

化合物Ⅷ: 无色针晶(石油醚), mp 234℃~ 235℃, Liebermann-Burchard 反应紫红色。 $^1\text{H NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 0.80(3H, s,  $\text{CH}_3$ ), 0.84(6H, s,  $\times \text{CH}_3$ ), 0.85(9H, s,  $\times \text{CH}_3$ ), 0.94(3H, s,  $\text{CH}_3$ ), 1.10(3H, s,  $\text{CH}_3$ ) 为 8 个甲基。 $^{13}\text{C NMR}$  中有 32 个碳峰, 30~42 范围内有 6 个季碳, 提示该化合物为齐墩果烷五环三萜化合物。IR 提示含有酯羰基 (1 738),  $^1\text{H NMR}$  2.03 处有一酰甲基, 碳谱中 171(s), 21.3(q) 峰的存在, 说明化合物中含有  $\text{CH}_3\text{COO}$ -基团, IR 谱 1 656  $\text{cm}^{-1}$  信号示有一双键,  $^1\text{H NMR}$  5.16(1H, t) 示为环内双键(因  $\delta > 5$ )。  $^{13}\text{C NMR}$  145(s), 121(d) 信号的存在, 提示该化合物为  $\Delta^{12}$  齐墩果烯类衍生物。根据以上分析为  $\beta$ -香树脂醇乙酸酯。且 EI-MS 与文献值<sup>[4]</sup>完全一致, 故可确定为  $\beta$ -香树脂醇乙酸酯。

化合物Ⅸ: 白色针羽晶, mp 210℃~ 211℃, Liebermann-Burchard 反应紫红色。IR(KBr)  $\text{cm}^{-1}$ : 1 735( $-\text{COOR}$ ), 1 240, 1 638( $\text{C}=\text{C}$ )。EI-MS( $m/z$ ): 468 ( $\text{M}^+$ ), 453 ( $\text{M} - \text{CH}_3$ ), 249, 218, 203, 189。  $^1\text{H NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 4.66(1H, br, H-30), 4.54

(1H, br, H-30), 4.45(1H, m, H-3), 2.03(3H, s, Ac), 1.66(3H, s,  $\text{CH}_3$ -29), 1.00(3H, s,  $\text{CH}_3$ ), 0.91(3H, s,  $\text{CH}_3$ ), 0.83(3H, s,  $\text{CH}_3$ ), 0.82(3H, s,  $\text{CH}_3$ ), 0.81(3H, s,  $\text{CH}_3$ ), 0.76(3H, s,  $\text{CH}_3$ )。  $^{13}\text{C NMR}$  与羽扇豆醇乙酯的文献值<sup>[9]</sup>完全一致, 故可确定为羽扇豆醇乙酯。

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## Minor Phenolic Constituents of Chinaberry-tree (*Melia azedarach*)

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**Abstract** Five minor ferulic acid esters (I ~ V) were identified in a petrol extract of *Melia azedarach* stem bark, one (I) of which was isolated with no impurity for the first time. By chemical and spectral methods, their structures were elucidated as hexacosylferulate (I); tetracosylferulate (II); pentacosylferulate (III); heptacosylferulate (IV) and octacosylferulate (V), respectively.

**Key words** *Melia azedarach* L. hexacosylferulate tetracosylferulate pentacosylferulate heptacosylferulate octacosylferulate

**摘要** 从苦楝茎皮中提取分离并鉴定了 5 个微量酚性化合物。它们的结构分别为阿魏酸二十六醇酯(I)、阿魏酸二十四醇酯(II)、阿魏酸二十五醇酯(III)、阿魏酸二十七醇酯(IV)、阿魏酸二十八醇酯(V)。均为从苦楝中首次分离得到。

**关键词** 苦楝 阿魏酸二十六醇酯(I) 阿魏酸二十四醇酯(II) 阿魏酸二十五醇酯(III) 阿魏酸二十七醇酯(IV) 阿魏酸二十八醇酯(V)

#### Introduction

*Melia azedarach* L. (*Meliaceae*) is widely distributed in Asia, Africa and other tropical

regions of the world. Different parts of the tree have long been used as a traditional folk medicine for the treatment of a variety of human ailments

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such as rheumatism, leprosy, scrofula, itch and eruptive skin disease<sup>[1]</sup>. Among others, antiviral, antihelminthic, emmenagogic and antitumor activities have also been reported<sup>[2]</sup>. In order to exploit its potential use as an antineoplastic agent, systematic chemical and pharmacological actions of the stem bark of *M. azedarach* L. have been studied by our group. Extensive investigation on a petrol extract of the stem bark has resulted in the isolation of hexacosylferulate (I) with no impurity for the first time and the determination of four other minor (II ~ V) long chain fatty alcohol esters of ferulic acid. The chemical structures of (I ~ V) were shown in Fig 1.

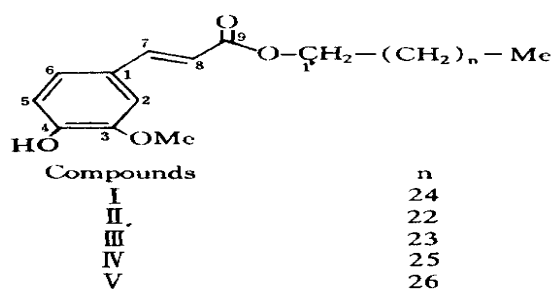


Fig. 1 The chemical structures of compounds I ~ V

# Results and Discussion

The petrol-soluble fraction of the stem bark of *M. azedarach* L. was separated by repeated open column chromatography and recrystallization (see experimental) to give a minor ferulic acid ester, hexacosylferulate (I), which was isolated in a pure state for the first time, and a mixt of four other minor ferulic acid esters (II ~ V).

Hexacosylferulate (I) was crystallized from petrol-EtOAc (8.5 : 1.5) as needles. Its molecular formula was determined as C<sub>36</sub>H<sub>62</sub>O<sub>4</sub> by HRF-AB-MS, and its IR spectrum, in addition to its positive results with FeCl<sub>3</sub> reagents and negative results with Emerson reagents, indicated that it was a ferulic acid ester<sup>[3]</sup>. This conclusion was confirmed by the observation of NOE 5.8% for signal δ7.04 when signal δ3.93 was irradiated. The <sup>1</sup>H NMR spectral data were similar to those of hexacosylacetoxylferulate except an acetoxyl peak at δ2.30 was missing and an additional peak appeared at δ5.87 (disappeared when D<sub>2</sub>O was added) as broad singlet for hydroxy group<sup>[4]</sup>. These results

are consistent with formula I as shown. Hexacosylferulate was isolated in the pure state for the first time. Assignments of the <sup>1</sup>H and <sup>13</sup>C NMR signals were shown in Table 1.

The mix esters II ~ V was composed of homologues of hexacosylferulate deducing from its similar spectral data (IR; <sup>1</sup>H, <sup>13</sup>C NMR) to those of compound I. FAB-MS indicated the presence of tetracosylferulate (II), pentacosylferulate (III), heptacosylferulate (IV) and octacosylferulate (V). HRFAB-MS confirmed their molecular formula as C<sub>34</sub>H<sub>58</sub>O<sub>4</sub>, C<sub>35</sub>H<sub>60</sub>O<sub>4</sub>, C<sub>37</sub>H<sub>64</sub>O<sub>4</sub> and C<sub>38</sub>H<sub>66</sub>O<sub>4</sub> respectively (see Table 2). Reversed phase chromatogram of the mixt revealed the existence of four homologues (see experimental). The mixt of compounds II ~ IV had been identified in *Spiranthes sinensis* (Pers.) Ames var. *amoean* (M. Bieberson) Hara<sup>[5]</sup>. Octacosylferulate (V) had also been isolated from *Tecomella undulata* (G. Don) Seem and *Gmelina arborea* Roxb<sup>[6,7]</sup>.

Table 1. <sup>1</sup>H and <sup>13</sup>C NMR Data of Compounds I ~ V (CDCl<sub>3</sub>)

position	<sup>13</sup> C δ	DEPT	<sup>1</sup> H δ	J <sub>H-H</sub> (Hz)
1	127.0	C	-	-
2	109.2	CH	7.04(d)	1.5
3	147.9	C	-	-
4	146.7	C	-	-
5	114.7	CH	6.92(d)	8.0
6	123.0	CH	7.07(dd)	1.5; 8.0
7	144.6	CH	7.61(d)	16.0
8	115.7	CH	6.30(d)	16.0
9	167.4	C=O	-	-
MeO	55.9	CH <sub>3</sub>	3.93(s)	-
HO	-	-	5.87(br. s)	-
1'	64.6	CH <sub>2</sub>	4.19(t)	6.7; 6.7
2	31.9	CH <sub>2</sub>	1.69(m)	-
3	26.0	CH <sub>2</sub>	1.64(m)	-
4 to (n-3)	28.8~129.7	CH <sub>2</sub>	1.25(m)	-
(n-2)	31.9	CH <sub>2</sub>	1.25(m)	-
(n-1)	22.7	CH <sub>2</sub>	1.25(m)	-
Me	14.1	CH <sub>3</sub>	0.88(t)	6.6; 6.6

It was reported that pharmaceuticals containing alkyl ferulates had been used for the treatment of alcoholism<sup>[8,9]</sup>. Ferulic acid and a few ferulic acid esters had been reported to possess allelopathic effects<sup>[10,11]</sup>. The isolation and determination of minor ferulic acid esters with long chain fatty alcohols occurring in lipid-soluble extract of *M. azedarach* L. is of interest, although

the biological significance is not yet clear and remains to be studied further.

Experimental

General Mps uncorr.; IR KBr; NMR <sup>1</sup>H, at 300 M Hz, <sup>13</sup>C(DEPT) at 75 M Hz, CDCl<sub>3</sub>; FAB-MS and HRFAB-MS negative ion mode; HPLC Varian HPLC system, ODS column, mobile phase MeOH-H<sub>2</sub>O-isopropyl alcohol-HOAc (78: 20: 1.5: 0.5), UV: λ 254 nm, flow rate: 1.0 mL/min.

Plant material *M.azedarach* L. was collected from Jishui county, Jiangxi province, China in Aug., 1995. The species was authenticated by Dr. J. Z. Deng, China Pharmaceutical University, where a vouched specimen has been deposited.

Extraction and separation The air-dried powdered stem bark (20 kg) was continuously extracted with refluxing 95% EtOH and the extracts concd. *in vacuo*. The residue was suspended in H<sub>2</sub>O and the mixt. was successively extracted with petrol, EtOAc and *n*-BuOH. The combined petrol layers were concd. to dryness to give a petrol fr. (200 g), which was subjected to CC (silica gel), eluting with petrol-EtOAc mixts of increasing polarity. Frs. were monitored by TLC. Fr. 83 (15 mg) (petrol-EtOAc 92: 8) showed positive results with FeCl<sub>3</sub> reagents. After repeated silica gel CC and recrystallization several times in petrol-EtOAc (8.5: 1.5), compound I (5 mg) as needles and the mixt (II ~ V) as white powder (4 mg) were isolated from fr. 83.

Hexacosylferulate I Needles; positive results with FeCl<sub>3</sub> reagents, negative results with Emerson reagents; mp 69°C ~ 70.5°C; HRFAB-MS (neg.) *m/z* 557.459 0 (calcd 557.457 0 for C<sub>36</sub>H<sub>61</sub>O<sub>4</sub>); FAB-MS (neg.) *m/z* 557 ([M-1]<sup>-</sup>, 100), 193 ([M-hexacosanyl]<sup>-</sup>, 31), 175 (21), 161 (20), 148 (23), 133 (27); IR<sub>max</sub><sup>KBr</sup> cm<sup>-1</sup>: 3 410, 2 910, 2 850, 1 710, 1 650, 1 600, 1 520, 1 470, 1 270, 1 175 and 980; <sup>1</sup>HNMR (CDCl<sub>3</sub>): 0.88 (3 H, t, J= 6.6 Hz, terminal methyl), 1.25 (44H, br. s, -(CH<sub>2</sub>)<sub>22</sub>-), 1.64 (2H, m, 3'-H), 1.69 (2 H, m, 2'-H), 3.93 (3H, s, 3-OMe), 4.19 (2H,

t, J= 6.7 Hz, 6.7 Hz, 1'-H), 5.87 (1H, br. s, disappeared when D<sub>2</sub>O was added, 4-OH), 6.30 (1H, d, J= 16.0 Hz, 8-H), 6.92 (1H, d, J= 8.0 Hz, 5-H), 7.04 (1H, d, J= 1.5 Hz, 2-H), 7.07 (1H, dd, J= 1.5 Hz, 8.0 Hz, 6-H), 7.61 (1H, d, J= 16.0 Hz, 7-H); <sup>13</sup>CNMR (CDCl<sub>3</sub>): 14.1 (terminal methyl), 22.7 (C-n-1), 26.0 (C-3'), 28.8~ 29.7 (C-4'-n-3), 31.9 (C-n-2), 31.9 (C-2'), 55.9 (aromatic-OMe), 64.6 (C-1'), 109.2 (C-2), 114.7 (C-5), 115.7 (C-8), 123.0 (C-6), 127.0 (C-1), 144.6 (C-7), 146.7 (C-4), 147.9 (C-3), 167.4 (C-9).

Compounds II ~ V The mixt was obtained as white powder; positive results with FeCl<sub>3</sub> reagents, negative results with Emerson reagents; IR spectrum similar to that of hexacosylferulate; the mixt was dissolved in isopropyl alcohol and further analyzed by HPLC to confirm the existence of compounds II ~ V, whose retention time was 8 minutes 12 seconds, 8 minutes 48 seconds, 9 minutes 18 seconds and 10 minutes 36 seconds, respectively. Their <sup>1</sup>H and <sup>13</sup>CNMR, FAB-MS and HRFAB-MS were shown in Tables 1, 2.

Table 2. FAB-MS and HRFAB-MS data of compounds II ~ V

compound	[M-1] <sup>-</sup> <i>m/z</i>	Elemental composition	Measured mass	Calculated mass	Major fragments ions <i>m/z</i>
I	557	C <sub>36</sub> H <sub>61</sub> O <sub>4</sub>	557.459 0	557.457 0	193, 175, 161, 148, 133
II	529	C <sub>34</sub> H <sub>57</sub> O <sub>4</sub>	529.427 8	557.425 7	
III	543	C <sub>35</sub> H <sub>59</sub> O <sub>4</sub>	543.443 5	543.441 3	
IV	571	C <sub>37</sub> H <sub>63</sub> O <sub>4</sub>	571.474 6	571.472 6	
V	585	C <sub>38</sub> H <sub>65</sub> O <sub>4</sub>	585.490 3	585.488 3	

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## 国产沉香中的三萜成分<sup>△</sup>

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**摘要** 从国产沉香 *Aquilaria sinensis* 中分得 14 个化合物, 其中羟基何帕酮为首次从该属植物中分到的三萜化合物, 在沉香的化学成分研究中, 尚未见该类化合物的报道。

**关键词** 国产沉香 化学成分 羟基何帕酮

### Triterpenoid from Chinese Eaglewood (*Aquilaria sinensis*)

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**Abstract** From *Aquilaria sinensis* (Lour.) Gilg 14 compounds were isolated and identified. Among them, a triterpenoid 3-oxo-22-hydroxyhopane, was obtained from this plant for the first time. The presence of triterpenoids has not been reported previously as a chemical constituent of this genus.

**Key words** *Aquilaria sinensis* (Lour.) Gilg chemical constituent 3-oxo-22-hydroxyhopane

国产沉香 (又称土沉香) 为瑞香料植物白木香 *Aquilaria sinensis* (Lour.) Gilg 含有黑色树脂的木质部, 是由于树干损后被真菌侵入后产生。白木香是我国珍贵的药用植物, 近年来由于采集沉香供药用, 损伤木材极为严重, 分布较为集中的林木已被破坏殆尽, 现仅有零星散生残存植株。主要分布在广东的高要、陆河、清远等地及海南文昌、琼海等地区<sup>[1]</sup>。在对沉香的形成及代谢的研究过程中, 我们对沉香的化学成分进行了研究。从国产沉香中分离得到 14 个化合物, 分别为: 苄基丙酮 (benzyl acetone), 对甲氧基苄基丙酮 (*p*-methoxybenzyl acetone), 沉香螺旋醇 (agarospirol),  $\beta$  沉香呋喃 ( $\beta$ -agarofuran), 二氢卡拉酮 (dihydrokarnone), 白木香醇 (baimuxinol), 去氢白木香醇 (dehydrobaimuxinol), 白木香醛 (baimuxinal), kusunol, 羟基何帕酮 (3-oxo-22-hydroxyhopane), 6-甲氧基-2-(2-苯乙基) 色酮, 6, 7-二甲氧基-2-(2-苯乙基) 色酮, 6-甲氧基-2-[2-(4-甲氧基苯) 乙基] 色酮, 6, 7-二甲氧基-2-[2-(4-甲氧基苯) 乙基] 色酮。其中羟基何帕酮为首次从该属植物中分到的三萜化合物, 在以前的化学成分报道中<sup>[2~4]</sup>, 尚未见该类型化合物的报道。羟基何帕酮的化学结构式见图 1。

#### 1 材料和仪器

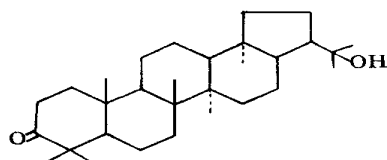


图 1 羟基何帕酮的化学结构式

国产沉香购自广东省药材公司。熔点用 MP-S2 显微熔点仪, 温度未经校正。红外光谱用 FTS-185 型仪。核磁共振谱用 DRX-400 型核磁共振谱仪。TMS 内标。EI-MS 用 QP-5000 型质谱仪。层析用硅胶为青岛海洋化工厂生产。

#### 2 提取与分离

国产沉香 5 kg 打粉, 用 95% 乙醇提取, 提取液浓缩后, 用 5%  $\text{Na}_2\text{CO}_3$  溶液皂化, 再用乙醚提取, 乙醚提取液浓缩后得中性部分浸膏。经反复硅胶层析分离, 以石油醚-乙酸乙酯梯度洗脱和制备 TLC 分离得 14 个化合物。

#### 3 结构鉴定

羟基何帕酮的结构:  $\text{C}_{30}\text{H}_{50}\text{O}_2$ , 无色针状晶体, mp  $253^\circ\text{C} \sim 255^\circ\text{C}$ , MS  $m/z$  442 ( $\text{M}^+$ ), 424, 409, 384, 381, 369, 313, 245, 207, 205, 189, 149 IR (KBr)  $\text{cm}^{-1}$ : 3 520, 2 920, 1 700, 1 440, 1 375  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.77 (s, 3H), 0.96 (s,

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