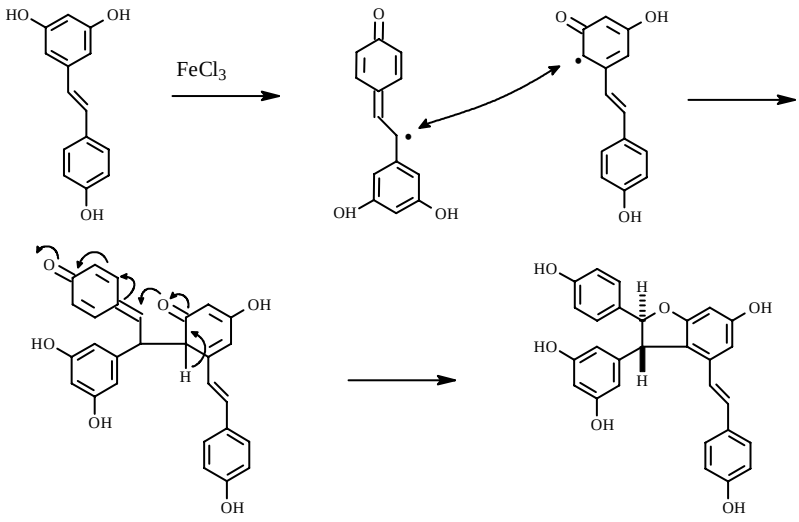
Scheme 1.



a. $FeCl_3$, MeOH b. $(Ac)_2O$, pyridine c. DDQ, 1,4-dioxane, refluxed d. K_2CO_3, MeOH

The dimerisation of resveratrol was the key step to form amurensin H, the mechanism of the oxidative coupling reaction was shown in **Scheme 2**.

Scheme 2.



Longcake and Pryce[4] studied the dimerisation of resveratrol by oxidative coupling reaction, but they failed to obtain ε-viniferin. Fortunately, we obtained ε-viniferin successfully by treating resveratrol with $FeCl_3$[5], which might be the similar reaction to the biosynthetic route of oligostilbenes.

References

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