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# An efficient and convenient formal synthesis of Jaspine B from D-xylose

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ABSTRACT

A formal synthesis of Jaspine B was completed in 42.4% overall yield with only three purification steps (one by crystallization and two by column chromatography). The key step in the synthesis involves a regio- and stereoselective epoxide ring-opening reaction and the configuration inversion of the C3-hydroxyl group through oxidation and reduction. All of the reagents and materials used were quite common and inexpensive.



Jaspine B (**1**), also known as pachastrissamine, is a naturally occurring novel anhydrosphingosine derivative, which was isolated by Higa and co-workers in 2002 from the Okinawa marine sponge *Pachastrissa sp.* (family Calthropellidae) and was found to possess cytotoxicity at an $IC_{50}$ level of 0.01 μg/mL against P388, A549, HT29, and Mell 28 cell lines.[1] Shortly thereafter, Debitus and co-workers reported the isolation of the same natural product from a different marine sponge *Jaspis sp.*[2]

Due to its impressive biological activity, novel structural features, and the lack of structure–activity relationship (SAR) studies on Jaspine B, much effort has been devoted to research of this interesting natural product.[3–6] However, SAR of this molecule is still scarce, which has prompted extensive synthetic studies of Jaspine B and its analogues.[7–12]

Most of the syntheses known for Jaspine B derive the asymmetry from the chiral pool of starting materials such as Garner's aldehyde,[13] or glucose.[14] A well-designed synthesis from D-xylose was also reported by Du.[15a] Unfortunately, the conversion of a mesylate derivative into an azido intermediate was quite slow and the yield was not satisfactory,[15b] as described in other reports.[11a,14] To explore a more economical and practical method, and to continue our successful efforts in the synthesis of higher carbon sugars and new amino sugars from D-xylose,[16] herein we report a practical and efficient synthesis of Jaspine B from D-xylose.

As shown in Scheme 1, Jaspine B can be retrosynthetically disconnected into aldehyde **1** according to Du's method. Aldehyde **1** can be accessed from **2** via hydrolysis. Acetal **2** can be obtained by benzylation of **3**, which, in turn, can be prepared from an 1,2-azido alcohol derivative **4** through a configuration change of the C3-hydroxy; group. Alcohol **4** can be derived from an epoxide **5** via a regio- and stereoselective epoxide ring-opening reaction as reported by Wightman.[17] The epoxide **5** can be easily prepared from D-xylose.[18]

First, D-xylose was treated with concentrated $H_2SO_4$ in acetone to give 1,2-acetal **7** in a 88% yield[19] (Scheme 2). Tosylation of **7** with tosyl chloride and pyridine in $CH_2Cl_2$ at room temperature afforded **6**, which could be crystallized in a 82% yield. Acid-catalyzed furan ring formation and epoxide generation led to **5** in a 94% yield. The 1,2-azido alcohol **4** was formed via ring-opening reaction of epoxide **5** with $NaN_3$ in a 95% yield.

Then the main problem was the configuration change of the C3-hydroxyl group of 1,2-azido alcohol **4**. Oxidation and stereoselective reduction were used due to steric hindrance. Thus, oxidation of 1,2-azido alcohol **4** followed by stereoselective reduction furnished a mixture of diastereomeric alcohols **3** and **4**. Reaction of this mixture of alcohols with benzyl bromide in the presence of potassium carbonate resulted in **2** and **2′** (Table 1), which could be separated easily via column chromatography due to a huge difference of $R_f$ value. Compound **2′** would be of use for preparing 3-*epi* Jaspine B.

The influence of reaction conditions of oxidation and reduction were examined as summarized in Table 1. When IBX was used as the oxidant, an excellent yield was observed (entry 4). Swern oxidation and PDC oxidation could also be used, and lower yields were observed (entries 1 and 2). However, no product was obtained by employing DMSO and acetic anhydride (entry 3). Thus, IBX was the best choice for the reaction. The influence of the reductant and temperature on yield and ratio of **3** and **4** were also studied (entries 4–6). When $NaBH_4$ was used as the reductant, or the temperature of the reduction reaction changed from 25 °C to −20 °C, no obvious variation in yields and ratio was observed. Therefore, the optimal reaction conditions were those outlined in entry 4.

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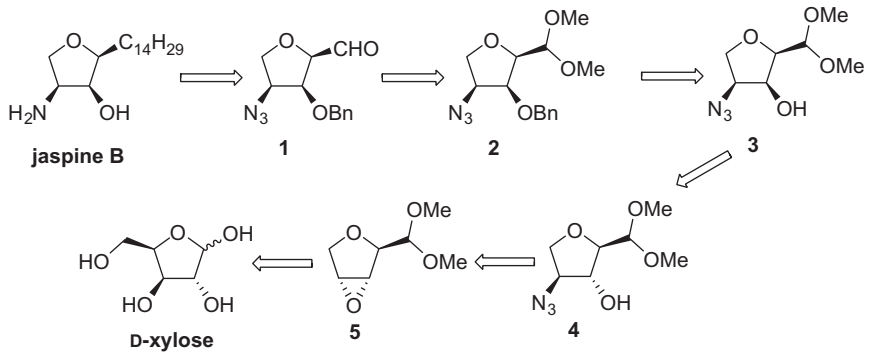
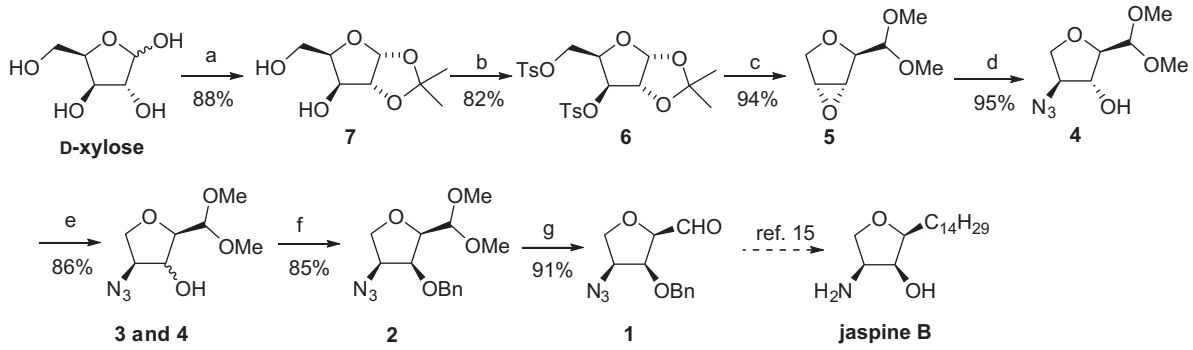
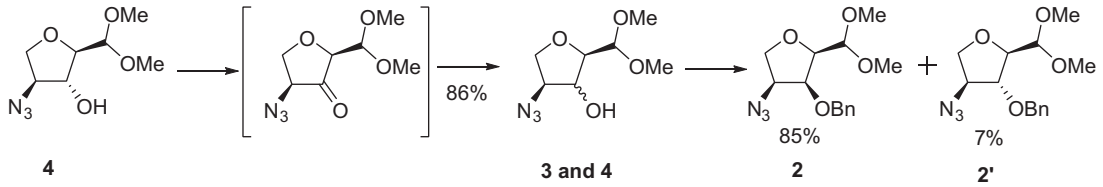



**Scheme 1.** Retrosynthetic analysis of Jaspine B.




**Scheme 2.** Synthesis of **1**. Reagents and conditions: (a) concd $H_2SO_4$, acetone, rt, then $Na_2CO_3$, rt; (b) tosyl chloride, pyridine, $CH_2Cl_2$, rt; (c) methanol, AcCl, reflux, then $K_2CO_3$, rt; (d) $NaN_3$, $NH_4Cl$, $H_2O$/ethanol, reflux; (e) IBX, EtOAc, reflux, then $KBH_4$, ethanol, rt; (f) BnBr, $K_2CO_3$, THF, reflux; (g) dioxane, 0.05 mol/L hydrochloric acid, 80 °C.

**Table 1**
Optimization of the oxidation and reduction reaction of **4** to **3**




| Entry | Oxidant | Reductant | Temperature[a] (°C) | Yield[b] | Ratio[c] (**3**:**4**) |
|---|---|---|---|---|---|
| 1 | PDC | $KBH_4$ | 25 | 35% | 12:1 |
| 2 | DMSO and oxalyl chloride | $KBH_4$ | 25 | 68% | 12:1 |
| 3 | DMSO and acetic anhydride | $KBH_4$ | 25 | 0 | —[d] |
| 4 | IBX | $KBH_4$ | 25 | 86% | 12:1 |
| 5 | IBX | $NaBH_4$ | 25 | 85% | 12:1 |
| 6 | IBX | $KBH_4$ | −20 | 86% | 12:1 |

[a] The temperature of reduction reaction.
[b] The crude yield of the mixture of compounds **3** and **4**.
[c] Determined by compound **2** and **2′**.
[d] Not tested.

The acetal of **2** was cleaved with 0.05 M hydrochloric acid to afford aldehyde **1** in a 91% yield. Finally, aldehyde **1** was synthesized in a 42.4% overall yield from D-xylose. Jaspine B and its analogues can be prepared from aldehyde **1** via Wittig reaction.

In summary, we have reported a practically efficient formal synthesis of Jaspine B in a high yield from inexpensive and easily available materials and reagents. The synthesis of the analogues of Jaspine B using this approach is currently underway. The biological activity of these analogues will be published elsewhere.

## 1. Experimental

### 1.1. General conditions

Melting points were measured on a WC-1 melting-point apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 341 polarimeter at 25 °C. Infrared spectra were recorded using KBr discs on a Bruker Vector-22 FTIR spectrometer. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker Advance

DPX-400 spectrometer using $CDCl_3$ as the solvent and TMS as internal standard. HRMS (high-resolution mass spectra) were taken with a Q-Tof Micromass spectrometer.

### 1.2. 1,2-*O*-Isopropylidene-3,5-di-*O*-*p*-toluenesulfonyl-α-D-xylofuranose (6)

A solution of **7**[19] (30.0 g, 158 mmol) and pyridine (38.2 mL, 473 mmol) in $CH_2Cl_2$ (300 mL) was cooled to 0 °C, TsCl (75.0 g, 395 mmol) was added to the mixture. After the mixture was stirred for 24 h at 0 °C to room temperature, saturated $NaHCO_3$ solution was added, and the reaction mixture was extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated. Crystallization of the crude product from ethanol gave compound **6** as a white solid (64.7 g, 82.3%) mp 100.4–102.1 °C; $[\alpha]_D^{25}$ −30 (*c* 1.0, $CHCl_3$); IR (KBr); 2932, 1308, 1191, 1176, 1096, 1065, 1051, 994, 841, 713, 666, 551 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.26 (s, 3H, $CH_3$), 1.42 (s, 3H, $CH_3$), 2.45 (s, 3H, $ArCH_3$), 2.48 (s, 3H, $ArCH_3$), 3.94–4.08 (m, 2H, H-5), 4.33 (td, *J* = 6.1, 3.0 Hz, 1H, H-4), 4.68 (d, *J* = 3.6 Hz, 1H, H-2), 4.77 (d, *J* = 3.0 Hz, 1H, H-3), 5.86 (d, *J* = 3.6 Hz, 1H, H-1), 7.37 (2d, *J* = 8.2 Hz, 4H, Ar-H), 7.75 (2d, *J* = 8.3 Hz, 4H, Ar-H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 21.7 ($ArCH_3$), 21.7 ($ArCH_3$), 26.2 ($CMe_2$), 26.5 ($CMe_2$), 65.9 ($CH_2$), 76.3 (CH), 81.3 (CH), 83.0 (CH), 104.8 (CH), 112.8 ($CMe_2$), 128.0 (ArC), 129.9 (ArC), 130.3 (ArC), 132.2 (ArC), 132.4 (ArC), 145.2 (ArC), 145.9 (ArC). HRMS: calcd for $C_{14}H_{19}N_3O_4Na$ $[M+Na]^+$ 521.0919, found: 521.0915.

### 1.3. (2*R*,3*R*,4*R*)-2-Dimethoxymethyl-3,4-epoxytetrahydrofuran (5)

A solution of the compound **6** (30.0 g, 60.2 mmol) in dry methanol (500 mL) containing AcCl (2.50 mL, 35.5 mmol) was heated at reflux for 24 h. The mixture was cooled to room temperature and stirred with anhydrous calcium carbonate (15.0 g, 108.5 mmol) overnight. The mixture was filtered and the solids washed with $CH_2Cl_2$. The combined filtrates were evaporated and the residue was partitioned between $CH_2Cl_2$ and brine, the organic layer was dried over $MgSO_4$, and concentrated under vacuum to give **5** as a syrup (9.1 g, 94.2%). This compound was used in the next step without further purification. A small sample was purified on a silica gel column (petroleum ether–EtOAc 1:1) to provide pure **5**: $[\alpha]_D^{25}$ +26 (*c* 1.1, $CHCl_3$); IR (KBr); 3467, 2941, 1737, 1713, 1365, 1201, 908, 854 $cm^{-1}$.$^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.44 (s, 3H, $CH_3$), 3.46 (s, 3H, $CH_3$), 3.76 – 3.88 (m, 3H, H-3, H-4, H-5$_\beta$), 3.98 (d, *J* = 10.1 Hz, 1H, H-5$_\alpha$), 4.08 (d, *J* = 4.4 Hz, 1H, H-2), 4.29 (d, *J* = 4.4 Hz, 1H, H-1). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 55.3 ($CH_3$), 56.2 ($CH_3$), 56.5 (CH), 56.7 (CH), 67.9 ($CH_2$), 77.6 (CH), 104.8 (CH). HRMS: calcd for $C_7H_{12}O_4Na$ $[M+Na]^+$ 183.0633, found: 183.0636.

### 1.4. (2*R*,3*R*,4*S*)-4-Azido-2-dimethoxymethyl-3-hydroxytetrahydrofuran (4)

A solution of epoxide **5** (10.0 g, 62.5 mmol), sodium azide (8.1 g, 124.6 mmol) and ammonium chloride (10.0 g, 188.7 mmol) in 95% ethanol (200 mL) was heated at reflux for 24 h. The residue formed after evaporation was extracted with $CH_2Cl_2$. The organic layer was dried over $MgSO_4$, and concentrated under vacuum to give **4** as a syrup (12.1 g, 95.4%). This compound was used in the next step without further purification. A small sample was purified on a silica gel column (petroleum ether–EtOAc, 1.5:1) to obtain pure **4**: $[\alpha]_D^{25}$ +30 (*c* 1.0, $CHCl_3$); IR (KBr); 3410, 2940, 2100, 1668, 1085 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.01 (s, 1H, OH), 3.45 (s, 3H, $CH_3$), 3.48 (s, 3H, $CH_3$), 3.77 (dd, *J* = 6.2, 5.0 Hz, 1H, H-2), 3.86 (dd, *J* = 9.6, 3.9 Hz, 1H, H-5$_\alpha$), 3.95–4.01 (m, 1H, H-4), 4.06 (dd, *J* = 9.6, 5.7 Hz, 1H, H-5), 4.22 (s, 1H, H-3), 4.39 (d, *J* = 6.3 Hz, 1H, H-1). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 54.2 ($CH_3$), 55.9 ($CH_3$), 66.8 (CH), 70.4 ($CH_2$), 77.5 (CH), 84.2 (CH), 104.5 (CH). HRMS: calcd for $C_7H_{13}N_3O_4$ Na $[M+Na]^+$ 226.0804, found: 226.0809.

### 1.5. Mixture of (2*R*,3*R*,4*S*)-4-azido-2-dimethoxymethyl-3-hydroxytetrahydrofuran (3) and (2*R*,3*R*,4*S*)-4-azido-2-dimethoxymethyl-3-hydroxytetrahydrofuran (4)

A solution of the compound **4** (10.0 g, 49.2 mmol), IBX (34.4 g, 123.7 mmol) in EtOAc (200 mL) was heated at reflux for 8 h. The mixture was filtered and the solids washed with EtOAc. The combined filtrates were evaporated. The residue was dissolved in ethanol (150 mL), $KBH_4$ (2.7 g, 49.2 mmol) was added, and the mixture was stirred at room temperature for 3 h, then quenched by the addition of saturated $NH_4Cl$ aqueous solution. The mixture was evaporated and the residue was partitioned between EtOAc and brine, the organic layer was dried over $Na_2SO_4$, and concentrated under vacuum to give the mixture of **3** and **4** as a syrup (8.6 g, 86.1%). This mixture was used in the next step without further purification.

### 1.6. (2*R*,3*R*,4*S*)-4-Azido-2-dimethoxymethyl-3-hydroxytetrahydrofuran (3)

A solution of the mixture of **3** and **4** (1.0 g, 4.92 mmol) and pyridine (0.8 mL, 10.0 mmol) in $CH_2Cl_2$ (10 mL) was cooled to 0 °C and then acetic anhydride (0.7 mL, 7.35 mmol) was added to the mixture. After the solution was stirred for 5 h at 0 °C to room temperature, saturated $NaHCO_3$ solution was added, and the reaction mixture was extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified on a silica gel column (petroleum ether–EtOAc 7:1) to get intermediate **I**. The material was dissolved in saturated $NH_3$–$CH_3OH$ (10 mL) and the mixture was stirred at room temperature for 3 h. Then, the mixture was evaporated and the residue was purified on a silica gel column (petroleum ether–EtOAc 1.5:1) to give pure **3**: $[\alpha]_D^{25}$ −10 (*c* 1.0, $CHCl_3$); IR (KBr); 3461, 2938, 2103, 1737, 1216 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.18 (s, 1H, OH) 3.44 (s, 3H, $CH_3$), 3.46 (s, 3H, $CH_3$), 3.86–4.04 (m, 4H, H-5$_\beta$, H-5$_\alpha$, H-4, H-2), 4.42 (s, 1H, H-3), 4.61 (d, *J* = 6.7 Hz, 1H, H-1). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 54.5 ($CH_3$), 55.3 ($CH_3$), 62.5 (CH), 68.8 ($CH_2$), 72.7 (CH), 79.9 (CH), 103.2 (CH). HRMS: calcd for $C_7H_{13}N_3O_4$ Na $[M+Na]^+$ 226.0804, found: 226.0801.

### 1.7. (2*R*,3*S*,4*S*)-4-Azido-2-dimethoxymethyl-3-benzyloxytetrahydrofuran (2) and (2*R*,3*R*,4*S*)-4-azido-2-dimethoxymethyl-3-benzyloxytetrahydrofuran (2′)

A solution of the mixture of **3** and **4** (6.0 g, 29.5 mmol), calcium carbonate (4.1 g, 29.5 mmol) and benzyl bromide (6.0 g, 35.4 mmol) in THF (100 mL) was heated at reflux for 5 h. The mixture was filtered and the solids washed with EtOAc. The combined filtrates were evaporated and the residue was partitioned between EtOAc and brine, the organic layer was dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified on a silica gel column (petroleum ether–EtOAc, 7:1) to afford **2** (7.4 g, 85.3%) and **2′** (0.62 g, 7.2%) as a syrup. Compound **2**: $[\alpha]_D^{25}$ +55 (*c* 1.0, $CHCl_3$); $R_f$ 0.3 (petroleum ether–EtOAc 5:1); IR (KBr); 3446, 2941, 2100, 1082, 781 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.38 (s, 3H, $CH_3$), 3.45 (s, 3H, $CH_3$), 3.84 (td, *J* = 7.6, 4.7 Hz, 1H, H-4), 3.94 (dd, *J* = 7.7, 4.2 Hz, 1H, H-3), 3.98–4.09 (m, 2H, H-5, H-5$_\alpha$), 4.20 (t, *J* = 4.4 Hz, 1H, H-2), 4.61–4.72 (m, 2H, $CH_2Ph$), 4.84 (d, *J* = 11.2 Hz, 1H, H-1), 7.30–7.49 (m, 5H, Ar-H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 53.5 ($CH_3$), 55.0 ($CH_3$), 61.5 (CH), 68.7 ($CH_2$), 74.4 ($CH_2$), 79.8 (CH), 80. 0(CH), 102.2 (CH), 127.9 (ArC), 127.9 (ArC), 128.4 (ArC), 137.6 (ArC). HRMS: calcd for $C_{14}H_{19}N_3O_4Na$ $[M+Na]^+$: 316.1273,

found: 316.1277. Compound **2′**: $[\alpha]_D^{25}$ +38 (*c* 1.0, $CHCl_3$); $R_f$ 0.7 (petroleum ether–EtOAc 5:1); IR (KBr); 2937, 2100, 1095, 738, 698 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.45 (s, 3H, $CH_3$), 3.47 (s, 3H, $CH_3$), 3.95–4.07 (m, 5H, H-4, H-3, H-2, H-5, H-5$_\alpha$), 4.37 (d, *J* = 6.3 Hz, 1H, H-1), 4.63 (q, *J* = 11.8 Hz, 2H, $CH_2Ph$), 7.30–7.42 (m, 5H, Ar-H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 54.1 ($CH_3$), 55.5 ($CH_3$), 65.7 (CH), 70.9 ($CH_2$), 72.1 ($CH_2$), 84.2 (CH), 84.5 (CH), 103.8 (CH), 128.0 (ArC), 128.0 (ArC), 128.5 (ArC), 137.3 (ArC). HRMS: calcd for $C_{14}H_{19}N_3O_4Na$ $[M+Na]^+$ 316.1273, found: 316.1273.

### 1.8. (2*R*,3*S*,4*S*)-4-Azido-3-(benzyloxy)tetrahydrofuran-2-carbaldehyde (1)

A solution of **2** (3.0 g, 10.2 mmol) in dioxane (10 mL) and 0.05 M hydrochloric acid (30 mL) was stirred at 80 °C for 3 h. The mixture was neutralized with saturated aqueous sodium carbonate and extracted with $CH_2Cl_2$, the organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified on a silica gel column (petroleum ether–EtOAc 5:1) to afford **1** (2.3 g, 90.8%): $[\alpha]_D^{25}$ +27 (*c* 0.2, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 4.06 (m, 3H), 4.32 (dd, *J* = 6.9, 1.8 Hz, 1H), 4.53 (dd, *J* = 6.7, 4.5 Hz, 1H), 4.70, 4.73 (2d, *J* = 11.7 Hz, 2H, $CH_2Ph$), 7.30–7.49 (m, 5H, ArH), 9.69 (d, *J* = 1.9 Hz, 1H, CHO). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 61.0 (CH), 70.5 ($CH_2$), 73.7 ($CH_2$), 81.5 (CH), 82.4 (CH), 128.0 (ArC), 128.3 (ArC), 128.6 (ArC), 136.6 (ArC), 200.5 (CHO). HRMS: calcd for $C_{14}H_{19}N_3O_4Na$ $[M+Na]^+$ 270.0855, found: 270.0857.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2012.01.013.

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