Chemical Constituents of *Maesa indica*

LAI Guo-Fang, WANG Yi-Fen, CAO Jian-Xin, LUO Shi-De*

State Key Laboratory of Phytochemistry and Plant Resource in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, 650204

【ABSTRACT】 **AIM:** To study the chemical constituents of *Maesa. indica*. **METHOD:** Compounds were separated by column chromatography on silica gel, Sephadex LH-20 and their structures were elucidated based on the spectral analyses including 1D NMR(^{1}HNMR, ^{13}CNMR) and 2D NMR(COSY, HMQC, HMBC). **RESULT:** Two triterpenoids aglycone and other four compounds were isolated from *M. indica* and identified as 22-*O*-(2-methylbutyryl)-28-al-12-en-olean-3β, 16α-diol (**1**), 22-*O*-hexanoyl-28-al-12-en-olean-3β, 16α-diol(**2**), 1, 12-bis(3, 3′-dihydroxy-4, 4′-dimethyl-5, 5′-dimethoxyphenyl) dodecane(**3**)], 3β, 16α, 22α, 28β-tetrahydroxy-13β, 28-epoxy-olean(**4**), (24*R*)-stigmast-7, 22(*E*)-dien-3α-ol(**5**), (24*R*)-stigmast-7, 22 (*E*)-dien-3β-D-glucopyranoside (**6**). **CONCLUSIONS:** Compound **1** was a new compound, and other compounds were obtained from *M. indica* for the first time.

【KEY WORDS】 *Maesa indica*; *Maesa* L.; Olean triterpenoids.

【CLC Number】 R284 【Document code】 A 【Article ID】 1672-3651(2003)02-0076-03

1 Introduction

Maesa indica (Roxb.) A. DC. is distributed in Yunnan province. It has been reported to exert antiviral activity against Rhaniket disease and Vaccinia viruses and was also used against the jaundise hepatitis in Chinese folk medicine[1]. Except that quercitin-3-rhamnoside has been reported from the leaves of *M. indica*, this plant has not systematically been studied. For this reason, chemical studies of this plant were undertaken. This paper mainly discussed the structure elucidation of compound(**1**).

2 Materials and apparatus

2.1 *Plant Material.*

The aerial of *Maesa indica* was collected at Xishuangbanna, Yunnan, P. R. China, in March 2002. The plant identity was established by Dr. Gao Xin-fen, and a voucher(No. 0547746) was deposited in the herbarium of Kunming Institute of Botany, Kunming, P.R. China.

2.2 *Apparatus and Material*

Column chromatography(CC): Qingdao silica gel (200-300 mesh), Sephadex LH-20 and TLC: Qingdao precoated plates, silica GF_{254} plates and mp: XPC-1 apparatus. IR Spectra: Bio-rad FTS spectrometer: in cm^{-1}. NMR Spectra: Bruker AM-400 or DRX-500 spectrometer, C5D5N and $CDCl_3$ solns; δ values(with ref. to the signal in C_5D_5N and $CDCl_3$ with TMS as internal standard; MS: Autospec 3000 spectrometer in *m/z*(rel. %).

2.3 *Extraction and Isolation*

The air-dried aerial parts(5 kg) were extracted thrice with 95% EtOH/H_2O at r.t. The solvent was evaporated at < 50° to give a deep-brown waxy residue, which was suspended in H_2O and partitioned with AcOEt(3 × 1000 ml), and BuOH(3 × 1000 ml) respectively. The AcOEt extract(38 g) was repeatedly chromatographed by silica gel(200 ~ 300 mesh) and Sephadex LH-20 to afford pure compounds **3**(32 mg), **4** (53 mg), **5**(106 mg), **6**(28 mg). The BuOH extract (20 g) was hydrolyzed with 5% HCl for 2 h, then partitioned with AcOEt, finally processed with $NaHCO_3$, NaCl, Na_2SO_4 to obtain the AcOEt extraction. Concentration of AcOEt solution was repeatedly chromatographed by silica gel(200 ~ 300 mesh) and Sephadex LH-20 to afford pure compounds **1** (24 mg), **2**(153 mg).

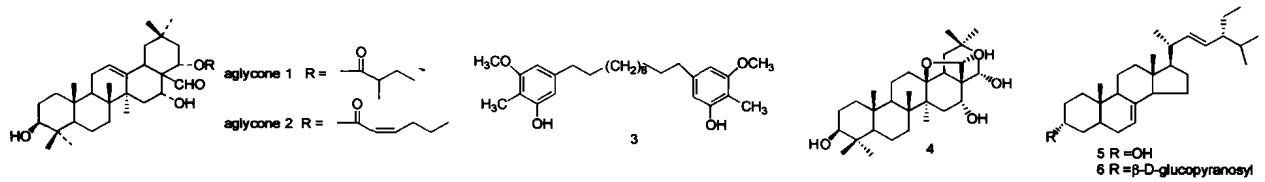
3 Results and Discussion

Compound(**1**), an amorphous powder. It was deduced to have a molecular formula of $C_{35}H_{56}O_5$ by high resolution positive FABMS(found $[M+1]^+$ 557.4190, calcd 557.4206). Its prominent fragment ions occurred

【Received date】 2003-01-12

【* Correponding author】 LUO Shi-De: Prof. Kunming Institute of Botany, Chinese Academy of Sciences, Tel: 0871-5223097 E-mail: shidehuo@hotmail.com

at *m/z* 455 [M-101], corresponding to the independent loss of a 2-methylbutyryloxy group, other fragment ions appeared at *m/z* 190,247, corresponding to the characteristic of the olean-type cleavage. Its IR spectrum showed absorption bands at 3465 br, 1731, 1462 cm^{-1}, which corresponded to hydroxyl groups, carboxyl group and olefinic bonds respectively. Its ^{1}HNMR spectrum exhibited the presence of three angular methyl group signals at δ0.92, 1.01 and 1.49 (each 3H, s), four geminal tertiary methyl group signals at δ 0.81, 1.12, 1.14 and 1.26 (each 3H, s), another methyl group signals at δ 0.99 and1.24 and one olefinic proton signal at δ 5.53(1H, brs). The ^{13}CNMR spectral data of compound **1** showed the presence of aldehyde carbon signal at δ 204.3, one ester carbonyl signal at δ 175.5, two olefinic carbon signals at δ 124.9 and 141.4, and three oxygenated methine signals at δ 78.7, 71.0, 66.9. ^{1}HNMR and ^{13}CNMR spectral data of compound **1** (see Table 1) were very similar to those of compound **2**, which indicated that compound **1** had the similar skeleton with that of compound **2**. However, in comparison of the ^{13}CNMR spectral data of **1** and those of **2**, the substituting group of **1** was one 2-methylbutyryl unit, which was also confirmed by two dimensional NMR techniques. HMQC and HMBC experiments showed the correlation between H-22 of the skeleton and C-1′ of 2 methylbutyryl unit. Based on the above evidence, the structure of compound **1** was established to be 22-*O*-(2-methylbutyryl)-28-al-12-en-olean-3β,16α-diol.



Tab 1 ^{13}CNMR data of compounds 1-2, 4-6

	1	2	4	5	6
1	39.1	39.1	39.6	37.0	37.1
2	28.1	28.1	28.3	26.7	29.7
3	78.7	78.1	78.2	74.1	79.5
4	39.4	39.4	39.6	33.8	34.1
5	55.8	55.8	55.5	40.5	40.7
6	18.7	18.8	18.3	29.4	29.6
7	32.2	31.2	34.5	117.1	117.2
8	42.0	42.1	42.3	139.5	139.2
9	47.1	47.1	50.5	49.0	49.4
10	37.3	37.3	33.1	34.4	34.3
11	23.7	23.8	19.3	21.4	21.5
12	124.9	124.5	33.4	39.5	39.5
13	141.4	142.3	87.5	43.0	43.1
14	40.1	40.2	44.1	55.6	55.8
15	33.2	33.4	36.8	23.1	23.0
16	66.9	67.8	70.1	28.5	28.4
17	56.3	55.2	52.9	55.9	56.6
18	40.5	41.7	47.4	12.1	12.0
19	45.9	46.0	38.7	12.5	12.9
20	31.5	31.8	37.3	40.1	40.2
21	44.0	44.1	46.8	21.0	21.0
22	71.0	70.3	68.1	138.2	138.3
23	28.8	28.8	28.8	129.5	129.4
24	16.5	16.6	16.5	51.3	51.2
25	15.6	15.7	16.6	31.6	31.9
26	17.4	17.5	18.9	19.2	19.0
27	27.3	27.4	19.5	21.3	21.5
28	204.3	204.3	98.6	25.5	25.4
29	33.6	33.2	33.4	13.1	13.0
30	25.1	24.9	26.1		
1	175.5	165.9			99.6
2	41.9	120.2			75.3
3	27.1	152.6			76.4
4	11.9	31.1			70.2
5	16.6	22.5			77.0
6		13.9			62.3

4 Structures Identification

Compound **1** (22-*O*-(2-methylbutyryl)-28-al-12-en-olean-3β,16α-diol) was obtained as white powder(Me_2CO). mp 105 ~ 108℃; EI-MS: *m/z* 556 [M^+]; Molecular formula: $C_{35}H_{56}O_5$, IR(KBr) ν 3465, 2954, 1731, 1654, 1462, 1383, 1260, 1190, 1155, 1105, 1067, 1040, 997 cm^{-1}. ^{1}HNMR(500 MHz, pyridine-d_5)(δ): 0.81(3H, s, C_{24}-H), 0.92(3H, s, C_{26}-H), 0.99(3H, t, *J* = 7.4, $C_{4'}$-H), 1.01(3H, s, C_{25}-H), 1.12(3H, s, C_{30}-H), 1.14(3H, s, C_{29}-H), 1.24(3H, d, *J* = 7.4, $C_{5'}$-H), 1.26(1H, 3H, s, C_{23}-H), 1.49(3H, s, C_{27}-H), 3.46(1H, m, C_3-H), 4.37(1H, brs, C_{16}-H), 6.59(1H, brs, C_{22}-H). ^{13}CNMR(100 MHz, pyridine-d5) spectral data(see Table).

Compound **2** (22-*O*-hexanoyl-28-al-12-en-olean-3α, 16β-diol) was obtained as white powder(Me_2CO). mp 100 ~ 102℃; $[\alpha]_D^{25}$-3.64°($CHCl_3$ 0.55); IR(KBr) ν 3519, 2954, 2869, 1724, 1641, 1464, 1179, 995 cm^{-1}. EI-MS: *m/z* 568[M^+]; Molecular formula: $C_{36}H_{56}O_5$, ^{1}HNMR(500 MHz, pyridine-d_5)(δ): 0.86 (3H, t, *J* = 12.0, $C_{6'}$-H), 0.81, 0.93, 1.03, 1.03, 1.22, 1.69, 1.77(each 3H, s), 3.45(1H, dd, *J* = 10.8, 5.2, C_3-H), 5.01 (1H, brs, C_{22}-H), 5.51(1H, brs, C_{12}-H), 5.66(1H, dd, *J* = 11.96, 5.40, C_{16}-H), 5.85(1H, d, *J* = 11.5, $C_{2'}$-H), 6.15(1H, m, $C_{3'}$-H). ^{13}CNMR(100 MHz, pyridine-d_5) spectral data(see Table 1): The spectral data of compound **2** was in accordance with those of the literature[2].

Compound **3** (1, 12-bis(3, 3′-dihydroxy-4, 4′-dimethyl-5, 5′-dimethoxyphenyl) dodecane was obtained as white solid. mp

76~78℃; EI-MS: *m/z* 442 [M$^+$]; Molecular formula: $C_{28}H_{42}O_4$, IR (KBr) ν 3325, 2926, 2948, 1620, 1595, 1462, 1227, 824, 662 cm^{-1}. ^{1}HNMR (400 MHz, pyridine-d_5) (δ): 2.56 (2-Me), 3.80 (5-OMe), 6.52 (1H, s, C_6-H), 6.84 (1H, s, C_2-H). ^{13}CNMR (100 MHz, pyridine-d_5) (δ): 9.1 (4, 4′-Me × 2), 30.1 (2, 11-CH_2 × 2), 32.1 (3-10, CH_2 × 8), 36.6 (1, 12-CH_2 × 2), 55.6 (5, 5′-OMe × 2), 102.8 (C-6, 6′), 109.2 (C-2, 2′), 110.5 (C-4, 4′), 141.8 (C-1, 1′), 157.5 (C-3, 3′), 159.5 (C-5, 5′). The spectral data of compound **3** was in accordance with those of the literature[3].

Compound **4** (3β, 16α, 22α, 28β-tetrahydroxy-13β, 28-epoxy-olean) was obtained as white powder (MeOH). mp 179~182℃; IR (KBr) ν 3411, 2850, 1078, 1052, 998 cm^{-1}. EI-MS: *m/z* 490; Molecular formula: $C_{30}H_{50}O_5$; ^{1}HNMR (400 MHz, pyridine-d_5) (δ): 0.94, 1.04, 1.14, 1.15, 1.23, 1.40, 1.65 (each 3H), 3.47 (1H, dd, *J* = 10.4, 5.5, C_3-H), 5.06 (1H, dd, *J* = 12.4, 5.5, C_{22}-H), 5.10 (1H, d, *J* = 6.1, C_{16}-H), 5.48 (1H, s, C_{28}-H). ^{13}CNMR (100 MHz, pyridine-d_5) spectral data (see Table): The spectral data of compound **4** was in accordance with those of the literature[4].

Compound **5** ((24R)-stigmast-7, 22 (E)-dien-3α-ol) was obtained as needle crystallis (Me_2CO). mp 161~162℃; IR (KBr) ν 3394, 2985, 2887, 1645, 1449, 1155, 1026, 846 cm^{-1}. EI-MS: *m/z* 412 [M$^+$], Molecular formula: $C_{29}H_{48}O$; ^{1}HNMR (400 MHz, $CDCl_3$) (δ): 0.54 (3H, s, C_{18}-H), 0.78 (3H, d, *J* = 7.1, C_{26}-H), 0.82 (3H, t, *J* = 7.2, C_{29}-H), 0.85 (3H, d, *J* = 6.5, C_{27}-H), 1.03 (3H, d, *J* = 6.5, C_{21}-H), 3.35 (1H, m, C_3-H), 5.18 (1H, m, C_7-7), 5.22 (1H, ddd, *J* = 16.1, 7.0, 7.0, C_{23}-H), 5.31 (1H, dd, *J* = 16.1, 7.0, C_{22}-H). ^{13}CNMR (100 MHz, $CDCl_3$) spectral data (see Table): The spectral data of compound **5** was in accordance with those of the literature[5].

Compound **6** ((24*R*)-stigmast-7, 22 (*E*)-dien-3β-*D*-glucopyranoside) was obtained as white powder (Me_2CO). mp 287~288℃; EI-MS: 574 [M$^+$]; Molecular formula: $C_{35}H_{58}O_6$; IR (KBr) ν 3400, 1639, 1023, 970 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) (δ): 0.54 (3H, s, C_{18}-H), 0.79 (3H, d, *J* = 7.1, C_{26}-H), 0.82 (3H, t, *J* = 7.2, C_{29}-H), 0.85 (3H, d, *J* = 6.5, C_{27}-H), 1.02 (3H, d, *J* = 6.5, C_{21}-H), 3.15 (1H, dd, *J* = 7.9, 8.0, $C_{2'}$-H), 3.27 (1H, dd, *J* = 8.7, 9.1, $C_{4'}$-H), 3.34 (1H, d, *J* = 9.0, $C_{5'}$-H), 3.35 (1H, m, C_3-H), 3.40 (1H, dd, *J* = 8.0, 8.7, $C_{3'}$-H), 3.80 (1H, dd, *J* = 12.1, 5.0, $C_{6'\beta}$-H), 3.81 (1H, dd, *J* = 12.1, 2.3, $C_{6'\alpha}$-H), 4.52 (1H, d, *J* = 7.9, $C_{1'}$-H), 5.16 (1H, m, C_7-7), 5.21 (1H, ddd, *J* = 16.1, 7.0, 7.0, C_{23}-H), 5.31 (1H, dd, *J* = 16.1, 7.0, C_{22}-H). ^{13}CNMR (100 MHz, $CDCl_3$) spectral data (see Table). The spectral data of compound 6 was in accordance with those of the literature[5].

References

[1] Koike K, Kudo M, Jia ZH, *et al*. New triterpenoid saponins from *Maesa japonica* [J]. *J Nat Prod*, 1999, **62**: 228-232.

[2] Monroe EW, Mansukh CW, Kevan G, *et al*. Plant antimutagenic agents, isolation and structure elucidation of maeeol, an inactive constituent of *Maesa Spp* [J]. *J Nat Prod*, 1988, **51**(6): 1226-1231.

[3] Giovanni A, Lorenzo DN, Federico G, *et al*. An Oleanane triterpene from *Anagallis arvensis* [J]. *Phytochemistry*, 1992, **31**(3): 929-933.

[4] Nusrat J, Wasim A, Abdul M. New steroidal glycosides from *Mimusops elengi* [J]. *J Nat Prod*, 1995, **58**(8): 1244-1247.

[5] Sindambiwe JB, Balde AM, Bruyne TD. Triterpenoid saponins from *Maesa lanceolata* [J]. *Phytochemistry*, 1996, **41**(1): 269-277.

包疮叶的化学成分研究

来国防, 王易芬, 曹建新, 罗士德*

中国科学院昆明植物研究所 植物化学与西部植物资源持续利用国家重点实验室, 昆明 650204

【摘 要】 **目的**: 研究包疮叶的化学成分。**方法**: 采用硅胶柱层析法进行分离, 根据光谱数据鉴定结构。**结果**: 从中分得 6 个化合物, 分别为: 22-*O*-(2-methylbutyryl)-28-al-12-en-olean-3β, 16α-diol (**1**), 22-*O*-hexanoyl-28-al-12-en-olean-3β, 16α-diol (**2**), 1, 12-bis (3, 3′-dihydroxy-4, 4′-dimethyl-5, 5′-dimethoxyphenyl) dodecane (**3**)], 3β, 16α, 22α, 28β-tetrahydroxy-13β, 28-epoxy-olean (**4**), (24*R*)-stigmast-7, 22 (*E*)-dien-3α-ol (**5**), (24*R*)-stigmast-7, 22 (*E*)-dien-3β-*D*-glucopyranoside (**6**)。**结论**: 化合物 **1** 为一新的齐墩果烷型甙元, 其它 5 个化合物均为首次从该植物中得到。

【关键词】 包疮叶; 杜茎山属; 齐墩果烷型三萜