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光白英的化学成分研究

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摘　要:利用硅胶柱色谱、Sephadex LH-20 柱色谱及高效制备薄层层析等手段对茄属植物光白英全草的化学成分进行分离纯化,根据化合物理化性质和波谱数据对其化学结构进行阐明,发现并鉴定了 16 个化合物,分别为:白英醇 E(**1**)、白英醇 F(**2**)、白英醇 A(**3**)、白英醇 B(**4**)、白英醇 C(**5**)、江西白英素 A(**6**)、江西白英素 D(**7**)、布卢门醇 A(**8**)、去氢催吐萝芙醇(**9**)、3β-羟基-5α,6α-环氧-7-大柱香波龙烯-9-酮(**10**)、布卢门醇 C(**11**)、东莨菪内酯(**12**)、(1′*S*,2*R*,5*S*,10*R*)-2-(1′,2′-dihydroxy -1′-methylethyl)-6,10-dimethylspiro[4,5]dec-6-en-8-one(**13**)、chakyunglupulin A(**14**)、9,10,13-三羟基-反-11-十八烯酸(**15**)、2-(1′,2′-dihydroxy-1′-methylethyl)-6,10-dimethyl-9-hydroxyspiro[4,5]dec-6-en-8-one(**16**)。化合物 **1** ~ **11**、**13**、**16** 为倍半萜;化合物 **1** ~ **16** 均为首次从光白英中发现。

关键词:光白英;化学成分;倍半萜

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Chemical Constituents from *Solanum borealisinense*

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Abstract: By means of column chromatography over silica gel, Sephadex LH-20 and preparative HPTLC. Sixteen compounds were isolated and purified from the whole plant of *Solanum borealisinense*. Their structures were elucidated on the basis of physico-chemical properties and spectral data as: lyratol E (**1**), lyratol F (**2**), lyratol A (**3**), lyratol B (**4**), lyratol C (**5**), solajiangxin A (**6**), solajiangxin D (**7**), blumenol A (**8**), dehydrovomifoliol (**9**), 3β-hydroxy-5α,6α-epoxy-7-megastigmen-9-one (**10**), blumenol C (**11**), scopoletin (**12**), (1′*S*,2*R*,5*S*,10*R*)-2-(1′,2′-dihydroxy-1′-methylethyl)-6,10-dimethylspiro[4,5]dec-6-en-8-one (**13**), chakyunglupulinA (**14**), 9,10,13-trihydroxy-(*E*)-11-octadecenoic acid (**15**), 2-(1′,2′-dihydroxy-1′-methylethyl)-6,10-dimethyl-9-hydroxyspiro[4,5]dec-6-en-8-one (**16**). Compounds **1**-**11**, **13** and **16** were sesquiterpenoids. For the first time, compounds **1**-**16** were obtained from *S. borealisinense*.

Key words: *Solanum borealisinense*; chemical constituent; sesquiterpenoid

光白英为茄科茄属植物光白英 *Solanum borealisinense* 的干燥全草,为多年生草本植物,主产于我国黑龙江、吉林、辽宁、河北、内蒙古、新疆等地,前苏联西伯利亚亦有分布[1]。文献调研发现,茄属许多植物有清热解毒、活血化瘀的功效,在临床上具有广泛的应用。例如,龙葵用于治疗感冒、牙痛、慢性支气管炎、乳腺炎、痢疾等病症,刺天茄用于治疗咽喉肿痛、咳嗽咯血、水肿、黄疸等病症,而白英用于治疗胆囊炎、胆结石、宫颈糜烂、白带异常等病症。迄今为止,尚未见有关同属植物光白英的研究报道[2]。

前期研究中,课题组从同属植物白英中发现一系列结构新颖的倍半萜,而细胞毒实验表明,这些倍半萜对淋巴癌 P388 细胞、人鼻咽癌 HONE-1 细胞、口腔上皮癌 KB 细胞及结肠癌 HT29 细胞具有良好的生长抑制作用。预实验中,以从白英中发现的新颖倍半萜为化学对照,应用 TLC、HPLC、HPLC-MS 等方法,发现光白英 95% 乙醇提取物中含有倍半萜。通过多种色谱分离技术,对光白英 95% 乙醇提取物进行了系统研究,共发现 16 个化合物,包括 13 个倍半萜(**1** ~ **11**、**13**、**16**)、1 个香豆素(**12**)、1 个具有新颖八元环的化合物(**14**)和 1 个直链烯酸化合物(**15**)。化合物 **1** ~ **16** 均为首次从光白英中发现,化合物 **14**、**15** 为首次从茄属植物中发现。此外,课题组前期对发现的倍半萜进行了细胞毒实验,研究结果表明倍半萜类化合物 **1** ~ **9** 对结肠癌 HT29 细

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胞、淋巴癌 P388 细胞、人鼻咽癌 HONE-1 细胞具有良好的生长抑制作用[3-7]。

1 材料与方法

1.1 仪器与材料

XT-4 微型熔点测定仪(温度未校正),Perkin-Elmer 241 型旋光仪,Autospec-Ultima ETOF 型质谱仪,AVANCE IIITM 500 型核磁共振仪(TMS 内标),Sephadex LH-20 为北京金欧亚进口分装产品,薄层色谱硅胶(GF_{254})、柱色谱硅胶(200 ~ 300 目)及高效制备薄层硅胶板(HPTLC,20 × 20 cm)均为青岛海洋化工厂产品,所用试剂均为分析纯。

光白英全草(*Solanum borealisinense* C. Y. Wu et S. C. Huang)于 2014 年 8 月采自新疆乌鲁木齐地区,由烟台大学药学院生药学教研室李桂生博士鉴定,标本(YP14079)保存于烟台大学药学院标本室。

1.2 提取与分离

取光白英干燥全草 25.0 kg,粉碎后用 95% 乙醇回流提取 3 次,每次 1 h。提取液减压浓缩后得总浸膏 1.1 kg。将总浸膏悬浮于水中,分别用石油醚、氯仿、乙酸乙酯、正丁醇反复萃取,萃取液分别合并,减压浓缩,得氯仿部位 245.3 g。氯仿部位通过硅胶柱色谱,环己烷-丙酮(95∶5 ~ 50∶50,v/v)梯度洗脱,TLC 检测并且合并相同流分,最后得到 10 个组分。组分 3(17.4 g)通过反复 Sephadex LH-20 柱层析(氯仿-甲醇洗脱,1∶1,v/v)及高效制备薄层色谱(20 × 20 cm,氯仿-丙酮展开,95∶5,v/v),得化合物 **2**(13 mg)、**3**(95 mg)、**5**(15 mg)、**12**(107 mg);组分 4(8.5 g)通过多次 Sephadex LH-20 柱层析(氯仿-甲醇洗脱,1∶1,v/v)与高效制备薄层色谱(氯仿-丙酮展开,90∶10,v/v),得化合物 **13**(62 mg)、**4**(28 mg)、**7**(19 mg);组分 **5**(16.0 g)通过反复 Sephadex LH-20 柱层析(氯仿-甲醇洗脱,1∶1,v/v)及高效制备薄层色谱(氯仿-丙酮展开,82∶18,v/v),得化合物 **6**(32 mg)、**10**(91 mg)、**11**(47 mg)、**16**(15 mg);组分 6(27.8 g)通过多次 Sephadex LH-20 柱层析(氯仿-甲醇洗脱,1∶1,v/v)及高效制备薄层色谱(氯仿-丙酮展开,76∶24,v/v),得化合物 **1**(10 mg)、**8**(14 mg)、**9**(38 mg)、**14**(77 mg)、**15**(233 mg)。

2 结构鉴定

化合物 1 白色粉末(氯仿);$[\alpha]_D^{25}$ -37.9° (*c* 0.28, CH_3OH);ESI-MS *m/z* 243 $[M+H]^+$;^1H NMR (500 MHz, $CDCl_3$) δ:1.46 (1H, t, *J* = 12.2 Hz, Ha-2), 1.35 (1H, dd, *J* = 12.2, 3.8 Hz, Hb-2), 4.06 (1H, m, H-3), 3.72 (1H, t, *J* = 11.9 Hz, H-4), 2.42 (1H, dq, *J* = 12.1, 7.1 Hz, H-5), 6.77 (1H, d, *J* = 15.8 Hz, H-7), 6.32 (1H, d, *J* = 15.8 Hz, H-8), 2.30 (3H, s, H_3-10), 0.88 (3H, s, H_3-11), 1.22 (3H, s, H_3-12), 1.07 (3H, d, *J* = 6.9 Hz, H_3-13);^{13}C NMR (125 MHz, $CDCl_3$) δ:39.1 (C-1), 38.2 (C-2), 72.5 (C-3), 75.7 (C-4), 31.9 (C-5), 81.5 (C-6), 151.4 (C-7), 130.2 (C-8), 199.5 (C-9), 28.0 (C-10), 27.1 (C-11), 27.5 (C-12), 24.1 (C-13)。以上数据与文献[3]报道的白英醇 E 的数据一致,故鉴定化合物 **1** 为白英醇 E。

化合物 2 无色片状结晶(丙酮);mp. 126 ~ 127 ℃;$[\alpha]_D^{25}$ -31.4° (*c* 0.34, CH_3OH);ESI-MS *m/z* 225 $[M+H]^+$;^1H NMR (500 MHz, DMSO-d_6) δ:1.27 (1H, t, *J* = 12.3 Hz, Ha-2), 2.15 (1H, dd, *J* = 11.9, 4.5 Hz, Hb-2), 4.13 (1H, m, H-3), 1.19 (1H, t, *J* = 12.0 Hz, Ha-4), 1.80 (1H, dd, *J* = 11.5, 5.0 Hz, Hb-4), 5.75 (1H, s, H-8), 2.11 (3H, s, H_3-10), 1.05 (3H, s, H_3-11), 1.31 (3H, s, H_3-12), 1.26 (3H, s, H_3-13);^{13}C NMR (125 MHz, DMSO-d_6) δ:36.0 (C-1), 49.7 (C-2), 62.4 (C-3), 50.0 (C-4), 71.0 (C-5), 119.2 (C-6), 198.3 (C-7), 100.0 (C-8), 209.6 (C-9), 26.6 (C-10), 32.1 (C-11), 29.2 (C-12), 30.8 (C-13)。以上数据与文献[3]报道的白英醇 F 的数据一致,故鉴定化合物 **2** 为白英醇 F。

化合物 3 无色油状物(氯仿);$[\alpha]_D^{25}$ +14.2° (*c* 0.90, $CHCl_3$);ESI-MS *m/z* 253 $[M+H]^+$;^1H NMR (500 MHz, $CDCl_3$) δ:7.33 (1H, d, *J* = 9.6 Hz, H-1), 5.97 (1H, d, *J* = 9.6 Hz, H-2), 2.36 (1H, m, H-4), 1.49 (1H, m, H-5), 1.15 (1H, m, Ha-6), 1.79 (1H, m, Hb-6), 1.45 (1H, m, H-7), 1.94 (1H, m, Ha-8), 1.46 (1H, m, Hb-8), 3.47 (1H, dd, *J* = 10.9, 4.6 Hz, H-9), 1.23 (3H, s, H_3-12), 1.25 (3H, s, H_3-13), 1.13 (3H, d, *J* = 7.0 Hz, H_3-14), 1.04 (3H, s, H_3-15);^{13}C NMR (125 MHz, $CDCl_3$) δ:156.1 (C-1), 126.8 (C-2), 201.5 (C-3), 41.9 (C-4), 46.6 (C-5), 24.1 (C-6), 46.7 (C-7), 31.6 (C-8), 74.1 (C-9), 41.4 (C-10), 72.6 (C-11), 27.5 (C-12), 27.1 (C-13), 12.0 (C-14), 11.4 (C-15)。以上数据与文献[4]报道的白英醇 A 的数据一致,故鉴定化合物 **3** 为白英醇 A。

化合物 4 无色油状物(氯仿);$[\alpha]_D^{25}$ +7.3°(*c* 0.81, $CHCl_3$);ESI-MS *m/z* 253 [M + H]$^+$;^{1}H NMR (500 MHz, $CDCl_3$) δ:3.51 (1H, dd, *J* = 11.4, 4.6 Hz, H-1), 2.17 (1H, m, Ha-2), 2.33 (1H, m, Hb-2), 5.46 (1H, br d, *J* = 4.9 Hz, H-3), 5.61 (1H, br s, H-6), 2.50 (1H, m, H-7), 1.57 (1H, m, Ha-8), 1.83 (1H, m, Hb-8), 1.31 (1H, m, Ha-9), 1.93 (1H, m, Hb-9), 3.53 (1H, d, *J* = 10.9 Hz, Ha-12), 3.70 (1H, d, *J* = 10.9 Hz, Hb-12), 1.17 (3H, s, H_3-13), 1.76 (3H, s, H_3-14), 0.91 (3H, s, H_3-15);^{13}C NMR (125 MHz, $CDCl_3$) δ:76.2 (C-1), 31.3 (C-2), 122.7 (C-3), 132.0 (C-4), 144.1 (C-5), 121.3 (C-6), 44.2 (C-7), 19.8 (C-8), 33.9 (C-9), 38.0 (C-10), 75.0 (C-11), 67.2 (C-12), 21.4 (C-13), 20.1 (C-14), 16.7 (C-15)。以上数据与文献[4]报道的白英醇 B 的数据一致,故鉴定化合物 **4** 为白英醇 B。

化合物 5 白色棱晶(丙酮);mp. 208 ~ 209 ℃;$[\alpha]_D^{25}$ +10.3°(*c* 0.84, $CHCl_3$);ESI-MS *m/z* 271 [M + H]$^+$;^{1}H NMR (500 MHz, C_5D_5N) δ:3.54 (1H, d, *J* = 9.0 Hz, H-1), 4.09 (1H, m, H-2), 2.94 (1H, dd, *J* = 12.6, 5.5 Hz, Ha-3), 2.43 (1H, dd, *J* = 12.6, 11.9 Hz, Hb-3), 1.94 (1H, dd, *J* = 10.5, 3,5 Hz, H-5), 1.61 (1H, m, Ha-6), 1.95 (1H, m, Hb-6), 1.98 (1H, m, H-7), 1.75 (1H, m, Ha-8), 2.16 (1H, m, Hb-8), 2.52 (1H, m, Ha-9), 1.37 (1H, m, Hb-9), 4.03 (1H, d, *J* = 10.7 Hz, Ha-12), 3.94 (1H, d, *J* = 10.7 Hz, Hb-12), 1.46 (3H, s, H_3-13), 1.07 (3H, s, H_3-14), 4.93 (1H, s, Ha-15), 4.73 (1H, s, Hb-15);^{13}C NMR (125 MHz, C_5D_5N) δ:84.7 (C-1), 72.4 (C-2), 43.9 (C-3), 150.1 (C-4), 49.0 (C-5), 25.5 (C-6), 45.8 (C-7), 22.8 (C-8), 39.0 (C-9), 40.2 (C-10), 75.1 (C-11), 69.9 (C-12), 23.7 (C-13), 12.2 (C-14), 108.1 (C-15)。以上数据与文献[5]报道的白英醇 C 的数据一致,故鉴定化合物 **5** 为白英醇 C。

化合物 6 白色粉末(丙酮);$[\alpha]_D^{25}$ +31.3°(*c* 0.80, $CHCl_3$);ESI-MS *m/z* 269 [M + H]$^+$;^{1}H NMR (500 MHz, DMSO-d_6) δ:3.38 (1H, br s, H-1), 5.71 (1H, s, H-3), 1.79 (1H, dd, *J* = 13.3, 3.6 Hz, Ha-6), 1.23 (1H, dd, *J* = 13.3, 6.0 Hz, Hb-6), 1.84 (1H, m, H-7), 1.60 (1H, br d, *J* = 12.8 Hz, Ha-8), 1.40 (1H, m, Hb-8), 2.29 (1H, br t, *J* = 13.6 Hz, Ha-9), 1.09 (1H, m, Hb-9), 1.06 (3H, s, H_3-12), 1.08 (3H, s, H_3-13), 0.80 (3H, s, H_3-14), 1.91 (3H, s, H_3-15), 6.65 (1H, br s, C_1-OH), 5.39 (1H, s, C_5-OH), 4.15 (1H, s, C_{11}-OH);^{13}C NMR (125 MHz, DMSO-d_6) δ:79.9 (C-1), 197.8 (C-2), 123.5 (C-3), 164.1 (C-4), 74.1 (C-5), 29.3 (C-6), 42.6 (C-7), 19.6 (C-8), 28.3 (C-9), 40.5 (C-10), 71.1 (C-11), 27.3 (C-12), 28.2 (C-13), 20.4 (C-14), 19.2 (C-15)。以上数据与文献[6]报道的江西白英素 A 的数据一致,故鉴定化合物 **6** 为江西白英素 A。

化合物 7 白色粉末(丙酮);$[\alpha]_D^{25}$ +17.8°(*c* 0.83, CH_3OH);ESI-MS *m/z* 269 [M + H]$^+$;^{1}H NMR (500 MHz, DMSO-d_6) δ:3.01 (1H, d, *J* = 9.0 Hz, H-1), 3.30 (1H, m, H-2), 1.91 (1H, br t, *J* = 12.7 Hz, Ha-3), 2.40 (1H, dd, *J* = 12.7, 5.4 Hz, Hb-3), 1.72 (1H, br d, *J* = 11.6 Hz, H-5), 1.13 (1H, m, Ha-6), 1.43 (1H, m, Hb-6), 2.19 (1H, m, H-7), 1.07 (1H, m, Ha-8), 1.48 (1H, m, Hb-8), 1.88 (1H, m, Ha-9), 1.09 (1H, m, Hb-9), 1.49 (1H, m, H-11), 1.04 (3H, d, *J* = 7.0 Hz, H_3-13), 0.55 (3H, s, H_3-14), 4.39 (1H, s, Ha-15), 4.74 (1H, s, Hb-15), 5.80 (1H, s, C_1-OH), 4.85 (1H, s, C_2-OH), 11.35 (1H, s, -COOH);^{13}C NMR (125 MHz, DMSO-d_6) δ:83.8 (C-1), 70.8 (C-2), 43.2 (C-3), 147.8 (C-4), 47.1 (C-5), 27.8 (C-6), 44.9 (C-7), 23.5 (C-8), 36.1 (C-9), 38.8 (C-10), 40.0 (C-11), 177.6 (C-12), 14.1 (C-13), 11.1 (C-14), 107.5 (C-15)。以上数据与文献[7]报道的江西白英素 D 的数据一致,故鉴定化合物 **7** 为江西白英素 D。

化合物 8 淡黄色油状物(氯仿);$[\alpha]_D^{25}$ +101.2°(*c* 0.78, $CHCl_3$);ESI-MS *m/z* 225 [M + H]$^+$;^{1}H NMR (500 MHz, DMSO-d_6) δ:2.07 (1H, d, *J* = 16.7 Hz, Ha-2), 2.36 (1H, d, *J* = 16.7 Hz, Hb-2), 5.79 (1H, s, H-4), 5.65 (1H, d, *J* = 15.7 Hz, H-7), 5.70 (1H, dd, *J* = 15.7, 4.6 Hz, H-8), 4.18 (1H, m, H-9), 1.12 (3H, d, *J* = 6.4 Hz, H_3-10), 0.92 (3H, s, H_3-12), 1.81 (3H, d, *J* = 1.3 Hz, H-13);^{13}C NMR (125 MHz, DMSO-d_6) δ:41.4 (C-1), 49.9 (C-2), 197.8 (C-3), 125.9 (C-4), 164.1 (C-5), 78.3 (C-6), 128.4 (C-7), 136.3 (C-8), 67.5 (C-9), 24.6 (C-10), 23.5 (C-11), 23.7 (C-12), 19.4 (C-13)。以上数据与文献[8]报道的布卢门醇 A 的数据一致,故鉴定化合物 **8** 为布卢门醇 A。

化合物 9 淡黄色油状物(氯仿);$[\alpha]_D^{25}$ +130.2°(*c* 0.81, CH_3OH);ESI-MS *m/z* 223 $[M+H]^+$;^1H NMR (500 MHz, $CDCl_3$) δ:2.34 (1H, d, *J* = 17.2 Hz, Ha-2), 2.50 (1H, d, *J* = 17.2 Hz, Hb-2), 5.97 (1H, s, H-4), 6.84 (1H, d, *J* = 15.7 Hz, H-7), 6.46 (1H, d, *J* = 15.6 Hz, H-8), 2.31 (3H, s, H_3-10), 1.89 (3H, s, H_3-11), 1.02 (3H, s, H_3-12), 1.10 (3H, s, H_3-13);^{13}C NMR (125 MHz, $CDCl_3$) δ:41.4 (C-1), 49.6 (C-2), 197.3 (C-3), 127.8 (C-4), 160.2 (C-5), 79.3 (C-6), 144.9 (C-7), 130.4 (C-8), 196.9 (C-9), 28.4 (C-10), 18.6 (C-11), 24.3 (C-12), 22.9 (C-13)。以上数据与文献[9]报道的去氢催吐萝芙醇数据一致,故鉴定化合物 **9** 为去氢催吐萝芙醇。

化合物 10 淡黄色油状物(氯仿);$[\alpha]_D^{25}$ -110.3°(*c* 0.48, CH_3OH);ESI-MS *m/z* 225 $[M+H]^+$;^1H NMR (500 MHz, $CDCl_3$) δ:1.25 (1H, m, Ha-2), 1.64 (1H, m, Hb-2), 3.90 (1H, m, H-3), 1.67 (1H, m, Ha-4), 2.41 (1H, dd, *J* = 14.6, 4.7 Hz, Hb-4), 7.03 (1H, d, *J* = 15.6 Hz, H-7), 6.31 (1H, d, *J* = 15.6 Hz, H-8), 2.28 (3H, s, H_3-10), 0.97 (3H, s, H_3-11), 1.20 (6H, s, H_3-12 and H_3-13);^{13}C NMR (125 MHz, $CDCl_3$) δ:35.3 (C-1), 46.9 (C-2), 64.0 (C-3), 40.6 (C-4), 67.5 (C-5), 69.5 (C-6), 142.3 (C-7), 130.0 (C-8), 197.8 (C-9), 28.6 (C-10), 25.1 (C-11), 29.5 (C-12), 20.0 (C-13)。以上数据与文献[10]报道的 3β-羟基-5α,6α-环氧-7-大柱香波龙烯-9-酮数据一致,故鉴定化合物 **10** 为 3β-羟基-5α,6α-环氧-7-大柱香波龙烯-9-酮。

化合物 11 淡黄色油状物(氯仿);$[\alpha]_D^{25}$ +81.9°(*c* 0.42, CH_3OH);ESI-MS *m/z* 211 $[M+H]^+$;^1H NMR (500 MHz, $CDCl_3$) δ:2.05 (1H, d, *J* = 17.5 Hz, Ha-2), 2.38 (1H, d, *J* = 17.5 Hz, Hb-2), 5.82 (1H, s, H-4), 1.86 (1H, m, H-6), 3.74 (1H, m, H-9), 1.20 (3H, d, *J* = 6.1 Hz, H_3-10), 1.09 (3H, s, H_3-11), 1.03 (3H, s, H_3-12), 2.00 (3H, s, H_3-13);^{13}C NMR (125 MHz, $CDCl_3$) δ:36.7 (C-1), 47.8 (C-2), 199.9 (C-3), 126.1 (C-4), 165.8 (C-5), 51.7 (C-6), 27.2 (C-7), 39.0 (C-8), 68.5 (C-9), 24.2 (C-10), 27.5 (C-11), 28.8 (C-12), 25.6 (C-13)。以上数据与文献[11]报道的布卢门醇 C 数据一致,故鉴定化合物 **11** 为布卢门醇 C。

化合物 12 淡黄色针状结晶(甲醇);mp. 202 ~ 204 ℃;ESI-MS *m/z* 193 $[M+H]^+$;^1H NMR (500 MHz, DMSO-d_6) δ:6.21 (1H, d, *J* = 9.4 Hz, H-3), 7.91 (1H, d, *J* = 9.4 Hz, H-4), 6.78 (1H, s, H-5), 7.22 (1H, s, H-8), 3.80 (3H, s, 6-OCH_3);^{13}C NMR (125 MHz, DMSO-d_6) δ:161.1 (C-2), 112.2 (C-3), 144.9 (C-4), 110.1 (C-5), 145.7 (C-6), 151.6 (C-7), 103.2 (C-8), 150.0 (C-9), 111.0 (C-10), 56.5 (6-OCH_3)。以上数据与文献[12]报道的东莨菪内酯的数据一致,故鉴定化合物 **12** 为东莨菪内酯。

化合物 13 淡黄色油状物(氯仿);$[\alpha]_D^{25}$ -120.8°(*c* 0.85, CH_3OH);ESI-MS *m/z* 253 $[M+H]^+$;^1H NMR (500 MHz, $CDCl_3$) δ:1.98 (1H, dd, *J* = 13.3, 7.6 Hz, Ha-1), 1.62 (1H, dd, *J* = 13.3, 11.5 Hz, Hb-1), 2.11 (1H, m, H-2), 1.84 (1H, m, Ha-3), 1.80 (1H, m, Hb-3), 1.68 (1H, m, Ha-4), 1.88 (1H, m, Hb-4), 5.77 (1H, s, H-7), 2.63 (1H, dd, *J* = 16.7, 4.6 Hz, Ha-9), 2.21 (1H, dd, *J* = 16.7, 4.3 Hz, Hb-9), 2.12 (1H, m, H-10), 3.53 (1H, d, *J* = 10.8 Hz, Ha-12), 3.40 (1H, d, *J* = 10.8 Hz, Hb-12), 1.19 (3H, s, H_3-13), 1.94 (3H, s, H_3-14), 0.98 (3H, d, *J* = 6.9 Hz, H_3-15);^{13}C NMR (125 MHz, $CDCl_3$) δ:37.1 (C-1), 46.2 (C-2), 27.4 (C-3), 34.5 (C-4), 49.9 (C-5), 166.9 (C-6), 125.7 (C-7), 199.3 (C-8), 42.1 (C-9), 38.0 (C-10), 73.6 (C-11), 69.6 (C-12), 21.7 (C-13), 20.4 (C-14), 15.8 (C-15)。以上数据与文献[13]报道的(1′S,2R,5S,10R)-2-(1′,2′-dihydroxy-1′-methylethyl)-6,10-dimethylspiro[4,5]dec-6-en-8-one 的数据一致,故鉴定化合物 **13** 为(1′*S*,2*R*,5*S*,10*R*)-2-(1′,2′-dihydroxy-1′-methylethyl)-6,10-dimethylspiro[4,5]dec-6-en-8-one。

化合物 14 白色粉末(氯仿);$[\alpha]_D^{25}$ +27.4°(*c* 0.56, CH_3OH);ESI-MS *m/z* 215 $[M+H]^+$;^1H NMR (500 MHz, $CDCl_3$) δ:5.71 (1H, s, H-2), 1.76 (1H, m, Ha-5), 2.47 (1H, m, Hb-5), 4.33 (1H, m, H-6), 1.53 (1H, m, Ha-7), 1.99 (1H, m, Hb-7), 1.27 (3H, s, H_3-9), 1.47 (3H, s, H_3-10), 1.79 (3H, s, H_3-11);^{13}C NMR (125 MHz, $CDCl_3$) δ:182.6 (C-1), 113.0 (C-2), 172.1 (C-3), 86.9 (C-4), 46.0 (C-5), 66.8 (C-6), 47.3 (C-7), 36.0 (C-8), 26.5 (C-9), 30.7 (C-10), 27.0 (C-11)。以上数据与文献[14]报道的 chakyunglupulin A 的数据一致,故鉴定化合物 **14** 为 chakyunglupulin A。

化合物 15 淡黄色雪花状晶体(氯仿);mp. 87 ~ 88 ℃;$[\alpha]_D^{25}$ -24.7°(*c* 0.64, CH_3OH);ESI-MS *m/z* 331 $[M + H]^+$;^1H NMR (500 MHz, DMSO-d_6) δ: 2.25 (2H, t, *J* = 7.4 Hz, H-2), 3.21 (1H, m, H-9), 4.18 (1H, dd, *J* = 5.8, 5.8 Hz, H-10), 5.36 (1H, dd, *J* = 15.8, 5.8 Hz, H-11), 5.42 (1H, dd, *J* = 15.8, 5.2 Hz, H-12), 4.30 (1H, dt, *J* = 11.0, 5.8 Hz, H-13);^{13}C NMR (125 MHz, DMSO-d_6) δ: 174.6 (C-1), 32.8 (C-2), 25.0 (C-3), 29.0 (C-4), 28.6 (C-5), 27.3 (C-6), 25.8 (C-7), 29.5 (C-8), 71.4 (C-9), 77.0 (C-10), 130.5 (C-11), 131.1 (C-12), 67.8 (C-13), 33.7 (C-14), 24.5 (C-15), 31.0 (C-16), 22.1 (C-17), 13.9 (C-18)。以上数据与文献[15]报道的 9,10,13-三羟基-反-11-十八烯酸的数据一致,故鉴定化合物 **15** 为 9,10,13-三羟基-反-11-十八烯酸。

化合物 16　淡黄色油状物(氯仿);$[\alpha]_D^{25}$ -95.5°(*c* 0.71, CH_3OH);ESI-MS *m/z* 269 $[M + H]^+$;^1H NMR (500 MHz, $CDCl_3$) δ: 2.19 (1H, m, Ha-1), 1.61 (1H, m, Hb-1), 2.17 (1H, m, H-2), 1.91 (1H, m, Ha-3), 1.75 (1H, m, Hb-3), 1.58 (1H, m, Ha-4), 2.26 (1H, m, Hb-4), 5.87 (1H, s, H-7), 3.85 (1H, d, *J* = 12.7 Hz, H-9), 2.10 (1H, m, H-10), 3.55 (1H, d, *J* = 10.8 Hz, Ha-12), 3.43 (1H, d, *J* = 10.8 Hz, Hb-12), 1.27 (3H, s, H_3-13), 2.07 (3H, s, H_3-14), 1.23 (3H, d, *J* = 6.7 Hz, H_3-15);^{13}C NMR (125 MHz, $CDCl_3$) δ: 37.1 (C-1), 48.5 (C-2), 28.6 (C-3), 31.3 (C-4), 51.7 (C-5), 172.9 (C-6), 122.0 (C-7), 199.2 (C-8), 74.1 (C-9), 47.6 (C-10), 73.4 (C-11), 69.8 (C-12), 22.6 (C-13), 22.5 (C-14), 12.3 (C-15)。以上数据与文献[16]报道的 2-(1′,2′-dihydroxy-1′-methylethyl)-6,10-dimethyl-9-hydroxyspiro[4,5]dec-6-en-8-one 的数据一致,故鉴定化合物 **16** 为 2-(1′,2′-dihydroxyl-1′-methylethyl)-6,10-dimethyl-9-hydroxyl-9-hydroxyspiro[4,5]dec-6-en-8-one。

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