DOI：10.11931/guihaia.gxzw201312033
黄永林，李典鹏，杨子明. 红背山麻杆叶的化学成分研究（Ⅳ）——多酚类化合物[J]. 广西植物，2015，35(4)：564－568
Huang YL，Li DP，Yang ZM. Chemical constituents from the leaves of *Alchornea trewioides* (4). Polyphenols[J]. Guihaia，2015，35(4)：564－568

Chemical constituents from the leaves of *Alchornea trewioides*（4）. Polyphenols

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Abstract：*Alchornea trewioides*，as atraditional Chinese medicine，was used to alleviate illness and discomfort in China，but the material basis of pharmacodynamic was unknown. In order to research for the material basis of pharmacodynamic from *A. trewioides* leaves，the fresh leaves of *A. trewioides* were extracted with 80% aqueous acetone and assigned by petroleum ether and water. The petroleum ether and water extracts were subjected to the column chromatography by MCI gel CHP 20P，Sephadex LH-20，and Toyopearl Butyl-650C，respectively，to yield nine polyphenols. Their structures were identified by means of ^{1}H NMR，^{13}C NMR，DEPT，and comparison with literature as：ellagic acid(**1**)，3-*O*-methylellagic acid(**2**)，decarboxyellagic acid(**3**)，1-*O*-galloyl-β-D-glucose(**4**)，1，6-di-*O*-galloyl-β-D-glucose(**5**)，corilagin(**6**)，phyllanthusiin D(**7**)，furosonin(**8**)，and geraniin(**9**)，respectively. Compounds **2**-**9** were obtained from *A. trewioides* for the first time.

Key words：*Alchornea trewioides*；chemical constituents；polyphenols；ellagic acid；extraction and separation
CLC number：Q946.91，R284.1　**Document code**：A　**Article ID**：1000-3142(2015)04-0564-05

红背山麻杆叶的化学成分研究(Ⅳ)——多酚类化合物

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摘　要：红背山麻杆(*Alchornea trewioides*)为山麻杆属植物，作为传统的中药被用来减轻疾病和身体不适，但它的药效物质基础尚未完全清楚。为了全面掌握红背山麻杆药效物质基础，采用80%丙酮对其新鲜叶进行提取，并利用MCI gel CHP 20P、Sephadex LH-20等色谱柱进行分离共得到9个化合物。这些化合物的结构经氢谱与碳谱比较分析鉴定为鞣花酸(**1**)、3-*O*-甲基没食子酸(**2**)、decarboxyellagic acid(**3**)、1-*O*-没食子酰基-β-D-葡萄糖(**4**)、1，6-二-*O*-没食子酰基-β-D-葡萄糖(**5**)、柯里拉京(**6**)、叶下珠鞣质D(**7**)、furosonin(**8**)、老鹳草素(**9**)。其中化合物**2**～**9**均为首次从该属植物中分离得到。

关键词：红背山麻杆；化学成分；多酚；鞣花酸；提取与分离

Alchornea trewioides，as atraditional Chinese medicine，was used to reduce illness，discomfort，and treated inflammation of the prostate gland，hematuria，and other diseases in China(Jiangsu New Medical College，1977). In previously，the polyphenols，such as flavonoids，quinic acids，phenylethanoids，and phenol-

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收稿日期：2014-12-26　**修回日期**：2015-02-09
基金项目：广西自然科学基金(2011GXNSFD018038)；广西科技合作与交流计划项目(桂科合1298014-10)；广西植物研究所基本业务费项目(桂植业13002)；广西植物功能物质研究与利用重点实验室开放基金(ZRJJ2013-7)。

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ic acids have been reported (Lu, 2012; Qin, 2012, Huang, 2013, 2014, 2015). However, the other main components of polyphenols have not been reported, and the material basis of pharmacodynamic is unknown. In order to grasp for the material basis of *A. trewioides*, 80% acetone extracts were subjected to the column chromatography by MCI gel CHP 20P, Sephadex LH-20, and Toyopearl Butyl-650C, respectively, to yield nine polyphenols. Their structures were identified by means of ^1H NMR, ^{13}C NMR, DEPT and comparison with literature. Compounds **2-9** were obtained from the *A. trewioides* for the first time.

1 Materials and Methods

^1H- and ^{13}C-NMR spectra were measured with a JEOL JNM-AL 400 spectrometer (Tokyo, Japan), operating at 400 MHz for ^1H, and 100 MHz for ^{13}C, or a Bruker Avance 500 spectrometer (Bruker Biospin AG, Faellanden, Switzerland), operating at 500 MHz for ^1H, and 125 MHz for ^{13}C. Coupling constants and chemical shifts were given in Hz and on a δ (ppm) scale, respectively. Column chromatography was used on MCI gel CHP 20P, Sephadex LH-20 and Toyopearl Butyl-650C. TLC was carried out on silica gel 60 F_{254} (Merck), with formic acid-formate-toluene-ethyl (2 ∶ 8 ∶ 2, or 1 ∶ 7 ∶ 1 v/v), and sports were visualized with a 2% ethanolic $FeCl_3$.

The leaves of *Alchornea trewioides* were collected in the Guilin Botanical Garden, Guangxi, China, in August 2011. The sample plant was identified by Prof. WEI Fa-Nan of Guangxi Institute of Botany, and a herbarium specimen (2011 0920N) was deposited in the Guangxi Institute of Botany.

2 Extraction and Isolation

The small pieces, fresh leaves of (5.35 kg) were extracted with 80% acetone for three times, at room temperature. The filtrate was evaporated by rotary evaporation to give an extract. The extract (610 g) was assigned between Et_2O (1 L) and H_2O (3 L) 3 times. The part of Et_2O-soluble fraction (Fr. E 5.46 g) was dissolved in EtOH and applied to a Sephadex LH-20 column (3.5 cm i. d.×45 cm) with 100%－0 EtOH (20% stepwise elution, each 300 mL) to give five fractions. The E-3 (0.67 g) was applied to a MCI gel CHP 20P column (2.5 cm i. d.×25 cm) with MeOH-H_2O (0 ∶ 100－100 ∶ 0) to obtain **3** (70 mg). The part of water-soluble fraction was dissolved in water and appliedto a Sephadex LH-20 column (10 cm i.d.×40 cm), eluting successively with H_2O, 20%, 40%, 60%, 80%, 100% MeOH-H_2O to yield 9 fractions (Fr. 1-9). The fraction 3 (6.51 g) was applied by a combination of column chromatography over Sephadex LH-20, MCI gel CHP 20P, and Toyopearl Butyl-650C to obtain **4** (45 mg) and **5** (28 mg). Fraction 6 (36.0 g) was separated by MCI gel CHP 20P column chromatography to give seven fractions. Fraction 6-4 (2.45 g) was separated by a column chromatography over Sephadex LH-20 column (4 cm i. d.×35 cm) with MeOH-H_2O (0 ∶ 100) to yield **6** (2.15 g). Fraction 7 (43.0 g) was applied by a MCI gel CHP 20P column with MeOH-H_2O (0 ∶ 100) to afford five fractions. Fraction 7-1 was further separated by MCI gel CHP 20P and Sephadex LH-20 column to give **6** (4.52 g), **8** (116 mg). Separation of fraction 7-2 using Sephadex LH-20 (3 cm i. d.×50 cm) with MeOH-H_2O (0 ∶ 100－100 ∶ 0), and finally with 60% acetone to afford **7** (476 mg). Separation of fraction 7-3 used Sephadex LH-20, Chromatorex ODS, and Toyopearl Butyl-650C to afford **1** (14 mg), **2** (31 mg), **9** (6.41 g).

3 Results and Analysis

Ellagic acid (**1**) amorphous white powder, $C_{14}H_6O_8$. ^1H-NMR (400 MHz, DMSO) β: 7.50 (2H, s, H-5, 5′); ^{13}C-NMR (125 MHz, DMSO) β: 106.8 (C-1, 1′), 109.7 (C-5, 5′), 112.6 (C-6, 6′), 136.3 (C-2, 2′), 140.6 (C-3, 3′), 148.1 (C-4, 4′), 159.1 (C-7, 7′) (Khac *et al.*, 1990).

3-*O*-Methylellagic acid (**2**) amorphous white powder, $C_{15}H_8O_8$. ^1H-NMR (500 MHz, DMSO) β: 4.03 (3H, s, 3-OMe), 7.43 (1H, s, H-5′), 7.50 (1H, s, H-5, 5′); ^{13}C-NMR (125 MHz, DMSO) β: 60.7 (C-OMe), 107.1 (C-6′), 110.7 (C-5′), 111.6 (C-5), 111.9

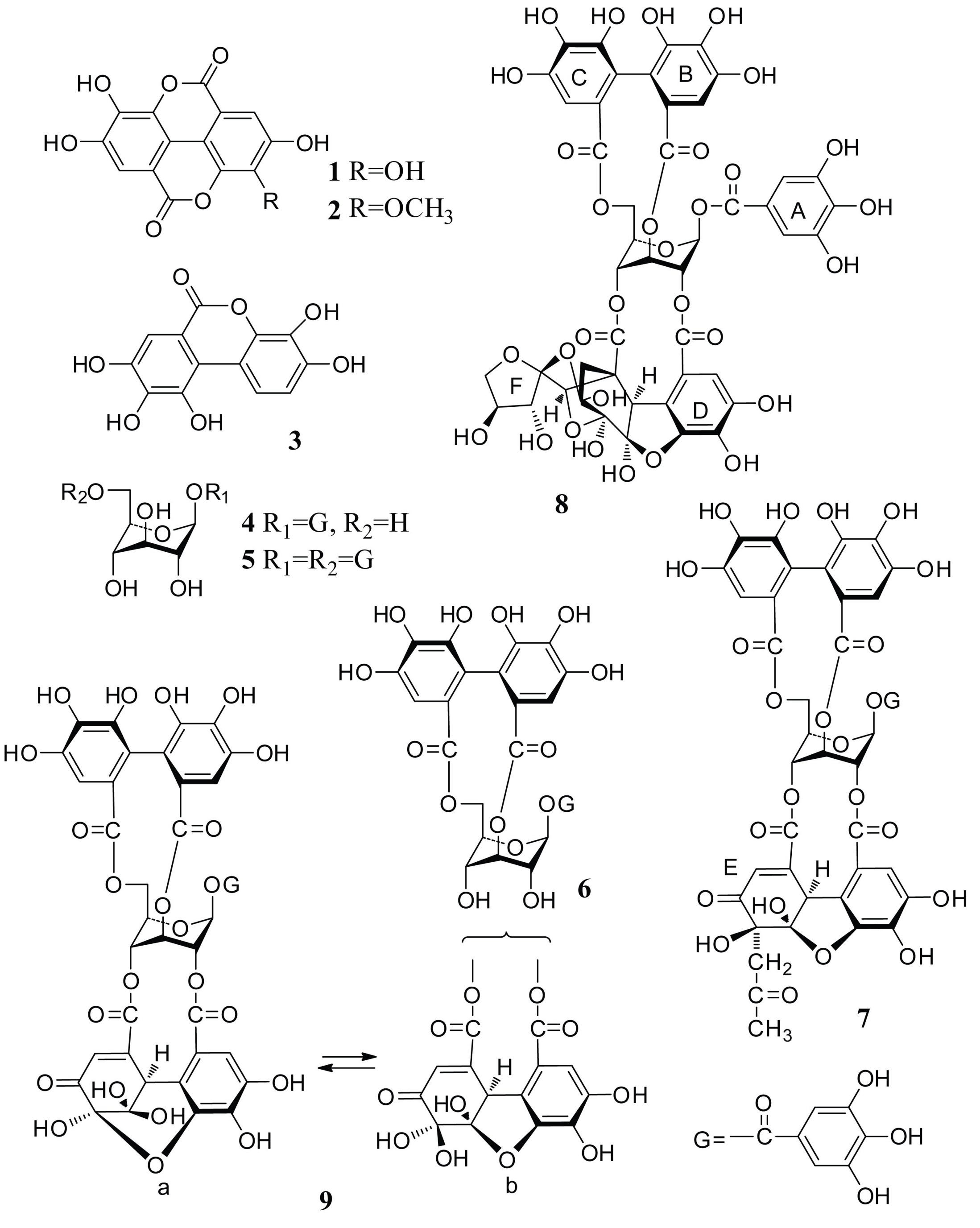

Fig. 1 Chemical structures of compounds **1**—**9**

(C-1), 112.5(C-6), 113.1(C-1′), 137.0(C-2′), 134.0(C-3′), 141.6(C-3), 140.9(C-2), 148.1(C-4′), 152.2(C-4), 158.6(C-7′), 158.8(C-7)(Bai *et al*., 2008).

Decarboxyellagic acid(**3**) amorphous white powder, $C_{13}H_8O_7$. ^{1}H-NMR(400 MHz, CD_3OD) β: 6.73(1H, d, *J*=8.1 Hz, H-5′), 7.41(1H, s, H-5), 8.42(1H, d, *J*=8.1 Hz, H-6′); ^{13}C-NMR (100 MHz, CD_3OD)β: 108.1(C-5), 112.1(C-6), 112.4(C-5′), 112.8(C-1′), 118.5(C-1), 119.1(C-6′), 133.3(C-3′), 141.1(C-3), 141.8(C-2′), 144.0(C-2), 146.4(C-4), 146.8(C-4′), 163.8(C-6)(Pfundstein *et al*., 2010).

1-*O*-Galloyl-β-D-glucose (**4**) amorphous brown powder, $C_{13}H_{16}O_{10}$. ^{1}H-NMR(500 MHz, acetone-d_6)β: 3.18 (1H, t, *J*=8.8 Hz, H-4), 3.21-3.55(3H，m，H-2，3，5)，3.46(1H，dd，*J*＝6.1，12.0 Hz，H-6ax)，3.64(1H，dd，*J*＝3.9，12.0 Hz，H-6eq)，5.53(1H，d，*J*＝8.5 Hz，H-1)，7.23(2H，s，H-2′，6′)；^{13}C-NMR(125 MHz，acetone-d_6)β：60.3(C-6)，69.6(C-4)，72.3(C-2)，75.6(C-5)，76.1(C-3)，93.4(C-1)，108.9(2C，C-2′，6′)，119.4(C-1′)，137.0(C-4′)，144.0(2C，C-3′，5′)，165.2(C-7′) (El-Ekkawy *et al*.，1995).

1,6-Di-*O*-galloyl-β-D-glucose (**5**) amorphous brown powder，$C_{20}H_{20}O_{14}$. ^{1}H-NMR(500 MHz，acetone-d_6)β：3.21-3.75(4H，m，H-2，3，4，5)，4.42(1H，dd，*J*＝6.5，12.0 Hz，H-6ax)，4.58(1H，dd，*J*＝2.7，12.0 Hz，H-6eq)，5.67(1H，d，*J*＝7.5 Hz，H-1)，7.08，7.15(each 2H，s，H-2′，6′ and 2″，6″)；^{13}C-NMR(125 MHz，acetone-d_6)β：63.3(C-6)，70.3(C-4)，73.6(C-2)，75.1(C-5)，76.8(C-3)，95.7(C-1)，107.9，108.0(each 2C，C-2′，6′ and 2′，6″)，119.3，119.4(C-1′，1″)，136.9，137.4(C-4′，4″)，143.9，144.0(each 2C，C-3′，5′ and 3″，5″)，165.1，165.1(C-7′，7″)(Yan *et al*.，2007).

Corilagin (**6**) amorphous brown powder，$C_{27}H_{22}O_{18}$. ^{1}H-NMR(500 MHz，acetone-d_6)β：4.08(1H，br s，H-2)，4.13(1H，dd，*J*＝8.5，11.0 Hz，H-6ax)，4.46(1H，br s，H-4)，4.52(1H，t，*J*＝8.5 Hz，H-5)，4.83(1H，br s，H-3)，4.91(1H，t，*J*＝11.0 Hz，H-6eq)，6.38(1H，s，H-1)，6.70(1H，s，H-ring B-5)，6.84(1H，s，H-ring C-5)，7.12(2H，s，H-ring A-2，6)；^{13}C-NMR(125 MHz，acetone-d_6)β：61.3(C-4)，63.5(C-6)，68.1(C-2)，69.9(C-3)，74.7(C-5)，93.5(C-1)，107.1(C-ring B-5)，109.1(C-ring C-5)，109.8(2C，C-ring A-2，6)，115.1(C-ring B-1)，115.8(C-ring C-1)，119.8(C-ring A-1)，124.7(C-ring C-2)，124.8(C-ring B-2)，135.7(C-ring C-3)，136.3(C-ring B-3)，138.5(C-ring A-4)，143.9(C-ring C-4)，144.0(C-ring B-4)，144.1(C-ring C-6)，144.5(C-ring B-6)，145.0(2C，C-ring A-3，5)，164.6(C-ring A-7)，166.5(C-ring C-6)，167.9(C-ring B-7) (Chung *et al*.，2003；Thitilertdecha *et al*.，2010).

Phyllanthusiin D (**7**) amorphous brown powder，$C_{44}H_{32}O_{27}$. ^{1}H-NMR(500 MHz，acetone-d_6)β：2.19(3H，s，H-ring E-9′)，2.98(1H，d，*J*＝15.5 Hz，H-ring E-7ax′)，3.47(1H，d，*J*＝15.5 Hz，H-ring E-7eq′)，4.40(1H，dd，*J*＝7.5，10.0 Hz，H-6ax)，4.78(1H，t，*J*＝7.5 Hz，H-6eq)，4.81(1H，t，*J*＝7.5 Hz，H-5)，4.91(1H，br s，H-ring E-1′)，5.43(1H，br s，H-4)，5.53(1H，br s，H-3)，5.56(1H，br s，H-2)，6.30(1H，s，H-ring E-3′)，6.57(1H，br s，H-glc-1)，6.65(1H，s，H-ring B-3)，7.07(1H，s，H-ring C-3)，7.17(2H，s，H-ring A-2，6)，7.23(1H，s，H-ring D-3)；^{13}C-NMR(125 MHz，acetone-d_6)β：31.0(C-ring E-9′)，49.1(C-ring E-7′)，51.1(C-ring E-1′)，61.5(C-3)，63.0(C-6)，65.8(C-4)，69.5(C-2)，72.3(C-5)，80.0(C-ring E-5′)，91.0(C-1)，107.0(C-ring C-3)，108.8(C-ring E-6′)，109.5(C-ring B-3)，109.8(2C，C-ring A-2，6)，112.5(C-ring D-3)，114.5(C-ring C-1)，116.0(C-ring D-1)，116.4(C-ring C-1)，119.3(C-ring A-1)，119.3(C-ring D-2)，123.5(C-ring B-2)，124.5(C-ring C-2)，126.0(C-ring E-3)，135.6(C-ring C-5)，136.5(C-ring D-5)，136.9(C-ring B-5)，139.6(C-ring A-4)，143.8(C-ring B-4)，144.1(C-ring B-6)，144.4(C-ring C-6)，144.6(C-ring C-4)，144.7(C-ring E-2′)，145.2(2C，C-ring A-3，5)，146.1(C-ring D-6)，146.8(C-ring D-4)，163.9(C-ring E-10′)，164.3(C-ring D-7)，164.6(C-ring A-7)，165.4(C-ring B-7)，167.7(C-ring C-7)，196.8(C-ring E-4′)，205.3(C-ring E-8′)(Foo *et al*.，1992；Yoshind *et al*.，1992).

Furosonin (**8**) amorphous brown powder，$C_{46}H_{36}O_{31}$. ^{1}H-NMR(500 MHz，acetone-d_6)β：1.63(1H，d，*J*＝14.0 Hz，H-ring E-3ax)，2.73(1H，d，*J*＝14.0 Hz，H-ring E-3eq)，3.93(1H，dd，*J*＝2.5，9.5 Hz，H-ring F-1ax)，4.09(1H，m，H-ring F-2)，4.12(1H，dd，*J*＝5.5，9.5 Hz，H-ring F-1eq)，4.16(1H，d，*J*＝1.5 Hz，H-ring F-3)，4.44(1H，t，*J*＝10.0 Hz，H-6ax)，4.73(1H，m，H-6eq)，4.75(1H，s，H-ring E-1)，4.91(1H，t，*J*＝9.0 Hz，H-5)，5.05(1H，s，H-ring F-5)，5.36(1H，br s，H-4)，5.61(1H，br s，H-2)，5.66(1H，br s，H-3)，6.53(1H，br s，H-1)，6.64(1H，s，H-ring B-3)，7.07(1H，s，H-ring C-3)，7.21(2H，s，H-ring A-2，6)，7.33(1H，s，H-ring D-3)；^{13}C-NMR(125 MHz，acetone-d_6)β：31.6(C-ring E-3)，51.2(C-ring E-1)，52.5(C-ring E-2)， 62.1(C-3)，63.2(C-6)，65.4(C-4)，69.7(C-2)，72.6(C-5)，74.4(C-ring F-1)，76.4(C-ring F-5)，76.5(C-ring F-2)，80.7(C-ring F-3)，90.9(C-1)，97.7(C-ring E-4)，98.1(C-ring E-6)，98.2(C-ring E-5)，106.8(C-ring C-3)，108.9(C-ring F-4)，109.6(C-ring C-3)，109.8(2C，C-ring A-2，6)，110.6(C-ring D-1)，113.9(C-ring D-3)，114.8(C-ring B-1)，116.3(C-ring C-1)，118.3(C-ring D-2)，119.0(C-ring A-1)，123.5(C-ring B-2)，124.6(C-ring C-2)，135.6(C-ring B-5)，137.1(C-ring C-5)，138.1(C-ring D-5)，139.4(C-ring A-4)，144.0(C-ring B-4)，144.1(C-ring C-4)，144.4(C-ring D-6)，144.5(C-ring B-6)，144.7(C-ring C-6)，145.1(C-ring D-4)，145.2(2C，C-ring A-3，5)，164.7(C-ring B-7)，165.1(C-ring D-7)，165.8(C-ring A-7)，168.1(C-ring C-7)，169.9(C-ring E-7)(Taniguchi *et al*.，2012).

Geraniin (**9**) amorphous brown powder，$C_{41}H_{28}O_{27}$. ^{1}H-NMR(500 MHz，acetone-d_6)β：4.33 [1H，dd，J=6.0，10.5 Hz，H(a)-6ax]，4.44 [1H，dd，J=8.0，10.5 Hz，H(b)-6ax]，4.76 [1H，d，J=1.6 Hz，H(b)-ring E-1′]，4.80 [1H，m，H(a)-5]，4.80 [1H，m，H(b)-5]，4.91 [1H，m，H(b)-6eq]，4.94 [1H，t，J=10.5 Hz，H(a)-6eq]，5.19 [1H，s，H(a)-ring E-1′]，5.54 [1H，br s，H(a)-4]，5.44 [1H，br s，H(b)-4]，5.50 [1H，br s，H(a)-3]，5.57 [1H，br s，H(b)-3]，5.58 [1H，br s，H(a)-2]，5.58 [1H，br s，H(b)-2]，6.27 [1H，d，J=1.6 Hz，H(b)-ring E-3′]，6.54 [1H，br s，H(b)-1]，6.58 [1H，s，H(a)-1]，6.58 [1H，s，H(a)-ring E-3′]，6.67 [1H，s，H(b)-ring C-3]，6.68 [1H，s，H(a)-ring C-3]，7.10 [1H，s，H(b)-ring B-3]，7.16 [1H，s，H(a)-ring B-3]，7.21 [2H，s，H(a)-ring A-2，6]，7.21 [2H，s，H(b)-ring A-2，6]，7.23 [1H，s，H(a)-ring D-3]，7.27 [1H，s，H(b)-ring D-3]；^{13}C-NMR(125 MHz，acetone-d_6)β：46.2 [C(a)-ring E-1′]，52.0 [C(b)-ring E-1′]，62.5 [C(b)-3]，63.8 [C(a)-6]，63.8 [C(b)-6]，63.9 [C(a)-3]，65.9 [C(a)-4]，66.0 [C(b)-4]，70.2 [C(a)-2]，70.6 [C(b)-2]，72.7 [C(a)-5]，73.3 [C(b)-5]，90.9 [C(a)-1]，91.8 [C(b)-1]，91.9 [C(b)-ring E-5′]，91.9 [C(b)-ring E-6′]，92.4 [C(a)-ring E-6′]，96.3 [C(a)-ring E-5′]，107.9 [C(b)-ring C-3]，108.0 [C(a)-ring C-3]，109.8 [C(b)-ring B-3]，110.6 [C(a)-ring B-3]，110.7 [2C，C(b)-ring A-2，6]，110.9 [2C，C(a)-ring A-2，6]，113.4 [C(b)-ring D-3]，113.5 [C(a)-ring D-3]，115.2 [C(b)-ring C-1]，115.3 [C(a)-ring C-1]，115.9 [C(a)-ring D-1]，117.0 [C(b)-ring B-1]，117.1 [C(b)-ring D-2]，117.2 [C(a)-ring B-1]，119.5 [C(a)-ring D-2]，120.1 [C(b)-ring A-1]，120.2 [C(b)-ring D-1]，120.7 [C(a)-ring A-1]，124.7 [C(b)-ring B-2]，124.8 [C(a)-ring B-2]，125.1 [C(b)-ring E-3′]，125.5 [C(b)-ring C-2]，125.7 [C(a)-ring C-2]，128.7 [C(a)-ring E-3′]，136.4 [C(b)-ring C-5]，136.5 [C(a)-ring C-5]，137.2 [C(b)-ring D-5]，137.7 [C(b)-ring B-5]，137.8 [C(a)-ring B-5]，139.0 [C(a)-ring D-5]，139.9 [C(a)-ring A-4]，140.0 [C(b)-ring A-4]，143.5 [C(a)-ring D-6]，144.6 [C(b)-ring B-4]，144.9 [C(a)-ring C-6]，144.9 [C(b)-ring B-6]，145.0 [C(a)-ring B-6]，145.2 [C(b)-ring C-6]，145.3 [C(a)-ring B-4]，145.4 [C(b)-ring C-4]，145.5 [C(a)-ring C-4]，145.8 [C(a)-ring D-4]，145.9 [2C，C(a)-ring A-3，5]，145.9 [2C，C(b)-ring A-3，5]，147.0 [C(b)-ring D-6]，147.6 [C(b)-ring D-4]，149.3 [C(b)-ring E-2′]，154.7 [C(a)-ring E-2′]，164.7 [C(a)-ring A-7]，164.9 [C(b)-ring A-7]，165.4 [C(b)-ring D-7]，165.5 [C(a)-ring D-7]，165.6 [C(a)-ring E-7′]，165.8 [C(b)-ring B-7]，165.9 [C(b)-ring E-7′]，166.2 [C(a)-ring B-7]，168.4 [C(b)-ring C-7]，168.5 [C(a)-ring C-7]，194.6 [C(b)-ring E-4′]，191.9 [C(a)-ring E-4′](Yoshind *et al*.，1992).

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