

地榆水溶性化学成分研究(II)

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摘要: 目的 研究地榆 *Sanguisorba officinalis* 水溶性化学成分。方法 采用大孔树脂(D101、HP-20)、透析袋、Toyopearl HW-40、反相硅胶 RP₁₈ 等柱色谱方法进行分离纯化, 并运用 ¹H-NMR、¹³C-NMR、ESI-MS 等多种波谱方法对化合物进行结构鉴定。结果 从地榆 10%乙醇部位中分离并鉴定了 25 个化合物, 分别为 4-(4'-hydroxyphenyl)-2-butanone-4'-O-β-D-glucopyranoside (1)、phenethanol-β-vicianoside (2)、junipetriolside A (3)、citroside A (4)、corchoionoside C (5)、adenosine (6)、tryptophan (7)、tachinoside (8)、d-mandelic acid-β-D-glucopyranoside (9)、(+)-(7S,8S)-guaiacylglycerol 8-O-β-D-glucopyranoside (10)、biophenol (11)、3,5-dihydroxyphenethyl alcohol 3-O-β-glucopyranoside (12)、syringin (13)、(2E,5E)-3,7-dimethyl-2,5-octadiene-1,7-diol (14)、(±)-3-hydroxy-3,7-dimethyloct-6-enoic acid (15)、(2Z)-2,6-dimethyl-2,7-octadiene-1,6-diol (16)、phlorizin (17)、(+)-cyclo-olivil-6-O-β-D-glucopyranoside (18)、5'-methoxy-8'-hydroxyl-(+)-isolariciresinol-4'-O-β-D-glucopyranoside (19)、phenethyl-6-O-α-L-arabinofuranosyl-β-D-glucoside (20)、gaultherin (21)、benzyl-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (22)、(2E)-7-hydroxy-3,7-dimethyl-2-octenyl-6-O-α-L-arabinofuranosyl-β-D-glucopyranoside (23)、3,3',4'-tri-O-methylelagic acid (24)、methyl-4-(β-D-glucopyranosyloxy)-3-hydroxy-5-methoxybenzoate (25)。结论 化合物 1~22 为首次从该植物中分离得到。

关键词: 地榆; 水溶性; junipetriolside A; citroside A; corchoionoside C

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Hydrosoluble chemical constituents in *Sanguisorba officinalis* (II)

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Abstract: Objective To study the chemical constituents in extract of *Sanguisorba officinalis*. **Methods** Compounds were isolated from 10% ethanol extracts by Macroporous resin (D101, HP-20), dialysis bag, reversed phase silica gel (RP₈, RP₁₈), Toyopearl HW-40 column chromatography and their structures were elucidated by NMR and MS data. **Results** Twenty-five compounds were isolated and their structures were elucidated as 4-(4'-hydroxyphenyl)-2-butanone-4'-O-β-D-glucopyranoside (1), phenethanol-β-vicianoside (2), junipetriolside A (3), citroside A (4), corchoionoside C (5), adenosine (6), tryptophan (7), tachinoside (8), d-mandelic acid-β-D-glucopyranoside (9), (+) (7S,8S)-guaiacylglycerol 8-O-β-D-glucopyranoside (10), biophenol (11), 3,5-dihydroxyphenethyl alcohol 3-O-β-glucopyranoside (12), syringin (13), (2E,5E)-3,7-dimethyl-2,5-octadiene-1,7-diol (14), (±)-3-hydroxy-3,7-dimethyloct-6-enoic acid (15), (2Z)-2,6-dimethyl-2,7-octadiene-1,6-diol (16), phlorizin (17), (+)-cyclo-olivil 6-O-β-D-glucopyranoside (18), 5'-methoxy-8'-hydroxyl-(+)-isolariciresinol-4'-O-β-D-glucopyranoside (19), phenethyl 6-O-α-L-arabinofuranosyl-β-D-glucoside (20), gaultherin (21), benzyl-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (22), (2E)-7-hydroxy-3,7-dimethyl-2-octenyl 6-O-α-L-arabinofuranosyl-β-D-glucopyranoside (23), 3,3',4'-tri-O-methylelagic acid (24), and methyl-4-(β-D-glucopyranosyloxy)-

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3-hydroxy-5-methoxybenzoate (25). **Conclusion** Compounds 1—22 were isolated from this plant for the first time.

Key words: *Sanguisorba officinalis* L.; hydrosolubility; junipetriolide A; citroside A; corchoionoside C

地榆来源于蔷薇科植物地榆 *Sanguisorba officinalis* L. 或长叶地榆 *S. officinalis* L. var. *longifolia* (Bert.) Yu et Li 的干燥根。其性微寒, 味苦、酸、涩, 归肝、大肠经。具有凉血止血、解毒敛疮的功效。地榆属植物在世界范围内 30 多种, 我国共 7 种, 是一种常用中药。研究发现, 地榆中含有丰富的营养物质和生理活性成分, 主要为鞣质、皂苷、黄酮类化合物, 尤以鞣质含量丰富。前期研究确定地榆 70%乙醇提取物经大孔吸附树脂分离的 30%、20%乙醇洗脱组分中主要含有酚苷类、皂苷类、木脂素类成分^[1-3], 前期的药理研究表明地榆具有很强的升高白细胞的作用, 为了进一步阐明其药效物质基础, 本实验对地榆根水溶性部位进行了系统的化学成分研究并分离得到 25 个化合物, 分别鉴定为 4-(4'-hydroxyphenyl)-2-butanone-4'-O- β -D-glucopyranoside (1)、phenethanol- β -vicianoside (2)、junipetriolide A (3)、citroside A (4)、corchoionoside C (5)、adenosine (6)、tryptophan (7)、tachinoside (8)、*d*-mandelic acid- β -D-glucopyranoside (9)、(+)-(7*S*,8*S*)-guaiacylglycerol 8-O- β -D-glucopyranoside (10)、biophenol (11)、3,5-dihydroxyphenethyl-alcohol 3-O- β -D-glucopyranoside (12)、syringin (13)、(2*E*,5*E*)-3,7-dimethyl-2,5-octadiene-1,7-diol (14)、($\pm$)-3-hydroxy-3,7-dimethyloct-6-enoic acid (15)、(2*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol (16)、phlorizin (17)、(+)-cyclo-olivil-6-O- β -D-glucopyranoside (18)、5'-methoxy-8'-hydroxyl-(+)-isolariciresinol-4'-O- β -D-glucopyranoside (19)、phenethyl-6-O- α -L-arabinofuranosyl- β -D-glucoside (20)、gaultherin (21)、benzyl-O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- β -D-glucopyranoside (22)、(2*E*)-7-hydroxy-3,7-dimethyl-2-octenyl-6-O- α -L-arabinofuranosyl- β -D-glucopyranoside (23)、3,3',4'-tri-O-methylelagic acid (24)、methyl-4-(β -D-glucopyranosyloxy)-3-hydroxy-5-methoxybenzoate (25)。其中, 化合物 1~22 为首次从该植物中分离得到。

1 仪器与材料

试剂均为分析纯 (成都科龙化工试剂厂); Toyopearl HW-40 (日本 Tosoh 公司); Diaion HP-20 (日本三菱公司); Dubhe C₁₈ (250 mm $\times$ 20 mm, 10

μ m, 江苏汉邦科技有限公司); YMC pack ODS-A (250 mm $\times$ 10 mm, 5 μ m, 日本 YMC 公司); 十万分之一电子天平 (瑞士奥豪斯 DV-215-CD, 上海顾村电光仪器厂); KQ-600DE 型数控超声波清洗器 (40 kHz, 600 W, 昆山市超声仪器有限公司); ZF-90 型暗箱式紫外透射仪 (上海顾村电光仪器厂); Bruker AM-400 型核磁共振仪 (德国 Bruker 公司); Micromass Xevo Triple-quadrupole 型质谱仪 (Waters 公司); 优普 UPT 系列超纯水器 (成都优普电子产品有限公司); NU3000 Serials UV/VIS 检测器、NP 7000 Serials 泵 (Hanbon Sci & Tech.)。

植物样品由成都地奥集团天府药业股份有限公司提供, 经成都中医药大学药学院中药鉴定教研室龙飞副教授鉴定为蔷薇科地榆属多年生草本植物地榆 *Sanguisorba officinalis* L.。标本 (20150920) 存放于成都中医药大学药学院中药化学实验室。

2 提取与分离

地榆干燥切片 10 kg, 粉碎, 经 33 倍量 70%乙醇渗漉提取, 旋转蒸干得浸膏 (3.75 kg)。将浸膏分散于水中, 过 D101、HP-20 大孔树脂柱, 乙醇-水 (0、10%、20%、30%、40%、50%、100%) 梯度洗脱, 将 10%乙醇洗脱部分 (120.0 g) 经透析袋, 再经 HPD-400 柱、MCI 柱、制备色谱 Dubhe C₁₈ (250 mm $\times$ 20 mm, 10 μ m, 江苏汉邦科技有限公司)、半制备色谱 YMC pack ODS-A (250 mm $\times$ 10 mm, 5 μ m, 日本 YMC 公司), 分离纯化得到化合物 1 (12.0 mg, 20 : 80, t_R =25 min)、2 (4.7 mg, 30 : 70, t_R =26 min)、3 (4.1 mg, 10 : 90, t_R =30 min)、4 (8.8 mg, 30 : 70, t_R =18 min)、5 (16.3 mg, 30 : 70, t_R =17 min)、6 (1.8 mg, 10 : 90, t_R =25 min)、7 (1.4 mg, 30 : 70, t_R =13 min)、8 (1.2 mg, 8 : 92, t_R =14 min)、9 (1.8 mg, 10 : 90, t_R =18 min)、10 (15.2 mg, 6 : 94, t_R =24 min)、11 (2.0 mg, 10 : 90, t_R =28 min)、12 (49.0 mg, 8 : 92, t_R =37 min)、13 (4.6 mg, 20 : 80, t_R =23 min)、14 (22.6 mg, 35 : 65, t_R =73 min)、15 (22.6 mg, 35 : 65, t_R =75 min)、16 (12.8 mg, 25 : 75, t_R =12 min)、17 (14.0 mg, 40 : 60, t_R =30 min)、18 (11.4 mg, 20 : 80, t_R =17 min)、19 (9.3 mg, 20 : 80, t_R =31 min)、20 (38.0 mg, 35 : 65, t_R =17 min)、21

(2.3 mg, 25 : 75, t_R = 26 min)、**22** (15.8 mg, 35 : 65, t_R = 13 min)、**23** (52.8 mg, 40 : 60, t_R = 18 min)、**24** (8.2 mg, 40 : 60, t_R = 16 min)、**25** (3.5 mg, 30 : 70, t_R = 20 min)。

3 结构鉴定

化合物**1**: 无色片状结晶(甲醇)。ESI-MS m/z : 325 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 7.17 (2H, d, J = 8.6 Hz, H-7, 9), 7.06 (2H, d, J = 8.6 Hz, H-6, 10), 4.91 (1H, d, J = 7.8 Hz, H-1'), 3.94 (1H, dd, J = 12.0, 1.9 Hz, H-6'a), 3.75 (1H, dd, J = 12.0, 5.1 Hz, H-6'b), 3.55~3.42 (4H, m, H-2'~5'), 2.90~2.77 (4H, m, H-3, 4), 2.17 (3H, s, H-1); ^{13}C -NMR (100 MHz, CD_3OD) δ : 30.0 (C-1), 30.0 (C-3), 46.0 (C-4), 62.5 (C-6'), 71.4 (C-4'), 74.9 (C-2'), 78.0 (C-5'), 78.1 (C-3'), 102.5 (C-1'), 117.8 (C-7, 9), 130.2 (C-6, 10), 136.4 (C-5), 157.5 (C-8), 211.1 (C-2)。以上数据与文献报道基本一致^[4], 故鉴定化合物**1**为4-(4'-hydroxyphenyl)-2-butanone-4'- O - β -D-glucopyranoside。

化合物**2**: 白色粉末。ESI-MS m/z : 413 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 7.32 (4H, d, J = 8.0 Hz, H-2, 3, 5, 6), 7.23 (1H, m, H-4), 4.36 (2H, d, J = 7.4 Hz, H-1', 1''), 3.77 (2H, d, J = 5.7 Hz, H-8), 2.99 (2H, t, J = 7.3 Hz, H-7); ^{13}C -NMR (100 MHz, CD_3OD) δ : 37.2 (C-7), 66.7 (C-5''), 69.5 (C-6'), 71.6 (C-4''), 71.8 (C-5'), 72.4 (C-4'), 74.2 (C-2''), 75.1 (C-2'), 76.9 (C-3''), 78.0 (C-3'), 104.4 (C-1''), 105.1 (C-1'), 127.2 (C-4), 129.4 (C-2, 6), 130.0 (C-3, 5), 140.1 (C-1)。以上数据与文献报道基本一致^[5], 故鉴定化合物**2**为phenethanol- β -vicianoside。

化合物**3**: 无定形粉末。ESI-MS m/z : 376 $[M+NH_4]^+$; 1H -NMR (400 MHz, CD_3OD) δ : 7.01 (1H, s, H-2), 6.88 (1H, d, J = 8.0 Hz, H-6), 6.80 (1H, d, J = 8.0 Hz, H-5), 4.61 (1H, d, J = 7.7 Hz, H-1'), 4.46 (1H, d, J = 9.5 Hz, H-7), 3.92 (1H, d, J = 12.0 Hz, H-6'a), 3.88 (3H, s, $-OCH_3$), 3.85~3.78 (1H, m, H-8), 3.74 (1H, dd, J = 12.0, 2.4 Hz, H-6'b), 3.60 (1H, d, J = 9.0 Hz, H-3'), 3.48 (1H, m, H-5'), 3.45 (1H, dd, J = 12.0, 5.2 Hz, H-9b), 3.39 (1H, m, H-4'), 3.38 (1H, dd, J = 12.0, 5.2 Hz, H-9a), 3.22~3.13 (1H, m, H-2'); ^{13}C -NMR (100 MHz, CD_3OD) δ : 56.4 ($-OCH_3$), 62.1 (C-9), 62.6 (C-6'), 71.9 (C-4'), 75.1 (C-3'), 79.8 (C-5'), 80.2 (C-7), 80.8 (C-2'), 82.7 (C-8), 99.8 (C-1'), 112.4 (C-2), 116.1 (C-5), 121.9 (C-6), 130.1 (C-1), 148.1

(C-4), 149.0 (C-3)。以上数据与文献报道基本一致^[6], 故鉴定化合物**3**为junipetriolside A。

化合物**4**: 淡黄色油状物。Molish 反应为阳性, 推测有糖苷的存在。ESI-MS m/z : 409 $[M+Na]^+$, 795 $[2M+Na]^+$, 确定化合物的相对分子质量为386, 结合 1H -NMR和 ^{13}C -NMR推测其分子式为 $C_{19}H_{30}O_8$, 不饱和度为5。 1H -NMR (400 MHz, CD_3OD) δ : 5.95 (1H, m, H-1'), 4.58 (1H, s, H-8), 4.32 (1H, m, H-3), 3.63 (1H, m, H-6'), 3.80 (1H, m, H-6'), 3.24~3.38 (3H, m, H-3'~5'), 3.16 (1H, m, H-2'), 2.54 (1H, d, J = 11.6 Hz, H-2), 2.25 (3H, s, H-10), 1.97 (1H, d, J = 12.5 Hz, H-4), 1.53 (3H, s, H-13), 1.44 (3H, s, H-11), 1.36 (1H, m, H-2), 1.91 (1H, m, H-4), 1.16 (3H, s, H-12); ^{13}C -NMR (100 MHz, CD_3OD) δ : 26.6 (C-13), 26.7 (C-10), 30.0 (C-12), 37.0 (C-1), 47.9 (C-4), 49.7 (C-2), 62.9 (C-6'), 63.8 (C-3), 71.7 (C-4'), 75.3 (C-2'), 77.8 (C-5'), 78.6 (C-3'), 78.7 (C-5), 98.7 (C-1'), 101.4 (C-8), 119.1 (C-6), 200.7 (C-9), 212.9 (C-7)。以上数据与文献报道基本一致^[7], 故鉴定化合物**4**为citroside A。

化合物**5**: 白色粉末。ESI-MS m/z : 385 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 6.03 (1H, dd, J = 15.6, 0.7 Hz, H-7), 5.95 (1H, m, H-4), 5.79 (1H, dd, J = 15.6, 7.2 Hz, H-8), 4.59 (1H, q, J = 6.7 Hz, H-9), 4.34 (1H, d, J = 7.7 Hz, H-1'), 3.91 (1H, dd, J = 11.9, 2.3 Hz, H-6'), 3.70 (1H, dd, J = 11.9, 6.1 Hz, H-6'), 3.38~3.17 (4H, m, H-2'~5'), 2.67 (1H, d, J = 16.9 Hz, H-2), 2.24 (1H, d, J = 16.9 Hz, H-2), 1.99 (3H, d, J = 1.3 Hz, H-11), 1.35 (3H, d, J = 6.5 Hz, H-10), 1.10 (3H, s, H-12), 1.08 (3H, s, H-13); ^{13}C -NMR (100 MHz, CD_3OD) δ : 19.6 (C-11), 22.2 (C-10), 23.5 (C-12), 24.7 (C-13), 42.4 (C-1), 50.7 (C-2), 62.8 (C-6'), 71.7 (C-4'), 74.6 (C-9), 74.9 (C-2'), 78.2 (C-5'), 78.4 (C-3'), 80.0 (C-6), 101.3 (C-1'), 127.1 (C-4), 133.7 (C-7), 133.7 (C-8), 167.1 (C-5), 201.3 (C-3)。以上数据与文献报道基本一致^[8], 故鉴定化合物**5**为corchoionoside C。

化合物**6**: 白色粉末。ESI-MS m/z : 268 $[M-H]^-$; 1H -NMR (400 MHz, $DMSO-d_6$) δ : 8.34 (1H, s, H-8), 8.13 (1H, s, H-2), 7.31 (2H, brd, $-NH_2$), 5.87 (1H, d, J = 6.1 Hz, Rib-H-1); ^{13}C -NMR (100 MHz, $DMSO-d_6$) δ : 61.7 (Rib-C-5), 70.6 (Rib-C-3), 73.4 (Rib-C-4), 85.9 (Rib-C-2), 87.9 (Rib-C-1), 119.3

(C-5), 139.9 (C-6), 149.1 (C-8), 152.4 (C-2), 156.1 (C-4)。以上数据与文献报道基本一致^[9], 故鉴定化合物 **6** 为 adenosine。

化合物 **7**: 白色粉末。ESI-MS m/z : 203 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 7.53 (1H, d, $J = 8.0$ Hz, H-4), 7.39 (1H, d, $J = 8.0$ Hz, H-7), 7.18 (1H, d, $J = 7.0$ Hz, H-6), 7.18 (1H, s, H-2), 7.10 (1H, d, $J = 7.0$ Hz, H-5), 4.00 (1H, m, H-2'), 3.53 (1H, m, H-1'a), 3.02 (1H, m, H-1'b), 1.79 (2H, d, $J = 6.7$ Hz, $-NH_2$); ^{13}C -NMR (100 MHz, CD_3OD) δ : 24.4 (C-1'), 59.8 (C-2'), 107.9 (C-3), 112.3 (C-7), 119.2 (C-4), 120.6 (C-5), 123.3 (C-3), 123.3 (C-3a), 127.6 (C-2), 138.6 (C-7a), 174.5 ($-COOH$)。以上数据与文献报道基本一致^[10], 故鉴定化合物 **7** 为 tryptophan。

化合物 **8**: 无色针晶 (甲醇)。ESI-MS m/z : 303 $[M+H]^+$; mp 208~210 $^{\circ}C$ 。 1H -NMR (400 MHz, CD_3OD) δ : 6.82 (1H, d, $J = 2.6$ Hz, H-2), 6.71 (1H, d, $J = 8.6$ Hz, H-5), 6.60 (1H, dd, $J = 8.6, 2.5$ Hz, H-6), 4.76 (1H, d, $J = 7.3$ Hz, H-1'), 3.94 (2H, m, H-6'), 3.84 (3H, s, $-OCH_3$), 3.85 (4H, m, H-2'~5'); ^{13}C -NMR (100 MHz, CD_3OD) δ : 56.4 (3- OCH_3), 62.7 (C-6'), 71.6 (C-4'), 75.0 (C-2'), 78.1 (C-5', 3'), 103.8 (C-1'), 103.8 (C-2), 110.0 (C-6), 116.0 (C-5), 143.0 (C-4), 149.3 (C-3), 152.8 (C-1)。以上数据与文献报道基本一致^[11], 故鉴定化合物 **8** 为 tachinoside。

化合物 **9**: 无定形粉末。ESI-MS m/z : 313 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 7.52 (2H, m, H-2, 6), 7.52 (2H, m, H-3, 5), 7.43 (1H, m, H-4), 5.36 (1H, s, H-7), 4.09 (1H, d, $J = 7.7$ Hz, H-1'); ^{13}C -NMR (100 MHz, CD_3OD) δ : 62.6 (C-6'), 71.6 (C-5'), 75.0 (C-4'), 77.6 (C-3'), 78.2 (C-2'), 79.4 (C-7), 100.2 (C-1'), 129.4 (C-3, 5), 129.6 (C-2, 6), 129.9 (C-4), 137.3 (C-1), 176.1 (C-8)。以上数据与文献报道基本一致^[12], 故鉴定化合物 **9** 为 *d*-mandelic acid- β -*D*-glucopyranoside。

化合物 **10**: 白色粉末。ESI-MS m/z : 399 $[M+Na]^+$; 1H -NMR (400 MHz, $DMSO-d_6$) δ : 6.95 (1H, d, $J = 1.5$ Hz, H-2), 6.74 (1H, dd, $J = 8.0, 1.5$ Hz, H-6), 6.69 (1H, d, $J = 8.0$ Hz, H-5), 4.47 (1H, m, $J = 6.5$ Hz, H-7), 4.27 (1H, d, $J = 8.0$ Hz, H-1'), 4.15 (2H, m, H-6'), 3.76 (3H, s, $-OCH_3$), 3.66 (1H, m, H-8), 3.59 (1H, m, H-3'), 3.47 (1H, m, H-5'), 3.45 (1H, m, H-9a), 3.39 (1H, m, H-4'), 3.38 (1H, m, H-9a), 3.13 (1H, m,

H-9b) 3.01 (1H, m, H-2'); ^{13}C -NMR (100 MHz, $DMSO-d_6$) δ : 55.6 ($-OCH_3$), 61.1 (C-6'), 61.3 (C-9), 70.1 (C-4'), 72.3 (C-7), 73.9 (C-2'), 76.4 (C-3'), 76.9 (C-5'), 86.7 (C-8), 104.0 (C-1'), 111.1 (C-2), 114.8 (C-5), 119.4 (C-6), 132.6 (C-1), 145.6 (C-4), 147.2 (C-3)。以上数据与文献报道基本一致^[13], 故鉴定化合物 **10** 为 (+)-(7*S*,8*S*)-guaiacylglycerol 8-*O*- β -*D*-glucopyranoside。

化合物 **11**: 无定形粉末。ESI-MS m/z : 339 $[M+Na]^+$; 1H -NMR (400 MHz, CD_3OD) δ : 7.10 (1H, d, $J = 8.2$ Hz, H-5), 6.73 (1H, s, H-2), 6.64 (1H, d, $J = 8.2$ Hz, H-6), 4.69 (1H, d, H-1'), 3.88 (1H, d, $J = 12.0$ Hz, H-6'), 3.72 (1H, d, $J = 12.0$ Hz, H-6'), 3.67 (2H, m, H-8), 3.65 (2H, m, H-2', 3'), 3.45~3.40 (2H, m, H-4', 5'), 2.71 (2H, t, $J = 7.1$ Hz, H-7); ^{13}C -NMR (100 MHz, CD_3OD) δ : 39.7 (C-7), 62.4 (C-6'), 64.3 (C-8), 71.3 (C-4'), 74.9 (C-2'), 77.7 (C-3'), 78.3 (C-5'), 104.8 (C-1'), 117.7 (C-2), 119.2 (C-5), 121.3 (C-6), 136.2 (C-1), 145.3 (C-3), 148.5 (C-4)。以上数据与文献报道基本一致^[14], 故鉴定化合物 **11** 为 biophenol。

化合物 **12**: 无定形粉末。ESI-MS m/z : 339 $[M+Na]^+$; 1H -NMR (400 MHz, CD_3OD) δ : 7.07 (1H, s, H-2), 6.78 (1H, d, $J = 1.2$ Hz, H-4), 6.75 (1H, d, $J = 1.2$ Hz, H-6), 4.75 (1H, d, $J = 7.3$ Hz, H-1'), 3.90 (1H, d, $J = 12.0$ Hz, H-6'a), 3.75 (1H, d, $J = 12.0$ Hz, H-6'b), 3.70 (2H, t, H-8), 3.49 (2H, d, H-2', 3'), 3.39 (2H, d, H-4', 5'), 2.71 (2H, t, $J = 7.0$ Hz, H-7); ^{13}C -NMR (100 MHz, CD_3OD) δ : 39.5 (C-7), 62.5 (C-6'), 64.3 (C-8), 71.4 (C-4'), 74.9 (C-2'), 77.6 (C-5'), 78.3 (C-3'), 104.4 (C-1'), 116.9 (C-4), 119.6 (C-2), 125.2 (C-6), 132.0 (C-1), 146.6 (C-3), 146.8 (C-5)。以上数据与文献报道基本一致^[15], 故鉴定化合物 **12** 为 3,5-dihydroxyphenethyl alcohol-3-*O*- β -glucopyranoside。

化合物 **13**: 白色无定形粉末。ESI-MS m/z : 390 $[M+NH_4]^+$; 1H -NMR (400 MHz, CD_3OD) δ : 6.81 (2H, s, H-3, 5), 6.61 (1H, d, $J = 15.9$ Hz, H-7), 6.38 (1H, dt, $J = 15.9, 5.6$ Hz, H-8), 4.93 (1H, d, $J = 7.4$ Hz, H-1'), 4.28 (2H, m, H-9), 3.92 (6H, s, $-OCH_3$), 3.78 (1H, m, H-6'), 3.66 (1H, m, H-6'), 3.48 (1H, m, H-3'), 3.42 (1H, m, H-4'), 3.39 (1H, m, H-2'), 3.21 (1H, m, H-5'); ^{13}C -NMR (100 MHz, CD_3OD) δ : 57.0 ($-OCH_3$), 57.0 ($-OCH_3$), 62.6 (C-6'), 63.6 (C-9), 71.4

(C-4'), 75.7 (C-2'), 77.8 (C-3'), 78.4 (C-5'), 105.4 (C-3, 5), 105.5 (C-1'), 130.1 (C-7), 131.3 (C-8), 135.3 (C-4), 135.9 (C-1), 154.4 (C-2, 6)。以上数据与文献报道基本一致^[16], 故鉴定化合物 **13** 为 syringin。

化合物 **14**: 无色油状物。ESI-MS m/z : 169 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 5.42 (1H, dt, J = 6.8, 17.1 Hz, H-5), 5.24 (1H, d, J = 17.1 Hz, H-6), 5.35~5.19 (1H, t, J = 17.1 Hz, H-2), 4.13 (2H, d, J = 6.8 Hz, H-1), 2.07 (2H, d, J = 6.8 Hz, H-4), 1.71 (3H, s, H-10), 1.22 (6H, s, H-8, 9); ^{13}C -NMR (100 MHz, CD_3OD) δ : 16.1 (C-10), 23.4 (C-6'), 29.2 (C-8, 9), 41.1 (C-4), 44.3 (C-6'), 59.5 (C-1), 71.3 (C-7), 125.0 (C-2, 5), 136.0 (C-3), 139.6 (C-6)。以上数据与文献报道基本一致^[17], 故鉴定化合物 **14** 为 (2*E*,5*E*)-3,7-dimethyl-2,5-octadiene-1,7-diol。

化合物 **15**: 无色油状物。ESI-MS m/z : 185 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 5.67 (1H, m, H-6), 3.31 (1H, m, H-2a), 2.12 (2H, m, H-5), 2.09 (1H, m, H-2b), 1.62 (3H, s, H-8), 1.49 (3H, s, H-9), 1.46 (2H, m, H-4), 1.17 (3H, s, H-10); ^{13}C -NMR (100 MHz, CD_3OD) δ : 18.4 (C-9, 5), 23.4 (C-8), 29.2 (C-10), 41.9 (C-4), 44.2 (C-2), 71.3 (C-3), 123.0 (C-6), 152.2 (C-7), 177.3 (C-1)。以上数据与文献报道基本一致^[18], 故鉴定化合物 **15** 为 ($\pm$)-3-hydroxy-3,7-dimethyloct-6-enoic acid。

化合物 **16**: 无色油状物。ESI-MS m/z : 169 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 5.95 (1H, dd, J = 17.4, 10.8 Hz, H-7), 5.31 (1H, t, J = 7.3 Hz, H-3), 5.24 (1H, dd, J = 17.4, 1.5 Hz, H-8a), 5.07 (1H, dd, J = 10.8, 1.5 Hz, H-8b), 4.11 (2H, s, H-1), 2.06 (2H, m, H-4), 1.80 (3H, s, H-9), 1.47~1.45 (m, 2H, H-5), 1.40 (3H, s, H-10); ^{13}C -NMR (100 MHz, CD_3OD) δ : 21.5 (C-9), 23.3 (C-4), 27.7 (C-10), 43.6 (C-5), 61.3 (C-1), 73.8 (C-6), 112.1 (C-8), 128.8 (C-3), 135.7 (C-2), 146.3 (C-7)。以上数据与文献报道基本一致^[19], 故鉴定化合物 **16** 为 (2*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol。

化合物 **17**: 无色针晶(甲醇)。mp 128~130 °C。ESI-MS m/z : 437 $[M+H]^+$; 1H -NMR (400 MHz, CD_3OD) δ : 7.09 (1H, d, J = 8.3 Hz, H-2, 6), 6.72 (1H, d, J = 8.3 Hz, H-3, 5), 6.21 (1H, d, J = 2.0 Hz, H-3'), 5.99 (1H, d, J = 2.0 Hz, H-5'), 5.07 (1H, d, J = 6.9 Hz, Glc-H-1), 3.34 (2H, t, J = 7.2 Hz, H- α), 2.91 (2H, t, J = 7.2 Hz, H- β); ^{13}C -NMR (100 MHz, CD_3OD) δ :

30.8 (C- β), 46.9 (C- α), 62.4 (Glc-C-6), 71.1 (Glc-C-4), 74.7 (Glc-C-2), 78.4 (Glc-C-3), 78.5 (Glc-C-5), 95.6 (C-5'), 98.4 (C-3'), 102.1 (Glc-C-1), 106.7 (C-1'), 116.1 (C-3, 5), 130.4 (C-2, 6), 133.9 (C-1), 156.3 (C-4), 162.3 (C-6'), 166.1 (C-2'), 167.5 (C-4'), 206.5 (C = O)。以上数据与文献报道基本一致^[20], 故鉴定化合物 **17** 为 phlorizin。

化合物 **18**: 无定形粉末。ESI-MS m/z : 539 $[M+H]^+$; 1H -NMR (400 MHz, CD_3OD) δ : 6.86 (1H, d, J = 8.0 Hz, H-5'), 6.77 (2H, s, H-2', 8), 6.73 (1H, d, J = 8.0 Hz, H-6'), 6.58 (1H, s, H-5), 4.42 (1H, d, H-1''), 4.09 (2H, m, H-3, 4), 3.91 (3H, s, -OCH₃), 3.83 (3H, s, -OCH₃), 3.27 (1H, d, J = 16.7 Hz, H-1 α), 2.71 (1H, d, J = 16.7 Hz, H-1 β); ^{13}C -NMR (100 MHz, CD_3OD) δ : 40.0 (C-1), 45.0 (C-4), 47.3 (C-3), 56.4 (-OCH₃), 56.8 (-OCH₃), 60.9 (C-3a), 62.0 (C-6''), 69.3 (C-2a), 70.8 (C-4''), 74.6 (C-2''), 74.9 (C-2), 77.8 (C-3''), 77.9 (C-5''), 103.4 (C-1''), 113.8 (C-8), 114.0 (C-2'), 116.1 (C-5'), 119.2 (C-5), 123.6 (C-6'), 129.8 (C-9), 134.1 (C-10), 138.2 (C-1'), 146.2 (C-6), 146.3 (C-4'), 148.9 (C-7), 149.1 (C-3') 以上数据与文献报道基本一致^[21], 故鉴定化合物 **18** 为 (+)-cyclo-olivil-6-*O*- β -*D*-glucopyranoside。

化合物 **19**: 白色无定形粉末。ESI-MS m/z : 591 $[M+Na]^+$; 1H -NMR (400 MHz, CD_3OD) δ : 6.80 (1H, d, J = 1.9 Hz, H-2), 6.76 (1H, d, J = 8.1 Hz, H-5), 6.67 (1H, s, H-2'), 6.63 (1H, dd, J = 8.1, 1.9 Hz, H-6), 4.89 (1H, d, J = 7.5 Hz, H-1''), 4.18 (1H, d, J = 8.5 Hz, H-7), 3.95 (2H, m, H-6''), 3.90 (3H, s, 3'-OCH₃), 3.84 (3H, s, 3-OCH₃), 3.77 (2H, m, H-9), 3.74 (2H, m, H-9'), 3.67 (1H, m, H-4''), 3.60 (1H, m, H-5''), 3.25 (1H, m, H-2''), 3.25 (1H, d, J = 16.3 Hz, H-7'), 3.22 (3H, s, 5'-OCH₃), 2.68 (1H, d, J = 16.4 Hz, H-7'), 2.07 (1H, m, H-8); ^{13}C -NMR (100 MHz, CD_3OD) δ : 40.7 (C-7'), 42.0 (C-7), 56.6 (3-OCH₃), 57.0 (3'-OCH₃), 60.8 (5'-OCH₃), 60.8 (C-9), 62.5 (C-6''), 69.3 (C-9'), 71.3 (C-4''), 74.9 (C-2''), 75.7 (C-8'), 77.8 (C-5''), 78.2 (C-3''), 104.7 (C-1''), 110.3 (C-2'), 113.9 (C-2), 116.0 (C-5), 122.3 (C-6), 127.4 (C-6'), 132.7 (C-1'), 138.8 (C-4'), 140.8 (C-1), 145.7 (C-4), 148.8 (C-3), 152.7 (C-5'), 153.3 (C-3')。以上数据与文献报道基本一致^[22], 故鉴定化合物 **19** 为 5'-methoxy-8'-hydroxyl-(+)-isolariciresinol-4'-*O*- β -*D*-glucopyranoside。

化合物 **20**: 白色粉末。ESI-MS m/z : 415 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 7.32 (4H, m, H-2, 3, 5, 6), 7.24 (1H, m, H-4), 5.04 (1H, s, H-1''), 4.38 (1H, d, $J = 7.8$ Hz, H-1'), 3.30 (1H, t, $J = 8.4$ Hz, H-8b), 3.26 (1H, t, $J = 8.4$ Hz, H-8a), 3.00 (2H, m, H-7); ^{13}C -NMR (100 MHz, CD_3OD) δ : 37.2 (C-7), 63.0 (C-5''), 68.1 (C-6'), 71.8 (C-8), 71.9 (C-4'), 75.0 (C-2'), 76.6 (C-5'), 77.9 (C-3'), 78.8 (C-3''), 83.1 (C-2''), 85.8 (C-4''), 104.3 (C-1'), 109.9 (C-1''), 127.2 (C-4), 129.3 (C-3, 5), 130.0 (C-2, 6), 139.9 (C-1)。以上数据与文献报道基本一致^[23], 故鉴定化合物 **20** 为 phenethyl-6- O - α -L-arabinofuranosyl- β -D-glucoside。

化合物 **21**: 无定形粉末。ESI-MS m/z : 469 $[M+Na]^+$; 1H -NMR (400 MHz, CD_3OD) δ : 7.81 (1H, dd, $J = 7.8, 1.7$ Hz, H-6), 7.63 (1H, ddd, $J = 8.5, 7.4, 1.8$ Hz, H-4), 7.50 (1H, dd, $J = 8.4, 0.8$ Hz, H-3), 7.17 (1H, td, $J = 7.7, 1.0$ Hz, H-5), 4.93 (1H, d, $J = 6.0$ Hz, H-1'), 4.37 (1H, d, $J = 6.8$ Hz, H-1''), 4.19~3.72 (11H, m, H-2', 3', 4', 5', 6'a, 6'b, 2'', 3'', 4'', 5''a, 5''b), 3.94 (3H, s, H-8); ^{13}C -NMR (100 MHz, CD_3OD) δ : 52.8 (C-8), 66.7 (C-5''), 69.5 (C-4''), 70.0 (C-3''), 71.5 (C-2''), 72.5 (C-5', 6'), 74.2 (C-4'), 75.0 (C-3'), 77.5 (C-2'), 77.5 (C-1'), 103.9 (C-1'), 105.1 (C-1''), 119.2 (C-3), 122.3 (C-1), 123.6 (C-5), 132.0 (C-6), 135.4 (C-4), 158.6 (C-2), 168.6 (C-7)。以上数据与文献报道基本一致^[24], 故鉴定化合物 **21** 为 gaultherin。

化合物 **22**: 无色油状物。ESI-MS m/z : 415 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 7.48 (2H, d, $J = 7.3$ Hz, H-2, 6), 7.39 (2H, t, $J = 7.3$ Hz, H-3, 5), 7.33 (1H, m, $J = 7.2$ Hz, H-4), 4.92 (1H, d, $J = 8.9$ Hz, H-1'), 4.87 (1H, d, $J = 7.2$ Hz, H-1''), 4.70 (1H, d, $J = 11.7$ Hz, H-7a), 4.39 (1H, d, $J = 7.7$ Hz, H-7b), 1.33 (3H, d, $J = 6.0$ Hz, H-6''); ^{13}C -NMR (100 MHz, CD_3OD) δ : 18.1 (C-6''), 68.1 (C-6'), 69.8 (C-5''), 71.7 (C-7), 71.8 (C-4'), 72.2 (C-2''), 72.4 (C-3''), 74.0 (C-4''), 75.1 (C-2'), 76.9 (C-5'), 78.1 (C-3'), 102.3 (C-1''), 103.2 (C-1'), 128.8 (C-4), 129.3 (C-3, 5), 129.3 (C-2, 6), 138.8 (C-1)。以上数据与文献报道基本一致^[25], 故鉴定化合物 **22** 为 benzyl- O - α -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- β -D-glucopyranoside。

化合物 **23**: 淡黄色黏稠物。ESI-MS m/z : 467 $[M-H]^-$; 1H -NMR (400 MHz, CD_3OD) δ : 5.45 (1H, t, $J = 6.6$ Hz, H-2), 5.05 (1H, s, H-1''), 4.39 (1H, m,

H-1), 4.37 (1H, d, $J = 7.8$ Hz, H-1'), 4.31 (1H, dd, $J = 11.8, 7.6$ Hz, H-1), 4.12 (1H, m, H-6''), 4.08 (1H, m, H-2''), 4.05 (1H, m, H-4''), 3.91 (1H, m, H-3''), 3.82 (1H, dd, $J = 11.9, 3.3$ Hz, H-5''), 3.75~3.71 (1H, m, H-5''), 3.65 (1H, m, H-6'), 3.50 (1H, m, H-5'), 3.38 (1H, t, H-3'), 3.36 (1H, t, H-4'), 3.26 (1H, t, H-2'), 2.12 (2H, t, $J = 7.0$ Hz, H-4), 1.77 (3H, s, H-10), 1.57 (2H, m, H-5), 1.48 (2H, m, H-6), 1.25 (6H, s, H-8, 9); ^{13}C -NMR (100 MHz, CD_3OD) δ : 16.4 (C-10), 23.3 (C-5), 29.2 (C-8, 9), 41.0 (C-4), 44.2 (C-6), 63.0 (C-5''), 66.3 (C-1), 68.0 (C-6'), 71.3 (C-7), 71.9 (C-4'), 74.9 (C-2'), 76.6 (C-5'), 77.9 (C-3'), 78.8 (C-3''), 83.1 (C-2''), 85.8 (C-4''), 102.6 (C-1'), 109.8 (C-1''), 121.4 (C-2), 142.2 (C-3)。以上数据与文献报道基本一致^[26], 故鉴定化合物 **23** 为 (2*E*)-7-hydroxy-3,7-dimethyl-2-octenyl-6- O - α -L-arabinofuranosyl- β -D-glucopyranoside。

化合物 **24**: 黄色粉末。ESI-MS m/z : 345 $[M+H]^+$; mp 287~289 °C。 1H -NMR (400 MHz, DMSO- d_6) δ : 7.60 (1H, s, H-5'), 7.52 (1H, s, H-5), 4.06 (3H, s, 3'-Me), 4.04 (3H, s, 3-Me), 3.99 (3H, s, 4'-Me); ^{13}C -NMR (100 MHz, DMSO- d_6) δ : 56.7 (4'-OCH₃), 61.0 (3'-OCH₃), 61.3 (3-OCH₃), 107.5 (C-5'), 111.2 (C-1), 111.7 (C-5), 112.0 (C-6), 112.5 (C-1'), 113.4 (C-6'), 140.2 (C-3), 140.9 (C-3'), 141.0 (C-4), 141.5 (C-2'), 152.6 (C-4), 153.8 (C-4'), 158.3 (C-7), 158.5 (C-7)。以上数据与文献报道基本一致^[27], 故鉴定化合物 **24** 为 3,3',4'-tri- O -methylellagic acid。

化合物 **25**: 白色针晶(甲醇)。mp 212~214 °C。ESI-MS m/z : 257 $[M+H]^+$; 1H -NMR (400 MHz, CD_3OD) δ : 7.23 (1H, d, $J = 2.0$ Hz, H-6), 7.21 (1H, d, $J = 1.9$ Hz, H-2), 4.85 (1H, d, $J = 7.9$ Hz, H-1'), 3.93 (3H, s, 7-OCH₃), 3.92 (3H, s, 3-OCH₃), 3.85 (1H, dd, $J = 12.0, 2.5$ Hz, H-6'b), 3.77 (1H, dd, $J = 12.0, 4.6$ Hz, H-6'a), 3.57~3.45 (4H, m, H-2'~5'); ^{13}C -NMR (100 MHz, CD_3OD) δ : 52.7 (7-OCH₃), 56.8 (3-OCH₃), 62.1 (C-6'), 70.9 (C-4'), 75.4 (C-2'), 77.7 (C-3'), 78.4 (C-5'), 105.8 (C-6), 106.2 (C-1'), 112.5 (C-2), 127.8 (C-1), 139.3 (C-4), 152.5 (C-3), 154.1 (C-5), 168.2 (C-7)。以上数据与文献报道基本一致^[24], 故鉴定化合物 **25** 为 methyl-4-(β -D-glucopyranosyloxy)-3-hydroxy-5-methoxybenzoate。

4 讨论

本实验通过植物化学研究手段, 从地榆中共分

离鉴定了 25 个单体化合物, 其中 1~22 为首次从该植物中分离得到, 在以往研究的基础上进一步阐明了地榆化学成分的组成。所分离得到的单体化学成分在后续工作中将进行分子水平上的升高白细胞的活性评价。

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