

北葶苈子黄酮苷类成分研究 II

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摘要: 为了解北葶苈子的化学成分, 从其 50% 乙醇提取物中分离鉴定了 8 个单体成分, 经理化性质和波谱数据分析, 分别鉴定为: 槲皮素-3-*O*- β -D-吡喃葡萄糖苷 (1)、槲皮素-3-*O*- β -D-葡萄糖醛酸苷 (2)、槲皮素-3,7-二-*O*- β -D-葡萄糖苷 (3)、槲皮素-3-*O*- β -D-葡萄糖-(1 \rightarrow 2)- β -D-葡萄糖苷 (4)、quercetin-3-*O*-[2-*O*-(6-*O*-*E*-sinapoyl)- β -D-glucopyranosyl]- β -D-glucopyranoside (5)、槲皮素-3-*O*-[(6-*O*-*trans*-咖啡酰基)- β -D-吡喃葡萄糖基(1 \rightarrow 2)- β -D-吡喃葡萄糖]-7-*O*- β -D-吡喃葡萄糖苷 (6)、isorhamnetin-3-*O*-sophoroside (7) 和异鼠李素-3-*O*- β -D-[2-*O*-(6-*O*-芥子酰基)- β -D-吡喃葡萄糖基]-吡喃葡萄糖苷 (8)。化合物 3 为首次从该种中分离得到, 化合物 2、4、6、7 为首次从独行菜属中分离得到, 且化合物 6 的 NMR 数据为首次报道。

关键词: 北葶苈子; 化学成分; 黄酮苷

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Flavonoid Glycosides from Seeds of *Lepidium apetalum* Willd. (II)

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Abstract: In order to understand the chemical constituents of *Lepidium apetalum* Willd., eight flavonoid glycosides were obtained from 50% EtOH extract of its seeds. On the basis of physicochemical and spectral data, they were identified as quercetin-3-*O*- β -D-glucoside (1), quercetin-3-*O*- β -D-glucuronide (2), quercetin-3,7-di-*O*- β -D-glucopyranoside (3), quercetin-3-*O*- β -D-glucosyl(1 \rightarrow 2)- β -D-glucoside (4), quercetin-3-*O*-[2-*O*-(6-*O*-*E*-sinapoyl)- β -D-glucopyranosyl]- β -D-glucopyranoside (5), quercetin-3-*O*-[(6-*O*-*trans*-caffeoyl)- β -D-glucopyranosyl(1 \rightarrow 2)- β -D-glucopyranosyl]-7-*O*- β -D-glucopyranoside (6), isorhamnetin-3-*O*-sophoroside (7) and isorhamnetin-3-*O*-[2-*O*-(6-*O*-*E*-sinapoyl)- β -D-glucopyranosyl]- β -D-glucopyranoside (8). Among them, compound 3 was isolated from this species for the first time, and compounds 2, 4, 6 and 7 were obtained from *Lepidium* genus for the first time. Meanwhile, the NMR data of compound 6 was reported firstly.

Key words: *Lepidium apetalum* seed; Chemical constituent; Flavonoid glycoside

葶苈子为十字花科(Cruciferae)植物独行菜 (*Lepidium apetalum* Willd.)和播娘蒿 [*Descurainia sophia* (Linn.) Webb. Ex Prantl] 的干燥成熟种子, 因来源不同, 有南北之分, 前者称为“北葶苈子”, 后者称为“南葶苈子”。北葶苈子主要分布于河北、辽宁、内蒙古、吉林等地, 南葶苈子主要分布于江苏、山东、安

徽、浙江等地。中医理论认为: 葶苈子味苦、辛, 性大寒, 临床常用于治疗痰涎壅肺, 喘咳痰多, 胸腹水肿, 小便不利等症。现代药理研究表明, 葶苈子具有强心、利尿、抗菌、抗癌、抗衰老等作用^[1-2], 但其药效物质和作用机制尚未明确。葶苈子的化学成分主要有脂肪类、黄酮、强心苷、生物碱、类萜类等^[2-5], 但缺乏

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系统性研究。我们对北葶苈子 50% 乙醇提取物的化学成分进行研究,从中分离鉴定了 8 个黄酮苷类

(图 1)成分。本文重点对其核磁共振波谱数据进行报道,为阐明其作用机制奠定物质基础。

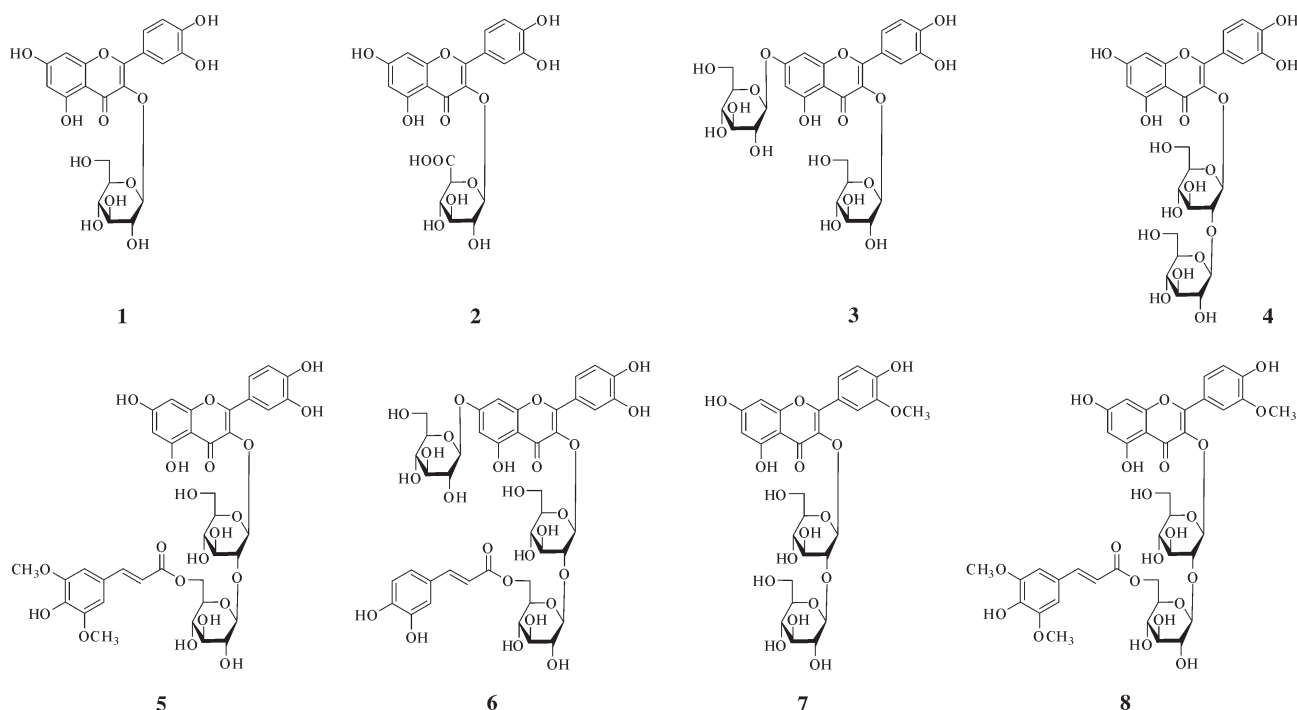


图 1 北葶苈子中化合物 1-8 的结构

Fig. 1 Structures of compounds 1-8 from seeds of *Lepidium apetalum*

1 材料和方法

1.1 材料

北葶苈子采购自河北省安国市,由天津中医药大学李天祥副教授鉴定为十字花科独行菜属独行菜(*Lepidium apetalum* Willd.)的干燥成熟种子。

1.2 仪器和试剂

Bruker 500 MHz NMR 超导核磁共振波谱仪[Avance III 500MR(瑞士 Bruker 公司)];安捷伦 6500 系列四级杆-飞行时间质谱仪[Agilent(美国 Agilent)];分析型高效液相色谱仪[Waters e2695(美国 Waters)];制备型高效液相色谱仪[LC-8A](日本岛津)。

D101 大孔吸附树脂(净品级,天津市海光化工有限公司);柱层析硅胶(100~200 目,青岛海洋化工厂), Chromatorex ODS MB 100-40/75 (40~75 μm , Fuji Silisia Chemical, Ltd., Japan);Sephadex LH-20 (Ge Healthcare Bio-Sciences AB, Sweden);HPLC

用分析柱/制备柱(Cosmosil 5C18-MS-II 250 mm \times 4.6 mm i.d./250 mm \times 20 mm i.d., Nacalai Tesque Inc., Japan)。

色谱纯及分析纯试剂购自天津市康科德科技有限公司。

1.3 提取和分离

干燥北葶苈子 10 kg,用 50% 乙醇(EtOH)加热回流提取 2 次,每次 2 h,减压回收溶剂,得浸膏。浸膏加水溶解,用 $\text{CHCl}_3\text{-H}_2\text{O}$ 萃取,将 H_2O 层萃取物除去氯仿后,经 D101 大孔吸附树脂($\text{H}_2\text{O} \rightarrow 95\% \text{EtOH}$)分离。取 95% EtOH 洗脱物(80 g)经硅胶柱层析[$\text{CHCl}_3\text{-MeOH}$ (100:0 \rightarrow 100:5, V/V) \rightarrow $\text{CHCl}_3\text{-MeOH-H}_2\text{O}$ (10:3:1 \rightarrow 6:4:1, 下层, V/V/V) \rightarrow MeOH], 得 Fr. 1~Fr. 16 共 16 个组分。Fr. 11 和 Fr. 12 组分分别经 ODS 柱色谱及制备型高效液相色谱分离,得到化合物 1 (3.5 mg)、4 (6.6 mg)、5 (68.0 mg)、7 (16.7 mg) 和 8 (7.0 mg)。Fr. 14 和 Fr. 16 组分采用 Sephadex LH-20 柱色谱结合 PHPLC 的方法分离,

得到化合物 **2** (4.1 mg)、**3** (5.9 mg) 和 **6** (18.0 mg)。

1.4 结构鉴定

化合物 1 黄色粉末。高分辨 Q-TOF-ESI-MS 准分子离子峰 m/z : 463.0879 [M - H]⁻ (Calcd for C₂₁H₁₉O₁₂, 463.0882, *diff.* 0.65), 分子式为 C₂₁H₂₀O₁₂。¹H NMR (500 MHz, DMSO-*d*₆): δ 6.07 (1H, br. s, H-6), 6.26 (1H, br. s, H-8), 7.56 (2H, m, H-2' and 6'), 6.79 (1H, d, *J* = 8.0 Hz, H-5'), 5.41 (1H, d, *J* = 7.5 Hz, H-1''), 3.09~3.59 (6H, m, H-2''~6'')。 ¹³C NMR (125 MHz, DMSO-*d*₆): δ 156.5 (C-2), 133.0 (C-3), 176.7 (C-4), 161.0 (C-5), 99.4 (C-6), 164.1 (C-7), 93.9 (C-8), 155.6 (C-9), 102.6 (C-10), 120.7 (C-1'), 115.8 (C-2'), 145.0 (C-3'), 149.0 (C-4'), 115.1 (C-5'), 121.4 (C-6'), 101.2 (C-1''), 74.1 (C-2''), 76.5 (C-3''), 69.9 (C-4''), 77.4 (C-5''), 60.9 (C-6'')。以上波谱数据与文献[6]报道基本一致, 鉴定该化合物为槲皮素-3-*O*-β-D-吡喃葡萄糖苷。

化合物 2 黄色粉末。高分辨 Q-TOF-ESI-MS 准分子离子峰 m/z : 477.0675 [M - H]⁻ (Calcd for C₂₁H₁₇O₁₃, 477.0675, *diff.* -0.08), 分子式为 C₂₁H₁₈O₁₃。 ¹H NMR (500 MHz, DMSO-*d*₆): δ 6.20 (1H, br. s, H-6), 6.39 (1H, br. s, H-8), 8.30 (1H, d, *J* = 1.5 Hz, H-2'), 6.83 (1H, d, *J* = 8.0 Hz, H-5'), 7.35 (1H, dd, *J* = 1.5, 8.0 Hz, H-6'), 5.24 (1H, d, *J* = 7.0 Hz, H-1''), 3.17~3.51 (4H, m, H-2''~5'')。 ¹³C NMR (125 MHz, DMSO-*d*₆): δ 157.6 (C-2), 134.0 (C-3), 177.5 (C-4), 160.9 (C-5), 98.9 (C-6), 164.6 (C-7), 93.7 (C-8), 156.4 (C-9), 103.6 (C-10), 120.5 (C-1'), 118.0 (C-2'), 144.8 (C-3'), 148.4 (C-4'), 115.3 (C-5'), 120.4 (C-6'), 103.0 (C-1''), 74.1 (C-2'', 5''), 76.6 (C-3''), 71.7 (C-4''), 171.9 (C-6'')。以上波谱数据与文献[7]报道基本一致, 鉴定该化合物为槲皮素-3-*O*-β-D-葡萄糖醛酸苷。

化合物 3 黄色粉末。高分辨 Q-TOF-ESI-MS 准分子离子峰 m/z : 625.1418 [M - H]⁻ (Calcd for C₂₇H₂₉O₁₇, 625.1410, *diff.* -1.24), 分子式为 C₂₇H₃₀O₁₇。 ¹H NMR (500 MHz, DMSO-*d*₆): δ 6.44 (1H, br. s, H-6), 6.76 (1H, br. s, H-8), 7.61 (1H, d, *J* = 1.5 Hz, H-2'), 6.87 (1H, d, *J* = 8.5 Hz, H-5'), 7.58 (1H, dd, *J* = 1.5, 8.5 Hz, H-6'), 5.49 (1H, d, *J* = 7.5 Hz, H-1''), 5.09 (1H, d, *J* = 7.5 Hz, H-1'''), 3.09~3.71 (12H, m, H-2''~6'', 2'''~6''')。 ¹³C NMR

(125 MHz, DMSO-*d*₆): δ 156.8 (C-2), 133.5 (C-3), 177.5 (C-4), 160.8 (C-5), 99.2 (C-6), 162.7 (C-7), 94.2 (C-8), 155.9 (C-9), 105.5 (C-10), 120.9 (C-1'), 116.3 (C-2'), 144.8 (C-3'), 148.6 (C-4'), 115.1 (C-5'), 121.5 (C-6'), 100.6 (C-1''), 74.0 (C-2''), 76.4 (C-3''), 69.8 (C-4''), 77.5 (C-5''), 60.9 (C-6''), 99.6 (C-1'''), 73.0 (C-2'''), 76.3 (C-3'''), 69.5 (C-4'''), 77.1 (C-5'''), 60.5 (C-6''')。以上波谱数据与文献[8]报道基本一致, 鉴定该化合物为槲皮素-3,7-二-*O*-β-D-葡萄糖苷。

化合物 4 黄色粉末。高分辨 Q-TOF-ESI-MS 准分子离子峰 m/z : 625.1421 [M - H]⁻ (Calcd for C₂₇H₂₉O₁₇, 625.1410, *diff.* -1.72), 分子式为 C₂₇H₃₀O₁₇。 ¹H NMR (500 MHz, DMSO-*d*₆): δ 6.20 (1H, br. s, H-6), 6.41 (1H, br. s, H-8), 7.56 (1H, br. s, H-2'), 6.88 (1H, d, *J* = 8.5 Hz, H-5'), 7.60 (1H, br. d, *ca.* *J* = 9 Hz, H-6'), 5.70 (1H, d, *J* = 7.5 Hz, H-1''), 3.53 (1H, dd, *J* = 7.5, 8.0 Hz, H-2''), 3.48 (1H, dd, *J* = 8.0, 8.0 Hz, H-3''), 3.15 (1H, dd, *J* = 8.0, 9.5 Hz, H-4''), 3.13 (1H, m, H-5''), [3.29 (1H, dd, *J* = 5.0, 11.5 Hz), 3.55 (1H, m, overlapped), H₂-6'', 4.61 (1H, d, *J* = 8.0 Hz, H-1'''), 3.08 (1H, dd, *J* = 8.0, 8.0 Hz, H-2'''), 3.19 (1H, dd, *J* = 8.0, 9.0 Hz, H-3'''), 3.18 (1H, dd, *J* = 9.0, 9.0 Hz, H-4'''), 3.10 (1H, m, H-5'''), [3.50 (1H, dd, *J* = 6.0, 14.0 Hz), 3.55 (1H, m, overlapped), H₂-6''']。 ¹³C NMR (125 MHz, DMSO-*d*₆): δ 155.4 (C-2), 132.9 (C-3), 177.3 (C-4), 161.2 (C-5), 98.6 (C-6), 164.2 (C-7), 93.4 (C-8), 156.2 (C-9), 103.7 (C-10), 121.0 (C-1'), 116.0 (C-2'), 144.7 (C-3'), 148.4 (C-4'), 115.3 (C-5'), 121.7 (C-6'), 97.9 (C-1''), 82.6 (C-2''), 76.4 (C-3''), 69.4 (C-4''), 76.7 (C-5''), 60.5 (C-6''), 104.1 (C-1'''), 74.3 (C-2'''), 76.4 (C-3'''), 69.5 (C-4'''), 77.4 (C-5'''), 60.6 (C-6''')。以上波谱数据与文献[9]报道基本一致, 鉴定该化合物为槲皮素-3-*O*-β-D-葡萄糖-(1→2)-β-D-葡萄糖苷。同时, 通过 2D-NMR 谱的解析, 对文献中报道的 C-2、9、10、2'、5'、1'' 位碳谱数据进行了更正。

化合物 5 黄色粉末。高分辨 Q-TOF-ESI-MS 准分子离子峰 m/z : 831.2013 [M - H]⁻ (Calcd for C₃₈H₃₉O₂₁, 831.1989, *diff.* -2.85), 分子式为 C₃₈H₄₀O₂₁。 ¹H NMR (500 MHz, DMSO-*d*₆): δ 6.20 (1H, br. s, H-6), 6.31 (1H, br. s, H-8), 7.58 (1H, br. s, H-2'), 6.92 (1H, d, *J* = 8.5 Hz, H-5'), 7.64 (1H, br. d, *ca.* *J* = 9 Hz, H-6'), 5.73 (1H, d, *J* = 7.5 Hz, H-1''),

3.55 (2H, m, overlapped, H-2'', 3''), 3.19 (1H, dd, $J = 9.0, 9.0$ Hz, H-4''), 3.15 (1H, m, H-5''), [3.34 (1H, m, overlapped), 3.55 (1H, m, overlapped), H₂-6''], 4.73 (1H, d, $J = 7.5$ Hz, H-1'''), 3.22 (1H, dd, $J = 7.5, 8.0$ Hz, H-2'''), 3.32 (1H, dd, $J = 8.0, 8.0$ Hz, H-3'''), 3.31 (1H, dd, $J = 8.0, 8.0$ Hz, H-4'''), 3.56 (1H, m, H-5'''), [4.25 (1H, br. d, ca. $J = 12$ Hz), 4.33 (1H, dd, $J = 5.0, 12.0$ Hz), H₂-6'''], 6.83 (2H, s, H-2''''', 6'''''), 7.41 (1H, d, $J = 16.0$ Hz, H-7'''''), 6.30 (1H, d, $J = 16.0$ Hz, H-8'''''), 3.78 (6H, s, 3''''', 5'''''-OCH₃)。 ¹³C NMR (125 MHz, DMSO-*d*₆): δ 155.5 (C-2), 133.0 (C-3), 177.4 (C-4), 161.2 (C-5), 98.5 (C-6), 163.9 (C-7), 93.4 (C-8), 156.1 (C-9), 103.9 (C-10), 121.2 (C-1'), 116.1 (C-2'), 144.8 (C-3'), 148.4 (C-4'), 115.3 (C-5'), 121.9 (C-6'), 97.9 (C-1''), 83.3 (C-2''), 76.4 (C-3''), 69.5 (C-4''), 77.4 (C-5''), 60.5 (C-6''), 104.4 (C-1'''), 74.5 (C-2'''), 76.3 (C-3'''), 69.5 (C-4'''), 73.9 (C-5'''), 63.1 (C-6'''), 124.3 (C-1'''), 105.9 (C-2'''), 6'''''), 147.9 (C-3''''', 5'''''), 138.2 (C-4'''''), 145.2 (C-7'''''), 114.4 (C-8'''''), 166.5 (C-9'''''), 55.9 (3''''', 5'''''-OCH₃)。以上波谱数据与文献[10]报道基本一致, 鉴定该化合物为 quercetin-3-*O*-[2-*O*-(6-*O*-*E*-sinapoyl)- β -D-glucopyranosyl]- β -D-glucopyranoside。同时, 通过 2D-NMR 谱的解析, 对文献中报道的 C-2'、5' 位碳谱数据进行了更正。

化合物 6 黄色粉末。高分辨 Q-TOF-ESI-MS 准分子离子峰 m/z : 949.2258 [M - H]⁻ (Calcd for C₄₂H₄₅O₂₅, 949.2255, *diff.* -0.27), 分子式为 C₄₂H₄₆O₂₅。 ¹H NMR (500 MHz, DMSO-*d*₆): δ 6.40 (1H, d, $J = 1.5$ Hz, H-6), 6.64 (1H, d, $J = 1.5$ Hz, H-8), 7.62 (1H, br. s, H-2'), 6.89 (1H, d, $J = 9.0$ Hz, H-5'), 7.61 (1H, br. d, ca. $J = 9$ Hz, H-6'), 5.73 (1H, d, $J = 7.5$ Hz, H-1''), 3.50 (2H, m, H-2'', 3''), 3.19 (1H, d, $J = 9.0, 9.0$ Hz, H-4''), 3.11 (1H, m, overlapped, H-5''), [3.27 (1H, dd, $J = 6.0, 11.0$ Hz), 3.49 (1H, m, overlapped), H₂-6''], 4.67 (1H, d, $J = 8.0$ Hz, H-1'''), 3.15 (1H, dd, $J = 8.0, 8.0$ Hz, H-2'''), 3.26 (1H, dd, $J = 8.0, 8.0$ Hz, H-3'''), 3.19 (1H, dd, $J = 9.0, 9.0$ Hz, H-4'''), 3.49 (1H, m, overlapped, H-5'''), [4.18 (1H, dd, $J = 5.0, 11.5$ Hz), 4.22 (1H, br. d, ca. $J = 11$ Hz), H₂-6'''], 6.90 (1H, d, $J = 1.5$ Hz, H-2'''''), 6.71 (1H, d, $J = 8.5$ Hz, H-5'''''), 6.78 (1H, dd, $J = 1.5, 8.5$ Hz, H-6'''''), 7.30 (1H, d, $J = 16.0$ Hz, H-7'''''), 6.00 (1H, d, $J =$

16.0 Hz, H-8'''''), 5.05 (1H, d, $J = 7.5$ Hz, H-1'''''), 3.26 (1H, dd, $J = 7.5, 8.0$ Hz, H-2'''''), 3.33 (1H, dd, $J = 8.5, 9.0$ Hz, H-3'''''), 3.19 (1H, m, overlapped, H-4'''''), 3.47 (1H, m, H-5'''''), [3.49 (1H, m, overlapped), 3.71 (1H, br. d, ca. $J = 11$ Hz), H₂-6''''')。 ¹³C NMR (125 MHz, DMSO-*d*₆): δ 155.7 (C-2), 133.1 (C-3), 177.4 (C-4), 160.7 (C-5), 99.1 (C-6), 162.5 (C-7), 94.1 (C-8), 155.9 (C-9), 105.4 (C-10), 120.9 (C-1'), 116.3 (C-2'), 144.8 (C-3'), 148.7 (C-4'), 115.2 (C-5'), 121.8 (C-6'), 97.7 (C-1''), 83.7 (C-2''), 76.3 (C-3''), 69.4 (C-4''), 77.5 (C-5''), 60.4 (C-6''), 104.5 (C-1'''), 74.4 (C-2'''), 76.1 (C-3'''), 69.5 (C-4'''), 73.9 (C-5'''), 63.2 (C-6'''), 125.3 (C-1'''), 114.9 (C-2'''), 145.3 (C-3'''), 148.2 (C-4'''), 115.6 (C-5'''), 120.9 (C-6'''), 144.9 (C-7'''), 113.5 (C-8'''), 166.4 (C-9'''), 99.6 (C-1'''''), 73.0 (C-2'''''), 76.3 (C-3'''''), 69.5 (C-4'''''), 77.0 (C-5'''''), 60.5 (C-6'''''), 结合 ¹H-¹H COSY、HSQC、HMBC 等 2D-NMR 谱鉴定该化合物为槲皮素-3-*O*-[(6-*O*-*trans*-咖啡酰基)- β -D-吡喃葡萄糖基(1 \rightarrow 2)- β -D-吡喃葡萄糖]-7-*O*- β -D-吡喃葡萄糖苷, 其核磁共振波谱数据为首次报道。

化合物 7 黄色粉末。高分辨 Q-TOF-ESI-MS 准分子离子峰 m/z : 639.1568 [M - H]⁻ (Calcd for C₂₈H₃₁O₁₇, 639.1567, *diff.* -0.20), 分子式为 C₂₈H₃₂O₁₇。 ¹H NMR (500 MHz, DMSO-*d*₆): δ 6.20 (1H, br. s, H-6), 6.45 (1H, br. s, H-8), 7.81 (1H, d, $J = 1.5$ Hz, H-2'), 6.93 (1H, d, $J = 8.5$ Hz, H-5'), 7.62 (1H, dd, $J = 1.5, 8.5$ Hz, H-6'), 5.76 (1H, d, $J = 7.0$ Hz, H-1''), 3.52 (2H, m, H-21'', 31''), 3.15 (1H, dd, $J = 9.0, 9.0$ Hz, H-4''), 3.14 (1H, m, H-5''), [3.33 (1H, dd, $J = 4.5, 11.5$ Hz), 3.54 (1H, m, overlapped), H₂-6''], 4.62 (1H, d, $J = 7.5$ Hz, H-1'''), 3.08 (1H, dd, $J = 7.5, 8.0$ Hz, H-2'''), 3.18 (1H, dd, $J = 8.0, 9.0$ Hz, H-3'''), 3.13 (1H, dd, $J = 9.0, 9.0$ Hz, H-4'''), 3.07 (1H, m, H-5'''), [3.44 (1H, dd, $J = 5.0, 11.5$ Hz), 3.53 (1H, m, overlapped), H₂-6'''], 3.86 (3H, s, 3'-OCH₃)。 ¹³C NMR (125 MHz, DMSO-*d*₆): δ 155.8 (C-2), 132.8 (C-3), 177.3 (C-4), 161.2 (C-5), 98.7 (C-6), 164.5 (C-7), 93.7 (C-8), 156.3 (C-9), 103.8 (C-10), 121.1 (C-1'), 113.1 (C-2'), 147.0 (C-3'), 149.5 (C-4'), 115.3 (C-5'), 122.7 (C-6'), 98.2 (C-1''), 82.0 (C-2''), 76.5 (C-3''), 69.5 (C-4''), 77.3 (C-5''), 60.5 (C-6''), 103.4 (C-1'''), 74.2 (C-2'''), 76.5

(C-3'''), 69.8 (C-4'''), 76.7 (C-5'''), 60.8 (C-6'''), 55.8 (3'-OCH₃)。以上波谱数据与文献[11]报道基本一致, 结合 ¹H-¹H COSY、HMBC 等二维谱鉴定该化合物为 isorhamnetin-3-O-sophoroside。

化合物 8 黄色粉末。高分辨 Q-TOF-ESI-MS 准分子离子峰 *m/z*: 845.2174 [M - H]⁻ (Calcd for C₃₉H₄₁O₂₁, 845.2146, *diff.* -3.33), 分子式为 C₃₉H₄₂O₂₁。¹H NMR (500 MHz, DMSO-*d*₆): δ 6.16 (1H, br. s, H-6), 6.34 (1H, br. s, H-8), 7.77 (1H, d, *J* = 1.5 Hz, H-2'), 6.89 (1H, d, *J* = 8.0 Hz, H-5'), 7.55 (1H, dd, *J* = 1.5, 8.0 Hz, H-6'), 5.74 (1H, d, *J* = 7.0 Hz, H-1''), 4.72 (1H, d, *J* = 7.5 Hz, H-1'''), 6.84 (2H, s, H-2''', 6'''), 7.40 (1H, d, *J* = 15.5 Hz, H-7'''), 6.32 (1H, d, *J* = 15.5 Hz, H-8'''), 3.11~3.59 (12H, m, H-2''~6'', 2'''~6'''), 3.74 (6H, s, 3''', 5'''-OCH₃), 3.83 (3H, s, 3'-OCH₃)。¹³C NMR (125 MHz, DMSO-*d*₆): δ 155.7 (C-2), 132.7 (C-3), 177.2 (C-4), 161.1 (C-5), 98.6 (C-6), 164.4 (C-7), 93.6 (C-8), 156.2 (C-9), 103.7 (C-10), 121.0 (C-1'), 113.0 (C-2'), 146.9 (C-3'), 149.4 (C-4'), 115.2 (C-5'), 122.6 (C-6'), 97.9 (C-1''), 82.1 (C-2''), 76.4 (C-3''), 69.4 (C-4''), 77.2 (C-5''), 60.2 (C-6''), 103.3 (C-1'''), 74.2 (C-2'''), 76.3 (C-3'''), 69.5 (C-4'''), 73.8 (C-5'''), 63.2 (C-6'''), 124.2 (C-1'''), 105.9 (C-2''', 6'''), 147.8 (C-3''', 5'''), 138.1 (C-4'''), 145.2 (C-7'''), 114.4 (C-8'''), 166.4 (C-9'''), 55.9 (3''', 5'''-OCH₃), 55.8 (3'-OCH₃)。以上波谱数据与文献[12]报道基本一致, 鉴定该化合物为异鼠李素-3-O-β-D-[2-O-(6-O-芥子酰基)-β-D-吡喃葡萄糖基]-吡喃葡萄糖苷。

2 结果和讨论

我国南北葶苈资源丰富, 葶苈子作为常用中草药在民间广泛使用且疗效显著。但至今, 葶苈子的临床使用仍是在单一的中医理论的指导下进行。为丰富其作用机制, 从而更加科学、有效、合理地应用于临床, 本文从药效物质基础出发, 首先对其化学成分进行了系统研究。

利用正相硅胶、反相 ODS 及 Sephadex LH-20 柱色谱和高效液相色谱制备等分离手段, 从北葶苈子 50% 乙醇提取物中分离得到了 8 个黄酮苷类单体成分。通过光谱分析及文献对照, 他们分别鉴定为槲皮素-3-O-β-D-吡喃葡萄糖苷 (1)、槲皮素-3-

O-β-D-葡萄糖醛酸苷 (2)、槲皮素-3,7-二-O-β-D-葡萄糖苷 (3)、槲皮素-3-O-β-D-葡萄糖-(1→2)-β-D-葡萄糖苷 (4)、quercetin-3-O-[2-O-(6-O-*E*-sinapoyl)-β-D-glucopyranosyl]-β-D-glucopyranoside (5)、槲皮素-3-O-[(6-O-*trans*-咖啡酰基)-β-D-吡喃葡萄糖基(1→2)-β-D-吡喃葡萄糖]-7-O-β-D-吡喃葡萄糖苷 (6), isorhamnetin-3-O-sophoroside (7)、异鼠李素-3-O-β-D-[2-O-(6-O-芥子酰基)-β-D-吡喃葡萄糖基]-吡喃葡萄糖苷 (8)。化合物 3 为首次从该种中分离得到, 化合物 2、4、6 和 7 为首次从独行菜属中分离得到, 并对化合物 6 的 NMR 数据进行了首次报道。

黄酮类化合物, 结构复杂多样, 具有多种生物活性, 如抗氧化、抗癌、抗肿瘤、抗心血管疾病等^[13]。据文献报道, 化合物 1、2 和 4 均有较强的抗氧化活性^[14-16]。本研究进一步完善了北葶苈子的物质基础, 为其活性成分的研究和作用机制的阐述奠定基础。

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