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水栀子果实化学成分研究(II)

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摘　要:利用多种色谱学技术从水栀子 *Gardenia jasminoides* var. *radicans* 果实中分离得到 11 个化合物,并应用多种波谱学手段将它们的结构分别鉴定为 *Z*-甲基-6-氧代-Z,4-庚二烯酸 *O*-β-D-龙胆二糖苷(**1**)、jasminoside O(**2**)、3,5-二甲氧基-4-羟基-苯甲醛(**3**)、5-羟甲基糠醛(**4**)、(5*R*,2*E*)-5-羟基-2-甲基-庚-2-烯-1,6-二酮(**5**)、1-*O*-对香豆酰基葡萄糖苷(**6**)、6,7-二甲氧基-4-羟基-1-萘甲酸(**7**)、10-*O*-*E*-*p*-香豆酰京尼平苷酸(**8**)、6′′-*O*-反式-肉桂酰基京尼平龙胆二糖苷(**9**)、丁香脂素(**10**)、松脂素(**11**)。以上化合物均为首次从该植物中分离得到。

关键词:水栀子;果实;化学成分

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Chemical Constituents in the Fruits of *Gardenia jasminoides* var. *radicans* (II)

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Abstract: Eleven compounds were isolated from the fruits of *Gardenia jasminoides* var. *radicans* by different chromatographic methods, and their structures were elucidated by spectroscopic characteristics and identified as Z-methyl-6-OXD-Z,4-heptadienoic acid *O*-β-D-gentiobioside (**1**), jasminoside O (**2**), 3,5-dimethoxy-4-hydroxy-benzaldehyde (**3**), 5-hydroxymethyl furfural (**4**), (5*R*,2*E*)-5-hydroxy-2-methyl-hepta-2-ene-1,6-dione (**5**), 1-*O*-*p*-coumaroyl-β-D-glucopyranose (**6**), 6,7-dimethoxy-4-hydroxy-1-naphthoic acid (**7**), 10-*O*-*E*-*p*-coumaroyl geniposidic acid (**8**), 6″-*O*-*trans*-cinnamoyl genipin gentiobioside (**9**), syringaresinol (**10**) and pinoresinol (**11**). All the eleven compounds were isolated from the fruits of *G. jasminoides* for the first time.

Key words: *Gardenia jasminoides* var. *radicans*; fruits; chemical constituents

水栀子(*Gardenia jasminoides* var. *radicans*)是茜草科(Rubiaceae)栀子属常绿灌木,我国长江以南大部分省区均有分布和人工栽培,主产于江西、湖南、湖北、浙江、福建、四川等省。水栀子可以根、叶、果实入药,具有解热凉血、镇静止痛、疏风解湿的功效。同时,它是提取天然色素的较好原料。因此,水栀子用途较广泛,经济价值高,是一种集绿化、观赏、药用等于一体的植物。迄今,有关栀子属其它品种植物的化学成分研究较透彻,但对水栀子化学成分研究的报道相对较少。为此,本课题组对水栀子的化学成分进行了较系统研究,从中得到 11 个化合物,分别鉴定为 Z-甲基-6-氧代-Z,4-庚二烯酸 *O*-β-D-龙胆二糖苷(**1**)、jasminoside O(**2**)、3,5-二甲氧基-4-羟基-苯甲醛(**3**)、5-羟甲基糠醛(**4**)、(5*R*,2*E*)-5-羟基-2-甲基-庚-2-烯-1,6-二酮(**5**)、1-*O*-对香豆酰基葡萄糖苷(**6**)、6,7-二甲氧基-4-羟基-1-萘甲酸(**7**)、10-*O*-*E*-*p*-香豆酰京尼平苷酸(**8**)、6′′-*O*-反式-肉桂酰基京尼平龙胆二糖苷(**9**)、丁香脂素(**10**)、松脂素(**11**)。以上化合物均为首次从该植物中分离得到。

1　仪器与材料

Bruker AVANCE III 300 MHz 核磁共振波谱仪(瑞士 Bruker 公司);Finnigan LCQ Advantage MAX 质谱仪(美国 Thermo 公司);UltiMate 3000 高效液相色谱仪(法国 Gilson 公司),GILSON 306 制备型高效液相色谱仪(法国 Gilson 公司),Welch Material Column XB-C_{18}分析色谱柱(4.6×250 mm,5 μm,上海月旭材料科技有限公司);Ultimate® XB-C_{18}制备色谱柱(10×250 mm,5 μm,上海月旭材料科技有限公司);Sephadex LH-20 葡聚糖凝胶(美国 Pharmacia 公司);薄层色谱硅胶预涂板(HSAF254,200×200 mm,烟台市化学工业研究所);ODS(50 μm,YMC,

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德国 Merck 公司)。

实验药材购于安徽亳州药材市场,经暨南大学药学院周光雄教授鉴定为水栀子 *Gardenia jasminoides* var. *radicans* 的果实,药材标本存放于暨南大学药学院生药学教研室中药标本室。

2 提取与分离

水栀子干燥果实 7.0 kg,粉碎,用体积分数 70% 乙醇渗漉提取 3 次,合并提取液,减压浓缩得稠浸膏 800 g。加水混悬,分别用石油醚、乙酸乙酯和正丁醇萃取,得各自萃取物 100、80 g 和 120 g。其中,乙酸乙酯部位浸膏 80 g,经硅胶柱层析,用氯仿-甲醇系统梯度洗脱,得到化合物 **1**(14.8 mg)。所得流分再经硅胶柱层析,以石油醚-乙酸乙酯系统梯度洗脱,经 ODS 反相柱、Sephadex LH-20 凝胶柱色谱和 HPLC 等分离纯化,分别得到化合物 **2**(5.6 mg)、**3**(6.2 mg)、**4**(5.1 mg)、**5**(4.9 mg)、**6**(8.5 mg)、**7**(12.7 mg)、**8**(19.8 mg)、**9**(102.5 mg)、**10**(3.2 mg)、**11**(3.7 mg)。

3 结构鉴定

化合物 1 浅黄色透明胶状物。分子式为 $C_{20}H_{30}O_{13}$,ESI-MS *m/z*:501 [M+Na]$^+$。^{1}H NMR (300 MHz,$CDCl_3$) δ:7.37 (1H,dd,J=15.3,11.4 Hz,H-4),7.29 (1H,d,J=11.4 Hz,H-3),6.49 (1H,d,J=15.3 Hz,H-5),5.76 (1H,d,J=7.6 Hz,H-1′),4.52 (1H,d,J=7.7 Hz,H-1″),4.25 (1H,dd,J=12.3,4.5 Hz,Hb-6″),4.09 (1H,dd,J=12.3,2.5 Hz,Ha-6″),3.95 (1H,dd,J=12.0,2.6 Hz,Hb-6′),3.58 (1H,dd,J=12.0,5.6 Hz,Ha-6′),3.15 ~ 3.60 (8H,m,糖基 H),2.36 (3H,s,H-7),2.05 (3H,s,2-CH_3);^{13}C NMR (75 MHz,$CDCl_3$) δ:165.3 (C-1),133.8 (C-2),137.5 (C-3),135.4 (C-4),136.0 (C-5),197.9 (C-6),29.5 (C-7),13.3 (2-CH_3),92.4 (C-1′),70.0 (C-2′),72.7 (C-3′),68.5 (C-4′),74.1 (C-5′),67.3 (C-6′),100.6 (C-1″),70.8 (C-2″),72.9 (C-3″),68.4 (C-4″),71.9 (C-5″),61.7 (C-6″)。以上数据与文献报道一致[1],故化合物 **1** 鉴定为 Z-甲基-6-氧代-Z,4-庚二烯酸 *O*-β-D-龙胆二糖苷。

化合物 2 黄色无定型粉末。分子式为 $C_{21}H_{34}O_{11}$,ESI-MS *m/z*:485 [M+Na]$^+$。^{1}H NMR (300 MHz,CD_3OD) δ:5.75 (1H,s,H-2),5.47 (1H,d,J=7.8 Hz,H-1′),5.06 ~ 5.14 (1H,m,H-6),4.28 (1H,d,J=7.4 Hz,H-1″),4.10 (1H,dd,J=11.2,1.8 Hz,Ha-6′),3.84 (1H,dd,J=11.4,5.3 Hz,Ha-5″),3.72 (1H,dd,J=11.3,5.3 Hz,Hb-6′),3.30 ~ 3.41 (7H,m,糖基 H),3.15 (1H,br. d,J=10.4 Hz,Hb-5″),2.19 (3H,d,J=1.1 Hz,H-10),1.69 (3H,s,H-8),1.62 (3H,s,H-9);^{13}C NMR (75 MHz,CD_3OD) δ:166.6 (C-1),115.9 (C-2),164.7 (C-3),42.2 (C-4),27.2 (C-5),124.2 (C-6),133.7 (C-7),26.0 (C-8),17.9 (C-9),19.4 (C-10),95.3 (C-1′),74.0 (C-2′),77.9 (C-3′),71.1 (C-4′),77.8 (C-5′),69.6 (C-6′),105.1 (C-1″),75.0 (C-2″),78.0 (C-3″),71.3 (C-4″),67.1 (C-5″)。以上数据与文献报道一致[2],故化合物 **2** 鉴定为 jasminoside O。

化合物 3 黄色油状物。分子式为 $C_9H_{10}O_4$,ESI-MS *m/z*:183 [M+H]$^+$。^{1}H NMR (300 MHz,CD_3OD) δ:9.74 (1H,s,CH=O),7.22 (2H,s,H-2,5),3.92 (6H,s,2 ×-OCH_3);^{13}C NMR (75 MHz,CD_3OD) δ:193.1 (C=O),149.8 (C-3,5),108.4 (C-2,6),57.0 (2 ×-OCH_3)。以上数据与文献报道一致[3],故化合物 **3** 鉴定为 3,5-二甲氧基-4-羟基-苯甲醛。

化合物 4 白色无定型粉末。分子式为 $C_6H_6O_3$,ESI-MS *m/z*:149 [M+Na]$^+$。^{1}H NMR (300 MHz,CD_3OD) δ:9.53 (1H,s,CH=O),7.39 (1H,d,J=3.5 Hz,H-3),6.59 (1H,d,J=3.5 Hz,H-4),4.62 (2H,s,H_2-6);^{13}C NMR (75 MHz,CD_3OD) δ:154.0 (C-2),125.1 (C-3),111.1 (C-4),163.3 (C-5),57.7 (C-6),179.6 (C=O)。以上数据与文献报道一致[4],故化合物 **4** 鉴定为 5-羟甲基糠醛。

化合物 5 浅黄色无定型粉末。分子式为 $C_8H_{12}O_3$,ESI-MS *m/z*:157 [M+H]$^+$。^{1}H NMR (300 MHz,CD_3OD) δ:7.30 (1H,t,J=1.6 Hz,H-3),5.33 (1H,t,J=6.4 Hz,H-5),2.87 (2H,m,H-4),2.19 (3H,s,H-7),1.87 (3H,s,2-CH_3);^{13}C NMR (75 MHz,CD_3OD) δ:176.3 (C-1),130.8 (C-2),151.2 (C-3),46.9 (C-4),78.9 (C-5),207.1 (C-6),30.4 (C-7),10.6 (2-CH_3)。以上数据与文献报道一致[5],故化合物 **5** 鉴定为(5*R*,2*E*)-5-羟基-2-甲基-庚-2-烯-1,6-二酮。

化合物 6 白色不定型粉末。分子式为 $C_{15}H_{18}O_8$,ESI-MS *m/z*:349 [M+Na]$^+$。^{1}H NMR (300

MHz,CD_3OD)δ:7.73 (1H,d,J = 15.9 Hz,H-7),7.49 (2H,t,J = 8.6 Hz,H-2,6),6.82 (2H,d,J = 8.6 Hz,H-3,5),6.38 (1H,d,J = 15.9 Hz,H-8),5.56 (1H,d,J = 15.9 Hz,H-1′),3.38 ~ 3.44 (4H,m,H-2′,3′,4′,5′),3.82 (1H,dd,J = 11.0,1.6 Hz,Ha-6′),3.69 (1H,dd,J = 12.0,4.4 Hz,Hb-6′);^{13}C NMR (75 MHz,CD_3OD)δ:127.2 (C-1),131.5 (C-2,6),117.0 (C-3,5),161.8 (C-4),148.1 (C-7),114.6 (C-8),167.9 (C = O),95.9 (C-1′),74.2 (C-2′),79.0 (C-3′),71.2 (C-4′),78.2 (C-5′),62.5 (C-6′)。以上数据与文献报道一致[6],故化合物**6** 鉴定为1-*O*-对香豆酰基葡萄糖苷。

化合物 7 白色无定型粉末。分子式为 $C_{13}H_{12}O_5$,ESI-MS m/z:249 [M + H]$^+$。^{1}H NMR (300 MHz,DMSO-d_6)δ:9.24 (1H,s,-OH),7.45 (1H,d,J = 8.5 Hz,H-2),7.42 (1H,s,H-5),7.20 (1H,s,H-8),6.84 (1H,d,J = 8.6 Hz,H-3),3.80 (6H,s,2 ×-OCH_3);^{13}C NMR (75 MHz,DMSO-d_6)δ:104.2 (C-1),123.6 (C-2),115.1 (C-3),151.2 (C-4),121.7 (C-4a),106.9 (C-5),147.5 (C-6),147.3 (C-7),112.7 (C-8),120.4 (C-8a),167.3 (-COOH),56.0 (6-OCH_3),55.6 (7-OCH_3)。以上数据与文献报道一致[7],故化合物**7** 鉴定为6,7-二甲氧基-4-羟基-1-萘甲酸。

化合物 8 无色透明胶状物。分子式为 $C_{25}H_{28}O_{12}$,ESI-MS m/z:543 [M + Na]$^+$。^{1}H NMR (300 MHz,CD_3OD)δ:7.62 (1H,d,J = 16.0 Hz,H-7″),7.51 (1H,s,H-3),7.49 (2H,d,J = 8.5 Hz,H-2″,6″),6.79 (2H,d,J = 8.5 Hz,H-3″,5″),6.35 (1H,d,J = 16.0 Hz,H-8″),5.89 (1H,s,H-7),5.18 (1H,d,J = 7.8 Hz,H-1),4.96 (1H,d,J = 2.6 Hz,Ha-10),4.85 (1H,dd,J = 5.3,2.6 Hz,Hb-10),4.71 (1H,d,J = 7.8 Hz,H-1′),3.90 (1H,d,J = 2.6 Hz,Ha-6′),3.65 (1H,d,J = 5.2 Hz,Hb-6′),3.06 ~ 3.45 (4H,m,糖基 H),3.22 (1H,m,H-5),2.85 (1H,d,J = 5.2 Hz,Ha-6),2.76 (1H,m,H-9),2.17 (1H,dd,J = 14.9,5.2 Hz,Hb-6);^{13}C NMR (75 MHz,CD_3OD)δ:98.2 (C-1),153.3 (C-3),112.7 (C-4),36.6 (C-5),40.0 (C-6),131.2 (C-7),139.7 (C-8),47.5 (C-9),63.5 (C-10),170.8 (C-11),100.5 (C-1′),74.9 (C-2′),77.8 (C-3′),71.4 (C-4′),78.2 (C-5′),62.7 (C-6′),127.3 (C-1″),131.2 (C-2″,6″),116.8 (C-3″,5″),161.1 (C-4″),146.8 (C-7″),114.8 (C-8″),169.3 (C-9″)。以上数据与文献报道一致[8],故化合物**8** 鉴定为10-*O*-*E*-*p*-香豆酰京尼平苷酸。

化合物 9 黄色无定型粉末。分子式为 $C_{32}H_{40}O_{16}$,ESI-MS m/z:703 [M + Na]$^+$。^{1}H NMR (300 MHz,CD_3OD)δ:7.72 (1H,d,J = 16.0 Hz,H-3‴),7.61 (2H,m,H-5‴,9‴),7.48 (1H,s,H-3),7.41 (2H,m,H-6‴,8‴),7.40 (1H,m,H-7‴),6.57 (1H,d,J = 16.0 Hz,H-2‴),5.83 (1H,s,H-7),5.14 (1H,d,J = 7.8 Hz,H-1),4.72 (1H,d,J = 7.9 Hz,H-1′),4.53 (1H,dd,J = 12.0,2.0 Hz,Ha-6″),4.41 (1H,d,J = 7.7 Hz,H-1″),4.33 (1H,m,Hb-6″),4.30 (1H,m,Ha-10),4.20 (1H,d,J = 14.5 Hz,Hb-10),4.11 (1H,dd,J = 11.9,1.5 Hz,Ha-6′),3.76 (1H,dd,J = 12.0,7.0 Hz,Hb-6′),3.68 (3H,s,11-OCH_3),3.57 (1H,m,H-5′),3.52 (1H,m,H-5″),3.42 (1H,m,H-3′),3.37 (1H,m,H-3″),3.35 (1H,m,H-4″),3.31 (1H,m,H-4′),3.27 (1H,m,H-2′),3.24 (1H,m,H-2″),3.14 (1H,m,H-5),2.80 (1H,dd,J = 16.5,8.5 Hz,Hb-6),2.69 (1H,t,J = 7.8 Hz,H-9),2.13 (1H,dd,J = 16.5,8.4 Hz,Hb-6);^{13}C NMR (75 MHz,CD_3OD)δ:98.9 (C-1),153.5 (C-3),112.4 (C-4),36.8 (C-5),39.8 (C-6),129.1 (C-7),144.8 (C-8),47.0 (C-9),61.6 (C-10),169.7 (C-11),51.9 (11-OCH_3),100.7 (C-1′),74.9 (C-2′),77.8 (C-3′),71.8 (C-4′),77.6 (C-5′),70.2 (C-6′),105.1 (C-1″),75.2 (C-2″),77.8 (C-3″),71.6 (C-4″),75.4 (C-5″),65.0 (C-6″),168.7 (C-1‴),118.7 (C-2‴),146.8 (C-3‴),135.8 (C-4‴),129.5 (C-5‴,9‴),130.2 (C-6‴,8‴),131.7 (C-7‴)。以上数据与文献报道一致[9],故化合物**9** 鉴定为6″-*O*-反式-肉桂酰基京尼平龙胆二糖苷。

化合物 10 无色透明胶状物。分子式为 $C_{22}H_{26}O_8$,ESI-MS m/z:859 [2M + Na]$^+$。^{1}H NMR (300 MHz,CD_3OD)δ:6.66 (4H,s,H-2,2′,6,6′),4.72 (2H,d,J = 4.4 Hz,H-7,7′),4.27 (2H,dd,J = 8.9,6.9 Hz,Ha-9,9′),3.88 (2H,m,Hb-9,9′),3.85 (12H,s,3,3′,5,5′-OCH_3),3.16 (2H,m,H-8,8′);^{13}C NMR (75 MHz,CD_3OD)δ:133.3 (C-1,1′),104.6 (C-2,2′,6,6′),149.5 (C-3,3′,5,5′),136.2 (C-4,4′),87.8 (C-7,7′),55.7 (C-8,8′),72.9 (C-9,9′),56.9 (3,3′,5,5′-OCH_3)。以上数据与文献

报道一致[10],故化合物 **10** 鉴定为丁香脂素。

化合物 11 无色透明胶状物。分子式为 $C_{20}H_{22}O_6$,ESI-MS *m/z*:739 [2M + Na]$^+$。^{1}H NMR (300 MHz,CD_3OD)δ:6.94 (2H,d,*J* = 1.5 Hz,H-2,2′),6.80 (2H,dd,*J* = 8.2,1.6 Hz,H-6,6′),6.76 (2H,d,*J* = 8.1 Hz,H-5,5′),4.69 (2H,d,*J* = 4.4 Hz,H-7,7′),4.22 (2H,dd,*J* = 9.0,6.8 Hz,Ha-9,9′),3.84 (6H,s,3,3′-OCH_3),3.81 (2H,m,Hb-9,9′),3.12 (2H,m,H-8,8′);^{13}C NMR (75 MHz,CD_3OD)δ:133.9 (C-1,1′),111.1 (C-2,2′),147.4 (C-3,3′),149.2 (C-4,4′),116.2 (C-5,5′),120.2 (C-6,6′),87.6 (C-7,7′),55.5 (C-8,8′),72.7 (C-9,9′),56.5 (3,3′-OCH_3)。以上数据与文献报道一致[10],故化合物 **11** 鉴定为松脂素。

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(上接第 62 页)

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