7.64(1H, s, H-4), 7.26(1H, s, H-2), 5.54(1H, t, J= 5.6 Hz, -OH), 5.16(2H, d, J= 8.0 Hz, anomeric-H), 4.60(2H, d, J= 5.2 Hz, -CH$_2$-), 3.19~3.72 (sugar-H). ^{13}CNMR(DMSO-d_6) δ 187.4(C-9), 181.9(C-10), 161.4(C-1), 158.1(C-8), 152.1(C-3), 135.8(C-6), 134.7(C-10a), 132.1(C-4a), 122.3(C-7), 120.6(C-2), 120.5(C-5), 115.9(C-4), 115.4(C-8a, 9a), 100.4(C-1′), 77.2(C-5′), 76.5(C-3′), 73.2(C-2′), 69.5(C-4′), 62.0(-CH$_2$-), 60.6(C-6′). 以上数据与文献对照基本一致[6],鉴定其结构为芦荟大黄素-8-O-β-D-吡喃葡萄糖苷。

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醉鱼草化学成分的研究

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醉鱼草 *Buddleja lindleyana* Fort. 为马钱科醉鱼草属植物,全草药用。醉鱼草属植物全世界约有 100种,分布于美洲、非洲和亚洲的热带至温带地区。我国产 29种,4变种,分布于全国各省区。醉鱼草性温、辛苦,有毒,具祛风杀虫、活血之功效。主治流行性感冒、哮喘、风湿关节痛、蛔虫、钩虫痛、疟腮等。该属植物化学成分的类型较多,并具有抗炎、细胞毒等活性,但对醉鱼草的研究报道较少[1]。本实验从醉鱼草中分离鉴定了 8个化合物,分别是 buddlejasaponinⅡ (Ⅰ), buddlejasaponinⅢ(Ⅱ),齐墩果酸(oleanolic acid,Ⅲ),α-菠甾醇葡萄糖苷(Ⅳ),1-二十六烷醇(1-hexacosanol,Ⅴ),二十九烷(nonacosane,Ⅵ),β-谷甾醇(β-sitosterol),Ⅶ),胡萝卜苷(daucosterol,Ⅷ)。化合物Ⅰ,Ⅱ,Ⅴ是首次从该植物中分得。

1 仪器及材料

熔点用 XT4-100X显微熔点仪测定,温度计未校正;红外光谱用 Nicolet-Impact 400测定,MS用 ZAB-2F质谱仪测定,NMR用 INOVA-500型核磁共振光谱仪测定;硅胶为青岛海洋化工厂产品;显色剂: 5% 硫酸乙醇溶液。醉鱼草采自广西,由广西中医学院生药教研室刘寿养教授鉴定,标本保存于中国医学科学院药物研究所标本室。

2 提取和分离

醉鱼草全草粗粉 2 kg,用 95% 乙醇回流提取,减压浓缩后,混悬于适量水中,依次用石油醚、乙酸乙酯、正丁醇萃取。回收溶剂得石油醚萃取物 34.4 g,乙酸乙酯萃取物 99.44 g,正丁醇萃取物 291.4 g。

乙酸乙酯萃取物经硅胶柱层析,以氯仿-甲醇(100∶5→50∶50)梯度洗脱,共得 A, B, C三个部分。B部分经硅胶柱层析以二氯甲烷-甲醇(30∶1→20∶1)梯度洗脱收集 59个馏分,Fr 1~2析出结晶为化合物Ⅵ(20 mg); Fr 8~16经硅胶柱层析以石油醚-二氯甲烷(2∶1)洗脱得化合物Ⅴ (15 mg); Fr 24~32经硅胶柱层析以石油醚-二氯甲烷(1∶1)洗脱得化合物Ⅶ(23 mg), Fr 47~59经硅胶柱层析以二氯甲烷-甲醇(30∶1→20∶1)梯度洗脱,收集 Fr 10~18部分的白色沉淀,经过 Sephadex LH-20,二氯甲烷为洗脱剂,反复纯化,得化合物Ⅳ(40 mg)。C部分经甲醇重结晶得化合物Ⅷ(22 mg)。

正丁醇萃取物经硅胶柱层析,以二氯甲烷-甲醇(30∶1→1∶1)梯度洗脱。Fr 6~10部分经硅胶柱层析,以二氯甲烷-甲醇(15∶1)洗脱,甲醇重结晶得化合物Ⅲ(20 mg)。Fr 78析出白色结晶,甲醇重结晶得化合物Ⅰ (100 mg), Fr 64~66硅胶柱层析,以二氯甲烷-甲醇-水(65∶35∶10,下层)洗脱,其 Fr 6~11部分再经过 Sephadex LH-20,以甲醇为洗脱

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剂,反复纯化得化合物Ⅱ (85 mg)。

3 结构鉴定

化合物Ⅰ:白色结晶, $[\alpha]_D^{25}$ + 32.2(c, 0.97, MeOH); Libearmann-Burchard和 Molish反应阳性;酸水解检出木糖和葡萄糖, FAB-MS *m/z*: 1 097 (M+ Na), 1 075(M+ H), 911([M+ H]$^+$ - Glc), 763([M+ H]$^+$ - Glc- Xyl), 599([M+ H]$^+$ - Glc- Xyl- Glc), 455([M+ H]- Glc- Xyl- Glc- Fuc); ^{1}HNMR和 ^{13}CNMR数据与文献报道的化合物 buddlejasaponinⅡ一致(碳谱归属见表 1)[2]。故确定该化合物为 buddlejasaponinⅡ (*O*-β-*D*-glucopyranosyl-(1→2)-*O*-[*O*-β-*D*-xylopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→3)]-6-deoxy-(3β, 4α, 16β)-13, 28-epoxy-16, 23-dihydroxyolenan-11-en-3-yl β-*D*-galactopyranoside)。

化合物Ⅱ:白色粉末, $[\alpha]_D^{25}$ + 38.2(c, 0.96, MeOH); Libearmann-Burchard和 Molish反应阳性; FAB-MS *m/z*: 935(M+ Na), 455(M- H- Xyl- Glc- Fuc);酸水解检出木糖和葡萄糖; ^{1}HNMR和 ^{13}CNMR数据与文献报道的化合物 buddle jasaponinⅢ一致(碳谱归属见表 1)[2],故确定该化合物为 buddle jasaponinⅢ (*O*-[*O*-β-*D*-xylopyranosyl-(1→4)-β-*D*-glucopyranosyl-(1→3)]-6-deoxy-(3β, 4α, 16β)-13, 28-epoxy-16, 23-dihydroxy-olenan-11-en-3-yl β-*D*-galactopyranoside)。

化合物Ⅲ:白色针状结晶(MeOH), mp 308 ℃~ 310 ℃, Liebarmann-Burchard反应阳性。 IR ν_{max}^{KBr} cm^{-1}: 3 423(OH), 1 697(C= O), 1 031(C-O);其碳谱数据与文献报道一致[3]。与齐墩果酸对照品共薄层, TLC行为一致。故化合物Ⅲ应为齐墩果酸。

化合物Ⅳ:白色粉末, Liebarmann-Burchard和 Molish反应阳性;其 ^{1}HNMR和 ^{13}CNMR数据与文献报道的化合物 α-菠甾醇葡萄糖苷一致[4],故该化合物确定为 α-菠甾醇葡萄糖苷。

化合物Ⅴ:白色针晶, mp 67 ℃~ 68 ℃, ^{1}HNMR(CDCl$_3$) δ 3.67(2H, t, CH_2-O), 0.89(3H, t, CH_3), 1.24~ 1.60(*n*H, *n*× CH_2); ^{13}CNMR (CDCl$_3$), δ 63.4(C_1), 33.1(C_2), 26.0(C_3), 29.7(C_4), 29.9(C_5-C_{23}), 32.2(C_{24}), 22.9(C_{25}), 14.4(C_{26})。数据与 1-二十六烷醇标准图谱一致[5],故该化合物确定为 1-二十六烷酸。

化合物Ⅵ:白色固体, mp 57 ℃~ 58 ℃, EI-MS *m/z*: 408[M]$^+$, ^{1}HNMR(CDCl$_3$, δ): 0.87(t, 6H, 2× CH_3), 1.28(br, s, *n*× CH_2)。数据与文献报道的二十九烷一致[1],与已知对照品薄层行为一致,故确定该化合物为二十九烷。

表 1 化合物Ⅰ和Ⅱ的 ^{13}CNMR化学位移(C_5D_5N)

Table 1 ^{13}CNMR chemical shift of compound Ⅰ and Ⅱ (in C_5D_5N)

序号	Ⅰ	Ⅱ	序号	Ⅰ	Ⅱ
1	38.7	38.7	16	64.4	64.1
2	25.8	26.1	17	47.0	47.0
3	82.5	81.6	18	52.2	52.2
4	43.9	43.8	19	37.7	37.7
5	47.8	47.4	20	31.6	31.6
6	17.7	17.6	21	34.7	34.7
7	31.6	31.6	22	26.1	25.8
8	42.2	42.2	23	65.1	64.1
9	53.1	53.1	24	12.7	13.1
10	36.2	36.2	25	18.7	18.8
11	132.2	132.2	26	20.1	20.1
12	131.1	131.2	27	20.9	20.9
13	84.0	84.0	28	73.1	73.1
14	45.7	45.7	29	33.7	33.7
15	36.3	36.2	30	23.8	23.8
Fuc			Glc(C_3 of fuc)		
1	104.2	106.0	1	105.1	106.5
2	77.2	71.8	2	75.1	75.5
3	84.9	85.6	3	76.4	76.3
4	72.2	72.2	4	80.7	80.7
5	70.5	71.8	5	76.6	76.8
6	17.7	17.8	6	61.6	61.7
Glc(C_3 of fuc)			Xyl		
1	104.1		1	105.6	105.6
2	76.3		2	75.0	75.0
3	78.8		3	78.4	78.4
4	72.2		4	70.8	70.8
5	77.6		5	67.4	67.4
6	63.2				

化合物Ⅶ:白色针状结晶(丙酮), mp 136 ℃~ 137 ℃, Liebarmann-Burchard反应阳性。 IR ν_{max}^{KBr} cm^{-1}: 3 428(OH), 2 935(C-H), 1 638(C= O), 1 465(CH_2), 1 381(CH_3), 1 054(C-O),与β-谷甾醇 IR标准图谱基本一致[6],并与已知对照品β-谷甾醇薄层行为一致,确定化合物Ⅲ为β-谷甾醇。

化合物Ⅷ:白色粉末(MeOH), mp 298 ℃~ 300 ℃, Liebarman-Burchard和 Molish反应阳性; IR ν_{max}^{KBr} cm^{-1}: 3 408(OH), 2 934(CH), 1 623(C= C), 1 463(CH_2), 1 381(CH_3), 1 024(C-O)以上数据与胡萝卜苷一致。与已知对照品共薄层, Rf值和斑点颜色一致,确定化合物Ⅷ为胡萝卜苷。

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Chemical constituents in volatile oil from plumule of *Nelumbo nucifera*

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莲子心挥发油成分分析

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The plumule of *Nelumbo nucifera* Gaertn., (PNN) has a good function in eliminating the heart-fire, lowering the high blood pressure and tonifying the heart which are related with the alkaloid constituents in PNN[1,2]. Great much investigation has been put on the alkaloid constituents, but little has been reported about the volatile oil from PNN so far. Now the analytic results by means of GC-MS are reported in the followings.

The 95% EtOH extract of PNN was partitioned with chloroform, the oil part in chloroform was esterified with 0.4 mol/L sodium hydroxyl methanol solution just before the GC-MS analysis, the analysis was performed on HP6890/HP5973 GC-MS (HP. USA.) at room temperature.

GC condition: HP-5.5% Prenyl Mennyl Siloxane 30 m× 0.25 mm, 0.25μm quartz capillary column; programmed temperature: 60℃ (3 min)→ 10℃/min→ 280℃ (10 min); inlet temperature: 280℃; carrier gas: Helium (99.999%) with the flux of 1.0 mL/min; sample size: 1μL; the split ratio is 40∶1.

Results The assuring constituents in PNN are listed in Table 1, among which several very important natural products show a high quantity. Vitamin E is well known a kind of antioxidants; sitosterol does well in preventing the atherosclerosis,

Table 1 Chemical constituents of volatile oil from PNN

No.	Compounds	Quality/%
1	9-hexadecenoic acid	91
2	14-methyl-pentadecanoic acid	97
3	hexadecanoic acid	97
4	heptadecanoic acid	98
5	9, 12-octadecadienoic acid	99
6	phytol	91
7	octadecanoic acid	98
8	9, 12-octadecadienoic acid (z, z)	95
9	3, 7, 11-trymethyl-2, 6, 10-dodecatrien-1-ol	91
10	eicosanoic acid	99
11	heneicosanoic acid	99
12	docosanoic acid	99
13	tetracosanoic acid	98
14	squalene	91
15	testosterone	93
16	gamma-tocopherol	98
17	gamma-sitosterol	95

the squalene plays an important role in cancer prevention and it can also ameliorate the blood circulation, and some fatty acid are constituents of cell membrane. Considering all the valuable constituents, PNN is sure to play more important role for people's health in the near future.

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