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Four Novel Oligostilbenes from the Roots of *Vitis amurensis*

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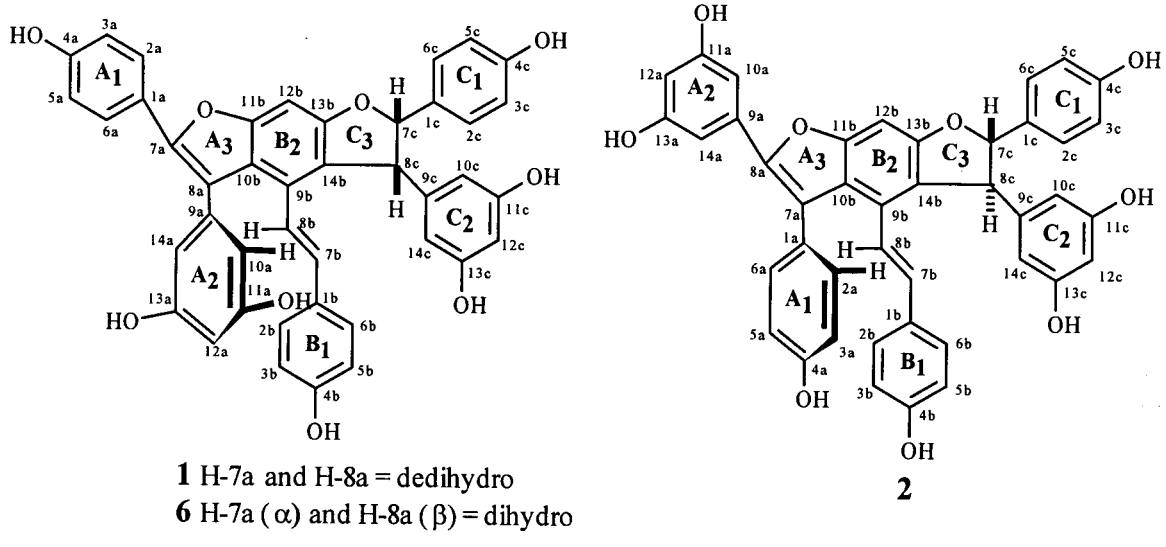
Abstract—Two novel resveratrol trimers, amurensins C (**1**), D (**2**), and two novel resveratrol pentamers, amurensins E (**3**), F (**4**) were isolated from the roots of *Vitis amurensis* Rupr. Their structures and relative or absolute configurations were determined by means of spectroscopic evidence, especially HMBC and NOE experiments. **2**, **3** and **4** are new types of resveratrol oligomers and are reported here for the first time. The pharmacological activities on anti-inflammation of all amurensins have been tested. Among them, compound **4** showed potent inhibition on biosynthesis of leukotriene B_4 (LTB_4).

Introduction

More and more attention has been focused on naturally occurring oligostilbenes because they have been found to have multi-faceted bioactivities. In 1993, Sotheeswaran and Pasupathy[1] divided naturally occurring oligostilbenes into two groups. Group A possessed at least one five-membered oxa-cyclic ring, while group B did not contain the five-membered heterocycle. They proposed that all oligostilbenes of group A were formed via the resveratrol dimer ϵ-viniferin (**8**). The heterocyclic rings of group A in the reported structures were generally dihydrobenzofuran types except for anigopreissin,[2] a resveratrol dimer with a completely unsaturated benzofuran system. Our research on bioactive oligostilbenes from the roots of *Vitis amurensis* resulted in the isolation of four novel oligostilbenes (**1**–**4**) besides amurensins A (**5**) and B (**6**) reported earlier (Scheme 1).[3] They were the first resveratrol trimers and pentamers with an unsaturated benzofuran ring. In the structures of **2**–**4**, the connections of the two resveratrol units were different from **8**. The positions of the 4-hydroxybenzene group (ring A_1) and the 3,5-dihydroxybenzene group (ring A_2) were interchanged. Compounds **2**–**4** are new types of resveratrol oligomers, and these might have biosynthetic implications for the research on naturally occurring oligostilbenes. Since the benzene group at the β-position of the



Scheme 1.

Keywords: *Vitis amurensis*; Vitaceae; amurensins C, D, E, F; oligostilbene; resveratrol; trimer; pentamer; benzofuran moiety.
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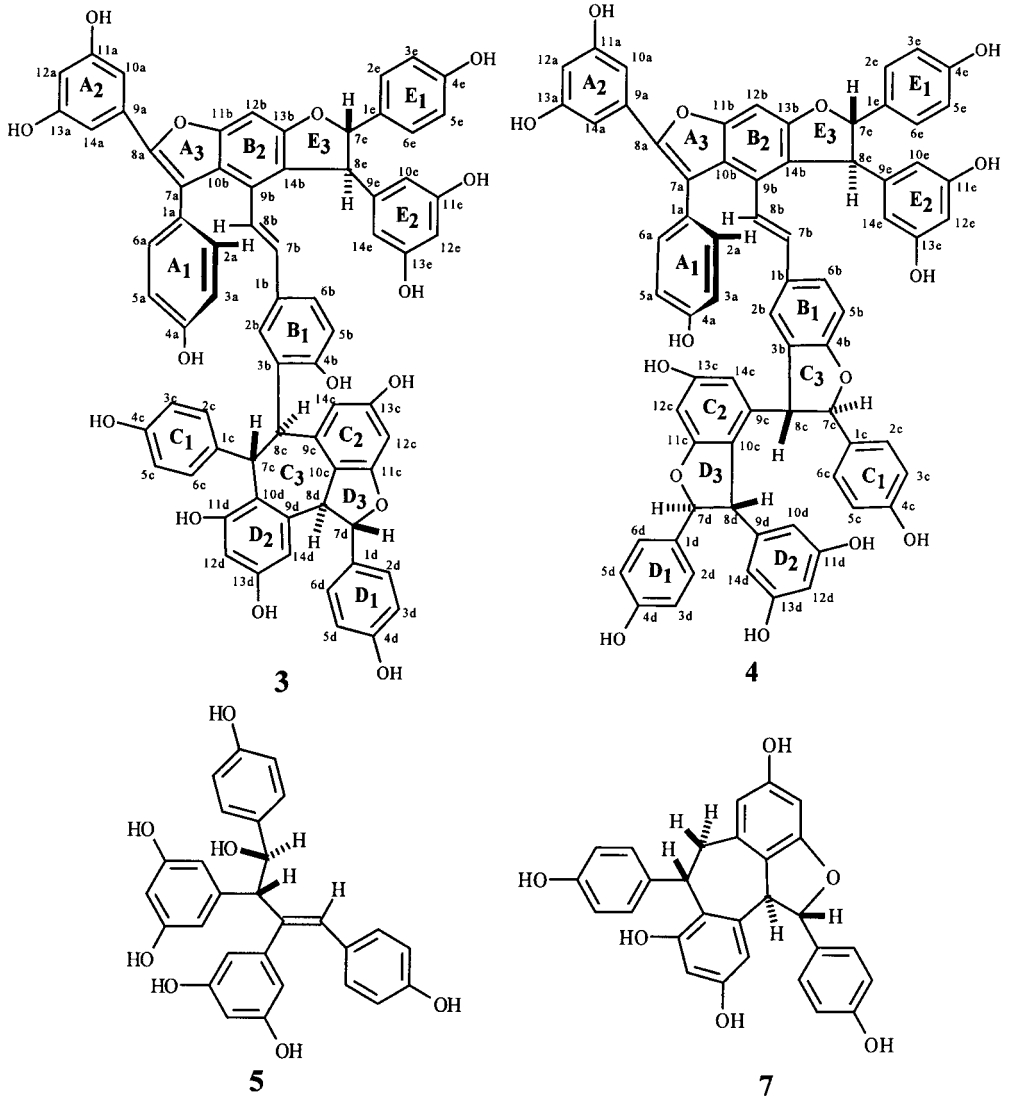


Scheme 2.

furan ring in each structure cannot rotate freely, some aromatic protons appeared as broad singlets or broad doublets in their ^{1}H NMR spectra at room temperature. The ^{1}H NMR features of **1**–**4** at different temperatures were studied as illustrated in Fig. 5 (Scheme 2).

Results and Discussion

Amurensin C (**1**) was obtained as a brown amorphous powder, which exhibited a strong yellow fluorescence under UV-254 light, $[\alpha]_D^{18}=+48.7°$ (*c* 0.079, MeOH). A molecular formula of $C_{42}H_{30}O_9$ deduced from the HRFAB-MS *m*/*z* 679.1956 $[MH]^+$ ($C_{42}H_{31}O_9$ requires 679.1968) together with its ^{1}H NMR spectral data suggested that **1** could be a resveratrol trimer. The UV spectrum (λ_{max} 340 nm) revealed the presence of a strong conjugated system in the structure. The ^{1}H NMR spectrum exhibited signals for three 4-hydroxybenzene moieties at δ 7.46 (2H, d, *J*=8.7 Hz) and 6.78 (2H, d, *J*=8.7 Hz), δ 7.06 (2H, d, *J*=8.5 Hz) and 6.63 (2H, d, *J*=8.5 Hz), δ 6.76 (2H, d, *J*=8.6 Hz) and 6.63 (2H, d, *J*=8.6 Hz); two 3,5-dihydroxybenzene moieties at δ 6.37 (1H, br s), 6.48 (1H, br s) and 6.53 (1H, t, *J*=2.2 Hz), δ 5.81 (2H, d, *J*=2.1 Hz) and 5.99 (1H, t, *J*=2.1 Hz); two aliphatic protons of a dihydrobenzofuran ring at δ 5.87 (1H, d, *J*=7.3 Hz) and 4.72 (1H, d, *J*=7.3 Hz); two *trans* olefinic protons at δ 6.67 (1H, d, *J*=16.7 Hz) and 6.95 (1H, d, *J*=16.7 Hz) and an aromatic proton at δ 7.05 (1H, s). The ^{13}C NMR spectrum exhibited the presence of two aliphatic carbons (δ 90.6 and 54.4) and two olefinic carbons (δ 133.3 and 121.8) besides 38 aromatic carbons. The ^{1}H and ^{13}C NMR features were similar to those of amurensin B[3] except that **1** showed only two aliphatic proton signals for one dihydrobenzofuran moiety in the ^{1}H NMR spectrum and two quaternary carbon signals more than amurensin B in the ^{13}C NMR spectrum, which meant that one dihydrobenzofuran moiety was changed into an unsaturated benzofuran moiety in **1**, therefore the signals of H-2(6)a were shifted to lower field at δ 7.46. Thus the planar structure of amurensin C is as shown in **1**, which was confirmed by long-range correlations in HMBC spectrum (Fig. 1a).

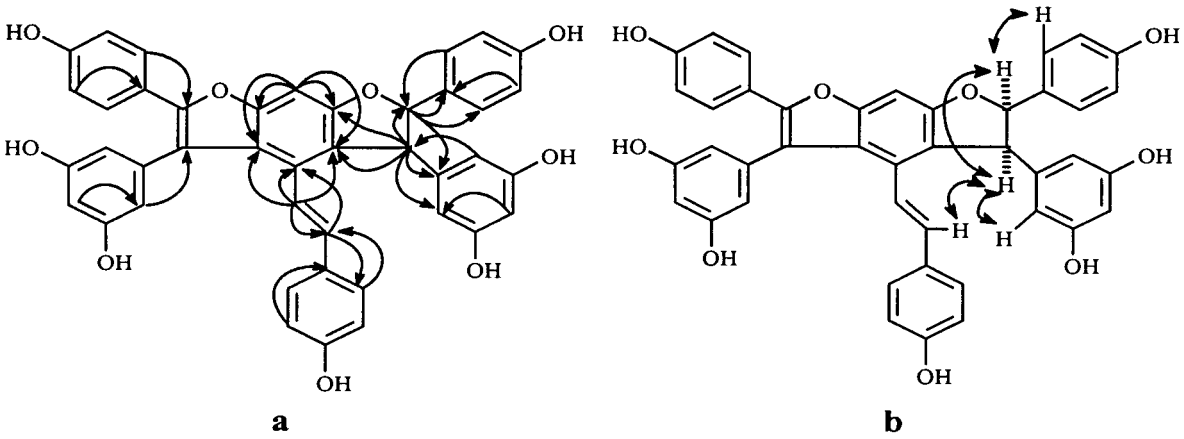


Figure 1. Long-range CH correlations in the HMBC spectrum (a) and significant NOE interactions in the NOESY spectrum (b) of **1**.

In order to clarify the stereochemistry of H-7c and H-8c, a NOESY (Fig. 1b) experiment was carried out. The NOEs between H-7c and H-8c, H-7c and H-2(6)c, H-8c and H-10(14)c indicated a *cis* orientation of ring C_1 and C_2. By consideration of the (7a*S*, 8a*S*) absolute configuration of (+)-ϵ-viniferin[4] and (7a*R*, 8a*R*) absolute configuration of (−)-ϵ-viniferin,[5] the relative configurations of C-7c and C-8c were determined to be *rel*-(7c*S*, 8c*R*).

Amurensin D (**2**) was obtained as a pale green amorphous powder, which exhibited a strong blue fluorescence under UV-254 light, $[\alpha]_D^{18}=+185.5°$ (*c* 0.059, MeOH). Its HRFAB-MS *m/z* 679.1965 $[MH]^+$ ($C_{42}H_{31}O_9$ requires 679.1968) gave a molecular formula of $C_{42}H_{30}O_9$, which in combination with ^{1}H NMR suggested that **2** was a resveratrol trimer. The UV spectrum was similar to that of **1**. The ^{1}H NMR spectrum also exhibited signals for three 4-hydroxybenzene moieties at δ 7.22 (2H, br d, J=8.3 Hz) and 6.96 (2H, br d, J=8.3 Hz), δ 7.22 (2H, d, J=8.6 Hz) and 6.81 (2H, d, J=8.6 Hz), δ 6.64 (2H, d, J=8.8 Hz) and 6.60 (2H, d, J=8.8 Hz); two 3,5-dihydroxybenzene moieties at δ 6.60 (2H, d, J=2.2 Hz) and 6.27 (1H, t, J=2.2 Hz), δ 6.18 (2H, d, J=2.0 Hz) and 6.18 (1H, t, J=2.0 Hz); two aliphatic protons of a dihydrobenzofuran ring at δ 5.47 (1H, d, J=3.5 Hz) and 4.63 (1H, d, J=3.5 Hz); two *trans* olefin protons at δ 6.49 (1H, d, J=16.7 Hz) and 6.62 (1H, d, J=16.7 Hz) and an aromatic proton at δ 7.05 (1H, s). Although, the ^{1}H NMR of **2** showed similar patterns to that of **1**, the chemical shift and shape of each signal was obviously different from that of **1**, suggesting that the connections between the three resveratrol units in **1** and **2** were different. In the HMBC spectrum of **2** (Fig. 2a), H-2(6)a showed long range couplings with C-7a (δ 119.7) and H-10(14)a had long range couplings with C-8a (δ 150.6), which indicated that ring A_1 was attached to C-7a and ring A_2 was attached to C-8a. Thus, the locations of the 4-hydroxybenzene moiety (ring A_1) and the 3,5-dihydroxybenzene moiety (ring A_2) at the benzofuran ring of **2** were interchanged compared with those of **1**. Therefore, the planar structure of amurensin D was concluded to be as shown in **2**. Amurensin D is a new type of oligostilbene and might have important implications for the biosynthetic research of this kind of compound.

The stereochemistry of **2** was established on the basis of NOE difference experiments. Irradiation of the doublet of H-7c or H-8c enhanced the signals of H-2(6)c and H-10(14)c, suggesting a *trans* orientation of H-7c and H-8c. The optical rotation of **2** was +185.5, similar to that of (+)-ϵ-viniferin. Therefore the absolute configuration of **2** was assigned as (7c*S*, 8c*S*).

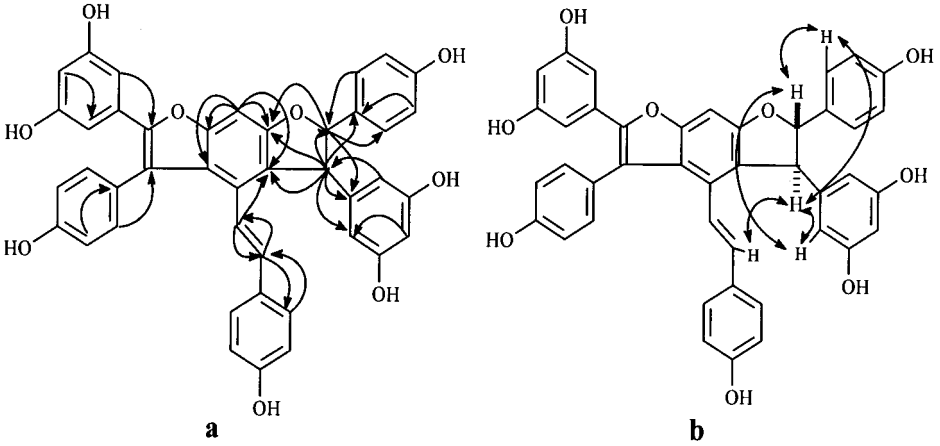


Figure 2. Long-range CH correlations in the HMBC spectrum (a) and significant NOE interactions in the NOESY spectrum (b) of **2**.

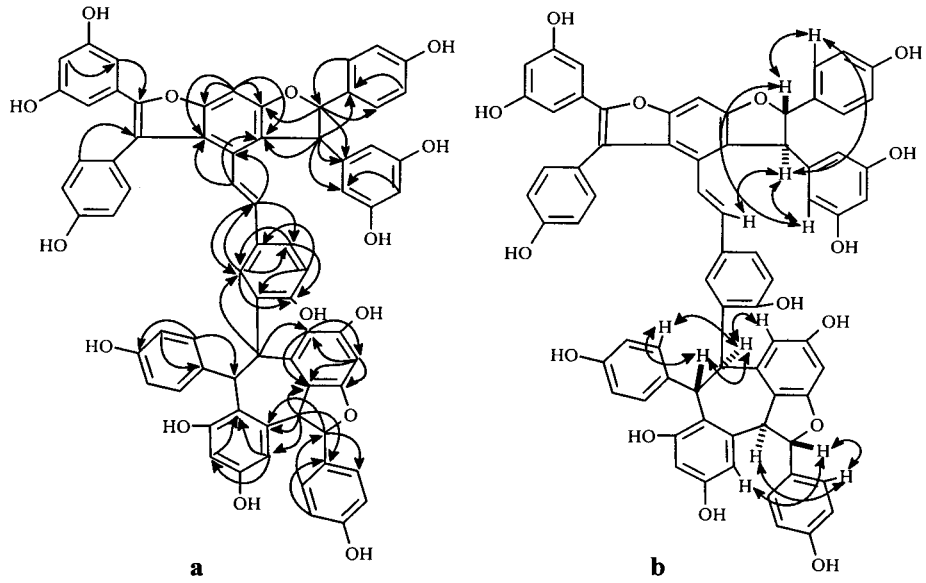


Figure 3. Long-range CH correlations in the HMBC spectrum (a) and significant NOE interactions in the NOESY spectrum (b) of **3**.

Amurensin E (**3**) was obtained as a brown amorphous powder, which exhibited a strong blue fluorescence under UV-254 light, $[\alpha]_D^{30}=+259.2°$ (*c* 0.052, MeOH). HRFAB-MS *m*/*z* 1131.3154 $[MH]^+$ ($C_{70}H_{51}O_{15}$ requires 1131.3228) gave a molecular formula of $C_{70}H_{50}O_{15}$, which in combination with ^1H and ^{13}C NMR of **3** suggested that it could be a resveratrol pentamer. The UV (λ_{max} 284, 338 nm) revealed the presence of a strong conjugated system in the structure. The following signals in the ^1H NMR spectrum of **3** revealed the presence of a H-3b substituted amurensin D moiety: signals for two 4-hydroxybenzene moieties at δ 7.08 (2H, br d, *J*=7.3 Hz) and 6.61 (2H, br d, *J*=7.3 Hz), δ 7.22 (2H, d, *J*=8.6 Hz) and 6.83 (2H, d, *J*=8.6 Hz); two 3,5-dihydroxybenzene moieties at δ 6.54 (2H, d, *J*=2.0 Hz) and 6.25 (1H, t, *J*=2.0 Hz), δ 6.00 (2H, br s) and 6.22 (1H, t, *J*=2.0 Hz); two aliphatic protons of a dihydrobenzofuran ring at δ 5.37 (1H, br s) and 4.50 (1H, br s); two *trans* olefin protons at δ 5.98 (1H, d, *J*=16.6 Hz) and 6.37 (1H, d, *J*=16.6 Hz); an aromatic proton at δ 6.98 (1H, s) and a 3-substituted 4-hydroxybenzene moiety at δ 6.60 (1H, d, *J*=8.1 Hz), 6.32 (1H, dd, *J*=8.1, 2.0 Hz) and 5.83 (1H, br s). The ^1H NMR spectrum of **3** also revealed the presence of a H-8c substituted ampelopsin B moiety[6] by the following signals: signals for two 4-hydroxybenzene moieties at δ 6.99 (2H, d, *J*=8.4 Hz) and 6.65 (2H, d, *J*=8.4 Hz), δ 7.15 (2H, d, *J*=8.4 Hz) and 6.83 (2H, d, *J*=8.4 Hz); four *meta*-coupled aromatic protons at δ 6.09 (1H, d, *J*=2.1 Hz), 6.03 (1H, br s), 6.08 (1H, br s) and 6.27 (1H, br s); two protons on a dihydrobenzofuran ring at δ 5.84 (1H, d, *J*=11.5 Hz) and 4.21 (1H, d, *J*=11.5 Hz) and two other aliphatic protons at δ 5.33 (1H, d, *J*=3.3 Hz) and 5.47 (1H, br s). Thus we propose that amurensin E should be composed from an amurensin D moiety and an ampelopsin B (**6**)[6] moiety formed through a linkage between C-3b and C-8c, as depicted in structure **3**. The ^1H NMR features of **3** were similar to those of vitisin A[7] except that **3** exhibited signals of one more resveratrol unit than vitisin A. The HMBC spectrum (Fig. 3a) of **3** supported the deduction. Amurensin E is the first resveratrol pentamer with an unsaturated benzofuran ring on which the positions of the 4-hydroxybezene moiety and the 3,5-dihydroxybenzene moiety are interchanged compared with ϵ-viniferin.

NOESY and NOE difference experiments (Fig. 3b) were carried out to identify the stereochemistry of **3**. The NOEs between H-2(6)c and H-8c revealed a *trans* orientation of H-7c and H-8c. Irradiation of the H-8d signal enhanced the H-2(6)d signal but no enhancement of the signals for H-7c and H-8c was observed, suggesting a *cis* orientation of H-8d and ring D_1 and a *trans* orientation of H-7c and H-8d. The NOEs between H-7e and H-10(14)e suggested a *cis* orientation of H-7e and ring E_2. On biosynthetic consideration, we propose the absolute configuration of **3** should be (7c*S*, 8c*S*, 7d*S*, 8d*S*, 7e*S*, 8e*S*) for the reason that only (+)-ϵ-viniferin was isolated from this plant.

Amurensin F (**4**) was obtained as a pale yellow amorphous powder, which exhibited strong blue fluorescence under UV-254 light, $[\alpha]_D^{30}=+23.0°$ (*c* 0.113, MeOH). Its HRFAB-MS *m*/*z* 1131.3154 $[MH]^+$ ($C_{70}H_{51}O_{15}$ requires 1131.3228) gave a molecular formula of $C_{70}H_{50}O_{15}$, which together with ^1H and ^{13}C NMR suggested that **4** was a resveratrol pentamer. The UV spectrum (λ_{max} 284, 341 nm) was similar to those of **3**. The following signals in the ^1H NMR spectrum of **4** revealed the presence of a H-3b substituted amurensin D moiety: signals for two 4-hydroxybenzene moieties at δ 7.08 (2H, br s) and 6.61 (2H, br s), δ 7.18 (2H, d, *J*=8.6 Hz) and 6.78 (2H, d, *J*=8.6 Hz); two 3,5-dihydroxybenzene moieties at δ 6.59 (2H, d, *J*=2.2 Hz)) and 6.27 (1H, t, *J*=2.2 Hz), δ 6.15 (2H, d, *J*=2.2 Hz) and 6.22 (1H, t, *J*=2.2 Hz); two aliphatic protons of a dihydrobenzofuran ring at δ 5.47 (1H, d, *J*=2.6 Hz) and 4.46 (1H, d, *J*=2.6 Hz); two *trans* olefin protons at δ 6.29 (1H, d, *J*=16.7 Hz) and 6.48 (1H, d, *J*=16.7 Hz); an aromatic proton at δ 7.04 (1H, s) and a 3-substituted 4-hydroxybenzene moiety at δ 6.66 (1H, d, *J*=8.3 Hz), 6.32 (1H, dd, *J*=8.3, 1.7 Hz) and 6.43 (1H, br s). The ^1H NMR spectrum of **4** also revealed the presence of an oxidative ϵ-viniferin moiety by signals as follow: signals for two 4-hydroxybenzene moieties at δ 7.24 (2H, d,

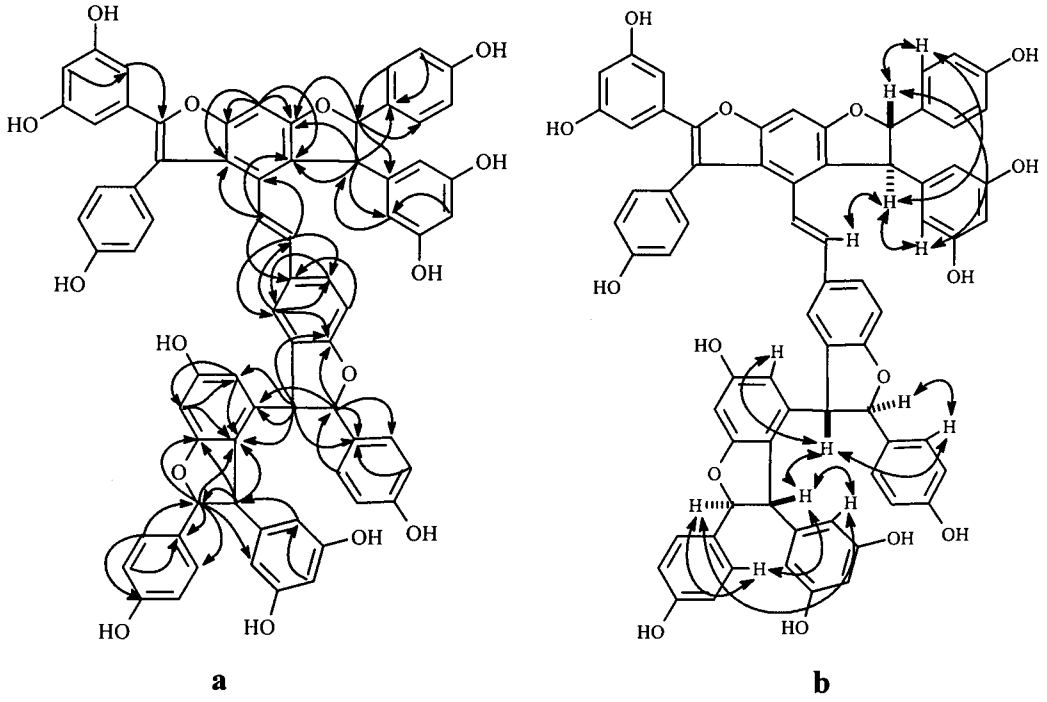


Figure 4. Long-range CH correlations in the HMBC spectrum (a) and significant NOE interactions in the NOESY spectrum (b) of **4**.

J=8.5 Hz) and 6.88 (2H, d, *J*=8.5 Hz), δ 6.49 (2H, d, *J*=8.6 Hz) and 6.55 (2H, d, *J*=8.6 Hz); one 3,5-dihydroxybenzene moiety at δ 6.18 (2H, d, *J*=2.2 Hz)) and 6.21 (1H, t, *J*=2.2 Hz); two *meta* coupled aromatic protons at δ 6.28 (1H, d, *J*=2.1 Hz) and 5.95 (1H, d, *J*=2.1 Hz) and four aliphatic protons of two dihydrobenzofuran moieties at δ 5.27 (1H, d, *J*=2.8 Hz) and 4.27 (1H, d, *J*=2.8 Hz), δ 5.36 (1H, d, *J*=3.4 Hz) and 4.75 (1H, d, *J*=3.4 Hz). Therefore, the structure of amurensin F should be formed by an amurensin D moiety and an ϵ-viniferin moiety with a dihydrobenzofuran group, which was confirmed by the HMBC spectrum of **4** (Fig. 4a). Amurensin F also belonged to the new type of oligostilbenes like amurensins D and E.

The stereochemistry of **4** was determined on the basis of NOE difference experiments (Fig. 4b). The NOEs between H-7c and H-2(6)c, 14c; H-7d and H-2(6)d, 10(14)d; H-7e and H-2(6)e, 10(14)e suggested a *trans* orientation of ring C_1 and C_2, D_1 and D_2, E_1 and E_2, respectively. The NOEs between H-8c and H-8d suggested a *cis* orientation of H-8c and H-8d. Since only (+)-ϵ-viniferin (7a*S*, 8a*S*) was isolated from this plant, the absolute configuration of amurensin F was established to be (7c*R*, 8c*R*, 7d*S*, 8d*S*, 7e*S*, 8e*S*) as shown in structure **4**, considering the biosynthesis of oligostilbenes.

In the ^{1}H NMR spectra of **1**–**4** at room temperature, some aromatic protons appeared as broad singlets or broad doublets. The ^{1}H NMR spectra of the four amurensins were carried out at various temperatures in order to study the phenomenon. All amurensins displayed different patterns at different temperatures. For example, in structure **2**, ring A_1 does not remain coplanar with rings A_2, A_3 and B_2 because of spatial congestion between H-2(6)a and H-8b, then ring A_1 cannot rotate freely. At the low temperature of −40°C, ring A_1 was stable as shown in structure **2**, H-2a and H-6a were in different chemical surroundings and appeared as two double doublets at δ 7.26 and 7.20, respectively; for the same reason, H-3a and H-5a also appeared as two double doublets at δ 7.01 and 6.97 (Fig. 5a), respectively. At the temperature of −20°C, ring A_1 could rotate a little, H-2a, 6a, 3a and 5a appeared as four doublets at δ 7.25, 7.20, 7.00 and 6.95 (Fig. 5b). At a temperature of 0°C, ring A_1 could overcome the steric hindrance and rotate more quickly with increasing temperature, H-2a and H-6a had the same chemical shifts and appeared as a broad singlet at δ 7.23, H-3a and H-5a at δ 6.98 (Fig. 5c). Ring A_1 rotated more and more quickly at a temperature of 20°C, thus H-2a and H-6a exhibited a broad doublet at δ 7.22, so did H-3a and H-5a at δ 6.96 (Fig. 5d). When the temperature was increased to 40°C, ring A_1 could rotate complete freely, H-2a and H-6a were in the same chemical surroundings and exhibited a sharp doublet at δ 7.22 as usual, and H-3(5)a at δ 6.96 (Fig. 5e). In summary, with increasing temperature, ring A_1 of **2** rotates more and more freely. The ^{1}H NMR spectra of **3** and **4** at various temperatures showed the same patterns with amurensin D with increasing temperature, but a small difference at the same temperature because of different steric hindrance. In structure **1**, H-10a and H-14a exhibited different features at various temperatures for the reason that ring A_2 could not rotate freely. As a consequence of the greater steric hindrance caused by two hydroxy groups on ring A_2, the A_2 ring rotates only freely at the higher temperature of 80°C, and H-10(14)a exhibited a sharp doublet. The ^{1}H NMR experiments of **1**–**4** at various temperatures further confirmed the accuracy of their structures, especially that the positions of ring A_1 and A_2 in each compound were correct.

In previous papers,[1,8] it was proposed that all naturally

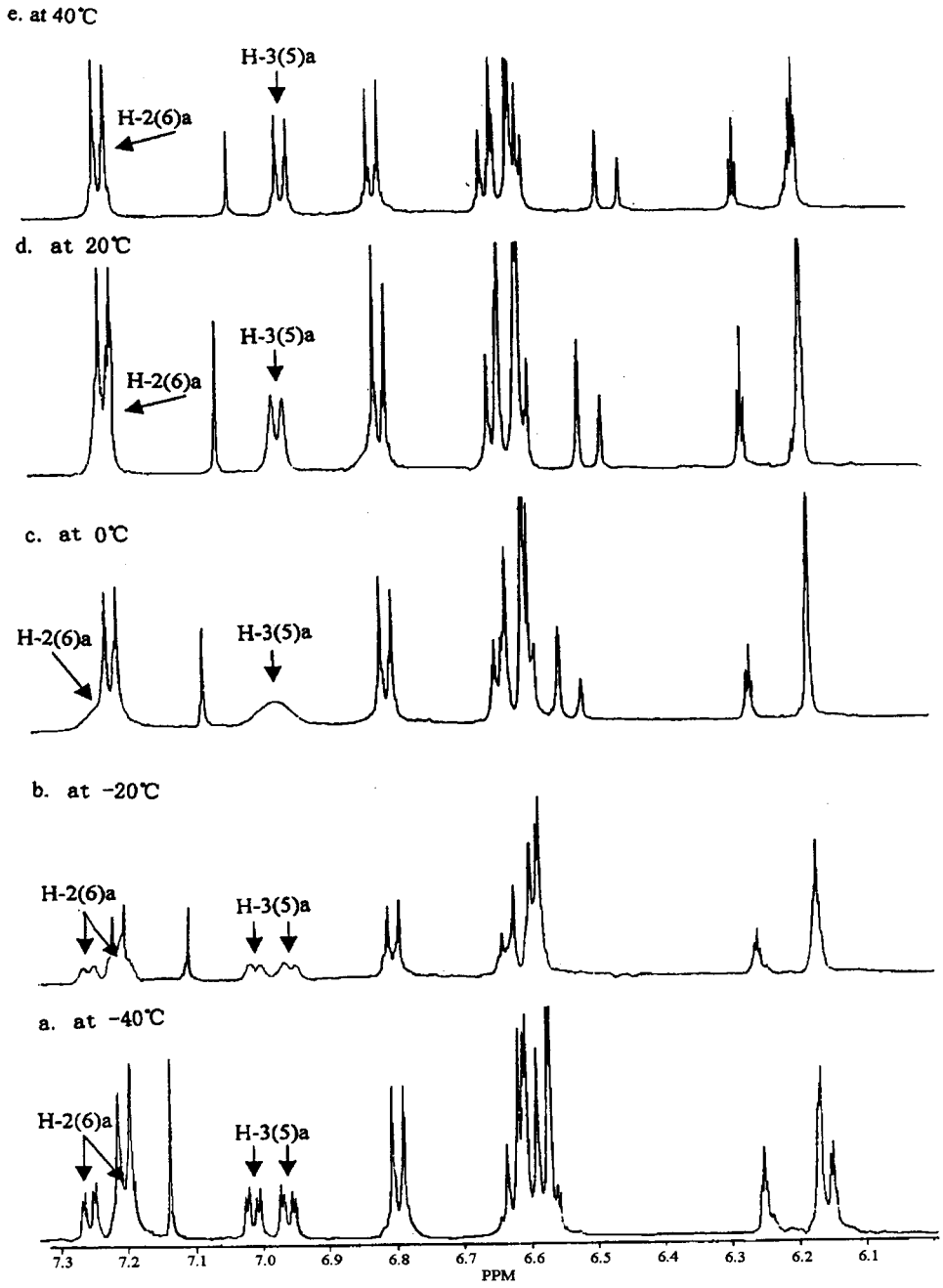
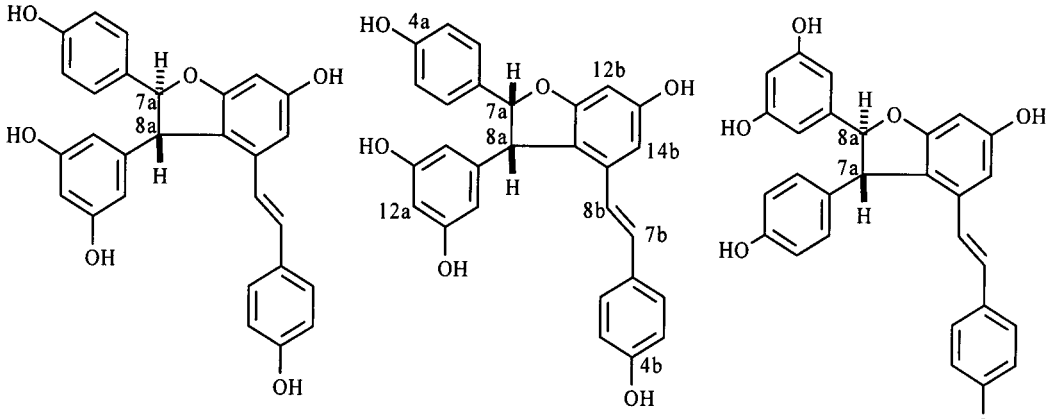


Figure 5. ^{1}H NMR spectra of **2** at different temperatures (in CD_3COCD_3).

occurring oligostilbenes of group A were formed from resveratrol via the dimer ϵ-viniferin (**8**). We considered that it was a main biogenetic route for oligostilbenes, but other biogenetic precursors might exist at the same time during biogenesis of oligostilbenes of group A because of appearance of amurensins B–F. Amurensins B and C, each with a *cis* dihydrobenzofuran moiety (ring C_3), might be formed from resveratrol via 7a,8a-*cis*-ϵ-viniferin (**9**), and amurensins D–F might be formed via iso-ϵ-viniferin (**10**) (Scheme 3). Unfortunately, **9** and **10** were not isolated from this plant. When resveratrol was treated with $FeCl_3$ in methanol at room temperature, only **8** and **9**, but not **10** was obtained, probably because of low yield or need to use other oxidants for treatment of resveratrol, which will be further investigated subsequently.

Of compounds **1**–**6**, the activities of leukotriene D_4 (LTD_4) receptor antagonism were tested, but unfortunately, none of them exhibited the obvious effect. The inhibitory rates of LTD_4 receptor antagonism for compounds **1**–**6** at concentrations of 10^{-5} mol L^{-1} were −35, −182, 29.4, −52.9, 17.6, and 5.9%, respectively, only compound **2** showed slight activity. Compound **4** exhibited strong inhibitory effect on biosynthesis of leukotriene B_4 (LTB_4) at concentration of 10^{-5} mol L^{-1} with an inhibitory rate of 67%, but it was not tested for other compounds because of scarcity of samples.



Scheme 3.

Experimental

General procedures

Optical rotations were determined on a Perkin–Elmer digital polarimeter. UV spectra were taken on a Shimadzu UV-300 spectrophotometer. IR spectra were run on a Perkin–Elmer 683 infrared spectrometer recorded as KBr pellet. The NMR spectra were carried out on a Bruker AM-500 using TMS as internal standard. The FAB-MS spectra were taken on a Autospec-Ulma-Tof mass spectrometer and HPLC on Waters 411.

Plant material

The roots of *Vitis amurensis* Rupr. were collected from Huairou Beijing in May 1997, identified as *Vitis amurensis* Rupr. by Prof. W. Z. Song of our institute. A voucher specimen (97021) was deposited in the herbarium of the Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College.

Isolation of 1–4

Dried and powdered roots of *Vitis amurensis* Rupr. (20 kg) were refluxed with 95% EtOH. The extract was concentrated in vacuo to yield 2.2 kg gum, which was mixed with silica gel (60–100 mesh), then eluted with $CHCl_3$, Me_2CO, MeOH (each 5000 mL) respectively to give four fractions. The acetone fraction (640 g) was subjected to a silica gel column eluted with $CHCl_3$–MeOH (100:1–100:30) to give A (27.5 g), B (30 g), C (25 g), D (230 g) and E (210 g) fractions. Fraction D was divided into D_1–D_4 by column chromatography (silica gel, 100–200 mesh, cyclohexane–acetone), D_1 was subjected to an ODS RP-18 column eluted with MeOH–H_2O (6:4) to afford **1** (11 mg), **2** (10 mg), and **3** (20 mg) was obtained from fraction D_3 by the same method. Fraction E was further divided into three fractions E_1–E_3 by column chromatography (ODS, RP-18, MeOH–H_2O (6:4–4:6)), the E_3 fraction was subjected to a sephadex HL-20 column eluted with EtOH to afford **4** (120 mg). Compounds **1**–**4** were further purified by Medium-Pressure Liquid Chromatography (ODS, RP-18 or RP-8, 40–63 μm), **1** (52 min, MeOH–H_2O=6:4), **2** (46 min, MeOH–H_2O=6:4), **3** (47 min, MeOH–H_2O=5.5:4.5), **4** (64 min, MeOH–H_2O=5.5:4.5).

Amurensin C (1). Brown amorphous powder; $[\alpha]_D^{18}$=+48.7° (*c* 0.079, MeOH); HRFAB-MS *m/z* 679.1956$[M+H]^+$ (calcd for $C_{42}H_{31}O_9$, 679.1968); UV

Table 1. ^1H and ^{13}C NMR spectral data for compounds **1** and **2** (all assignments were confirmed by ^1H–^1H COSY, ^1H–^{13}C COSY and HMBC spectra measured in CD_3COCD_3 at 500 and 125 MHz for ^1H (δ in ppm, *J* in Hz) and ^{13}C (δ in ppm) NMR, respectively)

Position no.	**1**		**2**	
	δ ^1H	δ ^{13}C	δ ^1H	δ ^{13}C
1a		123.2		126.5
2(6)a	7.46 (d, 8.7)	128.2	7.22 (br d, 8.3)	132.6
3(5)a	6.78 (d, 8.7)	116.0[a]	6.96 (br d, 8.3)	117.0
4a		158.2		158.2[a]
7a		150.4		119.7
8a		117.7		150.6
9a		138.0		133.6
10(14)a	6.37 (br s), 6.48 (br s)	109.6	6.60 (d, 2.2)	105.8
11(13)a		160.4		159.3
12a	6.53 (t, 2.2)	102.9	6.27 (t, 2.2)	103.3
1b		130.2		130.1
2(6)b	6.76 (d, 8.6)	128.4	6.64 (d, 8.8)	128.6
3(5)b	6.63 (d, 8.6)	116.1[a]	6.60 (d, 8.8)	116.9
4b		158.0		158.0
7b	6.67 (d, 16.7)	133.3	6.49 (d, 16.7)	133.9
8b	6.95 (d, 16.7)	121.8	6.62 (d, 16.7)	121.5
9b		128.7		130.3
10b		123.6		123.8
11b		154.9		155.7
12b	7.05 (s)	92.3	7.05 (s)	92.0
13b		159.7		160.7
14b		125.1		123.1
1c		129.2		134.1
2(6)c	7.06 (d, 8.5)	129.0	7.22 (d, 8.6)	127.7
3(5)c	6.63 (d, 8.5)	115.0	6.81 (d, 8.6)	116.2
4c		157.5		158.3[a]
7c	5.87 (d, 7.3)	90.6	5.47 (d, 3.5)	93.8
8c	4.72 (d, 7.3)	54.4	4.63 (d, 3.5)	58.0
9c		142.7		147.3
10(14)c	5.81 (d, 2.1)	108.6	6.18 (d, 2.0)	106.8
11(13)c		158.7		160.0
12c	5.99 (t, 2.1)	101.5	6.18 (t, 2.0)	102.1

[a] May be interchangeable in the same column.

(MeOH) λ_{max}: 278 nm (log ϵ=4.28), 309 nm (log ϵ= 4.30), 340 nm (log ϵ=4.30); IR (KBr) ν_{max}: 3363, 2925, 1697, 1599, 1512, 1454, 1338, 1238, 1149, 999 and 835 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1.

Amurensin D (2). Pale green amorphous powder; $[\alpha]_D$=+185.5° (*c* 0.059, MeOH); HRFAB-MS *m/z* 679.1965 $[M+H]^+$ (calcd for $C_{42}H_{31}O_9$, 679.1968); UV (MeOH) λ_{max}: 286 nm (sh) (log ϵ=4.29), 305 nm (log ϵ=4.32), 343 nm (log ϵ=4.41); IR (KBr) ν_{max}: 3379, 2925, 1697, 1604, 1514, 1446, 1319, 1238, 1155, 1003, 976, and 835 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1.

Amurensin E (3). Brown amorphous powder; $[\alpha]_D^{30}$= +259.2° (*c* 0.052, MeOH); HRFAB-MS *m/z* 1131.3154 $[M+H]^+$ (calcd for $C_{70}H_{51}O_{15}$, 1131.3228); UV (MeOH) λ_{max}: 284 nm (log ϵ=4.43) and 338 nm (log ϵ=4.46); IR (KBr) ν_{max}: 3386, 1612, 1514, 1446, 1336, 1228, 1153, 1005 and 835 cm^{-1}; ^1H and ^{13}C NMR data, see Table 2.

Amurensin F (4). Pale yellow amorphous powder; $[\alpha]_D^{30}$=+23.0° (*c* 0.113, MeOH); HRFAB-MS *m/z* 1131.3154 $[M+H]^+$ (calcd for $C_{70}H_{51}O_{15}$, 1131.3228); UV (MeOH) λ_{max}: 284 nm (log ϵ=4.37) and 341 nm (log ϵ=4.36); IR (KBr) ν_{max}: 3332, 1697, 1601, 1516, 1487, 1446, 1336, 1234, 1153, 1001 and 833 cm^{-1}; ^1H and ^{13}C NMR data, see Table 3.

7a,8a-*cis*-ϵ-Viniferin (9). Yellowish amorphous powder; EI-MS *m/z* 454 $[M]^+$, 360, 347, 331, 267, 107; IR (KBr) ν_{max}: 3303, 1697, 1604, 1514, 1448, 1336, 1238, 1171, 1124, 995, 960 and 833 cm^{-1}; UV (MeOH) λ_{max}: 284 nm (log ϵ=4.43), 321 nm (log ϵ=4.52); ^1H NMR (500 MHz, in CD_3COCD_3) δ 7.19 (2H, d, *J*=8.7 Hz, H-2a, H-6a), 7.01 (2H, d, *J*=8.6 Hz, H-2b, H-6b), 6.85 (2H, d, *J*=8.7 Hz, H-3a, H-5a), 6.75 (2H, d, *J*=8.6 Hz, H-3b, H-5b), 6.93 (1H, d, *J*=16.4 Hz, H-8b), 6.74 (1H, d, *J*=16.4 Hz, H-7b), 6.70 (1H, d, *J*=2.1 Hz, H-14b), 6.35 (1H, d, *J*=2.1 Hz, H-12b) 6.00 (1H, t, *J*=2.1 Hz, H-12a), 5.80 (2H, d, *J*=2.1 Hz, H-10a, H-14a), 5.83 (1H, d, *J*=8.1 Hz, H-7a), 4.65 1H, d, *J*=8.1 Hz, H-8a); NOE interactions in the NOESY spectrum: H-7a/H-8a, H-7a/H-2(6)a and H-8a/H-10(14)a.

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Table 2. ^1H and ^{13}C NMR spectral data for **3** (all assignments were confirmed by ^1H–^1H COSY, ^1H–^{13}C COSY and HMBC spectra measured in CD_3COCD_3 at 500 and 125 MHz for ^1H (δ in ppm, *J* in Hz) and ^{13}C (δ in ppm) NMR, respectively)

Position no.	δ ^1H	δ ^{13}C	Position no.	δ ^1H	δ ^{13}C
1a		126.0	1d		130.9
2(6)a	7.08 (br d, 7.3)	132.3	2(6)d	7.15 (d, 8.4)	130.1
3(5)a	6.61 (br d, 7.3)	116.6	3(5)d	6.77 (d, 8.4)	115.9
4a		157.7	4d		158.3
7a		119.6	7d	5.84 (d, 11.5)	88.5
8a		150.3	8d	4.21 (d, 11.5)	49.3
9a		133.5	9d		142.4
10(14)a	6.54 (d, 2.0)	105.6	10d		120.5
11(13)a		159.3[a]	11d		158.5
12a	6.25 (t, 2.0)	103.1	12d	6.08 (br s)	101.1
1b		128.9	13d		155.9
2b	5.83 (br s)	132.7	14d	6.27 (br s)	105.0
3b		132.3	1e		133.9
4b		154.8	2(6)e	7.22 (d, 8.6)	127.4
5b	6.60 (d, 8.1)	115.4	3(5)e	6.83 (d, 8.6)	116.2
6b	6.32 (dd, 8.1)	122.6	4e		157.7
7b	5.98 (d, 16.6)	134.3	7e	5.37 (br s)	93.3
8b	6.37 (d, 16.6)	120.7	8e	4.50 (br s)	56.7
9b		130.9	9e		147.2
10b		123.5	10(14)e	6.00 (br s)	106.7
11b		155.6	11(13)e		159.2[a]
12b	6.98 (s)	91.7	12e	6.22 (t, 2.0)	102.1
13b		160.2[a]			
14b		123.1			
1c		135.4			
2(6)c	6.99 (d, 8.4)	128.8			
3(5)c	6.65 (d, 8.4)	115.4			
4c		155.9			
7c	5.33 (d, 3.3)	40.7			
8c	5.47 (br s)	41.1			
9c		141.2			
10c		120.5			
11c		160.1[a]			
12c	6.09 (d, 2.1)	96.0			
13c		158.1			
14c	6.03 (br s)	110.1			

[a] May be interchangeable.

Table 3. ^{1}H and ^{13}C NMR spectral data for **4** (all assignments were confirmed by $^{1}H-^{1}H$ COSY, $^{1}H-^{13}C$ COSY and HMBC spectra measured in CD_3COCD_3 at 500 and 125 MHz for ^{1}H (δ in ppm, J in Hz) and ^{13}C (δ in ppm) NMR, respectively)

Position no.	δ ^{1}H	δ ^{13}C	Position no.	δ ^{1}H	δ ^{13}C
1a		126.1	1d		134.2
2(6)a	7.08 (br s)	132.4	2(6)d	7.24 (d, 8.5)	127.8
3(5)a	6.61 (overlap)	116.7	3(5)d	6.88 (d, 8.5)	116.3
4a		160.0	4d		158.1[a]
7a		119.6	7d	5.36 (d, 3.4)	94.3
8a		150.2	8d	4.75 (d, 3.4)	56.1
9a		133.5	9d		108.1
10(14)a	6.59 (d, 2.2)	105.7	10(14)d	6.18 (d, 2.2)	106.5
11(13)a		159.2	11(13)d		160.0
12a	6.27 (t, 2.2)	103.2	12d	6.21 (t, 2.2)	102.0[a]
1b		131.7	1e		133.9
2b	6.43 (s)	123.6	2(6)e	7.18 (d, 8.6)	127.6
3b		132.8[a]	3(5)e	6.78 (d, 8.6)	116.1
4b		160.0	4e		158.2[a]
5b	6.66 (d, 8.3)	109.9	7e	5.47 (d, 2.6)	93.5
6b	6.32 (dd, 8.3, 1.7)	128.7	8e	4.46 (d, 2.6)	57.4
7b	6.29 (d, 16.7)	133.8	9e		147.9
8b	6.48 (d, 16.7)	121.7	10(14)e	6.15 (d, 2.2)	106.6
9b		130.2	11(13)e		160.0
10b		123.7	12e	6.22 (t, 2.2)	102.2[a]
11b		155.5			
12b	7.04 (s)	92.1			
13b		160.1			
14b		123.4			
1c		132.7[a]			
2(6)c	6.49 (d, 8.6)	127.3			
3(5)c	6.55 (d, 8.6)	115.7			
4c		157.9			
7c	5.27 (d, 2.8)	92.1			
8c	4.27 (d, 2.8)	52.6			
9c		143.2			
10c		119.3			
11c		162.4			
12c	6.28 (d, 2.1)	96.3			
13c		160.0			
14c	5.95 (d, 2.1)	107.3			

[a] May be interchangeable.

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