# 腺梗豨莶化学成分研究

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**摘　要：目的**　研究腺梗豨莶 *Siegesbeckia pubescens* 的化学成分及其蛋白酪氨酸磷酸酶 1B（protein tyrosine phosphatase 1B，PTP1B）抑制活性。**方法**　综合运用硅胶柱色谱、Sephadex LH-20 凝胶柱色谱、MCI 柱色谱、半制备高效液相色谱（HPLC）等多种现代色谱技术对其化学成分进行分离纯化，利用质谱、核磁共振等波谱技术鉴定了单体化合物结构，并通过体外酶促反应对化合物进行 PTP1B 抑制剂活性评价。**结果**　从腺梗豨莶 75%乙醇提取物中分离鉴定了 32 个化合物，分别为对映-16β*H*,17-羟基贝壳杉烷-19-羧酸（**1**）、对映-16α,17-二羟基贝壳杉烷-19-羧酸（**2**）、豨莶酸（**3**）、对映-16β*H*,17-异丁酰氧基-18-羟基贝壳杉烷-19-羧酸（**4**）、对映-18-乙酰氧基-17 羟基-16β*H*-贝壳杉烷-19-羧酸（**5**）、奇壬醇（**6**）、对映-16-乙酰氧基-2α,15,19-三羟基海松烷-8(14)-烯（**7**）、darutoside（**8**）、对映-1β,3β,15,16-四羟基海松烷-8(14)-烯（**9**）、对映-(15*R*),16,19-三羟基海松烷-8(14)-烯-19-*O*-β-*D*-吡喃葡萄糖苷（**10**）、对映-15-乙酰氧基-2α,16,19-三羟基海松烷-8(14)-烯（**11**）、对映-2α,15*R*,16,19-四羟基海松烷-8(14)-烯（**12**）、16-*O*-acetyldarutoside（**13**）、15-*O*-acetyldarutoside（**14**）、对映-15,16,19-三羟基海松烷-8(14)-烯（**15**）、(4β,10*E*)-6α,14,15-trihydroxy-8β(tigloyloxy)-germacra-1(10),11(13)-diene-12-oic acid 12,6-lactone（**16**）、2-propenoicacid,2-methyl-2,3,3α,4,5,8,9,10,11,11α-decahydro-6,10-bis(hydroxyl-methyl)-3-methylene-2-oxocyclodeca[b]furan-4-yl ester（**17**）、(4β,10*E*)-6α,14,15-trihydroxy-8β-(isobutyryloxy)germacra-10,11(13)-diene-12-oic acid 12,6-lactone（**18**）、siegesbeckialide K（**19**）、(4β,10*E*)-6a,14,15-trihydroxy-8β-(senecioyloxy)-germacra-1(10),11(13)-diene-12-oic acid 12,6-lactone（**20**）、1(10)*E*,4*Z*-9α-ethoxy-6α,15-dihydroxy-8β-(tigloyloxy)-14-oxogermacra-1(10),4,11(13)-triene-12-oic acid 12,6-lactone（**21**）、17(13→4)-abeo-*ent*-3*S**,13*S**,16-trihydroxystrob-8(15)-ene（**22**）、strobol A（**23**）、2β,19-dihydroxy-15-devinyl-*ent*-pimar-8,11,13-triene（**24**）、阿亚黄素（**25**）、山柰酚-3-*O*-芸香糖苷（**26**）、3,5,3′-三羟基-7,4′-二甲氧基黄酮（**27**）、黑麦草内酯（**28**）、(6*R*,9*S*)-roseoside（**29**）、咖啡酸（**30**）、(–)-(7*R*,7′*R*,7″*R*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5-tetrameth-oxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol（**31**）、(–)-(7*R*,7′*R*,7″*S*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5-tetrameth-oxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol（**32**）。**结论**　化合物 **25**～**27**、**31**、**32** 为首次从豨莶草中分离得到。化合物 **1**、**2**、**4** 对 PTP1B 有一定的抑制作用。

**关键词：**腺梗豨莶；二萜；倍半萜；豨莶酸；奇壬醇；蛋白酪氨酸磷酸酶 1B；阿亚黄素；山柰酚-3-*O*-芸香糖苷；3,5,3′-三羟基-7,4′-二甲氧基黄酮

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# Chemical constituents from *Siegesbeckia pubescens*

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**Abstract: Objective**　The study focuses on the chemical constituents of S*iegesbeckia pubescens* and their inhibitory activity against protein tyrosine phosphatase 1B (PTP1B). **Methods**　A combination of silica gel column chromatography, Sephadex LH-20 gel

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column, MCI column, and semi-preparative HPLC was employed for the separation and purification of its chemical components. The structures of individual compounds were identified using mass spectrometry and nuclear magnetic resonance spectroscopy. Additionally, the inhibitory activity of the compounds against PTP1B was assessed through *in vitro* enzymatic assays. **Results** A total of 32 compounds were isolated and identified from the 75% ethanol extract of *S. pubescens*, which are as follows: *ent*-16β*H*,17-hydroxy-kauran-19-oic acid (**1**), *ent*-16α,17-dihydroxykauran-19-oic acid (**2**), siegesbeckic acid (**3**), *ent*-16βH,17-isobutyryloxy-18-hydroxy-kauran-19-oic acid (**4**), 18-acetoxy-*ent*-17-hydroxy-16β*H*-kauran-19-oicacid (**5**), kirenol (**6**), *ent*-16-acetoxy-2α,15,19-trihydroxypimar-8(14)-ene (**7**), darutoside (**8**), *ent*-1β,3β,15,16-tetrahydroxypimar-8(14)-ene (**9**), *ent*-(15*R*),16,19-trihydroxypimar-8(14)-ene-19-*O*-β-*D*-glucopyranoside (**10**), *ent*-15-acetoxy-2α,16,19-trihydroxypimar-8(14)-ene (**11**), *ent*-2α,15*R*,16,19-tetrahydroxypimar-8(14)-ene (**12**), 16-*O*-acetyldarutoside (**13**), 15-*O*-acetyldarutoside (**14**), *ent*-15,16,19-tetrahydroxypimar-8(14)-ene (**15**), (4β,10*E*)-6α,14,15-trihydroxy-8β(tigloyloxy)-germacra-1(10),11(13)-diene-12-oic acid 12,6-lactone (**16**), 2-propenoicacid,2-methyl-2,3,3α,4,5,8,9,10,11,11α-decahydro-6,10-bis(hydroxyl-methyl)-3-methylene-2-oxocyclodeca [b]furan-4-yl ester (**17**), (4β,10*E*)-6α,14,15-trihydroxy-8β-(isobutyryloxy)germacra-10,11(13)-diene-12-oic acid 12,6-lactone (**18**), siegesbeckialide K (**19**), (4β,10*E*)-6a,14,15-trihydroxy-8β-(senecioyloxy)-germacra-1(10),11(13)-diene-12-oic acid 12,6-lactone (**20**), 1(10)*E*,4*Z*-9α-ethoxy-6α,15-dihydroxy-8β-(tigloyloxy)-14-oxogermacra-1(10),4,11(13)-triene-12-oic acid 12,6-lactone (**21**), 17(13→4)-abeo-*ent*-3*S**,13*S**,16-trihydroxystrob-8(15)-ene (**22**), strobol A (**23**), 2β,19-dihydroxy-15-devinyl-*ent*-pimar-8,11,13-triene (**24**), ayanin (**25**), kaempferol 3-*O*-rutinoside (**26**), 3,5,3′-trihydroxy-7,4′-dimethoxyflavone (**27**), loliolide (**28**), (6*R*,9*S*)-roseoside (**29**), caffeic acid (**30**), (–)-(7*R*,7′*R*,7″*R*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5-tetrameth-oxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol (**31**), (–)-(7*R*,7′*R*,7″*S*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5-tetrameth-oxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol (**32**). **Conclusion** Compounds **25**—**27**, **31**, and **32** were isolated from *S. pubescens* for the first time. Compounds **1**, **2**, and **4** exhibited certain inhibitory effects on PTP1B.

**Key words:** *Siegesbeckia pubescens* Makino; diterpenes; sesquiterpenes; siegesbeckic acid; kirenol; protein tyrosine phosphatase 1B; ayanin; kaempferol 3-*O*-rutinoside; 3,5,3′-trihydroxy-7,4′-dimethoxyflavone

豨莶草 *Siegesbeckiae Herba* 为菊科豨莶属的一年生草本植物，别名有肥猪菜、肥猪草、粘糊菜、粘苍子等，主要分布于中国河北、四川、广西、云南、贵州等省区。豨莶草始载于《新修本草》：“主金疮，止痛、断血，生肉，除诸恶症。”《中国药典》2020 年版收载为菊科植物豨莶 *Siegesbeckia orientalis* L.、腺梗豨莶 *S. pubescens* Makino 或毛梗豨莶 *S. glabrescens* Makino 的干燥地上部分[1]，属于多基原品种。其味辛、苦，性寒，具有祛风湿、利关节、解毒之功。单味药制剂豨莶丸，具有清热祛湿、散风止痛之功效，多用于风湿疼痛的临床治疗[2]。虽然豨莶丸、豨桐胶囊等以豨莶草入药中成药品种上市应用多年，但豨莶草具体药效物质基础、作用机制尚不明确。国内外对豨莶草化学成分的研究表明，豨莶草包含多种化学成分类型，主要有二萜类、倍半萜类、黄酮类、甾醇类、有机酸类等[3]，现代研究主要集中在抗炎[4]、镇痛、抗血栓[5]、抗肿瘤[6]等领域。

本研究利用多种色谱技术对腺梗豨莶的化学成分进行研究，共分离鉴定 32 个化合物，分别为对映-16β*H*,17-羟基贝壳杉烷-19-羧酸（*ent*-16β*H*,17-hydroxy-kauran-19-oic acid，**1**）、对映-16α,17-二羟基贝壳杉烷-19-羧酸（*ent*-16α,17-dihydroxykauran-19-oic acid，**2**）、豨莶酸（siegesbeckic acid，**3**）、对映-16β*H*,17-异丁酰氧基-18-羟基贝壳杉烷-19-羧酸（*ent*-16β*H*,17-isobutyryloxy-18-hydroxy-kauran-19-oic acid，**4**）、对映-18-乙酰氧基-17 羟基-16β*H*-贝壳杉烷-19-羧酸（18-acetoxy-*ent*-17-hydroxy-16β*H*-kauran-19-oic acid，**5**）、奇壬醇（kirenol，**6**）、对映-16-乙酰氧基-2α,15,19-三羟基海松烷-8(14)-烯（2-propenoic acid,2-methyl-2,3,3α,4,5,8,9,10,11,11α-decahydro-6,10-bis(hydroxyl-methyl)-3-methylene-2-oxocyclodeca [b] furan-4-yl ester，**7**）、darutoside（**8**）、对映-1β,3β,15,16-四羟基海松烷-8(14)-烯 [*ent*-1β,3β,15,16-tetrahydroxy-pimar-8(14)-ene，**9**]、对映-(15*R*),16,19-三羟基海松烷-8(14)-烯-19-*O*-β-*D*-吡喃葡萄糖苷[*ent*-(15*R*),16,19-trihydroxypimar-8(14)-ene-19-*O*-β-*D*-glucopyrano-side，**10**]、对映-15-乙酰氧基-2α,16,19-三羟基海松烷-8(14)-烯 [*ent*-15-acetoxy-2α,16,19-trihydroxypimar-8(14)-ene，**11**]、对映-2α,15*R*,16,19-四羟基海松烷-8(14)-烯 [*ent*-2α,15*R*,16,19-tetrahydroxypimar-8(14)-ene，**12**]、16-*O*-acetyldarutoside（**13**）、15-*O*-acetyldarutoside（**14**）、对映-15,16,19-三羟基海松烷-8(14)-烯 [*ent*-15,16,19-tetrahydroxypimar-8(14)-ene

**15**] 、 (4β,10*E*)-6α,14,15-trihydroxy-8β(tigloyloxy) germacra-1(10),11(13)-diene-12-oic acid 12,6-lactone（**16**）、2-propenoicacid,2-methyl-2,3,3-α,4,5,8,9,10,11,11α-decahydro-6,10-bis(hydroxylmethyl)-3-methylene-2-oxocyclodeca[b]-furan-4-yl ester（**17**）、(4β,10*E*)-6α,14,15-trihydroxy-8β-(isobutyryloxy)germacra-10,11(13)-diene-12-oic acid 12,6-lactone （**18**）、siegesbeckialide K（**19**）、(4β,10*E*)-6a,14,15-trihydroxy-8β-(senecioyloxy)-germacra-1(10),11(13)-diene-12-oic acid 12,6-lactone（**20**）、1(10)*E*,4*Z*-9α-ethoxy-6α,15-dihydroxy-8β-(tigloyloxy)-14-oxogermacra-1(10),4,11(13)-triene-12-oic acid 12,6-lactone（**21**）、17(13→4)-abeo-*ent*-3*S**,13*S**,16-trihydroxystrob-8(15)-ene （**22**）、strobol A （**23**）、 2β,19-dihydroxy-15-devinyl-*ent*-pimar-8,11,13-triene（**24**）、阿亚黄素（ayanin，**25**）、山柰酚-3-*O*-芸香糖苷（kaempferol 3-*O*-rutinoside，**26**）、3,5,3′-三羟基-7,4′-二甲氧基黄酮（3,5,3′-trihydroxy-7,4′-dimethoxyflavone，**27**）、黑麦草内酯（loliolide，**28**）、(6*R*,9*S*)-roseoside（**29**）、咖啡酸（caffeic acid，**30**）、(–)-(7*R*,7′*R*,7″*R*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5-tetramethoxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol（**31**）、(–)-(7*R*,7′*R*,7″*S*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5-tetramethoxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol（**32**），结构见图 1。基于 Kim 等[7]发现的豨莶草中 C-17 位异丁酰氧基取代的贝壳杉烷型二萜对 PTP1B 酶活性具有显著抑制作用，开展部分化合物的 PTP1B 抑制剂筛选实验。其中化合物 **25**～**27**、**31**、**32** 为首次从豨莶草中分离得到。在 PTP1B 抑制剂活性评价实验中，化合物 **1**、**2**、**4** 表现出一定的抑制活性。

## 1 仪器与材料

Bruker AVANCE III 400 MHz、500 MHz、600 MHz、800 MHz 核磁共振仪（德国 Bruker 公司）；UPLC-IT-TOF 质谱仪（日本 Shuma dzu 公司）；Hitachi Chromaster 高效液相色谱仪（日本日立有限公司）；YMC-Triart $C_{18}$ 色谱柱（250 mm×10 mm，5 μm，日本 YMC 公司）；SENCO 旋转蒸发仪（上海申生科技有限公司）；DLSB-5L/25 型低温冷却液循环泵（巩义予华仪器有限公司）；多功能酶标仪 Flex Station 3（美国 Molecular Devices 公司）；HH-6 数显恒温水浴锅（国华电器有限公司）；MPR-440F 型冷藏冷冻箱（松下冷链有限公司）；AL204 型精密电子天平（上海托利多仪器有限公司）；DHS-500Spro 多功能混匀仪（天津德鸿盛生物）；96 孔酶标板（Costar 公司）；柱色谱硅胶（200～300 目）；薄层色谱硅胶 $GF_{254}$（中国青岛海洋化工有限公司）；Sephadex LH-20（瑞典 Pharmacia 生物技术有限公司）；MCI gel CHP-20P（苏州汇拓色谱分离纯化有限公司）。色谱级甲醇、乙腈（云南新蓝景）；甲醇、二氯甲烷、醋酸乙酯、石油醚、正丁醇（云南利妍科技有限公司）；水为超纯水；PTP1B 酶（北京义翘神州科技股份有限公司）；对硝基苯磷酸二钠 PNPP（美仑生物）；对照品 Suramin（批号 HY-B0879，美国 MedChemexpress 生物科技公司）。

豨莶草药材，经中国科学院广西植物研究所标本馆黄俞淞研究员鉴定为菊科豨莶属植物腺梗豨莶 *S. pubescens* Makino 的干燥全草。

## 2 方法

### 2.1 提取与分离

在室温下，将 25 kg 豨莶草干燥全草粉碎，用 75%乙醇回流提取 3 次，滤过后的滤液经浓缩得到 6 kg 浸膏。将粗提物与水 1∶1 混悬，分别用石油醚、二氯甲烷、醋酸乙酯和正丁醇萃取。取二氯甲烷部分（500 g）经硅胶（100～200 目）柱色谱分离，用二氯甲烷-甲醇（1∶0、50∶1、25∶1、10∶1、5∶1、2∶1、1∶1）洗脱，得到 7 个组分（Fr. 1～7）。

Fr. 2（55 g）经 MCI 柱色谱分离，用甲醇-水（10%～100%）梯度洗脱，得到 10 个组分（Fr. 2.1～2.10）。Fr.2.4 经硅胶柱色谱分离，用二氯甲烷-甲醇（40∶1～10∶1）梯度洗脱，得到 10 个组分（Fr. 2.4.1～2.4.10）。Fr. 2.4.3、Fr. 2.4.5 和 Fr. 2.4.8 挥干溶剂后重结晶，用甲醇洗涤，分别得到化合物 **1**（108 mg）、**2**（105 mg）、**3**（110 mg）。Fr. 2.4.4 经 Sephadex LH-20 柱色谱分离，用甲醇洗脱，每 30 mL 接一流分，TLC 检识后合并，经半制备 HPLC（乙腈-水 20%～80%）纯化得到化合物 **16**（$t_R$＝12.5 min，112 mg）、**17**（$t_R$＝16.7 min，5 mg）、**24**（$t_R$＝20 min，3 mg）。Fr. 2.5 经硅胶柱色谱分离，用二氯甲烷-丙酮（50∶1～8∶1）梯度洗脱，再经半制备 HPLC（45%乙腈-水）纯化得到化合物 **4**（$t_R$＝10.4 min，125 mg）、**18**（$t_R$＝13.7 min，3 mg）、**19**（$t_R$＝17 min，5 mg）、**20**（$t_R$＝20.5 min，6 mg）。Fr. 2.6 挥干溶剂后重结晶，用二氯甲烷和水依次洗涤得到化合物 **6**（150 mg），剩余样品经 Sephadex LH-20 柱色谱分离，用二氯甲烷-甲醇（1∶1）洗脱，得到 4 个组分（Fr.

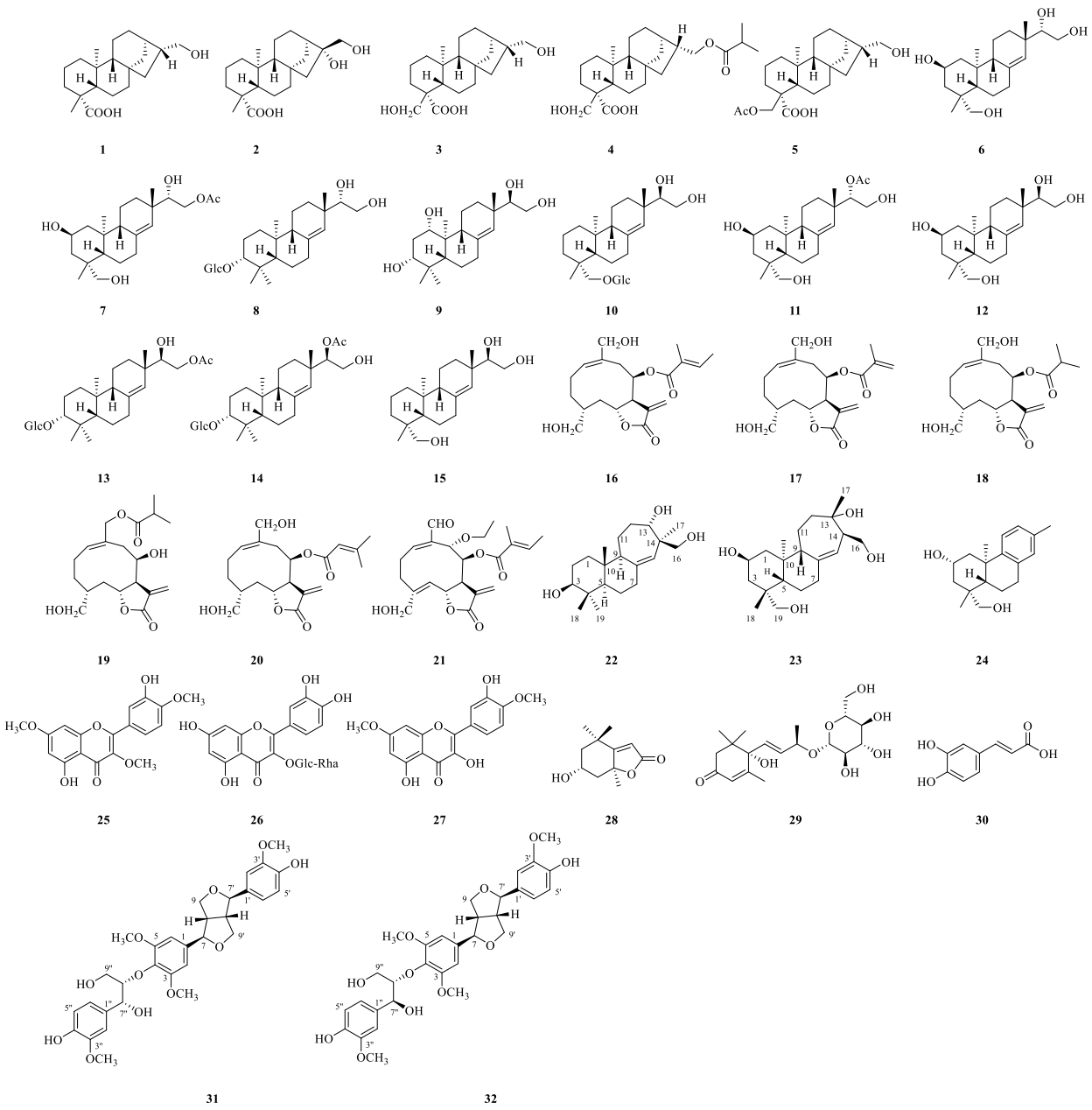

**图 1　化合物 1～32 的化学结构**

**Fig.1　Chemical structures of compounds 1—32**

2.6.1～2.6.4），Fr. 2.6.2 经半制备 HPLC（30%乙腈-水）纯化得到化合物 **5**（$t_R$＝15.8 min，108 mg）、**7**（$t_R$＝18.2 min，5.5 mg）、**28**（$t_R$＝19.5 min，3 mg）；Fr. 2.6.3 经半制备 HPLC（35%乙腈-水）纯化得到化合物 **22**（$t_R$＝11.2 min，4 mg）、**23**（$t_R$＝15.5 min，5 mg）。Fr. 2.8 经硅胶柱色谱分离，用二氯甲烷-甲醇（20∶1～5∶1）梯度洗脱，得到 5 个组分（Fr. 2.8.1～2.8.5）；Fr. 2.8.2 经硅胶柱色谱进一步纯化得到化合物 **8**（5 mg）、**10**（5 mg）；Fr. 2.8.4 经 Sephadex LH-20 柱色谱，甲醇洗脱后用半制备 HPLC（25%乙腈-水）纯化得到化合物 **13**（$t_R$＝20.6 min，6 mg）、**14**（$t_R$＝23.9 min，4 mg）。

Fr. 4（40 g）经 MCI 柱色谱分离，用甲醇-水（10%～100%）梯度洗脱，得到 8 个组分（Fr. 4.1～4.8）。Fr. 4.3 经 Sephadex LH-20 柱色谱分离，用甲醇洗脱，得到化合物 **25**（15 mg）。Fr. 4.4 经硅胶柱色谱分离，用二氯甲烷-甲醇（40∶1～10∶1）梯度洗脱，得到 3 个组分（Fr. 4.4.1～4.4.3）；Fr. 4.4.2 用半制备 HPLC（37%甲醇-水）纯化得到化合物 **27**（$t_R$＝13.5 min，12 mg）、**21**（$t_R$＝23.7 min，3 mg）；Fr. 4.4.3

经硅胶柱色谱进一步纯化得到化合物 **29**（5 mg）。Fr. 4.6 用半制备 HPLC（30%～70%乙腈-水）纯化得到化合物 **9**（$t_R$＝8.3 min，3 mg）、**15**（$t_R$＝17.6 min，6 mg），将剩余未完全分离的组分进行 2 次半制备 HPLC（26%乙腈-水）得到化合物 **26**（$t_R$＝10.5 min，4 mg）。

Fr. 6（50 g）经 MCI 柱色谱分离，用甲醇-水（10%～100%）梯度洗脱，得到 10 个组分（Fr. 6.1～6.10）。Fr. 6.5 经硅胶柱色谱分离，用二氯甲烷-甲醇（30∶1～8∶1）梯度洗脱，得到 3 个组分（Fr. 6.5.1～6.5.3）；Fr. 6.5.3 用半制备 HPLC（45%甲醇-水）纯化得到化合物 **11**（$t_R$＝15 min，5 mg）、**30**（$t_R$＝11 min，7 mg）。Fr. 6.7 经 Sephadex LH-20 柱色谱，二氯甲烷-甲醇（1∶1）洗脱，得到化合物 **12**（4.5 mg）。Fr.6.10 用半制备 HPLC（57%甲醇-水）纯化得到化合物 **31**（$t_R$＝20.2 min，4 mg）、**32**（$t_R$＝25.1 min，6 mg）。

### 2.2 PTP1B 抑制剂活性测定

缓冲液的配制：50 mmol/L HEPES，pH 7.4，含 150 mmol/L NaCl、1 mmol/L EDTA、0.01% 聚山梨酯 20。将待测化合物和阳性药 Suramin 用适量 DMSO 溶解，使终浓度为 50 μmol/L。酶标板每孔终体积为 100 μL，按以下顺序加入试剂：空白对照孔加入 60 μL 缓冲液、20 μL 酶溶液（终质量浓度 0.1 μg/μL）、20 μL 底物 pNPP（终浓度 1 mmol/L）。样品孔加入 50 μL 缓冲液、20 μL 待测样品、20 μL 酶溶液、10 μL pNPP。阳性对照孔加入 50 μL 缓冲液、20 μL Suramin（终浓度 50 μmol/L）、20 μL 酶溶液、10 μL pNPP。每组设置 3 个复孔，采用随机区组设计排列于酶标板，避免边缘效应。加入后立即以涡旋振荡器（1 000 r/min，10 s）混匀，确保溶液均一，37 ℃恒温孵育 30 min 后，快速加入 $Na_2CO_3$ 终止液，使用酶标仪在 405 nm 波长处测定各孔的吸光度（$A$）值，记录空白孔、实验孔和阳性对照孔的 $A$ 值，按公式计算抑制率。

$$抑制率=1-(A_{样品}-A_{无酶})/(A_{空白}-A_{无酶})$$

## 3 结果

### 3.1 结构鉴定

化合物 **1**：白色晶体（甲醇）；ESI-MS *m*/*z*: 321 $[M+H]^+$，分子式 $C_{20}H_{32}O_3$。$^1$H-NMR (400 MHz, Pyridine-$d_5$) $\delta$: 3.66 (2H, overlapped, H-17), 2.47 (1H, brd, $J$ = 13.1 Hz, H-3a), 2.36 (1H, m, H-13), 2.26 (1H, m, H-2a), 2.21 (1H, m, H-16), 2.16 (1H, m, H-6a), 2.05 (1H, m, H-6b), 1.90 (1H, overlapped, H-14a), 1.86 (1H, m, H-1a), 1.67 (1H, m, H-15a), 1.60 (2H, m, H-11), 1.54 (1H, overlapped, H-2b), 1.51 (2H, m, H-7), 1.46 (2H, m, H-12), 1.35 (3H, s, H-18), 1.16 (3H, s, H-20), 1.13 (1H, overlapped, H-15b), 1.10 (1H, overlapped, H-14b), 1.07(1H, m, H-3b), 1.04 (1H, overlapped, H-5), 1.01 (1H, m, H-9), 0.83 (1H, dt, $J$ = 13.3, 4.2 Hz, H-1b)；$^{13}$C-NMR (100 MHz, Pyridine-$d_5$) $\delta$: 180.1 (C-19), 66.9 (C-17), 57.0 (C-5), 55.6 (C-9), 45.7 (C-15), 45.0 (C-4), 44.1 (C-16), 43.8 (C-8), 42.1 (C-1), 41.1 (C-7), 39.9 (C-10), 38.6 (C-13), 38.6 (C-14), 37.3 (C-3), 31.8 (C-12), 29.3 (C-18), 23.1 (C-6), 19.8 (C-2), 19.1 (C-11), 15.9 (C-20)。以上数据与文献报道一致[7]，故鉴定化合物 **1** 为对映-16β*H*,17-羟基贝壳杉烷-19-羧酸。

化合物 **2**：白色晶体（甲醇）；ESI-MS *m*/*z*: 359 $[M+Na]^+$，分子式 $C_{20}H_{32}O_4$。$^1$H-NMR (400 MHz, Pyridine-$d_5$) $\delta$: 4.12 (1H, d, $J$ = 10.8 Hz, H-17a), 4.04 (1H, d, $J$ = 10.9 Hz, H-17b), 2.46 (1H, m, H-3a), 2.40 (1H, overlapped, H-14a), 2.28 (1H, m, H-13), 2.18 (1H, overlapped, H-6a), 2.04 (1H, overlapped, H-2a), 2.01 (1H, overlapped, H-14b), 1.99 (1H, overlapped, H-6b), 1.86 (1H, m, H-15a), 1.84 (1H, m, H-12a), 1.82 (1H, m, H-7a), 1.78 (1H, m, H-1a), 1.72 (1H, overlapped, H-15b), 1.63 (1H, m, H-11a), 1.55 (1H, m, H-11b), 1.52 (1H, m, H-7b), 1.49 (1H, m, H-2b), 1.47 (1H, m, H-12b), 1.33 (3H, s, H-18), 1.17 (3H, s, H-20), 1.09 (1H, m, H-3b), 1.06 (1H, overlapped, H-5), 1.03 (1H, m, H-9), 0.84 (1H, dt, $J$ = 13.3, 3.3 Hz, H-1b)；$^{13}$C-NMR (100 MHz, Pyridine-$d_5$) $\delta$: 180.0 (C-19), 81.5 (C-16), 66.3 (C-17), 56.8 (C-5), 56.1 (C-9), 53.6 (C-15), 45.7 (C-13), 44.8 (C-8), 43.7 (C-4), 42.6 (C-7), 40.8 (C-1), 39.8 (C-10), 38.5 (C-3), 37.6 (C-14), 29.1 (C-18), 26.6 (C-12), 22.7 (C-6), 19.6 (C-2), 18.8 (C-11), 15.8 (C-20)。以上数据与文献报道一致[8]，故鉴定化合物 **2** 为对映-16α,17-二羟基贝壳杉烷-19-羧酸。

化合物 **3**：白色针状晶体（甲醇）；ESI-MS *m*/*z*: 375 $[M+K]^+$，分子式 $C_{20}H_{32}O_4$。$^1$H-NMR (400 MHz, Pyridine-$d_5$) $\delta$: 4.40 (1H, d, $J$ = 10.8 Hz, H-18a), 4.01 (1H, d, $J$ = 10.3 Hz, H-18b), 3.65 (2H, dd, $J$ = 6.6, 2.4 Hz, H-17), 2.90 (1H, d, $J$ = 12.6 Hz, H-3a), 2.42 (1H, m, H-13), 2.36 (1H, m, H-2a), 2.21 (1H, m, H-16), 2.17 (2H, m, H-6), 1.94 (1H, overlapped, H-14a), 1.89 (1H,

overlapped, H-1a), 1.67 (1H, m, H-15a), 1.64 (2H, m, H-11), 1.61 (2H, overlapped, H-12), 1.57 (2H, overlapped, H-7), 1.53 (1H, m, H-2b), 1.50 (1H, m, H-15b), 1.45 (1H, m, H-14b), 1.24 (3H, s, H-20), 1.13 (1H, m, H-3b), 1.10 (1H, m, H-9), 1.07 (1H, m, H-5), 0.91 (1H, m, H-9)；$^{13}$C-NMR (100 MHz, Pyridine-$d_5$) $\delta$: 178.9 (C-19), 70.4 (C-18), 66.9 (C-17), 55.7 (C-9), 51.3 (C-5), 50.4 (C-4), 45.7 (C-15), 44.8 (C-8), 44.1 (C-16), 41.8 (C-7), 40.9 (C-1), 39.7 (C-10), 38.6 (C-13), 37.3 (C-14), 33.0 (C-3), 31.8 (C-12), 22.9 (C-6), 19.5 (C-2), 19.1 (C-11), 16.2 (C-20)。以上数据与文献报道一致[9]，故鉴定化合物 **3** 为豨莶酸。

化合物 **4**：白色针状晶体（甲醇）；ESI-MS *m*/*z*: 429 [M＋Na]$^+$，分子式 $C_{24}H_{38}O_5$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 3.85 (2H, d, $J$ = 7.6 Hz, H-17), 3.77 (1H, d, $J$ = 10.5 Hz, H-18), 3.46 (1H, d, $J$ = 10.5 Hz, H-18), 2.54 (1H, m, H-2′), 2.22 (1H, d-like, H-3), 2.10 (1H, m, H-16), 2.04 (1H, m, H-13), 1.90 (1H, m, H-1), 1.88 (1H, m, H-12), 1.76 (2H, m, H-6), 1.66 (2H, m, H-11), 1.60 (1H, m, H-15), 1.44 (4H, m, H-2, 7, 14), 1.26 (1H, m, H-5), 1.14 (7H, m, H-3, 3′, 4′), 1.06 (2H, m, H-9, 12), 1.00 (3H, s, H-20), 0.95 (1H, dd, $J$ = 13.5, 5.4 Hz, H-15), 0.83 (1H, m, H-1)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 179.9 (C-19), 179.0 (C-1′), 70.9 (C-18), 69.5 (C-17), 56.8 (C-9), 52.3 (C-5), 50.8 (C-4), 46.1 (C-15), 45.9 (C-8), 42.4 (C-7), 41.8 (C-1), 41.0 (C-16), 40.5 (C-10), 40.0 (C-13), 38.1 (C-12), 35.3 (C-2′), 33.1 (C-3), 32.4 (C-14), 23.4 (C-6), 19.9 (C-2), 19.8 (C-11), 19.4 (C-3′), 19.4 (C-4′), 16.4 (C-20)。以上数据与文献报道一致[10]，故鉴定化合物 **4** 为对映-16β*H*,17-异丁酰氧基-18-羟基贝壳杉烷-19-羧酸。

化合物 **5**：白色固体（甲醇）；ESI-MS *m*/*z*: 401 [M＋Na]$^+$，分子式 $C_{22}H_{34}O_5$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 4.37 (1H, d, $J$ = 10.4 Hz, H-18a), 3.95 (1H, d, $J$ = 10.4 Hz, H-18b), 3.30 (2H, overlapped, H-17), 2.26 (1H, d, $J$ = 13.3 Hz, H-3), 2.08 (1H, m, H-16), 2.02 (3H, s, 18-$CH_3COO$), 1.98 (1H, m, H-13), 1.94 (1H, m, H-2a), 1.91 (1H, m, H-1a), 1.85 (1H, d, $J$ = 11.9 Hz, H-12a), 1.75 (2H, m, H-6), 1.64 (2H, m, H-11), 1.58 (1H, m, H-15a), 1.54 (1H, m, H-14a), 1.45 (4H, overlapped, H-2b, 7, 14b), 1.27 (1H, dd, $J$ = 12.1, 2.4 Hz, H-5), 1.10 (1H, m, H-3b), 1.04 (2H, m, H-9, 12b), 1.01 (3H, s, H-20), 0.90 (1H, m, H-15b), 0.84 (1H, m, H-1b)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 178.7 (C-19), 172.6 (18-$CH_3COO$), 73.3 (C-18), 67.6 (C-17), 56.9 (C-9), 53.2 (C-5), 49.5 (C-4), 46.3 (C-15), 45.7 (C-8), 44.4 (C-16), 42.5 (C-7), 41.6 (C-1), 40.6 (C-10), 39.5 (C-13), 38.0 (C-14), 33.6 (C-3), 32.5 (C-12), 23.6 (C-6), 20.6 (18-$CH_3COO$), 19.9 (C-2), 19.7 (C-11), 16.2 (C-20)。以上数据与文献报道一致[9]，故鉴定化合物 **5** 为对映-18-乙酰氧基-17 羟基-16βH-贝壳杉烷-19-羧酸。

化合物 **6**：白色柱状晶体（甲醇）；ESI-MS *m*/*z*: 339 [M＋H]$^+$，分子式 $C_{20}H_{34}O_4$。$^1$H-NMR (400 MHz, Methanol-$d_4$) $\delta$: 5.18 (1H, s, H-14), 3.77 (1H, m, H-2), 3.69 (1H, overlapped, H-15), 3.66 (1H, overlapped, H-19a), 3.55 (1H, dd, $J$ = 9.0, 2.0 Hz, H-16a), 3.45 (1H, overlapped, H-16b), 3.32 (1H, d, $J$ = 11.1 Hz, H-19b), 2.28 (1H, m, H-6a), 2.18 (1H, m, H-6b), 2.05 (1H, m, H-11a), 1.99 (2H, m, H-7), 1.81 (1H, m, H-3a), 1.71 (1H, m, H-3b), 1.58 (2H, m, H-1), 1.31 (1H, m, H-5), 1.21 (1H, m, H-9), 1.05 (1H, overlapped, H-11b), 1.01 (3H, s, H-18), 0.93 (1H, m, H-12a), 0.89 (1H, m, H-12b), 0.84 (3H, s, H-17), 0.82 (3H, s, H-20)；$^{13}$C-NMR (100 MHz, Methanol-$d_4$) $\delta$: 139.3 (C-8), 130.1 (C-14), 77.5 (C-15), 65.6 (C-16), 65.2 (C-19), 64.3 (C-2), 56.5 (C-5), 52.5 (C-9), 49.1 (C-1), 45.1 (C-3), 41.4 (C-10), 40.5 (C-4), 38.5 (C-13), 37.4 (C-7), 33.2 (C-12), 28.1 (C-18), 23.3 (C-17), 23.0 (C-6), 19.7 (C-11), 17.2 (C-20)。以上数据与文献报道一致[11]，故鉴定化合物 **6** 为奇壬醇。

化合物 **7**：白色固体（甲醇）；分子式 $C_{22}H_{36}O_5$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 5.21 (1H, s, H-14), 4.22 (1H, dd, $J$ = 11.3, 2.5 Hz, H-16a), 4.01 (1H, dd, $J$ = 11.3, 9.0 Hz, H-16b), 3.77 (1H, m, H-2), 3.72 (1H, dd, $J$ = 8.9, 2.4 Hz, H-15), 3.68 (1H, d, $J$ = 11.1 Hz, H-19a), 3.32 (1H, m, H-19b), 2.30 (1H, m, H-6a), 2.18 (1H, m, H-6b), 2.05 (3H, s, 16-$CH_3COO$), 2.03 (1H, m, H-11a), 1.99 (2H, m, H-7), 1.83 (1H, m, H-3a), 1.72 (1H, m, H-3b), 1.56 (2H, m, H-1), 1.32 (1H, qd, $J$ = 12.9, 4.4 Hz, H-5), 1.22 (1H, dd, $J$ = 12.9, 2.1 Hz, H-9), 1.04 (1H, overlapped, H-11b), 1.01 (3H, s, H-18), 0.96 (1H, m, H-12a), 0.91 (1H, m, H-12b), 0.88 (3H, s, H-17), 0.80 (3H, s, H-20)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 173.1 (16-$CH_3COO$), 139.9 (C-8), 129.6 (C-14), 74.2 (C-15), 67.5 (C-16), 65.7 (C-2), 65.2 (C-19), 56.5 (C-5), 52.4 (C-9), 49.0 (C-1), 45.1 (C-3),

41.4 (C-13), 40.6 (C-4), 38.7 (C-10), 37.4 (C-7), 33.1 (C-12), 28.1 (C-18), 23.3 (C-17), 22.8 (C-6), 20.9 (16-$CH_3COO$), 19.6 (C-11), 17.1 (C-20)。以上数据与文献报道一致[12]，故鉴定化合物 **7** 为对映-16-乙酰氧基-2α,15,19-三羟基海松烷-8(14)-烯。

化合物 **8**：淡黄色油状物（甲醇）；分子式 $C_{26}H_{44}O_8$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 5.16 (1H, s, H-14), 4.33 (1H, d, $J$ = 7.7 Hz, H-1′), 3.86 (1H, dd, $J$ = 11.7, 2.3 Hz, H-6′a), 3.69 (1H, overlapped, H-15), 3.66 (1H, overlapped, H-6′b), 3.57 (1H, dd, $J$ = 9.0, 2.3 Hz, H-16a), 3.45 (1H, dd, $J$ = 11.1, 9.0 Hz, H-16b), 3.38 (1H, dd, $J$ = 11.7, 3.8 Hz, H-3), 3.34 (1H, ov, H-3′), 3.29 (1H, m, H-4′), 3.23 (1H, m, H-5′), 3.16 (1H, dd, $J$ = 9.1, 7.8 Hz, H-2′), 2.28 (1H,m, H-7a), 2.05 (1H, overlapped, H-7b), 1.98 (1H, m, H-12a), 1.80 (1H, m, H-2a), 1.76 (1H, m, H-1a), 1.71 (1H, m, H-9), 1.64 (1H, m, H-6a), 1.56 (3H, m, H-2b, 11), 1.39 (1H, m, H-6b), 1.16 (1H, overlapped, H-1b), 1.11 (1H, dd, $J$ = 12.2, 2.5 Hz, H-5), 1.05 (3H, s, H-18), 0.92 (1H, m, H-12b), 0.86 (3H, s, H-17), 0.84 (6H, overlapped, H-19, 20)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 139.9 (C-8), 129.6 (C-14), 101.9 (C-1′), 86.0 (C-3), 78.2 (C-5′), 77.7 (C-3′), 77.5 (C-15), 75.1 (C-2′), 71.9 (C-4′), 64.3 (C-16), 63.0 (C-6′), 56.2 (C-5), 52.1 (C-9), 39.4 (C-10), 39.0 (C-4), 38.5 (C-13), 38.1 (C-1), 37.1 (C-7), 33.3 (C-12), 29.2 (C-18), 24.4 (C-2), 23.4 (C-6), 23.0 (C-17), 19.4 (C-11), 17.3 (C-20), 15.3 (C-19)。以上数据与文献报道一致[12]，故鉴定化合物 **8** 为 darutoside。

化合物 **9**：无色油状物（甲醇）；分子式 $C_{20}H_{34}O_4$。$^1$H-NMR (800 MHz, Methanol-$d_4$) $\delta$: 5.19 (1H, s, H-14), 3.68 (1H, dd, $J$ = 11.2, 2.4 Hz, H-15), 3.62 (1H, dd, $J$ = 9.0, 2.4 Hz, H-16a), 3.49 (1H, dd, $J$ = 11.7, 4.5 Hz, H-16b), 3.46 (1H, dd, $J$ = 11.1, 9.0 Hz, H-1), 3.25 (1H, dd, $J$ = 12.1, 4.1 Hz, H-3), 2.28 (1H, m, H-7a), 2.03 (1H, m, H-11a), 1.97 (1H, m, H-7a), 1.88 (1H, m, H-2a), 1.86 (1H, m, H-11b), 1.84 (1H, m, H-2b), 1.79 (1H, m, H-7b), 1.73 (1H, m, H-9), 1.67 (1H, m, H-6a), 1.49 (1H, m, H-6b), 0.97 (3H, s, H-18), 0.93 (1H, m, H-12b), 0.87 (1H, m, H-5), 0.83 (3H, s, H-17), 0.82 (3H, s, H-19), 0.79 (3H, s, H-20)；$^{13}$C-NMR (200 MHz, Methanol-$d_4$) $\delta$: 139.9 (C-8), 130.4 (C-14), 77.5 (C-15), 77.5 (C-1), 76.7 (C-3), 64.4 (C-16), 54.1 (C-5), 52.9 (C-9), 45.2 (C-10), 40.2 (C-4), 38.9 (C-2), 38.2 (C-13), 37.6 (C-7), 33.8 (C-12), 28.8 (C-18), 23.1 (C-17), 23.0 (C-11), 22.6 (C-6), 16.1 (C-19), 9.4 (C-20)。以上数据与文献报道一致[13]，故鉴定化合物 **9** 为对映-1β,3β,15,16-四羟基海松烷-8(14)-烯。

化合物 **10**：淡黄色油状物（甲醇）；分子式 $C_{26}H_{44}O_8$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 5.14 (1H, s, H-14), 4.18 (1H, d, $J$ = 7.5 Hz, H-1′), 4.17 (1H, d, $J$ = 8.9 Hz, H-19a), 3.86 (dd, $J$ = 11.8, 2.3 Hz, 1H, H-6′a), 3.70 (1H, overlapped, H-16a), 3.67 (1H, overlapped, H-6′b), 3.56 (1H, dd, $J$ = 8.9, 2.3 Hz, H-15), 3.45 (1H, dd, $J$ = 11.1, 9.0 Hz, H-16b), 3.33 (1H, overlapped, H-3′), 3.29 (1H, overlapped, H-4′), 3.25 (1H, m, H-5′), 3.23 (1H, m, H-19b), 3.17 (1H, dd, $J$ = 8.9, 7.9 Hz, H-2′), 2.27 (1H, m, H-7a), 2.04 (1H, m, H-7b), 1.99 (1H, overlapped, H-3a), 1.97 (1H, overlapped, H-12a), 1.74 (3H, m, H-1a, 6a, 9), 1.56 (3H, m, H-2a, 11), 1.42 (1H, m, H-2b), 1.34 (1H, overlapped, H-6b), 1.21 (1H, dd, $J$ = 12.8, 2.3 Hz, H-5), 1.10 (1H, ddd, $J$ = 13.3, 13.1, 3.6 Hz, H-1b), 1.04 (3H, s, H-18), 0.97 (1H, m, H-3b), 0.91 (1H, m, H-12b), 0.83 (3H, s, H-17), 0.80 (3H, s, H-20)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 140.0 (C-8), 129.5 (C-14), 105.1 (C-1′), 78.2 (C-3′), 77.8 (C-5′), 77.5 (C-15), 75.3 (C-2′), 73.6 (C-19), 71.7 (C-4′), 64.3 (C-16), 62.7 (C-6′), 57.4 (C-5), 52.5 (C-9), 40.4 (C-1), 39.3 (C-4), 39.1 (C-10), 38.5 (C-13), 37.6 (C-7), 37.2 (C-3), 33.3 (C-12), 28.3 (C-18), 23.7 (C-6), 23.0 (C-17), 19.7 (C-11), 19.5 (C-2), 16.4 (C-20)。以上数据与文献报道一致[14]，故鉴定化合物 **10** 为对映-(15*R*),16,19-三羟基海松烷-8(14)-烯-19-*O*-β-*D*-吡喃葡萄糖苷。

化合物 **11**：白色针状结晶（甲醇）；分子式 $C_{22}H_{36}O_5$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 5.18 (1H, s, H-14), 5.04 (dd, $J$ = 9.1, 2.5 Hz, 1H, H-15), 3.80 (1H, m, H-2), 3.76 (1H, dd, $J$ = 12.1, 2.7 Hz, H-16a), 3.69 (1H, d, $J$ = 11.1 Hz, H-19a), 3.61 (1H, dd, $J$ = 12.0, 9.1 Hz, H-16b), 3.33 (1H, overlapped, H-19b), 2.30 (1H, m, H-6a), 2.18 (1H, m, H-6b), 2.09 (3H, s, 15-$CH_3COO$), 2.05 (1H, m, H-12a), 1.98 (2H, m, H-7), 1.82 (1H, m, H-3a), 1.74 (1H, m, H-3b), 1.67 (m, 1H), 1.59 (1H, m, H-1a), 1.52 (1H, m, H-1b), 1.33 (1H, dd, $J$ = 12.9, 4.4 Hz, H-5), 1.22 (1H, dd, $J$ = 12.9, 2.3 Hz, H-9), 1.02 (3H, s, H-18), 0.98 (1H, m, H-11b), 0.92 (3H, s, H-17), 0.88 (3H, s, H-20), 0.85 (1H, m, H-12b)；

$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 173.0 (15-$CH_3COO$), 140.7 (C-8), 128.6 (C-14), 79.6 (C-15), 65.7 (C-16), 65.2 (C-2), 62.3 (C-19), 56.4 (C-5), 52.3 (C-9), 49.0 (C-1), 45.0 (C-3), 41.4 (C-13), 40.7 (C-4), 38.0 (C-10), 37.4 (C-7), 33.5 (C-12), 28.1 (C-18), 23.7 (C-17), 23.3 (C-6), 21.1 (15-$CH_3COO$), 19.8 (C-11), 17.1 (C-20)。以上数据与文献报道一致[12]，故鉴定化合物 **11** 为对映-15-乙酰氧基-2α,16,19-三羟基海松烷-8(14)-烯。

化合物 **12**：白色固体（甲醇）；分子式 $C_{20}H_{34}O_4$。$^1$H-NMR (500 MHz, Pyridine-$d_5$) $\delta$: 5.78 (1H, s, H-14), 4.26 (1H, m, H-2), 4.12 (1H, m, H-16a), 4.06 (2H, m, H-19), 3.97 (1H, m, H-16b), 3.65 (1H, d, $J$ = 10.5 Hz, H-15), 2.92 (1H, m, H-3a), 2.35 (1H, m, H-1a), 2,32 (1H, m, H-7a), 2.11 (1H, m, H-7b), 1.91 (1H, m, H-12a), 1.83 (1H, m, H-9), 1.75 (1H, m, H-6a), 1.64 (2H, m, H-11), 1.36 (2H, m, H-1b), 1.33 (2H, m, H-3b, 5), 1.29 (4H, m, H-6b, 18), 1.20 (3H, s, H-17), 0.85 (3H, s, H-20)；$^{13}$C-NMR (125 MHz, Pyridine-$d_5$) $\delta$: 135.9 (C-8), 131.2 (C-14), 78.8 (C-15), 64.6 (C-19), 63.8 (C-16), 63.7 (C-2), 55.5 (C-5), 50.7 (C-9), 49.5 (C-1), 45.7 (C-3), 40.9 (C-4), 40.1 (C-10), 37.8 (C-13), 36.9 (C-7), 31.7 (C-12), 28.2 (C-18), 23.9 (C-17), 22.6 (C-6), 19.5 (C-11), 17.3 (C-20)。以上数据与文献报道一致[13]，故鉴定化合物 **12** 为对映-2α,15*R*,16,19-四羟基海松烷-8(14)-烯。

化合物 **13**：无色油状物（甲醇）；分子式 $C_{28}H_{46}O_9$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 5.19 (1H, s, H-14), 4.32 (1H, d, $J$ = 7.8 Hz, H-1′), 4.23 (1H, dd, $J$ = 11.3, 2.5 Hz, H-16a), 4.02 (1H, dd, $J$ = 11.3, 8.9 Hz, H-16b), 3.85 (1H, dd, $J$ = 11.8, 2.4 Hz, H-6′a), 3.72 (1H, dd, $J$ = 9.0, 2.5 Hz, H-15), 3.67 (1H, dd, $J$ = 11.7, 5.6 Hz, H-6′b), 3.39 (1H, dd, $J$ = 11.7, 3.8 Hz, H-3), 3.36 (1H, overlapped, H-3′), 3.28 (1H, m, H-4′), 3.23 (1H, m, H-5′), 3.16 (1H, dd, $J$ = 9.1, 7.8 Hz, H-2′), 2.29 (1H, m, H-7a), 2.06 (1H, overlapped, H-7b), 2.05 (3H, s, 16-$CH_3COO$), 2.00 (1H, m, H-12a), 1.80 (1H, m, H-2a), 1.75 (1H, m, H-1a), 1.71 (1H, m, H-9), 1.64 (1H, m, H-6a), 1.54 (3H, m, H-2b, 11), 1.40 (1H, m, H-6b), 1.18 (1H, m, H-1b), 1.12 (1H, dd, $J$ = 12.2, 2.5 Hz, H-5), 1.05 (3H, s, H-18), 0.95 (1H, m, H-12b), 0.88 (3H, s, H-17), 0.86 (3H, s, H-19), 0.82 (3H, s, H-20)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 173.1 (16-$CH_3COO$), 140.5 (C-8), 129.0 (C-14), 101.9 (C-1′), 86.0 (C-3), 78.3 (C-3′), 77.8 (C-5′), 75.2 (C-2′), 74.2 (C-15), 71.9 (C-4′), 67.5 (C-16), 63.0 (C-6′), 56.2 (C-5), 52.0 (C-9), 39.4 (C-4), 39.0 (C-10), 38.7 (C-13), 38.1 (C-1), 37.1 (C-7), 33.1 (C-12), 29.2 (C-18), 24.4 (C-2), 23.5 (C-6), 22.8 (C-17), 20.9 (16-$CH_3COO$), 19.3 (C-11), 17.4 (C-19), 15.2 (C-20)。以上数据与文献报道一致[15]，故鉴定化合物 **13** 为 16-*O*-acetyldarutoside。

化合物 **14**：无色油状物（甲醇）；分子式 $C_{28}H_{46}O_9$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 5.16 (1H, s, H-14), 5.05 (1H, dd, $J$ = 9.1, 2.5 Hz, H-15), 4.33 (1H, d, $J$ = 7.8 Hz, H-1′), 3.86 (1H, dd, $J$ = 11.7, 2.4 Hz, H-6′a), 3.77 (1H, dd, $J$ = 12.0, 2.4 Hz, H-16a), 3.67 (dd, $J$ = 11.8, 5.5 Hz, 1H, H-6′b), 3.61 (1H, dd, $J$ = 12.0, 9.1 Hz, H-16b), 3.39 (1H, ov, H-3), 3.36 (1H, m, H-3′), 3.34 (1H, m, H-4′), 3.23 (1H, m, H-5′), 3.16 (1H, dd, $J$ = 9.1, 7.8 Hz, H-2′), 2.30 (1H, m, H-7a), 2.09 (3H, s, 15-$CH_3COO$), 2.03 (1H, m, H-12a), 1.95 (1H, m, H-7b), 1.80 (1H, m, H-2a), 1.76 (1H, m, H-1a), 1.72 (1H, m, H-9), 1.67 (1H, m, H-6a), 1.58 (3H, m, H-2b, 11), 1.41 (1H, dd, $J$ = 12.8, 4.4 Hz, H-6b), 1.15 (1H, m, H-1b), 1.10 (1H, overlapped, H-5), 1.05 (3H, s, H-18), 0.92 (3H, s, H-17), 0.89 (3H, s, H-20), 0.87 (3H, s, H-19)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 173.1 (15-$CH_3COO$), 141.3 (C-8), 128.1 (C-14), 101.9 (C-1′), 86.0 (C-3), 79.6 (C-15), 78.3 (C-3′), 77.8 (C-5′), 75.2 (C-2′), 71.9 (C-4′), 63.0 (C-6′), 62.3 (C-16), 56.1 (C-5), 52.0 (C-9), 39.4 (C-4), 39.1 (C-10), 38.1 (C-13), 38.0 (C-7), 37.1 (C-1), 33.6 (C-12), 29.2 (C-18), 24.4 (C-2), 23.7 (C-6), 23.4 (C-17), 21.1 (15-$CH_3COO$), 19.5 (C-11), 17.3 (C-19), 15.3 (C-20)。以上数据与文献报道一致[14]，故鉴定化合物 **14** 为 15-*O*-acetyldarutoside。

化合物 **15**：白色粉末（甲醇）；分子式 $C_{20}H_{34}O_3$。$^1$H-NMR (600 MHz, Methanol-$d_4$) $\delta$: 5.14 (1H, s, H-14), 3.79 (1H, d, $J$ = 11.0 Hz, H-19a), 3.68 (1H, dd, $J$ = 11.1, 2.3 Hz, H-16a), 3.56 (1H, dd, $J$ = 9.0, 2.3 Hz, H-15), 3.45 (1H, dd, $J$ = 11.2, 9.1 Hz, H-16b), 3.35 (1H, m, H-19b), 2.26 (1H, m, H-7a), 2.03 (1H, m, H-7b), 1.93 (1H, m, H-12a), 1.89 (1H, m, H-3a), 1.76 (1H, m, H-9), 1.73 (1H, m, H-1a), 1.70 (1H, m, H-6a), 1.55 (1H, m, H-2a), 1.53 (1H, m, H-2b), 1.52 (1H, m, H-11a), 1.44 (1H, m, H-11b), 1.33 (1H, m, H-6b), 1.23 (1H, dd,

*J* = 12.9, 2.1 Hz, H-5), 1.10 (1H, td, *J* = 13.2, 3.8 Hz, H-1b), 0.96 (3H, s, H-18), 0.93 (1H, m, H-3b), 0.89 (1H, m, H-12b), 0.83 (3H, s, H-17), 0.78 (3H, s, H-20)；$^{13}$C-NMR (150 MHz, Methanol-$d_4$) $\delta$: 139.9 (C-8), 129.6 (C-14), 77.6 (C-15), 64.9 (C-19), 64.3 (C-16), 57.3 (C-5), 52.5 (C-9), 40.4 (C-1), 39.7 (C-4), 39.2 (C-10), 38.5 (C-13), 37.6 (C-7), 36.5 (C-3), 33.3 (C-12), 27.8 (C-18), 23.6 (C-6), 23.0 (C-17), 19.7 (C-11), 19.5(C-2), 16.4 (C-20)。以上数据与文献报道一致[16]，故鉴定化合物 **15** 为对映-15,16,19-三羟基海松烷-8(14)-烯。

化合物 **16**：无色油状物（甲醇）；ESI-MS *m*/*z*: 365 [M＋H]$^+$，分子式 $C_{20}H_{28}O_6$。$^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 6.79 (1H, m, H-3′), 6.26 (1H, d, *J* = 1.9 Hz, H-13a), 5.69 (1H, m, H-1), 5.66 (1H, m, H-13b), 5.32 (1H, m, H-8), 4.93 (1H, m, H-6), 4.14 (1H, s, H-14), 3.44 (2H, m, H-15), 3.15 (1H, s, H-7), 2.71 (1H, dd, *J* = 13.9, 10.2 Hz, H-9a), 2.58 (1H, dd, *J* = 5.2, 13.2 Hz, H-9b), 2.29 (2H, m, H-2), 2.02(1H, m, H-3a), 1.98(1H, m, H-5a), 1.89 (1H, m, H-4), 1.77(3H, overlapped, H-4′), 1.76 (3H, overlapped, H-5′), 1.53 (1H, m, H-5b), 1.14 (1H, m, H-3b)；$^{13}$C-NMR (125 MHz, $CDCl_3$) $\delta$: 169.9 (C-12), 167.3 (C-1′), 138.9 (C-3′), 136.9 (C-11), 133.5 (C-10), 131.3 (C-1), 128.0 (C-2′), 123.8 (C-13), 79.1 (C-6), 77.3 (C-8), 67.9 (C-14), 67.7 (C-15), 48.0 (C-7) , 42.2 (C-4), 40.5 (C-5), 30.9 (C-3), 30.3 (C-9), 26.6 (C-2), 14.6 (C-4′), 12.0 (C-5′)。以上数据与文献报道一致[17]，故鉴定化合物 **16** 为 (4β,10*E*)-6α,14,15-trihydroxy-8β-(tigloyloxy)-germacra-1(10),11(13)-diene-12-oic acid 12,6-lactone。

化合物 **17**：无色油状物（甲醇）；分子式 $C_{19}H_{26}O_6$。$^1$H-NMR (400 MHz, Methanol-$d_4$) $\delta$: 6.21 (1H, d, *J* = 1.9 Hz, H-13a), 6.03 (1H, m, H-3′a), 5.83 (1H, m, H-13b), 5.70 (1H, t, *J* = 8.2 Hz, H-1), 5.60 (1H, m, H-3′b), 5.36 (1H, m, H-8), 5.08 (1H, m, H-6), 4.08 (2H, m, H-14), 3.32 (3H, overlapped, H-7, 15), 2.81 (1H, dd, *J* = 13.8, 10.0 Hz, H-9a), 2.57 (1H, m, H-9b), 2.34 (2H, m, H-2), 1.98 (1H, m, H-3a), 1.95(1H, m, H-5a), 1.87 (3H, s, H-4′), 1.86 (1H, overlapped, H-4), 1.51 (1H, m, H-5b), 1.12 (1H, m, H-3b)；$^{13}$C-NMR (100 MHz, Methanol-$d_4$) $\delta$: 172.1 (C-12), 167.6 (C-1′), 139.1 (C-11), 137.3 (C-2′), 135.0 (C-10), 132.2 (C-1), 126.8 (C-3′), 124.5 (C-13), 81.0 (C-6), 79.0 (C-8), 68.2 (C-15), 67.8 (C-14), 49.1 (C-7), 43.1 (C-4), 41.4 (C-5), 31.4 (C-3), 31.4 (C-9), 27.2 (C-2), 18.3 (C-4′)。以上数据与文献报道一致[18]，故鉴定化合物 **17** 为 2-propenoicacid,2-methyl-2,3,3α,4,5,8,9,10,11,11α-decahydro-6,10-bis-(hydroxyl-methyl)-3-methylene-2-oxocyclod-eca[β]furan-4-yl ester。

化合物 **18**：无色油状物（氯仿）；分子式 $C_{19}H_{28}O_6$。$^1$H-NMR (600 MHz, $CDCl_3$) $\delta$: 6.28 (1H, d, *J* = 2.0 Hz, H-13a), 5.67(2H, m, H-1 and H-13b), 5.35 (1H, m, H-8), 4.87 (1H, m, H-6), 4.15 (2H, s, H-14), 3.44(2H, m, H-15), 3.11 (1H, m, H-7), 2.69 (1H, m, H-9), 2.49 (1H, m, H-2′), 2.30 (2H, m, H-2), 1.99 (2H, m, H-3, 5a), 1.88 (1H, m, H-4), 1.54 (1H, m, H-5b), 1.10 (3H, d, *J* = 7.0 Hz, H-3′), 1.08 (3H, d, *J* = 7.0 Hz, H-4′)；$^{13}$C-NMR (150 MHz, $CDCl_3$) $\delta$: 176.6 (C-1′), 170.0 (C-12), 136.8 (C-11), 133.3 (C-10), 131.7 (C-1), 123.9 (C-13), 79.2 (C-6), 76.1 (C-8), 68.0 (C-15), 67.9 (C-14), 47.8 (C-7), 42.3 (C-4), 40.5 (C-5), 34.3 (C-2′), 30.9 (C-9), 30.4 (C-3), 26.6 (C-2), 19.1 (C-4′), 18.8 (C-3′)。以上数据与文献报道一致[19]，故鉴定化合物 **18** 为 (4β,10*E*)-6α,14,15-trihydroxy-8β-(isobutyryloxy) germacra-10,11(13)-diene-12 oic acid 12,6-lactone。

化合物 **19**：无色油状物（甲醇）；分子式 $C_{19}H_{28}O_6$。$^1$H NMR (600 MHz, Methanol-$d_4$) $\delta$: 6.24 (1H, d, *J* = 2.0 Hz, H-13a), 5.77 (1H, d, *J* = 1.8 Hz, H-13b), 5.66 (1H, m, H-1), 4.93 (1H, ov, H-6), 4.62 (1H, d, *J* = 12.8 Hz, H-14a), 4.55 (1H, d, *J* = 12.7 Hz, H-14b), 4.12 (1H, m, H-8), 3.35 (2H, m, H-15), 3.01 (1H, brs, H-7), 2.74 (1H, m, H-9a), 2.60 (1H, m, H-2′), 2.30 (3H, m, H-2 and H-9b), 1.94 (1H, m, H-3a), 1.90 (1H, m, H-5a), 1.79 (1H, m, H-4), 1.44 (1H, m, H-5b), 1.19 (3H, s, H-3′), 1.17 (3H, s, H-4′), 1.05 (1H, m, H-3b)；$^{13}$C NMR (150 MHz, Methanol-$d_4$) $\delta$: 178.5 (C-1′), 172.8 (C-12), 140.7 (C-11), 133.8 (C-1), 131.7 (C-10), 123.1 (C-13), 80.6 (C-6), 75.7 (C-8), 69.5 (C-14), 68.2 (C-15), 50.1 (C-7), 43.3 (C-4), 41.3 (C-5), 35.3 (C-2′), 35.0 (C-9), 31.2 (C-3), 27.4 (C-2), 19.4 (C-3′), 19.4 (C-4′)。以上数据与文献报道一致[20]，故鉴定化合物 **19** 为 siegesbeckialide K。

化合物 **20**：无色油状物（氯仿）；分子式 $C_{20}H_{28}O_6$。$^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 6.27 (1H, m, H-13a), 5.67 (2H, m, H-1, 13b), 5.58 (1H, s, H-2′), 5.37 (1H, m, H-8), 4.87 (1H, m, H-6), 4.16 (2H, s, H-

14), 3.45 (2H, m, H-15), 3.13 (1H, m, H-7), 2.70 (1H, m, H-9a), 2.58 (1H, m, H-9b), 2.30 (2H, m, H-2), 2.11 (3H, s, H-5′), 1.98 (2H, m, H-3b, 5), 1.94 (1H, m, H-4), 1.87 (3H, s, H-4′), 1.59 (1H, m, H-5), 1.16 (1H, m, H-3a)；$^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 170.2 (C-12), 166.0 (C-1′), 159.1 (C-3′), 136.8 (C-11), 133.6 (C-10), 131.4 (C-1), 123.8 (C-13), 115.3 (C-2′), 79.4 (C-6), 75.5 (C-8), 67.9 (C-14), 67.7 (C-15), 47.8 (C-7), 42.2 (C-4), 40.5 (C-5), 31.0 (C-9), 30.4 (C-3), 27.6 (C-4′), 26.5 (C-2), 20.5 (C-5′)。以上数据与文献报道一致[17]，故鉴定化合物 **20** 为 (4β,10*E*)-6α,14,15-trihydroxy-8β-(senecioyloxy)-germacra-1(10),11(13)-diene-12-oic acid 12,6-lactone。

化合物 **21**：无色油状物（氯仿）；分子式 $C_{22}H_{28}O_7$。$^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 9.50 (1H, d, *J* = 2.1 Hz, H-14), 6.82 (1H, dq, *J* = 7.0, 1.5 Hz, H-3′), 6.74 (1H, dd, *J* = 10.2, 7.4 Hz, H-1), 6.57 (1H, dd, *J* = 8.4, 1.7 Hz, H-8), 6.25 (1H, d, *J* = 3.5 Hz, H-13a), 5.90 (1H, d, *J* = 3.1 Hz, H-13b), 5.22 (1H, t, *J* = 10.2 Hz, H-6), 5.03 (1H, d, *J* = 10.6 Hz, H-5), 4.50 (1H, d, *J* = 12.6 Hz, H-15), 4.39 (1H, d, *J* = 12.6 Hz, H-15), 3.93 (1H, dd, *J* = 8.4, 2.2 Hz, H-9), 3.37 (1H, m, 7-$CH_2CH_3$), 3.09 (1H, m, 7-$CH_2CH_3$), 2.84 (1H, m, H-3b), 2.71 (1H, m, H-2a), 2.63 (1H, m, H-7), 2.56(1H, m, H-2b), 2.02 (1H, m, H-3a), 1.83 (3H, m, H-5′), 1.80 (3H, m, H-4′), 1.02 (3H, t, *J* = 7.0 Hz, 7-$CH_2CH_3$)；$^{13}$C-NMR (125 MHz, $CDCl_3$) $\delta$: 194.5 (C-14), 169.7 (C-12), 166.7 (C-1′), 155.5 (C-1), 141.8 (C-10), 139.7 (C-4), 137.8 (C-3′), 133.9 (C-11), 129.6 (C-5), 128.4 (C-2′), 122.9 (C-13), 76.2 (C-9), 73.9 (C-6), 69.8 (C-8), 64.6 (7-OEt), 61.0 (C-15), 51.2 (C-7), 32.8 (C-3), 27.6 (C-2), 15.1 (7-OEt), 14.6 (C-4′), 12.4 (C-5′)。以上数据与文献报道一致[17]，故鉴定化合物 **21** 为 1(10)*E*,4*Z*-9α-ethoxy-6α,15-dihydroxy-8β-(tigloyloxy)-14-oxogermacra-1(10),4,11(13)-triene-12-oic acid 12,6-lactone。

化合物 **22**：无色油状物（甲醇）；分子式 $C_{20}H_{34}O_3$。$^1$H-NMR (400 MHz, Methanol-$d_4$) $\delta$: 5.17 (1H, overlapped, H-15), 3.69 (1H, dd, *J* = 10.9, 2.2 Hz, H-16a), 3.57 (1H, dd, *J* = 8.9, 2.3 Hz, H-13), 3.46 (1H, dd, *J* = 11.0, 9.0 Hz, H-16b), 3.19 (1H, m, H-3), 2.28 (1H, ddd, *J* = 14.2, 4.6, 2.1 Hz, H-7a), 2.06 (1H, m, H-7b), 1.98 (1H, m, H-12a), 1.74 (1H, m, H-1a), 1.70 (1H, m, H-9), 1.63 (1H, m, H-6a), 1.59 (2H, m, H-2), 1.53 (2H, m, H-11), 1.38 (1H, qd, *J* = 12.8, 4.5 Hz, H-6b), 1.20 (1H, m, H-1b), 1.07 (1H, dd, *J* = 11.3, 1.8 Hz, H-5), 0.99 (3H, s, H-18), 0.92 (1H, m, H-12b), 0.83 (3H, s, H-17), 0.82 (3H, s, H-20), 0.81 (3H, s, H-19)；$^{13}$C-NMR (100 MHz, Methanol-$d_4$) $\delta$: 139.8 (C-8), 129.6 (C-15), 79.8 (C-3), 77.5 (C-13), 64.3 (C-16), 55.7 (C-5), 52.1 (C-9), 40.1 (C-4), 39.1 (C-10), 38.5 (C-14), 38.4 (C-1), 37.1 (C-7), 33.3 (C-12), 29.1 (C-18), 28.3 (C-2), 23.4 (C-6), 23.0 (C-17), 19.3 (C-11), 16.5 (C-19), 15.3 (C-20)。以上数据与文献报道一致[21]，故鉴定化合物 **22** 为 17(13→4)-abeo-*ent*-3*S**,13*S**,16-trihydroxystrob-8(15)-ene。

化合物 **23**：无色油状物（甲醇）；分子式 $C_{20}H_{34}O_4$。$^1$H-NMR (600 MHz, Methanol-$d_4$) $\delta$: 4.94 (1H, d, *J* = 5.0 Hz, H-15), 3.81 (1H, m, H-2), 3.79 (1H, dd, *J* = 10.2, 7.4 Hz, H-16a), 3.66 (1H, d, *J* = 11.1 Hz, H-19a), 3.56 (1H, *J* = 10.2, 7.6 Hz, H-16b), 3.33 (1H, overlapped, H-19b), 2.90 (1H, m, H-14), 2.22 (1H, m, H-7a), 2.17 (1H, m, H-3a), 1.97 (1H, m, H-1a), 1.92 (1H, m, H-7b), 1.90 (1H, overlapped, H-9), 1.88 (1H, m, H-11a), 1.82 (1H, m, H-6a), 1.73 (1H, dd, *J* = 14.7, 8.0 Hz, H-12a), 1.53 (1H, m, H-11b), 1.50 (1H, m, H-12b), 1.39 (1H, qd, *J* = 13.0, 4.2 Hz, H-6b), 1.25 (1H, dd, *J* = 13.0, 2.6 Hz, H-5), 1.07 (3H, s, H-17), 1.02 (1H, overlapped, H-1b), 1.00 (3H, s, H-20), 0.99 (3H, s, H-18), 0.87 (1H, t, *J* = 12.3 Hz, H-3b)；$^{13}$C-NMR (150 MHz, Methanol-$d_4$) $\delta$: 143.3 (C-8), 122.4 (C-15), 77.7 (C-13), 65.5 (C-19), 65.4 (C-16), 64.8 (C-2), 61.1 (C-9), 57.5 (C-5), 48.3 (C-1), 46.0 (C-14), 45.2 (C-3), 42.6 (C-10), 41.5 (C-12), 41.4 (C-4), 40.5 (C-7), 28.0 (C-18), 25.4 (C-17), 25.1 (C-6), 19.5 (C-11), 16.6 (C-20)。以上数据与文献报道一致[13]，故鉴定化合物 **23** 为 strobol A。

化合物 **24**：无色油状物（甲醇）；分子式 $C_{18}H_{26}O_2$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 7.13 (1H, d, *J* = 8.1 Hz, H-12a), 6.89 (1H, d, *J* = 7.9 Hz, H-11a), 6.82 (1H, s, H-14), 3.97 (1H, m, H-2), 3.73 (1H, d, *J* = 11.1 Hz, H-19a), 3.43 (1H, d, *J* = 11.2 Hz, H-19b), 2.88 (1H, m, H-7a), 2.78 (1H, m, H-7b), 2.61 (1H, m, H-1a), 2.24 (1H, m, H-3a), 2.22 (3H, s, H-17), 1.98 (1H, m, H-6a), 1.70 (1H, m, H-6b), 1.42 (1H, dd, *J* = 12.6, 1.6 Hz, H-5), 1.25 (1H, t, *J* = 11.8 Hz, H-1b), 1.17 (3H, s, H-20), 1.08 (3H, s, H-18), 0.93 (1H, m, H-3b)；

$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 147.4 (C-9), 135.8 (C-13), 135.4 (C-8), 130.5 (C-14), 127.6 (C-12), 125.1 (C-11), 65.6 (C-19), 65.5 (C-2), 52.3 (C-5), 48.9 (C-1), 45.1 (C-3), 41.2 (C-4), 40.1 (C-10), 31.8 (C-7), 27.8 (C-18), 27.1 (C-20), 20.9 (C-17), 20.0 (C-6)。以上数据与文献报道一致[13]，故鉴定化合物 **24** 为 2β,19-dihydroxy-15-devinyl-*ent*-pimar-8,11,13-triene。

化合物 **25**：黄色结晶（甲醇）；分子式 $C_{18}H_{16}O_7$。$^1$H-NMR (500 MHz, DMSO-$d_6$) $\delta$: 9.45 (1H, s, 3′-OH), 7.59 (2H, m, H-2′, 6′), 7.11 (1H, d, $J$ = 9.0 Hz, H-5′), 6.73 (1H, d, $J$ = 2.1 Hz, H-8), 6.37 (1H, d, $J$ = 2.1 Hz, H-6), 3.86 (6H, m, 7, 4′-$OCH_3$), 3.80 (3H, s, 3-$OCH_3$)；$^{13}$C-NMR (125 MHz, DMSO-$d_6$) $\delta$: 178.1 (C-4), 165.2 (C-7), 160.9 (C-5), 156.3 (C-2), 155.7 (C-9), 150.4 (C-4′), 146.4 (C-3′), 138.2 (C-3), 122.2 (C-6′), 120.5 (C-1′), 115.1 (C-2′), 111.9 (C-5′), 105.2 (C-10), 97.8 (C-6), 92.3 (C-8), 59.8 (4′-$OCH_3$), 56.1 (7-$OCH_3$), 55.7 (3-$OCH_3$)。以上数据与文献报道一致[22]，故鉴定化合物 **25** 为阿亚黄素。

化合物 **26**：黄色固体（甲醇）；分子式 $C_{27}H_{30}O_{15}$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 8.07 (2H, d, $J$ = 8.9 Hz, H-2′, 6′), 6.89 (2H, d, $J$ = 8.9 Hz, H-3′, 5′), 6.41 (1H, d, $J$ = 2.1 Hz, H-8), 6.21 (1H, d, $J$ = 2.1 Hz, H-6), 5.13 (1H, d, $J$ = 7.1 Hz, H-1″), 4.52 (1H, d, $J$ = 1.6 Hz, H-1‴), 3.81 (1H, m, H-6″a), 3.63 (1H, m, H-6″b), 3.52 (1H, dd, $J$ = 9.4, 3.4 Hz, H-2″), 3.41 (5H, m, H-2‴, 3″, 3‴, 4″, 4‴), 3.26 (2H, m, H-5″, 5‴), 1.12 (3H, d, $J$ = 6.2 Hz, H-6‴)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 179.4 (C-4), 166.3 (C-7), 163.0 (C-5), 161.5 (C-4′), 159.4 (C-9), 158.6 (C-2), 135.5 (C-3), 132.4 (C-2′, 6′), 122.8 (C-1′), 116.1 (C-3′, 5′), 105.6 (C-10), 104.6 (C-1‴), 102.4 (C-1″), 100.1 (C-6), 95.0 (C-8), 78.1 (C-2″), 77.2 (C-3‴), 75.8 (C-5″), 73.9 (C-3″), 72.3 (C-2‴), 72.1 (C-4‴), 71.4 (C-4″), 69.7 (C-5‴), 68.6 (C-6″), 17.9 (C-6‴)。以上数据与文献报道一致[23]，故鉴定化合物 **26** 为山柰酚-3-*O*-芸香糖苷。

化合物 **27**：黄色固体（甲醇）；分子式 $C_{17}H_{14}O_7$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 7.63 (1H, dd, $J$ = 8.6, 2.3 Hz, H-6′), 7.60 (1H, d, $J$ = 2.2 Hz, H-2′), 7.06 (1H, d, $J$ = 8.6 Hz, H-5′), 6.36 (1H, d, $J$ = 2.0 Hz, H-10), 6.18 (1H, d, $J$ = 2.0 Hz, H-8), 3.94 (3H, s, 4′-$OCH_3$), 3.79 (3H, s, 3-$OCH_3$)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 179.9 (C-4), 166.9 (C-7), 163.3 (C-5), 158.6 (C-9), 157.4 (C-8), 151.6 (C-4′), 147.6 (C-3′), 139.8 (C-3), 124.3 (C-1′), 122.1 (C-6′), 116.1 (C-2′), 112.3 (C-5′), 105.8 (C-10), 100.2 (C-6), 94.8 (C-8), 60.6 (3-$OCH_3$), 56.4 (4′-$OCH_3$)。以上数据与文献报道一致[24]，故鉴定化合物 **27** 为 3,5,3′-三羟基-7,4′-二甲氧基黄酮。

化合物 **28**：无色油状物（甲醇）；分子式 $C_{11}H_{16}O_3$。$^1$H-NMR (400 MHz, Methanol-$d_4$) $\delta$: 5.75 (1H, s, H-7), 4.22 (1H, t, $J$ = 3.5 Hz, H-3), 2.42 (1H, dt, $J$ = 13.6, 2.6 Hz, H-4a), 1.99 (1H, dt, $J$ = 14.4, 2.7 Hz, H-2a), 1.76 (3H, s, H-11), 1.73 (1H, overlapped, H-4b), 1.53 (1H, dd, $J$ = 14.4, 3.7 Hz, H-2b), 1.47 (3H, s, H-9), 1.28 (3H, s, H-10)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 185.7 (C-8), 174.4 (C-6), 113.3 (C-7), 89.0 (C-5), 67.2 (C-3), 48.0 (C-2), 46.4 (C-4), 37.2 (C-1), 31.0 (C-10), 27.4 (C-11), 27.0 (C-9)。以上数据与文献报道一致[25]，故鉴定化合物 **28** 为黑麦草内酯。

化合物 **29**：黄色油状物（甲醇）；分子式 $C_{19}H_{30}O_8$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 5.98 (1H, d, $J$ = 15.6 Hz, H-7), 5.87 (1H, m, H-4), 5.73 (1H, dd, $J$ = 15.6, 7.2 Hz, H-8), 4.54 (1H, m, H-9), 4.27 (1H, d, $J$ = 7.8 Hz, H-1′), 3.85 (1H, dd, $J$ = 11.8, 2.2 Hz, H-6′a), 3.63 (1H, dd, $J$ = 11.8, 5.9 Hz, H-6′b), 3.27 (1H, m, H-3′), 3.23 (1H, m, H-4′), 3.20 (1H, m, H-2′), 3.16 (1H, m, H-5′). 2.56 (1H, d, $J$ = 17.1 Hz, H-2a), 2.17 (1H, m, H-2b), 1.95 (3H, d, $J$ = 1.4 Hz, 5-Me), 1.30 (3H, overlapped, 9-Me), 1.04 (3H, s, 1-Me), 1.02 (3H, s, 1-Me)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 201.3 (C-3), 167.1 (C-5), 133.8 (C-7), 133.7 (C-8), 127.1 (C-4), 101.2 (C-1′), 78.4 (C-3′), 78.2 (C-5′), 75.0 (C-2′), 74.6 (C-9), 71.7 (C-4′), 62.8 (C-6′), 50.8 (C-2), 42.4 (C-1), 24.7 (1-Me), 23.5 (1-Me), 22.2 (9-Me), 19.6 (5-Me)。以上数据与文献报道一致[26]，故鉴定化合物 **29** 为 (6*R*,9*S*)-roseoside。

化合物 **30**：黄色粉末（甲醇）；分子式 $C_9H_8O_4$。$^1$H-NMR (600 MHz, Methanol-$d_4$) $\delta$: 7.53 (1H, d, $J$ = 15.9 Hz, H-7), 7.03 (1H, d, $J$ = 2.1 Hz, H-8), 6.93 (1H, dd, $J$ = 8.1, 2.1 Hz, H-6), 6.78 (1H, d, $J$ = 8.2 Hz, H-5), 6.22 (1H, d, $J$ = 15.9 Hz, H-2)；$^{13}$C-NMR (150 MHz, Methanol-$d_4$) $\delta$: 171.0 (C-9), 149.5 (C-4), 147.0 (C-3), 146.8 (C-7), 127.8 (C-1), 122.8 (C-6), 116.5 (C-2), 115.5 (C-5), 115.1 (C-8)。以上数据与文献报道一致[27]，故鉴定化合物 **30** 为咖啡酸。

化合物 **31**：无色油状（甲醇）；分子式 $C_{31}H_{36}O_{11}$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 6.97 (1H, d, $J$ = 2.0 Hz, H-2′), 6.95 (1H, d, $J$ = 2.0 Hz, H-2″), 6.82 (1H, dd, $J$ = 8.3, 1.9 Hz, H-5′), 6.78 (1H, m, H-5″), 6.76 (1H, m, H-6′), 6.72 (1H, dd, $J$ = 8.1, 1.5 Hz, H-6″), 6.68 (2H, s, H-2, 6), 4.89 (1H, m, H-7″), 4.75 (1H, d, $J$ = 2.9 Hz, H-7′), 4.71 (1H, d, $J$ = 4.0 Hz, H-7), 4.26 (2H, m, H-9a, 9′a), 3.89 (2H, m, H-9b, 9′b), 3.86 (3H, s, 3-OMe), 3.82 (9H, m, 5, 3′, 3″-OMe), 3.13 (2H, m, H-8, 8′)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 154.6 (C-3, 5), 149.1 (C-3″), 148.6 (C-3′), 147.3 (C-4′), 146.9 (C-4″), 138.9 (C-1), 136.1 (C-4), 133.8 (C-1′), 133.7 (C-1″), 120.7 (C-6′), 120.1 (C-6″), 116.1 (C-5′), 115.6 (C-5″), 111.4 (C-2′), 111.0 (C-2″), 104.2 (C-2, 6), 87.5 (C-8″), 87.3 (C-7), 87.3 (C-7′), 74.0 (C-7″), 72.9 (C-9), 72.8 (C-9′), 61.7 (C-9″), 56.7 (3, 5-OMe), 56.4 (3′, 5′-OMe), 56.3 (3″, 5″-OMe), 55.7 (C-8′), 55.3 (C-8)。以上数据与文献报道一致[28]，故鉴定化合物 **31** 为 (–)-(7*R*,7′*R*,7″*R*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5-tetramethoxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol。

化合物 **32**：无色油状（甲醇）；分子式 $C_{31}H_{36}O_{11}$。$^1$H-NMR (500 MHz, Methanol-$d_4$) $\delta$: 6.99 (1H, d, $J$ = 2.0 Hz, H-2′), 6.95 (1H, d, $J$ = 1.9 Hz, H-2″), 6.85 (1H, dd, $J$ = 8.1, 1.9 Hz, H-5′), 6.82 (1H, dd, $J$ = 8.2, 1.9 Hz, H-5″), 6.77 (1H, d, $J$ = 8.1 Hz, H-6′), 6.73 (1H, d, $J$ = 8.1 Hz, H-6″), 6.69 (2H, s, H-2, 6), 4.86 (1H, overlapped, H-7″), 4.73 (2H, d, $J$ = 4.6 Hz, H-7, 7′), 4.26 (2H, m, H-9a, 9′a), 4.09 (1H, m, H-8″), 3.89 (2H, m, H-9b, 9′b), 3.86 (9H, m, 5, 3′, 3″-OMe), 3.82 (3H, s, 3-OMe), 3.35 (1H, m, H-9″b), 3.13 (2H, m, H-8, 8′)；$^{13}$C-NMR (125 MHz, Methanol-$d_4$) $\delta$: 154.3 (C-3, 5), 149.1 (C-3″), 148.7 (C-3′), 147.4 (C-4′), 147.1 (C-4″), 139.1 (C-1), 136.6 (C-4), 133.7 (C-1′), 133.5 (C-1″), 120.8 (C-6′), 120.1 (C-6″), 116.1 (C-5′), 115.8 (C-5″), 111.6 (C-2′), 111.0 (C-2″), 104.2 (C-2, 6), 88.8 (C-8″), 87.5 (C-7), 87.2 (C-7′), 74.4 (C-7″), 72.9 (C-9), 72.7 (C-9′), 61.8 (C-9″), 56.7 (3, 5-OMe), 56.4 (3′, 5′-OMe), 56.3 (3″, 5″-OMe), 55.8 (C-8′), 55.3 (C-8)。以上数据与文献报道一致[29]，故鉴定化合物 **32** 为 (–)-(7*R*,7′*R*,7″*S*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5-tetramethoxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol。

### 3.2 PTP1B 抑制剂活性评价

结合分离所得化合物的结构类型及构效关系，选择其中量大的成分，开展了 PTP1B 抑制剂活性筛选实验。基于 PTP1B 与底物对硝基苯磷酸酯（pNPP）水解后会产生去磷酸化的对硝基苯酚，该产物在 405 nm 处有较强的光吸收。通过测定 405 nm 处的吸光度变化，可以定量分析 PTP1B 的酶活性，进而评估抑制剂的体外酶促反应效果。本研究对化合物 **1**～**6**、**13**、**16** 进行了活性筛选，结果显示化合物 **1**、**2**、**4** 对 PTP1B 具有一定的抑制效果，结果见表 1。

**表 1 化合物 1～6、13、16 的 PTP1B 抑制活性**

**Table 1 PTP1B inhibitory activity of compounds 1—6, 13, 16**

| 样品 | 抑制率/% |
|---|---|
| **1** | 32.56±2.14 |
| **2** | 38.30±0.83 |
| **3** | 12.58±1.01 |
| **4** | 42.38±1.66 |
| **5** | 9.84±0.31 |
| **6** | 12.40±0.84 |
| **13** | 14.42±0.97 |
| **16** | −1.98±0.99 |
| Suramin | 59.92±0.43 |
| 空白对照 | −0.94±0.53 |

## 4 讨论

豨莶草作为临床常用中药材，药典收载了多个基原，该研究选择腺梗豨莶为研究对象，以期明确不同基原药材之间质量差异。从腺梗豨莶醇提取物的二氯甲烷部位中分离鉴定了 32 个化合物，发现主要成分为二萜、倍半萜、黄酮、木脂素和酚酸类。其中，化合物 **25**～**27**、**31**、**32** 为首次从豨莶草属植物中分离得到；化合物 **1**、**2**、**4** 对 PTP1B 有一定的抑制作用。这些化合物的发现不仅丰富了豨莶草的化学成分研究，也为进一步研究其药效作用机制、相关新药开发以及中药资源可持续开发利用提供了新的思路和方向。

**利益冲突** 所有作者均声明不存在利益冲突

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