

蒙药土木香的化学成分研究

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摘要: 研究蒙药土木香的化学成分, 采用 RP-HPLC、硝酸银硅胶色谱等方法分离纯化, 应用 NMR、MS 等波谱技术鉴定化合物结构, 共分离鉴定了 22 个单体化合物, 分别为 5 α , 6 α -dihydroxy-eudesma-11(13)-dien-12, 8 β -olide (1)、4 α -hydroxy-5-methoxy-5, 8 α -dimethyl-3-methylenedecahydronaphtho[2, 3-b]furan-2-one (2)、木香烯内酯 (3)、土木香内酯 (4)、异土木香内酯 (5)、11, 13-二氢土木香内酯 (6)、alloalantolactone (7)、4 α , 5 β -环氧-1 (10)、11 (13)-吉玛烷-12, 8 α -交酯 (8)、septuplinolide (9)、8-epi-ivangustin (10)、santamarine (11)、racemosalactone A (12)、3-oxo-eudesma-4 (11)-dien-12, 8 β -olide (13)、telekin (14)、igalane (15)、macrophyllilactone E (16)、4 α , 15-环氧异土木香内酯 (17)、11, 13-dihydroxy-alantolactone (18)、1 (2)、4 (15)、11 (3)-eudesma-trien-12, 8 β -olide (19)、亚麻酸 (20)、亚油酸 (21)、油酸 (22)。化合物 1 是新倍半萜内酯类化合物, 化合物 2、3、9~14、17、19~22 为首次从该属植物中分离得到, 化合物 4~8、15、16、18 为土木香药材中已报道的化合物。

关键词: 蒙药土木香; 硝酸银硅胶柱色谱; 化学成分

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Chemical constituents from Mongolian medicine *Inulae Radix*MAO Ting¹, MAO Le², ZHANG Ping³, GAO Bai-qing¹, ZHANG Yong^{4*}¹The Third Affiliated Hospital of Inner Mongolia Medical University; ²The Third Affiliated Hospital of Baotou Medical College of Inner Mongolia Scientific and Technological University, Baotou 014040, China;³Inner Mongolia Medical University, Hohhot 010110, China; ⁴The First Affiliated Hospital of Baotou Medical College of Inner Mongolia Scientific and Technological University, Baotou 014040, China

Abstract: To study the chemical constituents from the roots of the Mongolian medicine *Inulae Radix*. The compounds were separated and purified by RP-HPLC and silver nitrate silica gel chromatography, and the structures of the compounds were identified by applying NMR and MS spectroscopy. Twenty-two monomeric compounds were isolated and identified as follows: 5 α , 6 α -dihydroxy-eudesma-11(13)-dien-12, 8 β -olide (1), 4 α -hydroxy-5-methoxy-5, 8 α -dimethyl-3-methylenedecahydronaphtho[2, 3-b]furan-2-one (2), 1 (10), 4 (5), 11 (13)-germa-cradiene-8, 12-olide (3), alantolactone (4), isovalantolactone (5), 11, 13-dihydro-5 (6)-dine-alantolactone (6), alloalantolactone (7), 4 α , 5 β -epoxy-1 (10), 11 (13)-germacra-dien-12, 8 α -olide (8), sseptuplinolide (9), 8-epi-ivangustin (10), santamarine (11), racemosalactone A (12), 3-oxo-eudesma-4 (11)-dien-12, 8 β -olide (13), telekin (14), igalane (15), macrophyllilactone E (16), 4 α , 15-epoxy-isovalantolactone (17), 11, 13-dihydroxy-alantolactone (18), 1 (2), 4 (15), 11 (3)-eudesma-trien-12, 8 β -olide (19), linolenic (20), linoleic acid (21), oleic acid (22). Compound 1 was a new sesquiterpenes. Compounds 2, 3, 9-14, 17, 19-22 were isolated from genus *Inula* for the first time. Compounds 4-8, 15, 16, 18 have been reported from *Inulae Radix*.

Key words: Mongolian medicine *Inulae Radix*; silver nitrate silica gel column chromatography; chemical constituents

蒙药土木香, 是菊科旋覆花属植物土木香 (*Inula helenium* L.) 的干燥根, 是蒙医常用清热类药, 性

甘、苦、辛, 味腻、燥、锐、重、平, 具清巴达干热、解赫依血相让、温中消食、健脾开欲、止刺痛等功效, 主治未成熟热、感冒头痛、恶心寒战、赫依血引起胸闷气喘、不思饮食等症^[1]。以本品为君药的蒙药复方“四味土木香散”为治疗瘟病热证的经典方和基础

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方,1977年作为蒙药经典验方载入《中华人民共和国药典》,该方辨证加味可形成62方^[2],在蒙医药中具有重要地位和价值。土木香中已分离鉴定了40多种化合物,主要为倍半萜内酯类、少量黄酮、氨基酸、三萜、生物碱、植物甾醇等^[3-6],药理作用突出有效,具有抗肿瘤、抗菌、抗炎、驱虫、镇痛、保肝及降糖等多重活性^[7-10]。故本研究对“查干汤”中君药土木香进行更加深入的研究,以期提取出更有价值的有效成分,进一步为后续土木香药代动力学研究做好前期准备,更进一步为蒙药复方“查干汤”抗流感药效物质基础的研究奠定科学的理论依据。

1 材料与方法

1.1 材料

土木香(济南人和中药饮片公司,批号20120619,产地河北),由内蒙古医科大学药用植物教研室主任包保全教授鉴定为菊科旋覆花属植物土木香 *Inula helenium* L. 的干燥根。

1.2 仪器和试剂

Bruker Avance III 500 MHz 核磁共振仪(瑞士 Bruker 公司);SHIMADZU LC-20AT 高效液相色谱仪(UV, RID-10A 检测器,日本岛津公司);IR Affinity-1(日本岛津公司);电子天平(型号 AL-204,梅特勒-托利多仪器上海有限公司);SGW-5 自动旋光仪(型号 SGW-5,上海仪电科仪);双光束紫外可见分光光度计(型号 TU-1901,北京普析通用仪器);硝酸银(分析纯,国药集团化学试剂有限公司);薄层色谱硅胶 GF₂₅₄(青岛海洋化工厂);柱层析硅胶(200-300 目,中国青岛海洋公司);乙腈(美国 Fisher);甲醇(美国 Fisher);四氢呋喃(美国 Fisher);其余试剂均为分析纯,实验用水为超纯水。

1.3 方法

称取 1.0 kg 土木香超微粉,采用 8 倍量乙酸乙酯加热回流,提取 3 次,依次 2 h、1 h、30 min,提取液合并过滤,减压浓缩,用水萃取,乙酸乙酯层减压浓缩,冷冻干燥,得浸膏 32.38 g。采用中低压高效液相色谱法,上样 32.38 g 浸膏,用 75% 的四氢呋喃制备,得 1、2、3、4 共四部分。第 4 部分的 10 g 样品经 HPLC 色谱法,70% 乙腈等度洗脱,得化合物 4(3.7 g, $t_R = 13.5$ min)、6(2.8 mg, $t_R = 16.5$ min)、7(19.0 mg, $t_R = 18.5$ min)、20(15.4 mg, $t_R = 12.0$ min)、21(5.0 mg, $t_R = 22.5$ min)、22(6.4 mg, $t_R = 34.0$ min);第 1、2、3 部分合并 22 g,采用自制的 10% 硝酸银硅胶(200~300 目)柱色谱,洗脱剂环己烷-乙

酸乙酯四个梯度(15:1, 5:1, 3:1, 2:1),8 倍柱体积(8 000 mL)洗脱,200 mL 为一个流分。第一部分 Fr1(15:1)得 37 个流分,10% 硝酸银薄层色谱鉴别,展开剂环己烷-乙酸乙酯(3:1),显色剂 2% 香草醛-浓硫酸,以土木香内酯和异土木香内酯为混合对照品,得化合物 4(4.3 g)、5(2.2 g);第二部分 Fr2(5:1)得 38 个流分,10% 硝酸银薄层色谱鉴别,合并相同流分 Fr2(1~20 号流分)得化合物 5(2.5 g);Fr2(21~38 号流分)经 HPLC 色谱法 80% 甲醇纯化,得化合物 1(7.2 mg, $t_R = 32.0$ min)、2(4.3 mg, $t_R = 27.0$ min)、17(5.0 mg, $t_R = 25.0$ min)。第三部分 Fr3(3:1)得 40 个流分,10% 硝酸银薄层色谱鉴别,合并相同流分,Fr3-1(1~7 号流分)和 Fr3-3(21~40 号流分),经 HPLC 色谱法 70% 甲醇纯化,得化合物 8(12.4 mg, $t_R = 17.5$ min)、9(3.8 mg, $t_R = 19.5$ min)、10(23.0 mg, $t_R = 21.0$ min)、11(5.8 mg, $t_R = 23.5$ min)、12(1.6 mg, $t_R = 27.0$ min)、15(6.0 mg, $t_R = 12.0$)、16(8.0 mg, $t_R = 10.5$ min)。Fr3-2(8~20 号流分)经 HPLC 色谱法 65% 甲醇纯化,得化合物 3(25.0 mg, $t_R = 58.5$ min)、13(5.0 mg, $t_R = 13.5$ min)、14(4.6 mg, $t_R = 25.0$ min)、15(13.0 mg, $t_R = 50.0$ min);第四部分 Fr4(2:1)得 40 个流分,Fr4(15~25 号)经 HPLC 色谱法 80% 甲醇纯化,得化合物 18(4.5 mg, $t_R = 8.5$ min)、19(2.0 mg, $t_R = 13.0$ min)。

2 结构鉴定

化合物 1 白色针状结晶(CHCl_3); $[\alpha]_D^{26.2} + 56.99$ (c 0.73, CHCl_3);HR-ESI-MS: m/z 289.141 0 $[M + Na]^+$ (calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4\text{Na}$, 289.139 7);结合 ^{13}C NMR 谱,确定其分子式为 $\text{C}_{15}\text{H}_{22}\text{O}_4$;UV (MeOH) λ_{\max} ($\log \epsilon$) 211(1.51) nm;IR 光谱显示该化合物含有羟基($3\ 405\ \text{cm}^{-1}$)、双键($1\ 650\ \text{cm}^{-1}$)以及羰基($1\ 770\ \text{cm}^{-1}$); ^1H NMR(500 MHz, CDCl_3):2 个甲基氢信号:1.13(3H, s), 1.06(3H, d, $J = 7.0$ Hz), 2 个环外亚甲基氢信号:6.43(1H, d, $J = 3.0$ Hz), 5.79(1H, d, $J = 2.5$ Hz), 2 个氧化的次甲基氢信号:4.70(1H, m), 2.92(1H, d, $J = 2.5$ Hz); ^{13}C NMR(125 MHz, CDCl_3)显示有 15 个碳原子,1 个酯羰基碳(δ_c 169.5), 2 个双键碳信号(δ_c 136.6、 δ_c 123.6), 3 个连氧碳(δ_c 61.1、 δ_c 67.4、 δ_c 75.1), 2 个甲基碳信号(δ_c 16.4、 δ_c 17.9);HMBC 谱中, H-14(δ_H 1.13, 3H, s)与 C-1(δ_c 37.3), C-5(δ_c 67.4), C-9

($\delta_{\text{C}} 39.4$), C-10($\delta_{\text{C}} 32.5$) 相关, H-15($\delta_{\text{H}} 1.06$, 3H, d, $J = 7.0$ Hz) 与 C-3($\delta_{\text{C}} 29.4$), C-4($\delta_{\text{C}} 37.6$), C-5($\delta_{\text{C}} 67.4$) 相关, H-6($\delta_{\text{H}} 2.92$, 1H, d, $J = 2.5$ Hz) 与 C-5($\delta_{\text{C}} 67.4$), C-7($\delta_{\text{C}} 37.0$), C-8($\delta_{\text{C}} 75.1$) 相关, H-13a($\delta_{\text{H}} 6.43$, 1H, d, $J = 3.0$ Hz) 和 H-13b($\delta_{\text{H}} 5.79$, 1H, d, $J = 2.5$ Hz) 与 C-7($\delta_{\text{C}} 37.0$), C-11($\delta_{\text{C}} 136.7$), C-12($\delta_{\text{C}} 169.5$) 相关; 结合 HSQC 谱图归属, 连氧碳($\delta_{\text{C}} 67.4$) 为季碳, 连氧碳($\delta_{\text{C}} 61.1$) 上有一个($\delta_{\text{H}} 2.92$, 1H, d, $J = 2.5$ Hz), 连氧碳($\delta_{\text{C}} 75.1$) 上有一个($\delta_{\text{H}} 4.70$, 1H, m); $^1\text{H}-^1\text{H}$ COSY 谱中, H-6($\delta_{\text{H}} 2.92$) 与 H-7($\delta_{\text{H}} 3.69$) 相关, H-7($\delta_{\text{H}} 3.69$) 与 H-8($\delta_{\text{H}} 4.70$)、H-13a($\delta_{\text{H}} 6.43$)、H-13b($\delta_{\text{H}} 5.79$) 相关, 综合以上, 判断化合物 **1** 具有典型的 α -甲基基 γ -内酯结构。化合物 **1** 的相对构型通过二维同核 Overhauser 效应 NOESY 谱进行确认, 天然的桉叶烷型倍半萜内酯类化合物中 H-8 为 α 构型^[11], NOESY 谱中 H-8 和 H-7、H-9 α 相关, 说明 H-7、H-9 α 均为 α 构型; H-9 β 与 H-6、H-14 相关, H-6 又与 H-1a、H-13、H-14、H-15 相关, 则表明 H-6、H-14、H-15 均为 β 构型, C₆-OH 则为 α 构型; (HMBC、 $^1\text{H}-^1\text{H}$ COSY 相关信号及相对构型见图 1、NOESY 相关信号见图 2); 结合参考文献^[12] 报道的天然桉叶烷型倍半萜内酯类化合物的骨架构型, 定义 C₅-OH 为 α 构型; 综上, 经核磁数据比对及 SCIFinder 数据库检索确定为新化合物 **5 α** , 6 α -dihydroxy-eudesma-11(13)-dien-12, 8 β -olide (核磁数据见表 1)。化合物 **1** 的详细结构鉴定数据

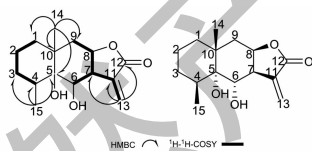


图 1 化合物 **1** 的 HMBC、 $^1\text{H}-^1\text{H}$ COSY 关键相关信号及相对构型

Fig. 1 Key HMBC and $^1\text{H}-^1\text{H}$ COSY correlations and relative configuration of compound **1**

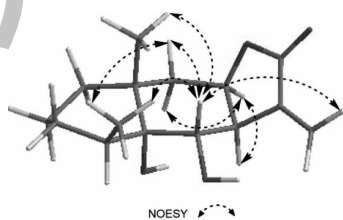


图 2 化合物 **1** 的 NOESY 谱关键相关信号
Fig. 2 Key NOESY correlations of compound **1**

原始图谱可从本刊官网免费下载 (www. trew. ac. cn)。

表 1 化合物 **1** 的 ^1H NMR 和 ^{13}C NMR 数据 (500 和 125 MHz, CDCl_3)

Table 1 ^1H NMR and ^{13}C NMR data for compound **1** (500 and 125 MHz, CDCl_3)

No.	δ_{H}	δ_{C}
1	1.39(1H, m); 1.07(1H, m)	37.3
2	1.81(1H, m); 1.51(1H, m)	23.9
3	1.83(1H, m); 1.52(1H, m)	29.4
4	1.45(1H, m)	37.6
5	-	67.4
6	2.92(1H, d, $J = 2.5$ Hz)	61.1
7	3.69(1H, m)	37.0
8	4.70(1H, m)	75.1
9	1.58(1H, dd, $J = 15.0, 1.8$ Hz, H-9a); 1.89(1H, dd, $J = 15.0, 4.4$ Hz, H-9b)	39.4
10	-	32.5
11	-	136.7
12	-	169.5
13	6.43(1H, d, $J = 3.0$ Hz); 5.79(1H, d, $J = 2.5$ Hz)	123.6
14	1.13(3H, s)	16.4
15	1.06(3H, d, $J = 7.0$ Hz)	17.9

化合物 **2** 白色油状物; UV (MeOH) λ_{max} (log ϵ) 207 (0.89) nm; HR-ESI-MS: m/z 289.141 0 [M + Na]⁺ (calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4\text{Na}$, 289.139 7); IR (丙酮) ν_{max} 3 448、1 650、1 747 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ : 6.32 (1H, d, $J = 3.5$ Hz, H-13a), 5.61 (1H, d, $J = 3.0$ Hz, H-13b), 4.75 (1H, m, H-8), 3.25 (1H, m, H-7), 2.1 (1H, m, H-6), 1.85 (1H, m, H-9), 1.8 (1H, m, H-6), 1.65 (1H, m, H-9), 1.65 ~ 2.0 (2H, m, H-3), 1.45 (1H, m, H-2), 1.39 (3H, s, H-15), 1.26 (1H, m, H-2), 1.25 (1H, m, H-1), 1.06 (3H, s, H-14); ^{13}C NMR (125 MHz, CDCl_3) δ : 34.9 (C-1), 16.5 (C-2), 32.2 (C-3), 62.5 (C-4), 65.9 (C-5), 29.7 (C-6), 37.5 (C-7), 74.7 (C-8), 41.9 (C-9), 32.3 (C-10), 138.8 (C-11), 170.0 (C-12), 122.9 (C-13), 22.9 (C-14), 19.7 (C-15)。以上数据与文献^[13] 报道一致, 故鉴定化合物 **2** 为 4 α -Hydroxy-5-methoxy-5, 8 α -dimethyl-3-methylenedecahydronaphtho [2,3-b]furan-2-one。

化合物 **3** 白色针状结晶 (CHCl_3); $[\alpha]_{\text{D}}^{25} + 19.7$ (c 1.34, CHCl_3); HR-ESI-MS: m/z 255.135 2

$[M + Na]^+$ (calcd for $C_{15}H_{20}O_2Na$, 255.1355); UV (MeOH) λ_{max} ($\log \epsilon$) 208 (1.22); IR (丙酮) ν_{max} 3525, 1650, 1763 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ : 6.28 (1H, d, $J = 3.3$ Hz, H-13a), 5.60 (1H, d, $J = 3.3$ Hz, H-13b), 4.90 (1H, dd, $J = 10.8, 4.5$ Hz, H-1), 4.70 (1H, d, $J = 9.6$ Hz, H-5), 4.1 (1H, m, H-6), 1.50 (3H, s, H-15), 1.5 (3H, s, H-14); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 127.7 (C-1), 31.3 (C-2), 25.0 (C-3), 130.9 (C-4), 137.0 (C-5), 38.8 (C-6), 49.5 (C-7), 84.4 (C-8), 47.0 (C-9), 133.4 (C-10), 139.7 (C-11), 169.8 (C-12), 120.8 (C-13), 16.7 (C-14), 16.3 (C-15)。以上数据与文献^[14]报道一致,故鉴定化合物 **3** 为木香烯内酯。

化合物 4 白色无定型粉末; $[\alpha]_D^{25.6} + 72.56$ (c 5.4, $CHCl_3$); HR-ESI-MS: m/z 233.1538 $[M + H]^+$ (calcd for $C_{15}H_{21}O_2$, 233.1536); UV (MeOH) λ_{max} ($\log \epsilon$) 210 (1.13) nm; 1H NMR (500 MHz, $CDCl_3$) δ : 6.20 (1H, br s, H-13a), 5.63 (1H, br s, H-13b), 5.15 (1H, d, $J = 3.0$ Hz, H-6), 4.83 (1H, m, H-8), 2.11 (1H, d, $J = 14.5$ Hz, H-9a), 1.20 (3H, s, H-14), 1.09 (3H, d, $J = 7.0$ Hz, H-15); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 16.8 (C-1), 32.7 (C-2), 41.7 (C-3), 37.6 (C-4), 149.0 (C-5), 118.8 (C-6), 39.5 (C-7), 76.5 (C-8), 42.7 (C-9), 32.7 (C-10), 139.9 (C-11), 170.5 (C-12), 121.6 (C-13), 28.6 (C-14), 22.6 (C-15)。以上数据与文献^[15]报道一致,故鉴定化合物 **4** 为土木香内酯。

化合物 5 白色无定型粉末; $[\alpha]_D^{25.5} + 27.28$ (c 0.5, $CHCl_3$); HR-ESI-MS: m/z 233.1538 $[M + H]^+$ (calcd for $C_{15}H_{21}O_2$, 233.1536); UV (MeOH) λ_{max} ($\log \epsilon$) 212 (0.66) nm; 1H NMR (500 MHz, $CDCl_3$) δ : 6.13 (1H, s, H-13a), 5.59 (1H, s, H-13b), 4.77 (1H, br s, H-15a), 4.50 (1H, m, H-8), 4.44 (1H, br s, H-15b), 2.98 (1H, m, H-7), 2.34 (1H, d, $J = 13.0$ Hz, H-3), 2.34 (1H, d, $J = 12.5$ Hz, H-5), 2.2 (1H, d, $J = 15.5$ Hz, H-1a), 1.74 (1H, dd, $J = 13.0, 7.0$ Hz, H-6a), 1.40 (1H, dd, $J = 18.0, 11.0$ Hz, H-6b), 1.25 (1H, dd, $J = 13.5, 4.0$ Hz, H-9a), 0.83 (3H, s, H-14); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 41.4 (C-1), 22.7 (C-2), 36.8 (C-3), 148.9 (C-4), 46.2 (C-5), 27.5 (C-6), 40.6 (C-7), 76.8 (C-8), 42.2 (C-9), 34.3 (C-10), 142.3 (C-11), 170.6 (C-12), 120.0 (C-

13), 17.7 (C-14), 106.6 (C-15), 以上数据与文献^[16]报道一致,故鉴定化合物 **5** 为异土木香内酯。

化合物 6 白色结晶 ($CHCl_3$); $[\alpha]_D^{25.7} - 18.57$ (c 0.42, $CHCl_3$); HR-ESI-MS: m/z 235.1702 $[M + H]^+$ (calcd for $C_{15}H_{23}O_2$, 235.1692); UV (MeOH) λ_{max} ($\log \epsilon$) 205 (1.23) nm; 1H NMR (500 MHz, $CDCl_3$) δ : 5.17 (1H, d, $J = 3.0$ Hz, H-6), 4.74 (1H, m, H-8), 3.03 (1H, m, H-7), 2.48 (1H, m, H-4), 2.88 (1H, m, H-11), 2.12 (1H, d, $J = 15.0$ Hz, H-9a), 1.25 (3H, s, H-14), 1.23 (3H, d, $J = 5.0$ Hz, H-13), 1.13 (3H, d, $J = 10.0$ Hz, H-15); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 16.8 (C-1), 33.1 (C-2), 42.3 (C-3), 38.5 (C-4), 150.6 (C-5), 115.5 (C-6), 40.4 (C-7), 76.7 (C-8), 42.9 (C-9), 32.9 (C-10), 38.8 (C-11), 179.2 (C-12), 10.7 (C-13), 28.7 (C-14), 23.0 (C-15)。以上数据与文献^[17]报道一致,故鉴定化合物 **6** 为 11,13-二氢土木香内酯。

化合物 7 白色无定型粉末; $[\alpha]_D^{25.7} + 74.2$ (c 1.0, $CHCl_3$); m/z 233.1545 $[M + H]^+$ (calcd for $C_{15}H_{21}O_2$, 233.1536); UV (MeOH) λ_{max} ($\log \epsilon$) 206 (0.80) nm; 1H NMR (500 MHz, $CDCl_3$) δ : 6.24 (1H, br s, H-13a), 5.62 (1H, br s, H-13b), 4.50 (1H, t, $J = 5.0$ Hz, H-8a), 3.06 (1H, m, H-7a), 1.74 (2H, d, $J = 10.0$ Hz, H-9), 1.66 (3H, s, H-15), 1.08 (3H, s, H-14); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 37.0 (C-1), 18.7 (C-2), 31.9 (C-3), 127.2 (C-4), 131.3 (C-5), 27.6 (C-6), 41.0 (C-7), 76.5 (C-8), 42.5 (C-9), 33.5 (C-10), 140.3 (C-11), 170.9 (C-12), 121.4 (C-13), 19.2 (C-14), 26.8 (C-15)。以上数据与文献^[18]报道一致,故鉴定化合物 **7** 为 alloanantolactone。

化合物 8 白色结晶 ($CHCl_3$); $[\alpha]_D^{25.9} + 148.77$ (c 1.3, $CHCl_3$); HR-ESI-MS: m/z 271.1303 $[M + Na]^+$ (calcd for $C_{15}H_{20}O_3Na$, 271.1304); UV (MeOH) λ_{max} ($\log \epsilon$) 209 (1.46) nm; 1H NMR (500 MHz, $CDCl_3$) δ : 6.36 (1H, d, $J = 3.0$ Hz, H-13a), 5.61 (1H, d, $J = 2.5$ Hz, H-13b), 4.44 (1H, d, $J = 10.5$ Hz, H-8), 2.89 (1H, m, $J = 12.0$ Hz, H-7), 2.75 (1H, d, $J = 10.5$ Hz, H-9b), 2.53 (1H, d, $J = 8.0$ Hz, H-5), 2.12 (1H, d, $J = 6.5$ Hz, H-6a), 2.09 (1H, d, $J = 4.5$ Hz, H-9a), 1.73 (3H, s, H-14), 1.63 (1H, m, H-6), 1.30 (1H, s, H-15); ^{13}C NMR

(125 MHz, CDCl_3) δ : 126.9 (C-1), 22.5 (C-2), 36.4 (C-3), 59.8 (C-4), 61.7 (C-5), 34.6 (C-6), 40.9 (C-7), 80.3 (C-8), 45.6 (C-9), 131.2 (C-10), 138.7 (C-11), 169.4 (C-12), 123.3 (C-13), 18.5 (C-14), 15.4 (C-15)。以上数据与文献^[19]报道一致,故鉴定化合物 **8** 为 $4\alpha, 5\beta$ -环氧-1(10), 11(13)-吉玛烷-12, 8α -交酯。

化合物 9 白色针状结晶 (CHCl_3); $[\alpha]_{\text{D}}^{26} + 15.2$ (c 0.5, CHCl_3); HR-ESI-MS: m/z 251.164 0 $[M + H]^+$ (calcd for $\text{C}_{15}\text{H}_{23}\text{O}_3$, 251.164 1); UV (MeOH) λ_{max} ($\log \varepsilon$) 206 (0.91) nm; ^1H NMR (500 MHz, CDCl_3) δ : 6.13 (1H, br s, H-13a), 5.59 (1H, brs, H-13b), 4.47 (1H, td, $J = 4.5$ Hz, H-8), 2.97 (1H, m, H-7), 2.07 (1H, dd, $J = 15.5, 1.5$ Hz, H-9), 1.21 (3H, s, H-15), 1.13 (3H, s, H-14); ^{13}C NMR (125 MHz, CDCl_3) δ : 41.9 (C-1), 17.3 (C-2), 41.5 (C-3), 71.2 (C-4), 48.8 (C-5), 24.9 (C-6), 41.1 (C-7), 76.7 (C-8), 44.4 (C-9), 32.5 (C-10), 142.2 (C-11), 170.5 (C-12), 120.1 (C-13), 20.0 (C-14), 30.3 (C-15)。以上数据与文献^[14]报道一致,故鉴定化合物 **9** 为 septuplinolide。

化合物 10 白色油状物; HR-ESI-MS: m/z 249.148 4 $[M + H]^+$ (calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3$, 249.148 5); UV (MeOH) λ_{max} ($\log \varepsilon$) 206 (0.78) nm; ^1H NMR (500 MHz, CDCl_3) δ : 6.11 (1H, d, $J = 3.0$ Hz, H-13a), 5.46 (1H, d, $J = 3.0$ Hz, H-13b), 4.09 (1H, m, H-8), 3.02 (1H, dd, $J = 14.0, 3.0$ Hz, H-6a), 2.60 (1H, dd, $J = 11.5, 4.0$ Hz, H-9b), 2.28 (1H, m, H-7), 1.67 (1H, s, H-15), 1.45 (1H, t, $J = 12.0$ Hz, H-9a), 1.09 (1H, s, H-14); ^{13}C NMR (125 MHz, CDCl_3) δ : 76.8 (C-1), 26.8 (C-2), 31.8 (C-3), 127.9 (C-4), 129.9 (C-5), 20.0 (C-6), 48.9 (C-7), 80.4 (C-8), 41.9 (C-9), 41.7 (C-10), 139.5 (C-11), 170.9 (C-12), 117.3 (C-13), 19.2 (C-14), 19.7 (C-15)。以上数据与文献^[14]报道一致,故鉴定化合物 **10** 为 8-epi-ivangustin。

化合物 11 白色油状物; HR-ESI-MS: m/z 249.148 4 $[M + H]^+$ (calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3$, 249.148 5); UV (MeOH) λ_{max} ($\log \varepsilon$) 211 (1.59) nm; ^1H NMR (500 MHz, CDCl_3) δ : 6.08 (1H, d, $J = 3.0$ Hz, H-13a), 5.39 (1H, d, $J = 3.0$ Hz, H-13b), 5.35 (1H, br s, H-3), 3.99 (1H, t, $J = 11.0$ Hz, H-6), 3.60 (1H, dd, $J = 10.0, 6.6$ Hz, H-1), 2.48 (1H, ddd, $J =$

12.0, 11.0, 3.0 Hz, H-7), 1.73 (3H, s, H-15), 0.88 (3H, s, H-14); ^{13}C NMR (125 MHz, CDCl_3) δ : 76.7 (C-1), 32.8 (C-2), 118.8 (C-3), 135.3 (C-4), 51.2 (C-5), 79.1 (C-6), 50.0 (C-7), 20.6 (C-6), 34.3 (C-9), 40.0 (C-10), 139.3 (C-11), 170.8 (C-12), 117.2 (C-13), 11.1 (C-14), 22.2 (C-15)。以上数据与文献^[14]报道一致,故鉴定化合物 **11** 为 santamarine。

化合物 12 白色粉末状; $[\alpha]_{\text{D}}^{26} + 39.33$ (c 0.3, CHCl_3), HR-ESI-MS: m/z 251.164 1 $[M + H]^+$ (calcd for $\text{C}_{15}\text{H}_{23}\text{O}_3$, 251.164 0); UV (MeOH) λ_{max} ($\log \varepsilon$) 215 (2.25) nm; ^1H NMR (500 MHz, CDCl_3) δ : 6.13 (1H, d, $J = 0.5$ Hz, H-13a), 5.55 (1H, d, $J = 0.5$ Hz, H-13b), 4.56 (1H, t, $J = 5.5$ Hz, H-8), 3.38 (1H, m, H-7), 1.87 (1H, dd, $J = 13.0, 12.5$ Hz, H-6), 1.52 (1H, dt, $J = 13.5, 4.5$ Hz, H-1a), 1.15 (3H, s, H-14), 1.03 (3H, s, H-15); ^{13}C NMR (125 MHz, CDCl_3) δ : 35.3 (C-1), 16.2 (C-2), 28.1 (C-3), 41.0 (C-4), 74.7 (C-5), 36.1 (C-6), 37.9 (C-7), 76.8 (C-8), 39.3 (C-9), 35.5 (C-10), 142.2 (C-11), 170.9 (C-12), 120.1 (C-13), 23.3 (C-14), 16.7 (C-15)。以上数据与文献^[20]报道一致,故鉴定化合物 **12** 为 racemosalactoneA。

化合物 13 白色针状结晶 (CHCl_3); $[\alpha]_{\text{D}}^{26} + 41.92$ (c 0.52, CHCl_3); HR-ESI-MS: m/z 269.114 4 $[M + \text{Na}]^+$ (calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3\text{Na}$, 269.114 8); UV (MeOH) λ_{max} ($\log \varepsilon$) 247 (1.29) nm; ^1H NMR (500 MHz, CDCl_3) δ : 6.38 (1H, d, $J = 3.0$ Hz, H-13a), 5.73 (1H, d, $J = 2.5$ Hz, H-13b), 4.62 (1H, m, H-8), 3.23 (1H, m, H-7), 3.06 (1H, dd, $J = 12.5, 7.5$ Hz, H-6a), 2.24 (1H, t, $J = 12.5$ Hz, H-6b), 2.05 (1H, td, $J = 13.5, 5.0$ Hz, H-1a), 1.95 (1H, dd, $J = 5.0, 4.5$ Hz, H-9a), 1.80 (1H, d, $J = 3.0$ Hz, H-9b), 1.25 (3H, s, H-14), 1.84 (3H, s, H-15); ^{13}C NMR (125 MHz, CDCl_3) δ : 34.7 (C-1), 33.9 (C-2), 197.9 (C-3), 130.1 (C-4), 158.7 (C-5), 29.7 (C-6), 39.6 (C-7), 74.6 (C-8), 42.6 (C-9), 35.3 (C-10), 138.6 (C-11), 169.8 (C-12), 123.1 (C-13), 25.1 (C-14), 11.2 (C-15)。以上数据与文献^[21]一致,故鉴定化合物 **13** 为 3-oxo-eudesma-4(11)-dien-12, 8β -olide。

化合物 14 白色针状结晶 (CHCl_3); $[\alpha]_{\text{D}}^{26} + 131.2$ (c 0.5, CHCl_3); HR-ESI-MS: m/z 249.157 0 $[M + H]^+$ (calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3$, 249.148 5); UV

(MeOH) λ_{\max} (log ϵ) 211 (1.02) nm; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 6.16 (1H, d, $J = 3.0$ Hz, H-13a), 5.60 (1H, d, $J = 2.5$ Hz, H-13b), 4.88 (1H, br s, H-15a), 4.71 (1H, br s, H-15b), 4.57 (1H, td, $J = 5.5, 5.0$ Hz, H-8), 3.36 (1H, m, H-7), 2.55 (1H, m, H-3), 2.18 (1H, m, H-3), 2.04 (1H, dd, $J = 15.5, 5.0$ Hz, H-9), 1.92 (1H, dd, $J = 15.5, 5.0$ Hz, H-9), 1.83 (1H, m, H-1), 1.79 (1H, d, $J = 9.5$ Hz, H-6), 1.77 (1H, s, H-6), 1.18 (1H, m, H-1), 1.61 (2H, m, H-2), 0.97 (3H, s, H-14); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ : 35.4 (C-1), 21.6 (C-2), 31.8 (C-3), 150.1 (C-4), 74.3 (C-5), 33.8 (C-6), 37.6 (C-7), 76.8 (C-8), 35.6 (C-9), 36.5 (C-10), 142.1 (C-11), 170.7 (C-12), 120.3 (C-13), 21.8 (C-14), 109.1 (C-15)。以上数据与文献^[22]报道的一致,故鉴定化合物 **14** 为 telekin。

化合物 15 白色粉末状; $[\alpha]_{\text{D}}^{26} + 26$ (c 1.5, CHCl_3); HR-ESI-MS: m/z 233.153 8 $[\text{M} + \text{H}]^+$ (calcd for $\text{C}_{15}\text{H}_{21}\text{O}_2$, 233.153 6); UV (MeOH) λ_{\max} (log ϵ) 215 (1.31) nm; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 6.34 (1H, d, $J = 3.0$ Hz, H-13a), 5.71 (1H, dd, $J = 17.5, 10.5$ Hz, H-1), 5.56 (1H, d, $J = 3.0$ Hz, H-13b), 4.95 (1H, m, H-2), 4.91 (1H, m, H-3a), 4.88 (1H, dd, $J = 17.0, 10.5$ Hz, H-2), 4.87 (1H, m, H-8), 4.68 (1H, m, H-3b), 3.29 (1H, m, H-7), 2.18 (1H, m, H-6), 2.01 (1H, d, $J = 2.5$ Hz, H-5), 1.98 (1H, m, H-6), 1.94 (1H, m, H-9), 1.72 (1H, br s, H-15), 1.3 (1H, m, H-9), 1.04 (3H, s, H-14); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ : 147.3 (C-1), 111.0 (C-2), 113.0 (C-3), 145.8 (C-4), 46.0 (C-5), 26.5 (C-6), 39.2 (C-7), 75.9 (C-8), 42.8 (C-9), 39.6 (C-10), 137.3 (C-11), 170.5 (C-12), 120.4 (C-13), 16.4 (C-14), 24.8 (C-15)。以上数据与文献^[19]报道一致,故鉴定化合物 **15** 为 igalane。

化合物 16 黄色油状物; $[\alpha]_{\text{D}}^{26} + 124.63$ (c 1.08, CHCl_3); HR-ESI-MS: m/z 249.148 4 $[\text{M} + \text{H}]^+$ (calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3$, 249.148 5); UV (MeOH) λ_{\max} (log ϵ) 280 (1.21) nm; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 6.36 (1H, s, H-6), 4.80 (1H, dd, $J = 13.5, 5.5$ Hz, H-8), 4.44 (2H, m, H-13), 1.27 (3H, t, $J = 4.0$ Hz, H-14), 2.78 (1H, m, H-4), 2.18 (1H, dd, $J = 13.0, 5.5$ Hz, H-9), 1.27 (3H, m, H-15); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ : 34.1 (C-1), 39.8 (C-2), 18.1 (C-3),

40.7 (C-4), 163.6 (C-5), 112.7 (C-6), 158.9 (C-7), 76.5 (C-8), 43.3 (C-9), 38.7 (C-10), 118.3 (C-11), 174.8 (C-12), 55.5 (C-13), 29.5 (C-14), 20.7 (C-15)。以上数据与文献^[23]报道一致,故鉴定化合物 **16** 为 macrophyllilactone E。

化合物 17 黄色油状物; $[\alpha]_{\text{D}}^{26} + 14.58$ (c 0.48, CHCl_3); HR-ESI-MS: m/z 271.130 0 $[\text{M} + \text{Na}]^+$ (calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Na}$, 271.130 4); UV (MeOH) λ_{\max} (log ϵ) 212 (1.20) nm; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 6.11 (1H, d, $J = 1.0$ Hz, H-13a), 5.55 (1H, d, $J = 0.1$ Hz, H-13b), 4.48 (1H, td, $J = 5.0, 1.5$ Hz, H-8), 2.91 (1H, m, H-7), 2.67 (1H, dd, $J = 4.5, 2.0$ Hz, H-15a), 2.55 (1H, d, $J = 4.5$ Hz, H-15b), 2.21 (1H, dd, $J = 15.5, 1.5$ Hz, H-9), 1.67 (1H, m, H-6), 1.50 (1H, dd, $J = 16.0, 4.5$ Hz, H-9), 0.98 (3H, s, H-14), 0.95 (1H, m, H-6); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ : 41.4 (C-1), 20.3 (C-2), 35.3 (C-3), 58.5 (4), 44.2 (C-5), 23.1 (C-6), 40.4 (C-7), 76.5 (C-8), 41.9 (C-9), 34.3 (C-10), 141.8 (C-11), 170.5 (C-12), 120.5 (C-13), 18.6 (C-14), 50.8 (C-15)。以上数据与文献^[24]报道一致,故鉴定化合物 **17** 为 4 α ,15-epoxy-isoalantolactone。

化合物 18 白色油状物; $[\alpha]_{\text{D}}^{26} - 26.45$ (c 0.62, CHCl_3); HR-ESI-MS: m/z 289.141 1 $[\text{M} + \text{Na}]^+$ (calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4\text{Na}$, 289.141 0); UV (MeOH) λ_{\max} (log ϵ) 206 (0.78) nm; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 5.13 (1H, m, H-8), 3.93 (1H, d, $J = 12.0$ Hz, H-13a), 3.74 (1H, m, H-13b), 2.98 (1H, dd, $J = 5.0, 2.0$ Hz, H-7), 2.15 (1H, dd, $J = 15.0, 3.5$ Hz, H-9a), 1.22 (3H, s, H-15), 1.12 (3H, d, $J = 7.5$ Hz, H-14); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ : 42.1 (C-1), 16.8 (C-2), 38.4 (C-3), 32.8 (C-4), 152.7 (C-5), 112.4 (C-6), 44.7 (C-7), 77.7 (C-8), 42.4 (C-9), 32.9 (C-10), 77.2 (C-11), 177.7 (C-12), 64.0 (C-13), 22.9 (C-14), 28.6 (C-15)。以上数据与文献^[25]一致,故鉴定化合物 **18** 为 11,13-dihydroxy-alantolactone。

化合物 19 白色油状物; $[\alpha]_{\text{D}}^{26} - 17.0$ (c 1.0, CHCl_3); HR-ESI-MS: m/z 231.138 2 $[\text{M} + \text{H}]^+$ (calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2$, 231.138 3); UV (MeOH) λ_{\max} (log ϵ) 206 (0.74) nm; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 6.18 (1H, d, $J = 1.7$ Hz, H-13a), 5.60 (1H, d, $J =$

1.5 Hz, H-13b), 5.0 (1H, m, H-2), 4.86 (1H, m, H-15a), 4.60 (1H, m, H-15b), 4.58 (1H, m, H-8), 3.05 (1H, m, H-7), 2.11 (1H, m, H-1), 2.05 (1H, m, H-5), 1.89 (2H, m, H-9), 1.78 (1H, m, H-6), 1.71 (2H, m, H-3), 1.04 (3H, s, H-14); ^{13}C NMR (125 MHz, CDCl_3) δ : 148.1 (C-1), 111.3 (C-2), 24.4 (C-3), 146.0 (C-4), 48.9 (C-5), 30.2 (C-6), 40.2 (C-7), 76.1 (C-8), 40.1 (C-9), 38.3 (C-10), 141.1 (C-11), 170.5 (C-12), 120.9 (C-13), 19.3 (C-14), 112.9 (C-15)。以上数据与参考文献^[26]一致,故鉴定化合物 **19** 为 1(2), 4(15), 11(3)-eudesma-trien-12, 8 β -olide。

化合物 20 黄色油状物; HR-ESI-MS: m/z 277.217 3 [M-H]⁻ (calcd for $\text{C}_{18}\text{H}_{29}\text{O}_2$, 277.216 2); UV (MeOH) λ_{max} (log ϵ) 209 (1.0) nm; ^1H NMR (500 MHz, CDCl_3) δ : 5.35 ~ 5.29 (6H, m, H-9, 10, 12, 13, 15, 16), 2.81 (2H, s, H-11), 2.80 (2H, m, H-14), 2.36 (2H, t, $J = 7.5$ Hz, H-20), 2.11 ~ 2.05 (2H, m, H-17), 2.11 ~ 2.05 (2H, m, H-8), 1.62 (2H, m, H-3), 1.32 (8H, m, H-4, 5, 6, 7), 0.98 (3H, t, $J = 7.5$ Hz, H-18); ^{13}C NMR (125 MHz, CDCl_3) δ : 179.3 (C-1), 33.9 (C-2), 24.8 (C-3), 29.1 (C-4), 29.1 (C-5), 29.2 (C-6), 29.6 (C-7), 27.0 (C-8), 132.0 (C-9), 130.3 (C-10), 25.7 (C-11), 128.3 (C-12), 128.3 (C-13), 25.6 (C-14), 127.8 (C-15), 127.2 (C-16), 20.6 (C-17), 14.3 (C-18)。以上数据与文献^[27]报道一致,故鉴定化合物 **20** 为亚麻酸。

化合物 21 黄色油状物; HR-ESI-MS: m/z 279.232 6 [M-H]⁻ (calcd for $\text{C}_{18}\text{H}_{31}\text{O}_2$, 279.231 8); UV (MeOH) λ_{max} (log ϵ) 206 (1.27) nm; ^1H NMR (500 MHz, CDCl_3) δ : 5.36 (4H, m, H-9, 10, 12, 13), 2.77 (2H, t, $J = 7.5$ Hz, H-11), 2.35 (2H, t, $J = 7.5$ Hz, H-2), 2.05 (4H, m, H-8, 14), 1.65 (2H, m, H-3), 1.26 ~ 1.34 (14H, m, H-4, 5, 6, 7, H-15, 16, 17), 0.89 (3H, t, $J = 6.5$ Hz, H-18); ^{13}C NMR (125 MHz, CDCl_3) δ : 178.4 (C-1), 33.8 (C-2), 22.7 (C-3), 29.7 ~ 29.0 (C-4, 5, 6, 7, 15), 27.3 (C-8), 130.3 (C-9), 130.0 (C-10), 4.8 (C-11), 128.1 (C-12), 127.9 (C-13), 27.2 (C-14), 31.9 (C-16), 22.7 (C-17), 14.1 (C-18)。以上数据与文献^[28]的报道一致,故鉴定化合物 **21** 为亚油酸。

化合物 22 白色针状结晶 (CHCl_3); HR-ESI-MS: m/z 281.248 3 [M-H]⁻ (calcd for $\text{C}_{18}\text{H}_{33}\text{O}_2$,

281.247 5); UV (MeOH) λ_{max} (log ϵ) 203 (0.33) nm; ^1H NMR (500 MHz, CDCl_3) δ : 5.35 (2H, d, H-9, 10), 2.35 (2H, t, $J = 7.5$ Hz, H-2), 2.01 (4H, m, H-8, 11), 1.60 ~ 1.66 (2H, m, H-3), 1.25 ~ 1.29 (20H, m, H-4 ~ 7, H-12 ~ 17), 0.88 (3H, t, $J = 6.5$ Hz, H-18); ^{13}C NMR (125 MHz, CDCl_3) δ : 179.9 (C-1), 34.2 (C-2), 24.8 (C-3), 29.8 ~ 29.4 (C-4 ~ 7, C-12 ~ 15), 29.2 (C-8, 11), 130.0 (C-9), 129.7 (C-10), 32.1 (C-16), 22.9 (C-17), 14.27 (C-18)。以上数据与文献^[29]报道一致,故鉴定化合物 **22** 为油酸。

3 讨论与结论

本实验对蒙药土木香化学成分进行研究,采用乙酸乙酯有机溶剂提取法、10%硝酸银硅胶柱色谱及薄层色谱法、反相高效液相法进行分离纯化,依据理化性质及波谱技术鉴定了 22 个单体化合物,其中化合物 **3**、**8** 为吉马烷型、化合物 **20** ~ **22** 为脂肪酸,其余化合物均为桉叶烷型。通过采用亲脂性有机溶剂乙酸乙酯对土木香进行提取分离,虽提取率较低,但可针对性地锁定挥发油倍半萜内酯类成分,具有专属性强、纯净度高、易回收浓缩等特点。采用硝酸银硅胶柱色谱法可对土木香内酯和异土木香内酯主成分进行高效快速的分离制备,具有分离效果好、纯度高、产量大、操作简单等优点。硝酸银见光易分解,故实验过程均为避光操作。

蒙药土木香应用广泛、历史悠久,倍半萜内酯是主要特征性成分。通过对蒙药土木香乙酸乙酯层化学成分研究,使我们对蒙药名贵药材土木香有了较为全面的认识,进一步为开发其药用价值和制订相关质量标准提供了科学依据。土木香药源广、价格低廉、副作用少、疗效显著,今后可进一步探究其有效活性成分,深入研究其药理活性,为临床应用提供更精准的参考价值。

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