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三七根茎的化学成分研究(Ⅱ)*

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摘要: 研究三七[*Panax notoginseng* (Burk.) F. H. Chen]根茎的化学成分. 利用 D_{101} 大孔吸附树脂柱、硅胶柱、RP - 8 和 RP - 18 柱进行化合物的分离纯化, 根据其理化性质和光谱数据进行结构鉴定. 从三七根茎部分分离鉴定出 5 个化合物, 分别为人参皂苷三七皂苷 T_5 (Notoginsenoside T_5, Ⅰ), 人参皂苷 F_1 (Gin senoside F_1, Ⅱ), 人参皂苷 F_2 (Ginsenoside F_2, Ⅲ), 三七皂苷 E (Notoginsenoside E, Ⅳ), 人参皂苷 Ⅱ (Ginsenoside Ⅱ, Ⅴ). Ⅴ为首次从该植物中分离获得, Ⅰ～Ⅳ为首次从该植物根茎中分离获得.

关键词: 三七根茎; 人参皂苷; 三七皂苷
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三七[*Panax notoginseng* (Burk.) F. H. Chen]为五加科人参属植物, 主要分布于我国的云南、广西, 是我国特有的名贵中药材, 具有化淤止血、活血定痛之功效. 传统主要应用于人体内外各种出血之症及跌打损伤、瘀滞肿痛. 三七的化学成分与药理研究已经比较深入, 研究表明三七含皂苷、黄酮、三七素等活性物质. 药理研究表明对防治心脑血管疾病有显著作用, 还具有降血脂、降血糖、降血压、抗炎症、抗疲劳、耐缺氧、抗衰老和提高机体免疫力等活性[1]. 三七中皂苷成分是三七的主要有效成分之一, 文献报道已从三七的不同部位分离得到 70 多个单体皂苷成分[2], 而对根茎作为其主要药用部位研究相对较少, 本文从产自文山的三七根茎中分离得到 5 种单体皂苷, 分别是三七皂苷 T_5 (Notoginsenoside T_5, Ⅰ), 人参皂苷 F_1 (Ginsenoside F_1 Ⅱ), 人参皂苷 F_2 (Ginsenoside F_2, Ⅲ), 三七皂苷 E (Notoginsenoside E, Ⅳ), 人参皂苷 Ⅱ (Ginsenoside Ⅱ, Ⅴ), 其中化合物 Ⅴ为首次从该植物中分离获得, 化合物 Ⅰ～Ⅳ为首次从该植物根茎中分离获得.

1 实验部分

1.1 仪器与材料 三七根茎由文山州三七研究所提供. 熔点用 XRC - Ⅰ型显微熔点仪测定(温度计未校正); 旋光用 JASCO - 20 旋光仪测定; 质谱用 VG Auto Spec - 3000 型质谱仪测定; NMR 用 Bruker AV - 400 超导核磁共振仪测定, C_5D_5N 为溶剂, TMS 内标. 青岛海洋化工厂生产的硅胶, Merck、FUJI 公司生产的 RP - 8、RP - 18 为柱层析材料; TLC 用青岛化工厂生产的硅胶 G 预制薄板和 Merck 公司生产的 RP - 8 F_{254} 和 RP - 18 F_{254} 预制薄板. 展开剂: ① V(氯仿) : V(甲醇) : V(水) = 9 : 1 : 0.1, 7 : 3 : 0.31; ② V(甲醇) : V(水) = 7 : 3 ～8 : 2. 显色剂: 10 % H_2SO_4 - CH_3CH_2OH 溶液.

1.2 提取与分离 三七根茎 48.0 kg 粉碎, 以 6 倍量的 80 %乙醇回流提取 3 次, 过滤后残渣以 6 倍量的 40 %乙醇回流提取 3 次. 合并 80 %及 40 %醇提液, 浓缩得醇提物 18.6 kg; 残渣再以 6 倍量的水煮提 2 次,

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每次 2 h,过滤后浓缩滤液得水提物 1.7 kg. 乙醇提取物用少量水溶解后,经 D_{101}大孔吸附树脂柱层析,分别用水、80 %乙醇洗脱,收集 80 %乙醇洗脱液减压浓缩得粗三七总皂苷 8.6 kg. 总皂苷部分经硅胶柱层析(氯仿/甲醇/水,体积比 8∶2∶0.2～6.5∶3.5∶0.5),TLC 检查合并后得 10 个流分. 流分 2 反复经硅胶柱(氯仿/甲醇/水,体积比 90∶10∶1),MCI CHP - 20P 柱、RP - 8 柱、RP - 18 柱(甲醇/水,体积比 8∶2)层析得到化合物 Ⅱ(20 mg). 流分 5 反复经硅胶柱(氯仿/甲醇/水,体积比 80∶20∶2),MCI CHP - 20P 柱、RP - 8 柱、RP - 18 柱(甲醇/水,体积比 7∶3)层析得到化合物 Ⅰ(100 mg)和 Ⅲ(15 mg). 流分 7 反复经硅胶柱(氯仿/甲醇/水,体积比 70∶30∶3),MCI CHP - 20P 柱、RP - 8 柱、RP - 18 柱(甲醇/水,体积比 7∶3)层析得到化合物 Ⅳ(5 g)和 Ⅴ(300 mg).

2 结构鉴定

2.1 化合物 Ⅰ 白色粉末,m.p:161～163 ℃,$[\alpha]_D^{16.8}$ = + 20.6 °(c = 0.5,CH_3OH),FAB - MS$^-$ m/z (%):751([M - 1]$^-$,100). ^{1}H NMR (400 MHz,C_5D_5N) δ:0.81 (3H,s,H - 30),0.97(3H,s,H - 19),1.20(3H,s,H - 18),1.46(3H,s,H - 29),1.59(3H,s,H - 27),1.66(3H,s,H - 26),2.06(3H,s,H - 28),4.89(1H,br. d,J = 13.5 Hz,H - 21),5.12(1H,br. d,J = 13.5 Hz,H - 21),4.93(1H,d,J = 7.0 Hz,H - 1′),5.29(1H,t,H - 24),5.76(1H,d,J = 6.6 Hz,H - 1″);^{13}C NMR(100 MHz,C_5D_5N) δ:39.6(t,C - 1),27.8(t,C - 2),78.0(d,C - 3),40.3(s,C - 4),61.4(d,C - 5),79.5(d,C - 6),45.0(t,C - 7),41.3(s,C - 8),50.6(d,C - 9),39.7(s,C - 10),30.8(t,C - 11),71.3(d,C - 12),48.3(d,C - 13),51.2(s,C - 14),32.6(t,C - 15),27.1(t,C - 16),52.1(d,C - 17),17.4(q,C - 18),17.8(q,C - 19),155.5(s,C - 20),108.2(t,C - 21),33.8(t,C - 22),32.9(t,C - 23),125.4(d,C - 24),131.2(s,C - 25),25.8(q,C - 26),17.8(q,C - 27),31.7(q,C - 28),16.7(q,C - 29),16.8(q,C - 30),103.6(d,C - 1′),80.2(d,C - 2′),78.1(d,C - 3′),72.4(d,C - 4′),78.8(d,C - 5′),62.9(t,C - 6′),104.9(d,C - 1″),75.9(d,C - 2″),78.9(d,C - 3″),71.3(d,C - 4″),67.3(t,C - 5″). 该光谱数据与文献报道的三七皂苷 T_5(Notoginsenoside T_5)[3]一致.

2.2 化合物 Ⅱ 白色粉末,m.p:185～187 ℃,$[\alpha]_D^{25}$ = + 36.6 °(c = 1.12,CH_3OH);FAB - MS$^-$ m/z (%):585([M]$^-$,100);^{1}H NMR(400 MHz,C_5D_5N) δ:0.96(3H,s,H - 30),1.00(3H,s,H - 19),1.08(3H,s,H - 18),1.44(3H,s,H - 28),1.55(3H,s,H - 29),1.58(3H,s,H - 26),1.61(3H,s,H - 27),1.98(3H,s,H - 21),5.22(1H,d,J = 6.3 Hz,H - 1′),5.74(1H,br. s,H - 24);^{13}C NMR(100 MHz,C_5D_5N) δ:39.4(t,C - 1),28.2(t,C - 2),78.3(d,C - 3),40.4(s,C - 4),61.8(d,C - 5),67.8(d,C - 6),47.5(t,C - 7),41.2(s,C - 8),49.9(d,C - 9),39.6(s,C - 10),31.0(t,C - 11),70.2(d,C - 12),49.2(d,C - 13),51.4(s,C - 14),30.8(t,C - 15),26.7(t,C - 16),51.6(d,C - 17),17.6(q,C - 18),17.5(q,C - 19),83.3(s,C - 20),22.4(q,C - 21),36.2(t,C - 22),23.2(t,C - 23),126.0(d,C - 24),131.0(s,C - 25),25.8(q,C - 26),17.8(q,C - 27),32.0(q,C - 28),16.6(q,C - 29),17.4(q,C - 30),98.3(d,C - 1′),75.2(d,C - 2′),78.5(d,C - 3′),71.7(d,C - 4′),79.4(d,C - 5′),62.9(t,C - 6′). 该光谱数据与文献报道的人参皂苷 F_1(Ginsenoside F_1)[4]一致.

2.3 化合物 Ⅲ 白色粉末,m.p:184～186 ℃,$[\alpha]_D^{25}$ = + 21.1 °(c = 1.14,CH_3OH);FAB - MS$^-$ m/z (%):785([M]$^-$,100),622([M - H - 162]$^-$,10);^{1}H NMR(400 MHz,C_5D_5N) δ:0.83(3H,s,H - 19),0.95(3H,s,H - 30),0.98(3H,s,H - 18),1.21(3H,s,H - 29),1.29(3H,s,H - 28),1.57(3H,s,H - 26),1.95(3H,s,H - 21),1.61(3H,s,H - 27),4.94(1H,d,J = 7.2 Hz,H - 1″),5.19(1H,d,J = 7.7 Hz,H - 1′),5.59(1H,br. s,H - 24);^{13}C NMR(100 MHz,C_5D_5N) δ:39.2(t,C - 1),26.8(t,C - 2),88.8(d,C - 3),39.7(s,C - 4),56.4(d,C - 5),18.5(t,C - 6),35.2(t,C - 7),40.1(s,C - 8),50.2(d,C - 9),37.0(s,C - 10),30.9(t,C - 11),70.2(d,C - 12),49.5(d,C - 13),51.6(s,C - 14),30.8(t,C - 15),26.7(t,C - 16),

51.5(d,C-17),16.0(q,C-18),16.3(q,C-19),83.3(s,C-20),22.4(q,C-21),36.2(t,C-22),23.3(t,C-23),126.0(d,C-24),131.0(s,C-25),25.8(q,C-26),17.8(q,C-27),28.2(q,C-28),16.8(q,C-29),17.4(q,C-30),107.0(d,C-1′),75.8(d,C-2′),78.8(d,C-3′),71.9(d,C-4′),78.4(d,C-5′),63.1(t,C-6′),98.3(d,C-1″),75.2(d,C-2″),79.4(d,C-3″),71.6(d,C-4″),78.4(d,C-5″),62.9(t,C-6″). 该光谱数据与文献报道的人参皂苷 F_2(Ginsenoside F_2)[4]一致.

2.4　化合物Ⅳ　白色粉末,m.p:202～204 ℃,$[\alpha]_D^{24}$ = +19.2°(*c* = 0.1,CH_3OH);FAB-MS⁻ *m/z*:979([M]⁻,50),889([M]⁻ - $CH_2CCH_3CH_3OOH$,23),797([M]⁻ - $C_6H_{12}O_6$,12),325(48),159(46),119(100);^{1}H NMR(400 MHz,C_5D_5N) δ:0.81(3H,s,H-19),0.86(3H,s,H-30),0.98(3H,s,H-18),1.10(3H,s,H-29),1.27(3H,s,H-28),1.56(3H,s,H-26),1.56(3H,s,H-27),1.57(3H,s,H-21),3.24(1H,dd,H-3),3.99(1H,m,H-12),6.06(1H,d,*J* = 15.0 Hz,H-24),6.14(1H,m,H-23),4.92(1H,d,*J* = 7.2 Hz,H-1′),5.39(1H,d,*J* = 7.0 Hz,H-1″),5.22(1H,d,*J* = 7.6 Hz,H-1‴);^{13}C-NMR(100 MHz,C_5D_5N) δ:38.6(t,C-1),25.6(t,C-2),87.9(d,C-3),38.0(s,C-4),55.3(d,C-5),17.3(t,C-6),34.0(t,C-7),38.9(s,C-8),49.0(d,C-9),35.8(s,C-10),29.8(t,C-11),69.4(d,C-12),48.4(d,C-13),50.4(s,C-14),29.5(t,C-15),25.3(t,C-16),51.2(d,C-17),14.8(q,C-18),15.2(q,C-19),82.0(s,C-20),22.2(q,C-21),38.5(t,C-22),125.4(d,C-23),137.0(d,C-24),80.2(s,C-25),24.1(q,C-26),24.3(q,C-27),27.0(q,C-28),15.5(q,C-29),16.0(q,C-30),104.0(d,C-1′),82.2(d,C-2′),77.0(d,C-3′),70.5(d,C-4′),77.2(d,C-5′),61.7(t,C-6′),104.9(d,C-1″),76.0(d,C-2″),77.0(d,C-3″),70.4(d,C-4″),77.7(d,C-5″),61.6(t,C-6″),97.2(d,C-1‴),74.2(d,C-2‴),76.8(d,C-3‴),70.5(d,C-4‴),77.2(d,C-5‴),61.7(t,C-6‴). 该光谱数据与文献报道的三七皂苷 E(Notoginsenoside E)[5]一致.

2.5　化合物Ⅴ　白色粉末,m.p:193～195 ℃,$[\alpha]_D^{28.9}$ +13.13°(*c* = 0.33,CH_3OH);FAB-MS⁻ *m/z*(%):977([M]⁻,53),797([M]⁻ - $C_6H_{12}O_6$,12),781(12),765(15),159(38),119(100),^{1}H NMR(400 MHz,C_5D_5N) δ:0.77(3H,s,H-18),0.91(3H,s,H-30),0.92(3H,s,H-19),1.08(3H,s,H-29),1.26(3H,s,H-28),1.21(3H,s,H-21),1.89(3H,s,H-27),3.01(1H,m,H-22),3.24(1H,dd,*J* = 11.7,4.4 Hz,H-3),3.26(1H,m,H-22),4.15(1H,m,H-12),4.71(1H,dd,H-24),5.02(1H,d,H-26),4.91(1H,d,*J* = 7.8 Hz,H-1′),5.36(1H,d,*J* = 4.4 Hz,H-1″),5.17(1H,s,*J* = 7.8 Hz,H-1‴);^{13}C NMR(100 MHz,C_5D_5N) δ:39.4(t,C-1),26.7(t,C-2),89.1(d,C-3),39.2(s,C-4),56.4(d,C-5),18.5(t,C-6),35.2(t,C-7),40.1(s,C-8),50.3(d,C-9),37.0(s,C-10),30.8(t,C-11),70.4(d,C-12),49.5(d,C-13),51.7(s,C-14),31.0(t,C-15),26.8(t,C-16),51.5(d,C-17),16.4(q,C-18),16.0(q,C-19),83.4(s,C-20),22.8(q,C-21),32.8(t,C-22),26.8(t,C-23),90.0(d,C-24),146.1(s,C-25),113.5(t,C-26),17.8(q,C-27),28.2(q,C-28),16.7(q,C-29),17.4(q,C-30),105.2(d,C-1′),83.4(d,C-2′),78.0(d,C-3′),71.6(d,C-4′),78.4(d,C-5′),62.8(t,C-6′),106.0(d,C-1″),77.2(d,C-2″),78.2(d,C-3″),71.7(d,C-4″),78.4(d,C-5″),62.9(t,C-6″),98.3(d,C-1‴),75.2(d,C-2‴),79.2(d,C-3‴),71.7(d,C-4‴),77.2(d,C-5‴),62.0(t,C-6‴). 该光谱数据与文献报道的人参皂苷 Ⅱ(Ginsenoside Ⅱ)[6]一致.

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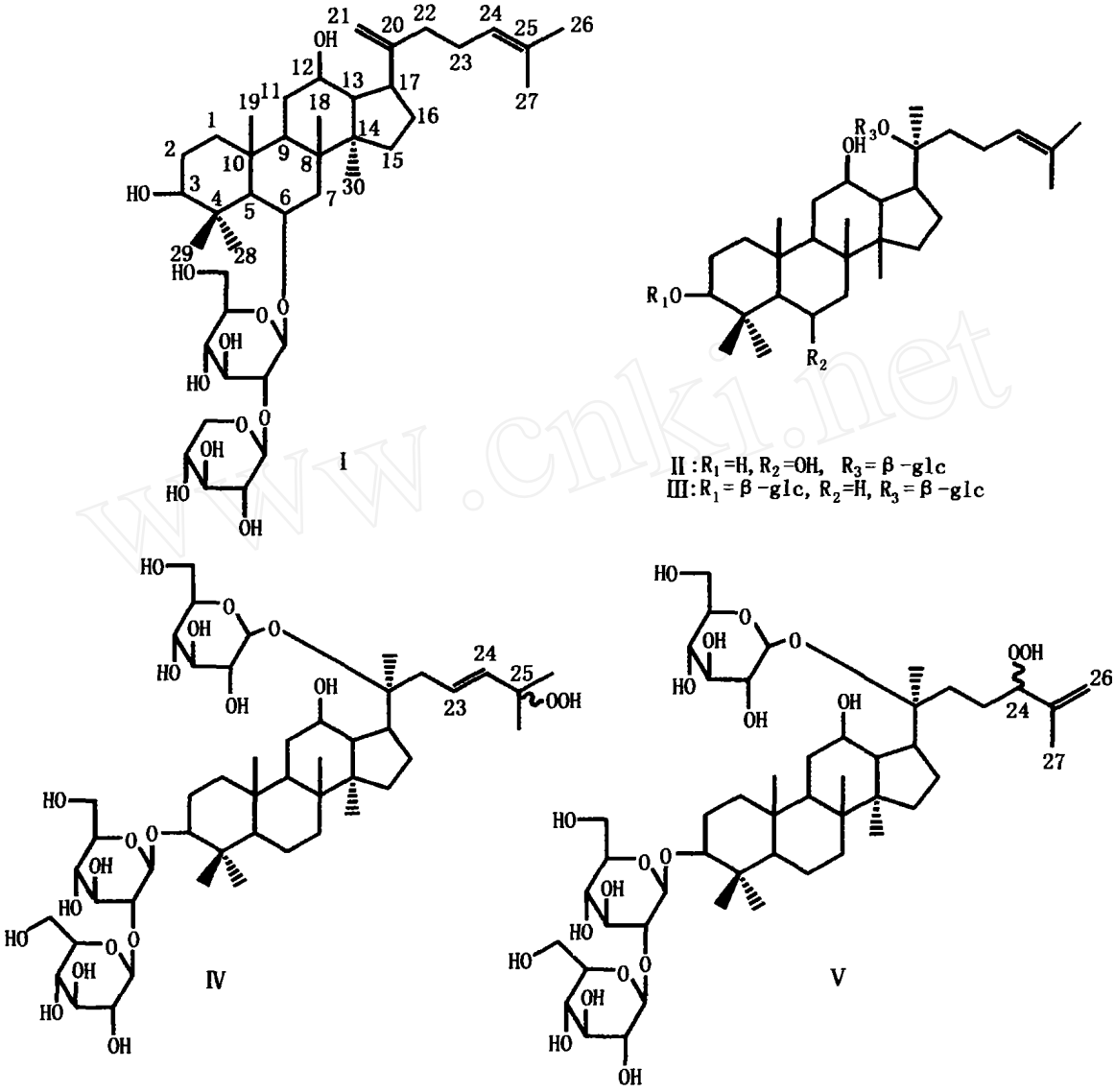

图 1 化合物 I～ V的结构

Fig. 1 Structures of compounds Ⅰ—Ⅴ

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Study on preparation of active zinc oxide by ammonia complex method

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Abstract: Active zinc oxide was yielded by calcining zinc subcarbonate at high temperature, which was prepared from zinc sulfate by ammonia complex method with $NH_3 \cdot H_2O$-NH_4HCO_3. The product was characterized by DTA-TG, specific surface area analyzer, XRD and SEM. The factors such as evaporating ammonia time, ageing time, calcining temperature and calcining time were investigated in detail. The optimum technical conditions to produce active zinc oxide were obtained. Active zinc oxide with specific surface area of 68.151 m^2/g was obtained under optimum conditions.

Key words: active zinc oxide; ammonia complex method; zinc subcarbonate

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Studies on chemical constituents from Rhizomes of *Panax Notoginseng* (Ⅱ)

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Abstract: To study the chemical constituents of rhizomes of *Panax notoginseng*. The compounds were isolated and purified by various chromatogragraphic methods. All compounds were identified on the basis of spectral analysis and physicochemical data. Five compounds were isolated from the rhizomes of *Panax notoginseng* (Burk.) F. H. Chen and identified as notoginsenoside T_5 (Ⅰ), ginsenoside F_1 (Ⅱ), ginsenoside F_2 (Ⅲ), notoginseno side E (Ⅳ), ginsenoside Ⅱ (Ⅴ). Conclusion Compound Ⅴ was isolated from this plant for the first time and compounds Ⅰ—Ⅳ was obtained from the rhizomes of this plant for the first time.

Key words: rhizomes of *Panax notoginseng*; ginsenoside; notoginsenoside