

砂茴香化学成分研究

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摘要:目的 研究砂茴香化学成分。方法 采用硅胶柱色谱、薄层色谱、半制备高效液相色谱、核磁共振波谱及高分辨质谱等方法,对砂茴香的化学成分进行了研究。结果 从砂茴香中分离鉴定了33个化合物,分别为棕榈酸(1)、油酸(2)、亚油酸(3)、亚麻酸(4)、去氢镰叶芹醇(5)、镰叶芹醇(6)、 β -谷甾醇(7)、2,6,11,15-四甲基-2,6,10,14-十六碳四烯(8)、arteordoy A(9)、镰叶芹二醇(10)、去氢镰叶芹二醇(11)、伞形戊烯内酯(12)、圆锥茎阿魏酮(13)、金合欢阿魏酮 A(14)、托里阿魏酮(15)、多花素宁(16)、assafoetidol B(17)、乙酰托里阿魏诺醇(18)、托里阿魏诺醇(19)、克乐利素(20)、圆锥茎阿魏醇(21)、多胶阿魏素(22)、金合欢基阿魏醇 A(23)、托里阿魏素(24)、去乙酰基克乐利素(25)、assafoetidol A(26)、卡拉阿魏醇(27)、14'-羟基-卡拉阿魏醇(28)、古蓬阿魏酸(29)、6,7-二甲氧基香豆素(30)、香草醛(31)、7-羟基香豆素(32)和6,7-二羟基香豆素(33)。结论 化合物5~6、9~11为该属中首次分离得到,其他均为该植物中首次分离得到。

关键词:阿魏属;砂茴香;炔;倍半萜香豆素;化学成分

doi:10.11669/cpj.2024.23.003 中图分类号:R284 文献标志码:A 文章编号:1001-2494(2024)23-2216-10

Chemical Constituents from *Ferula bungeana* Kitagawa

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ABSTRACT: OBJECTIVE To investigate the chemical constituents from *Ferula bungeana* Kitagawa. **METHODS** The chemical constituents from *Ferula bungeana* Kitagawa were investigated by silica gel chromatography, TLC, preparative HPLC, NMR, and HR-MS. **RESULTS** Thirty-three compounds were isolated from *Ferula bungeana* Kitagawa and identified, namely palmitic acid(1), oleic acid(2), linoleic acid(3), linolenic acid(4), dehydrofalcariol(5), falcariol(6), β -itosterol(7), 2,6,11,15-tetramethyl-2,6,10,14-hexadecanetetraene(8), arteordoy A(9), falcariindiol(10), dehydrofalcariindiol(11), umbelliprenin(12), conferone(13), farnesiferone A(14), ferukrinone(15), polyanthinin(16), assafoetidol B(17), actylfekryol(18), fekryol(19), kellerin(20), mogoltacin(21), gummosin(22), farnesiferol A(23), ferukrin(24), deacetylkellerin(25), assafoetidol A(26), karatavicinol(27), 14'-hydroxy-karatavicinol(28), galbanic acid(29), 6,7-dimethoxycoumarin(30), vanillin(31), 7-hydroxycoumarin(32) and 6,7-dihydroxycoumarin(33). **CONCLUSION** Compounds 5-6, 9-11 are isolated in this genus for the first time, and others are isolated from this plant for the time.

KEY WORDS: *Ferula* genus; *Ferula bungeana* Kitagawa; alkyne; sesquiterpene coumarin; chemical constituent

阿魏属植物在中国约有26种,其中7种为中国特有种,13种具有药用价值,主要产于中国新疆和内蒙古^[1-2]。阿魏属植物中已分离得到化学成分有倍半萜-香豆素杂化合物^[3-8]、倍半萜及其衍生物^[9-13]、苯丙素类^[14-17]和其他类^[18-19],然而砂茴香化学成分尚未见到研究报道。砂茴香(*Ferula bun-*

geana Kitagawa),又名硬阿魏,来源于伞形科阿魏属植物砂茴香,以根、种子、全草入药。其在内蒙古境内分布较广,资源丰富,是具有潜在开发利用价值的天然资源。民间相传砂茴香对结核病防治有显著效果,且未见毒副作用。为了摸清砂茴香的化学信息,本实验采用硅胶柱色谱、薄层色谱及半制备高效液

基金项目:蒙药研发国家地方联合工程研究中心开放基金项目资助(MDK2023040);内蒙古自治区中蒙药重点实验室开放基金项目资助(MYX2022-K06)

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相色谱法对砂茴香进行分离,并鉴定了 33 个化合物。

1 实验材料

LC-20Ap 半制备高效液相色谱仪, AUW220D 型电子天平(日本岛津公司); Bruker AVAI VCE III-500 型核磁共振波谱仪(布鲁克公司); KQ-600DB 型超声波仪(昆山市超声仪器有限公司); XBridge® BEH C₁₈ OBD™ Prep Column C₁₈ 色谱柱(美国沃特斯公司); 甲醇(色谱纯,美国飞世尔科学公司); LH-20 葡聚糖凝胶(北京普瑞因生物色谱技术有限公司); 硅胶(200~300 目,青岛海洋化工厂); 硅胶 G-TLC 薄层预制板(青岛海洋化工厂); 其他试剂均为分析纯。砂茴香采集于内蒙古锡林浩特市,经药用植物学红艳副教授鉴定为伞形科阿魏属植物砂茴香(*Ferula bungeana* Kitagawa)的全草(编号:20220602)。样品保存于内蒙古民族大学蒙医药学院蒙药化学与分析实验室备用。

2 提取分离

2.1 乙醇提取物的制备

砂茴香 20.4 kg,用 20 倍量的体积分数 95% 乙醇回流提取 2 次,每次 4 h,减压回收溶剂,得到体积分数 95% 乙醇提取物(3 806 g),其收率为 18.7%。

2.2 不同溶剂萃取物的制备

取砂茴香体积分数 95% 乙醇提取物加水适量,搅拌成混悬液。混悬液依次用二氯甲烷、乙酸乙酯和正丁醇萃取,萃取至萃取液减压回收无产生固体为止,合并萃取物,自然晾干,即得 3 种溶剂萃取物,分别为 713、50.6 和 105.6 g,其得率分别为 18.7%、1.3% 和 2.8%。因从砂茴香乙酸乙酯和正丁醇萃取物中没分到化合物,故接下来实验中没报道其分离过程。

2.3 二氯甲烷萃取物的分离

称取砂茴香二氯甲烷萃取物 700 g,加适量二氯甲烷湿润,再加少量硅胶,拌样均匀,自然晾干。用湿法拌样后的样品装入硅胶(200~300 目)柱色谱,采用石油醚-丙酮(100:1→5:1)进行梯度洗脱,流份为 500 mL,每个流份减压回收溶剂至干,加二氯甲烷 10 mL,溶解,溶液经 TLC 检测合并相同部分,得到 10 个流分(Fr. 1~10)。

Fr. 1 (18 g) 经硅胶柱色谱(石油醚-丙酮=100:1)洗脱,得到化合物 1(2.7 g)。母液浓缩至 5 mL,再用 TLC(展开剂为石油醚-丙酮=25:1)制备,得到化合物 2(135 mg)。Fr. 2 (2 g) 经硅胶柱色谱(石油醚-丙酮=100:1)洗脱,再用 TLC(展开剂为石油醚-丙酮=20:1)制备,得到化合物 3(35 mg)和 4(28 mg)。Fr. 3 (23 g) 经硅胶柱色谱(石油醚-丙酮=90:1)洗脱,得到化合物 7(1.2 g)。母液经 TLC 检测,分段为 2 份(Fr. 3A 和 Fr. 3B)。Fr. 3A 用 TLC(展开剂为石油醚-丙酮=18:1)制备,得到化合物 5(23 mg)和 6(87 mg); Fr. 3B 用 TLC(展开剂为石油醚-丙酮=17:1)制备,得到化合物 8(69 mg)和 9(24 mg)。Fr. 4(5 g) 经硅胶柱色谱(石油醚-丙酮=80:1)洗脱,再用 TLC(展开剂为石油醚-丙酮=17:1)制备,得到化合物 10(86 mg)和 11(35 mg)。Fr. 7 (65 g) 经硅胶柱色谱(石油醚-丙酮=60:1→40:1)梯度洗脱,经 TLC 检测合并相同部分,得到 2 个流分(Fr. 7A 和 Fr. 7B)。Fr. 7A (36 g) 经硅胶柱色谱(石油醚-丙酮=70:1→50:1)梯度洗脱,得化合物 12(1.5 g)。母液经 TLC 检测,分段为 2 份(Fr. 7A-1 和 Fr. 7A-2)。Fr. 7A-1 和 Fr. 7A-2 再经 Sephadex LH-20 葡聚糖凝胶柱色谱(三氯甲烷-甲醇=1:3 洗脱),洗脱液分别用半制备型高效液相色谱仪进行分离,流动相分别为甲醇-水(65:35)和甲醇-水(61:39),得到化合物 13(76 mg)、14(55 mg)、15(47 mg)、16(52 mg)、17(39 mg)和 18(81 mg)。Fr. 7B(7 g) 经 Sephadex LH-20 葡聚糖凝胶柱色谱(三氯甲烷-甲醇=1:3 洗脱),洗脱液用半制备型高效液相色谱仪(甲醇-水=57:43)进行分离,得到化合物 19(38 mg)和 20(61 mg)。Fr. 8 (74 g) 经硅胶柱色谱(石油醚-丙酮=40:1→20:1)梯度洗脱,得化合物 21(3.5 g)。母液经 TLC 检测,分段为 2 份(Fr. 8A 和 Fr. 7B)。Fr. 8A 经硅胶柱色谱(石油醚-丙酮=50:1→30:1)梯度洗脱 3 次,得化合物 22(31 mg)和 23(29 mg)。Fr. 8B 经硅胶柱色谱(石油醚-丙酮=30:1→10:1)梯度洗脱 3 次,得到化合物 24(57 mg)和 25(18 mg)。Fr. 9 (46 g) 经硅胶柱色谱(石油醚-丙酮=20:1→10:1)梯度洗脱,经 TLC 检测合并相同部分,得到 2 个流分(Fr. 9A 和 Fr. 9B)。Fr. 9A 和 Fr. 9B 分别再经 Sephadex LH-20 葡聚糖凝胶柱色谱洗脱,洗脱液分别用半制备型高效液相色谱仪进行分离,流动相分别为甲

醇-水(49:51)和甲醇-水(45:55),得到化合物26(38 mg)、27(74 mg)、30(19 mg)和31(27 mg)。Fr. 10(27 g)加甲醇溶解,溶液用半制备型高效液相色谱仪进行分离,流动相为甲醇-水(41:59),得到化合物28(25 mg)、29(73 mg)、32(20 mg)和33(17 mg)。

3 结构鉴定

化合物1:白色蜡状固体,易溶于二氯甲烷、乙醚等有机溶剂。其¹H-NMR(500 MHz, CDCl₃)和¹³C-NMR(125 MHz, CDCl₃)数据与文献[20]对照,鉴定化合物1为棕榈酸。

化合物2:淡黄色油状物,易溶于二氯甲烷、乙醚等有机溶剂。其¹H-NMR(500 MHz, CDCl₃)和¹³C-NMR(125 MHz, CDCl₃)数据与文献[21]对照,鉴定化合物2为油酸。

化合物3:淡黄色油状物,易溶于二氯甲烷、乙醚等有机溶剂。其¹H-NMR(500 MHz, CDCl₃)和¹³C-NMR(125 MHz, CDCl₃)数据与文献[21]对照,鉴定化合物3为α-亚油酸。

化合物4:淡黄色油状物,易溶于二氯甲烷、乙醚等有机溶剂。其¹H-NMR(500 MHz, CDCl₃)和¹³C-NMR(125 MHz, CDCl₃)数据与文献[22]对照,鉴定化合物4为α-亚麻酸。

化合物5:淡黄色油状物,易溶于乙醚、二氯甲烷等有机溶剂。¹H-NMR(500 MHz, CDCl₃) δ: 1.33~1.36(6H, m, H-12, 13, 14), 1.98(2H, t, *J*=6.5 Hz, H-11), 2.03(2H, t, *J*=6.5 Hz, H-15), 3.11(2H, d, *J*=6.5 Hz, H-8), 4.90(1H, m, H-3), 4.96(1H, d, *J*=16.5 Hz, H-17a), 5.03(1H, dd, *J*=16.5, 2.0 Hz, H-17b), 5.19(1H, brd, *J*=10.0 Hz, H-1b), 5.29(1H, m, H-9), 5.41(1H, brd, *J*=12.0 Hz, H-1a), 5.55(1H, m, H-10), 5.78(1H, m, H-16), 5.89(1H, m, H-2)。¹³C-NMR(125 MHz, CDCl₃) δ: 8.0(C-8), 28.0(C-11), 28.5(C-14), 29.0(C-13), 29.3(C-12), 34.0(C-15), 64.1(C-3), 65.0(C-6), 71.5(C-5), 75.0(C-4), 80.6(C-7), 115.1(C-17), 118.2(C-1), 122.3(C-9), 133.3(C-10), 135.8(C-2), 138.8(C-16)。与文献[23]对照,鉴定化合物5为去氢镰叶芹醇。

化合物6:淡黄色油状物,易溶于乙醚、二氯甲烷等有机溶剂。¹H-NMR(500 MHz, CDCl₃) δ: 0.90(3H, s, H-17), 1.28~1.30(8H, m, H-12, 13, 14,

15), 1.34(2H, m, H-16), 2.05(2H, m, H-11), 3.06(2H, d, *J*=7.0 Hz, H-8), 4.94(1H, brs, H-3), 5.27(1H, d, *J*=10.0 Hz, H-1a), 5.40(1H, m, H-9), 5.50(1H, d, *J*=10.0 Hz, H-1b), 5.56(1H, m, H-10), 5.97(1H, m, H-2)。¹³C-NMR(125 MHz, CDCl₃) δ: 14.1(C-17), 17.7(C-8), 22.7(C-16), 27.2(C-11), 29.1(C-12), 29.2(C-13), 29.3(C-14), 31.8(C-15), 63.6(C-3), 64.0(C-6), 71.3(C-5), 74.2(C-4), 80.3(C-7), 117.1(C-1), 121.9(C-9), 133.1(C-10), 136.2(C-2)。与文献[24]对照,鉴定化合物6为镰叶芹醇。

化合物7:无色针状结晶,易溶于乙醚、二氯甲烷等有机溶剂。其¹H-NMR(500 MHz, CDCl₃)和¹³C-NMR(125 MHz, CDCl₃)数据与文献[25]对照,鉴定化合物7为β-谷甾醇。

化合物8:白色固体粉末,易溶于乙醚、二氯甲烷等有机溶剂。其¹H-NMR(500 MHz, CDCl₃)和¹³C-NMR(125 MHz, CDCl₃)数据与文献[26]对照,鉴定化合物8为2,6,11,15-四甲基-2,6,10,14-十六碳四烯。

化合物9:淡黄色油状物,易溶于乙醚、二氯甲烷等有机溶剂。¹H-NMR(500 MHz, CDCl₃) δ: 1.30~1.33(6H, m, H-11, 12, 13), 1.39(2H, m, H-14), 1.45(2H, m, H-10), 1.72(2H, m, H-9), 2.03(2H, m, H-15), 4.44(1H, m, H-8), 4.91(1H, m, H-17a), 4.95(1H, m, H-3), 5.01(1H, m, H-17b), 5.31(1H, brd, *J*=10.0 Hz, H-1a), 5.48(1H, brd, *J*=17.0 Hz, H-1b), 5.83(1H, m, H-16), 5.97(1H, m, H-2)。¹³C-NMR(125 MHz, CDCl₃) δ: 25.0(C-10), 28.8(C-11), 28.9(C-14), 29.0(C-13), 29.4(C-12), 34.0(C-15), 37.3(C-9), 63.0(C-8), 64.0(C-3), 69.0(C-6), 70.5(C-5), 77.5(C-4), 81.3(C-7), 114.5(C-17), 117.8(C-1), 136.0(C-2), 138.9(C-16)。与文献[27]对照,鉴定化合物9为arteordoyne A。

化合物10:淡黄色油状物,易溶于乙醚、二氯甲烷等有机溶剂。¹H-NMR(500 MHz, CDCl₃) δ: 0.89(3H, t, *J*=7.0 Hz, H-17), 1.28~1.32(10H, m, H-12, 13, 14, 15, 16), 2.12(2H, m, H-11), 4.96(1H, m, H-3), 5.23(1H, d, *J*=8.5 Hz, H-8), 5.28(1H, brd, *J*=10.0 Hz, H-1a), 5.50(1H, brd, *J*=17.0 Hz, H-1b), 5.52(1H, m, H-9), 5.62(1H, m, H-10), 5.95(1H, m, H-2)。¹³C-NMR(125 MHz, CDCl₃) δ: 14.1(C-17), 22.7(C-16), 27.7(C-11), 29.0(C-13),

29.1(C-12), 29.3(C-14), 31.8(C-15), 58.5(C-8), 63.4(C-3), 68.7(C-6), 70.3(C-5), 78.7(C-4), 79.8(C-7), 117.4(C-1), 127.6(C-9), 134.6(C-10), 135.8(C-2)。与文献[28]对照, 鉴定化合物 10 为镰叶芹二醇。

化合物 11: 淡黄色油状物, 易溶于乙醚、二氯甲烷等有机溶剂。¹H-NMR(500 MHz, CDCl₃) δ: 1.36 ~ 1.40(6H, m, H-12, 13, 14), 2.03(2H, brt, *J* = 6.5 Hz, H-15), 2.11(2H, brt, *J* = 6.5 Hz, H-11), 4.89(1H, m, H-3), 4.95(1H, dd, *J* = 17.0, 8.0 Hz, H-17a), 5.00(1H, dd, *J* = 17.0, 1.5 Hz, H-17b), 5.19(1H, brd, *J* = 8.0 Hz, H-8), 5.30(1H, brd, *J* = 10.0 Hz, H-1a), 5.50(1H, brd, *J* = 17.0 Hz, H-1b), 5.53(1H, brd, *J* = 7.5 Hz, H-9), 5.63(1H, m, H-10), 5.79(1H, m, H-16), 5.90(1H, m, H-2)。¹³C-NMR(125 MHz, CDCl₃) δ: 27.5(C-11), 28.1(C-13), 28.3(C-14), 28.9(C-12), 34.0(C-15), 59.1(C-8), 63.3(C-3), 68.6(C-6), 70.7(C-5), 78.5(C-4), 80.3(C-7), 115.2(C-17), 118.1(C-1), 127.2(C-9), 134.1(C-10), 136.1(C-2), 138.9(C-16)。与文献[28]对照, 鉴定化合物 11 为去氢镰叶芹二醇。

化合物 12: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR(500 MHz, CDCl₃) δ: 1.18(3H, s, H-13'), 1.60(3H, s, H-14'), 1.61(3H, s, H-15'), 1.78(3H, s, H-12'), 2.02(2H, m, H-1'), 2.07(2H, m, H-2'), 2.11(2H, m, H-7'), 2.12(2H, m, H-6'), 4.61(2H, d, *J* = 6.5 Hz, H-11'), 5.07(1H, m, H-3'), 5.10(1H, m, H-5'), 5.48(1H, m, H-9'), 6.26(1H, d, *J* = 9.5 Hz, H-3), 6.82(1H, d, *J* = 2.5 Hz, H-8), 6.86(1H, dd, *J* = 8.5, 2.5 Hz, H-6), 7.38(1H, d, *J* = 8.5 Hz, H-5), 7.65(1H, d, *J* = 9.5 Hz, H-4)。¹³C-NMR(125 MHz, CDCl₃) δ: 16.1(C-15'), 16.8(C-12'), 17.7(C-14'), 25.7(C-13'), 26.1(C-2'), 26.5(C-6'), 39.3(C-7'), 39.7(C-1'), 65.5(C-11'), 101.6(C-8), 112.4(C-9), 112.9(C-3), 113.2(C-6), 118.0(C-9'), 123.1(C-5'), 124.3(C-3'), 128.7(C-5), 131.7(C-4'), 135.6(C-10'), 142.4(C-8'), 143.5(C-4), 155.9(C-10), 161.3(C-2), 162.1(C-7)。与文献[29]对照, 鉴定化合物 12 为伞形戊烯内酯。

化合物 13: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR(500 MHz, CDCl₃) δ: 1.11(3H, s, H-13'), 1.16(3H, s, H-14'), 1.17(3H, s, H-15'), 1.68(1H, m, H-1'a), 1.70(1H, m, H-5'),

1.76(3H, s, H-12'), 2.02(1H, m, H-6'a), 2.14(1H, m, H-6'b), 2.32(1H, m, H-1'b), 2.33(1H, m, H-9'), 2.34(2H, m, H-2'), 4.12(1H, dd, *J* = 10.0, 5.0 Hz, H-11'a), 4.21(1H, dd, *J* = 10.0, 4.0 Hz, H-11'b), 5.63(1H, m, H-7'), 6.29(1H, d, *J* = 9.5 Hz, H-3), 6.84(1H, d, *J* = 2.5 Hz, H-8), 6.88(1H, dd, *J* = 8.5, 2.5 Hz, H-6), 7.40(1H, d, *J* = 8.5 Hz, H-5), 7.67(1H, d, *J* = 9.5 Hz, H-4)。¹³C-NMR(125 MHz, CDCl₃) δ: 14.5(C-15'), 21.6(C-12'), 22.3(C-14'), 23.9(C-6'), 25.3(C-13'), 34.4(C-2'), 35.8(C-10'), 38.5(C-1'), 47.5(C-4'), 51.1(C-5'), 53.1(C-9'), 66.7(C-11'), 101.3(C-8), 112.9(C-9), 113.1(C-3), 113.2(C-6), 123.7(C-7'), 128.8(C-5), 132.4(C-8'), 143.3(C-4), 155.9(C-10), 161.1(C-2), 161.8(C-7), 216.1(C-3')。与文献[30]对照, 鉴定化合物 13 为圆锥茎阿魏酮。

化合物 14: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR(500 MHz, CDCl₃) δ: 1.06(3H, s, H-13'), 1.15(3H, s, H-14'), 1.19(3H, s, H-15'), 1.57(2H, m, H-6'), 1.69(1H, brd, *J* = 15.0 Hz, H-1'a), 1.78(1H, dd, *J* = 10.0, 2.0 Hz, H-5'), 1.98(1H, m, H-1'b), 2.08(1H, m, H-7'a), 2.33(1H, m, H-7'b), 2.35(1H, m, H-9'), 2.38(1H, m, H-2'a), 2.81(1H, m, H-2'b), 4.02(1H, dd, *J* = 10.0, 5.0 Hz, H-11'a), 4.25(1H, dd, *J* = 10.0, 4.0 Hz, H-11'b), 4.61(1H, s, H-12'a), 4.90(1H, s, H-12'b), 6.23(1H, d, *J* = 9.5 Hz, H-3), 6.77(1H, d, *J* = 2.5 Hz, H-8), 6.79(1H, dd, *J* = 8.5, 2.5 Hz, H-6), 7.33(1H, d, *J* = 8.5 Hz, H-5), 7.61(1H, d, *J* = 9.5 Hz, H-4)。¹³C-NMR(125 MHz, CDCl₃) δ: 20.3(C-15'), 21.2(C-14'), 23.8(C-6'), 25.6(C-13'), 32.8(C-2'), 35.0(C-7'), 36.1(C-1'), 37.5(C-10'), 47.5(C-5'), 47.9(C-4'), 56.1(C-9'), 68.0(C-11'), 101.6(C-8), 112.2(C-12'), 112.6(C-9), 112.8(C-6), 113.1(C-3), 128.6(C-5), 143.1(C-4), 146.1(C-8'), 155.8(C-10), 161.0(C-7), 161.5(C-2), 215.5(C-3')。与文献[31]对照, 鉴定化合物 14 为金合欢阿魏酮 A。

化合物 15: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR(500 MHz, CDCl₃) δ: 1.06(3H, s, H-15'), 1.08(3H, s, H-14'), 1.14(3H, s, H-13'), 1.31(3H, s, H-12'), 1.48(1H, m, H-6'a), 1.57(1H, m, H-5'), 1.58(1H, m, H-7'a), 1.68(1H,

m, H-6' b), 1.74 (1H, m, H-1' a), 1.86 (1H, m, H-9'), 1.98 (1H, m, H-7' b), 2.03 (1H, m, H-1' b), 2.47 (1H, m, H-2' a), 2.56 (1H, m, H-2' b), 4.20 (1H, dd, $J = 10.0, 6.0$ Hz, H-11' a), 4.38 (1H, dd, $J = 10.0, 5.0$ Hz, H-11' b), 6.26 (1H, d, $J = 9.5$ Hz, H-3), 6.86 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 6.90 (1H, d, $J = 2.5$ Hz, H-8), 7.35 (1H, d, $J = 8.5$ Hz, H-5), 7.65 (1H, d, $J = 9.5$ Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ : 15.5 (C-15'), 21.3 (C-14'), 21.4 (C-6'), 24.0 (C-12'), 26.1 (C-13'), 33.8 (C-2'), 37.3 (C-10'), 38.5 (C-1'), 43.1 (C-7'), 47.5 (C-4'), 54.5 (C-5'), 58.0 (C-9'), 66.5 (C-11'), 72.3 (C-8'), 101.6 (C-8), 112.9 (C-9), 113.1 (C-6), 113.4 (C-3), 128.8 (C-5), 143.3 (C-4), 155.9 (C-10), 161.1 (C-7), 161.5 (C-2), 216.3 (C-3')。与文献[32]对照, 鉴定化合物 15 为托里阿魏酮。

化合物 16: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ : 0.89 (3H, s, H-15'), 0.91 (3H, s, H-13'), 0.94 (3H, s, H-14'), 2.11 (3H, s, COCH₃), 1.45 (1H, m, H-6' a), 1.57 (1H, m, H-6' b), 1.59 (1H, m, H-1' a), 1.67 (1H, m, H-5'), 1.73 (1H, m, H-1' b), 1.76 (1H, m, H-2' a), 1.93 (1H, m, H-2' b), 2.17 (1H, m, H-7' b), 2.36 (1H, m, H-9'), 2.51 (1H, m, H-7' a), 4.02 (1H, m, H-11' a), 4.23 (1H, dd, $J = 13.6, 6.5$ Hz, H-11' b), 4.56 (1H, brs, H-12' a), 4.71 (1H, m, H-3'), 4.94 (1H, brs, H-12' b), 6.27 (1H, d, $J = 9.5$ Hz, H-3), 6.85 (1H, d, $J = 2.5$ Hz, H-8), 6.86 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 7.39 (1H, d, $J = 8.5$ Hz, H-5), 7.66 (1H, d, $J = 9.5$ Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ : 15.3 (C-15'), 21.3 (COCH₃), 21.9 (C-14'), 23.2 (C-6'), 23.3 (C-2'), 28.1 (C-13'), 32.5 (C-1'), 36.9 (C-4'), 37.4 (C-7'), 38.7 (C-10'), 49.3 (C-5'), 54.8 (C-9'), 65.6 (C-11'), 77.8 (C-3'), 101.4 (C-8), 107.8 (C-12'), 112.5 (C-9), 113.0 (C-3), 113.1 (C-6), 128.7 (C-5), 143.4 (C-4), 146.4 (C-8'), 155.9 (C-10), 161.2 (C-2), 162.3 (C-7), 170.5 (COCH₃)。与文献[33]对照, 鉴定化合物 16 为多花素宁。

化合物 17: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ : 1.01 (3H, s, H-15'), 1.11 (3H, s, H-14'), 1.22 (3H, s, H-13'), 1.62 (1H, m, H-1' a), 1.73 (1H, m, H-1'

b), 1.75 (1H, m, H-2' a), 1.93 (1H, m, H-2' b), 2.01 (3H, s, COCH₃), 2.10 (1H, $J = 12.0$ Hz, H-5'), 2.34 (1H, m, H-9'), 3.66 (1H, dd, $J = 12.0, 10.0$ Hz, H-6'), 4.03 (1H, d, $J = 10.0$ Hz, H-7'), 4.06 (1H, dd, $J = 10.0, 6.0$ Hz, H-11' a), 4.35 (1H, dd, $J = 10.0, 5.0$ Hz, H-11' b), 4.66 (1H, brs, H-3'), 4.87 (1H, brs, H-12' a), 5.17 (1H, brs, H-12' b), 6.27 (1H, d, $J = 9.5$ Hz, H-3), 6.78 (1H, d, $J = 2.5$ Hz, H-8), 6.84 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 7.37 (1H, d, $J = 8.5$ Hz, H-5), 7.64 (1H, d, $J = 9.5$ Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ : 15.7 (C-14'), 16.8 (C-15'), 21.3 (COCH₃), 23.0 (C-2'), 28.7 (C-13'), 30.2 (C-1'), 37.5 (C-10'), 37.7 (C-4'), 45.2 (C-5'), 56.6 (C-9'), 68.3 (C-11'), 74.8 (C-6'), 77.5 (C-7'), 79.9 (C-3'), 101.4 (C-8), 110.3 (C-12'), 112.5 (C-9), 113.0 (C-3), 113.2 (C-6), 128.8 (C-5), 143.4 (C-4), 145.7 (C-8'), 155.9 (C-10), 161.1 (C-2), 161.9 (C-7), 170.1 (COCH₃)。与文献[34]对照, 鉴定化合物 17 为 assafoetidnol B。

化合物 18: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ : 0.92 (3H, d, $J = 7.0$ Hz, H-13'), 1.16 (3H, s, H-12'), 1.20 (2H, m, H-7'), 1.40 (2H, m, H-2'), 1.44 (3H, s, H-14'), 1.60 (3H, s, H-15'), 1.69 (1H, m, H-1' a), 1.73 (1H, m, H-1' b), 1.86 (1H, m, H-8'), 2.01 (3H, s, COCH₃), 2.92 (1H, m, H-10'), 2.50 (2H, d, $J = 12.0$ Hz, H-6'), 3.69 (1H, d, $J = 8.0$ Hz, H-11' a), 3.88 (1H, d, $J = 8.0$ Hz, H-11' b), 4.05 (1H, brs, H-3'), 6.27 (1H, d, $J = 9.5$ Hz, H-3), 6.78 (1H, d, $J = 2.5$ Hz, H-8), 6.84 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 7.37 (1H, d, $J = 8.5$ Hz, H-5), 7.64 (1H, d, $J = 9.5$ Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ : 16.0 (C-13'), 19.6 (C-14'), 19.8 (C-15'), 21.0 (COCH₃), 22.5 (C-12'), 23.4 (C-1'), 24.4 (C-6'), 26.8 (C-2'), 31.7 (C-7'), 35.0 (C-8'), 40.8 (C-9'), 43.0 (C-10'), 65.0 (C-3'), 71.7 (C-11'), 101.1 (C-8), 112.3 (C-9), 112.6 (C-3), 113.2 (C-6), 124.6 (C-4'), 128.5 (C-5), 129.8 (C-5'), 143.4 (C-4), 155.9 (C-10), 161.3 (C-2), 162.6 (C-7), 170.3 (COCH₃)。与文献[35]对照, 鉴定化合物 18 为乙酰托里阿魏诺醇。

化合物 19: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ : 0.89 (3H, d, $J = 7.0$ Hz, H-13'), 1.15 (3H, s,

H-12'), 1.23 (2H, m, H-7'), 1.39 (3H, s, H-14'), 1.43 (2H, m, H-2'), 1.61 (3H, s, H-15'), 1.71 (1H, m, H-1'a), 1.75 (1H, m, H-1'b), 1.88 (1H, m, H-8'), 2.46 (2H, d, $J = 12.0$ Hz, H-6'), 2.91 (1H, m, H-10'), 3.71 (1H, d, $J = 8.0$ Hz, H-11'a), 3.89 (1H, d, $J = 8.0$ Hz, H-11'b), 4.01 (1H, brs, H-3'), 6.23 (1H, d, $J = 9.5$ Hz, H-3), 6.71 (1H, d, $J = 2.5$ Hz, H-8), 6.88 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 7.33 (1H, d, $J = 8.5$ Hz, H-5), 7.61 (1H, d, $J = 9.5$ Hz, H-4)。 $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 15.9 (C-13'), 19.3 (C-14'), 20.3 (C-15'), 22.5 (C-12'), 23.5 (C-1'), 24.6 (C-6'), 26.8 (C-2'), 31.7 (C-7'), 34.8 (C-8'), 41.0 (C-9'), 43.3 (C-10'), 66.3 (C-3'), 72.6 (C-11'), 101.3 (C-8), 112.1 (C-9), 112.5 (C-3), 113.2 (C-6), 124.4 (C-4'), 128.5 (C-5), 129.6 (C-5'), 143.5 (C-4), 155.9 (C-10), 161.1 (C-2), 162.9 (C-7)。与文献[36]对照, 鉴定化合物 19 为托里阿魏诺醇。

化合物 20: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。 $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.03 (3H, s, H-13'), 1.07 (3H, s, H-15'), 1.09 (3H, s, H-14'), 1.13 (1H, m, H-1'a), 1.29 (3H, s, H-12'), 1.45 (1H, m, H-6'a), 1.56 (1H, m, H-9'), 1.58 (1H, m, H-2'a), 1.71 (1H, m, H-6'b), 1.76 (2H, m, H-7'), 1.80 (1H, m, H-1'b), 2.01 (3H, s, COCH_3), 2.06 (1H, m, H-5'), 2.07 (1H, m, H-2'b), 4.21 (1H, dd, $J = 10.0, 5.0$ Hz, H-11'a), 4.30 (1H, dd, $J = 10.0, 3.0$ Hz, H-11'b), 4.86 (1H, t, $J = 3.0$ Hz, H-3'), 6.26 (1H, d, $J = 9.5$ Hz, H-3), 6.89 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 6.93 (1H, d, $J = 2.5$ Hz, H-8), 7.46 (1H, d, $J = 8.5$ Hz, H-5), 7.76 (1H, d, $J = 9.5$ Hz, H-4)。 $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 16.8 (C-15'), 19.8 (COCH_3), 20.3 (C-14'), 21.1 (C-6'), 23.0 (C-13'), 23.8 (C-2'), 31.4 (C-12'), 32.0 (C-1'), 38.8 (C-4'), 40.6 (C-7'), 43.2 (C-10'), 46.0 (C-5'), 58.6 (C-9'), 68.6 (C-11'), 75.0 (C-8'), 75.8 (C-3'), 101.8 (C-8), 113.2 (C-3), 114.5 (C-9), 115.0 (C-6), 128.9 (C-5), 144.1 (C-4), 155.8 (C-10), 161.3 (C-2), 162.1 (C-7), 171.1 (COCH_3)。与文献[37]对照, 鉴定化合物 20 为克乐利素。

化合物 21: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。 $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 0.94 (3H, s, H-15'), 0.95 (3H, s, H-14'), 0.99 (3H,

s, H-13'), 1.61 (1H, m, H-1'a), 1.71 (1H, m, H-6'a), 1.74 (3H, s, H-12'), 1.76 (1H, m, H-1'b), 1.78 (1H, m, H-2'a), 1.80 (1H, m, H-5'), 1.91 (1H, m, H-2'b), 1.98 (1H, m, H-6'b), 2.34 (1H, m, H-9'), 3.50 (1H, m, H-3'), 4.06 (1H, dd, $J = 9.5, 1.0$ Hz, H-11'a), 4.21 (1H, dd, $J = 9.5, 3.0$ Hz, H-11'b), 5.57 (1H, m, H-7'), 6.27 (1H, d, $J = 9.5$ Hz, H-3), 6.84 (1H, d, $J = 2.5$ Hz, H-8), 6.86 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 7.39 (1H, d, $J = 8.5$ Hz, H-5), 7.66 (1H, d, $J = 9.5$ Hz, H-4)。 $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 14.8 (C-15'), 21.8 (C-12'), 22.4 (C-14'), 23.2 (C-2'), 25.1 (C-6'), 28.1 (C-13'), 31.8 (C-1'), 35.6 (C-10'), 37.2 (C-4'), 43.4 (C-5'), 53.5 (C-9'), 67.1 (C-11'), 75.8 (C-3'), 101.3 (C-8), 112.5 (C-9), 113.0 (C-3), 113.1 (C-6), 123.8 (C-7'), 128.7 (C-5), 132.5 (C-8'), 143.5 (C-4), 155.9 (C-10), 161.3 (C-2), 162.1 (C-7)。与文献[38]对照, 鉴定化合物 21 为圆锥茎阿魏醇。

化合物 22: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。 $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 1.10 (3H, s, H-13'), 1.20 (3H, s, H-14'), 1.23 (3H, s, H-15'), 1.55 (2H, m, H-6'), 1.59 (1H, brd, $J = 12.0$ Hz, H-1'a), 1.69 (1H, dd, $J = 10.0, 2.0$ Hz, H-5'), 1.71 (1H, m, H-2'a), 1.76 (1H, m, H-2'b), 1.87 (1H, m, H-1'b), 2.07 (1H, m, H-7'a), 2.26 (1H, m, H-7'b), 2.40 (1H, m, H-9'), 3.68 (1H, m, H-3'), 4.06 (1H, dd, $J = 10.0, 5.0$ Hz, H-11'a), 4.31 (1H, dd, $J = 10.0, 4.0$ Hz, H-11'b), 4.59 (1H, s, H-12'a), 4.89 (1H, s, H-12'b), 6.22 (1H, d, $J = 9.5$ Hz, H-3), 6.75 (1H, d, $J = 2.5$ Hz, H-8), 6.80 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 7.36 (1H, d, $J = 8.5$ Hz, H-5), 7.63 (1H, d, $J = 9.5$ Hz, H-4)。 $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 15.6 (C-15'), 21.3 (C-14'), 23.8 (C-6'), 25.8 (C-2'), 28.5 (C-13'), 33.4 (C-1'), 36.8 (C-7'), 37.8 (C-4'), 38.3 (C-10'), 47.2 (C-5'), 54.3 (C-9'), 65.7 (C-11'), 75.6 (C-3'), 101.4 (C-8), 107.3 (C-12'), 112.4 (C-9), 112.9 (C-3), 113.2 (C-6), 128.7 (C-5), 143.3 (C-4), 146.7 (C-8'), 156.0 (C-10), 161.2 (C-7), 161.8 (C-2)。与文献[39]对照, 鉴定化合物 22 为多胶阿魏素。

化合物 23: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。 $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 0.96 (3H, s, H-15'), 0.99 (3H, s, H-13'), 1.33

(1H, dd, $J = 14.0, 5.0$ Hz, H-2' a), 1.36 (3H, s, H-14'), 1.39 (1H, d, $J = 10.0$ Hz, H-5'), 1.55 (2H, m, H-6'), 1.65 (2H, m, H-1'), 1.68 (1H, m, H-2' b), 2.10 (1H, dd, $J = 6.0, 5.0$ Hz, H-9'), 2.20 (1H, dd, $J = 14.0, 13.0$ Hz, H-7' a), 2.66 (1H, dd, $J = 14.0, 5.0$ Hz, H-7' b), 3.21 (1H, dd, $J = 11.0, 5.0$ Hz, H-3'), 4.05 (1H, dd, $J = 10.0, 5.0$ Hz, H-11' a), 4.27 (1H, dd, $J = 10.0, 6.0$ Hz, H-11' b), 4.75 (1H, brs, H-12' a), 4.84 (1H, bss, H-12' b), 6.22 (1H, d, $J = 9.5$ Hz, H-3), 6.77 (1H, d, $J = 2.5$ Hz, H-8), 6.80 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 7.31 (1H, d, $J = 8.5$ Hz, H-5), 7.64 (1H, d, $J = 9.5$ Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ : 15.9 (C-15'), 23.2 (C-14'), 24.1 (C-6'), 27.1 (C-1'), 31.2 (C-13'), 35.3 (C-2'), 38.3 (C-10'), 39.2 (C-4'), 43.6 (C-7'), 47.3 (C-5'), 56.0 (C-9'), 67.5 (C-11'), 78.8 (C-3'), 101.4 (C-8), 112.5 (C-12'), 112.7 (C-9), 112.8 (C-3), 113.2 (C-6), 128.7 (C-5), 141.2 (C-8'), 143.5 (C-4), 155.7 (C-10), 161.3 (C-2), 161.9 (C-7)。与文献[34]对照, 鉴定化合物 23 为金合欢基阿魏醇 A。

化合物 24: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ : 0.97 (3H, s, H-15'), 1.01 (3H, s, H-13'), 1.16 (3H, s, H-14'), 1.28 (3H, s, H-12'), 1.35 (1H, dd, $J = 14.0, 5.0$ Hz, H-2' a), 1.37 (1H, d, $J = 10.0$ Hz, H-5'), 1.55 (2H, m, H-6'), 1.58 (1H, m, H-9'), 1.67 (2H, m, H-1'), 1.70 (1H, m, H-2' b), 1.77 (2H, m, H-7'), 3.22 (1H, dd, $J = 11.0, 5.0$ Hz, H-3'), 4.21 (1H, dd, $J = 10.0, 3.0$ Hz, H-11' a), 4.33 (1H, dd, $J = 10.0, 2.0$ Hz, H-11' b), 6.21 (1H, d, $J = 9.5$ Hz, H-3), 6.78 (1H, d, $J = 2.5$ Hz, H-8), 6.82 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 7.34 (1H, d, $J = 8.5$ Hz, H-5), 7.65 (1H, d, $J = 9.5$ Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ : 15.8 (C-15'), 23.5 (C-14'), 24.3 (C-6'), 27.6 (C-1'), 28.8 (C-12'), 30.2 (C-13'), 34.9 (C-2'), 38.7 (C-4'), 40.5 (C-7'), 44.1 (C-10'), 47.5 (C-5'), 58.6 (C-9'), 69.1 (C-11'), 74.3 (C-8'), 78.9 (C-3'), 102.2 (C-8), 113.2 (C-3), 113.8 (C-6), 114.1 (C-9), 129.1 (C-5), 145.3 (C-4), 156.0 (C-10), 162.1 (C-2), 162.8 (C-7)。与文献[40]对照, 鉴定化合物 24 为托里阿魏素。

化合物 25: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ :

0.96 (3H, s, H-13'), 1.13 (1H, t, $J = 3.0$ Hz, H-1' a), 1.16 (3H, s, H-14'), 1.21 (3H, s, H-15'), 1.29 (3H, s, H-12'), 1.45 (1H, m, H-6' a), 1.55 (1H, m, H-9'), 1.57 (1H, m, H-2' a), 1.73 (1H, m, H-6' b), 1.76 (2H, m, H-7'), 1.81 (1H, d, $J = 12.0$ Hz, H-1' b), 2.06 (1H, m, H-2' b), 2.13 (1H, m, H-5'), 3.34 (1H, t, $J = 2.5$ Hz, H-3'), 4.23 (1H, dd, $J = 10.0, 3.0$ Hz, H-11' a), 4.30 (1H, dd, $J = 10.0, 2.0$ Hz, H-11' b), 6.25 (1H, d, $J = 9.5$ Hz, H-3), 6.93 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 6.96 (1H, d, $J = 2.5$ Hz, H-8), 7.53 (1H, d, $J = 8.5$ Hz, H-5), 7.87 (1H, d, $J = 9.5$ Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ : 17.8 (C-15'), 20.5 (C-6'), 21.3 (C-14'), 23.9 (C-2'), 25.3 (C-13'), 28.6 (C-12'), 31.6 (C-1'), 37.3 (C-5'), 40.8 (C-7'), 41.6 (C-4'), 43.5 (C-10'), 59.0 (C-9'), 69.4 (C-11'), 71.3 (C-3'), 74.1 (C-8'), 102.0 (C-8), 113.2 (C-3), 114.0 (C-6), 114.2 (C-9), 129.1 (C-5), 145.3 (C-4), 156.3 (C-10), 162.1 (C-2), 162.6 (C-7)。与文献[40]对照, 鉴定化合物 25 为去乙酰基克乐利素。

化合物 26: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ : 0.97 (3H, s, H-15'), 1.01 (3H, s, H-13'), 1.11 (1H, t, $J = 3.0$ Hz, H-1' a), 1.17 (3H, s, H-14'), 1.40 (1H, d, $J = 10.0$ Hz, H-5'), 1.55 (1H, m, H-2' a), 1.79 (1H, d, $J = 12.0$ Hz, H-1' b), 2.03 (1H, m, H-2' b), 2.09 (1H, dd, $J = 7.0, 5.0$ Hz, H-9'), 2.20 (1H, dd, $J = 14.0, 13.0$ Hz, H-7' a), 2.60 (1H, dd, $J = 14.0, 5.0$ Hz, H-7' b), 3.36 (1H, t, $J = 2.5$ Hz, H-3'), 3.97 (1H, m, H-6'), 4.05 (1H, dd, $J = 10.0, 5.0$ Hz, H-11' a), 4.26 (1H, dd, $J = 10.0, 6.0$ Hz, H-11' b), 4.71 (1H, brs, H-12' a), 4.81 (1H, bss, H-12' b), 6.24 (1H, d, $J = 9.5$ Hz, H-3), 6.76 (1H, d, $J = 2.5$ Hz, H-8), 6.81 (1H, dd, $J = 8.5, 2.5$ Hz, H-6), 7.35 (1H, d, $J = 8.5$ Hz, H-5), 7.66 (1H, d, $J = 9.5$ Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ : 17.9 (C-15'), 21.9 (C-14'), 24.1 (C-2'), 25.6 (C-13'), 31.8 (C-1'), 38.7 (C-10'), 41.8 (C-4'), 43.1 (C-7'), 50.9 (C-5'), 55.9 (C-9'), 67.8 (C-11'), 70.5 (C-6'), 73.1 (C-3'), 102.5 (C-8), 112.7 (C-12'), 113.2 (C-3), 114.1 (C-6), 114.5 (C-9), 129.1 (C-5), 141.3 (C-8'), 145.3 (C-4), 156.1 (C-10), 161.9 (C-2), 162.6 (C-7)。与文献[34]对照, 鉴定化合物 26 为 assafoetidol A。

化合物 27: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ: 1.16 (3H, s, H-14'), 1.19 (3H, s, H-13'), 1.53 (2H, m, H-2'), 1.60 (3H, brs, H-12'), 1.73 (3H, brs, H-15'), 2.23 (2H, t, *J* = 6.0 Hz, H-1'), 2.35 (2H, t, *J* = 6.0 Hz, H-7'), 2.43 (1H, m, H-6'), 3.36 (1H, dd, *J* = 10.0, 2.5 Hz, H-3'), 4.53 (2H, d, *J* = 6.0 Hz, H-11'), 5.14 (1H, brd, *J* = 6.0 Hz, H-5'), 5.45 (1H, t, *J* = 6.0 Hz, H-9'), 6.21 (1H, d, *J* = 9.5 Hz, H-3), 6.75 (1H, d, *J* = 2.5 Hz, H-8), 6.80 (1H, dd, *J* = 8.5, 2.5 Hz, H-6), 7.30 (1H, d, *J* = 8.5 Hz, H-5), 7.62 (1H, d, *J* = 9.5 Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ: 16.3 (C-15'), 17.0 (C-13'), 23.7 (C-14'), 26.1 (C-12'), 26.2 (C-2'), 30.2 (C-6'), 36.8 (C-7'), 39.2 (C-1'), 65.3 (C-11'), 73.2 (C-4'), 78.0 (C-3'), 101.5 (C-8), 112.4 (C-3), 113.0 (C-6), 113.5 (C-9), 118.2 (C-9'), 124.0 (C-5'), 128.9 (C-5), 135.4 (C-10'), 144.0 (C-8'), 144.2 (C-4), 156.0 (C-10), 161.6 (C-7), 162.0 (C-2)。与文献[41]对照, 鉴定化合物 27 为卡拉阿魏醇。

化合物 28: 白色粉末, 易溶于乙醚、二氯甲烷、乙酸乙酯等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ: 1.31 (3H, s, H-13'), 1.58 (3H, brs, H-12'), 1.46 (2H, m, H-2'), 1.68 (3H, brs, H-15'), 2.33 (2H, t, *J* = 6.0 Hz, H-7'), 2.37 (1H, m, H-6'), 2.41 (2H, t, *J* = 6.0 Hz, H-1'), 3.67 (1H, dd, *J* = 10.0, 2.5 Hz, H-3'), 3.96 (1H, d, *J* = 12.0 Hz, H-14'a), 4.06 (1H, d, *J* = 12.0 Hz, H-14'b), 4.56 (2H, d, *J* = 6.0 Hz, H-11'), 5.15 (1H, brd, *J* = 6.0 Hz, H-5'), 5.50 (1H, t, *J* = 6.0 Hz, H-9'), 6.22 (1H, d, *J* = 9.5 Hz, H-3), 6.77 (1H, d, *J* = 2.5 Hz, H-8), 6.83 (1H, dd, *J* = 8.5, 2.5 Hz, H-6), 7.33 (1H, d, *J* = 8.5 Hz, H-5), 7.62 (1H, d, *J* = 9.5 Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ: 16.7 (C-15'), 17.7 (C-13'), 26.3 (C-12'), 27.1 (C-2'), 31.2 (C-6'), 36.6 (C-7'), 39.1 (C-1'), 66.1 (C-11'), 68.3 (C-14'), 75.3 (C-4'), 79.1 (C-3'), 101.2 (C-8), 112.9 (C-3), 113.3 (C-6), 113.5 (C-9), 118.0 (C-9'), 124.4 (C-5'), 128.9 (C-5), 135.3 (C-10'), 144.1 (C-8'), 144.3 (C-4), 155.9 (C-10), 161.8 (C-7), 162.0 (C-2)。与文献[41]对照, 鉴定化合物 28 为 14'-羟基-卡拉阿魏醇。

化合物 29: 白色粉末, 易溶于乙醚、二氯甲烷、

乙酸乙酯等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ: 0.93 (3H, brs, H-15'), 1.14 (3H, d, *J* = 6.5 Hz, H-12'), 1.19 (1H, m, H-7'a), 1.62 (3H, s, H-13'), 1.70 (2H, m, H-1'), 1.72 (3H, s, H-14'), 1.75 (1H, m, H-9'), 1.92 (1H, m, H-7'b), 1.83 (1H, m, H-8'), 2.37 (2H, m, H-2'), 2.50 (1H, m, H-6'), 3.97 (1H, dd, *J* = 10.0, 5.0 Hz, H-11'a), 4.02 (1H, dd, *J* = 10.0, 7.0 Hz, H-11'b), 5.13 (1H, brd, *J* = 10.0 Hz, H-5'), 6.24 (1H, d, *J* = 9.5 Hz, H-3), 6.77 (1H, d, *J* = 2.5 Hz, H-8), 6.82 (1H, dd, *J* = 8.5, 2.5 Hz, H-6), 7.35 (1H, d, *J* = 8.5 Hz, H-5), 7.63 (1H, d, *J* = 9.5 Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ: 18.1 (C-13'), 20.7 (C-12'), 21.0 (C-15'), 26.3 (C-14'), 29.1 (C-2'), 33.2 (C-1'), 36.1 (C-8'), 40.1 (C-7'), 47.0 (C-9'), 49.3 (C-6'), 53.1 (C-10'), 69.3 (C-11'), 101.2 (C-8), 112.5 (C-9), 112.6 (C-6), 113.2 (C-3), 125.3 (C-5'), 128.7 (C-5), 132.1 (C-4'), 143.5 (C-4), 156.0 (C-10), 161.2 (C-2), 162.1 (C-7), 178.9 (C-3')。与文献[32]对照, 鉴定化合物 29 为古蓬阿魏酸。

化合物 30: 白色针状结晶, 易溶于乙醚、二氯甲烷等有机溶剂。¹H-NMR (500 MHz, CDCl₃) δ: 3.90 (3H, s, 6-OCH₃), 3.92 (3H, s, 7-OCH₃), 6.32 (1H, d, *J* = 9.5 Hz, H-3), 7.20 (1H, s, H-8), 7.37 (1H, s, H-5), 7.91 (1H, d, *J* = 9.5 Hz, H-4)。¹³C-NMR (125 MHz, CDCl₃) δ: 56.5 (6-OCH₃), 56.7 (7-OCH₃), 103.1 (C-8), 110.5 (C-5), 112.8 (C-9), 113.7 (C-3), 143.1 (C-4), 144.6 (C-6), 146.5 (C-7), 155.8 (C-10), 161.1 (C-2)。与文献[42]对照, 鉴定化合物 30 为 6,7-二甲氧基香豆素。

化合物 31: 白色针状结晶, 易溶于乙醚、二氯甲烷等有机溶剂。其¹H-NMR (500 MHz, CDCl₃) 和¹³C-NMR (125 MHz, CDCl₃) 数据与文献[43]对照, 鉴定化合物 31 为香草醛。

化合物 32: 白色针状结晶, 在紫外灯下 (365 nm) 具有天蓝色荧光, 易溶于乙醚、二氯甲烷等有机溶剂。其¹H-NMR (500 MHz, CDCl₃) 和¹³C-NMR (125 MHz, CDCl₃) 数据与文献[44]对照, 鉴定化合物 32 为 7-甲氧基香豆素。

化合物 33: 白色针状结晶, 在紫外灯下 (365 nm) 具有天蓝色荧光, 易溶于乙醚、二氯甲烷等有机溶剂。其¹H-NMR (500 MHz, CDCl₃) 和¹³C-NMR (125 MHz, CDCl₃) 数据与文献[44]对照, 鉴定化合物 33 为 6,7-二羟基香豆素。

4 讨论

砂茴香是我国特有且具药用价值的阿魏属植物之一,在内蒙古境内分布较广,资源丰富,是具有潜在开发利用价值的天然资源。近几年,民间相传砂茴香对结核病防治有显著效果,且未见毒副作用。目前,对于砂茴香的化学成分方面研究尚未见到报道。本实验对砂茴香进行了系统的化学成分研究。

借助于现代色谱和波谱技术从砂茴香二氯甲烷萃取物中分离鉴定了33个化合物,其中倍半萜香豆素类18个、炔类5个、脂肪酸类4个、香豆素类3个和其他类3个。化合物5~6、9~11为该属中首次分离得到,其他化合物均为该植物中首次分离得到,为该植物后续研究打下了前期的实验基础。

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(收稿日期:2024-05-13)