

## Two New Sesquiterpenes from a Kind of TCM Pieces, Curcumae Radix

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**Abstract:** Phytochemical study on the ethanol extract of the Curcumae Radix pieces, authenticated as the radixes of *Curcuma wenyujin* Y.H. Chen et C. Ling, led to the isolation of two new sesquiterpenes, (1R,4R,5S,7S)-curwenyujinone (**1**) and zedoalactone H (**2**), along with five known sesquiterpenes, zedoalactone E (**3**), zedoarolide B (**4**), gweicurculactone (**5**), curdionolide A (**6**), curcumenone (**7**) and one diterpene compound, curcuminol D (**8**). Their structures were elucidated on the basis of extensive spectroscopic analysis and computational ECD simulations.

**Keywords:** Curcumae Radix; (1R,4R,5S,7S)-curwenyujinone; zedoalactone H; sesquiterpenes. © 2014 ACG Publications. All rights reserved.

### 1. Introduction

*C. wenyujin* belongs to the Zingiberaceae family and is a common Traditional Chinese Medicine (TCM) that has been used to treat the Oketsu syndromes (various syndromes caused by the obstruction of blood circulation such as arthralgia, psychataxia, and dysmenorrhea) [1] for thousands of years. The genus *Curcuma* has been reported to be rich in diarylheptanoids and sesquiterpenoids [2-5]. These substances showed various pharmacological properties, such as anticancer [6,7], vasorelaxant [8], hepatoprotective [9], anti-inflammatory [10,11] and immunological activities [12]. There were also reports about the antidepressant effect of curcumin [13] which is considered one of the major constituents of *curcuma* radixes. However, study about the chemical analysis of *curcuma* drugs showed that curcumin in *C. wenyujin* was hardly detected [14]. So, maybe there exist other constituents involved in the antidepressant effect of *curcuma* radixes.

In order to study the bioactive constituents with antidepressant effect, we have investigated the Curcumae Radix pieces (Yujin pieces), authenticated as the radixes of *Curcuma wenyujin*, and

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obtained two new sesquiterpenes together with six known compounds. This article mainly describes the isolation and characterization of these compounds.

## 2. Materials and Methods

### 2.1. Apparatus and reagents

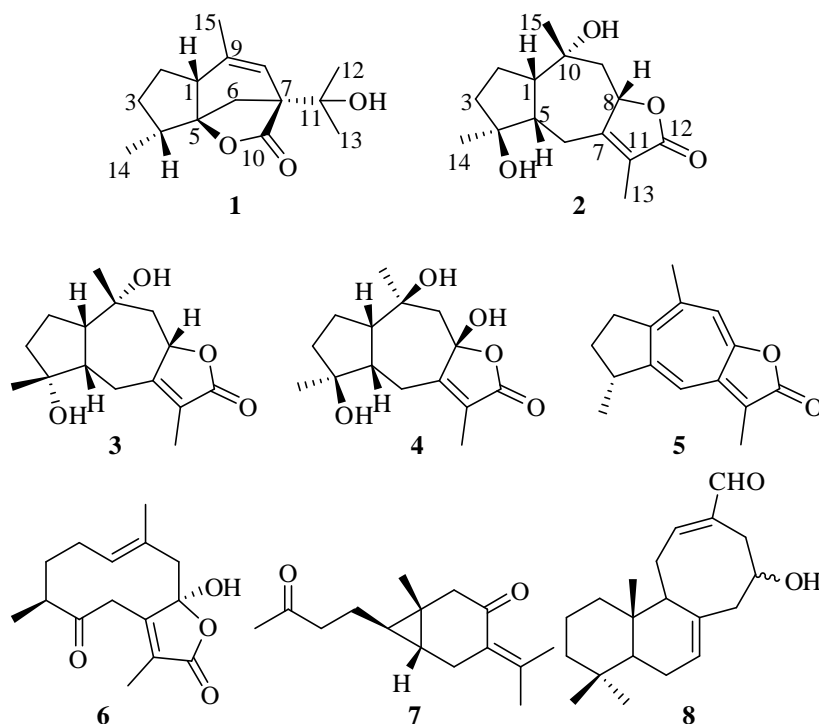
All reagents were of HPLC or analytical grade and were purchased from Tianjin Damao Chemical Company. Column chromatography (CC): silica gel (SiO<sub>2</sub>, 200-300/400-500 mesh, Qingdao Marine Chemical Factory, Qingdao, China); Sephadex LH-20: (GE Healthcare UK Ltd, Buckinghamshire, England); TLC: silica gel GF254 (SiO<sub>2</sub>, 400-500 mesh, Qingdao Marine Chemical Factory, Qingdao, China). Prep. HPLC: Waters 2489, ODS column (C-18, 5  $\mu$ m, 250 $\times$ 10 mm). IR Spectra: Spectrum 65 spectrometer (PerkinElmer, Waltham, MA, USA). UV and CD: Jasco J-815 polarimeter (JASCO Corporation, Tokyo, Japan). NMR Experiments: BrukerAV-III spectrometer (Bruker, Zurich, Switzerland). HR-ESI-MS: Synapt G2 mass spectrometer (Waters, Milford, MA, USA).

### 2.2. Plant material

The *Curcumae Radix* pieces were obtained from Anguo county, Hebei province of P.R. China, in June, 2010. The plant material was identified by Prof. Tian-xiang Li, Tianjin University of Traditional Chinese Medicine, P.R. China. A voucher specimen (No. B11224322) was deposited in the traditional Chinese medicine research and development center, Tianjin university of traditional Chinese medicine.

### 2.3. Extraction and isolation

*C. wenyujin* drugs (5 kg) were extracted successively with petroleum ether and 70% EtOH. The 70% EtOH extract (142 g) was evaporated under reduced pressure and distributed in water before being partitioned with petroleum ether (PE), ethyl acetate (EA), and n-butanol (BU) Successively. The PE fraction (10 g) was chromatographed on silica gel column, gradiently eluted with petroleum ether-acetone (100:0-0:100) to obtain 13 fractions CP1-CP13. Fraction CP4 was subjected to preparative HPLC with C18 column using MeOH-H<sub>2</sub>O (63:37), then was purified by semi-preparative HPLC with MeOH/H<sub>2</sub>O (41:59) to yield compound **1** ( $t_R$ =150.63 min, 5.6 mg) and **7** ( $t_R$ =168.18 min, 13.2 mg). Fraction CP9 was submitted to silica gel column using petroleum ether-ethyl acetate (5:1 to 0:1), which afforded three sub-fractions CP91-CP93. CP93 was purified by semi-preparative HPLC using MeOH-H<sub>2</sub>O (70:30) to obtain compound **8** ( $t_R$ =59.85 min, 13.4 mg). The EA fraction (10 g) was chromatographed on silica gel using the CH<sub>2</sub>Cl<sub>2</sub>-MeOH gradient solvent system (100:0-0:100) to give 8 fractions CE1-CE8. Fraction CE2 was purified by Sephadex LH-20 with MeOH to afford compound **5** (5.0 mg). Fraction CE4 was rechromatographed on silica gel using a gradient of petroleum ether-ethyl acetate (5:1-1:5) which gave 5 subfractions (CE41-CE45). CE45 was further purified by semi-preparative HPLC using MeOH-H<sub>2</sub>O (28:72) to yield compound **2** ( $t_R$ =60.82 min, 14.3 mg) and **3** ( $t_R$ =78.53 min, 4.8 mg). CE42 was subjected to preparative HPLC and further purified by semi-preparative HPLC with MeOH/H<sub>2</sub>O (42:58) to yield compound **6** ( $t_R$ =50.95 min, 22.8 mg). CE6 was submitted to Sephadex LH-20 (CH<sub>2</sub>Cl<sub>2</sub>-MeOH 1:1) and further purified by semi-preparative HPLC with MeOH/H<sub>2</sub>O (18:82) to obtain compound **4** ( $t_R$ =40.32 min, 6.0 mg).



**Figure 1.** The chemical structures of compounds **1-8**.

(1*R*,4*R*,5*S*,7*S*)-curwenyujinone (**1**): colorless oil. UV (MeOH)  $\lambda_{\max}$ : 193, 341 nm; IR (KBr)  $\nu_{\max}$  ( $\text{cm}^{-1}$ ): 3503, 2976, 2959, 2931, 2874, 1742, 1637, 1468, 1455, 1394, 1384, 1357, 1158, 1099; CD (MeOH,  $c = 2.6 \times 10^{-3}$ )  $\lambda_{\max}$  ( $\Delta\epsilon$ ): 230 (-10.29) nm; HRESI-MS:  $m/z$  273.1467 [ $\text{M}+\text{Na}$ ] $^+$  (calcd. for  $\text{C}_{15}\text{H}_{22}\text{NaO}_3^+$ : 273.1461);  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ ) and  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO}-d_6$ ): see Table 1.

zedoalactone H (**2**): colourless oil. UV (MeOH)  $\lambda_{\max}$ : 223 nm; IR (KBr)  $\nu_{\max}$  ( $\text{cm}^{-1}$ ): 3431, 2970, 2936, 2879, 2865, 2128, 1736, 1673, 1463, 1385, 1353, 1215, 1156, 1109; CD (MeOH,  $c = 1.9 \times 10^{-3}$ )  $\lambda_{\max}$  ( $\Delta\epsilon$ ): 207 (-16.18), 253 (-3.45) nm; HRESI-MS:  $m/z$  267.1595 [ $\text{M}+\text{H}$ ] $^+$  (calcd. for  $\text{C}_{15}\text{H}_{23}\text{O}_4^+$ : 267.1591),  $m/z$  289.1412 [ $\text{M}+\text{Na}$ ] $^+$  (calcd. for  $\text{C}_{15}\text{H}_{22}\text{NaO}_4^+$ : 289.1410);  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ ) and  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO}-d_6$ ): see Table 2.

#### 2.4. Computational methods

Considering the free rotation of C7-C11 bond in **1**, a stochastic conformational search was firstly conducted using Discovery Studio 3.0 software applying standard settings of systematic method (energy was set for 20) and three low energy conformers were found. Geometric optimizations of the conformers were then finished with Gaussian 09 using AM1 method. The optimized conformers were energy minimized with Gaussian 09 using the B3LYP density functional and a 6-31G(d) basis set. Time-dependent density functional theory (TDDFT) calculations were performed using the B3LYP/6-31G(d) optimized structures applying the B3LYP functional and the same basis set. Finally, the calculation results were boltzman averaged to yield the depicted spectrum [15], the closest match with the experimental CD spectrum.

Full output of the calculations can be obtained from the corresponding author on request.

### 3. Results and Discussion

#### 3.1. Structure elucidation

Curcumae Radix pieces were extracted successively with petroleum ether and 70% EtOH. From the crude extracts, two new sesquiterpenes, (1*R*,4*R*,5*S*,7*S*)-curwenyujinone (**1**), zedoalactone H (**2**)

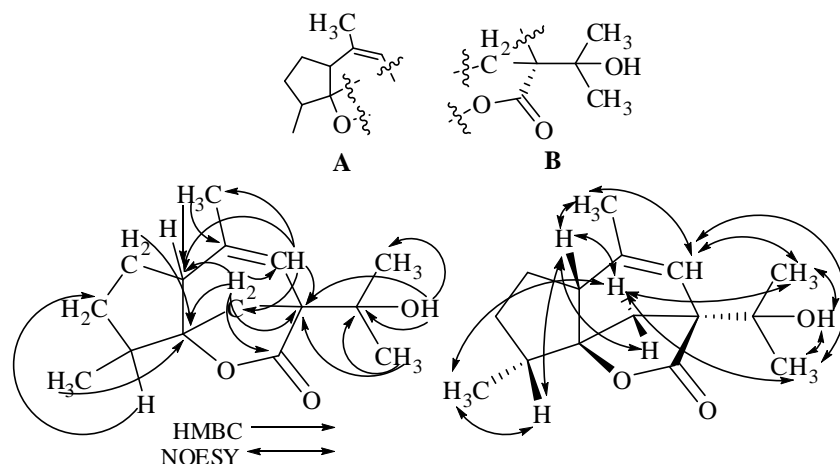
were isolated by a combination of column chromatography and preparative HPLC, together with six known compounds, zedoalactone E (**3**) [16], zedoarolide B (**4**) [17], gweicurculactone (**5**) [18], curdionolide A (**6**) [19], curcumenone (**7**) [20] and curcuminol D (**8**) [21].

Compound **1** was obtained as a colorless oil. The molecular formula of this compound was assigned to be C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>, as deduced from its HRESI-MS at *m/z* 273.1467 ([M+Na]<sup>+</sup>, calcd. 273.1461) and NMR data. The IR spectrum showed absorption bands due to a lactone ester (1742 cm<sup>-1</sup>), a double bond (1637 cm<sup>-1</sup>) and a hydroxyl group (3503 cm<sup>-1</sup>). The <sup>1</sup>H NMR spectrum showed four methyl signal peaks including two singlets at δ<sub>H</sub> 1.19, and 1.32, a triplet at δ<sub>H</sub> 1.68 (*J* = 1.2 Hz), and a doublet at δ<sub>H</sub> 0.97 (*J* = 6.6 Hz). In addition to this, there were an olefinic proton singlet at δ<sub>H</sub> 5.70 (1H, br s), and a hydroxyl singlet at δ<sub>H</sub> 4.45 with none HSQC and HMBC correlations. The <sup>13</sup>C NMR spectrum displayed total fifteen C-atom resonances, comprising those for four Me groups, three CH<sub>2</sub> groups, three CH groups (including one olefinic C-atoms), and five quaternary C-atoms (including an olefinic C-atoms, an ester CO group and two oxygenated aliphatic carbons). The presence of moieties A and B were confirmed by a HMBC experiment, which showed the correlations from H-14 (3H, δ<sub>H</sub> 0.97) to C-3 (δ<sub>C</sub> 30.1), C-4 (δ<sub>C</sub> 37.8) and C-5 (δ<sub>C</sub> 90.5), from H-2 (2H, δ<sub>H</sub> 1.86, 1.38) to C-5, from H-15 (3H, δ<sub>H</sub> 1.68) to C-1 (δ<sub>C</sub> 50.7), C-8 (δ<sub>C</sub> 122.3) and C-9 (δ<sub>C</sub> 139.3), indicating the presence of moiety A; the other correlations from H-12 (3H, δ<sub>H</sub> 1.31), H-13 (3H, δ<sub>H</sub> 1.19) to C-7 (δ<sub>C</sub> 57.0) and C-11 (δ<sub>C</sub> 69.7), from 11-OH (1H, δ<sub>H</sub> 4.45) to C-12 (δ<sub>C</sub> 25.4), C-7 and C-11, and from H-6 (2H, δ<sub>H</sub> 2.47, 1.79) to C-1, C-7, C-5 and C-8, suggested the presence of moiety B. The planar structure of **1**, combining moiety A and moiety B by 6, 8-carbon atoms, was deduced from the HMBC correlations from H-6 to C-1, C-5 and C-8, and from H-8 (1H, δ<sub>H</sub> 5.70) to C-1, C-15 (δ<sub>C</sub> 20.7), C-6 (δ<sub>C</sub> 35.9) and C-7.

**Table 1.** <sup>1</sup>H NMR (600 MHz) and <sup>13</sup>C NMR (150 MHz) spectral data of compound **1** in DMSO-*d*<sub>6</sub>.

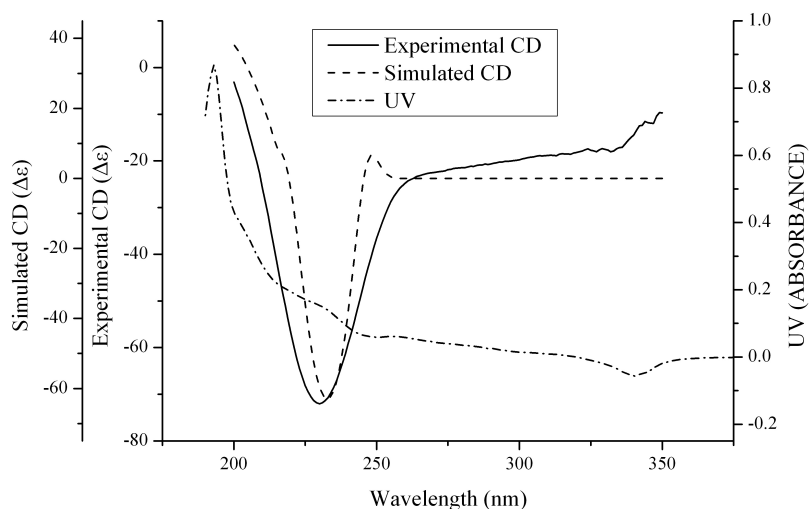
Position	δ <sub>C</sub>	δ <sub>H</sub> (J in Hz)
1	50.7	2.52 (1H, dd, 8.4, 9.6)
2	23.5	1.86 (1H, m) 1.38 (1H, m)
3	30.1	2.05 (1H, m) 1.35 (1H, m)
4	37.8	2.11 (1H, m)
5	90.5	—
6	35.9	2.47 (1H, dd, 10.8, 1.2) 1.79 (1H, d, 10.8)
7	57.0	—
8	122.3	5.70 (1H, br s)
9	139.3	—
10	176.3	—
11	69.7	—
12	25.4	1.31 (3H, s)
13	27.0	1.19 (3H, s)
14	12.9	0.97 (3H, d, 6.6)
15	20.7	1.68 (3H, br s)
11-OH	—	4.45 (1H, s)

The relative configuration of **1** was obtained by a NOESY experiment, in which correlations of Me-11/H-6 $\alpha$ , Me-12/H-6 $\alpha$ , Me-4/H-6 $\alpha$ , H-6 $\beta$ /H-1 and H-6 $\beta$ /H-4 indicated that H-1, C<sub>5</sub>-O bond, H-4 were  $\beta$ -oriented and that C<sub>7</sub>-C<sub>11</sub> bond, Me-4 were  $\alpha$ -oriented. Hence, the structure of **1** was confirmed as shown, named as curwenyujinone.



**Figure 2.** The main moieties and the Key HMBC and NOESY correlations of compound **1**.

Finally, the absolute stereochemistry of **1** was established based on the following CD spectral evidence. Some 45 years ago based on the lactone sector rule derived by Klyne and co-workers, A. C. Beecham [22,23] proposed an important and simple CD empirical rule that the sign of the  $n \rightarrow \pi^*$  Cotton effect in bridged ring lactones based on the bicyclo [3,2,1] octane skeleton depends upon the location of  $C_4$  relative to the planar lactone system, while choosing the seven-membered ring as the object of observation. If  $C_4$  is above the lactone plane, the sign of the  $n \rightarrow \pi^*$  Cotton effect ( $\sim 225$  nm) is positive, otherwise the sign is negative. The CD curve of **1** showed a negative Cotton effect (230 nm, MeOH) that attributed to the lactone  $n \rightarrow \pi^*$  transition. Furthermore, experimental CD spectrum of **1** was compared to the theoretical spectra of the (1*R*,4*R*,5*S*,7*S*)-enantiomer of compound **1** obtained by time-dependent DFT quantum mechanics (TDDFT) [B3LYP/6–31G(d)]. The excellent agreement of the experimental and simulated spectra (Graph 1) confirmed the above empirical deduction. Thus, **1** was assigned as (1*R*,4*R*,5*S*,7*S*)-curwenyujinone.



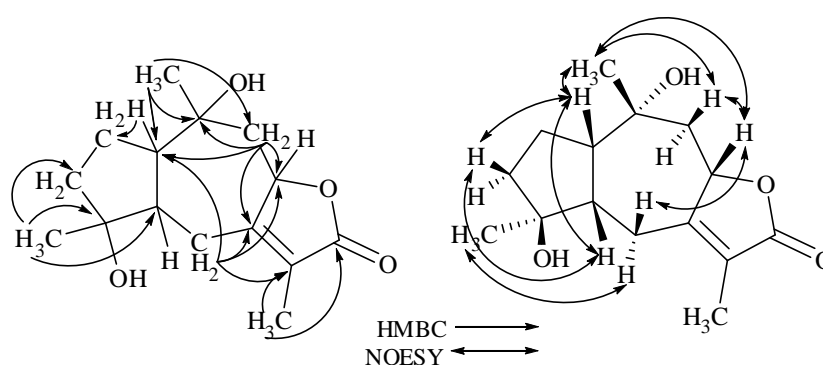
**Graph 1.** The UV, experimental and simulated CD curves of compound **1**.

Compound **2** was isolated as a colourless oil, with a molecular formula assigned as  $C_{15}H_{22}O_4$  on the basis of HRESI-MS ( $m/z$  267.1595 [ $M+H$ ] $^+$ , calcd. 267.1591;  $m/z$  289.1412 [ $M+Na$ ] $^+$ , calcd. 289.1410) and NMR data. Its IR spectrum had absorption bands at 3431, 1736, 1673 and 1109  $cm^{-1}$ , suggesting the presence of hydroxy and  $\alpha,\beta$ -unsaturated  $\gamma$ -lactone functionalities. The  $^1H$  and  $^{13}C$  NMR of **2** resembled those of **3** (Table 2), a known one firstly isolated by Lou Y. group in 2009 [15]. Thus, **2** was considered to be a stereoisomer of zedoalactone E (**3**), and this was confirmed by 2D NMR spectra, showing the same correlations as those for **3**. The relative configuration of **2** was determined by NOE correlations. The NOE correlation of H-1/H-5 indicated that the H-1 and H-5 had

a *cis*-configuration. Furthermore, the correlations of H-15/H-1 and H-8/H-15 suggested that H-1, 5, and 8 were in the same-orientation and were randomly assigned as  $\beta$ -orientation. While the correlations of H-6 $\beta$ /H-8 and H-6 $\alpha$ /H-14 concluded that H-14 and H-8 were in the *trans*-orientation. Thus, compound **2** was determined to be 4 $\beta$ ,10 $\alpha$ -dihydroxy-1,5,8  $\beta$ H-guai-7(11)-en-12,8-olide, named as zedoalactone H.

**Table 2.**  $^1\text{H}$  NMR (600 MHz) and  $^{13}\text{C}$  NMR (150 MHz) spectral data of compound **2**, **3** in  $\text{DMSO-}d_6$ .

Position	<b>2</b>		<b>3</b>	
	$\delta_{\text{C}}$	$\delta_{\text{H}}$ (J in Hz)	$\delta_{\text{C}}$	$\delta_{\text{H}}$ (J in Hz)
1	52.0	2.50 (1H, dd, 7.8, 10.4)	52.0	2.77 (1H, m)
2	24.9	1.65 (1H, m)	24.5	1.59 (1H, m)
		1.47 (1H, m)		1.27 (1H, m)
3	38.1	1.58 (1H, m)	37.3	1.54 (2H, t, 7.8, 6.7)
		1.65 (1H, m)		
4	80.3	—	80.4	—
5	50.3	1.86 (1H, ddd, 3.6, 7.8, 13.8)	47.4	2.07 (1H, dd, 4.8, 10.2)
6	24.6	1.95 (1H, t, 12.6)	24.5	2.63 (1H, dd, 18.0, 4.8)
		2.60 (1H, dd, 3.6, 12.0)		2.30 (1H, dd, 10.2, 18.0)
7	163.4	—	166.0	—
8	80.8	4.97 (1H, m)	79.5	5.19 (1H, d, 10.8)
9	38.8	2.28 (1H, dd, 7.2, 15.0)	40.7	1.62 (1H, dd, 11.4, 13.2)
		1.73 (1H, dd, 3.6, 15.6)		2.04 (1H, ddd, 1.8, 3.6, 10.2)
10	72.0	—	71.0	—
11	120.8	—	120.4	—
12	175.0	—	174.5	—
13	8.2	1.69 (3H, d, 1.8)	8.8	1.70 (3H, s)
14	25.2	1.20 (3H, s)	25.7	1.23 (3H, s)
15	30.5	1.10 (3H, s)	32.2	1.16 (3H, s)
-OH	—	4.40 (1H, br s)	—	4.73 (1H, br s)
		4.13 (1H, br s)		4.37 (1H, br s)



**Figure 3.** The key HMBC and NOESY correlations of compound **2**.

Other six known compounds were also identified by comparison of their spectroscopic data with those reported in the literatures. The chemical structures of compounds **1–8** are shown in Figure 1.

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## Supporting Information

Supporting Information accompanies this paper on <http://www.acgpubs.org/RNP>

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