

# 吉林人参根和根茎的化学成分研究

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**【摘要】** 采用 Amberlite XAD-4 大孔吸附树脂和硅胶柱色谱以及高效液相色谱等方法系统性研究人参根和根茎的化学成分;通过谱学数据分析鉴定化合物的结构。从人参根和根茎的 70% 乙醇提取物中分离得到 28 个皂苷类化合物,分别鉴定为高丽人参皂苷 R<sub>1</sub>(**1**), 人参皂苷 Rg<sub>1</sub>(**2**), 人参皂苷 Rf(**3**), 三七皂苷 R<sub>2</sub>(**4**), 人参皂苷 Rg<sub>2</sub>(**5**), 三七皂苷 Fe(**6**), 吉林人参苷醇(**7**), 人参皂苷 Re<sub>5</sub>(**8**), 三七皂苷 N(**9**), 三七皂苷 R<sub>1</sub>(**10**), 人参皂苷 Re<sub>2</sub>(**11**), 人参皂苷 Re<sub>1</sub>(**12**), 人参皂苷 Re(**13**), 人参皂苷 Rs<sub>2</sub>(**14**), 人参皂苷 Ro 甲酯(**15**), 人参皂苷 Rd(**16**), 人参皂苷 Re<sub>3</sub>(**17**), 人参皂苷 Re<sub>4</sub>(**18**), 20-葡萄糖基-人参皂苷 Rf(**19**), 人参皂苷 Ro(**20**), 人参皂苷 Rc(**21**), 西洋参皂苷 R<sub>1</sub>(**22**), 人参皂苷 Ra<sub>2</sub>(**23**), 人参皂苷 Rb<sub>1</sub>(**24**), 人参皂苷 Ra<sub>1</sub>(**25**), 人参皂苷 Ra<sub>3</sub>(**26**), 人参皂苷 Rb<sub>2</sub>(**27**), 三七皂苷 R<sub>4</sub>(**28**)。所有化合物均系 20(S)-原人参二醇型或原人参三醇型皂苷。化合物 **1** 为首次从吉林栽培人参根和根茎中分离得到;化合物 **6** 为首次从人参根和根茎中分离得到;并首次对化合物 **6, 14, 19** 的氢谱信号进行了归属。

**【关键词】** 人参;化学成分;三七皂苷 Fe;人参皂苷 Rs<sub>2</sub>;20-葡萄糖基-人参皂苷 Rf

传统中药人参 *Ginseng Radix et Rhizoma* 系五加科人参属植物人参 *Panax ginseng* C. A. Mey. 的干燥根和根茎<sup>[1]</sup>, 始载于我国历史上第一部记载药物的著作《神农本草经》, 列为上品, 记载其“味甘, 微寒, 主补五脏, 安精神, 定魂魄, 止惊悸, 除邪气, 明目, 开心益智, 久服轻身延年”, 亚洲各国广泛应用, 为著名的补益药之一。人参的特征性化学成分主要为四环三萜达玛烷型人参皂苷(ginsenoside)<sup>[2-3]</sup>, 具有改善记忆障碍、延缓衰老、提高免疫功能、抗氧化、改善心血管系统功能、抗应激、壮阳等作用, 一直是国内外医药领域的研究热点<sup>[3]</sup>。人参主要分布于我国东北, 以及朝鲜和俄罗斯与我国接壤地带;野生人参数量日益减少, 现在主要依靠人工种植, 我国已在吉林省的靖宇、长白、集安、抚松等县建立了人参规范化种植基地(GAP)。为保证人参药材的质量及为其质量评价提供物质基础, 本研究对吉林省长

白县“人参规范化种植基地”栽培人参的皂苷成分进行了系统研究, 从其根和根茎的 70% 乙醇提取物中分离鉴定了 28 个化合物, 所有化合物均系 20(S)-原人参二醇型或原人参三醇型皂苷。前文<sup>[4]</sup>已报道化合物人参皂苷 Rf(**3**), 吉林人参苷醇(**7**)和人参皂苷 Re<sub>5</sub>(**8**)的化学结构鉴定, 本文报道其他 25 个化合物的结构鉴定。

## 1 材料

Bruker AV 400 型核磁共振波谱仪, 吡啶-*d*<sub>5</sub>(py-*d*<sub>5</sub>)为溶剂, 三甲基硅烷为内标; MDS SCIEX API QSTAR 型质谱仪(ESI-TOF-MS); 创新通恒 LC 3000 半制备型高效液相色谱(SP-HPLC)仪系统, 包括 P3050 二元泵, CXTH-3000 色谱工作站; Daisogel C<sub>18</sub> 色谱柱(30 mm × 250 mm, 10 μm)。柱色谱硅胶(200~300目)和薄层色谱(TLC)硅胶板 GF254 均为青岛海洋化工厂产品; Amberlite XAD-4 非离子型大孔树脂(20~60目; Sigma Chemical Co., St. Louis, MO, USA); 分析纯三氯甲烷、甲醇、正丁醇均为北京化工厂产品; 色谱纯甲醇和乙腈均为天津西华特种试剂厂产品; 水为娃哈哈纯净水, 用时经 Millipore Milli-Q 水处理系统处理为去离子水。

研究材料于 2012 年 9 月采自吉林省长白县“人参规范化种植基地”, 经北京大学药学院杨秀伟教

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授鉴定为人参 *P. ginseng* 的干燥根和根茎, 凭证标本(No. 201209JLRS)存放在北京大学药学院天然药物及仿生药物国家重点实验室。

## 2 提取与分离

干燥的人参根和根茎粗粉(6 kg)用70%乙醇(每次48 L)回流提取6次,第1次2 h,以后每次1 h;浓缩提取液,得干膏1 307 g(按投料计算收率为21.8%,下同)。将此干膏加蒸馏水(3 L)混悬,用水饱和的正丁醇萃取6次,每次正丁醇用量为3 L;合并正丁醇萃取液,减压浓缩,得正丁醇萃取物300 g(5%)和残留的水层997.6 g(16.63%)。

将上述正丁醇萃取物300 g用适量的蒸馏水溶解,经Amberlite XAD-4大孔吸附树脂柱色谱,依次用水,60%,95%乙醇洗脱,体积流量分别为15,20,15 L,分别得到相应的洗脱部位84.2 g(1.40%),189.0 g(3.15%),24.7 g(0.41%)。60%乙醇洗脱部位189.0 g经硅胶柱色谱,三氯甲烷-甲醇-水(5:1:0.1~4:1:0.1~3:1:0.1~2:1:0.1~1:1:0.1)梯度洗脱,TLC检测合并相同组分,得到9个流分,命名为F1(5.6 g),F2(4.4 g),F3(3.3 g),F4(34.5 g),F5(18.3 g),F6(26.4 g),F7(31.2 g),F8(50.0 g)和F9(5.0 g)。

F4(34.5 g)经硅胶柱色谱,三氯甲烷-甲醇-水(3:1:0.1~2:1:0.1)梯度洗脱,TLC检测合并相同组分,得到6个流分F4-1~F4-6。F4-2经SP-HPLC(甲醇-水70:30)分离,得到2个流分F4-2-1和F4-2-2;后者经SP-HPLC(乙腈-水30:70)纯化,得到化合物**1**(12.2 mg)。F4-3经SP-HPLC(甲醇-水70:30)分离,得到2个流分F4-3-1和F4-3-2。F4-3-1再经SP-HPLC(甲醇-水50:50)分离,得到4个流分F4-3-1-1~F4-3-1-4。F4-3-1-4经SP-HPLC(乙腈-水25:75)纯化,得到化合物**2**(4.223 g)。F4-3-2经SP-HPLC(乙腈-水30:70)纯化,得到化合物**3**(1.378 g),**4**(970 mg),**5**(193 mg)。

F5(18.3 g)经硅胶柱色谱,三氯甲烷-甲醇-水(4.5:1.5:0.2~2:1:0.2)梯度洗脱,TLC检测合并相同组分,得到5个流分F5-1~F5-5。F5-3经SP-HPLC(甲醇-水75:25)分离,得到6个流分F5-3-1~F5-3-6。F5-3-6经SP-HPLC(乙腈-水35:65)纯化,得到化合物**6**(9 mg)。F5-4经SP-HPLC(甲醇-水75:25)分离,得到3个流分F5-4-1~F5-4-3。F5-4-1再经SP-HPLC(甲醇-水50:50)分离,得到4个流分F5-4-1-1~F5-4-1-4。F5-4-1-1经SP-HPLC(乙腈-水

20:80)纯化,得到化合物**7**(13.2 mg)。F5-4-1-2经SP-HPLC(乙腈-水19:81)纯化,得到化合物**8**(12.6 mg),**9**(11.2 mg)。F5-4-1-3经SP-HPLC(乙腈-水20:80)纯化,得到化合物**10**(358 mg)。F5-4-1-4采用流分F5-4-1-3同样的方法纯化,得到化合物**11**(54 mg),**12**(7 mg),**13**(2.388 g)。

F6(26.4 g)经硅胶柱色谱,三氯甲烷-甲醇-水(4.5:1.5:0.2~2:1:0.2)梯度洗脱,TLC检测合并相同组分,得到5个流分F6-1~F6-5。F6-3经SP-HPLC(甲醇-水70:30)分离,得到4个流分F6-3-1~F6-3-4。F6-3-2经SP-HPLC(乙腈-水33:67)纯化,得到化合物**14**(10 mg)。F6-3-3和F6-3-4皆经SP-HPLC(乙腈-水35:65)纯化,分别得到化合物**15**(196 mg),**16**(1.876 g)。F6-4经SP-HPLC(甲醇-水70:30)分离,得到5个流分F6-4-1~F6-4-5。F6-4-1再经SP-HPLC(甲醇-水50:50)分离,得到4个流分F6-4-1-1~F6-4-1-5。F6-4-1-2经SP-HPLC(乙腈-水20:80)纯化,得到化合物**17**(67 mg),**18**(8 mg)。F6-4-1-3采取与F6-4-1-2同样的方法纯化,得到化合物**19**(367 mg)。F6-4-2经SP-HPLC(乙腈-水30:70)纯化,得到化合物**20**(2.038 g)。

F7(31.2 g)经硅胶柱色谱,三氯甲烷-甲醇-水(2:1:0.1~1:1:0.1)梯度洗脱,TLC检测合并相同组分,得到4个流分F7-1~F7-4。F7-3经SP-HPLC(甲醇-水70:30)分离,得到4个流分F7-3-1~F7-3-4。F7-3-3经SP-HPLC(乙腈-水3:70)纯化,得到化合物**21**(2.835 g)。F7-3-4经SP-HPLC(乙腈-水33:67)纯化,得到化合物**22**(110 mg)。

F8(50.0 g)经硅胶柱色谱,三氯甲烷-甲醇-水(1:0.5:0.1~1:1:0.1)梯度洗脱,TLC检测合并相同组分,得到6个流分F8-1~F8-6。F8-4经SP-HPLC(甲醇-水70:30)分离,得到5个流分F8-4-1~F8-4-5。F8-4-3经SP-HPLC(乙腈-水28:72)纯化,得到化合物**23**(108 mg)。F8-4-4经SP-HPLC(乙腈-水30:70)纯化,得到化合物**24**(1.290 g),**25**(140 mg),**26**(88 mg)。F8-4-5采取与F8-4-4相同的方法纯化,得到化合物**27**(418 mg)。

F9(5.0 g)经硅胶柱色谱,三氯甲烷-甲醇-水(1:0.5:0.1~1:1:0.1)梯度洗脱,TLC检测合并相同组分,得到5个流分F9-1~F9-5。F9-3经SP-HPLC(甲醇-水70:30)分离,得到3个流分F9-3-1~F9-3-3。F9-3-2经SP-HPLC(乙腈-水28:72)纯化,

得到化合物 **28** (8 mg)。

### 3 结构鉴定

分离得到的 28 个化合物在 TLC 板上展开后喷雾 10% 浓硫酸乙醇试液皆呈紫色斑点; Liberman-Burchard 反应阳性, 提示为三萜皂苷类化合物。根据苷元的 <sup>13</sup>C-NMR 波谱信号特征并与对照品原人参二醇或原人参三醇、齐墩果酸的比较, 鉴定了它们相应的苷元; 分析其 C-17, 20 ~ 22 的 <sup>13</sup>C-NMR 信号的化学位移, 26 个皆呈 20(S)-原人参二醇或原人参三醇型特征<sup>[5]</sup>; 2 个呈齐墩果酸型特征。

化合物 **1** 白色粉末。ESI-MS  $m/z$  891.5 [M + Na]<sup>+</sup>, 867.5 [M - H]<sup>-</sup>; <sup>1</sup>H-NMR (py-*d*<sub>5</sub>, 400 MHz)

$\delta$ : 7.06 (1H, dq,  $J = 15.4, 6.9$  Hz, H-3''), 6.02 (1H, d,  $J = 15.4$  Hz, H-2''), 5.24 (1H, t,  $J = 6.7$  Hz, H-24), 5.18 (1H, d,  $J = 7.8$  Hz, 20-glu-H-1'''), 5.03 (1H, d,  $J = 7.8$  Hz, 6-glu-H-1'), 4.37 (1H, dd,  $J = 11.0, 3.4$  Hz, H-6 $\beta$ ), 4.13 (1H, m, H-12 $\alpha$ ), 3.47 (1H, dd,  $J = 11.7, 5.2$  Hz, H-3 $\alpha$ ), 2.05 (3H, s, 3H, s, H-28), 1.70 (3H, d,  $J = 6.1$  Hz, H-4''), 1.61 (3H, s, H-21), 1.57 (6H, s, H-26, H-27), 1.54 (3H, s, H-29), 1.20 (3H, s, H-18), 1.04 (3H, s, H-19), 0.91 (3H, s, H-30); <sup>13</sup>C-NMR 数据见表 1。以上数据与文献[6]基本一致, 鉴定为高丽人参皂苷 R<sub>1</sub> (koryogin-senoside R<sub>1</sub>)。

表 1 20(S)-原人参三醇型皂苷 **1, 2, 4, 9 ~ 13, 17 ~ 19** 的 <sup>13</sup>C-NMR 数据 (py-*d*<sub>5</sub>, 100 MHz)

Table 1 <sup>13</sup>C-NMR data (py-*d*<sub>5</sub>, 100 MHz) for 20(S)-protopanaxatriol-type saponins **1, 2, 4, 9 ~ 13** and **17 ~ 19**

No.	<b>1</b>	<b>2</b>	<b>4</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>17</b>	<b>18</b>	<b>19</b>
1	39.5	39.4	39.4	39.4	39.5	39.4	39.3	39.4	39.4	39.4	39.4
2	27.9	27.9	27.8	27.9	27.8	27.9	27.9	27.8	27.9	28.0	27.8
3	78.6	78.6	78.8	78.6	78.3	78.6	78.6	78.2	78.6	78.6	78.7
4	40.3	40.3	40.2	40.3	40.2	40.3	40.3	40.0	40.4	40.4	40.2
5	61.4	61.4	61.3	61.3	61.3	61.4	61.4	60.8	61.3	61.4	61.4
6	80.0	79.6	79.4	80.3	78.0	80.4	80.1	78.2	80.3	80.1	79.9
7	45.5	45.1	45.0	44.8	44.9	45.1	45.0	46.0	44.9	45.1	44.9
8	41.3	41.1	41.1	41.0	41.1	41.1	41.0	41.2	41.0	41.1	41.1
9	50.0	50.0	50.1	49.9	49.9	50.0	49.9	49.5	50.0	50.0	50.0
10	39.7	39.7	39.6	39.6	39.6	39.7	39.6	39.7	39.6	39.7	39.6
11	30.9	30.9	32.1	30.9	31.0	31.0	30.9	31.0	31.0	30.9	30.9
12	70.1	70.1	71.0	70.1	70.1	70.1	70.2	70.1	70.1	70.2	70.1
13	49.2	49.2	48.2	49.1	49.2	49.2	49.0	49.1	49.2	49.1	49.2
14	51.4	51.3	51.7	51.3	51.4	51.3	51.3	51.4	51.3	51.3	51.4
15	31.0	30.6	31.2	30.6	30.7	30.6	30.6	30.7	30.6	30.6	30.7
16	26.7	26.6	27.0	26.6	26.6	26.6	26.6	26.6	26.6	26.6	26.6
17	51.6	51.5	54.8	51.5	51.5	51.4	51.8	51.6	51.4	51.5	51.5
18	17.7	17.5	17.6	17.5	17.7	17.5	17.5	17.5	17.5	17.5	17.6
19	17.7	17.5	17.7	17.5	17.7	17.5	17.5	17.6	17.5	17.5	17.5
20	83.2	83.2	73.0	83.3	83.2	83.3	83.5	83.2	83.3	83.4	83.2
21	22.3	22.3	25.8	22.3	22.3	22.3	22.4	22.3	22.2	22.3	22.3
22	36.1	36.1	35.8	36.1	36.1	36.1	36.0	36.1	36.1	36.1	36.1
23	23.2	23.2	23.0	23.2	23.2	23.2	23.3	23.2	23.1	23.1	23.2
24	125.9	125.9	126.3	125.9	126.0	126.0	125.9	126.0	126.0	126.0	126.0
25	130.9	130.9	130.8	130.9	130.9	130.9	130.9	130.9	130.9	131.0	130.9
26	25.8	25.7	26.8	25.7	25.8	25.8	25.7	25.8	25.7	25.8	25.7
27	17.8	17.7	17.3	17.7	17.5	17.7	17.7	17.7	17.7	17.9	17.7
28	31.5	31.7	31.7	31.7	31.7	31.7	31.7	32.2	31.7	31.8	32.0
29	16.5	16.4	16.7	16.3	17.2	16.3	16.3	17.2	16.3	16.4	16.7
30	17.3	17.1	16.8	17.1	16.7	17.1	17.1	17.3	17.2	17.1	17.1
	6-glu	6-glu	6-glu	6-glu	6-glu	6-glu	6-glu	6-glu	6-glu	6-glu	6-glu
1'	106.1	106.0	103.6	105.6	103.5	105.7	106.0	101.9	105.6	106.0	103.8
2'	75.4	75.4	79.9	74.8	80.1	73.7	75.5	79.4	75.5	75.5	79.3

续表 1

No.	1	2	4	9	10	11	12	13	17	18	19
3'	79.2	80.1	78.8	78.9	78.8	89.4	79.6	78.4	79.4	79.7	78.0
4'	71.7	71.8	71.3	81.3	71.3	70.9	71.8	72.3	71.9	71.8	71.7
5'	75.1	78.1	80.2	76.4	79.5	77.6	78.1	78.6	78.2	78.1	79.9
6'	65.1	63.0	62.9	62.1	62.9	62.3	63.1	63.1	62.9	63.1	62.9
	(E)-but-2-enoyl	20-glu	2'-xyl	4'-glu	2'-xyl	3'-glu	20-glu	2'-rha	20-glu	20-glu	2'-glu
1''	166.5	98.2	104.9	103.0	104.9	102.2	98.1	101.9	98.2	98.1	103.9
2''	123.2	75.1	75.8	74.4	75.8	74.3	73.4	72.4	74.8	75.0	76.0
3''	144.8	79.3	78.0	75.3	79.3	75.6	88.5	72.6	78.9	79.3	78.2
4''	17.5	71.7	71.7	71.9	71.7	71.9	70.7	74.2	81.3	72.2	72.3
5''		78.2	67.3	75.5	67.3	74.8	77.7	69.5	76.5	76.5	79.5
6''		62.9		62.8		62.5	62.3	18.8	62.2	68.5	63.3
	20-glu			20-glu	20-glu	20-glu	3''-glu	20-glu	4''-glu	6''-ara(f)	20-glu
1'''	98.3			98.2	98.2	98.2	102.0	98.3	103.0	110.1	98.2
2'''	75.1			75.1	75.1	75.1	74.3	75.2	74.5	83.4	75.1
3'''	79.3			79.3	79.9	79.4	75.6	79.3	75.3	78.8	78.4
4'''	71.5			71.6	71.7	71.7	72.0	71.7	71.7	86.0	71.7
5'''	78.3			78.2	78.8	78.3	74.6	78.3	75.1	62.6	77.8
6'''	62.9			62.8	62.9	62.9	62.4	62.9	62.8		62.9

注: glu. glucopyranosyl; xyl. xylopyranosyl; rha. rhamnopyranosyl; ara(f). arabinofuranosyl; (E)-but. *trans*-butenoyl.

化合物2 白色粉末。ESI-MS  $m/z$  823.5 [M + Na]<sup>+</sup>, 799.5 [M - H]<sup>-</sup>; <sup>1</sup>H-NMR (py-*d*<sub>5</sub>, 400 MHz)  $\delta$ : 5.22 (1H, t,  $J$  = 7.2 Hz, H-24), 5.15 (1H, d,  $J$  = 7.8 Hz, 20-glu-H-1''), 5.01 (1H, d,  $J$  = 7.7 Hz, 6-glu-H-1'), 4.50 (1H, dd,  $J$  = 12.5, 2.1 Hz, 6-glu-H-6'a), 4.47 (1H, dd,  $J$  = 12.5, 2.3 Hz, 20-glu-H-6''a), 4.39 (1H, dd,  $J$  = 12.5, 2.4 Hz, 6-glu-H-6'b), 4.38 (1H, dd,  $J$  = 11.4, 2.4 Hz, H-6 $\beta$ ), 4.36 (1H, dd,  $J$  = 12.5, 2.8 Hz, 20-glu-H-6''b), 4.08 (1H, m, H-12 $\alpha$ ), 3.49 (1H, dd,  $J$  = 11.3, 3.9 Hz, H-3 $\alpha$ ), 2.05 (3H, s, H-28), 1.59 (3H, s, H-21), 1.57 (6H, s, H-26, H-27), 1.56 (3H, s, H-29), 1.14 (3H, s, H-18), 1.02 (3H, s, H-19), 0.79 (3H, s, H-30); <sup>13</sup>C-NMR 数据见表1。以上数据与文献[7]基本一致, 鉴定为人参皂苷 Rg<sub>1</sub> (ginsenoside Rg<sub>1</sub>)。

化合物4 白色粉末。ESI-MS  $m/z$  793.5 [M + Na]<sup>+</sup>, 769.5 [M - H]<sup>-</sup>; <sup>1</sup>H-NMR (py-*d*<sub>5</sub>, 400 MHz)  $\delta$ : 5.76 (1H, d,  $J$  = 7.1 Hz, 2'-xyl-H-1''), 5.31 (1H, t,  $J$  = 7.0 Hz, H-24), 4.92 (1H, d,  $J$  = 7.2 Hz, 6-glu-H-1'), 4.47 (1H, dd,  $J$  = 11.7, 2.4 Hz, 6-glu-H-6'a), 4.32 (1H, dd,  $J$  = 10.6, 2.9 Hz, H-6 $\beta$ ), 4.32 (1H, t,  $J$  = 10.5 Hz, 2'-xyl-H-5''a), 4.30 (1H, dd,  $J$  = 11.7, 2.7 Hz, 6-glu-H-6'b), 3.87 (1H, m, H-12 $\alpha$ ), 3.64

(1H, t,  $J$  = 10.5 Hz, 2'-xyl-H-5''b), 3.48 (1H, dd,  $J$  = 11.3, 5.0 Hz, H-3 $\alpha$ ), 2.06 (3H, s, H-28), 1.64 (3H, s, H-26), 1.61 (3H, s, H-27), 1.44 (3H, s, H-29), 1.37 (3H, s, H-21), 1.14 (3H, s, H-18), 0.94 (3H, s, H-19), 0.78 (3H, s, H-30); <sup>13</sup>C-NMR 数据见表1。以上数据与文献[8]基本一致, 鉴定为三七皂苷 R<sub>2</sub> (notoginsenoside R<sub>2</sub>)。

化合物5 白色粉末。ESI-MS  $m/z$  807.5 [M + Na]<sup>+</sup>, 783.5 [M - H]<sup>-</sup>; <sup>1</sup>H-NMR (py-*d*<sub>5</sub>, 400 MHz) 和 <sup>13</sup>C-NMR (py-*d*<sub>5</sub>, 100 MHz) 数据与笔者前报[5]的一致, 鉴定为20(S)-人参皂苷 Rg<sub>2</sub> [20(S)-ginsenoside Rg<sub>2</sub>]。

化合物6 白色粉末。ESI-MS  $m/z$  915.4 [M - H]<sup>-</sup>; <sup>1</sup>H-NMR (py-*d*<sub>5</sub>, 400 MHz)  $\delta$ : 5.64 (1H, br s, 6''-ara(f)-H-1'''), 5.29 (1H, t,  $J$  = 6.9 Hz, H-24), 5.13 (1H, d,  $J$  = 7.8 Hz, 20-glu-H-1''), 4.92 (1H, d,  $J$  = 7.8 Hz, 3-glu-H-1'), 4.14 (1H, m, H-12 $\alpha$ ), 4.13 (1H, m, H-12), 3.34 (1H, dd,  $J$  = 11.4, 3.9 Hz, H-3 $\alpha$ ), 1.63 (3H, s, H-27), 1.62 (3H, s, H-21), 1.59 (3H, s, H-26), 1.28 (3H, s, H-28), 0.97 (3H, s, H-29), 0.93 (3H, s, H-30), 0.92 (3H, s, H-19), 0.78 (3H, s, H-18); <sup>13</sup>C-NMR 数据见表2。以上数据与文献[9]基本一致, 鉴定为三七皂苷 Fe (notoginsenoside Fe)。

表2 20(S)-原人参二醇型皂苷 **6**, **14**, **16**, **21** ~ **28** 的<sup>13</sup>C-NMR 数据(py-d<sub>5</sub>, 100 MHz)Table 2 <sup>13</sup>C-NMR data(py-d<sub>5</sub>, 100 MHz) for 20(S)-protopanaxadiol-type saponins **6**, **14**, **16** and **21** - **28**

No.	<b>6</b>	<b>14</b>	<b>16</b>	<b>21</b>	<b>22</b>	<b>23</b>	<b>24</b>	<b>25</b>	<b>26</b>	<b>27</b>	<b>28</b>
1	39.2	39.1	39.2	39.2	39.2	39.2	39.2	39.2	39.2	39.1	39.2
2	26.6	26.5	26.8	26.6	26.6	26.6	26.8	26.6	26.6	26.7	26.6
3	88.8	89.1	88.9	89.0	89.2	88.9	89.0	88.9	89.0	88.9	88.9
4	39.7	39.6	39.7	39.7	39.7	39.7	40.1	39.7	39.7	39.6	39.7
5	56.4	56.3	56.4	56.4	56.4	56.4	56.4	56.4	56.4	56.3	56.4
6	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4
7	35.1	35.0	35.1	35.1	35.1	35.1	35.2	35.1	35.1	35.1	35.1
8	40.0	39.9	40.0	40.0	40.0	40.0	39.7	40.0	40.0	40.0	40.0
9	50.2	50.1	50.2	50.2	50.2	50.2	50.2	50.2	50.2	50.2	50.2
10	36.9	36.8	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9	36.9
11	30.7	30.6	30.9	30.8	30.8	30.8	30.8	30.8	30.7	30.7	30.8
12	70.2	70.2	70.2	70.2	70.1	70.2	70.2	70.1	70.1	70.2	70.1
13	49.4	49.3	49.5	49.4	49.5	49.4	49.5	49.5	49.5	49.4	49.5
14	51.4	51.3	51.6	51.4	51.4	51.4	51.6	51.4	51.4	51.6	51.4
15	30.8	30.7	30.7	30.7	30.7	30.7	30.7	30.7	30.8	30.7	30.7
16	26.8	26.7	26.6	26.8	26.8	26.8	26.6	26.7	26.8	26.6	26.6
17	51.6	51.6	51.4	51.6	51.6	51.5	51.4	51.5	51.6	51.4	51.5
18	16.3	16.2	16.3	16.3	16.2	16.3	16.3	16.2	16.3	16.2	16.3
19	16.0	15.9	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0
20	83.4	83.3	83.3	83.3	83.4	83.5	83.5	83.5	83.5	83.5	83.5
21	22.4	22.3	22.4	22.4	22.4	22.4	22.4	22.3	22.3	22.3	22.4
22	36.1	36.0	36.1	36.1	36.1	36.1	36.2	36.2	36.2	36.1	36.2
23	23.2	23.1	23.2	23.2	23.2	23.1	23.2	23.1	23.2	23.2	23.2
24	126.0	125.9	125.9	126.0	125.9	126.1	126.0	125.9	126.0	125.9	126.0
25	131.0	131.0	130.9	131.0	131.0	131.0	131.0	131.1	131.1	131.1	131.0
26	25.8	25.7	25.7	25.8	25.8	25.8	25.8	25.8	25.8	25.8	25.8
27	17.9	17.8	17.7	17.9	17.9	17.9	17.9	17.9	18.0	17.8	18.0
28	28.1	27.9	28.1	28.1	28.0	28.1	28.1	28.1	28.1	28.1	28.1
29	16.8	16.4	16.6	16.6	16.4	16.6	16.6	16.6	16.6	16.6	16.6
30	17.4	17.3	17.4	17.4	17.4	17.4	17.4	17.4	17.4	17.3	17.4
	3-glu	3-glu	3-glu	3-glu	3-glu	3-glu	3-glu	3-glu	3-glu	3-glu	3-glu
1'	107.0	104.8	105.1	105.1	104.9	105.1	105.1	105.1	105.0	105.1	106.1
2'	75.8	84.2	83.5	83.4	84.3	83.4	83.6	83.5	83.5	83.5	83.5
3'	79.3	77.8	78.3	78.0	77.9	77.5	78.0	78.3	78.3	78.2	78.1
4'	72.1	72.0	71.7	72.1	71.5	71.9	71.7	71.6	71.6	72.1	71.6
5'	78.4	78.0	78.3	78.3	78.1	78.4	78.1	78.1	78.0	78.1	78.1
6'	63.1	62.5	62.9	62.9	62.8	62.8	62.8	62.7	62.9	62.6	62.8
	20-glu	2'-glu	2'-glu	2'-glu	2'-glu	2'-glu	2'-glu	2'-glu	2'-glu	2'-glu	2'-glu
1''	98.1	106.1	106.0	106.1	106.2	106.1	106.1	106.1	106.1	106.0	106.0
2''	75.0	76.4	77.1	77.2	76.7	77.2	77.2	77.2	77.2	77.1	77.0
3''	78.8	78.7	79.3	79.2	79.2	79.3	78.2	79.3	79.3	79.2	79.3
4''	71.9	70.9	71.7	71.7	71.6	71.6	71.7	71.9	71.6	71.8	71.5
5''	76.6	75.2	77.9	78.1	75.3	78.1	78.4	77.9	77.9	77.9	78.3
6''	68.5	64.7	62.9	62.7	64.7	62.6	62.7	62.9	62.6	62.8	62.7
	6''-ara (f)	20-glu	20-glu	20-glu	20-glu	20-glu	20-glu	20-glu	20-glu	20-glu	20-glu
1'''	110.1	98.0	98.3	98.1	98.0	98.1	98.1	98.0	98.1	98.1	98.1
2'''	83.4	74.9	75.1	75.0	74.8	75.0	74.9	74.8	74.8	74.9	74.8
3'''	78.8	78.4	78.2	78.2	78.3	78.2	78.3	78.7	78.2	78.3	78.3
4'''	86.0	71.3	71.7	71.7	71.6	71.6	71.7	71.6	71.6	71.6	71.5
5'''	62.6	76.6	78.1	76.5	77.0	76.4	77.1	76.9	77.1	76.7	77.0
6'''		68.4	62.7	68.5	71.6	68.0	70.3	69.8	69.6	69.2	71.6

续表2

No.	6	14	16	21	22	23	24	25	26	27	28
		6 <sup>'''</sup> -ara(f)	6 <sup>'''</sup> -ara(f)	6 <sup>'''</sup> -Ara(f)6 <sup>'''</sup> -glu		6 <sup>'''</sup> -ara(f)	6 <sup>'''</sup> -glu	6 <sup>'''</sup> -ara(p)	6 <sup>'''</sup> -glu	6 <sup>'''</sup> -ara(p)	6 <sup>'''</sup> -glu
1 <sup>'''</sup>		110.0		110.1	105.3	108.1	105.4	105.1	105.1	104.6	105.5
2 <sup>'''</sup>		83.2		83.5	75.2	90.5	75.3	72.9	74.2	72.1	75.1
3 <sup>'''</sup>		79.1		78.8	78.3	78.3	78.3	73.9	87.5	74.1	77.2
4 <sup>'''</sup>		85.9		86.0	71.4	85.6	71.7	78.3	71.4	68.5	71.6
5 <sup>'''</sup>		62.7		62.6	78.5	62.5	79.3	65.7	78.1	65.6	76.9
6 <sup>'''</sup>					62.8		62.9		62.4		69.9
						2 <sup>'''</sup> -xyl		4 <sup>'''</sup> -xyl	3 <sup>'''</sup> -xyl		6 <sup>'''</sup> -xyl
1 <sup>'''</sup>						104.4		107.0	106.5		105.1
2 <sup>'''</sup>						74.9		75.4	75.5		74.8
3 <sup>'''</sup>						77.9		78.4	77.2		77.9
4 <sup>'''</sup>						71.0		71.0	70.9		71.1
5 <sup>'''</sup>						67.3		67.3	67.4		67.1
Ac-CH <sub>3</sub>		20.8			20.9						
Ac-CO		170.9			171.0						

注:ara(f). arabinofuranosyl; ara(p). arabinopyranosyl; glu. glucopyranosyl; xyl. xylopyranosyl; Ac. acetyl.

化合物 **9** 白色粉末。ESI-MS  $m/z$  839.5  $[M + Na]^+$ , 915.4  $[M - H]^-$ ; <sup>1</sup>H-NMR (py-*d*<sub>5</sub>, 400 MHz)  $\delta$ : 5.87(1H, d,  $J = 3.7$  Hz, 4'-glu-H-1''), 5.22(1H, t,  $J = 6.8$  Hz, H-24), 5.15(1H, d,  $J = 7.7$  Hz, 20-glu-H-1'''), 4.87(1H, d,  $J = 7.8$  Hz, 6-glu-H-1'), 4.31(1H, m, H-6 $\beta$ ), 4.10(1H, m, H-12 $\alpha$ ), 3.49(1H, dd,  $J = 11.4, 4.7$  Hz, H-3), 3.48(1H, dd,  $J = 11.4, 4.7$  Hz, H-3 $\alpha$ ), 2.01(3H, s, H-28), 1.58(6H, s, H-26, H-27), 1.57(6H, s, H-21, H-29), 1.12(3H, s, H-18), 0.99(3H, s, H-19), 0.76(3H, s, H-30); <sup>13</sup>C-NMR 数据见表1。以上数据与文献[10]基本一致, 鉴定为三七皂苷 N(notoginsenoside N)。

化合物 **10** 白色粉末。ESI-MS  $m/z$  955.5  $[M + Na]^+$ , 931.5  $[M - H]^-$ ; <sup>1</sup>H-NMR (py-*d*<sub>5</sub>, 400 MHz)  $\delta$ : 5.77(1H, d,  $J = 7.2$  Hz, 2'-xyl-H-1''), 5.22(1H, t,  $J = 6.9$  Hz, H-24), 5.16(1H, d,  $J = 7.8$  Hz, 20-glu-H-1'''), 4.91(1H, d,  $J = 7.2$  Hz, 6-glu-H-1'), 4.45(1H, br d,  $J = 10.8$  Hz, 6-glu-Ha-6'), 4.37(1H, t,  $J = 10.5$  Hz, 2'-xyl-H-5''a), 4.30(1H, dd,  $J = 10.8, 3.5$  Hz, H-6 $\beta$ ), 4.29(1H, br d,  $J = 10.8$  Hz, 6-glu-H-6'b), 4.10(1H, m, H-12 $\alpha$ ), 3.65(1H, t,  $J = 10.5$  Hz, 2'-xyl-H-5''b), 3.46(1H, dd,  $J = 11.2, 5.7$  Hz, H-3 $\alpha$ ), 2.06(3H, s, H-28), 1.57(9H, s, H-21, H-26, H-27), 1.45(3H, s, H-29), 1.11(3H, s, H-18), 0.94(3H, s, H-19), 0.77(3H, s, H-30); <sup>13</sup>C-NMR 数据见表1。以上数据与文献[7]基本一致, 鉴定为三七皂

苷 R<sub>1</sub>(notoginsenoside R<sub>1</sub>)。

化合物 **11** 白色粉末。ESI-MS  $m/z$  985.5  $[M + Na]^+$ , 961.5  $[M - H]^-$ ; <sup>1</sup>H-NMR (py-*d*<sub>5</sub>, 400 MHz)  $\delta$ : 5.89(1H, d,  $J = 3.7$  Hz, 3'-glu-H-1''), 5.22(1H, t,  $J = 6.8$  Hz, H-24), 5.16(1H, d,  $J = 7.7$  Hz, 20-glu-H-1'''), 4.92(1H, d,  $J = 7.6$  Hz, 6-glu-H-1'), 4.47(1H, br d,  $J = 12.8$  Hz, 3'-glu-Ha-6''), 4.45(1H, br d,  $J = 12.8$  Hz, 20-glu-Ha-6'''), 4.33(1H, dd,  $J = 10.5, 2.9$  Hz, H-6 $\beta$ ), 4.41(1H, br d,  $J = 12.8$  Hz, 6-glu-Ha-6'), 4.30(1H, br d,  $J = 12.8$  Hz, 3'-glu-H-6''b), 4.28(1H, br d,  $J = 12.8$  Hz, 20-glu-H-6''b), 4.27(1H, br d,  $J = 12.8$  Hz, 6-glu-H-6'b), 4.12(1H, m, H-12 $\alpha$ ), 3.45(1H, dd,  $J = 11.3, 5.4$  Hz, H-3 $\alpha$ ), 1.96(3H, s, H-28), 1.57(3H, s, H-21), 1.56(6H, s, H-26, H-27), 1.50(3H, s, H-29), 1.13(3H, s, H-18), 0.99(3H, s, H-19), 0.77(3H, s, H-30); <sup>13</sup>C-NMR 数据见表1。以上数据与文献[11]基本一致, 鉴定为人参皂苷 Re<sub>2</sub>(ginsenoside Re<sub>2</sub>)。

化合物 **12** 白色粉末。ESI-MS  $m/z$  985.5  $[M + Na]^+$ , 961.5  $[M - H]^-$ ; <sup>1</sup>H-NMR (py-*d*<sub>5</sub>, 400 MHz)  $\delta$ : 5.85(1H, d,  $J = 3.7$  Hz, 3''-glu-H-1'''), 5.20(1H, t,  $J = 6.6$  Hz, H-24), 5.08(1H, d,  $J = 7.6$  Hz, 20-glu-H-1'''), 5.00(1H, d,  $J = 7.6$  Hz, 6-glu-H-1'), 4.50(1H, br d,  $J = 10.7$  Hz, 6-glu-Ha-6'), 4.49(1H, dd,  $J = 10.9, 2.1$  Hz, 3''-glu-H-6''a), 4.39(1H, dd,  $J = 12.8, 3.1$  Hz, 20-glu-H-6''a), 4.37(1H, dd,  $J =$

11.0, 3.8 Hz, H-6 $\beta$ ), 4.35 (1H, br d,  $J = 10.7$  Hz, 6-glu-Ha-6'), 4.25 (1H, br d,  $J = 10.9$  Hz, 3''-glu-Hb-6''), 4.21 (1H, br d,  $J = 12.8$  Hz, 20-glu-Hb-6''), 3.99 (1H, m, H-12 $\alpha$ ), 3.48 (1H, dd,  $J = 11.4, 5.7$  Hz, H-3 $\alpha$ ), 2.05 (3H, s, H-28), 1.58 (9H, s, H-26, H-27, H-29), 1.52 (3H, s, H-21), 1.11 (3H, s, H-18), 0.98 (3H, s, H-19), 0.74 (3H, s, H-30);  $^{13}\text{C-NMR}$  数据见表1。以上数据与文献[11]基本一致, 鉴定为人参皂苷 Re<sub>1</sub> (ginsenoside Re<sub>1</sub>)。

化合物 13 白色粉末。ESI-MS  $m/z$  969.6 [M + Na]<sup>+</sup>, 945.5 [M - H]<sup>-</sup>;  $^1\text{H-NMR}$  (py- $d_5$ , 400 MHz)  $\delta$ : 6.49 (1H, br s, 2'-rha-H-1''), 5.24 (1H, d,  $J = 6.6$  Hz, 6-glu-H-1'), 5.23 (1H, t,  $J = 6.8$  Hz, H-24), 5.16 (1H, d,  $J = 7.8$  Hz, 20-glu-H-1'''), 4.66 (1H, dd,  $J = 9.8, 2.9$  Hz, H-6 $\beta$ ), 4.50 (1H, br d,  $J = 10.9$  Hz, 20-glu-Hb-6'''), 4.47 (1H, br d,  $J = 10.7$  Hz, 6-glu-H-6'a), 4.31 (1H, br d,  $J = 10.7$  Hz, 6-glu-H-6'b), 4.23 (1H, br d,  $J = 10.9$  Hz, 20-glu-H-6''b), 4.11 (1H, m, H-12 $\alpha$ ), 3.44 (1H, dd,  $J = 11.2, 5.0$  Hz, H-3 $\alpha$ ), 2.10 (3H, s, H-28), 1.76 (3H, d,  $J = 6.2$  Hz, 2'-rha-H-6''), 1.58 (3H, s, H-21), 1.57 (6H, s, H-26, H-27), 1.35 (3H, s, H-29), 1.16 (3H, s, H-18), 0.95 (3H, s, H-19), 0.94 (3H, s, H-30);  $^{13}\text{C-NMR}$  数据见表1。以上数据与文献[7]基本一致, 鉴定为人参皂苷 Re (ginsenoside Re)。

化合物 14 白色粉末。ESI-MS  $m/z$  1143.6 [M + Na]<sup>+</sup>, 1119.6 [M - H]<sup>-</sup>;  $^1\text{H-NMR}$  (py- $d_5$ , 400 MHz)  $\delta$ : 5.62 [1H, br s, 6'''-ara (f)-H-1''''], 5.29 (1H, t,  $J = 6.0$  Hz, H-24), 5.28 (1H, d,  $J = 7.4$  Hz, 2'-glu-H-1''), 5.10 (1H, d,  $J = 7.7$  Hz, 20-glu-H-1'''), 4.87 (1H, d,  $J = 7.7$  Hz, 3-glu-H-1'), 4.08 (1H, m, H-12 $\alpha$ ), 3.23 (1H, dd,  $J = 11.4, 4.1$  Hz, H-3), 2.02 (-CH<sub>3</sub>), 1.63 (3H, s, H-27), 1.61 (3H, s, H-21), 1.59 (3H, s, H-26), 1.29 (3H, s, H-28), 1.09 (3H, s, H-29), 0.93 (3H, s, H-30), 0.93 (3H, s, H-19), 0.80 (3H, s, H-18);  $^{13}\text{C-NMR}$  数据见表2。以上数据与文献[12]基本一致, 鉴定为人参皂苷 Rs<sub>2</sub> (ginsenoside Rs<sub>2</sub>)。

化合物 15 白色粉末。ESI-MS  $m/z$  979.5 [M + Na]<sup>+</sup>, 955.5 [M - H]<sup>-</sup>;  $^1\text{H-NMR}$  (py- $d_5$ , 400 MHz)  $\delta$ : 6.31 (1H, d,  $J = 8.0$  Hz, 28-glu-H-1'''), 5.39 (1H, d,  $J = 7.5$  Hz, 2'-glu-H-1''), 5.39 (1H, brs,

H-12), 4.95 (1H, d,  $J = 7.0$  Hz, 3-glu A-H-1'), 4.47 (1H, br d,  $J = 12.0$  Hz, 2''-glu-H-6''a), 4.44 (1H, br d,  $J = 12.0$  Hz, 2''-glu-H-6''b), 4.38 (1H, br d,  $J = 11.5$  Hz, 28-glu-H-6''a), 4.35 (1H, br d,  $J = 11.5$  Hz, 28-glu-H-6''b), 3.70 (3H, s, 6'-OCH<sub>3</sub>), 3.22 (1H, dd,  $J = 12.1, 4.4$  Hz, H-3 $\alpha$ ), 1.24 (3H, s, H-27), 1.22 (3H, s, H-23), 1.06 (6H, s, H-24, H-26), 0.89 (3H, s, H-29), 0.86 (3H, s, H-30), 0.81 (3H, s, H-25);  $^{13}\text{C-NMR}$  (py- $d_5$ , 100 MHz)  $\delta$ : 38.6 (C-1), 26.5 (C-2), 89.3 (C-3), 39.5 (C-4), 55.8 (C-5), 18.5 (C-6), 33.1 (C-7), 39.9 (C-8), 48.0 (C-9), 36.9 (C-10), 23.4 (C-11), 122.8 (C-12), 144.1 (C-13), 42.1 (C-14), 28.2 (C-15), 23.7 (C-16), 47.0 (C-17), 41.7 (C-18), 46.2 (C-19), 30.7 (C-20), 34.0 (C-21), 32.5 (C-22), 28.1 (C-23), 16.7 (C-24), 15.5 (C-25), 17.4 (C-26), 26.1 (C-27), 176.4 (C-28), 23.6 (C-29), 33.1 (C-30), 52.0 (-OCH<sub>3</sub>); 3-glu A,  $\delta$ : 105.3 (C-1'), 82.5 (C-2'), 77.5 (C-3'), 72.8 (C-4'), 76.7 (C-5'), 170.4 (C-6'); 2'-glu,  $\delta$ : 105.9 (C-1''), 77.0 (C-2''), 77.9 (C-3''), 71.7 (C-4''), 78.3 (C-5''), 62.7 (C-6''); 28-glu,  $\delta$ : 95.7 (C-1'''), 74.1 (C-2'''), 79.3 (C-3'''), 71.1 (C-4'''), 78.9 (C-5'''), 62.2 (C-6''')。以上数据与文献[13]基本一致, 鉴定为人参皂苷 Ro 甲酯 (ginsenoside Ro methyl ester)。

化合物 16 白色粉末。ESI-MS  $m/z$  969.5 [M + Na]<sup>+</sup>, 945.5 [M - H]<sup>-</sup>;  $^1\text{H-NMR}$  (py- $d_5$ , 400 MHz)  $\delta$ : 5.35 (1H, d,  $J = 7.4$  Hz, 2'-glu-H-1''), 5.22 (1H, t,  $J = 6.8$  Hz, H-24), 5.17 (1H, d,  $J = 7.8$  Hz, 20-glu-H-1'''), 4.90 (1H, d,  $J = 7.2$  Hz, 3-glu-H-1'), 4.54 (1H, br d,  $J = 11.8$  Hz, 3-glu-H-6'a), 4.47 (1H, br d,  $J = 12.0$  Hz, 2'-glu-H-6'a), 4.46 (1H, br d,  $J = 11.5$  Hz, 20-glu-H-6''a), 4.32 (1H, br d,  $J = 11.8$  Hz, 3-glu-H-6'b), 4.31 (1H, br d,  $J = 12.0$  Hz, 2'-glu-H-6''b), 4.30 (1H, br d,  $J = 11.5$  Hz, 20-glu-H-6''b), 4.08 (1H, m, H-12 $\alpha$ ), 3.24 (1H, dd,  $J = 11.6, 3.5$  Hz, H-3 $\alpha$ ), 1.60 (3H, s, H-21), 1.57 (6H, s, H-26, H-27), 1.26 (3H, s, H-28), 1.08 (3H, s, H-29), 0.93 (6H, s, H-18, H-30), 0.79 (3H, s, H-19);  $^{13}\text{C-NMR}$  数据见表2。以上数据与文献[7]基本一致, 鉴定为人参皂苷 Rd (ginsenoside Rd)。

化合物 17 白色粉末。ESI-MS  $m/z$  985.5

$[M + Na]^+$ , 961.5  $[M - H]^-$ ;  $^1H$ -NMR (py- $d_5$ , 400 MHz)  $\delta$ : 5.87 (1H, d,  $J = 3.7$  Hz, 4''-glu-H-1'''), 5.22 (1H, t,  $J = 6.6$  Hz, H-24), 5.15 (1H, d,  $J = 7.8$  Hz, 20-glu-H-1''), 4.88 (1H, d,  $J = 7.8$  Hz, 6-glu-H-1'), 4.55 (1H, br d,  $J = 10.8$  Hz, 4''-glu-H-6''' a), 4.47 (1H, dd,  $J = 11.8, 2.4$  Hz, 6-glu-H-6' a), 4.40 (1H, m, H-6 $\beta$ ), 4.38 (2H, br d,  $J = 12.5$  Hz, 20-glu-H-6''), 4.35 (1H, br d,  $J = 11.8$  Hz, 6-glu-H-6' a), 4.30 (1H, br d,  $J = 10.8$  Hz, 4''-glu-H-6''' b), 4.12 (1H, m, H-12 $\alpha$ ), 3.49 (1H, dd,  $J = 11.4, 3.9$  Hz, H-3 $\alpha$ ), 2.01 (3H, s, H-28), 1.58 (6H, s, H-26, H-29), 1.56 (6H, s, H-21, 27), 1.13 (3H, s, H-18), 0.99 (3H, s, H-19), 0.77 (3H, s, H-30);  $^{13}C$ -NMR 数据见表1。以上数据与文献[11]基本一致, 鉴定为人参皂苷 Re<sub>3</sub> (ginsenoside Re<sub>3</sub>)。

化合物 18 白色粉末。ESI-MS  $m/z$  955.5  $[M + Na]^+$ , 931.5  $[M - H]^-$ ;  $^1H$ -NMR (py- $d_5$ , 400 MHz)  $\delta$ : 5.65 (1H, br s, 6''-ara(f)-H-1'''), 5.29 (1H, t,  $J = 6.0$  Hz, H-24), 5.10 (1H, d,  $J = 7.6$  Hz, 20-glu-H-1''), 5.01 (1H, d,  $J = 7.8$  Hz, 6-glu-H-1'), 4.66 (1H, dd,  $J = 10.8, 1.7$  Hz, 20-glu-H-6'' a), 4.51 (1H, dd,  $J = 11.7, 2.4$  Hz, 6-glu-H-6' a), 4.41 (1H, 1H, dd,  $J = 10.6, 3.1$  Hz, H-6 $\beta$ ), 4.34 (1H, br d,  $J = 11.7$  Hz, 6-glu-H-6' a), 4.30 (1H, dd,  $J = 11.8, 3.0$  Hz, 6''-ara(f)-H-5''' a), 4.13 (1H, m, H-12 $\alpha$ ), 4.19 (1H, dd,  $J = 11.8, 2.4$  Hz, 6''-ara(f)-H-5''' b), 4.07 (1H, br d,  $J = 10.8$  Hz, 20-glu-H-6''' b), 3.49 (1H, dd,  $J = 11.5, 4.6$  Hz, H-3 $\alpha$ ), 2.05 (3H, s, H-28), 1.63 (3H, s, H-27), 1.59 (9H, s, H-21, 26, 29), 1.14 (3H, s, H-18), 1.01 (3H, s, H-19), 0.77 (3H, s, H-30);  $^{13}C$ -NMR 数据见表1。以上数据与文献[11]基本一致, 鉴定为人参皂苷 Re<sub>4</sub> (ginsenoside Re<sub>4</sub>)。

化合物 19 白色粉末。ESI-MS  $m/z$  985.5  $[M + Na]^+$ , 961.5  $[M - H]^-$ ;  $^1H$ -NMR (py- $d_5$ , 400 MHz)  $\delta$ : 5.92 (1H, d,  $J = 7.2$  Hz, 6-glu-H-1'), 5.22 (1H, t,  $J = 6.2$  Hz, H-24), 5.15 (1H, d,  $J = 7.8$  Hz, 20-glu-H-1'''), 4.88 (1H, d,  $J = 7.6$  Hz, 2'-glu-H-1''), 4.47 (1H, br d,  $J = 12.2$  Hz, 3-glu-H-6' a), 4.46 (1H, br d,  $J = 11.5$  Hz, 20-glu-H-6''' a), 4.45 (1H, br d,  $J = 11.8$  Hz, 2'-glu-H-6'' a), 4.35 (1H, br d,  $J = 12.2$  Hz, 3-glu-H-6' b), 4.33 (1H, 1H, dd,  $J = 11.0, 2.6$  Hz, H-6 $\beta$ ), 4.31 (1H, br d,  $J = 11.8$  Hz, 2'-glu-H-6''' b),

4.28 (1H, br d,  $J = 11.5$  Hz, 20-glu-H-6''' b), 4.08 (1H, m, H-12 $\alpha$ ), 3.44 (1H, dd,  $J = 10.8, 4.3$  Hz, H-3 $\alpha$ ), 2.06 (3H, s, H-28), 1.57 (9H, s, H-26, 27, 29), 1.46 (3H, s, H-21), 1.10 (3H, s, H-18), 0.93 (3H, s, H-19), 0.77 (3H, s, H-30);  $^{13}C$ -NMR 数据见表1。以上数据与文献[14]基本一致, 鉴定为20-葡萄糖基人参皂苷 Rf (20-gluco-ginsenoside Rf)。

化合物 20 白色粉末。ESI-MS  $m/z$  979.5  $[M + Na]^+$ , 955.5  $[M - H]^-$ ;  $^1H$ -NMR (py- $d_5$ , 400 MHz)  $\delta$ : 6.30 (1H, d,  $J = 8.0$  Hz, 28-glu-H-1'''), 5.39 (1H, d,  $J = 7.8$  Hz, 2'-glu-H-1''), 5.39 (1H, brs, H-12), 4.97 (1H, d,  $J = 6.4$  Hz, 3-glu A-H-1'), 4.47 (1H, dd,  $J = 10.2, 2.5$  Hz, 2''-glu-H-6'' a), 4.44 (1H, br d,  $J = 10.2$  Hz, 2''-glu-H-6'' b), 4.38 (1H, dd,  $J = 11.5, 3.9$  Hz, 28-glu-H-6'' a), 4.35 (1H, br d,  $J = 11.5$  Hz, 28-glu-H-6'' b), 3.24 (1H, dd,  $J = 12.4, 4.3$  Hz, H-3 $\alpha$ ), 1.25 (3H, s, H-27), 1.24 (3H, s, H-23), 1.07 (6H, s, H-24, H-26), 0.89 (3H, s, H-29), 0.86 (3H, s, H-30), 0.81 (3H, s, H-25);  $^{13}C$ -NMR (py- $d_5$ , 100 MHz)  $\delta$ : 38.7 (C-1), 26.6 (C-2), 89.2 (C-3), 39.5 (C-4), 55.8 (C-5), 18.5 (C-6), 32.5 (C-7), 39.9 (C-8), 48.0 (C-9), 36.9 (C-10), 23.4 (C-11), 122.8 (C-12), 144.1 (C-13), 42.1 (C-14), 28.2 (C-15), 23.7 (C-16), 47.0 (C-17), 41.7 (C-18), 46.2 (C-19), 30.8 (C-20), 34.0 (C-21), 33.1 (C-22), 28.1 (C-23), 16.7 (C-24), 15.5 (C-25), 17.5 (C-26), 26.1 (C-27), 176.4 (C-28), 23.6 (C-29), 33.1 (C-30); 3-glu A,  $\delta$ : 105.3 (C-1'), 82.8 (C-2'), 77.1 (C-3'), 73.2 (C-4'), 77.7 (C-5'), 172.9 (C-6'); 2'-glu,  $\delta$ : 106.0 (C-1''), 77.9 (C-2''), 78.2 (C-3''), 71.1 (C-4''), 77.9 (C-5''), 62.7 (C-6''); 28-glu,  $\delta$ : 95.7 (C-1'''), 74.1 (C-2'''), 79.3 (C-3'''), 71.6 (C-4'''), 78.9 (C-5'''), 62.2 (C-6''')。以上数据与文献[15]基本一致, 鉴定为人参皂苷 Ro (ginsenoside Ro)。

化合物 21 白色粉末。ESI-MS  $m/z$  1101.6  $[M + Na]^+$ , 1077.6  $[M - H]^-$ ;  $^1H$ -NMR (py- $d_5$ , 400 MHz)  $\delta$ : 5.64 (1H, d,  $J = 1.4$  Hz, 6'''-ara(f)-H-1'''), 5.35 (1H, d,  $J = 7.5$  Hz, 2'-glu-H-1''), 5.29 (1H, t,  $J = 6.8$  Hz, H-24), 5.11 (1H, d,  $J = 7.7$  Hz, 20-glu-H-1'''), 4.89 (1H, d,  $J = 7.5$  Hz, 3-glu-H-1'), 4.65 (1H, dd,  $J = 10.8, 2.0$  Hz, 20-glu-H-6''' a), 4.55



(1H, br d,  $J = 11.2$  Hz, 2'-glu-H-6''a), 4.47 (1H, br d,  $J = 11.3$  Hz, 3-glu-H-6'a), 4.34 (1H, br d,  $J = 11.3$  Hz, 3-glu-H-6'b), 4.32 [1H, br d,  $J = 10.9$  Hz, 6''-ara(f)-H-5'''a], 4.30 (1H, br d,  $J = 11.2$  Hz, 2'-glu-H-6''b), 4.28 (1H, br d,  $J = 10.8$  Hz, 20-glu-H-6'''b), 4.20 [1H, br d,  $J = 10.9$  Hz, 6''-ara(f)-H-5'''b], 4.09 (1H, m, H-12 $\alpha$ ), 3.24 (1H, dd,  $J = 11.6, 4.2$  Hz, H-3 $\alpha$ ), 1.64 (3H, s, H-27), 1.61 (3H, s, H-26), 1.59 (3H, s, H-21), 1.26 (3H, s, H-28), 1.08 (3H, s, H-29), 0.93 (3H, s, H-30), 0.92 (3H, s, H-18), 0.78 (3H, s, H-19);  $^{13}\text{C-NMR}$  数据见表2。以上数据与文献[16]基本一致, 鉴定为人参皂苷 Rc (ginsenoside Rc)。

化合物 22 白色粉末。ESI-MS  $m/z$  1 173.6 [M + Na] $^+$ , 1 149.6 [M - H] $^-$ ;  $^1\text{H-NMR}$  (py- $d_5$ , 400 MHz)  $\delta$ : 5.30 (1H, d,  $J = 7.5$  Hz, 2'-glu-H-1''), 5.29 (1H, t,  $J = 6.4$  Hz, H-24), 5.11 (1H, d,  $J = 7.8$  Hz, 20-glu-H-1'''), 5.08 (1H, d,  $J = 7.7$  Hz, 6'''-glu-H-1''''), 4.88 (1H, d,  $J = 8.0$  Hz, 3-glu-H-1'), 4.29 (1H, m, H-12 $\alpha$ ), 3.24 (1H, dd,  $J = 11.6, 4.0$  Hz, H-3 $\alpha$ ), 2.02 (3H, s, Ac-CH $_3$ ), 1.63 (6H, s, H-26, 27), 1.58 (3H, s, H-21), 1.30 (3H, s, H-28), 1.10 (3H, s, H-29), 0.94 (6H, s, H-18, 30), 0.81 (3H, s, H-19);  $^{13}\text{C-NMR}$  数据见表2。以上数据与文献[17]基本一致, 鉴定为西洋参皂苷 R $_1$  (quinquenoside R $_1$ )。

化合物 23 白色粉末。ESI-MS  $m/z$  1 233.6 [M + Na] $^+$ , 1 209.6 [M - H] $^-$ ;  $^1\text{H-NMR}$  (py- $d_5$ , 400 MHz)  $\delta$ : 5.70 [1H, br s, 6'''-ara(f)-H-1''''], 5.34 (1H, d,  $J = 7.6$  Hz, 2'-glu-H-1''), 5.29 (1H, t,  $J = 6.4$  Hz, H-24), 5.12 (1H, d,  $J = 7.5$  Hz, 20-glu-H-1'''), 5.08 (1H, d,  $J = 7.4$  Hz, 2'''-xyl-H-1''''), 4.89 (1H, d,  $J = 7.6$  Hz, 3-glu-H-1'), 4.19 (1H, m, H-12 $\alpha$ ), 3.23 (1H, dd,  $J = 11.6, 3.8$  Hz, H-3 $\alpha$ ), 1.65 (6H, s, H-26, H-27), 1.57 (3H, s, H-21), 1.25 (3H, s, H-28), 1.07 (3H, s, H-29), 0.92 (6H, s, H-18, H-30), 0.78 (3H, s, H-19);  $^{13}\text{C-NMR}$  数据见表2。以上数据与文献[18]基本一致, 鉴定为人参皂苷 Ra $_2$  (ginsenoside Ra $_2$ )。

化合物 24 白色粉末。ESI-MS  $m/z$  1 131.6 [M + Na] $^+$ , 1 107.6 [M - H] $^-$ ;  $^1\text{H-NMR}$  (py- $d_5$ , 400 MHz)  $\delta$ : 5.34 (1H, d,  $J = 7.6$  Hz, 2'-glu-H-1''), 5.29 (1H, t,  $J = 6.6$  Hz, H-24), 5.10 (1H, d,  $J = 7.8$  Hz, 20-glu-H-1'''), 5.07 (1H, d,  $J = 7.7$  Hz, 6'''-glu-H-

1''''), 4.89 (1H, d,  $J = 7.5$  Hz, 3-glu-H-1'), 4.29 (1H, m, H-12 $\alpha$ ), 3.24 (1H, dd,  $J = 11.6, 4.2$  Hz, H-3 $\alpha$ ), 1.64 (6H, s, H-26, 27), 1.59 (3H, s, H-21), 1.26 (3H, s, H-28), 1.09 (3H, s, H-29), 0.94 (6H, s, H-18, H-30), 0.80 (3H, s, H-19);  $^{13}\text{C-NMR}$  数据见表2。以上数据与文献[16]基本一致, 鉴定为人参皂苷 Rb $_1$  (ginsenoside Rb $_1$ )。

化合物 25 白色粉末。ESI-MS  $m/z$  1 233.6 [M + Na] $^+$ , 1 209.6 [M - H] $^-$ ;  $^1\text{H-NMR}$  (py- $d_5$ , 400 MHz)  $\delta$ : 5.35 (1H, d,  $J = 7.4$  Hz, 2'-glu-H-1''), 5.28 (1H, t,  $J = 6.8$  Hz, H-24), 5.09 (1H, d,  $J = 7.4$  Hz, 20-glu-H-1'''), 5.09 (1H, d,  $J = 7.4$  Hz, 4'''-xyl-H-1''''), 4.91 [1H, d,  $J = 5.7$  Hz, 6'''-ara(p)-H-1''''], 4.90 (1H, d,  $J = 5.9$  Hz, 3-glu-H-1'), 4.20 (1H, m, H-12 $\alpha$ ), 3.24 (1H, dd,  $J = 11.4, 4.1$  Hz, H-3 $\alpha$ ), 1.63 (3H, s, H-27), 1.62 (3H, s, H-26), 1.59 (3H, s, H-21), 1.26 (3H, s, H-28), 1.08 (3H, s, H-29), 0.95 (3H, s, H-30), 0.93 (3H, s, H-18), 0.78 (3H, s, H-19);  $^{13}\text{C-NMR}$  数据见表2。以上数据与文献[18]基本一致, 鉴定为人参皂苷 Ra $_1$  (ginsenoside Ra $_1$ )。

化合物 26 白色粉末。ESI-MS  $m/z$  1263.6 [M + Na] $^+$ , 1239.6 [M - H] $^-$ ;  $^1\text{H-NMR}$  (py- $d_5$ , 400 MHz)  $\delta$ : 5.35 (1H, d,  $J = 7.6$  Hz, 2'-glu-H-1''), 5.31 (1H, t,  $J = 6.8$  Hz, H-24), 5.26 (1H, d,  $J = 7.6$  Hz, 6'''-glu-H-1''''), 5.10 (1H, d,  $J = 7.6$  Hz, 3'''-xyl-H-1''''), 5.10 (1H, d,  $J = 7.6$  Hz, 20-glu-H-1'''), 4.90 (1H, d,  $J = 7.5$  Hz, 3-glu-H-1'), 4.20 (1H, m, H-12 $\alpha$ ), 3.24 (1H, dd,  $J = 11.4, 4.2$  Hz, H-3 $\alpha$ ), 1.65 (3H, s, H-27), 1.63 (3H, s, H-26), 1.60 (3H, s, H-21), 1.26 (3H, s, H-28), 1.08 (3H, s, H-29), 0.94 (6H, s, H-18, H-30), 0.81 (3H, s, H-19);  $^{13}\text{C-NMR}$  数据见表2。以上数据与文献[19]基本一致, 鉴定为人参皂苷 Ra $_3$  (ginsenoside Ra $_3$ )。

化合物 27 白色粉末。ESI-MS  $m/z$  1 101.6 [M + Na] $^+$ , 1 077.6 [M - H] $^-$ ;  $^1\text{H-NMR}$  (py- $d_5$ , 400 MHz)  $\delta$ : 5.34 (1H, d,  $J = 7.6$  Hz, 2'-glu-H-1''), 5.29 (1H, t,  $J = 6.3$  Hz, H-24), 5.11 (1H, d,  $J = 7.7$  Hz, 20-glu-H-1'''), 4.97 [1H, d,  $J = 6.0$  Hz, 6'''-ara(p)-H-1''''], 4.89 (1H, d,  $J = 7.5$  Hz, 3-glu-H-1'), 4.09 (1H, m, H-12 $\alpha$ ), 3.23 (1H, dd,  $J = 11.5, 4.0$  Hz, H-3 $\alpha$ ), 1.62 (3H, s, H-27), 1.61 (3H, s, H-26), 1.59 (3H, s, H-21), 1.25 (3H, s, H-28), 1.07 (3H, s, H-29), 0.92

(6H, s, H-18, 30), 0.78 (3H, s, H-19);  $^{13}\text{C}$ -NMR 数据见表2。以上数据与文献[16]基本一致, 鉴定为人参皂苷  $\text{Rb}_2$  (ginsenoside  $\text{Rb}_2$ )。

化合物 **28** 白色粉末。ESI-MS  $m/z$  1 263.6  $[\text{M} + \text{Na}]^+$ , 1 239.7  $[\text{M} - \text{H}]^-$ ;  $^1\text{H}$ -NMR (py- $d_5$ , 400 MHz)  $\delta$ : 5.35 (1H, d,  $J = 7.6$  Hz, 2'-glu-H-1''), 5.28 (1H, t,  $J = 6.5$  Hz, H-24), 5.11 (1H, d,  $J = 7.7$  Hz, 20-glu-H-1'''), 4.93 (1H, d,  $J = 7.5$  Hz, 6'''-xyl-1'''''), 4.90 (1H, d,  $J = 7.7$  Hz, 3-glu-H-1'), 4.90 (1H, d,  $J = 7.7$  Hz, 6'''-glu-H-1'''''), 4.20 (1H, m, H-12 $\alpha$ ), 3.24 (1H, dd,  $J = 11.5, 3.6$  Hz, H-3 $\alpha$ ), 1.63 (3H, s, H-27), 1.61 (3H, s, H-26), 1.58 (3H, s, H-21), 1.26 (3H, s, H-28), 1.08 (3H, s, H-29), 0.94 (3H, s, H-30), 0.93 (3H, s, H-18), 0.79 (3H, s, H-19);  $^{13}\text{C}$ -NMR数据见表2。以上数据与文献[20]基本一致, 鉴定为三七皂苷  $\text{R}_4$  (notoginsenoside  $\text{R}_4$ )。

#### 4 结论与讨论

上述28个化合物中, 化合物**1**为首次从吉林栽培人参根和根茎中分离得到, 化合物**6**为首次从人参根和根茎中分离得到; 本文并首次对化合物**6**, **14**, **19**的氢谱信号进行了归属。另有意义的是近年从传统中药三七(Notoginseng Radix et Rhizoma)亦分离鉴定出化合物**1**[<sup>21-22</sup>]。人参属植物可分为2个类群: 第一类群根状茎短而通常直立, 具胡萝卜状肉质根; 在地理分布上以分布区狭小和间断为特征; 在化学成分上以含达玛烷型四环三萜皂苷元的皂苷为主, 如人参、西洋参 *P. quinquefolium* L.、三七 *P. notoginseng* (Burk.) F. H. Chen 等是这一类群的代表性植物, 是人参属的古老类群。第二类群根状茎长而匍匐, 肉质根常不发达或无; 在地理分布上以分布区较广而连续为特征; 在化学成分上以含齐墩果烷型五环三萜皂苷元的皂苷为主, 是人参属的进化类群, 代表性植物如姜状三七 *P. zingiberensis* C. Y. Wu et K. M. Feng、屏边三七 *P. stipuleanatus* H. T. Tsai et K. M. Feng、竹节参 *P. japonicus* C. A. Mey. 及其变种狭叶竹节参 *P. japonicus* C. A. Mey. var. *angustifolius* (Burk.) Cheng et Chun 和珠子参 *P. japonicus* C. A. Mey. var. *major* (Burk.) C. Y. Wu et K. M. Feng 等。本文从人参分离得到化合物**1**, 为人参属植物第一类群的化学分类提供了一定的佐证; 亦提示韩国产高丽参与吉林产人参内在物质基础的一致性。

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## Chemical constituents from the roots and rhizomes of *Panax ginseng* cultivated in Jilin province

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[Abstract] The chemical constituents of the roots and rhizomes of *Panax ginseng* were systematically investigated by various column chromatographic methods including Amberlite XAD-4 macroporous adsorptive resins and silica gel as well as high-performance liquid chromatography, and their chemical structures were identified by physico-chemical properties and spectral analyses. Twenty-eight compounds were isolated from the 70% ethanolic-aqueous extract and identified as koryoginsenoside R<sub>1</sub> (**1**), ginsenoside R<sub>g</sub> (**2**), ginsenoside R<sub>f</sub> (**3**), notoginsenoside R<sub>2</sub> (**4**), ginsenoside R<sub>g</sub><sub>2</sub> (**5**), notoginsenoside Fe (**6**), ginsenjilanol (**7**), ginsenoside R<sub>e</sub><sub>5</sub> (**8**), notoginsenoside N (**9**), notoginsenoside R<sub>1</sub> (**10**), ginsenoside R<sub>e</sub><sub>2</sub> (**11**), ginsenoside R<sub>e</sub><sub>1</sub> (**12**), ginsenoside R<sub>e</sub> (**13**), ginsenoside R<sub>s</sub><sub>2</sub> (**14**), ginsenoside R<sub>o</sub> methyl ester (**15**), ginsenoside R<sub>d</sub> (**16**), ginsenoside R<sub>e</sub><sub>3</sub> (**17**), ginsenoside R<sub>e</sub><sub>4</sub> (**18**), 20-gluco-ginsenoside R<sub>f</sub> (**19**), ginsenoside R<sub>o</sub> (**20**), ginsenoside R<sub>c</sub> (**21**), quinquenoside-R<sub>1</sub> (**22**), ginsenoside R<sub>a</sub><sub>2</sub> (**23**), ginsenoside R<sub>b</sub><sub>1</sub> (**24**), ginsenoside R<sub>a</sub><sub>1</sub> (**25**), ginsenoside R<sub>a</sub><sub>3</sub> (**26**), ginsenoside R<sub>b</sub><sub>2</sub> (**27**), and notoginsenoside R<sub>4</sub> (**28**). All isolated compounds are 20(*S*)-protopanaxadiol or protopanaxatriol type triterpenoid saponins. Compound **1** was isolated from the roots and rhizomes of *P. ginseng* cultivated in Jilin province for the first time and compound **6** was isolated from the roots and rhizomes of *P. ginseng* for the first time. The <sup>1</sup>H-NMR data of compounds **6**, **14** and **19** were assigned for the first time.

[Key words] *Panax ginseng*; chemical constituents; notoginsenoside Fe; ginsenoside R<sub>s</sub><sub>2</sub>; 20-gluco-ginsenoside R<sub>f</sub>

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