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糙叶五加中三萜皂苷等次生代谢产物的研究及其化学分类学意义

王　翔[1#],李小军[1#],李　芝[1],张晓丹[2],陆昌洙[3],刘向前[1*]

[1]湖南中医药大学药学院,长沙 410208;[2] 浙江理工大学生命科学学院,杭州 310018;

[3]庆熙大学药学院,韩国 首尔 130-701

摘　要:基于化学分类学意义的成分研究,采用多种柱层析手段和波谱学方法,从糙叶五加叶中分离鉴定了23种化合物,包括3种黄酮类物质(**1**~**3**)、一个有机酸(**4**)、16种三萜皂苷(**5**~**20**)、一个蒽醌(**21**)、一个甾体皂苷(**22**)和一个脑苷脂(**23**)。化合物**5**、**6**、**11**、**12**、**14**、**15**、**17**、**19**和**20**为首次从五加属植物中分离得到;化合物**8**、**13**和**21**为首次从五加科中分得。同时基于这些分离所得的次生代谢产物进一步探讨它们在化学分类上的意义。

关键词:五加科;糙叶五加;三萜皂苷;蒽醌;黄酮

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Chemotaxonomic Significance of Triterpenoid Saponins and Other Secondary Metabolites from *Acanthopanax henryi*

WANG Xiang[1#], LI Xiao-jun[1#], LI Zhi[1], ZHANG Xiao-dan[2], YOOK Chang-soo[3], LIU Xiang-qian[1*]

[1] *School of Pharmacy, Hunan University of Chinese Medicine, No. 300 Xueshi Road, Changsha 410208, China*; [2] *College of Life Science, Zhejiang Sci-Tech University, Hangzhou 310018, China*;

[3] *College of Pharmacy, Kyung-Hee University, Seoul 130-701, Korea*

Abstract: Phytochemical investigation of the leaves of *Acanthopanax henryi* led to the isolation of 23 compounds, including three flavonoids (**1-3**), one organic acid (**4**), sixteen triterpenoid saponins (**5-20**), one anthraquinone (**21**), one steroidal glycoside (**22**) and one cerebroside (**23**). The structures of the isolates were elucidated by spectroscopic methods and comparison with the reported spectral data. All of these compounds except for **1-3**, **10** and **23** have previously been isolated from *A. henryi*. Compounds **5**, **6**, **11**, **12**, **14**, **15**, **17**, **19** and **20** have been reported from the *Acanthopanax* genus and compounds **8**, **13**, and **21** are new compounds within Araliaceae. The chemotaxonomic significance of this investigation based on the isolated compounds is summarized.

Key words: Araliaceae; *Acanthopanax henryi*; triterpenoid saponins; Anthraquinone; flavonoids

Introduction

Acanthopanax henryi (*Eleutherococcus henryi*) (Oliv.) Harms (Araliaceae) is a deciduous shrub or tree that grows in forest margins or shrubbery up to an altitude of 1000-3200 m. It is often found in eastern China such as Hunan, Anhui and Zhejiang Provinces[1]. *A. henryi* is a plant with a number of medicinal effects[2], it is usually used for the treatment of rheumatism pain, spasm of numbness, edema and so on.

Previous phytochemical investigations of *A. henryi* resulted in the isolation of a variety of secondary metabolites, including steroids, fatty acids, lignans and phenylpropanoids[3]. In particular, six caffeoyl quinic acid derivates, five flavonoids, one triterpene saponin and one cerebroside were reported[4]. Additionally, we isolated four fatty acids, two steroids and four flavonoids from the leaves of *A. henryi*[5].

Materials and Methods

General experimental procedures

Melting points (uncorrected) were measured using a Boetius micromelting point apparatus. ^{1}H NMR (600

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# These authors contributed equally to this work.

* Corresponding author　Tel: 86-731-88458240; E-mail: lxq0001cn@163.com

MHz), ^{13}C NMR (150 MHz) and 2D NMR were recorded at room temperature in MeOH or pyridine-d_5 using Bruker ACF-500 NMR spectrometer and chemical shifts were given in δ (ppm) value relative to TMS as internal standard. Mass spectra were obtained on an Agilent 1200 Series LC/MSD Trap Mass spectrometer (ESI-MS). HR-MS were obtained on an Agilent 6530 Q-TOF high resolution Mass spectrometer. Column chromatography was carried out on silica gel (200-300 mesh and 100-200 mesh, Qingdao Marine Chemical Co., Ltd., Qingdao, China), Sephadex LH-20 (Merck) and D101 macroporous resin (Tianjin Guangfu Chemical Co., Ltd., Tianjin, China). RP-TLC was performed on a precoated RP-18F_{254s} (Merck) plates. TLC was conducted on self-made silica gel G (Qingdao Marine Chemical Industry, Qingdao, China) plates and spots were visualized by spraying with 10% H_2SO_4 in ethanol (v/v) followed by heating at 105 ℃.

Plant materials

The leaves of *A. henryi* (Oliv.) Harms were collected in October 2012 in Xinhua, Hunan Province, China, and authenticated by Prof. Liu, X. Q. The voucher specimen (NO. 20121125) has been deposited in The School of Pharmacy, Hunan University of Chinese Medicine.

Extraction and isolation

Dried leaves of *A. henryi* (Oliv.) Harms (10 kg) were cut into small pieces and extracted with MeOH (3 × 100 L) by soaking three times at room temperature. The solutions from the extractions were combined and concentrated under reduced pressure to yield a dark-green residue (0.8 kg). It was then suspended in water and partitioned with petroleum ether (boiling point 60-90 ℃). The aqueous layer was fractionated into five fractions (F1-5) by column chromatography on a macroporous resin using a gradient of EtOH/H_2O (0%, 30%, 50%, 75%, and 95%).

F1 (100.0 mg) was subjected to a Sephadex LH-20 column chromatography and eluted with H_2O to give **4** (30.0 mg). Yellow powder **1** (32.8 g) was obtained from F2 (130.0 g) by successive recrystallizations with MeOH. F3 (14.0 g) was subjected to silica gel column chromatography and was eluted with $CHCl_3$/MeOH/H_2O (25∶1∶0/1∶1∶0.2) to obtain **15** subfractions (F3.1-3.15). Small crystals were obtained from F3.2 (260.0 mg), which were collected by removal of the supernatant. Recrystallization from $CHCl_3$ yielded compound **21** (7.0 mg). F3.3 (119.0 mg) was purified on a silica gel column chromatography and eluted with a gradient of $CHCl_3$/MeOH/H_2O (15∶1∶0/6∶1∶0.1). This was then purified on a reversed phase C_{18} gel (MeOH/H_2O, 10∶90/100∶0) to give **5** (12.0 mg) and **22** (35.0 mg). F3.4 (0.8 g) was further refractionated on a Sephadex LH-20 column ($CHCl_3$/MeOH, 1∶1) to afford **7** (45.0 mg). F3.5 (113.8 mg) was further chromatographed on silica gel column chromatography using $CHCl_3$/MeOH/H_2O (10∶1∶0/5∶1∶0.1) to obtain **7** (20.0 mg), **8** (12.0 mg) and **23** (8.0 mg). F3.6 (115.0 mg) was also subjected to silica gel column chromatography and eluted with a gradient consisting of $CHCl_3$/MeOH/H_2O (10∶1∶0.1/5∶1∶0.1) to yield **9** (20.0 mg). F3.7 (1.2 g) was first purified by silica gel column chromatography by eluting with $CHCl_3$/MeOH/H_2O (10∶1∶0.1/6∶1∶0.1). This was then recrystallized from MeOH to obtain 10 (600.0 mg) and **11** (200.0 mg). F3.8 (613.0 mg) was purified on silica gel column chromatography by eluting with $CHCl_3$/MeOH/H_2O (7∶1∶0.1/4∶1∶0.1). This was followed by decolorization by a Sephadex LH-20 CC (MeOH) to give **12** (35.0 mg). Compound **13** (30.0 mg) was obtained as needle crystals from F3.9 (180.0 mg) by recrystallization from MeOH. F3.10 (0.58 g) was subjected to silica gel column chromatography, with a gradient of $CHCl_3$/MeOH/H_2O (7∶1∶0.1/3∶1∶0.1) as the solvent. This was followed by purification by preparative HPLC (CH_3CN/H_2O, 6∶4) to gain **14** (22.0 mg). F3.11 (0.67 g) was first separated on silica gel column chromatography and eluted with $CHCl_3$/MeOH/H_2O (6∶1∶0.1/2∶1∶0.1) to afford six subfractions (F3.11.1-3.11.6). F3.11.2 and F3.11.3 (106.0 mg) were then subjected to silica gel column chromatography and finally purified on a Sephadex LH-20 (MeOH) to yield **15** (35.0 mg), **16** (35.0 mg) and **17** (30.0 mg). F3.12 (75.0 mg) was purified on silica gel column chromatography, using $CHCl_3$/MeOH/H_2O (4∶1∶0.1/1∶1∶0.2) as the mo-

bile phase to give four sub-fractions (F3. 12. 1-3. 12. 4). F3. 12. 2-3. 12. 4 were further separated by Sephadex LH-20 (MeOH) to produce **18** (15. 0 mg), **19** (51. 0 mg) and **20** (60. 0 mg). Finally, F4 (14. 0 g) was subjected to silica gel column chromatography and eluted with $CHCl_3$/MeOH/H_2O (15∶1∶0/1∶1∶0. 2) to give **10** subfractions (F4. 1-4. 10). Yellow powder **2** (4. 1 g) was purified from F4. 4 (130. 0 g) by successive recrystallizations from MeOH. F4. 10 (75. 0 mg) was purified on silica gel column chromatography and eluted with $CHCl_3$/MeOH/H_2O (6∶1∶0. 1/3∶1∶0. 1) to obtain **3** (25. 0 mg).

Results and Discussion

Rutin (**1**) Yellow amorphous powder; HCl-Mg and Molish tests were positive; NP-TLC analysis: The R_f values of compound 1 and standard (rutin) were same on NP-TLC using three different solvent system $CHCl_3$/MeOH/H_2O, CH_3COCH_3/MeOH, and EtOAc/MeOH.

Isoquercitrin (**2**) Yellow amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 159. 0 (C-2), 135. 6 (C-3), 179. 5 (C-4), 163. 0 (C-5), 99. 9 (C-6), 166. 1 (C-7), 94. 7 (C-8), 158. 5 (C-9), 105. 7 (C-10), 123. 1 (C-1′), 116. 0 (C-2′), 145. 9 (C-3′), 148. 6 (C-4′), 117. 6 (C-5′), 122. 2 (C-6′), 104. 4 (glu-C-1″), 75. 7 (glu-C-2″), 78. 1 (glu-C-3″), 71. 2 (glu-C-4″), 78. 4 (glu-C-5″), 62. 6 (glu-C-6″).

Quercetin (**3**) Yellow amorphous powder; HCl-Mg test was positive; Molish test was negative; NP-TLC analysis: The R_f values of compound **3** and standard (quercetin) were same on NP-TLC using three different solvent system $CHCl_3$/MeOH/H_2O, CH_3COCH_3/MeOH, and EtOAc/MeOH.

Fumaric acid (**4**) Colorless needles; ^{13}C NMR (150 MHz, pyridine-d_5): δ 165. 93 (C-1, C-1′), 133. 95 (C-2, C-2′).

Ursolic acid 3-*O*-α-L-arabinopyranoside (**5**) White needles; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39. 4 (C-1), 27. 2 (C-2), 89. 2 (C-3), 40. 0 (C-4), 56. 4 (C-5), 18. 9 (C-6), 34. 0 (C-7), 40. 4 (C-8), 48. 4 (C-9), 37. 4 (C-10), 24. 1 (C-11), 126. 1 (C-12), 139. 1 (C-13), 43. 0 (C-14), 29. 2 (C-15), 25. 4 (C-16), 48. 5 (C-17), 54. 0 (C-18), 40. 0 (C-19), 39. 8 (C-20), 31. 6 (C-21), 37. 9 (C-22), 28. 7 (C-23), 16. 1 (C-24), 17. 4 (C-25), 17. 9 (C-26), 24. 4 (C-27), 180. 3 (C-28), 18. 0 (C-29), 21. 9 (C-30); C-3-ara: 108. 0 (C-1′), 73. 4 (C-2′), 75. 1 (C-3′), 70. 0 (C-4′), 67. 2 (C-5′).

Eechinocystic acid 3-*O*-α-L-arabinopyranoside (**6**) White needles; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39. 9 (C-1), 27. 9 (C-2), 90. 3 (C-3), 40. 3 (C-4), 57. 3 (C-5), 19. 5 (C-6), 34. 4 (C-7), 40. 8 (C-8), 48. 3 (C-9), 38. 0 (C-10), 24. 6 (C-11), 123. 6 (C-12), 145. 2 (C-13), 42. 8 (C-14), 36. 7 (C-15), 75. 4 (C-16), 48. 3 (C-17), 42. 2 (C-18), 47. 9 (C-19), 31. 6 (C-20), 32. 9 (C-21), 36. 4 (C-22), 28. 7 (C-23), 17. 1 (C-24), 16. 2 (C-25), 17. 9 (C-26), 27. 4 (C-27), 181. 3 (C-28), 33. 6 (C-29), 25. 1 (C-30); C-3-ara: 107. 3 (C-1′), 73. 0 (C-2′), 74. 5 (C-3′), 69. 7 (C-4′), 66. 5 (C-5′).

Eleutheroside K (**7**) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39. 3 (C-1), 27. 0 (C-2), 89. 3 (C-3), 40. 0 (C-4), 56. 4 (C-5), 19. 0 (C-6), 33. 7 (C-7), 40. 4 (C-8), 48. 4 (C-9), 37. 5 (C-10), 24. 2 (C-11), 122. 9 (C-12), 145. 4 (C-13), 42. 6 (C-14), 28. 8 (C-15), 24. 3 (C-16), 47. 2 (C-17), 42. 5 (C-18), 47. 0 (C-19), 31. 4 (C-20), 34. 7 (C-21), 33. 6 (C-22), 28. 6 (C-23), 17. 5 (C-24), 16. 0 (C-25), 17. 9 (C-26), 26. 6 (C-27), 180. 2 (C-28), 33. 8 (C-29), 24. 3 (C-30); C-3-ara: 105. 3 (C-1′), 76. 4 (C-2′), 74. 3 (C-3′), 69. 1 (C-4′), 65. 2 (C-5′); rha (1→2) ara: 102. 2 (C-1″), 73. 1 (C-2″), 72. 9 (C-3″), 74. 6 (C-4″), 70. 4 (C-5″), 19. 1 (C-6″).

Prosapogenin CP_{2b} (**8**) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39. 4 (C-1), 27. 0 (C-2), 89. 2 (C-3), 40. 0 (C-4), 56. 4 (C-5), 19. 0 (C-6), 33. 7 (C-7), 40. 2 (C-8), 48. 4 (C-9), 37. 5 (C-10), 24. 2 (C-11), 123. 0 (C-12), 145. 4 (C-13), 42. 6 (C-14), 28. 8 (C-15), 24. 3 (C-16), 47. 2 (C-17), 42. 5 (C-18), 47. 0 (C-19), 31. 4 (C-20), 34. 7 (C-21), 33. 6 (C-22), 28. 6 (C-23), 17. 0 (C-24), 16. 0 (C-25), 17. 5 (C-26), 26. 6 (C-27), 180. 4 (C-28), 33. 7 (C-29), 24. 3 (C-30); C-3-ara: 105. 8 (C-1′), 81. 2 (C-2′), 74. 3 (C-3′), 69. 1 (C-4′), 65. 2 (C-5′); xyl (1→2) ara: 106. 7 (C-1″),

74.6 (C-2″), 74.9 (C-3″), 69.7 (C-4″), 67.5 (C-5″).

Tauroside D (**9**) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.4 (C-1), 27.0 (C-2), 89.3 (C-3), 40.0 (C-4), 56.5 (C-5), 19.1 (C-6), 34.0 (C-7), 40.4 (C-8), 47.7 (C-9), 37.6 (C-10), 24.2 (C-11), 122.9 (C-12), 145.6 (C-13), 42.6 (C-14), 36.6 (C-15), 75.2 (C-16), 49.4 (C-17), 41.9 (C-18), 47.8 (C-19), 31.4 (C-20), 33.4 (C-21), 36.7 (C-22), 28.6 (C-23), 17.5 (C-24), 16.1 (C-25), 17.9 (C-26), 27.7 (C-27), 180.5 (C-28), 33.8 (C-29), 25.2 (C-30); C-3-ara: 105.3 (C-1′), 76.4 (C-2′), 74.3 (C-3′), 69.2 (C-4′), 65.2 (C-5′); rha (1→2) ara: 102.4 (C-1″), 73.1 (C-2″), 72.9 (C-3″), 74.6 (C-4″), 70.4 (C-5″), 19.1 (C-6″).

Guaianin N (**10**) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.3 (C-1), 27.2 (C-2), 89.2 (C-3), 40.1 (C-4), 56.4 (C-5), 19.0 (C-6), 33.3 (C-7), 40.2 (C-8), 48.5 (C-9), 37.6 (C-10), 24.3 (C-11), 123.0 (C-12), 145.2 (C-13), 42.7 (C-14), 28.4 (C-15), 24.2 (C-16), 47.2 (C-17), 42.5 (C-18), 47.0 (C-19), 31.5 (C-20), 34.7 (C-21), 34.0 (C-22), 28.6 (C-23), 17.5 (C-24), 16.0 (C-25), 17.9 (C-26), 26.7 (C-27), 180.4 (C-28), 33.8 (C-29), 24.3 (C-30); C-3-ara: 107.9 (C-1′), 72.1 (C-2′), 86.6 (C-3′), 69.8 (C-4′), 67.5 (C-5′); glu (1→3) ara: 106.9 (C-1″), 76.2 (C-2″), 78.9 (C-3″), 72.1 (C-4″), 79.2 (C-5″), 63.2 (C-6″).

Matesaponin J$_2$ (**11**) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.4 (C-1), 27.2 (C-2), 89.2 (C-3), 40.2 (C-4), 56.4 (C-5), 19.0 (C-6), 34.7 (C-7), 40.5 (C-8), 48.5 (C-9), 37.5 (C-10), 24.1 (C-11), 126.2 (C-12), 139.7 (C-13), 43.0 (C-14), 29.2 (C-15), 24.2 (C-16), 47.2 (C-17), 42.5 (C-18), 40.3 (C-19), 40.0 (C-20), 31.5 (C-21), 38.0 (C-22), 28.8 (C-23), 17.5 (C-24), 16.1 (C-25), 17.9 (C-26), 24.4 (C-27), 180.7 (C-28), 18.0 (C-29), 21.9 (C-30); C-3-ara: 107.9 (C-1′), 72.1 (C-2′), 86.6 (C-3′), 69.8 (C-4′), 67.5 (C-5′); glu (1→3) ara: 106.9 (C-1″), 76.2 (C-2″), 78.9 (C-3″), 72.1 (C-4″), 79.2 (C-5″), 63.2 (C-6″).

Echinocystic acid 3-*O*-β-D-glucopyranosyl-(1→3)-*O*-α-L-arabinopyranoside (**12**) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.4 (C-1), 27.2 (C-2), 89.2 (C-3), 40.1 (C-4), 56.5 (C-5), 19.0 (C-6), 34.0 (C-7), 40.2 (C-8), 47.7 (C-9), 37.6 (C-10), 24.3 (C-11), 122.9 (C-12), 145.6 (C-13), 42.6 (C-14), 36.6 (C-15), 75.3 (C-16), 49.4 (C-17), 41.9 (C-18), 47.8 (C-19), 31.5 (C-20), 36.7 (C-21), 33.3 (C-22), 28.6 (C-23), 17.5 (C-24), 16.1 (C-25), 18.0 (C-26), 27.7 (C-27), 180.5 (C-28), 33.8 (C-29), 25.2 (C-30); C-3-ara: 107.9 (C-1′), 72.4 (C-2′), 84.6 (C-3′), 69.8 (C-4′), 67.5 (C-5′); glu (1→3) ara: 106.9 (C-1″), 76.2 (C-2″), 78.9 (C-3″), 72.1 (C-4″), 79.1 (C-5″), 63.2 (C-6″).

Hemslonin A (**13**) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.5 (C-1), 28.6 (C-2), 79.3 (C-3), 39.9 (C-4), 56.3 (C-5), 19.3 (C-6), 33.0 (C-7), 40.4 (C-8), 48.7 (C-9), 37.9 (C-10), 23.9 (C-11), 123.0 (C-12), 144.9 (C-13), 42.6 (C-14), 28.8 (C-15), 24.3 (C-16), 47.6 (C-17), 42.2 (C-18), 46.8 (C-19), 31.2 (C-20), 34.1 (C-21), 33.7 (C-22), 29.3 (C-23), 17.0 (C-24), 16.2 (C-25), 18.1 (C-26), 26.6 (C-27), 177.0 (C-28), 33.6 (C-29), 24.6 (C-30); C-28-glu: 96.2 (C-1′), 74.4 (C-2′), 79.0 (C-3′), 71.4 (C-4′), 78.5 (C-5′), 69.9 (C-6′); glu′ (1→6) glu: 105.8 (C-1″), 75.7 (C-2″), 78.9 (C-3″), 72.0 (C-4″), 78.6 (C-5″), 63.1 (C-6″).

Cussonoside B (**14**) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 38.5 (C-1), 27.6 (C-2), 78.6 (C-3), 39.6 (C-4), 55.4 (C-5), 18.1 (C-6), 33.0 (C-7), 41.5 (C-8), 47.3 (C-9), 36.7 (C-10), 23.2 (C-11), 122.5 (C-12), 143.5 (C-13), 41.9 (C-14), 29.2 (C-15), 22.6 (C-16), 48.2 (C-17), 41.2 (C-18), 45.8 (C-19), 31.6 (C-20), 33.5 (C-21), 36.2 (C-22), 27.5 (C-23), 16.5 (C-24), 15.1 (C-25), 20.2 (C-26), 27.4 (C-27), 177.2 (C-28), 32.1 (C-29), 24.9 (C-30); C-28-glu: 94.3 (C-1′), 75.4 (C-2′), 78.5 (C-3′), 69.5 (C-4′), 76.7 (C-5′), 68.0 (C-6′); glu′ (1→6) glu: 102.8 (C-1″), 73.9 (C-2″), 75.3 (C-3″), 78.1

(C-4″), 76.6 (C-5″), 60.5 (C-6″); rha (1→4) glu′: 101.5 (C-1‴), 70.9 (C-2‴), 72.4 (C-3‴), 72.4 (C-4‴), 69.3 (C-5‴), 16.1 (C-6‴).

Oleanolic acid 3-*O*-[*β*-D-glucopyranosyl-(1→3)]-*β*-D-galactopyranosyl-(1→2)-*O*-*α*-L- arabinopyranoside (15) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.3 (C-1), 27.1 (C-2), 89.4 (C-3), 40.2 (C-4), 56.4 (C-5), 19.0 (C-6), 33.7 (C-7), 40.4 (C-8), 48.4 (C-9), 37.5 (C-10), 24.2 (C-11), 123.1 (C-12), 145.3 (C-13), 42.6 (C-14), 28.8 (C-15), 24.3 (C-16), 47.2 (C-17), 42.5 (C-18), 47.0 (C-19), 31.4 (C-20), 34.7 (C-21), 34.0 (C-22), 28.6 (C-23), 17.3 (C-24), 16.0 (C-25), 17.3 (C-26), 26.6 (C-27), 180.6 (C-28), 33.8 (C-29), 24.3 (C-30); C-3-ara: 105.8 (C-1′), 78.2 (C-2′), 83.5 (C-3′), 69.0 (C-4′), 66.0 (C-5′); gal (1→2) ara: 105.7 (C-1″), 74.0 (C-2″), 75.8 (C-3″), 70.2 (C-4″), 76.8 (C-5″), 61.9 (C-6″); glu (1→3) ara: 105.4 (C-1‴), 75.9 (C-2‴), 78.8 (C-3‴), 72.0 (C-4‴), 79.0 (C-5‴), 63.1 (C-6‴).

Ciwujianoside C$_3$ (16) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.5 (C-1), 27.2 (C-2), 89.2 (C-3), 40.0 (C-4), 56.4 (C-5), 19.0 (C-6), 33.0 (C-7), 40.6 (C-8), 48.6 (C-9), 37.5 (C-10), 24.3 (C-11), 123.4 (C-12), 144.6 (C-13), 42.6 (C-14), 29.2 (C-15), 25.1 (C-16), 48.9 (C-17), 42.2 (C-18), 46.7 (C-19), 31.2 (C-20), 34.0 (C-21), 37.4 (C-22), 28.8 (C-23), 17.4 (C-24), 16.1 (C-25), 17.9 (C-26), 26.5 (C-27), 177.0 (C-28), 33.6 (C-29), 24.2 (C-30); C-3-ara: 107.9 (C-1′), 73.4 (C-2′), 75.1 (C-3′), 70.0 (C-4′), 67.2 (C-5′); C-28-glu: 96.1 (C-1″), 74.4 (C-2″), 79.2 (C-3″), 71.4 (C-4″), 78.5 (C-5″), 69.7 (C-6″); glu (1→6) glu: 105.4 (C-1‴), 75.8 (C-2‴), 77.7 (C-3‴), 78.8 (C-4‴), 77.0 (C-5‴), 61.8 (C-6‴); rha (1→4) glu′: 103.2 (C-1⁗), 73.1 (C-2⁗), 73.3 (C-3⁗), 74.5 (C-4⁗), 70.8 (C-5⁗), 19.0 (C-6⁗).

Ursolic acid 3-*O*-*α*-L-arabinopyranosyl-28-*O*-*α*-L-rhamnopyranosyl-(1→4)-*O*-*β*-D- glucopyranosyl-(1→6)-*O*-*β*-D-glucopyranoside (17) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.3 (C-1), 27.2 (C-2), 89.2 (C-3), 40.0 (C-4), 56.4 (C-5), 19.1 (C-6), 34.5 (C-7), 40.6 (C-8), 48.6 (C-9), 37.5 (C-10), 24.3 (C-11), 126.6 (C-12), 138.9 (C-13), 43.0 (C-14), 29.2 (C-15), 25.1 (C-16), 48.9 (C-17), 42.2 (C-18), 39.8 (C-19), 39.6 (C-20), 31.3 (C-21), 37.3 (C-22), 28.7 (C-23), 17.4 (C-24), 16.3 (C-25), 18.0 (C-26), 24.2 (C-27), 176.7 (C-28), 18.2 (C-29), 21.8 (C-30); C-3-ara: 108.0 (C-1′), 73.4 (C-2′), 75.1 (C-3′), 70.0 (C-4′), 67.2 (C-5′); C-28-glu: 96.1 (C-1″), 74.4 (C-2″), 79.2 (C-3″), 71.4 (C-4″), 78.5 (C-5″), 69.9 (C-6″); glu′ (1→6) glu: 105.5 (C-1‴), 75.8 (C-2‴), 77.7 (C-3‴), 78.8 (C-4‴), 77.0 (C-5‴), 61.8 (C-6‴); rha (1→4) glu′: 103.2 (C-1⁗), 73.1 (C-2⁗), 73.3 (C-3⁗), 74.3 (C-4⁗), 70.8 (C-5⁗), 19.0 (C-6⁗).

Momordin Ib (18) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.1 (C-1), 26.9 (C-2), 89.5 (C-3), 40.0 (C-4), 56.3 (C-5), 19.0 (C-6), 33.7 (C-7), 40.2 (C-8), 48.5 (C-9), 37.5 (C-10), 24.2 (C-11), 123.1 (C-12), 145.3 (C-13), 42.8 (C-14), 28.8 (C-15), 24.3 (C-16), 47.2 (C-17), 42.5 (C-18), 47.0 (C-19), 30.5 (C-20), 34.7 (C-21), 33.7 (C-22), 28.7 (C-23), 17.5 (C-24), 16.0 (C-25), 17.9 (C-26), 26.7 (C-27), 180.7 (C-28), 33.8 (C-29), 24.3 (C-30); C-3-gluA: 107.4 (C-1′), 75.9 (C-2′), 78.7 (C-3′), 74.1 (C-4′), 77.6 (C-5′), 172.9 (C-6′).

Araliasaponin II (19) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.3 (C-1), 27.2 (C-2), 89.2 (C-3), 40.1 (C-4), 56.4 (C-5), 19.1 (C-6), 33.0 (C-7), 40.4 (C-8), 48.6 (C-9), 37.5 (C-10), 23.9 (C-11), 123.4 (C-12), 144.6 (C-13), 42.6 (C-14), 28.8 (C-15), 24.3 (C-16), 47.5 (C-17), 42.2 (C-18), 46.7 (C-19), 31.2 (C-20), 34.5 (C-21), 33.0 (C-22), 28.6 (C-23), 18.0 (C-24), 16.1 (C-25), 17.5 (C-26), 26.6 (C-27), 177.0 (C-28), 33.6 (C-29), 24.2 (C-30); C-3-ara: 107.9 (C-1′), 72.4 (C-2′), 86.6 (C-3′), 69.8 (C-4′), 67.5 (C-5′); glu (1→3) ara: 106.9 (C-1″), 76.2 (C-2″), 78.9 (C-3″), 72.1 (C-4″), 79.2 (C-5″), 63.2 (C-6″); C-28-glu′: 96.2 (C-1‴), 74.4 (C-2‴), 78.9 (C-3‴), 71.4 (C-4‴), 78.5 (C-

5‴),69.9 (C-6‴); glu″(1→6)glu′: 105.8 (C-1⁗), 75.6 (C-2⁗), 78.9 (C-3⁗), 72.0 (C-4⁗),79.2 (C-5⁗),63.1 (C-6⁗).

Begoniifolide A (**20**) White amorphous powder; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 39.3 (C-1), 27.2 (C-2), 89.2 (C-3), 40.1 (C-4), 56.4 (C-5), 18.2 (C-6), 33.0 (C-7), 40.4 (C-8), 48.6 (C-9), 37.5 (C-10), 23.8 (C-11), 123.4 (C-12), 144.6 (C-13), 42.6 (C-14), 28.8 (C-15), 24.3 (C-16), 47.5 (C-17), 42.2 (C-18), 46.7 (C-19), 31.2 (C-20), 34.5 (C-21), 33.0 (C-22), 28.6 (C-23), 18.0 (C-24), 16.1 (C-25), 17.5 (C-26), 26.6 (C-27), 177.0 (C-28), 33.6 (C-29), 24.2 (C-30); C-3-ara: 107.9 (C-1′), 72.4 (C-2′), 84.6 (C-3′), 69.8 (C-4′), 67.5 (C-5′); glu(1→3)ara: 106.9 (C-1″), 76.2 (C-2″), 78.9 (C-3″), 72.1 (C-4″), 79.2 (C-5″), 63.2 (C-6″); C-28-glu′: 96.1 (C-1‴), 74.2 (C-2‴), 78.8 (C-3‴), 71.4 (C-4‴), 78.5 (C-5‴), 69.9 (C-6‴); glu″(1→6)glu′: 105.8 (C-1⁗), 75.8 (C-2⁗), 77.7 (C-3⁗), 79.2 (C-4⁗), 77.0 (C-5⁗), 61.8 (C-6⁗); rha(1→4)glu″: 103.3 (C-1⁗′), 73.1 (C-2⁗′), 73.3 (C-3⁗′), 74.5 (C-4⁗′), 70.8 (C-5⁗′), 19.0 (C-6⁗′).

Glyceroyl-1,6,8-trihydroxy-3-methyl-9,10-dioxo-2-anthracene carboxylate (**21**) Orange red needles; ^{13}C NMR (150 MHz, CD_3OD): δ 160.2 (C-1), 130.2(C-2), 146.3 (C-3), 121.9 (C-4), 134.9 (C-4a), 110.6 (C-5), 166.8 (C-6), 109.2 (C-7), 166.8 (C-8), 110.4 (C-8a), 191.5 (C-9), 115.4 (C-9), 182.6 (C-10), 136.7 (C-10a), 67.7 (C-1′), 71.2 (C-2′), 64.2 (C-14), 20.3 (3-Me), 167.7 (2-COO).

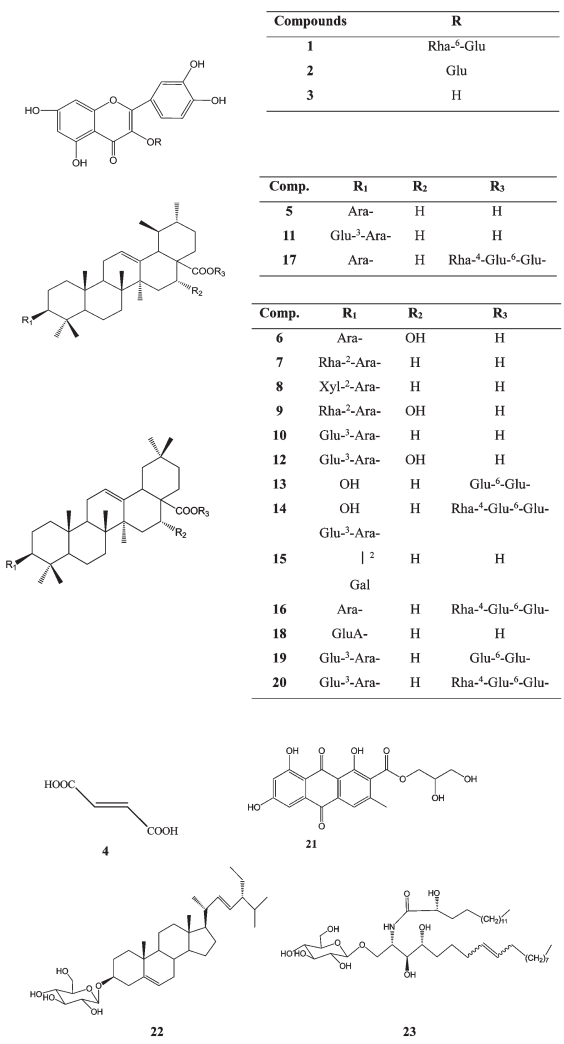
Stigmasterol-3-*O*-β-D-glucopyranoside (**22**) Colorless needles; ^{13}C NMR (150 MHz, pyridine-d_5) δ: 37.4 (C-1), 30.3 (C-2), 78.6 (C-3), 39.4 (C-4), 141.4 (C-5), 122.4 (C-6), 32.1 (C-7), 32.2 (C-8), 50.4 (C-9), 37.0 (C-10), 21.3 (C-11), 39.8 (C-12), 42.5 (C-13), 56.8 (C-14), 24.5 (C-15), 29.4 (C-16), 56.0 (C-17), 12.6 (C-18), 19.6 (C-19), 40.8 (C-20), 26.2 (C-21), 139.3 (C-22), 129.9 (C-23), 51.4 (C-24), 32.2 (C-25), 21.8 (C-26), 19.9 (C-27), 25.8 (C-28), 13.0 (C-29); C-3-glu: 103.0 (C-1′), 75.8 (C-2′), 79.0 (C-3′), 72.2 (C-4′), 78.5 (C-5′), 63.3 (C-6′).

1-*O*-β-D-glucopyranosyl-(2*S*, 3*S*, 4*R*, 7*Z*)-2-(2′-hydrooxypalmitoylamino)-8-octadec-ene-1,3,4-triol (**23**) White needles; ^{13}C NMR (pyridine-d_5, 150 MHz): δ 14.8 (Me), 23.4, 26.3, 27.1, 30.0, 30.1, 30.1, 30.3, 30.4, 32.6 (C-7), 33.5 (C-10), 33.8, 34.4, 36.1 (all CH_2), 52.2 (C-2), 63.1 (glu-C-6″), 71.0 (C-1), 71.9 (glu-C-4″), 72.9 (C-4,2′), 75.3 (glu-C-2″), 76.4 (C-3), 78.9 (glu-C-3″), 79.0 (glu-C-5″), 106.1 (glu-C-1″), 131.2 (C-9), 131.3 (C-8), 176.1 (C-1′).

The structures of the isolated compounds were elucidated from their spectroscopic data, including MS, ^{1}H and ^{13}C NMR and compared to data from the literature. Compounds 1-23 were identified as rutin (**1**)[4], isoquercitrin (**2**)[4], quercetin (**3**)[5], fumaric acid (**4**)[6], ursolic acid 3-*O*-α-L-arabinopyranoside (**5**)[7], echinocystic acid 3-*O*-α-L-arabinopyranoside (**6**)[8], eleutheroside K (**7**)[9], prosapogenin CP_{2b} (**8**)[10], tauroside D (**9**)[11], guaianin N (**10**)[9], matesaponin J_2 (**11**)[9], echinocystic acid 3-*O*-β-D-glucopyranosyl-(1→3)-*O*-α-L-arabinopyranoside (**12**)[12], hemslonin A (**13**)[13], cussonoside B (**14**)[14], oleanolic acid 3-*O*-[β-D-glucopyranosyl-(1→3)]-β-D-galactopyranosyl-(1→2)-*O*-α-L-arabinopyranoside (**15**)[15], ciwujianoside C_3 (**16**)[16], ursolic acid 3-*O*-α-L-arabinopyranosyl-28-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranoside (**17**)[17], momordin Ib (**18**)[18], araliasaponin II (**19**)[19], begoniifolide A (**20**)[20], glyceroyl-1,6,8-trihydroxy-3-methyl-9,10-dioxo-2-anthracene carboxylate (**21**)[21], stigmasterol-3-*O*-β-D-glucopyranoside (**22**)[22] and 1-*O*-β-D-glucopyranosyl-(2*S*, 3*S*, 4*R*, 8E/Z)-2-(2′-hydrooxypalmitoylamino)-8-octadecene-1, 3, 4- triol (**23**)[23], respectively (Fig. 1).

In this study, **23** compounds were isolated from the leaves of *A. henryi*, including three flavonoids (**1-3**), one organic acid (**4**), sixteen triterpenoid saponins (**5-20**), one anthraquinone (**21**), one steroidal glycoside (**22**), and one cerebroside (**23**). Among them, compounds **8**, **13**, and **21** are newly found within Araliace-

ae. Compounds **5**, **6**, **11**, **12**, **14**, **15**, **17**, **19** and **20** were previously reported from the *Acanthopanax* genus. All compounds, excluding **1-3**, **10** and **23**, were all isolated for the first time from *A. henryi*.



Compounds	R
1	Rha-^{6}-Glu
2	Glu
3	H

Comp.	R_1	R_2	R_3
5	Ara-	H	H
11	Glu-^{3}-Ara-	H	H
17	Ara-	H	Rha-^{4}-Glu-^{6}-Glu-

Comp.	R_1	R_2	R_3
6	Ara-	OH	H
7	Rha-^{2}-Ara-	H	H
8	Xyl-^{2}-Ara-	H	H
9	Rha-^{2}-Ara-	OH	H
10	Glu-^{3}-Ara-	H	H
12	Glu-^{3}-Ara-	OH	H
13	OH	H	Glu-^{6}-Glu-
14	OH	H	Rha-^{4}-Glu-^{6}-Glu-
15	Glu-^{3}-Ara- |^{2} Gal	H	H
16	Ara-	H	Rha-^{4}-Glu-^{6}-Glu-
18	GluA-	H	H
19	Glu-^{3}-Ara-	H	Glu-^{6}-Glu-
20	Glu-^{3}-Ara-	H	Rha-^{4}-Glu-^{6}-Glu-

Fig. 1 Chemical structures of the isolated compounds 1-23

Among these triterpenoid saponins, compounds **8** and **13**, which were previously isolated from a species of the Araliaceae family, were initially reported from *Clematis chinensis* Osbeck (Ranunculaceae) and *Bupleurum rotundifolium* L. (Apiaceae). These compounds may play roles as fingerprints for *A. henryi* to differentiate it from other species within the Araliaceae family. Compounds **7**, **16** and **18** have previously been isolated from *Acanthopanax senticosus* (Rupr. et Maxim) Harms, and compound **9** was isolated from *Acanthopanax sieboldianus* Makino. This is indicative of close relationships among *A. henryi*, *A. senticosus* and *A. sieboldianus*. Moreover, this demonstrates that these species from the genus *Acanthopanax* may have similar biosynthetic pathways and genetic information. Compounds **5**, **10**, **11**, **16**, **17**, and **20** have been reported from *Scheffleropsis angkae* (Craib.) Grushv. et N. Skvorts (*Schefflera*), and compounds **6**, **12** and **19** were previously obtained from *Aralia elata* (Miq.) Seem and *Aralia decaisneana* Hance (*Aralia*). This demonstrates that these genera, *Acanthopanax*, *Schefflera* and *Aralia*, all of which belong to the Araliaceae family, have close biological relationships. Compound **14** was isolated from *Hedera caucasigena* Pojark (Caucasian ivy) and *Kalopanax pictus* (Thunb.) Nakai [*Kalopanax septemlobus* (Thunb.) Koidz.], which demonstrates an intimate relationship between the genera *Hedera* and *Kalopanax* (Araliaceae). Compound **15** was initially isolated from *Tetrapanax papyrifer* (Hook.) K. Koch (Araliaceae), indicating the relationship between *Tetrapanax* and *Acanthopanax*. These accumulating chemotaxonomic evidences suggest that *A. henryi* may have close phylogenetic relations with the Araliaceae species mentioned above. Pentacyclic triterpenoid saponins in which the sugars are linked to the hydroxyl at position 3 and/or the carboxyl at position 28 can serve as essential chemotaxonomic biomarkers for *A. henryi*. Additionally, previous phytochemical investigations on the *Acanthopanax* species indicate that triterpenoid saponins may be of systematic and evolutionary importance. Such species include, *Acanthopanax brachypus* Harms[24,25], *Acanthopanax chiisanensis* Nakai[26], *Acanthopanax divaricatus* var. albeofructus[27], *Acanthopanax gracylistylus* W. W. Smith var. gracilistylus[28], and *Acanthopanax sessiliflorus* (Rupr. & Maxim.) Seem. var. sessiliflorus. Furthermore, flavonoids **1-3** have been purified from *A. henryi*, which is consistent with previous reports of this species. Compound **4** is an organic acid which was once reported from *Acanthopanax koreanum* Nakai suggesting that there are some similar organic acid metabolic pathways between *A. henryi* and *A. koreanum*. Anthraquinone, **21** is the first to be isolated from the *Acanthopanax* species. It has only been reported previously in *Clinopodium polycephalum* (Vaniot) C. Y. Wu et Hsuan ex P. S. Hsu (Labiatae), *Didymocarpus leucoca-*

lyx C. B. C_{LARKE} (gesneriaceae), *Aspergillus variecolor* B-17 (Mucedinaceae), and *Gentiana loureirii* (G. Don) Griseb. (Gentianaceae). Therefore, this new finding in *A. henryi* may also be considered as a fingerprint for this species. Steroidal glycoside **22** obtained from *A. sessiliflorus* shows a close relationship between *A. henryi* and *A. sessiliflorus*. However, due to the wide distribution of this compound in multiple species of plants, it does not serve as a feature of chemotaxonomy for *A. henryi*. Cerebroside **23** was previously isolated from *Aralia elata* (Miq.) Seem[29], indicating that there is a genetic relationship between the genera *Acanthopanax* and *Aralia*. In summary, the chemotaxonomic data from this study supports a close relation between *A. henryi* and other species in the Araliaceae family. Further chemotaxonomic investigations are needed to further evaluate these relationships. Additionally, the identification of prosapogenin CP_{2b}, hemslonin A, and glyceroyl-1,6,8-trihydroxy-3-methyl-9,10-dioxo-2- anthracene carboxylate may be used as characteristic chemotaxonomic markers to differentiate *A. henryi* from other species of Araliaceae. The saponins containing a pentacyclic triterpene skeleton may serve as a fingerprint for *A. henryi* (Oliv.) Harms.

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