

三七叶化学成分的研究

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摘要: 从三七叶乙醇提取物中分离到 16 个化合物, 分别鉴定为人参皂甙(ginsenoside) Rh₂(1), F₂(4), Rg₃(5), Rg₁(7), Rd(8), Re(11), Rb₃(13), Rb₁(14), Rc(15), 七叶胆皂甙(gypenoside) XIII(2), IX(9), XVII(10), 三七皂甙(notoginsenoside) R₁(12), Fa(16), 甘草素(liquiritigenin) (3), 以及芹糖甘草甙(liquiritin apioside) (6)。其中化合物 1, 2, 3 和 6 首次分离自该植物中, 化合物 1~8 及 10~12 首次从三七叶中分离到。研究结果进一步证实, 三七叶以含原人参二醇型皂甙为主, 同时含有微量的原人参三醇型皂甙和黄酮类化合物。

关键词: 三七; 三七茎叶; 皂甙; 黄酮

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A Further Investigation on the Chemical Constituents from the Leaves of *Panax notoginseng*

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Abstract: Sixteen compounds were isolated from the ethanol extract of the leaves of *Panax notoginseng*. They were identified as ginsenoside Rh₂(1), F₂(4), Rg₃(5), Rg₁(7), Rd(8), Re(11), Rb₃(13), Rb₁(14), Rc(15); gypenoside XIII(2), IX(9), XVII(10); notoginsenoside R₁(12), Fa(16); liquiritigenin (3) and liquiritin apioside (6), respectively. It is noticed that compounds 1, 2, 3 and 6 are isolated from *P. notoginseng* for the first time, and compounds 1~8 and 10~12 are isolated from the leaves of this plant for the first time. It is also confirmed that the leaves of *notoginseng* mainly contain protopanaxdiol saponins along with protopanaxtriol saponins and flavonoids of small quantity.

Key words: *Panax notoginseng*; leaves; saponins; flavonoids

三七 (*Panax notoginseng* (Burk.) F. H. Chen) 为常用中药, 其药用部分为地下的根部。三七叶在民间常用为茶饮, 亦可药用。其性温, 味辛, 用于止血、消肿、定痛、治吐血、衄血、便血、外伤出血、痈肿疮毒等。《本草纲目》称三七茎叶“治折伤、跌扑出血, 敷之即止, 青肿经夜即散, 余功同根”。现代药理研究表明, 三七叶有镇静安神和抗衰老作用, 对血液系统、心血管系统、神经系统和代谢系统的生理作用与三七根相似。八十年代开发的安眠镇静药物“七叶安神片”即是以三七叶提取物为原料。三七叶富含皂甙成分, 早年, 我们曾从三七叶中分离到已知的人参皂甙(ginsenoside) Rb₁, Rb₃, Rc 和七叶胆皂甙(gypenoside) IX, 以及 3 个新的达玛烷型四环三萜配糖体: 三七皂甙(notoginsenoside) Fa, Fc 和 Fe。这些

化合物均为 20-(S)-原人参二醇型皂甙^[1]。而后, 有报道从三七叶中分离到黄酮类化合物槲皮素及其 3-O-槐糖甙^[2]。本文报道我们对三七叶化学成分的研究。

1 实验部分

1.1 仪器和材料

熔点用四川大学科仪厂生产的 XRC-I 型显微熔点仪测定, 温度计未校正。旋光用 JASCO-20 仪测定。FAB-MS 和 EI-MS 用 VG Auto Spec-3000 型质谱仪测定。NMR 用 Bruker AM-400 和 Bruker DRX-500 超导核磁共振仪测定, pyridine-*d*₅ 和 DMSO-*d*₆ 为溶剂, TMS 为内标。日本三菱化工公司生产的 Diaion HP-20、青岛化工厂生产的硅胶、Merck 公司生产的键合硅胶 RP-8 为柱层析材料; TLC 用青岛化工厂生产的硅胶 H 预制薄板和 Merck 公司生产的 HP RP-8 F₂₅₄ 薄板; 展开剂: (1) 氯仿: 甲醇: 水 (7: 3: 0.5);

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(2) 甲醇:水 (7:3); 显色剂: 10% H₂SO₄-EtOH 液。

1.2 提取分离

三七叶水提取物 250 g, 通过 Diaion HP-20 柱层析处理, 从甲醇洗脱部位得总皂甙 (180 g), 经硅胶柱层析分离, 氯仿: 甲醇: 水 (7:3:0.5) 洗脱, 得到 4 个洗脱部位 (Fr. I-IV)。Fr. II 用硅胶柱层析分离, 氯仿: 甲醇: 水 (7.5:2:0.2) 洗脱, 得到 3 个洗脱部位 (II-1, II-2, II-3), 各部位再经 RP-8 反相硅胶柱层析分离, 含水甲醇洗脱, 得到化合物 1 (20 mg), 2 (20 mg), 3 (80 mg), 4 (40 mg), 5 (100 mg), 6 (20 mg) 和 7 (40 mg)。Fr. III 经硅胶柱层析分离, 氯仿: 甲醇: 水 (7:2:0.3) 洗脱, 得到 2 个部位 (Fr. III-1, III-2), 再经 RP-8 反相硅胶柱层析分离, 得到化合物 8 (200 mg), 9 (250 mg), 10 (220 mg), 11 (15 mg) 和 12 (15 mg)。Fr. IV 经硅胶柱层析分离, 氯仿: 甲醇: 水 (7:3:0.5) 洗脱, 得到 3 个部位 (Fr. IV-1, IV-2, IV-3), 再经 RP-8 反相硅胶柱层析分离, 含水甲醇洗脱, 得到化合物 13 (1.4 g), 14 (1 g), 15 (30 mg) 和 16 (30 mg)。

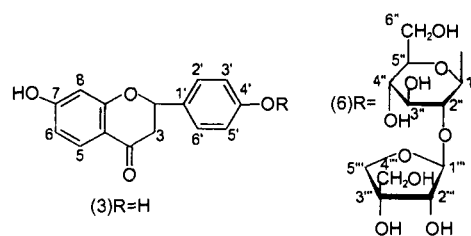


图 1 从三七叶中分离到的 16 个化合物的结构

Fig. 1 The structures of compounds 1 ~ 16 isolated from the leaves of notoginseng

2 结构鉴定

得到的化合物 1 ~ 16 经谱学分析 (表 1) 并与标准品对照比较, 分别鉴定为: 人参皂甙 Rh₂ 的 20(S) 和 (R) 异构体混合物 (1)^[3], 七叶胆皂甙 (gypenoside) XIII (2)^[4], 甘草素 (liquiritigenin) (3)^[5], 人参皂甙 F₂ (4)^[6], 20(S)-人参皂甙 Rg₃ (5)^[7], 甘草苜糖甙 (liquiritin apioside) (6)^[8], 人参皂甙 Rg₁ (7)^[9], 人参皂甙 Rd (8)^[10], 七叶胆皂甙 IX (9)^[4], 七叶胆皂甙 XVII (10)^[11], 人参皂甙 Re (11)^[12], 三七皂甙 (notoginsenoside) R₁ (12)^[13], 人参皂甙 Rb₃ (13)^[3], 人参皂甙 Rb₁ (14)^[10], 人参皂甙 Rc (15)^[10], 三七皂甙 Fa (16)^[7] (图 1)。其中, 2 个黄酮类化合物的¹³C 和¹H NMR 化学位移, 结合 2D-NMR 的 HMQC, HMBC 和¹H, ¹H-COSY 试验确定归属, 首次进行了全指定 (表 2)。

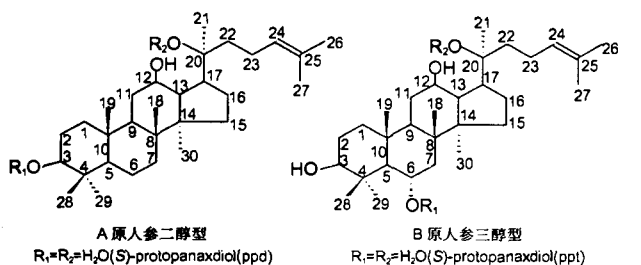
人参皂甙 Rh₂ (1) 白色粉末, FAB-MS (Negative) *m/z* (%): 621 [M-H]⁻ (100), 459 [M-H-162]⁻ (7); ¹³C NMR (pyridine-*d*₅, 100 MHz) (见表 1)。

七叶胆皂甙 XIII (2) 白色粉末, mp. 156 ~ 158 °C, [α]_D²⁵ = +26.5° (c 0.30, MeOH); FAB-MS (Negative) *m/z* (%): 753 [M-H]⁻ (100), 621 [M-H-132]⁻ (14); ¹³C NMR (pyridine-*d*₅, 100 MHz) (见表 1)。

甘草素 (3) 黄色粉末, mp. 203 ~ 205 °C; EI-MS *m/z* (%): 256 (100), 239 (14), 228 (7), 163 (22), 137 (87), 120 (66), 110 (11), 77 (18); ¹H NMR (DMSO-*d*₆, 500 MHz) 和 ¹³C NMR (DMSO-*d*₆, 125 MHz) (见表 2)。

人参皂甙 F₂ (4) 白色粉末, mp. 160 ~ 163 °C; [α]_D²⁵ = +22.4° (c 0.4, MeOH); FAB-MS (Negative) *m/z* (%): 783 [M-H]⁻ (100), 621 [M-H-132]⁻ (14); ¹³C NMR (pyridine-*d*₅, 100 MHz) (见表 1)。

20(S)-人参皂甙 Rg₃ (5) 白色粉末, mp. 175 ~



| | R ₁ | R ₂ |
|---|----------------------|-------------------|
| A 原人参二醇型 R ₁ =R ₂ =H ₂ O(S)-protopanaxadiol(ppd) | | |
| Ginsenoside Rh ₂ (1) | -glc | -H |
| Gypenoside XIII (2) | -H | -glc(6-1)xyl |
| Ginsenoside F ₂ (4) | -glc | -glc |
| Ginsenoside Rg ₃ (5) | -glc(2-1)glc | -H |
| Ginsenoside Rd (8) | -glc(2-1)glc | -glc |
| Gypenoside IX (9) | -glc | -glc(6-1)xyl |
| Gypenoside XVII (10) | -glc | -glc(6-1)glc |
| Ginsenoside Rb ₃ (13) | -glc(2-1)glc | -glc(6-1)xyl |
| Ginsenoside Rb ₁ (14) | -glc(2-1)glc | -glc(6-1)glc |
| Ginsenoside Rc (15) | -glc(2-1)glc | -glc(6-1)ara(fur) |
| Notoginsenoside Fa (16) | -glc(2-1)glc(2-1)xyl | -glc(6-1)glc |
| B 原人参三醇型 R ₁ =R ₂ =H ₂ O(S)-protopanaxadiol(ppd) | | |
| Ginsenoside Rg ₁ (7) | -glc | -glc |
| Ginsenoside Re (11) | -glc(2-1)rha | -glc |
| Notoginsenoside R ₁ (12) | -glc(2-1)xyl | -glc |

177 °C; $[\alpha]_D^{24} = -5.3^\circ$ (c 0.47, C_5H_5N); FAB-MS (Negative) m/z (%): 783 [M-H] $^-$ (100), 621 [M-H-132] $^-$ (20); ^{13}C NMR (pyridine- d_5 , 100 MHz)(见表1)

甘草芹糖甙(6) 黄色粉末, mp. 211 ~ 214 °C; FAB-MS (Negative) m/z (%): 549 [M-H] $^-$ (100), 417 [M-H-132] $^-$ (36), 255 [M-H-132-162] $^-$ (15); 1H NMR (DMSO- d_6 , 500 MHz) 和 ^{13}C NMR (DMSO- d_6 , 125 MHz)(见表2)。

人参皂甙 R_{G1}(7) 白色粉末, mp. 191 ~ 194 °C; $[\alpha]_D^{27} = +19.5^\circ$ (c 0.68, MeOH); FAB-MS (Negative) m/z (%): 800 [M] $^-$ (100), 637 [M-H-162] $^-$ (10); ^{13}C NMR (pyridine- d_5 , 100 MHz)(见表1)。

人参皂甙 Rd(8) 白色粉末, mp: 176 ~ 179 °C; $[\alpha]_D^{25} = +16.8^\circ$ (c 0.55, MeOH); FAB-MS (Negative) m/z (%): 946 [M] $^-$ (100), 783 [M-H-162] $^-$ (12), 621 [M-H-(2 × 162)] $^-$; ^{13}C NMR (pyridine- d_5 , 100 MHz)(见表1)。

七叶胆皂甙 IX(9) 白色粉末, mp. 171 ~ 174 °C; $[\alpha]_D^{26} = +10.7^\circ$ (c 0.30, MeOH); FAB-MS (Negative) m/z (%): 916 [M] $^-$ (100), 783 [M-H-132] $^-$ (11), 621 [M-H-132-162] $^-$; ^{13}C NMR (pyridine- d_5 , 100 MHz)(见表1)。

七叶胆皂甙 XVII(10) 白色粉末, mp. 176 ~ 179 °C; $[\alpha]_D^{27} = +18.3^\circ$ (c 0.30, MeOH); FAB-MS (Negative) m/z (%): 946 [M] $^-$ (100), 783 [M-H-162] $^-$ (14), 621 [M-H-(2 × 162)] $^-$ (6); ^{13}C NMR (pyridine- d_5 , 100 MHz): (见表1)。

人参皂甙 Re(11) 白色粉末, mp. 200 ~ 203 °C; $[\alpha]_D^{26} = +0.0^\circ$ (c 0.75, MeOH); FAB-MS (Nega-

tive) m/z (%): 946 [M] $^-$ (100), 799 [M-H-146] $^-$ (24), 637 [M-H-146-162] $^-$ (12), 475 [M-H-146-(2 × 162)] $^-$ (4); ^{13}C NMR (pyridine- d_5 , 100 MHz)(见表1)。

三七皂甙 R₁(12) 白色粉末, mp. 211 ~ 214 °C; $[\alpha]_D^{26} = +17.5^\circ$ (c 0.64, MeOH); FAB-MS (Negative) m/z (%): 932 [M] $^-$ (100), 799 [M-H-132] $^-$ (20), 637 [M-H-132-162] $^-$ (12), 475 [M-H-132-(2 × 162)] $^-$ (5); ^{13}C NMR (pyridine- d_5 , 100 MHz)(见表1)。

人参皂甙 Rb₃(13) 白色粉末, mp. 192 ~ 195 °C; $[\alpha]_D^{25} = +7.2^\circ$ (c 0.31, MeOH); FAB-MS (Negative) m/z (%): 1077 [M-H] $^-$ (100), 945 [M-H-132] $^-$ (14), 915 [M-H-162] $^-$ (6), 783 [M-H-132-162] $^-$ (10); ^{13}C NMR(pyridine- d_5 , 100 MHz)(见表1)。

人参皂甙 Rb₁(14) 白色粉末, mp. 195 ~ 197 °C; $[\alpha]_D^{26} = +11.5^\circ$ (c 0.56, MeOH); FAB-MS (Negative) m/z (%): 1107 [M-H] $^-$ (100), 945 [M-H-162] $^-$ (17), 783 [M-H-(2 × 162)] $^-$ (8); ^{13}C NMR (pyridine- d_5 , 100 MHz)(见表1)。

人参皂甙 Rc(15) 白色粉末, mp. 193 ~ 196 °C; $[\alpha]_D^{26} = +2.1^\circ$ (c 0.37, MeOH); FAB-MS (Negative) m/z (%): 1077 [M-H] $^-$ (100), 945 [M-H-132] $^-$ (12), 783 [M-H-132-162] $^-$ (7); ^{13}C NMR (pyridine- d_5 , 100 MHz)(见表1)。

三七皂甙 Fa(16) 白色粉末, mp. 193 ~ 196 °C; $[\alpha]_D^{26} = +2.1^\circ$ (c 0.37, MeOH); FAB-MS (Negative) m/z (%): 1247 [M-H] $^-$ (100), 1107 [M-H-132] $^-$ (19), 945 [M-H-132-162] $^-$ (8), 783 [M-H-132-(2 × 162)] $^-$ (5); ^{13}C NMR (pyridine- d_5 , 100 MHz)(见表1)。

表1 三七茎叶皂甙的 ^{13}C NMR 化学位移 (ppm) (甙元部分)

Table 1 ^{13}C NMR data of saponins from the leaves of *notoginseng* (ppm)(aglycone part)

| ppd | 1 | 1(R) | 2 | 4 | 5 | 8 | 9 | 10 | 13 | 14 | 15 | 16 | ppt | 7 | 11 | 12 | |
|-----|------|------|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1 | 39.5 | 39.3 | - | 39.6 | 39.3 | 39.2 | 39.3 | 39.3 | 39.2 | 39.4 | 39.1 | 39.0 | 39.2 | 39.2 | 39.7 | 39.4 | 39.7 |
| 2 | 28.2 | 26.8 | - | 28.3 | 26.8 | 26.9 | 26.8 | 26.7 | 26.6 | 26.7 | 26.6 | 26.6 | 26.7 | 28.0 | 27.9 | 27.6 | 27.7 |
| 3 | 77.9 | 88.9 | - | 78.2 | 88.8 | 89.0 | 89.1 | 88.9 | 88.8 | 89.1 | 89.3 | 89.3 | 89.0 | 78.3 | 78.7 | 78.1 | 78.2 |
| 4 | 39.5 | 39.8 | - | 39.5 | 39.7 | 39.7 | 39.8 | 39.7 | 39.6 | 39.7 | 39.6 | 39.6 | 39.8 | 40.2 | 40.3 | 39.7 | 40.2 |
| 5 | 56.3 | 56.5 | - | 56.5 | 56.5 | 56.5 | 56.6 | 56.5 | 56.3 | 56.5 | 56.3 | 56.3 | 56.5 | 61.7 | 61.5 | 60.8 | 61.3 |
| 6 | 18.7 | 18.6 | - | 18.9 | 18.5 | 18.5 | 18.6 | 18.5 | 18.4 | 18.5 | 18.6 | 18.3 | 18.5 | 67.6 | 78.1 | 74.6 | 78.0 |
| 7 | 35.2 | 35.3 | - | 35.3 | 35.2 | 35.2 | 35.2 | 35.2 | 35.1 | 35.1 | 35.1 | 35.1 | 35.2 | 47.4 | 45.1 | 45.7 | 45.0 |
| 8 | 40.0 | 40.2 | - | 40.2 | 40.1 | 40.0 | 40.2 | 40.1 | 40.0 | 40.1 | 39.9 | 39.9 | 40.1 | 41.1 | 41.2 | 41.3 | 41.2 |
| 9 | 50.4 | 49.3 | - | 50.4 | 50.3 | 50.4 | 50.3 | 50.3 | 50.1 | 50.2 | 50.1 | 50.1 | 50.2 | 50.1 | 50.1 | 49.5 | 50.0 |
| 10 | 37.3 | 37.1 | - | 37.5 | 37.0 | 37.0 | 37.0 | 37.0 | 36.9 | 37.0 | 36.8 | 36.8 | 36.9 | 39.3 | 39.5 | 39.2 | 39.7 |
| 11 | 32.0 | 32.3 | - | 30.9 | 30.9 | 32.0 | 31.0 | 30.8 | 30.6 | 30.8 | 30.8 | 30.7 | 30.8 | 31.9 | 30.9 | 30.9 | 31.0 |

| | | | | | | | | | | | | | | | | | |
|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 12 | 70.9 | 70.9 | 71.1 | 70.3 | 70.2 | 71.0 | 70.3 | 70.3 | 70.1 | 70.2 | 70.1 | 70.2 | 70.2 | 70.9 | 70.3 | 70.2 | 70.2 |
| 13 | 48.5 | 48.7 | 50.8 | 49.3 | 49.5 | 48.6 | 49.6 | 49.5 | 49.4 | 49.5 | 49.3 | 49.5 | 49.5 | 48.1 | 49.1 | 48.7 | 49.2 |
| 14 | 51.6 | 51.9 | - | 51.5 | 51.5 | 51.8 | 51.8 | 51.7 | 51.3 | 51.5 | 51.3 | 51.4 | 51.4 | 51.5 | 51.4 | 51.5 | 51.5 |
| 15 | 31.8 | 31.5 | - | 30.9 | 30.8 | 31.4 | 30.9 | 30.8 | 30.6 | 30.8 | 30.8 | 30.8 | 30.8 | 31.3 | 30.8 | 30.9 | 30.9 |
| 16 | 26.8 | 26.8 | - | 26.8 | 26.7 | 26.8 | 26.8 | 26.7 | 26.6 | 26.7 | 26.6 | 26.6 | 26.8 | 26.8 | 26.7 | 26.5 | 26.7 |
| 17 | 54.7 | 54.8 | 50.5 | 51.7 | 51.7 | 54.8 | 51.5 | 51.5 | 51.5 | 51.7 | 51.5 | 51.6 | 51.7 | 54.6 | 51.7 | 51.7 | 51.6 |
| 18 | 16.2 | 16.5 | - | 16.5 | 16.3 | 15.9 | 16.4 | 16.3 | 16.2 | 16.2 | 16.2 | 16.2 | 16.3 | 17.5 | 17.6 | 17.5 | 17.6 |
| 19 | 15.8 | 16.0 | - | 16.2 | 16.0 | 16.4 | 16.1 | 16.1 | 16.0 | 16.1 | 15.9 | 15.9 | 16.0 | 17.4 | 17.6 | 17.5 | 17.6 |
| 20 | 72.9 | 73.0 | - | 83.6 | 83.4 | 73.0 | 83.5 | 83.5 | 83.3 | 83.5 | 83.5 | 83.1 | 83.5 | 73.9 | 83.4 | 83.3 | 83.4 |
| 21 | 26.9 | 27.2 | 22.8 | 22.4 | 22.5 | 27.1 | 22.5 | 22.4 | 22.3 | 22.3 | 22.6 | 22.2 | 22.4 | 26.9 | 22.5 | 22.3 | 22.4 |
| 22 | 35.8 | 36.0 | 43.3 | 36.2 | 36.2 | 35.9 | 36.2 | 36.2 | 36.1 | 36.2 | 36.1 | 36.0 | 36.2 | 35.7 | 36.1 | 35.8 | 36.1 |
| 23 | 22.9 | 23.1 | 22.7 | 23.2 | 23.3 | 23.0 | 23.3 | 23.2 | 23.1 | 23.1 | 23.1 | 23.1 | 23.2 | 22.9 | 23.3 | 23.2 | 23.2 |
| 24 | 126.2 | 126.2 | 126.4 | 126.0 | 126.0 | 126.4 | 126.0 | 126.0 | 126.0 | 126.0 | 125.8 | 125.9 | 126.0 | 126.2 | 126.0 | 126.0 | 126.0 |
| 25 | 130.6 | 130.0 | - | 131.0 | 131.0 | 130.8 | 131.0 | 131.0 | 130.8 | 130.9 | 131.0 | 131.0 | 131.1 | 130.5 | 131.0 | 131.0 | 131.0 |
| 26 | 25.8 | 25.9 | - | 25.9 | 25.8 | 25.9 | 25.8 | 25.8 | 25.7 | 25.7 | 25.8 | 25.7 | 25.8 | 25.8 | 25.9 | 25.8 | 25.8 |
| 27 | 17.6 | 17.5 | - | 17.8 | 17.8 | 17.7 | 17.9 | 18.0 | 17.8 | 17.9 | 17.9 | 17.8 | 18.0 | 17.7 | 17.9 | 17.8 | 17.8 |
| 28 | 28.6 | 28.2 | - | 28.8 | 28.2 | 28.2 | 28.2 | 28.2 | 28.0 | 28.0 | 28.0 | 28.0 | 28.1 | 31.9 | 31.8 | 32.2 | 31.7 |
| 29 | 16.4 | 16.9 | - | 16.5 | 16.8 | 16.6 | 16.7 | 16.8 | 16.7 | 16.5 | 16.4 | 16.5 | 16.7 | 16.4 | 16.5 | 17.2 | 16.8 |
| 30 | 17.0 | 16.9 | - | 17.2 | 17.4 | 17.1 | 17.5 | 17.5 | 17.5 | 17.5 | 17.4 | 17.4 | 17.4 | 17.0 | 17.2 | 17.5 | 17.2 |

表 1(续) 三七茎叶皂甙的¹³C NMR 化学位移 (ppm) (糖链部分)Table 1(continued) ¹³C NMR data of saponins from the leaves of *notoginseng* (ppm) (sugar part)

| | 1 | 2 | 4 | 5 | 8 | 9 | 10 | 13 | 14 | 15 | 16 | 7 | 11 | 12 | | |
|-------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------|-------|-------------|-------|-------|-------|--|
| 3-inner | | | glc | glc | glc | glc | glc | glc | glc | glc | glc | 6-inner | glc | glc | glc | |
| 1 | 106.9 | | 107.0 | 105.2 | 105.1 | 106.8 | 106.7 | 105.1 | 105.0 | 105.1 | 104.8 | 1 | 106.0 | 101.9 | 103.5 | |
| 2 | 75.8 | | 75.8 | 83.5 | 83.5 | 75.7 | 75.6 | 83.4 | 83.1 | 83.1 | 83.0 | 2 | 75.5 | 79.3 | 80.2 | |
| 3 | 78.8 | | 79.3 | 78.3 | 78.7 | 79.2 | 79.0 | 77.7 | 77.2 | 77.8 | 77.8 | 3 | 80.0 | 78.2 | 79.0 | |
| 4 | 72.0 | | 71.7 | 71.7 | 71.8 | 71.6 | 71.6 | 71.7 | 71.6 | 71.5 | 71.8 | 4 | 71.9 | 72.2 | 71.8 | |
| 5 | 78.3 | | 78.3 | 78.2 | 78.0 | 78.2 | 78.6 | 77.3 | 78.2 | 77.8 | 77.9 | 5 | 79.5 | 78.2 | 80.0 | |
| 6 | 63.2 | | 63.2 | 62.8 | 62.9 | 63.1 | 62.9 | 62.9 | 62.7 | 62.6 | 62.8 | 6 | 63.1 | 63.1 | 63.0 | |
| 3-terminal | | | | glc | glc | | | glc | glc | glc | glc | 6-terminal | | rha | xyl | |
| 1 | - | | - | 106.1 | 105.9 | - | - | 105.6 | 105.6 | 105.7 | 103.2 | 1 | - | 101.9 | 104.8 | |
| 2 | - | | - | 77.2 | 77.0 | - | - | 76.7 | 76.7 | 76.8 | 84.5 | 2 | - | 72.4 | 75.8 | |
| 3 | - | | - | 79.8 | 79.2 | - | - | 78.1 | 78.8 | 78.9 | 78.3 | 3 | - | 72.6 | 79.0 | |
| 4 | - | | - | 71.7 | 71.8 | - | - | 71.7 | 71.5 | 71.6 | 71.2 | 4 | - | 74.1 | 71.7 | |
| 5 | - | | - | 78.0 | 78.0 | - | - | 78.1 | 78.0 | 78.0 | 77.8 | 5 | - | 69.5 | 67.2 | |
| 6 | - | | - | 62.8 | 62.9 | - | - | 62.8 | 62.6 | 62.6 | 62.9 | 6 | - | 18.7 | - | |
| | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |
| 20-inner | | glc | glc | | glc | glc | glc | glc | glc | glc | glc | 20-inner | glc | glc | glc | |
| 1 | | 98.1 | 98.3 | | 98.3 | 98.1 | 98.1 | 98.1 | 98.0 | 98.0 | 98.1 | 1 | 98.2 | 98.3 | 98.3 | |
| 2 | | 74.9 | 75.2 | | 75.2 | 74.7 | 75.2 | 74.8 | 74.9 | 75.0 | 75.2 | 2 | 75.2 | 75.1 | 75.1 | |
| 3 | | 79.3 | 78.4 | | 78.4 | 78.7 | 78.3 | 79.0 | 78.2 | 78.6 | 78.6 | 3 | 79.2 | 79.2 | 79.9 | |
| 4 | | 71.9 | 71.8 | | 71.8 | 72.0 | 71.6 | 71.7 | 71.6 | 71.5 | 71.7 | 4 | 71.4 | 71.6 | 71.7 | |
| 5 | | 76.9 | 78.0 | | 78.0 | 76.8 | 76.9 | 76.7 | 76.7 | 76.3 | 77.0 | 5 | 78.1 | 78.5 | 79.0 | |
| 6 | | 70.2 | 62.9 | | 62.9 | 70.0 | 71.6 | 69.9 | 71.5 | 68.3 | 70.7 | 6 | 62.8 | 63.0 | 63.0 | |
| 20-terminal | | xyl | | | | xyl | glc | xyl | glc | ara (f) | glc | 20-terminal | | | | |
| 1 | | 105.8 | - | | - | 105.6 | 105.1 | 105.3 | 105.0 | 109.9 | 105.3 | 1 | - | - | - | |
| 2 | | 74.9 | - | | - | 74.7 | 74.6 | 74.5 | 75.0 | 83.5 | 74.9 | 2 | - | - | - | |

| | | | | | | | | |
|---|------|------|------|------|------|------|------|---|
| 3 | 77.9 | 77.7 | 78.0 | 78.8 | 78.0 | 78.6 | 78.3 | 3 |
| 4 | 71.1 | 71.0 | 71.6 | 70.8 | 71.5 | 86.1 | 71.6 | 4 |
| 5 | 67.0 | 66.8 | 78.1 | 66.5 | 78.0 | 62.7 | 78.2 | 5 |
| 6 | - | - | 62.7 | - | 62.6 | - | 63.0 | 6 |

表 2 三七茎叶黄酮类化合物的¹H、¹³C NMR 数据(ppm), J(Hz)
Table 2 ¹H, ¹³C NMR data of flavonoids from the leaves of *notoginseng*

| | 3 | | 6 | |
|------|-----------------|--|-----------------|--|
| | ¹³ C | ¹ H | ¹³ C | ¹ H |
| 2 | 79.6 | 5.37(1H, dd, J = 12.9, 2.9) | 78.9 | 5.49(1H, dd, J = 12.9, 2.1) |
| 3 | 43.9 | 2.70(1H, dd, J = 17.0, 2.9) 3.05(1H, d, J = 16.0) | 43.3 | 2.68(1H, dd, J = 17.0, 2.4) 3.04(1H, d, J = 16.2) |
| 4 | 190.4 | - | 190.2 | - |
| 5 | 128.6 | 7.66(1H, d, J = 8.6) | 128.6 | 7.64(1H, d, J = 8.7) |
| 6 | 109.8 | 6.51(1H, d, J = 8.6) | 110.8 | 6.50(1H, d, J = 8.6) |
| 7 | 165.8 | - | 165.0 | - |
| 8 | 100.7 | 6.36 (1H, s) | 102.8 | 6.34(1H, d, J = 2.0) |
| 9 | 163.2 | - | 163.3 | - |
| 10 | 114.6 | - | 113.6 | - |
| 1' | 130.6 | - | 132.6 | - |
| 2' | 127.5 | 7.30(1H, A ₂ B ₂ Q-A, J = 8.8) | 128.3 | 7.43(1H, A ₂ B ₂ Q-A, J = 8.5) |
| 3' | 113.9 | 6.78(1H, A ₂ B ₂ Q-B, J = 8.8) | 116.2 | 7.06(1H, A ₂ B ₂ Q-B, J = 8.5) |
| 4' | 159.6 | - | 157.5 | - |
| 5' | 113.9 | 6.78(1H, A ₂ B ₂ Q-B, J = 8.8) | 116.2 | 7.06(1H, A ₂ B ₂ Q-B, J = 8.5) |
| 6' | 127.5 | 7.30(1H, A ₂ B ₂ Q-A, J = 8.8) | 128.3 | 7.43(1H, A ₂ B ₂ Q-A, J = 8.5) |
| glc | | | | |
| 1" | | | 98.8 | 4.95(1H, d, J = 7.4) |
| 2" | | | 76.0 | |
| 3" | | | 76.3 | 3.35-3.65 (4H, m) |
| 4" | | | 70.1 | |
| 5" | | | 77.1 | |
| 6" | | | 60.8 | 3.70(1H, dd, J = 12.0, 5.4) 3.89 (1H, dd, J = 12.0, 2.2) |
| api | | | | |
| 1''' | | | 108.9 | 5.38(d, J = 1.6) |
| 2''' | | | 77.0 | 3.95(d, J = 1.6) |
| 3''' | | | 79.5 | |
| 4''' | | | 64.5 | 3.54(2H, s) |
| 5''' | | | 74.2 | 4.25 (1H, m) 3.80 (1H, m) |

3 结论

早期,我们从三七叶中仅分离得到原人参二醇

型的四环三萜皂甙。本项进一步的研究结果表明,三七叶中亦含有少量的原人参三醇型四环三萜皂甙。在三七根部含量高的原人参三醇型的人参皂甙

Rg₁ 以及 Re 和三七皂甙 R₁ 等亦少量存在于茎叶中。前人报道三七茎叶中的槲皮素及其配糖体, 我们未能分离和检测到。我们从三七叶中分离鉴定到的黄酮类化合物是甘草素 (liquiritigenin) 和甘草芹糖甙 (liquiritin apioside)。这在人参属植物中是首次发现。本研究的结果将有助于对三七叶的综合利用及其产品的深度开发。

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