酸枣仁芽的化学成分分离鉴定

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［摘要］ **目的**：研究酸枣仁芽的化学成分，从物质基础的角度探寻萌发对酸枣仁活性的影响。**方法**：将干燥的酸枣仁芽粉碎后石油醚浸泡提取，除去油脂类成分，残渣干燥后再用甲醇加热回流提取，减压浓缩后得酸枣仁芽甲醇浸膏，将浸膏溶解，采用硅胶，C_{18} 反相硅胶，LH-20 型羟丙基葡聚糖凝胶等多种柱色谱方法进行分离纯化，并利用 NMR 和 MS 等现代波谱技术，结合参考文献确定化合物的化学结构。**结果**：从酸枣仁芽中分离鉴定 13 个化合物，分别为酸枣仁皂苷 B（**1**），酸枣仁皂苷 D（**2**），酸枣仁皂苷 A（**3**），白桦脂酸（**4**），白桦脂醇（**5**），羽扇豆醇（**6**），麦珠子酸（**7**），美洲茶酸（**8**），齐墩果酸（**9**），熊果酸（**10**），木兰花碱（**11**），荷叶碱（**12**），当药黄素（**13**）。**结论**：以上化合物均首次从酸枣仁芽中分离得到。经对比，发现酸枣仁芽的化学成分与传统药用部位种子相似，主要为三萜及皂苷类、黄酮类、生物碱类化合物等，为酸枣仁芽药用资源的开发利用提供了一定的化学依据。

［关键词］ 酸枣仁芽；三萜及皂苷；化学成分
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Chemical Constituents from Sprout of *Ziziphi jujuba* var. *spinosa*

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［**Abstract**］ **Objective**: To investigate the chemical constituents from sprout of *Ziziphi jujuba* var. *spinosa*, and explore the effect of germination on the activity of *Z. jujuba* var. *spinosa* seed from the perspective of material basis. **Method**: The dry sprout of *Z. jujuba* var. *spinosa* was crushed and extracted with petroleum ether to remove oils and fats, then the residues were dried and received reflux extraction with methanol. The solvent was decompressed and recovered to obtain methanol fractions. The fractions were dissolved, isolated and purified by column chromatography technologies such as silica gel, RP C_{18} and Sephadex LH-20, and the structures of the compounds were identified by nuclear magnetic resonance (NMR), mass spectrometry (MS) and reference liteature. **Result**: The 13 compounds were isolated from the sprout of *Z. jujuba* var. *spinosa* and identified as jujuboside B (**1**), jujuboside D (**2**), jujuboside A (**3**), betulinic acid (**4**), betulin (**5**), lupeol (**6**), alphitolic acid (**7**), ceanothic acid (**8**), oleanolic acid (**9**), ursolic acid (**10**), magnoflorine (**11**), nuciferine (**12**) and swertisin (**13**). **Conclusion**: All the above compounds were isolated from the sprout of of *Z. jujuba* var. *spinosa* for the first time. The study showed that the chemical constituents from the sprout were quite similar with those from the seeds of *Z. jujuba* var. *spinosa*, mainly including triterpenoids and saponins, flavonoids, alkaloid, etc. Overall, the results described in this study could provide certain chemical basis for further resources

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exploitation and utilization of the sprout of *Z. jujuba* var. *spinosa*.

[**Key words**] sprout of *Ziziphi jujuba* var. *spinosa*; triterpenoids and saponins; chemical constituents

酸枣仁为枣属植物酸枣的种子,其味甘、酸,性平,归心、肝、胆经,具有养心益肝、宁心安神、敛汗的功效,临床常用于虚烦不眠,惊悸多梦等[1],作为一种药食同源物质被誉为“东方睡果”。研究发现,酸枣仁的化学成分复杂多样,含有三萜及皂苷类、黄酮类、生物碱、脂肪酸等,其中三萜及皂苷的含量相对较高,并具有镇静催眠、抗心律失常、抗惊厥等多种药理活性[2-4]。

萌发是种子特有的生理过程,而萌发过程中种子内部代谢增强,会产生能量和代谢产物,同时也激活内部的生物合成,导致内部化学物质发生变化[5]。项目组对酸枣仁萌发的研究发现,酸枣仁萌发处理可使酸枣仁皂苷 A 和斯皮诺素的含量减少,酸枣仁皂苷 B 的含量升高;萌发后镇静催眠、抗心肌缺血缺氧活性优于萌发前[6]。为进一步探讨酸枣仁萌发前后的物质基础差别,本研究对酸枣仁芽的化学成分进行了系统分离,以期从物质基础层面为酸枣仁芽的应用提供科学依据。结果从酸枣仁芽中分离鉴定了 13 个化合物,分别为酸枣仁皂苷 B(**1**),酸枣仁皂苷 D(**2**),酸枣仁皂苷 A(**3**),白桦脂酸(**4**),白桦脂醇(**5**),羽扇豆醇(**6**),麦珠子酸(**7**),美洲茶酸(**8**),齐墩果酸(**9**),熊果酸(**10**),木兰花碱(**11**),荷叶碱(**12**),当药黄素(**13**)。以上化合物均首次从酸枣仁芽中分离得到,为酸枣仁萌发前后的对比研究,以及酸枣仁芽的药效研究与资源开发奠定了实验依据。

1 材料

AV-400 型超导核磁共振仪(德国 Bruker),VG AUTO Spec-300 型质谱仪(美国应用生物系统公司),Z-1000 型旋转蒸发仪(上海爱郎仪器有限公司),AL104 型电子分析天[平梅特勒-托利多仪器(上海)有限公司],UV 用 ZF70 三用紫外分光仪(上海旦鼎国际贸易有限公司),SB-2000 型电热恒温水浴锅(上海爱郎仪器有限公司),DHG-9240A 型电热鼓风干燥箱(上海一恒科技有限公司)。

RP C_{18}(40 ~ 60 μm,德国 Merk 公司),LH-20 型羟丙基葡聚糖凝胶(Sephadex LH-20, Amersham Biosciences 公司),柱色谱硅胶 G(100 ~ 200,200 ~ 300 目,青岛海洋化工厂),GF_{254} 薄层板(德国 Merck 公司)。显色剂 10% 硫酸甲醇溶液、香草醛-高氯酸甲醇溶液、碘化铋钾试剂等。其他溶剂有甲醇、三氯甲烷、丙酮、石油醚、乙醇、乙酸乙酯均为工业试剂,经重蒸使用。

酸枣仁购于菊花村药材市场,经云南中医学院张洁副教授鉴定为鼠李科植物酸枣 *Ziziphus jujuba* var. *spinosa* 的成熟种子。发芽条件为酸枣仁使用温水(35 ℃)浸泡 24 h 后,置于沙床,25 ℃条件下进行萌发,萌发时间为 8 d。

2 提取与分离

取干燥的酸枣仁芽 15 kg,粉碎后用石油醚冷浸处理 3 次,除去其中的油脂类成分(2.6 kg)。残渣干燥后再用甲醇加热回流提取 3 次,回收甲醇后得到浸膏 1.8 kg。浸膏用甲醇溶解后用脱脂棉过滤,浓缩滤液后用硅胶拌样,用硅胶柱色谱分离(三氯甲烷-甲醇梯度洗脱,100∶0,50∶1,20∶1,10∶1,3∶1,0∶1),经薄层色谱检识,合并得到 6 个馏分(Fr. 1 ~ Fr. 6)。Fr. 3(314 g)经硅胶柱色谱以三氯甲烷-甲醇(50∶1 ~ 20∶1)洗脱,依次经 Sephadex LH-20 柱色谱,RP C_{18}柱色谱得化合物 **9**(34 mg),**10**(12 mg),**11**(7 mg),**12**(11 mg);Fr. 4(263 g)经硅胶柱色谱以三氯甲烷-甲醇(30∶1 ~ 10∶1)洗脱,依次经 Sephadex LH-20 柱色谱,RP C_{18}柱色谱得化合物 **4**(21 mg),**5**(43 mg),**6**(17 mg),**7**(8 mg),**8**(8 mg),**13**(50 mg);Fr. 6(272 g)经硅胶柱色谱以三氯甲烷-甲醇(6∶1 ~ 1∶9)洗脱,以 Sephadex LH-20 柱纯化得化合物 **1**(150 mg),**2**(40 mg),**3**(220 mg)。

3 结构鉴定

化合物 **1** 白色粉末,$C_{52}H_{84}O_{21}$;(+)ESI-MS *m/z* 1 068 $[M+Na]^+$。^{1}H-NMR(400 MHz, CD_3OD) δ: 5.07(1H, br s, H-1″), 5.04(1H, d, J = 8.2 Hz, H-24), 4.62(1H, d, J = 7.2 Hz, H-1‴″), 4.58(1H, m, H-23), 4.52(1H, d, J = 7.6 Hz, H-1‴), 4.34(1H, d, J = 5.5 Hz, H-1′), 1.62(3H, s, H-27), 1.59(3H, s, H-26), 1.58(3H, d, J = 6.6 Hz, H-6″), 1.31(3H, s, H-21), 1.11(3H, s, H-28), 1.07(3H, s, H-18), 1.03(3H, s, H-29), 0.63(3H, s, H-19)。^{13}C-NMR(100 MHz, CD_3OD) δ: 135.3(C-25), 124.9(C-24), 110.1(C-16), 104.2(C-1′), 102.9(C-1‴″), 102.1(C-1‴), 100.4(C-1″), 88.4(C-3), 81.1(C-2‴), 80.4(C-3′), 76.9(C-5‴), 76.7(C-3‴), 76.3(C-3‴″), 74.5(C-2‴″), 74.1(C-2′), 72.5(C-4″), 70.9(C-2″), 70.7(C-3″), 69.9(C-4‴), 69.6

(C-4‴'),68.9(C-5″),68.7(C-20),68.3(C-23),68.1(C-4′),66.1(C-5‴'),65.6(C-30),63.3(C-5′),61.2(C-6‴'),56.1(C-5),53.2(C-17),53.1(C-14),52.8(C-9),45.1(C-22),39.2(C-4),38.8(C-1),38.8(C-15),37.9(C-13),37.1(C-8),36.9(C-10),35.7(C-7),28.2(C-12),27.7(C-21),27.2(C-28),25.8(C-2),24.4(C-26),21.2(C-11),17.8(C-18),17.8(C-6),17.0(C-27),16.6(C-6″),15.8(C-29),15.5(C-19)。以上数据与文献[7]报道对照基本一致,故鉴定化合物**1**为酸枣仁皂苷 B。

化合物**2** 白色粉末,$C_{58}H_{94}O_{26}$;(+)ESI-MS *m/z* 1 230[M+Na]$^+$。^{1}H-NMR(400 MHz,CD_3OD)δ:5.85(1H,s,H-1‴),5.49(1H,m,H-23),5.18(1H,d,*J*=6.8 Hz,H-1⁗),5.17(1H,d,H-24),4.81(1H,d,*J*=7.2 Hz,H-1″),4.79(1H,d,*J*=7.2 Hz,H-1⁗),4.70(1H,d,*J*=4.8 Hz,H-1′),1.67(3H,s,H-27),1.64(3H,s,H-26),1.51(3H,d,H-6″),1.36(3H,s,H-21),1.03(3H,s,H-28),1.00(3H,s,H-18),0.90(3H,s,H-29),0.66(3H,s,H-19)。^{13}C-NMR(100 MHz,CD_3OD)δ:135.3(C-25),124.9(C-24),110.0(C-16),105.1(C-1‴'),104.7(C-1⁗),104.0(C-1′),103.2(C-1‴),101.3(C-1″),88.2(C-3),82.4(C-3′),81.7(C-2‴),79.7(C-3‴'),77.2(C-3⁗),76.6(C-3‴'),76.6(C-5⁗),76.3(C-5‴'),75.5(C-2⁗),73.9(C-2′),73.8(C-2⁗),73.2(C-4″),73.0(C-4⁗),70.8(C-6‴'),70.5(C-3″),70.2(C-4⁗),69.7(C-4‴'),68.5(C-23),68.5(C-20),68.3(C-4′),68.3(C-2″),68.1(C-5⁗),66.6(C-5″),66.1(C-30),63.7(C-5′),61.4(C-6⁗),56.1(C-5),53.2(C-17),53.0(C-14),52.8(C-9),44.0(C-22),39.0(C-4),38.6(C-1),37.1(C-8),36.9(C-13),36.7(C-10),35.8(C-15),35.5(C-7),28.2(C-21),27.8(C-12),27.1(C-28),26.0(C-2),24.4(C-26),21.1(C-11),17.8(C-27),17.0(C-6),17.0(C-18),15.8(C-6″),15.5(C-29),15.4(C-19)。以上数据与文献[8]报道对照基本一致,故鉴定化合物**2**为酸枣仁皂苷 D。

化合物**3** 白色粉末,$C_{58}H_{94}O_{26}$;(+)ESI-MS *m/z* 1 230[M+Na]$^+$。^{1}H-NMR(400 MHz,CD_3OD)δ:5.90(1H,s,H-1‴),5.57(1H,s,H-24),5.34(1H,d,*J*=6.8 Hz,H-1⁗),4.96(1H,d,*J*=7.0 Hz,H-1‴),4.88(1H,d,*J*=7.0 Hz,H-1⁗),4.86(1H,d,*J*=4.4 Hz,H-1′),1.70(3H,s,H-27),1.64(3H,s,H-26),1.51(3H,d,*J*=6.7 Hz,H-6″),1.39(3H,s,H-21),1.15(3H,s,H-28),1.03(3H,s,H-18),0.96(3H,s,H-29),0.70(3H,s,H-19)。^{13}C-NMR(100 MHz,CD_3OD)δ:135.3(C-25),124.9(C-24),110.0(C-16),105.9(C-1‴'),104.6(C-1⁗),103.5(C-1′),102.2(C-1‴),100.4(C-1″),88.4(C-3),81.4(C-3′),81.4(C-2‴),76.8(C-5⁗),76.6(C-3‴'),76.4(C-3‴),76.2(C-3⁗),75.5(C-5‴),75.4(C-2⁗),74.7(C-2⁗),74.4(C-2′),73.7(C-4″),72.5(C-2″),72.5(C-3″),70.8(C-4⁗),70.8(C-4‴),70.3(C-4⁗),69.6(C-6‴),68.8(C-5″),68.3(C-23),68.1(C-20),67.4(C-4′),66.2(C-5⁗),65.4(C-30),62.4(C-5′),61.3(C-6⁗),56.1(C-5),53.2(C-17),53.0(C-14),52.8(C-9),44.0(C-22),39.2(C-4),38.5(C-1),37.1(C-8),36.9(C-13),36.7(C-10),35.8(C-15),35.5(C-7),28.2(C-21),27.8(C-12),27.3(C-28),25.8(C-2),24.4(C-26),21.1(C-11),17.8(C-27),17.7(C-6),17.0(C-18),16.7(C-6″),15.8(C-29),15.5(C-19)。以上数据与文献[8]报道对照基本一致,故鉴定化合物**3**为酸枣仁皂苷 A。

化合物**4** 白色粉末,$C_{30}H_{48}O_3$;(+)ESI-MS *m/z* 479[M+Na]$^+$。^{1}H-NMR(400 MHz,C_5D_5N)δ:4.77(1H,d,*J*=1.8 Hz,H-29),4.56(1H,d,*J*=1.8 Hz,H-29),3.33(1H,m,H-3),1.61(3H,s,H-30),1.05(3H,s,H-27),0.89(3H,s,H-26),0.88(3H,s,H-25),0.83(3H,s,H-24),0.65(3H,s,H-23)。^{13}C-NMR(100 MHz,C_5D_5N)δ:180.1(C-28),151.9(C-20),111.2(C-29),79.4(C-3),57.9(C-17),57.2(C-5),52.3(C-9),51.1(C-19),49.1(C-18),44.1(C-14),42.4(C-8),40.8(C-4),40.6(C-1),39.9(C-13),38.8(C-22),38.8(C-10),36.1(C-7),34.2(C-16),32.5(C-15),31.6(C-21),29.9(C-24),29.6(C-2),27.4(C-12),22.5(C-11),20.8(C-30),20.1(C-6),17.7(C-23),17.6(C-25),17.6(C-26),16.2(C-27)。以上数据与文献[9]报道对照基本一致,故鉴定化合物**4**为白桦脂酸。

化合物**5** 白色粉末,$C_{30}H_{50}O_2$;(+)ESI-MS *m/z* 465[M+Na]$^+$。^{1}H-NMR(400 MHz,C_5D_5N)δ:4.73(1H,s,*J*=1.8 Hz,H-29a),4.54(1H,s,*J*=1.8 Hz,H-29b),3.89(1H,d,*J*=9.8 Hz,H-28a),3.47(1H,d,*J*=9.8 Hz,H-28b),3.26(1H,t,*J*=8.0 Hz,H-3),2.42(1H,m,H-19),1.57(3H,s,H-30),1.00(3H,s,H-27),0.85(3H,s,H-23),0.84(3H,s,H-

25), 0.81 (3H, s, H-26), 0.66 (3H, s, H-24)。^{13}C-NMR (100 MHz, C_5D_5N) δ: 151.1 (C-20), 110.8 (C-29), 79.0 (C-3), 60.4 (C-28), 56.8 (C-5), 51.7 (C-9), 50.1 (C-18), 49.5 (C-17), 49.3 (C-19), 43.9 (C-14), 42.2 (C-8), 40.4 (C-4), 40.2 (C-1), 38.5 (C-13), 38.4 (C-10), 35.8 (C-7), 35.6 (C-22), 31.3 (C-21), 30.9 (C-16), 29.6 (C-23), 29.2 (C-2), 28.5 (C-15), 25.8 (C-12), 22.0 (C-11), 20.2 (C-30), 19.7 (C-6), 17.3 (C-25), 17.1 (C-24), 16.3 (C-26), 15.9 (C-27)。以上数据与文献[9]报道对照基本一致,故鉴定化合物 **5** 为白桦脂醇。

化合物 **6**　白色粉末, $C_{30}H_{50}O$; (+) ESI-MS *m/z* 449 [M + Na]$^+$。^{1}H-NMR (400 MHz, C_5D_5N) δ: 4.69 (1H, s, H-29a), 4.55 (1H, s, H-29b), 4.27 (1H, d, *J* = 5.3 Hz, 3-OH), 3.31 (1H, t, H-3), 2.37 (1H, td, H-19), 1.65 (3H, s, H-30), 0.99 (3H, s, H-27), 0.92 (3H, s, H-26), 0.88 (3H, s, H-23), 0.78 (3H, s, H-28), 0.77 (3H, s, H-25), 0.66 (3H, s, H-24)。^{13}C-NMR (100 MHz, C_5D_5N) δ: 150.7 (C-20), 110.1 (C-29), 77.3 (C-3), 55.4 (C-5), 50.3 (C-9), 48.3 (C-18), 47.9 (C-19), 43.0 (C-17), 42.9 (C-14), 40.9 (C-8), 40.0 (C-22), 38.9 (C-4), 38.7 (C-1), 38.1 (C-13), 37.2 (C-10), 35.6 (C-16), 34.3 (C-7), 29.7 (C-21), 28.6 (C-23), 27.6 (C-2), 27.5 (C-15), 25.2 (C-12), 20.9 (C-11), 19.5 (C-30), 18.4 (C-6), 18.3 (C-28), 16.4 (C-25), 16.3 (C-26), 16.2 (C-24), 14.8 (C-27)。以上数据与文献[10]报道对照基本一致,故鉴定化合物 **6** 为羽扇豆醇。

化合物 **7**　白色粉末, $C_{30}H_{46}O_4$; (+) ESI-MS *m/z* 493 [M + Na]$^+$。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 4.78 (1H, d, *J* = 1.7 Hz, H-29a), 4.57 (1H, d, *J* = 1.7 Hz, H-29b), 3.54 (1H, m, H-2), 3.32 (1H, m, H-3), 1.63 (3H, s, H-30), 1.02 (3H, s, H-27), 0.91 (3H, s, H-26), 0.88 (3H, s, H-25), 0.82 (3H, s, H-24), 0.66 (3H, s, H-23)。^{13}C-NMR (100 MHz, DMSO-d_6) δ: 180.2 (C-28), 152.5 (C-20), 111.8 (C-29), 79.4 (C-3), 66.7 (C-2), 57.2 (C-17), 55.1 (C-5), 52.2 (C-9), 51.0 (C-19), 49.7 (C-18), 43.5 (C-14), 42.9 (C-8), 40.6 (C-4), 40.3 (C-1), 39.6 (C-13), 38.6 (C-22), 38.2 (C-10), 35.9 (C-7), 33.8 (C-16), 31.5 (C-15), 31.2 (C-21), 27.9 (C-24), 27.4 (C-12), 22.1 (C-11), 20.6 (C-30), 20. (C-6), 18.7 (C-23), 17.6 (C-25), 17.4 (C-26), 16.1 (C-27)。以上数据与文献[11]报道对照基本一致,故鉴定化合物 **7** 为麦珠子酸。

化合物 **8**　白色粉末, $C_{30}H_{46}O_5$; (+) ESI-MS *m/z* 509 [M + Na]$^+$。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 10.32 (2H, s, 2 × COOH), 4.85 (1H, d, *J* = 1.8 Hz, H-29a), 4.59 (1H, d, *J* = 1.8 Hz, H-29b), 3.85 (1H, s, H-3), 2.85 (1H, m, H-19), 2.40 (1H, s, H-1), 1.62 (3H, s, H-30), 1.03 (3H, s, H-23), 0.92 (3H, s, H-25), 0.87 (3H, s, H-24), 0.83 (3H, s, H-26), 0.77 (3H, s, H-27)。^{13}C-NMR (100 MHz, DMSO-d_6) δ: 180.1 (C-28), 179.5 (C-2), 151.6 (C-20), 111.7 (C-29), 84.3 (C-3), 65.6 (C-1), 57.2 (C-5), 55.2 (C-17), 52.1 (C-18), 51.2 (C-10), 49.8 (C-19), 43.3 (C-9), 42.7 (C-4), 40.8 (C-8), 39.8 (C-14), 38.9 (C-13), 38.4 (C-22), 36.1 (C-7), 33.9 (C-16), 31.8 (C-23), 31.4 (C-21), 28.4 (C-15), 27.8 (C-12), 22.4 (C-11), 21.1 (C-30), 20.6 (C-24), 19.1 (C-6), 18.1 (C-25), 17.9 (C-26), 16.5 (C-27)。以上数据与文献[12]报道对照基本一致,故鉴定化合物 **8** 为美洲茶酸。

化合物 **9**　白色粉末, $C_{30}H_{48}O_3$; (+) ESI-MS *m/z* 479 [M + Na]$^+$。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 11.94 (1H, s, H-28), 5.09 (1H, t, *J* = 3.6 Hz, H-12), 4.21 (1H, d, 3-OH), 3.23 (1H, dd, *J* = 10.1, 5.0 Hz, H-3), 2.85 (1H, dd, *J* = 10.2, 4.6 Hz, H-18), 1.03 (3H, s, H-27), 0.83 (3H, s, H-30), 0.81 (3H, s, H-29), 0.79 (3H, s, H-26), 0.65 (3H, s, H-25), 0.63 (3H, s, H-23), 0.61 (3H, s, H-24)。^{13}C-NMR (100 MHz, DMSO-d_6) δ: 179.0 (C-28), 143.3 (C-13), 122.0 (C-12), 77.3 (C-3), 55.3 (C-5), 47.6 (C-9), 46.2 (C-17), 45.9 (C-19), 41.8 (C-14), 41.3 (C-18), 39.4 (C-8), 38.9 (C-4), 38.6 (C-1), 37.1 (C-10), 33.8 (C-21), 33.3 (C-29), 32.9 (C-7), 32.6 (C-22), 30.9 (C-20), 28.7 (C-23), 27.7 (C-15), 27.4 (C-2), 26.1 (C-27), 23.9 (C-30), 23.4 (C-16), 23.1 (C-11), 18.5 (C-6), 17.3 (C-26), 16.5 (C-24), 15.6 (C-25)。以上数据与文献[13]报道对照基本一致,故鉴定化合物 **9** 为齐墩果酸。

化合物 **10**　白色粉末, $C_{30}H_{48}O_3$; (+) ESI-MS *m/z* 479 [M + Na]$^+$。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 11.98 (1H, s, H-28), 5.17 (1H, t, *J* = 3.7 Hz, H-12), 4.78 (1H, d, 3-OH), 3.22 (1H, dd, *J* = 10.8, 4.8 Hz, H-3), 2.61 (1H, m, H-18), 1.14 (3H, s, H-27), 1.02 (3H, s, H-23), 0.93 (3H, s, H-30), 0.88 (3H, s, H-25), 0.83 (3H, s, H-29), 0.74 (3H, s, H-24), 0.67

(3H, s, H-26)。^{13}C-NMR (100 MHz, DMSO-d_6) δ:179.7(C-28),146.1(C-13),126.7(C-12),78.2(C-3),55.4(C-5),54.6(C-18),47.9(C-9),46.8(C-17),43.4(C-1),42.8(C-8),41.9(C-19),41.2(C-20),39.7(C-4),39.5(C-10),38.8(C-22),33.2(C-7),32.6(C-21),28.6(C-15),27.9(C-23),27.3(C-2),25.9(C-16),24.5(C-11),24.8(C-27),21.6(C-30),19.5(C-6),18.7(C-26),17.4(C-29),15.9(C-25),15.6(C-24)。以上数据与文献[14]报道对照基本一致,故鉴定化合物 **10** 为熊果酸。

化合物 **11** 白色针状结晶,$C_{20}H_{24}NO_4$;(+)ESI-MS *m/z* 343 [M + H]$^+$。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 6.71 (1H, d, *J* = 8.0 Hz, H-9), 6.48 (1H, d, *J* = 8.0 Hz, H-8), 6.31 (1H, s, H-3), 3.86 (3H, s, 2-OCH_3), 3.68 (3H, s, 1-OCH_3), 3.46 (6H, s, 2 × N-CH_3)。^{13}C-NMR (100 MHz, DMSO-d_6) δ: 155.3 (C-2), 154.8 (C-10), 151.4 (C-1), 150.9 (C-11), 136.4 (C-7a), 134.6 (C-11′), 132.7 (C-1b), 131.2 (C-3a), 130.9 (C-1a), 130.6 (C-9), 129.3 (C-8), 114.8 (C-3), 67.5 (C-6), 58.7 (C-5), 56.3 (2-OCH_3), 56.0 (10-OCH_3), 53.8 (NCH_3), 43.5 (NCH_3), 37.7 (C-7), 34.7 (C-4)。以上数据与文献[15]报道对照基本一致,故鉴定化合物 **11** 为木兰花碱。

化合物 **12** 白色针状晶体,$C_{19}H_{21}NO_2$;(+)ESI-MS *m/z* 296 [M + H]$^+$。^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.71 (1H, d, *J* = 7.8 Hz, H-11), 7.12 (1H, m, H-8), 6.86 (1H, m, H-9), 6.67 (1H, m, H-10), 6.51 (1H, s, H-3), 3.86 (3H, s, 2-OCH_3), 3.56 (3H, s, 1-OCH_3), 3.22 (1H, m, H-6a), 3.16 (1H, m, Ha-4), 3.09 (1H, m, Ha-7), 3.03 (1H, m, Ha-5), 2.68 (1H, m, Hb-4), 2.61 (1H, m, Hb-7), 2.55 (3H, s, N-CH_3), 2.51 (1H, m, Hb-5)。^{13}C-NMR (100 MHz, $CDCl_3$) δ: 156.3 (C-2), 149.0 (C-1), 139.9 (C-7a), 135.7 (C-11a), 132.5 (C-11), 131.8 (C-1b), 131.6 (C-3a), 131.2 (C-9), 131.0 (C-1a), 130.6 (C-8), 130.5 (C-10), 115.3 (C-3), 66.8 (C-6), 63.1 (1-OCH_3), 58.9 (2-OCH_3), 56.4 (C-5), 50.9 (N-CH_3), 38.2 (C-7), 32.1 (C-4)。以上数据与文献[16]报道对照基本一致,故鉴定化合物 **12** 为荷叶碱。

化合物 **13** 黄色粉末,$C_{22}H_{22}O_{10}$;(−)ESI-MS *m/z* 445 [M − H]$^-$。^{1}H-NMR (400 MHz, DMSO-d_6) δ: 12.08 (1H, s, 5-OH), 9.14 (1H, s, 4′-OH), 7.92 (2H, d, *J* = 7.7 Hz, H-2′, 6′), 6.92 (2H, d, *J* = 7.7 Hz, H-3′, 5′), 6.74 (1H, s, H-3), 6.48 (1H, s, H-8), 4.58 (1H, d, *J* = 7.8 Hz, H-1″), 4.06 (1H, d, *J* = 7.8 Hz, H-2″), 3.78 (3H, s, 7-OCH_3), 3.24 (1H, m, H-3″), 3.20 (1H, m, H-5″), 3.15 (1H, m, H-4″), 3.10 (1H, d, *J* = 8.0 Hz, H-6″)。^{13}C-NMR (100 MHz, DMSO-d_6) δ: 197.4 (C-4), 165.9 (C-7), 164.3 (C-2), 162.3 (C-5), 161.6 (C-4′), 158.1 (C-9), 129.3 (C-2′, 6′), 122.4 (C-1′), 116.9 (C-3′, 5′), 110.8 (C-6), 105.1 (C-10), 103.9 (C-3), 93.4 (C-8), 76.5 (C-3″), 77.2 (C-5″), 73.1 (C-1″), 73.8 (C-2″), 70.9 (C-4″), 66.2 (C-6″), 57.2 (7-OCH_3)。以上数据与文献[17]报道对照基本一致,故鉴定化合物 **13** 为当药黄素。

4 讨论

药用种子的萌发炮制是我国人民在几千年医药实践中总结出的宝贵财富,以“麦芽”为代表的萌发较为经典。前期研究发现,酸枣仁萌发处理可使酸枣仁皂苷 A 和斯皮诺素的含量减少,酸枣仁皂苷 B 的含量升高;酸枣仁芽品的镇静催眠、抗心肌缺血缺氧活性及优于萌发前。在分离鉴定的 13 个化合物中,包括 3 个三萜皂苷类,7 个三萜类,2 个生物碱类及 1 个黄酮类化合物。文献研究表明,本文分离得到的部分化合物所具有镇静催眠、抗心肌缺血缺氧活性,如酸枣仁皂苷 A,B,D 均具有抑制组胺释放及小鼠自发活动[18-19],麦珠子酸可与地西泮竞争结合苯二氮卓受体[20]。此外,酸枣仁皂苷 A 还可抑制心肌细胞的 Ica-L 而保护心脏[21]、荷叶碱可上调 ABCA1 表达而降低血脂[22]、当药黄素能降血糖及扩张微血管[23]、木兰花碱抗心律失常[24]等。研究结果显示,酸枣仁芽的化学成分及药理活性与传统药用部位很相似,为酸枣仁芽药用资源的开发利用提供了一定的化学依据。

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