银中杨落叶的化学成分及活性研究

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摘 要：目的 研究银中杨 *Populus alba* × *P. berolinensis* 落叶的化学成分及水杨苷衍生物对 SGC-7901 细胞的抑制活性。**方法** 采用硅胶柱色谱和高效液相色谱等进行分离纯化，依据理化性质及波谱数据分析进行结构鉴定，利用 MTT 法对水杨苷衍生物进行人胃癌 SGC-7901 细胞体外增殖的抑制活性实验。**结果** 从银中杨落叶中分离得到 16 个化合物，分别鉴定为颤杨苷（1）、白杨苷（2）、3′-*O*-苯甲酰基水杨苷（**3**）、4′-*O*-苯甲酰基水杨苷（**4**）、水杨苷（**5**）、特里杨苷（**6**）、poliothrysin benzoate（**7**）、邻苯二酚（**8**）、苯甲酸（**9**）、tremulacinol（**10**）、6′-*O*-苯甲酰基水杨苷-7-水杨酸酯（**11**）、水杨醇（**12**）、salicortin（**13**）、7-*O*-乙酰基-3′-*O*-苯甲酰基水杨苷（**14**）、7-*O*-乙酰基-4′-*O*-苯甲酰基水杨苷（**15**）、6′-*O*-乙酰基-2′-*O*-苯甲酰基水杨苷（**16**）。MTT 实验表明，特里杨苷类衍生物化合物 **7**、**11**～**13** 对 SGC-7901 细胞体外增殖均显示一定抑制活性，IC_{50} 分别为 71.0、122.5、212.7、257.8 μmol/L。**结论** 化合物 **4**、**7**、**10**、**11**、**14**～**16** 为首次从该植物中分离得到，化合物 **7** 对人胃癌 SGC-7901 细胞体外增殖具有抑制作用。

关键词：银中杨；白杨苷；水杨苷；特里杨苷；水杨醇；7-*O*-乙酰基-3′-*O*-苯甲酰基水杨苷
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Chemical constituents from fallen leaves of *Populus alba* × *P. berolinensis*

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Abstract: Objective To study the chemical constituents from the fallen leaves of *Populus alba* × *P. berolinensis* and the inhibitory activity of salicin derivatives against SGC-7901 cell. **Methods** The chemical constituents were isolated and purified on the basis of silica gel column chromatography and HPLC. The structural elucidation was performed according to the physicochemical properties and spectroscopic analysis. The inhibitory activity of salicin derivatives on human gastric carcinoma cells SGC-7901 *in vitro* proliferation was determined by MTT method. **Results** Sixteen compounds were isolated and identified as tremuloidin (**1**), populin (**2**), chaenomeloidin (**3**), 4′-*O*-benzoylsalicin (**4**), salicin (**5**), tremulacin (**6**), poliothrysin benzoate (**7**), catechol (**8**), benzoic acid (**9**), tremulacinol (**10**), 6′-*O*-benzoylsalicin-7-salicylate (**11**), salicylol (**12**), salicortin (**13**), 7-*O*-acetyl-3′-*O*-benzoylsalicin (**14**), 7-*O*-acetyl-4′-*O*-benzoylsalicin (**15**), and 6′-*O*-acetyl-2′-*O*-benzoylsalicin (**16**), respectively. The inhibitory activity of compounds **7** and **11**—**13** on the *in vitro* proliferation of SGC-7901 cell was indicated by MTT and IC_{50} values were 71.0, 122.5, 212.7, and 257.8 μmol/L. **Conclusion** Compounds **4**, **7**, **10**, **11**, **14**—**16** are isolated from this plant for the first time. Compound **7** shows the inhibitory activity against SGC-7901 *in vitro* proliferation.

Key words: *Populus alba* × *P. berolinensis* L.; populin; salicin; tremulacin; salicylol; 7-*O*-acetyl-3′-*O*-benzoylsalicin

杨属植物在我国古代就作药用，具有抗菌、抗炎、镇痛、抗病毒、对心血管系统的保护作用等多种药理活性，用于治疗肝炎、痢疾、淋浊、咳嗽痰喘等症[1]。银中杨 *Populus alba* × *P. berolinensis* L. 属白杨派与黑杨派派间杂种，具有适应性强、不飞絮、抗寒、耐旱、抗病虫害等优点，是城市绿化、美化、防风、防砂用林以及用材林的理想树种，在我国东北和内蒙古等地得到了广泛种植，由于杨树具有树冠大、枝条生长速度快、树叶大而密等特点，树叶资源丰富。为进一步开发银中杨树叶资源的应用途径，在对夏季采集银中杨树叶化学成分进行研究的基础上[2]，本实验将初冬采集的银中杨落叶用水煮提取，提取液依次用醋酸乙酯和正丁醇萃取，制得萃取物，并分别对 2 种溶剂萃取物的化学成分

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进行研究，从中分离得到 16 个化合物，分别鉴定为颤杨苷（tremuloidin，**1**）、白杨苷（populin，**2**）、3′-*O*-苯甲酰基水杨苷（chaenomeloidin，**3**）、4′-*O*-苯甲酰基水杨苷（4′-*O*-benzoylsalicin，**4**）、水杨苷（salicin，**5**）、特里杨苷（tremulacin，**6**）、poliothrysin benzoate（**7**）、邻苯二酚（catechol，**8**）、苯甲酸（benzoic acid，**9**）、tremulacinol（**10**）、6′-*O*-苯甲酰基水杨苷-7-水杨酸酯（6′-*O*-benzoylsalicin-7-salicylate，**11**）、水杨醇（salicylol，**12**）、salicortin（**13**）、7-*O*-乙酰基-3′-*O*-苯甲酰基水杨苷（7-*O*-acetyl-3′-*O*-benzoylsalicin，**14**）、7-*O*-乙酰基-4′-*O*-苯甲酰基水杨苷（7-*O*-acetyl-4′-*O*-benzoylsalicin，**15**）、6′-*O*-乙酰基-2′-*O*-苯甲酰基水杨苷（6′-*O*-acetyl-2′-*O*-benzoylsalicin，**16**）。其中化合物 **4**、**7**、**10**、**11**、**14**～**16** 为首次从该植物中分离得到；利用 MTT 法对水杨苷和特里杨苷类化合物进行人胃癌细胞 SGC-7901 体外增殖的抑制活性实验，结果表明水杨苷及其苯甲酸酯类没有活性，而特里杨苷类化合物苯甲酰基连接位置对人胃癌 SGC-7901 细胞体外增殖抑制活性具有较大影响。

1 材料与仪器

X—6 显微熔点测定仪（北京泰克仪器有限公司）；Magna FTIR—750 型傅里叶变换红外光谱仪（美国 Nicolet 公司）；上海精科实业有限公司，WFH—204B 型紫外分光光度计；Bruker AM—400 型核磁共振波谱仪；美国鲁道夫公司 Autopol V 型旋光仪；高效液相色谱仪：Hitachi L—7100 泵，Hitachi L—3350 示差折光检测器，GL Scirnces Inc. Inertsil PREP-ODS Φ 10 mm×250 mm 不锈钢柱；柱色谱用硅胶（200～300 目，青岛海洋化工厂），薄层色谱硅胶板（烟台化工厂）。

银中杨落叶，2010 年 11 月 12 日采集于齐齐哈尔大学校园，经齐齐哈尔大学沙伟教授鉴定为银中杨 *Populus alba* × *P. berolinensis* L.，标本（PB-20101112）收藏于齐齐哈尔大学天然产物研究室。

2 提取和分离

干燥银中杨落叶 2.0 kg，加入 12 L 水煮沸，保温 1.0 h，冷却至室温滤过，重复 3 次。合并水煮液并浓缩至 500 mL 左右，每次用醋酸乙酯 1.0 L 萃取，共 3 次，合并醋酸乙酯层浓缩得醋酸乙酯萃取物 54.1 g。醋酸乙酯萃取后的水层每次用正丁醇 1.0 L 萃取，共 3 次，合并正丁醇层浓缩得正丁醇萃取物 120.9 g。醋酸乙酯萃取物 54.1 g 经多次硅胶柱色谱、半制备 HPLC 等分离操作，得化合物 **1**（54.0 mg）、**2**（0.9 g）、**3**（3.3 g）、**5**（0.9 g）、**6**（15.1 mg）、**7**（74.9 mg）、**8**（6.9 g）、**9**（28.1 mg）、**10**（16.9 mg）、**11**（32.4 mg）、**12**（32.5 mg）、**13**（68.8 mg）、**14**（50.6 mg）。正丁醇萃取物 20.0 g 经多次硅胶柱色谱、半制备 HPLC 等分离操作，得化合物 **4**（32.4 mg）、**5**（3.6 g）、**15**（30.0 mg）、**16**（24.1 mg）。

3 结构鉴定

化合物 **1**：白色颗粒（EtOAc），mp 199.2～201.5 ℃；IR ν_{max}^{KBr} (cm^{-1}): 3 414 (-OH), 1 717 (C = O)；$[\alpha]_D^{17}$+16° (*c* 1.25, MeOH)；UV λ_{max}^{MeOH} (nm): 234, 270。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 7.97 (2H, d, *J* = 8.0 Hz, H-2″, 6″), 7.65 (1H, t, *J* = 8.0 Hz, H-4″), 7.52 (2H, t, *J* = 8.0 Hz, H-3″, 5″), 7.31 (1H, d, *J* = 7.4 Hz, H-3), 7.17 (1H, t, *J* = 7.4 Hz, H-5), 7.08 (1H, d, *J* = 7.4 Hz, H-6), 6.98 (1H, t, *J* = 7.42 Hz, H-4), 5.49 (1H, d, *J* = 5.7 Hz, 3′-OH), 5.34 (1H, d, *J* = 5.5 Hz, 4′-OH), 5.25 (1H, d, *J* = 7.6 Hz, H-1′), 5.06 (1H, dd, *J* = 9.5, 8.1 Hz, H-2′), 4.88 (1H, t, *J* = 5.7 Hz, 7-OH), 4.71 (1H, t, *J* = 5.3 Hz, 6′-OH), 4.37 (1H, dd, *J* = 15.1, 5.7 Hz, H-7a), 4.10 (1H, dd, *J* = 15.1, 5.7 Hz, H-7b), 3.80～3.30 (5H, m, H-3′～6′)；^{13}C-NMR (100 MHz, DMSO-d_6) δ: 165.5 (C-7″), 153.8 (C-1), 133.8 (C-4″), 131.6 (C-2), 130.3 (C-1″), 129.7 (C-2″, 6″), 129.2 (C-3″, 5″), 127.8 (C-5), 126.8 (C-3), 122.4 (C-4), 114.4 (C-6), 98.7 (C-1′), 77.7 (C-5′), 74.7 (C-2′), 74.3 (C-3′), 70.4 (C-4′), 61.0 (C-6′), 58.7 (C-7)。以上数据与文献报道一致[2]，故鉴定化合物 **1** 为颤杨苷。

化合物 **2**：白色针晶（EtOAc），mp 218.5～220.0 ℃；IR ν_{max}^{KBr} (cm^{-1}): 3 406 (-OH)；1 720 (C = O)；$[\alpha]_D^{17}$ −28.0° (*c* 1.25, MeOH)；UV λ_{max}^{MeOH} (nm): 232, 274。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 7.99 (2H, brd, *J* = 8.0 Hz, H-2″, 6″), 7.68 (1H, t, *J* = 8.0 Hz, H-4′), 7.56 (2H, t, *J* = 8.0 Hz, H-3″, 5″), 7.35 (1H, brd, *J* = 7.0 Hz, H-3), 7.06 (1H, t, *J* = 7.0 Hz, H-5), 6.98 (1H, brd, *J* = 7.0 Hz, H-6), 7.02 (1H, t, *J* = 7.7 Hz, H-4), 5.48 (1H, d, *J* = 4.3 Hz, 4′-OH), 5.41 (1H, d, *J* = 4.4 Hz, 3′-OH), 5.27 (1H, brs, H-2′), 4.98 (1H, t, *J* = 5.2 Hz, 7-OH), 4.85 (1H, d, *J* = 6.8 Hz, H-1′), 4.63 (2H, m, H-6′, H-7), 4.45 (1H, dd, *J* = 14.4, 6.0 Hz, H-7), 4.30 (1H, dd, *J* = 11.6, 7.6 Hz, H-6′), 3.77 (1H, t, *J* = 8.0 Hz, H-4′), 3.50～3.20 (3H, m, H-2′, 3′, 5′)；^{13}C-NMR (100 MHz, DMSO-d_6) δ: 165.9 (C-7″), 154.7 (C-1), 133.8 (C-4″), 131.9 (C-2), 130.1 (C-1″), 129.6 (C-2″, 6″),

129.1 (C-3″, 5″), 127.7 (C-5), 127.6 (C-3), 122.2 (C-4), 115.0 (C-6), 101.4 (C-1′), 76.7 (C-3′), 74.2 (C-5′), 73.7 (C-2′), 70.6 (C-4′), 64.7 (C-6′), 58.6 (C-7)。以上数据与文献报道一致[2]，故鉴定化合物 **2** 为白杨苷。

化合物 **3**：白色针晶（EtOAc），mp 192.3～193.6 ℃；$[\alpha]_D^{17}$ −35.2° (*c* 1.25, MeOH)；UV λ_{max}^{MeOH} (nm): 233, 274。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 8.04 (2H, brd, *J* = 7.1 Hz, H-2″, 6″), 7.67 (1H, t, *J* = 7.1 Hz, H-4′), 7.55 (2H, t, *J* = 7.1 Hz, H-3″, 5″), 7.38 (1H, d, *J* = 7.7 Hz, H-3), 7.21 (1H, t, *J* = 7.7 Hz, H-5), 7.13 (1H, brd, *J* = 7.7 Hz, H-6), 7.02 (1H, t, *J* = 7.7 Hz, H-4), 5.68 (1H, d, *J* = 5.7 Hz, 4′-OH), 5.34 (1H, d, *J* = 5.5 Hz, 2′-OH), 5.17 (1H, t, *J* = 8.9 Hz, H-3′), 5.02 (1H, d, *J* = 7.6 Hz, H-1′), 5.01 (1H, t, *J* = 5.8 Hz, 7-OH), 4.70 (1H, t, *J* = 5.4 Hz, 6′-OH), 4.64 (1H, dd, *J* = 14.4, 5.8 Hz, H-7), 4.48 (1H, dd, *J* = 14.4, 5.8 Hz, H-7), 3.80～3.30 (5H, m, H-2′～6′)；^{13}C-NMR (100 MHz, DMSO-d_6) δ: 165.8 (C-7″), 154.7 (C-1), 133.5 (C-4″), 132.0 (C-2), 130.8 (C-1″), 129.8 (C-2″, 6″), 129.0 (C-3″, 5″), 128.1 (C-5), 127.6 (C-3), 122.4 (C-4), 115.1 (C-6), 101.2 (C-1′), 78.9 (C-3′), 77.1 (C-5′), 71.9 (C-2′), 68.0 (C-4′), 60.8 (C-6′), 58.6 (C-7)。以上数据与文献报道一致[2]，故鉴定化合物 **3** 为 3′-*O*-苯甲酰基水杨苷。

化合物 **4**：白色针晶（EtOAc），mp 192.0～192.5 ℃；IR ν_{max}^{KBr} (cm^{-1}): 3 414 (-OH), 1 717 (C=O)；$[\alpha]_D^{17}$+18.2° (*c* 1.25, MeOH)；UV λ_{max}^{MeOH} (nm): 234, 273。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 8.09 (2H, d, *J* = 8.1 Hz, H-2″, 6″), 7.64 (1H, t, *J* = 8.1 Hz, H-4″), 7.52 (2H, t, *J* = 8.1 Hz, H-3″, 5″), 7.38 (1H, d, *J* = 7.8 Hz, H-3), 7.29 (1H, t, *J* = 7.8 Hz, H-5), 7.28 (1H, d, *J* = 7.8 Hz, H-6), 7.07 (1H, t, *J* = 7.8 Hz, H-4), 5.15 (1H, t, *J* = 7.4 Hz, H-4′), 5.01 (1H, d, *J* = 7.6 Hz, H-1′), 4.81 (1H, d, *J* = 13.0 Hz, H-7), 4.61 (1H, d, *J* = 13.0 Hz, H-7), 3.50～3.20 (5H, m, H-2′, 3′, 5′, 6′)；^{13}C-NMR (100 MHz, DMSO-d_6) δ: 165.9 (C-7″), 155.6 (C-1), 133.1 (C-4″), 130.8 (C-2), 129.8 (C-1″), 129.4 (C-2″, 6″), 128.6 (C-5), 128.5 (C-3), 128.2 (C-3″, 5″), 122.5 (C-4), 115.8 (C-6), 105.5 (C-1′), 74.8 (C-3′), 74.4 (C-5′), 73.9 (C-2′), 71.4 (C-4′), 60.8 (C-6′), 59.5 (C-7)。以上数据与文献报道基本一致[3]，故鉴定化合物 **4** 为 4′-*O*-苯甲酰基水杨苷。

化合物 **5**：白色针状晶体（MeOH），mp 215.4～217 ℃；IR ν_{max}^{KBr} (cm^{-1}): 3 367 (-OH), 1 589, 1 494, 1 454 (Ph)；$[\alpha]_D^{17}$ −47.2° (*c* 1.25, MeOH)。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 7.36 (1H, d, *J* = 7.8 Hz, H-3), 7.20 (1H, t, *J* = 7.8 Hz, H-5), 7.09 (1H, d, *J* = 7.8 Hz, H-6), 7.01 (1H, t, *J* = 7.8 Hz, H-4), 5.35 (1H, d, *J* = 4.6 Hz, 4′-OH), 5.08 (1H, d, *J* = 4.3 Hz, 3′-OH), 5.02 (1H, d, *J* = 5.3 Hz, 2′-OH), 4.98 (1H, t, *J* = 5.9 Hz, 7-OH), 4.76 (1H, d, *J* = 7.6 Hz, H-1′), 4.65 (1H, dd, *J* = 14.4, 6.4 Hz, H-7), 4.57 (1H, t, *J* = 5.6 Hz, 6′-OH), 4.45 (1H, dd, *J* = 14.4, 6.4 Hz, H-7), 3.71 (1H, m, H-6′), 3.48 (1H, m, H-6′), 3.38～3.15 (4H, m, H-2′～5′)；^{13}C-NMR (100 MHz, DMSO-d_6) δ: 155.2 (C-1), 132.3 (C-2), 128.2 (C-5), 127.7 (C-3), 122.2 (C-4), 115.3 (C-6), 101.9 (C-1′), 83.1 (C-5′), 82.4 (C-3′), 73.9 (C-2′), 70.2 (C-4′), 61.3 (C-6′), 58.7 (C-7)。以上数据与文献报道一致[2]，故鉴定化合物 **5** 为水杨苷。

化合物 **6**：白色针晶（EtOAc），mp 94.2～95.1 ℃；IR ν_{max}^{KBr} (cm^{-1}): 3 429 (-OH), 1 723 (C = O)；$[\alpha]_D^{17}$ −51.2° (*c* 1.25, MeOH)；UV λ_{max}^{MeOH} (nm): 231, 273。^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.11 (2H, d, *J* = 7.8 Hz, H-2‴, 6‴), 7.60 (1H, t, *J* = 7.8 Hz, H-4‴), 7.47 (2H, t, *J* = 7.8 Hz, H-3‴, 5‴), 7.35 (1H, t, *J* = 7.8 Hz, H-5), 7.33 (1H, d, *J* = 7.8 Hz, H-3), 7.10 (1H, d, *J* = 7.8 Hz, H-6), 7.05 (1H, t, *J* = 7.8 Hz, H-4), 6.08 (1H, m, H-3″), 5.77 (1H, dd, *J* = 9.8, 1.7 Hz, H-2″), 5.37 (1H, d, *J* = 11.8 Hz, H-7), 5.25 (1H, m, H-2′), 5.23 (1H, d, *J* = 11.8 Hz, H-7), 5.10 (1H, d, *J* = 7.6 Hz, H-1′), 4.00～3.15 (5H, m, H-3′～6′), 2.87 (1H, m, H-5″), 2.65 (1H, m, H-4″), 2.59 (1H, m, H-5″), 2.50 (1H, m, H-4″)；^{13}C-NMR (100 MHz, $CDCl_3$) δ: 205.9 (C-6″), 170.1 (C-7″), 168.8 (C-7‴), 155.5 (C-1), 133.6 (C-4‴), 132.2 (C-3″), 131.1 (C-5), 130.8 (C-3), 130.1 (C-2‴,6‴), 130.0 (C-1‴), 128.5 (C-3‴, 5‴), 127.4 (C-2″), 124.2 (C-6), 123.0 (C-4), 115.2 (C-2), 101.1 (C-1′), 78.8 (C-1″, 5′), 76.1 (C-3′), 72.0 (C-2′), 69.4 (C-4′), 62.2 (C-7), 62.1 (C-6′), 35.2 (C-5″), 26.8 (C-4″)。以上数据与文献报道一致[2]，故鉴定化合物 **6** 为特里杨苷。

化合物 **7**：白色针晶（EtOAc），mp 76.6～78.7 ℃；IR ν_{max}^{KBr} (cm^{-1}): 3 430 (-OH), 1 721 (C = O)；$[\alpha]_D^{17}$ −106.4° (*c* 1.25, MeOH)；UV λ_{max}^{MeOH} (nm): 232, 274。

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.00 (2H, d, J = 7.6 Hz, H-2″, 6″), 7.51 (1H, t, J = 7.6 Hz, H-4″), 7.38 (2H, t, J = 7.6 Hz, H-3″, 5″), 7.19 (1H, d, J = 7.6 Hz, H-3), 7.07 (1H, t, J = 7.6 Hz, H-5), 7.05 (1H, d, J = 7.6 Hz, H-6), 6.94 (1H, t, J = 7.6 Hz, H-4), 5.99 (1H, m, H-5‴), 5.75 (1H, t, J = 9.8 Hz, H-6‴), 5.29 (1H, d, J = 12.0 Hz, H-7a), 5.19 (1H, d, J = 12.0 Hz, H-7b), 4.91 (1H, d, J = 7.6 Hz, H-1′), 4.72 (1H, d, J = 7.6 Hz, H-6′), 4.48 (1H, m, H-6′), 3.81 (2H, m, H-2′, 3′), 3.74 (1H, t, J = 7.6 Hz, H-5′), 3.66 (1H, t, J = 7.6, H-4′), 2.78 (1H, m, H-3‴), 2.54 (1H, m, H-4‴), 2.49 (1H, m, H-3‴), 2.38 (1H, m, H-4‴); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 206.2 (C-2‴), 172.0 (C-7‴), 166.8 (C-7″), 155.7 (C-1), 133.3 (C-4″), 132.3 (C-5‴), 130.7 (C-3), 130.5 (C-5), 130.0 (C-1″), 129.9 (C-2″, 6″), 128.5 (C-3″, 5″), 127.7 (C-6‴), 124.5 (C-2), 123.8 (C-4), 115.7 (C-6), 100.9 (C-1′), 78.5 (C-1‴), 76.4 (C-3′), 74.1 (C-5′), 73.6 (C-2′), 70.5 (C-4′), 64.4 (C-7), 64.2 (C-6′), 35.4 (C-3‴), 26.7 (C-4‴)。以上数据与文献报道一致[4]，故鉴定化合物 **7** 为 poliothrysin benzoate。

化合物 **8**：无色片状晶体（EtOAc），mp 104～105 ℃；三氯化铁反应显墨绿色。^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.87 (2H, m, H-3, 6), 6.81 (2H, m, H-4, 5), 5.18 (2H, s, Ar-OH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 145.5 (C-1, 2), 119.3 (C-4, 5), 115.7 (C-3, 6)。以上数据与文献报道一致[2]，故鉴定化合物 **8** 为邻苯二酚。

化合物 **9**：无色片状晶体（EtOAc），mp 121～122 ℃。^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.13 (2H, d, J = 7.6 Hz, H-2, H-6), 7.62 (1H, t, J = 7.6 Hz, H-4), 7.49 (2H, t, J = 7.6 Hz, H-3, 5)。以上数据与苯甲酸对照品的谱图完全一致，故鉴定化合物 **9** 为苯甲酸。

化合物 **10**：白色针晶（EtOAc），mp 94.2～95.1 ℃； IR ν_{max}^{KBr} (cm^{-1}): 3 429 (-OH), 1723 (C=O); $[\alpha]_D^{17}$ −51.2° (c 1.25, MeOH); UV λ_{max}^{MeOH} (nm): 231, 273。^{1}H-NMR (400 MHz, CD_3OD) δ: 8.13 (2H, d, J = 7.8 Hz, H-2″, 6″), 7.63 (1H, t, J = 7.8 Hz, H-4″), 7.51 (2H, t, J = 7.8 Hz, H-3″, 5″), 7.40 (1H, d, J = 7.4 Hz, H-3), 7.34 (1H, t, J = 7.4 Hz, H-5), 7.26 (1H, d, J = 7.4 Hz, H-6), 7.04 (1H, t, J = 7.4 Hz, H-4), 5.91 (1H, m, H-5‴), 5.57 (1H, t, J = 9.2 Hz, H-6‴), 5.34 (1H, d, J = 9.2 Hz, H-7), 5.32 (1H, m, H-2′), 5.30 (1H, d, J = 7.6 Hz, H-1′), 5.15 (1H, d, J = 9.2 Hz, H-7), 3.93 (1H, d, J = 9.2 Hz, H-6′), 3.86 (1H, dd, J = 6.3, 3.8 Hz, H-2‴), 3.82 (1H, t, J = 7.9 Hz, H-3′), 3.78 (1H, m, H-6′), 3.77 (1H, m, H-4′), 3.62 (1H, m, H-5′), 2.21 (1H, m, H-4‴), 2.12 (1H, m, H-4‴), 2.07 (1H, m, H-3‴), 1.88 (1H, m, H-3‴); ^{13}C-NMR (100 MHz, CD_3OD) δ: 174.6 (C-7‴), 167.8 (C-7″), 156.7 (C-1), 134.2 (C-4″), 132.1 (C-6‴), 131.7 (C-1″), 130.8 (C-2″, 6″), 130.7 (C-5), 129.9 (C-2″, 6″), 129.5 (C-3″, 5″), 127.5 (C-5‴), 126.6 (C-2), 123.5 (C-4), 116.4 (C-6), 102.5 (C-1′), 79.4 (C-5′), 78.9 (C-2′), 77.0 (C-1‴), 74.7 (C-2‴), 73.3 (C-3′), 69.5 (C-4′), 65.8 (C-7), 62.2 (C-6′), 27.0 (C-4‴), 24.0 (C-3‴)。以上数据与文献报道一致[5]，故鉴定化合物 **10** 为 tremulacinol。

化合物 **11**：浅黄色脂状物。^{1}H-NMR (400 MHz, CD_3OD) δ: 8.01 (2H, d, J = 7.6 Hz, H-2″, 6″), 7.80 (1H, d, J = 7.8 Hz, H-6‴), 7.62 (1H, t, J = 7.6 Hz, H-4″), 7.59 (3H, m, H-3″, 5″, 4‴), 7.57 (1H, m, H-5‴), 7.14 (1H, m, H-3‴), 7.11 (1H, d, J = 7.6 Hz, H-3), 7.02 (1H, t, J = 7.6 Hz, H-4), 6.91 (1H, d, J = 7.6 Hz, H-6), 6.81 (1H, t, J = 7.6 Hz, H-5), 5.63 (1H, d, J = 9.2 Hz, H-7), 5.57 (1H, d, J = 9.2 Hz, H-7), 4.88 (1H, d, J = 7.4 Hz, H-1′), 4.35 (1H, m, H-6′), 4.15 (1H, m, H-6′), 3.80～3.00 (4H, m, H-2′～5′); ^{13}C-NMR (100 MHz, CD_3OD) δ: 170.0 (C-7‴), 166.9 (C-7″), 161.5 (C-1‴), 155.3 (C-1), 135.9 (C-4‴), 133.3 (C-4″), 130.2 (C-3), 130.0 (C-5, 2″, 6″), 129.9 (C-6‴), 129.8 (C-1″), 128.5 (C-3″, 5″), 125.2 (C-2), 123.1 (C-4), 119.4 (C-5‴), 117.7 (C-3‴), 116.0 (C-6), 112.5 (C-2‴), 101.7 (C-1′), 76.4 (C-5′), 74.3 (C-3′), 73.6 (C-2′), 64.2 (C-7), 62.2 (C-6′)。以上数据与文献报道基本一致[6]，故鉴定化合物 **11** 为 6′-*O*-苯甲酰基水杨苷-7-水杨酸酯。

化合物 **12**：白色颗粒（EtOAc），mp 84.1～86.6 ℃。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 9.28 (1H, s, Ar-OH), 7.28 (1H, d, J = 7.4 Hz, H-6), 7.03 (1H, t, J = 7.4 Hz, H-4), 6.77 (1H, t, J = 7.4 Hz, H-5), 6.74 (1H, t, J = 7.4 Hz, H-3), 4.93 (1H, t, J = 4.4 Hz, 7-OH), 4.47 (2H, d, J = 4.4 Hz, H-7); ^{13}C-NMR (100 MHz, DMSO-d_6) δ: 154.6 (C-2), 129.0 (C-6), 127.8 (C-1, C-4), 119.1 (C-5), 115.0 (C-3), 58.7 (C-7)。以上数据与文献报道一致[2]，故鉴定化合物 **12** 为水杨醇。

化合物 **13**：白色针晶（EtOAc），mp 84.9～86.3 ℃； IR ν_{max}^{KBr} (cm^{-1}): 3 419 (-OH), 1 723 (C=O);

UV λ_{max}^{MeOH} (nm): 226, 273。^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.22 (1H, d, J = 8.0 Hz, H-3), 7.20 (1H, t, J = 8.0 Hz, H-5), 7.02 (1H, d, J = 8.0 Hz, H-6), 6.96 (1H, t, J = 8.0 Hz, H-4), 5.98 (1H, m, H-5″), 5.70 (1H, d, J = 9.6 Hz, H-6″), 5.26 (1H, d, J = 12.0 Hz, H-7), 5.13 (1H, d, J = 12.0 Hz, H-7), 4.88 (1H, d, J = 7.6 Hz, H-1′), 3.80～3.20 (6H, m, H-2′～6′), 2.80 (1H, m, H-3″), 2.60～2.30 (3H, m, H-3″, 4″); ^{13}C- NMR (100 MHz, $CDCl_3$) δ: 206.2 (C-2″), 170.1 (C-7″), 155.4 (C-1), 132.1 (C-6″), 130.1 (C-5), 129.8 (C-5″), 127.6 (C-3), 122.5 (C-4), 115.6 (C-6), 101.0 (C-1′), 78.3 (C-1″), 78.2 (C-5′), 75.9 (C-3′), 73.3 (C-2′), 69.8 (C-4′), 64.1 (C-4′), 61.0 (C-7), 35.4 (C-3″), 26.4 (C-4″)。以上数据与文献报道一致[7]，故鉴定化合物 **13** 为 salicortin。

化合物 **14**：白色针晶（EtOAc），mp 98.2～100.1 ℃； IR ν_{max}^{KBr} (cm^{-1}): 3 439 (-OH), 1 743 (C=O)。^{1}H-NMR (400 MHz, $CDCl_3$), δ 8.12 (2H, d, J = 7.8 Hz, H-2″, 6″), 7.62 (1H, t, J = 7.8 Hz, H-4″), 7.48 (2H, t, J = 7.8 Hz, H-3″, 5″), 7.37 (1H, d, J = 8.0 Hz, H-3), 7.35 (1H, t, J = 8.0 Hz, H-5), 7.14 (1H, d, J = 8.0 Hz, H-6), 7.09 (1H, t, J = 8.0 Hz, H-4), 5.06 (1H, d, J = 12.0 Hz, H-7), 5.05 (1H, t, J = 8.1 Hz, H-3′), 5.04 (1H, d, J = 12.0 Hz, H-7), 5.00 (1H, d, J = 7.6 Hz, H-1′), 3.90 (1H, d, J = 9.2 Hz, H-6′), 3.80 (1H, dd, J = 9.2, 7.6 Hz, H-6′), 3.59 (1H, m, H-2′), 3.58 (1H, m, H-5′), 3.53 (1H, m, H-4′), 2.01 (3H, s, -OAc)；^{13}C-NMR (100 MHz, $CDCl_3$) δ: 171.6 (-OAc), 167.5 (C-7″), 155.5 (C-1), 133.4 (C-4″), 130.5 (C-2), 130.2 (C-1′), 130.0 (C-2″, 6″), 129.5 (C-5, 3″, 5″), 125.4 (C-3), 123.0 (C-4), 115.6 (C-6), 102.0 (C-1′), 78.1 (C-5′), 76.0 (C-2′), 72.0 (C-3′), 69.2 (C-4′), 62.0 (C-6′), 61.5 (C-7), 21.0 (-OAc)。以上数据与文献报道一致[5]，故鉴定化合物 **14** 为 7-*O*-乙酰基-3′-*O*-苯甲酰基水杨苷。

化合物 **15**：白色针晶（EtOAc），mp 102.1～103.6 ℃； IR ν_{max}^{KBr} (cm^{-1}): 3 418 (-OH), 1 741 (C=O)。^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.10 (2H, d, J = 7.8 Hz, H-2″, 6″), 7.61 (1H, t, J = 7.8 Hz, H-4″), 7.46 (2H, t, J = 7.8 Hz, H-3″, 5″), 7.37 (1H, d, J = 8.0 Hz, H-3), 7.33 (1H, t, J = 8.0 Hz, H-5), 7.12 (1H, d, J = 8.0 Hz, H-6), 7.05 (1H, t, J = 8.0 Hz, H-4), 5.08 (1H, d, J = 11.9 Hz, H-7), 5.06 (1H, t, J = 8.2 Hz, H-4′), 5.04 (1H, d, J = 11.9 Hz, H-7), 5.01 (1H, d, J = 7.6 Hz, H-1′), 3.92 (1H, d, J = 9.6 Hz, H-6′), 3.80 (1H, dd, J = 9.6, 7.4 Hz, H-6′), 3.62 (1H, m, H-2′), 3.58 (1H, m, H-5′), 3.55 (1H, m, H-4′), 2.01 (3H, s, -OAc)；^{13}C-NMR (100 MHz, $CDCl_3$) δ: 171.5 (-OAc), 167.2 (C-7″), 155.6 (C-1), 133.7 (C-4″), 130.8 (C-2), 130.4 (C-1′), 130.0 (C-2″, 6″), 128.5 (C-3″, 5″), 128.3 (C-5), 125.5 (C-3), 124.0 (C-4), 116.0 (C-6), 102.1 (C-1′), 78.1 (C-5′), 76.2 (C-2′), 72.1 (C-3′), 69.5 (C-4′), 62.5 (C-6′), 61.7 (C-7), 21.0 (-OAc)。以上数据与文献报道一致[5]，故鉴定化合物 **15** 为 7-*O*-乙酰基-4′-*O*-苯甲酰基水杨苷。

化合物 **16**：白色针晶（EtOAc），mp 106.5～107.0 ℃； IR ν_{max}^{KBr} (cm^{-1}): 3 445 (-OH), 1 746 (C=O)。^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.11 (2H, d, J = 7.7 Hz, H-2″, 6″), 7.61 (1H, t, J = 7.7 Hz, H-4″), 7.46 (2H, t, J = 7.7 Hz, H-3″, 5″), 7.33 (1H, d, J = 8.0 Hz, H-3), 7.25 (1H, t, J = 8.0 Hz, H-5), 7.20 (1H, d, J = 8.0 Hz, H-6), 7.09 (1H, t, J = 8.0 Hz, H-4), 5.15 (1H, t, J = 8.1 Hz, H-2′), 4.90 (1H, d, J = 7.6 Hz, H-1′), 4.87 (1H, d, J = 13.0 Hz, H-7), 4.52 (1H, d, J = 9.2 Hz, H-6′), 4.49 (1H, d, J = 13.0 Hz, H-7), 4.46 (1H, dd, J = 9.2, 7.6 Hz, H-6′), 3.80 (1H, m, H-3′), 3.75 (1H, m, H-5′), 3.53 (1H, m, H-4′), 2.15 (3H, s, -OAc)；^{13}C-NMR (100 MHz, $CDCl_3$) δ: 171.4 (-OAc), 167.7 (C-7″), 157.0 (C-1), 133.6 (C-4″), 130.7 (C-2), 130.0 (C-2″, 6″), 129.9 (C-1′), 129.7 (C-5), 129.2 (C-3), 128.5 (C-3″, 5″), 123.5 (C-4), 116.9 (C-6), 103.2 (C-1′), 78.2 (C-3′), 74.2 (C-5′), 72.3 (C-2′), 69.0 (C-4′), 63.1 (C-6′), 61.9 (C-7), 20.8 (-OAc)。以上数据与文献报道一致[5]，故鉴定化合物 **16** 为 6′-*O*-乙酰基-2′-*O*-苯甲酰基水杨苷。

4 生物活性测试

采用 MTT 法对化合物 **1**、**4**、**5**、**7**、**11**～**13** 进行人胃癌细胞 SGC-7901 体外增殖的抑制作用实验，结果表明，特里杨苷类衍生物化合物 **7**、**11**～**13** 均显一定的活性，其 IC_{50} 值分别为 71.0、122.5、212.7、257.8 μmol/L，其中化合物 **7** 的活性最强。

参考文献

[1] 江苏新医学院. 中药大辞典 [M]. 上海: 上海科学技术出版社. 1985.

[2] 吕伟强, 丁 宇, 刘继梅, 等. 银中杨树叶化学成分研究 [J]. 天然产物研究与开发, 2013, 25(5): 620-623.

[3] Shi H M, Wen J, Jia C Q, *et al*. Two new phenolic glycosides from the barks of *Hydnocarpus annamensis*

and their anti-inflammatory and anti-oxidation activities [J]. *Planta Med*, 2006, 72(1): 948-950.

[4] Simon G, Alexander I, Prter G W. Poliothrysins: novel hydroxycyclohexenone esters from the leaves of *Poliothryszs sinenszs* [J]. *Nat Prod Lett*, 1993, 3(1): 59-64.

[5] Tsutomu I, Kaori N, Kazuko T, *et al*. Isolation of salicin derivatives from *Homalium cochinchinensis* and their antiviral activities [J]. *J Nat Prod*, 2004, 67(4): 659-663.

[6] Mizuo M, Masayak A, Chiemmi I, *et al*. Chaenomeloidin: A phenolic glucoside from leaves of *Salix chaenomeloides* [J]. *J Nat Prod*, 1991, 54 (5): 1447-1450.

[7] Theodore P E, Thomas P C, Paul B R. Structurally intriguing glucosides from Alaskan little tree Willow (*Salix arbusculoides*) [J]. *J Nat Prod*, 1995, 58(2): 1897-1990.