◆植物科学◆

线叶报春苣苔化学成分研究*

罗　彭,邓祖帅,王佳佳,沈章阳,潘为高**
(广西中医药大学,广西南宁　530200)

摘要:为了研究广西地域特色壮药植物线叶报春苣苔[*Primulina linearifolia* (W. T. Wang) Yin Z. Wang]的化学成分,探索其传统药效的物质基础,本研究采用硅胶柱色谱、大孔树脂(D101)柱色谱、聚酰胺柱色谱、反相ODS柱色谱、Sephadex LH-20柱色谱和重结晶方法对其全草的乙醇提取物进行分离纯化,并根据波谱数据和理化性质鉴定化合物的结构。结果表明:从线叶报春苣苔全草的乙醇提取物中分离得到17个化合物,分别鉴定为二十七酸(**1**)、芥酸单甘油酯(**2**)、β-谷甾醇(**3**)、β-扶桑甾醇氧化物(**4**)、三十一烷酸对羟基苯乙酯(**5**)、香草酸(**6**)、熊果酸(**7**)、1-二十八酸甘油酯(**8**)、胡萝卜苷(**9**)、木通苯乙醇苷A(**10**)、5,7,3′,4′-四羟基-6-C-β-D-葡萄糖二氢黄酮碳苷(**11**)、大车前苷(**12**)、α-菠甾醇-3-*O*-β-D-葡萄糖苷(**13**)、1,8-二氮杂环十四烷-2,9-二酮(**14**)、24-三十四碳烯酸(**15**)、正三十四烷酸(**16**)、正四十二烷(**17**)。化学成分研究为该广西地域特色植物传统药效的物质基础研究、质量标准制定和深度开发应用提供了重要借鉴。

关键词:线叶报春苣苔;分离纯化;化学成分;壮药

中图分类号:R931.6　　**文献标识码**:A　　**文章编号**:1005-9164(2023)05-0883-08
DOI:10.13656/j.cnki.gxkx.20231121.007

线叶报春苣苔[*Primulina linearifolia* (W. T. Wang) Yin Z. Wang]为苦苣苔科(Gesneriaceae)报春苣苔属(*Primulina*)多年生草本,壮药名为接骼红,中药名为接骨草,广西地域性壮族药用植物,主要分布于中国广西南部,例如南宁市邕宁区、大新县、隆安县、武鸣区[1];其根状茎可供药用,有清热解毒之效,用于调气道、续筋骨、散瘀肿,治疗劳伤咳嗽、骨折、跌打肿痛等病症[1,2]。

本课题组前期报道了线叶报春苣苔含有多种醌类成分(蒽醌、α-萘尼酮、萘骈萘尼酮),并具有优良抗肿瘤作用[3],但关于该植物的其他成分,国内外目前尚无研究报道,仅有植物生理方面的报道[4]。其同属植物的化学成分或药理研究方面,蚂蝗七[*P. fimbrisepala* (Hand.-Mazz.) Yin Z. Wang]含有黄酮和甾醇苷类[5];牛耳朵[*P. eburnea* (Hance) Yin Z. Wang]含有蒽醌和苯乙醇苷类,其苯乙醇苷类具有抗

收稿日期:2022-08-03　　修回日期:2022-09-18
*广西自然科学基金项目(2022JJA140371),广西高校中青年教师科研基础能力提升项目(2019KY0329)和广西一流学科建设开放课题(2019XK047,2019XK132)资助。
【第一作者简介】
罗　彭(1982-),女,副教授,博士,主要从事民族药活性成分研究,E-mail:lcl40261461@163.com。
【**通信作者简介】
潘为高(1977-),男,教授,博士,主要从事天然活性成分与结构改造研究,E-mail:agao81706672@163.com。
【引用本文】
罗彭,邓祖帅,王佳佳,等.线叶报春苣苔化学成分研究[J].广西科学,2023,30(5):883-890.
LUO P,DENG Z S,WANG J J,et al. Chemical Constituents from *Primulina linearifolia* (W. T. Wang) Yin Z. Wang [J]. Guangxi Sciences,2023,30(5):883-890.

癌活性[6-8];报春苣苔(*P. tabacum* Hance)含有的阿克苷具有抗肿瘤及抗肿瘤转移、抗凋亡作用[9,10];红药[*P. longgangensis* (W. T. Wang) Yan Liu & Yin Z. Wang]含蒽醌、香草酸、车前草苷、三萜及苷类等[11-13]。

除了上述典籍记载的药用价值[1,2],根据历次广西植物资源普查科考研究得知,在桂南马山、武鸣、隆安等区县,民间也称线叶报春苣苔为红接骨草、吊石牛,全草用于劳伤咳嗽、崩漏、肝炎,外治跌打损伤、骨折、消肿,是壮族民间赤脚医生的常用药。但该药用植物除其所含醌类被报道外[4],其他化学成分未见有相关研究,药效物质基础不明,药材质量标准尚未制定。本研究较系统地对其化学成分进行研究,拟为该药用植物传统药效的物质基础研究、质量标准制定和开发应用提供借鉴。

1 材料与方法

1.1 植物药材

线叶报春苣苔药材采集于广西南宁市隆安县,生长于该县山地的石山荫处及疏林中石上,经广西中医药大学朱意麟实验师和韦松基教授鉴定为苦苣苔科报春苣苔属线叶报春苣苔[*Primulina linearifolia* (W. T. Wang) Yin Z. Wang]。药材全株,阴干、粉碎,于 4 ℃密闭保存备用。

1.2 仪器与试剂

Waters Auto Spec Premier P776 质谱仪(Waters,美国);Bruker Avance-500 型和 Bruker AM-800 型核磁共振波谱仪(Bruker,瑞士);ZF-2 三用紫外仪(上海市安亭电子仪器厂);XT4-100A 显微熔点测定仪(北京市科仪电光仪器厂)。

柱层析硅胶 GF254(200 - 300 目、300 - 400 目)和薄层用硅胶 G 板(青岛海洋化工有限公司);D101 大孔吸附树脂(上海展云化工有限公司);聚酰胺柱色谱填料(80 - 120 目,100 - 200 目,常州市长丰化工有限公司);Sephadex LH-20(法玛西亚公司,瑞典);ODS 柱色谱填料(YMC 公司,日本);MCI(三菱化学公司,日本);乙醇、石油醚、乙酸乙酯、二氯甲烷、三氯甲烷、丙酮、甲醇(分析纯,成都市科隆化学品有限公司)。

1.3 方法

线叶报春苣苔全草粗粉 8.65 kg,用 15 倍量 85%乙醇,在 60 ℃条件下热搅拌,重复提取 3 次,每次 12 h;滤渣在相同条件下,用 15 倍量 50%乙醇重复提取 3 次,每次 12 h。合并提取液,减压浓缩,浓缩液水浴挥干至无醇味,并加适量水混悬,依次用石油醚(沸程 60 - 90 ℃)、乙酸乙酯、正丁醇萃取,将萃取液分别减压浓缩,得石油醚部位(140.0 g)、乙酸乙酯部位(160.0 g)、正丁醇部位(205.0 g)、水部位(203.0 g)。

取石油醚部位 130.0 g,经硅胶柱层析(100 - 200 目),用石油醚-乙酸乙酯(100∶1→50∶1→25∶1→15∶1→8∶1→5∶1→3∶1→2∶1→1∶1→0∶1,*V*/*V*)梯度洗脱,得 20 个流分;各流分分别经硅胶柱色谱(200 - 300 目,流动相为石油醚-乙酸乙酯或石油醚-丙酮)反复分离,并结合 Sephadex LH-20 柱色谱(三氯甲烷∶甲醇=1∶1,*V*/*V*)和重结晶进行纯化,最终获得 10 个化合物:**1**(5 mg)、**2**(4 mg)、**3**(300 mg)、**4**(5 mg)、**5**(3 mg)、**6**(3 mg)、**7**(3 mg)、**8**(5 mg)、**9**(150 mg)、**10**(30 mg)。

取乙酸乙酯部位 130.0 g,用硅胶柱色谱(100 - 200 目)分离,先以石油醚-乙酸乙酯(100∶1→15∶1,*V*/*V*)洗脱,接着用三氯甲烷-甲醇(100∶1→25∶1→15∶1→8∶1→5∶1→3∶1→2∶1→1∶1→0∶1,*V*/*V*)洗脱;各流分经硅胶柱色谱(200 - 300 目,流动相为石油醚-二氯甲烷)反复分离,并结合 Sephadex LH-20 柱色谱(三氯甲烷∶甲醇=1∶1,*V*/*V*)和重结晶进行纯化,最终获得 4 个化合物:**11**(7 mg)、**12**(6 mg)、**13**(9 mg)、**14**(6 mg)。

取正丁醇部位 150.0 g,用大孔树脂(D101)柱色谱进行分离,采用水→30%乙醇→50%乙醇→70%乙醇→无水乙醇梯度洗脱;所得各流分,根据极性等特性差异,分别用聚酰胺柱色谱(100 - 200 目,水→30%乙醇→50%乙醇→70%乙醇→无水乙醇洗脱)或硅胶柱色谱(200 - 300 目,三氯甲烷-甲醇:20∶1→10∶1→0∶1,*V*/*V*)或反相 ODS 柱色谱(水→30%乙醇→50%乙醇→70%乙醇→100%乙醇)进一步分离,最终获得 3 个化合物:**15**(7 mg)、**16**(9 mg)、**17**(8 mg)。

2 结果与分析

化合物 **1**:无色粉末,m. p. 87 - 89 ℃。EI-MS (*m*/*z*):410[M]$^+$。^{1}H-NMR (500 MHz,$CDCl_3$) δ:0.88 (3H,t,J = 7.1 Hz,H-27),1.25 (46H,m,H-4 - 26),1.63 (2H,m,H-3),2.35 (2H,t,J = 7.5 Hz,H-2);^{13}C-NMR and DEPT (125 MHz,$CDCl_3$) δ:14.1 (CH_3,C - 27),22.7 (CH_2,C - 26),24.7

(CH_2,C-3),29.1 - 29.7 (CH_2,C-4 - 24),31.9 (CH_2,C-25),34.1 (CH_2,C-2),180.3 (qC,C-1)。以上数据与文献[14]报道基本一致,化合物 **1** 鉴定为二十七酸(Heptacosanoic acid,$C_{27}H_{54}O_2$)。

化合物 **2**:白色粉末,m. p. 52 - 53 ℃。EI-MS (m/z):412 $[M]^+$。^{1}H-NMR (500 MHz,$CDCl_3$) δ:5.35 (2H,m,H-13,14),4.21 (1H,dd,J = 11.5,5.0 Hz,H-1′a),4.15 (1H,dd,J = 11.5,5 Hz,H-1′b),3.93 (1H,m,H-2′),3.70 (1H,dd,J = 11.5,6.0 Hz,H-3′a),3.60 (1H,dd,J = 11.5,6.0 Hz,H-3′b),2.35 (2H,t,J = 7.6 Hz,H-2),2.20 (2H,t,J = 7.5 Hz,H-15),2.00 (2H,m,H-12),1.63 (2H,m,H-3),1.26 (28H,m,H-4 - 11,H-16 - 21),0.88 (3H,t,J = 7.5 Hz,H-22);^{13}C-NMR and DEPT (125 MHz,$CDCl_3$) δ:174.4 (qC,C-1),129.9 (CH,C-13),129.9 (CH,C-14),70.2 (CH,C-2′),65.2 (CH_2,C-1′),63.3 (CH_2,C-3′),35.9 (CH_2,C-2),34.1 (CH_2,C-12,15),31.9 (CH_2,C-20),29.8,29.6,29.6,29.5,29.5,29.4,29.4,29.3,29.2,29.1,27.2,25.5 (CH_2,C-4 - 11,C-16 - 19),24.9 (CH_2,C-3),22.7 (CH_2,C-21),14.1 (CH_3,C-22)。对照文献[15]的核磁数据,化合物 **2** 鉴定为芥酸单甘油酯(Monoerucin,$C_{25}H_{48}O_4$)。

化合物 **3**:无色针状结晶,m. p. 141 - 142 ℃。EI-MS (m/z):414 $[M]^+$。^{1}H-NMR (500 MHz,$CDCl_3$) δ:5.35 (1H,m,H-6),3.52 (1H,m,H-3);^{13}C-NMR and DEPT (125 MHz,$CDCl_3$) δ:140.5 (qC,C-5),121.9 (CH,C-6),71.9 (CH,C-3),56.8 (CH,C-14),56.1 (CH,C-17),50.3 (CH,C-9),46.0 (CH,C-24),42.2 (qC,C-13),40.0 (CH_2,C-4),39.7 (CH_2,C-12),37.3 (CH_2,C-1),36.6 (qC,C-10),36.2 (CH,C-20),34.0 (CH_2,C-22),31.8 (CH_2,C-7),31.8 (CH,C-8),31.1 (CH_2,C-2),29.3 (CH,C-25),28.4 (CH_2,C-16),26.2 (CH_2,C-23),24.5 (CH_2,C-15),23.1 (CH_2,C-28),21.3 (CH_2,C-11),20.1 (CH_3,C-27),19.5 (CH_3,C-19),19.0 (CH_3,C-26),18.9 (CH_3,C-21),12.3 (CH_3,C-29),12.0 (CH_3,C-18)。对照文献[16]的核磁数据,化合物 **3** 鉴定为 β-谷甾醇(β-Sitosterol,$C_{29}H_{50}O$)。

化合物 **4**:无色针状结晶,易溶于三氯甲烷,m. p. 85 - 87 ℃。EI-MS (m/z):412$[M]^+$。^{1}H-NMR (500 MHz,$CDCl_3$) δ:5.72 (1H,s,H-4),2.40 (2H,m,H-2);^{13}C-NMR and DEPT (125 MHz,$CDCl_3$) δ:11.9 (CH_3,C-18),11.9 (CH_3,C-29),17.4 (CH_3,C-26),18.7 (CH_3,C-21),19.0 (CH_3,C-19),19.8 (CH_3,C-27),21.0 (CH_2,C-11),23.0 (CH_2,C-28),24.2 (CH_2,C-15),26.0 (CH,C-25),28.2 (CH_2,C-16),29.1 (CH_2,C-23),32.0 (CH_2,C-2),32.9 (CH_2,C-6),33.8 (CH_2,C-7),34.0 (CH_2,C-22),35.6 (CH_2,C-1),35.7 (CH,C-8),36.1 (CH,C-20),38.6 (qC,C-10),39.6 (CH_2,C-12),42.4 (qC,C-13),45.8 (CH,C-24),53.8 (CH,C-9),55.8 (CH,C-17),56.0 (CH,C-14),123.7 (CH,C-4),171.7 (qC,C-5),199.7 (qC,C-3)。以上数据与文献[17]报道基本一致,化合物 **4** 鉴定为 β-扶桑甾醇氧化物(β-sitostenone,$C_{29}H_{48}O$)。

化合物 **5**:无色片状结晶,m. p. 76 - 77 ℃。EI-MS (m/z):586 $[M]^+$。^{1}H-NMR (800 MHz,$CDCl_3$) δ:7.08 (2H,d,J = 8.4 Hz,H-2,6),6.76 (2H,J = 8.4 Hz,H-3,5),4.23 (2H,t,J = 7.1 Hz,H-8),2.86 (2H,t,J = 7.1 Hz,H-7),2.27 (2H,t,J = 7.6 Hz,H-2′),1.58 (2H,m,H-3′),1.25 (64H,m,H-4′ - 30′),0.88 (3H,t,J = 7.1 Hz,H-31′);^{13}C-NMR and DEPT (200 MHz,$CDCl_3$) δ:173.9 (qC,C-1′),154.2 (qC,C-4),130.1 (CH,C-2,6),129.9 (qC,C-1),115.3 (CH,C-3,5),64.9 (C-8),34.3 (C-7),34.3 (C-2′),31.9 (C-29′),29.1 - 29.7 (C-4′-28′),24.9 (C-3′),22.7 (C-30′),14.1 (CH_3,C-31′)。对照文献[18]的 Heitziethanoid A 光谱数据,化合物 **5** 结构鉴定为三十一烷酸对羟基苯乙酯[Hentriacontanoic acid,2 - (4 - hydroxyphenyl) ethyl ester,$C_{39}H_{70}O_3$]。

化合物 **6**:无色簇状结晶,m. p. 210 - 212 ℃。EI-MS (m/z):168 $[M]^+$。^{1}H-NMR (800 MHz,CD_3OD) δ:7.51 (1H,d,J = 1.9 Hz,H-2),7.55 (1H,dd,J = 8.3,1.9 Hz,H-6),6.83 (1H,d,J = 8.3 Hz,H-5),3.87 (3H,s,OCH_3);^{13}C-NMR and DEPT (200 MHz,CD_3OD) δ:169.5 (qC,C-7),151.3 (qC,C-4),147.5 (qC,C-3),124.6 (CH,C-6),122.3 (qC,C-1),115.0 (CH,C-5),113.0 (CH,C-2),56.1 (OCH_3)。以上数据与文献[19]报道基本一致,故化合物 **6** 鉴定为香草酸(Vanillic acid,$C_8H_8O_4$)。

化合物 **7**:无色片状结晶,m. p. 290 - 291 ℃。EI-MS (m/z):456$[M]^+$。^{1}H-NMR (800 MHz,$CDCl_3$) δ:5.25 (1H,t,J = 3.8 Hz,H-12),3.22 (1H,dd,J = 11.5,4.6Hz,H-3);^{13}C-NMR and DEPT (200 MHz,$CDCl_3$) δ:181.8 (qC,C-28),137.9 (qC,C-13),125.8 (CH,C-12),79.0 (CH,C-3),55.2 (CH,C-5),52.6 (CH,C-18),47.9 (qC,C-17),47.5 (CH,C-9),42.0 (qC,C-14),39.5 (qC,C-

10),39.0 (CH,C-20),38.8 (CH,C-19),38.7 (qC,C-4),38.6 (CH_2,C-22),37.0 (qC,C-8),36.7 (CH_2,C-1),32.9 (CH_2,C-7),30.6 (CH_2,C-21),28.1 (CH_3,C-23),28.0 (CH_2,C-2),27.2 (CH_2,C-15),24.1 (CH_2,C-16),23.6 (CH_3,C-27),23.3 (CH_2,C-11),21.2 (CH_3,C-30),18.3 (CH_2,C-6),17.0 (CH_3,C-26),17.0 (CH_3,C-29),15.6 (CH_3,C-24),15.5 (CH_3,C-25)。化合物 **7** 光谱数据与熊果酸数据[20]基本一致,故确定化合物 **7** 为熊果酸(Ursolic acid,$C_{30}H_{48}O_3$)。

化合物 **8**:白色粉末,m. p. 92 - 94 ℃。EI-MS (m/z): 498 $[M]^+$。^{1}H-NMR (800 MHz,CD_3OD) δ:4.05 (2H,m,H-1′),3.81 (1H,m,H-2′),3.55 (1H,dd,J = 11.5,4.2 Hz,H-3′a),3.48 (1H,dd,J = 11.5,6.2 Hz,H-3′b),2.28 (2H,t,J = 7.6 Hz,H-2),1.55 (2H,t,J = 7.6 Hz,H-3),1.14 - 1.38 (48H,m,H-4 - 27),0.81 (3H,t,J = 7.0 Hz,H-28);^{13}C-NMR and DEPT (200 MHz,CD_3OD) δ: 174.6 (qC,C-1),70.0 (CH,C-2′),65.2 (CH_2,C-1′),63.2 (CH_2,C-3′),34.9 (CH_2,C-2),31.9 (CH_2,C-26),29.1 - 29.7 (CH_2,C4 - 25),24.9 (CH_2,C-3),22.7 (CH_2,C-27),14.0 (CH_3,C-28)。对照文献[21]中的二十二(或二十四)酸甘油酯波谱数据进行归属,化合物 **8** 鉴定为 1-二十八酸甘油酯(1-Octacosanoyl glyceride,$C_{31}H_{62}O_4$)。

化合物 **9**:白色粉末,m. p. 301 - 303 ℃,易溶于三氯甲烷、甲醇。EI-MS (m/z): 398 $[M-C_6H_{11}O_6]^+$。^{1}H-NMR (500 MHz,Pyridine-d_6) δ: 5.33 (1H,m,H-6),4.36 (1H,d,J = 7.9 Hz,H-1′),3.79 - 3.81 (1H,m,H-3′),3.68 - 3.70 (1H,m,H-4′),3.53 - 3.57 (1H,m,H-3),3.35 - 3.37 (2H,m,H-6′),3.23 - 3.24 (1H,m,H-5′),3.16 - 3.19 (1H,m,H-2′);^{13}C-NMR and DEPT (125 MHz,Pyridine-d_6) δ:140.7 (qC,C-5),122.4 (CH,C-6),101.5 (CH,C-1′),79.5 (CH,C-3),76.9 (CH,C-3′),76.3 (CH,C-5′),74.0 (CH,C-2′),70.6 (CH,C-4′),62.1 (CH_2,C-6′),57.1 (CH,C-17),56.4 (CH,C-14),50.6 (CH,C-9),46.2 (CH,C-24),42.7 (qC,C-13),40.1 (CH_2,C-12),39.0 (CH_2,C-4),37.6 (CH_2,C-1),37.1 (qC,C-10),36.5 (CH,C-20),34.3 (CH_2,C-22),32.3 (CH_2,C-7),32.3 (CH,C-8),29.9 (CH_2,C-25),29.5 (CH,C-16),28.6 (CH_2,C-2),26.4 (CH_2,C-23),24.6 (CH_2,C-15),23.4 (CH_2,C-28),21.4 (CH_2,C-11),20.0 (CH_3,C-21),19.6 (CH_3,C-26),19.2 (CH_3,C-19),19.0 (CH_3,C-27),12.2 (CH_3,C-18),12.1 (CH_3,C-29)。以上数据与文献[22,23]报道基本一致,故化合物 **9** 鉴定为胡萝卜苷(Daucosterol,$C_{35}H_{60}O_6$)。

化合物 **10**:灰白色固体,m. p. 187 - 189 ℃。ESI-MS (m/z):477$[M-H]^-$。^{1}H-NMR (800 MHz,CD_3OD) δ:6.70 (1H,d,J = 2.0 Hz,H-2),6.69 (1H,d,J = 8.0 Hz,H-5),6.53 (1H,dd,J = 8.0,2.0 Hz,H-6),3.62 (2H,m,H-8),2.77 (2H,m,H-7)(phenethyl alcohol moiety);7.56 (1H,d,J = 15.8 Hz,H-7′),7.01 (1H,d,J = 2.0 Hz,H-2′),6.88 (1H,dd,J = 8.0,2.0 Hz,H-6′),6.76 (1H,d,J = 8.0 Hz,H-5′),6.22 (1H,d,J = 15.8 Hz,H-8′)(caffeic acid moiety);4.83 (1H,t,J = 9.6 Hz,H-4″),4.31 (1H,d,J = 7.8 Hz,H-1″),3.70 (1H,m,H-3″),3.54 (1H,m,H-5″),3.43 (1H,m,H-2″),3.31 (2H,m,H-6″)(glucose moiety)。^{13}C-NMR and DEPT (200 MHz,CD_3OD) δ: 144.9 (qC,C-3),143.5 (qC,C-4),130.7 (qC,C-1),120.7 (CH,C-6),116.3 (CH,C-2),115.6 (CH,C-5),71.4 (CH_2,C-8),35.7 (CH_2,C-7)(phenethyl alcohol moiety);168.2 (qC,C-9′),148.6 (qC,C-4′),147.3 (CH,C-7′),145.6 (qC,C-3′),126.8 (qC,C-1′),122.6 (CH,C-6′),115.8 (CH,C-5′),114.6 (CH,C-2′),113.7 (CH,C-8′)(caffeic acid moiety);103.3 (CH,C-1″),78.0 (CH,C-4″),75.1 (CH,C-2″),74.7 (CH,C-5″),74.3 (CH,C-3″),61.6 (CH_2,C-6″)(glucose moiety)。对照文献[10,24]的核磁数据,化合物 **10** 鉴定为木通苯乙醇苷 A(Calceolarioside A,$C_{23}H_{26}O_{11}$)。

化合物 **11**:白色粉末,溶于甲醇,盐酸-镁粉反应呈阳性,m. p. 254 - 255 ℃。EI-MS (m/z): 450 $[M]^+$。^{1}H-NMR (500 MHz,CD_3OD) δ:6.89(1H,s,H-2′),6.76(2H,s,H-5′,6′),5.95(1H,s,H-8),5.30 (1H,dd,J = 12.3,3.0 Hz,H-2),4.78(1H,d,J = 9.9 Hz,H-1″),4.10(1H,m,H-2″),3.85 (1H,d,J = 12.0 Hz,H-6″),3.71 (1H,dd,J = 12.0,5.4 Hz,H-6″),3.35 - 3.43 (3H,m,H-3″,4″,5″),3.10 (1H,dd,J = 17.2,12.3 Hz,H-3),2.75 (1H,dd,J = 17.2,3.0 Hz,H-3);^{13}C-NMR and DEPT (125 MHz,CD_3OD) δ:198.1 (qC,C-4),167.3 (qC,C-7),164.3 (qC,C-5),164.2 (qC,C-9),146.9 (qC,C-4′),146.5 (qC,C-3′),131.6 (qC,C-1′),119.2 (CH,C-6′),116.2 (CH,C-5′),114.7 (CH,C-2′),105.9 (qC,C-6),103.2 (qC,C-10),96.3 (CH,C-8),82.5 (CH,C-5″),80.5 (CH,C-3″),80.2 (CH,C-2),75.2 (CH,C-1″),72.6 (CH,C-2″),71.8 (CH,C-

4″),62.9 (CH_2,C-6″),44.0 (CH_2,C-3)。化合物**11**光谱数据与文献中5,7,3′,4′-四羟基-6-C-β-D-葡萄糖二氢黄酮碳苷的数据[25]一致,故鉴定其为5,7,3′,4′-四羟基-6-C-β-D-葡萄糖二氢黄酮碳苷(5,7,3′,4′-tetrahydroxy-6-C-β-D-glucosyl-dihydroflavonol,$C_{21}H_{22}O_{11}$)。

化合物**12**:灰白色固体,易吸潮,m.p.136-138 ℃。经$FeCl_3$-K_3[Fe(CN)$_6$]试剂鉴别,显蓝色,可能为酚类物质。ESI-MS (m/z):639 $[M-H]^-$。^{1}H-NMR (500 MHz,CD_3OD) δ:6.71 (1H,d,J=2.0 Hz,H-2),6.69 (1H,d,J=8.0 Hz,H-5),6.57 (1H,dd,J=8.0,2.0 Hz,H-6),3.66 (2H,m,H-8),2.79 (2H,m,H-7)(phenethyl alcohol moiety);7.60 (1H,d,J=15.9 Hz,H-7′),7.09 (1H,d,J=2.0 Hz,H-2′),6.99 (1H,dd,J=8.0,2.0 Hz,H-6′),6.80 (1H,d,J=8.0 Hz,H-5′),6.34 (1H,d,J=15.9 Hz,H-8′)(caffeic acid moiety);4.41 (1H,t,J=7.9 Hz,H-1″),4.03 (1H,m,H-4″),3.94 (1H,t,J=9.3Hz,H-3″),3.50 (2H,m,H-6″),3.25 (1H,m,H-5″),3.16 (1H,m,H-2″)(glucose moiety 1);4.55 (1H,t,J=7.8 Hz,H-1‴),3.74 (1H,m,H-4‴),3.72 (1H,m,H-3‴),3.54 (2H,m,H-6‴),3.32 (1H,m,H-5‴),3.19 (1H,m,H-2‴)(glucose moiety 2)。^{13}C-NMR and DEPT (125 MHz,CD_3OD) δ:146.1 (qC,C-3),144.6 (qC,C-4),131.4 (qC,C-1),121.4 (CH,C-6),117.2 (CH,C-2),116.4 (CH,C-5),72.2 (CH_2,C-8),36.5 (CH_2,C-7)(phenethyl alcohol moiety);168.6 (qC,C-9′),149.7 (qC,C-4′),147.5 (CH,C-7′),146.8 (qC,C-3′),127.7 (qC,C-1′),123.2 (CH,C-6′),116.6 (CH,C-5′),115.3 (CH,C-2′),115.2 (CH,C-8′)(caffeic acid moiety);103.9 (CH,C-1″),84.3 (CH,C-3″),76.0 (CH,C-2″),75.8 (CH,C-5″),70.9 (CH,C-4″),62.3 (CH_2,C-6″)(glucose moiety 1);105.8 (CH,C-1‴),77.8 (CH,C-3‴),77.6 (CH,C-5‴),75.0 (CH,C-2‴),71.1 (CH,C-4‴),62.4 (CH_2,C-6‴)(glucose moiety 2)。对照文献[26,27]的核磁数据,确定化合物**12**为大车前苷(Plantamajoside,$C_{29}H_{36}O_{16}$)。

化合物**13**:白色粉末,10% H_2SO_4显紫色,易溶于三氯甲烷、甲醇、乙醇,m.p.278-280 ℃。ESI-MS (m/z):575 $[M+H]^+$。^{1}H-NMR (500 MHz,$CDCl_3$+CD_3OD) δ:5.07-5.16 (1H,m,H-22,23),5.02 (1H,m,H-7),5.00 (1H,d,J=7.6 Hz,H-1′),4.01 (1H,m,H-3);^{13}C-NMR and DEPT (125 MHz,$CDCl_3$+CD_3OD) δ:139.5 (qC,C-8),138.4 (CH,C-22),129.8 (CH,C-23),117.7 (CH,C-7),102.2 (CH,C-1′),78.4 (CH,C-3′),78.0 (CH,C-5′),77.5 (CH,C-3),75.2 (CH,C-2′),71.9 (CH,C-4′),63.0 (CH_2,C-6′),56.3 (CH,C-17),55.3 (CH,C-14),51.4 (CH,C-24),49.7 (CH,C-9),43.5 (qC,C-13),40.5 (CH,C-5),40.3 (CH,C-20),39.7 (CH_2,C-12),37.4 (CH_2,C-1),34.7 (qC,C-10),34.6 (CH_2,C-4),32.1 (CH,C-25),30.1 (CH_2,C-2,6),28.6 (CH_2,C-16),25.5 (CH_2,C-28),23.3 (CH_2,C-15),21.7 (CH_2,C-11),21.3 (CH_3,C-27),21.2 (CH_3,C-21),19.3 (CH_3,C-26),12.8 (CH_3,C-19),12.2 (CH_3,C-29),12.1(CH_3,C-18)。对照文献[28]的核磁数据,化合物**13**鉴定为α-菠甾醇-3-*O*-β-D-葡萄糖苷(α-spinasteryl-3-*O*-β-D-glucoside,$C_{35}H_{58}O_6$)。

化合物**14**:白色粉末,易溶于三氯甲烷、甲醇,m.p.338 ℃。EI-MS (m/z):226 $[M]^+$。^{1}H-NMR (500 MHz,$CDCl_3$) δ:7.31 (1H,s,NH,H-1),7.28 (1H,s,NH,H-1),3.05 (4H,m,H-7,14),2.05 (4H,m,H-3,10),1.49 (4H,m,H-4,11),1.38 (4H,t,H-6,13),1.19 (4H,t,H-5,12);^{13}C-NMR (125 MHz,$CDCl_3$) δ:174.4 (qC,C-2,9),39.0 (CH_2,C-7,14),35.9 (CH_2,C-3,10),28.7 (CH_2,C-6,13),26.0 (CH_2,C-5,12),25.2 (CH_2,C-4,11)。对照文献[29]的核磁数据,化合物**14**鉴定为1,8-二氮杂环十四烷-2,9-二酮(1,8-diazacyclotetradecane-2,9-dinoe,$C_{12}H_{22}N_2O_2$)。

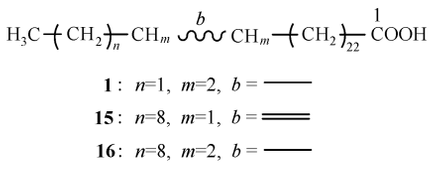
化合物**15**:无色油状物。EI-MS (m/z):506 $[M]^+$。^{1}H-NMR (500 MHz,C_5D_5N) δ:5.45 (2H,m,H-24,25),2.43 (2H,m,H-2),2.06 (2H,m,H-23),1.83 (2H,m,H-26),1.23 (54H,m,H-3-22,H-27-33),0.83 (3H,m,H-34);^{13}C-NMR (125 MHz,C_5D_5N) δ:180.1 (qC,C-1),130.2 (CH,C-24,25),36.3 (CH_2,C-2),32.1 (CH_2,C-23,26),27.5-30.1 (CH_2,m,C-4-22,C-27-32),26.3 (CH_2,C-3),23.0 (CH_2,C-33),14.3 (CH_3,C-34)。与文献[30]中的n-Tetratriacont-24-enoic acid光谱数据基本吻合,故化合物**15**鉴定为24-三十四碳烯酸(n-Tetratriacont-24-enoic acid,$C_{34}H_{66}O_2$)。

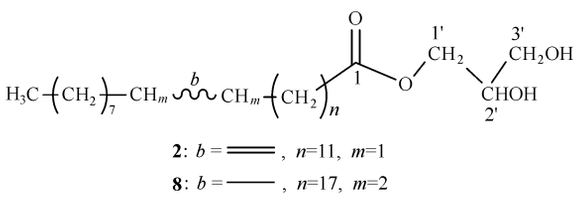
化合物**16**:白色粉末,m.p.110 ℃。EI-MS (m/z):508 $[M]^+$。^{1}H-NMR (500 MHz,C_5D_5N) δ:2.22 (2H,m,H-2),1.63 (2H,m,H-3),1.25 (60H,m,H-4-33),0.88 (3H,m,H-34);^{13}C-NMR (125 MHz,C_5D_5N) δ:180.1 (qC,C-1),35.9 (CH_2,C-2),31.9 (CH_2,C-32),29.3-29.7 (CH_2,m,C-4-31),25.7 (CH_2,C-3),22.7 (CH_2,C-33),14.1 (CH_3,C-34)。化合物**16**鉴定为正三十四烷酸(n-Tetratria-

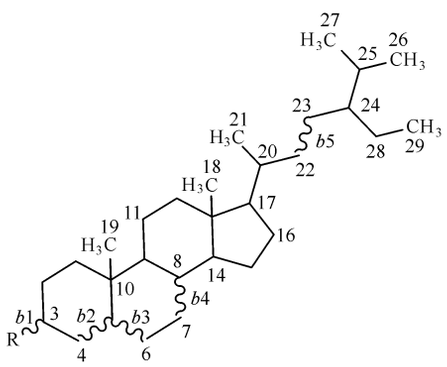
contanoic acid,$C_{34}H_{68}O_2$)[31]。

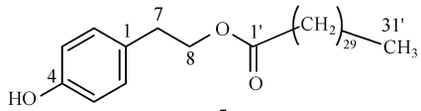
化合物 **17**:白色片状结晶,m. p. 83 ℃。EI-MS (m/z):590 $[M]^+$。^{1}H-NMR (500 MHz,$CDCl_3$) δ:1.25 (80H,m,H-2 - 41),0.88 (6H,t,J = 7.0 Hz,H-1,42);^{13}C-NMR (125 MHz,$CDCl_3$) δ:31.9 (CH_2,C-3,40),29.3 - 29.7 (CH_2,m,C-4 - 39),22.7 (CH_2,C-2,41),14.1 (CH_3,C-1,42)。化合物 **17** 鉴定为正四十二烷 (Alkane C42,n-$C_{42}H_{86}$)[32]。

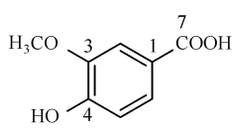
化合物 **1** - **17** 的结构式如图 1 所示。

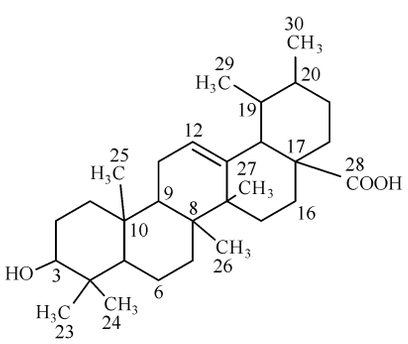


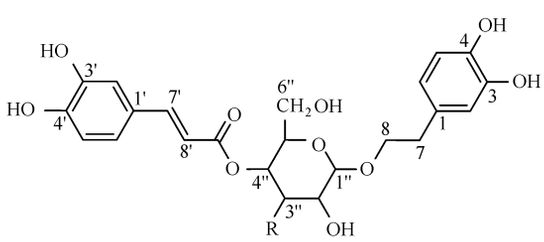


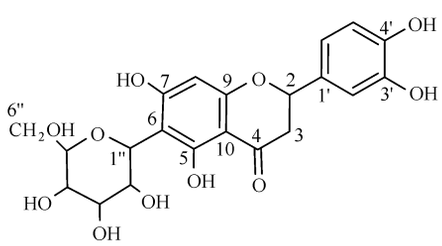


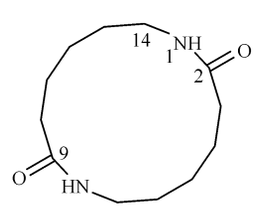












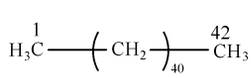


图 1　化合物 **1** - **17** 的结构式

Fig. 1　Structures of compounds **1** - **17**

3 讨论

三萜或甾类成分最显著的生理活性为抗炎、保肝等。线叶报春苣苔所含的1个五环三萜和4个甾体类(包括苷),很可能是其具有清热解毒、治跌打损伤、散瘀肿(消肿)、治疗肝炎等药效的重要物质基础。本研究发现线叶报春苣苔含有2个苯乙醇-咖啡酰糖苷,该类成分为阿克替苷的同系物,阿克替苷具有神经和组织保护、抗氧化、抗衰老、保肝等多种生理活性,是肉苁蓉、藏波罗花中的重要滋补成分[33],这与线叶报春苣苔用于跌打损伤治疗的记载相吻合。线叶报春苣苔含有的二氢黄酮苷类成分亦具有多种生理活性。另外,课题组前期从线叶报春苣苔中亦分离获得了系列蒽醌、α-董尼酮和萘骈董尼酮类成分,并报道了其优良抗癌特性[3]。醌类成分具有显著的抗菌(抗感染)、止血等作用,这与线叶报春苣苔具有清热解毒、治劳伤咳嗽、治崩漏的药效记载相吻合。总之,化学成分研究为该植物传统药效作用的物质基础研究、质量标准制定及深度开发应用提供了重要借鉴。

4 结论

本研究从线叶报春苣苔中获得17个化合物,按类别可分为饱和或不饱和脂肪酸(**1**、**15**、**16**)、脂肪酸单甘油酯(**2**、**8**)、甾体或其苷类(**3**、**4**、**9**、**13**)、苯乙醇脂肪酸酯(**5**)、苯甲酸类(**6**)、五环三萜(**7**)、苯乙醇-咖啡酰糖苷(**10**、**12**)、二氢黄酮碳苷(**11**)、环双内酰胺(**14**)、饱和烷烃(**17**),其中多数是生物活性功能性成分,该研究为广西地域特色壮药植物线叶报春苣苔的质量标准研究和深度开发应用提供了良好借鉴。

参考文献

[1] 中国科学院中国植物志编辑委员会.中国植物志:第六十九卷[M].北京:科学出版社,1990:382.
[2] 李振宇,王印政.中国苦苣苔科植物[M].郑州:河南科学技术出版社,2005:242-243.
[3] 罗彭,邓祖帅,潘为高,等.线叶报春苣苔中醌类成分及抗癌差异性研究[J].化学研究与应用,2021,33(10):1964-1971.
[4] 潘春柳,吕惠珍,彭玉德,等.外源激素处理对线叶报春苣苔种子萌发的影响[J].种子,2011,30(1):24-27.
[5] 周立东,余竞光,郭伽,等.蚂蝗七根的化学成分研究[J].中国中药杂志,2001,26(2):114-117.
[6] 陈文娟.苦苣苔科植物牛耳朵化学成分及其活性研究[D].桂林:广西师范大学,2010.
[7] CHEN Y Y,CHEN W J,LI D P,et al. Preparative isolation and purification of five phenylethanoid glycosides from *Primulina eburnean* [J]. Chemistry of Natural Compounds,2011,47(4):615-618.
[8] CAI X H,LUO X D,ZHOU J,et al. Quinones from *Primulina eburnean* [J]. Journal of Natural Products,2005,68(5):797-799.
[9] 白贞芳,王晓琴,肖培根,等.苯乙醇苷类化合物在苦苣苔科药用植物中分布规律[J].中国中药杂志,2013,38(24):4267-4270.
[10] MULANI S K,GUH J H,MONG K K T. A general synthetic strategy and the anti-proliferation properties on prostate cancer cell lines for natural phenylethanoid glycosides [J]. Organic & Biomolecular Chemistry,2014,12:2926-2937.
[11] DUAN W J,BAI A Y,LIN X J,et al. Isolation and purification of highly polar antioxidants from *Primulina longgangensis* by combination of macroporous resin and HSCCC [J]. Chromatographia,2014,77:707-713.
[12] 王满元,杨岚,屠呦呦.红药化学成分的研究[J].中国中药杂志,2006,31(4):307-308.
[13] 黄海疆,贺兰云.红药根的化学成分研究[J].中国中药杂志,2014,39(6):1040-1042.
[14] 周勤梅,彭成,蒙春旺,等.益母草中脂肪族化合物的研究[J].中草药,2015,46(9):1283-1286.
[15] 李晓君,陈铁,李梦雪,等.紫苏内生真菌 *Penicillium* sp. 12Y25 化学成分及抑菌活性研究[J].西北农林科技大学学报(自然科学版),2015,43(10):64-69,76.
[16] 邹娟,赵臣亮,何康,等.银叶凤尾蕨化学成分的研究[J].中成药,2019,41(10):2388-2393.
[17] YU C X,YU Y F,ZHAO Y,et al. Chemical constituents of *Sonchus brachyotus* [J]. Chemistry of Natural Compounds,2020,56(2):370-372.
[18] KAMOLDINOV K S,ESHBAKOVA K A,BOBAKULOV K M,et al. A new hydroxyphenylethyl hentriacontanoate from *Fraxinus syriaca* [J]. Chemistry of Natural Compounds,2017,53(4):618-619.
[19] LI S C,JIN Y J,XUE X,et al. Bioactive chemical constituents of *Cercis chinensis* [J]. Chemistry of Natural Compounds,2022,58(1):138-140.
[20] 任杰,潘善庆,赵小芳,等.野茉莉叶化学成分研究[J].中草药,2019,50(1):30-35.
[21] MATSUMARU T,IKENO R,SHUCHI Y,et al. Synthesis of glycerolipids containing simple linear acyl chains or aromatic rings and evaluation of their Mincle signaling activity [J]. Chemical Communications,2019,55:711-714.
[22] NGUYEN T M H,NGUYEN T T O,LE N T,et al. Preliminary observation on the fibrinolytic activity of *Dimocarpus longan* seed [J]. Chemistry of Natural Compounds,2021,57(5):945-948.
[23] 陈玩珊,胡新华,原文鹏.酸模叶的化学成分研究[J].中华中医药杂志,2019,34(8):3769-3771.
[24] LIU Y G,LI X X,XIONG D C,et al. Synthetic pheny-

lethanoid glycoside derivatives as potent neuroprotective agents [J]. European Journal of Medicinal Chemistry,2015,95:313-323.
[25] HE J B,ZHAO P,HU Z M,et al. Molecular and structural characterization of a promiscuous *C*-glycosyltransferase from *Trollius chinensis* [J]. Angewandte Chemie International Edition,2019,58:11513-11520.
[26] YUAN X,ZHAO J,WANG H X,et al. Antiproliferative activity of phenylpropanoids isolated from *Lagotis brevituba* maxim [J]. Phytotherapy Research,2017,31(10):1509-1520.
[27] BUDZIANOWSKA A,BUDZIANOWSKI J. A new flavonoid,a new phenylethanoid glycoside and related compounds isolated from the inflorescences of *Plantago lanceolata* L [J]. Natural Product Research,2022,36(15):3813-3824.
[28] 王梦月,詹志斌,熊英,等. 木鳖子脂溶性成分研究[J]. 中国中药杂志,2018,43(6):1175-1181.
[29] ABE Y,MUTSUGA M,OHNO H,et al. Isolation and quantification of polyamide cyclic oligomers in kitchen utensils and their migration into various food simulants [J]. PLoS One,2016,11(7):e0159547.
[30] JAMEEL M,ALI A,ALI M. Extraction and isolation of new compounds from traditional herbal medicine; *Clerodendrum phlomidis* Linn. [J]. Future Journal of Pharmaceutical Sciences,2017,3(2):118-123.
[31] ALI A,JAMEEL M,ALI M. New fatty acid,aromatic ester and monoterpenic benzyl glucoside from the fruits of *Withania coagulans* Dunal [J]. Natural Product Research,2015,29(14):1307-1314.
[32] SIDDIQUI A A,WANI S M,RAJESH R,et al. Isolation and hypotensive activity of five new phytoconstituents from chloroform extract of flowers of *Hibiscus rosasinensis* Linn. [J]. Indian Journal of Chemistry (Section B),2005,44(4):806-811.
[33] PAN W G,JIANG S P,LUO P,et al. Isolation,purification and structure identification of two phenolic glycosides from the roots of *Incarvillea younghusbandii* Sprague and their antioxidant activities [J]. Acta Pharmaceutica Sinica,2011,46(4):422-427.

Chemical Constituents from *Primulina linearifolia* (W. T. Wang) Yin Z. Wang

LUO Peng,DENG Zushuai,WANG Jiajia,SHEN Zhangyang,PAN Weigao**
(Guangxi University of Chinese Medicine,Nanning,Guangxi,530200,China)

Abstract: *Primulina linearifolia* (W. T. Wang) Yin Z. Wang is a valuable Zhuang nationality medicinal crop at traditional herbs market. In order to identify its chemical basis for the traditional medicinal effects,silica gel column chromatography,macroporous resin (D101) column chromatography,polyamide column chromatography,ODS column chromatography,Sephadex LH20 column chromatography and recrystallization methods were applied in separation and purification of ethanol extract from the whole herb. Based on chemical properties and spectral analysis,17 compounds were characterized:Heptacosanoic acid (**1**),Monoerucin (**2**),β-Sitosterol (**3**),β-sitostenone (**4**),Hentriacontanoic acid,2-(4-hydroxyphenyl)ethyl ester (**5**),Vanillic acid (**6**),Ursolic acid (**7**),1-Octacosanoyl glyceride (**8**),Daucosterol (**9**),Calceolarioside A (**10**),5,7,3′,4′-tetrahydroxy-6-C-β-D-glucosyl-dihydroflavonol (**11**),Plantamajoside(**12**),α-spinasteryl-3-*O*-β-D-glucoside(**13**),1,8-diazacyclotetradecane-2,9-dinoe (**14**),n-Tetratriacont-24-enoic acid (**15**),n-Tetratriacontanoic acid (**16**),Alkane C42 (**17**). This study will provide theoretical reference for the traditional medicine exploration.

Key words: *Primulina linearifolia* (W. T. Wang) Yin Z. Wang; isolation and purification; chemical constituents; Zhuang medicine

责任编辑:陆媛峰