Studies on the Chemical Constituents of Turpinia arguta Seem
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Abstract. From the Turpinia arguta Seem, twelve compounds were isolated and identified as
corosolic acid-28-O-\beta-D-glucopyranosyl ester(1), pomolic acid(2), ursolic acid(3), quercetin (4),
 rhoifolin (5), apigenin-7-O-rutinoside(6), quercetin-3- O-a-L-arabinopyranoside(7), p-hydroxy
cinnamic acid(8), caffeic acid(9), gallic acid, (10) 3,4-dihydroxybenzonic acid(11), p-
hydroxybenzoic acid(12). Their structures were determined by \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR spectral data.

Introduction

Turpinia arguta Seem is distributed in the southern part of China. The leaves of Turpiniae arguta
Seem has been used as an antibacterial, anti-inflamatory and analgesia agent in China for
thousands. Flavonoids, megastigmanes and triterpenoids have been identified as constituents of the
plant\textsuperscript{1,2}. In the present paper, twelve compounds were isolated and identified as corrosolic
cacid-28-O-\beta-D-glucopyranosyl ester(1), pomolic acid(2), ursolic acid(3), quercetin (4),
 rhoifolin (5), apigenin-7-O-rutinoside(6), quercetin-3- O-a-L-arabinopyranoside(7), p-hydroxy
cinnamic acid(8), caffeic acid(9), gallic acid, (10) 3,4-dihydroxybenzonic acid(11), p-
hydroxybenzoic acid(12) by means of \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR spectral data.

Experimental

General experimental procedures All melting points were determined on a X-4A
micro-melting point apparatus and are uncorrected. IR spectra were recorded with an American
Nicolet IMPACT-400 Fourier Transform Infrared Spectrometer. \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR, HSQC and
HMBC were recorded on an American Varian company INOVA-400 and SYSTEM-600 FT NMR
spectrometer. Silica gel (200–300 mesh; Qingdao Marine Chemical Plant) was used for column
chromatography.

Plant material Turpinia arguta Seem were collected at Ganzhou, Jiangxi Province, China in
September of 2013 and authenticated by Professor Q. Lui, Jiangxi University of Traditional Chinese
Medicine. A voucher specimen (13-09-18) of the plant is deposited at the Herbarium of Jiangxi
University of Traditional Chinese Medicine.

Extraction and isolation The leaves of Turpiniae arguta Seem was reduced to a coarse powder
and refluxed with 95% ethanol three times. After evaporation of ethanol in vacuo, the aqueous
residue was diluted with water and was extracted with chloroform, ethyl acetate and n-butanol
saturated with water to give the respective extracts after solvent removal. The ethyl acetate-solution
portion(58g) was subjected to column chromatography on silica gel using a gradient mixture of
chloroform-methanol (from 95:5 to 50:50) as eluting solvent to afford compound 2, 3, 4, 11, 12. The n-butanol-solution portion was evaporated, and the part extract (90g) was fractionated by silica gel column chromatography, eluted with CHCl₃–MeOH–H₂O (6:4:1) to give five fractions (Fractions I–V). Fraction III was subjected to a silica-gel column eluted with CHCl₃–MeOH–H₂O (7:3:1) and preparative HPLC [H₂O–MeOH (60:40), 5ml/min, monitored at 285 nm] to give compound 5–10. Fraction V was subjected to preparative HPLC [H₂O–CH₃CN (70:30), 5ml/min, monitored at 210 nm] to afford compound 1.

Results and discussion

**Compound 1** was white powder, mp 242–244°C. ¹H-NMR (C₅D₅N, 400 MHz) δ: 0.96 (3H, d, J=6Hz), 0.99 (3H, d, J=6.2 Hz), 1.01 (3H, s), 1.07 (3H, s), 1.23 (3H, s), 1.28 (3H, s), 3.36 (1H, d, J=9Hz), 4.15 (1H, td, J=11,4Hz), 5.54 (1H, t, J=3Hz). ¹³C-NMR (C₅D₅N, 100 MHz) δ: 48.1(C-1), 68.8(C-2), 83.1(C-3), 39.3(C-4), 55.2(C-5), 18.7(C-6), 33.1(C-7), 40.4(C-8), 48.2(C-9), 38.2(C-10), 23.8(C-11), 125.8(C-12), 139.4(C-13), 42.6(C-14), 28.1(C-15), 24.6(C-16), 48.1(C-17), 53.2(C-18), 39.5(C-19), 39.3(C-20), 31.8(C-21), 37.6(C-22), 36.7(C-23), 29.6(C-23), 17.0(C-24), 17.2(C-25), 17.6(C-26), 23.6(C-27), 177.6(C-28), 17.2(C-29), 21.5 (C-30), 95.2(C-1’), 74.1(C-2’), 79.3(C-3’), 71.2(C-4’), 78.2(C-5’), 62.3 (C-6’). On the basis of relevant reference [3] and its spectral data, its structure was elucidated to be corosolic acid-28- O-β-D-glucopyranosyl ester.

**Compound 2** was white powder, mp 298-300°C. ¹H-NMR (CDCl₃ , 400MHz) δ: 0.88 (3H, s), 1.05 (3H, d, J=6 Hz), 1.11 (3H, s), 1.16 (3H, s), 1.18 (3H, s), 1.37 (3H, s), 1.69 (3H, s), 3.25 (1H, dd, J=11,5 Hz), 5.59 (1H, t, J=3 Hz). ¹³C-NMR (CDCl₃, 100MHz) δ: 39.7(C-1), 26.4(C-2), 78.0(C-3), 39.3(C-4), 56.3(C-5), 18.6(C-6), 33.3(C-7), 40.5(C-8), 47.4(C-9), 37.2(C-10), 23.9(C-11), 128.2(C-12), 139.1(C-13), 42.3(C-14), 29.4(C-15), 25.6(C-16), 48.8(C-17), 53.3(C-18), 72.5(C-19), 42.2(C-20), 26.8(C-21), 37.6(C-22), 27.9(C-23), 17.3(C-24), 16.0(C-25), 17.0(C-26), 24.5(C-27), 180.9(C-28), 27.3(C-29), 16.3(C-30). On the basis of relevant reference [4] and its spectral data, its structure was elucidated to be pomolic acid.

**Compound 3** was white powder, mp 270–271°C. ¹H NMR (C₅D₅N, 400MHz) δ: 0.91 (3H, s), 0.98 (3H, d, J=6.0 Hz), 1.02 (3H, d, J=6.4 Hz), 1.03 (3H, s), 1.12 (3H, s), 1.29 (3H, s), 3.42 (1H, dd, J=10,7Hz), 5.54 (1H, t, J=3.2 Hz). ¹³C-NMR (C₅D₅N, 100MHz) δ: 39.1(C-1), 28.1(C-2), 78.1(C-3), 39.2(C-4), 55.3(C-5), 18.3(C-6), 33.3(C-7), 40.4(C-8), 48.1(C-9), 37.0(C-10), 23.7(C-11), 126.2(C-12), 139.3(C-13), 42.6(C-14), 28.8(C-15), 12.9(C-16), 48.0(C-17), 53.2(C-18), 39.5(C-19), 39.2(C-20), 31.8(C-21), 37.5(C-22), 27.9(C-23), 15.3(C-24), 16.0(C-25), 17.7(C-26), 23.5(C-27), 179.9(C-28), 17.3(C-29), 21.3 (C-30). On the basis of relevant reference [5] and its spectral data, its structure was elucidated to be ursolic acid.

**Compound 4** was obtained as a yellow needle crystals, mp 311–313°C. ¹H NMR (DMSO-d₆, 400 MHz) δ: 12.47 (1H, s), 7.66(1H, d, J=2.2 Hz), 7.52(1H, d, J=7.8 Hz), 6.86 (1H, d, J=8.4 Hz), 6.38 (1H, d, J = 2.0 Hz), 6.16(1H, d, J = 2.0 Hz). ¹³C NMR (DMSO-d₆, 100 MHz) δ: 175.7 (C-4), 164.4 (C-7), 160.6 (C-9), 156.1 (C-5), 147.7 (C-4’), 146.6 (C-2), 145.0 (C-3’), 135.6 (C-3), 121.9 (C-1’), 119.9 (C-6’), 115.5 (C-5’), 114.9 (C-2’), 102.7 (C-10), 98.3 (C-6), 93.3 (C-8). On the basis of spectral data[6], its structure was elucidated to be quercetin.
Compound 5 were pale yellow granules, soluble in methanol, mp248-250°C. 1H NMR (DMSO-d6, 400 MHz) δ: 12.96 (1H, s, OH), 10.43 (1H, s, OH), 7.94 (2H, d, J = 8.8 Hz, H-2', 6'), 6.94 (2H, d, J = 8.8 Hz, H-3', 5'), 6.87 (1H, s, H-3), 6.79 (1H, d, J = 2.1 Hz, H-8), 6.38 (1H, d, J = 2.1 Hz, H-6). 13C-NMR (DMSO-d6, 100 MHz) δ: 182.45 (C-4), 164.74 (C-2), 161.86 (C-7), 161.58 (C-5), 157.45 (C-9), 129.05 (C-2', 6), 121.46 (C-1'), 116.50 (C-3', 5'), 105.89 (C-10), 103.71 (C-3), 100.93(C-1''), 98.27 (C-6), 98.32 (C-1''), 94.98 (C-8), 77.68 (C-2''), 77.48 (C-3''), 76.72 (C-5''), 72.33 (C-4''), 70.94 (C-4''), 70.86 (C-3''), 70.11 (C-2''), 68.81 (C-5''), 60.93 (C-6''), 18.54 (C-6''). The above data is consistent with the literatures, this compound is identified as rhoifolin.

Compound 6 was obtained as an amorphous solid. 1H- NMR(DMSO-d6,600MHz) δ: 7.92(2H, d, J=9.0Hz, H-2', H-6'), 6.92 (2H, d, J=9.0Hz, H-3', H-5''), 6.83 (1H,s), 6.76 (1H,d,J=2.4Hz,8-H'), 6.44(1H,d,J=2.4 Hz ,6-H). 13C-NMR(150MHz,DMSO-d6) δ: 181.9 (C-4'),162.8 (C-5'),161.1 (C-7),156.8 (C-9),128.6 (C-2',C-6''),116.2 (C-3',C-5''),105.3 (C-10), 100.5 (C-1''), 99.8 (C-1''), 99.4 (C-6), 94.7 (C-8), 76.2 (C-5''), 75.5 (C-3'), 73.0 (C-4''), 72.0 (2''), 70.7 (C-4''), 70.3 (C-3''), 69.5 (C-2''), 68.2 (C-5''), 66.0 (C-6''), 17.7 (C-6''). On the basis of relevant reference [7] and its spectral data, its structure was elucidated to be apigenin- 7-O-rutinoside.

Compound 7 was obtained as a yellow powder. 1H-NMR(DMSO-d6,600MHz)δ: 7.64(1H,dd,J=9.2 Hz, H-6''), 7.50(1H,d,J= 1.8 Hz, H-2''), 6.83(1H,d,J= 8.4 Hz, H-5''), 6.38(1H, d, J=1.8Hz, H-8), 6.18(1H,d,J=1.2Hz, H-6), 5.26 (1H,d,J=5.4Hz, H-1''). 13C-NMR(DMSO-d6,125MHz) δ: 177.4 (C-4), 164.6 (C-7), 161.1 (C-5), 156.3 (C-9), 156.1 (C-2), 148.6 (C-4''), 145.0 (C-3''), 133.6 (C-3), 122.0 (C-6''), 120.8 (C-1''), 115.7 (C-5''), 115.3 (C-2''), 103.7 (C-10), 101.4 (C-1''), 98.7 (C-6), 93.5 (C-8), 71.6 (C-2''), 70.7 (C-3''), 60.0 (C-4''), 64.2 (C-5''). On the basis of spectral data[8], its structure was elucidated to be quercetin-3-O-a-L-arabinopyranoside.

Compound 8 was white powder, soluble in methanol, mp217-219 ºC. 1H-NMR (DMSO-d6,400MHz) δ: 12.15 (1H, s, OH), 9.95 (1H, s, OH), 6.28 (1H, d, J = 16Hz, H-3), 7.49 (1H, d, J = 16Hz, H-2), 6.78 (2H, J = 8.8 Hz, H-6,8), 7.50 (2H, d, J = 8.8 Hz, H-5,9). 13C-NMR (DMSO-d6,100MHz) δ: 168.40 (C-1), 160.05 (C-7), 144.63 (C-3), 130.55 (C-5,9), 125.73 (C-4), 116.20 (C-6,8), 115.79 (C-2). The above data is consistent with the literature, so it is identified as p-hydroxy cinnamic acid.

Compound 9 was obtained as a yellow powder, mp: 201-203°C, 1H-NMR (CD3OD,600MHz) δ: 6.23(d, J=15 Hz), 7.53(d, J=15 Hz), 6.73(d, J=8.4Hz), 6.93(dd, J=7.8 Hz,1.8Hz), 7.03(d, J =1.8 Hz). 13C-NMR (CD3OD,150MHz) δ:171.6(COOH), 115.3 (C-6), 116.1 (C-5), 117.0 (C-2), 122.9 (C-8), 128.1 (C-1), 146.9 (C-3), 147.0 (C-8), 149.5 (C-4), 171.6 (C-9). On the basis of relevant reference [9] and its spectral data, its structure was elucidated to be cafffeic acid.

Compound 10 was obtained as a yellow needle crystal, soluble in methanol, mp201-203°C, 1H-NMR (DMSO-d6,400MHz) δ: 12.22 (1H, s, OH), 9.18 (2H, s, OH), 8.92 (1H, s, OH), 6.92 (2H, s, H-2,6), 13C-NMR (DMSO-d6,100MHz) δ: 167.91 (COOH), 145.86 (C-3,5), 138.44 (C-4), 120.89 (C-1), 109.17 (C-2,6). The above data is consistent with the literature, it is identified as gallic acid.
**Compound 11** was obtained as colorless needles, mp: 210~212°C. UV\(_\text{λ}\)\(_{\text{max}}\text{(MeOH)}\): 206nm. IR\(_\text{KBr}\) cm\(^{-1}\): 3207, 1676, 1601, 1529, 1298, 1466, 1419, 1381, 1130, 1095, 941, 766, 638, 577. EI-MS m/z (%): 154(M\(^+\),85), 137(100), 119(3), 110(31), 97(5), 91(6), 81(22), 69(3), 63(32), 53(34), 44(35), 41(6). \(^1\)H-NMR (CD\(_3\)OD, 400MHz)\(\delta\): 7.47(1H, s, H-2) 7.45(1H, d, H-6), 6.82(1H, s, H-5). \(^{13}\)C-NMR (CD\(_3\)OD, 100MHz)\(\delta\): 170.2, 151.5(C-4), 146.0(C-3), 123.9(C-1), 123.1(C-6), 117.7(C-2), 115.7(C-5). On the basis of spectral data, its structure was elucidated to be 3, 4-dihydroxybenzonic acid.

**Compound 12** was white powder. \(^1\)H-NMR (CD\(_3\)OD,400MHz)\(\delta\): 7.86(2H, d, J=8.4 Hz), 6.82(2H, d, J=8.4 Hz). \(^{13}\)C-NMR(CD\(_3\)OD,100MHz)\(\delta\): 163.4(C-1),132.7(C-3),116.2(C-2),123.1(C-4) . On the basis of spectral data[10], its structure was elucidated to be p-hydroxybenzoic acid.

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**References**

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