SO-$d_6$): 174.5(C-1, 7), 33.6(C-2, 6), 28.4, (C-4), 28.4(C-3, 5), 24.5(C-8, 9). EI-MS m(rel.int): 171 (M- 17, 25), 152(40), 137(10), 124(20), 111(45), 98(20), 83(54), 73(24), 69(46), 60(56), 55(100). 综合上述数据推定此化合物结构为 4, 4′-二甲基-1, 7庚二酸。该化合物虽有文献[4]提及,但无光谱数据报道。

化合物II: 白色结晶, mp> 300℃ (氧化),易溶于水。EI-MS m/z (rel.int.): 181($M^+$ + H, 5), 144 (5), 102(10), 73(100), 60(25); $^1$HNMR(DMSO-$d_6$): 4.63(1H, s, HO), 2.96(1H, s, H); $^{13}$CNMR (DMSO-$d_6$) δ: 74.2。以上数据与文献[2,3]报道一致,可确定此化合物结构为肌醇。

化合物III: 白色针晶, mp 152℃~ 154℃,溶于氯仿,磷钼酸呈紫红色斑点。与豆甾醇对照品混合熔点不下降,薄层层析 Rf值, IR, EI-MS与豆甾醇一致。确定III为豆甾醇。

化合物IV: 白色粉末, mp 272℃~ 273℃,溶于甲醇, IR $\nu_{max}^{KBr}$ ($cm^{-1}$): 3 420, 1 640, 1 480, 1 390。EI-MS m/z (rel.int.): 412(苷元, 10), 394(20), 382 (9), 275(10), 255(20)。与维太菊苷对照品混合熔点不下降,薄层层析 Rf值, IR均与维太菊苷一致。确定化合物IV为维太菊苷。

化合物V: 白色结晶, PC与 TLC检识与对照品鼠李糖一致。FAB-MS m/z: 165($M^+$ + 1); EI-MS m/z (rel.int): 146($M^+$ - 18, 10), 115(20), 103 (70), 85(20), 73(100), 69(50), 57(90), 43(65)。薄层层析和质谱数据结合证实此化合物为鼠李糖。

化合物VI: 白色结晶 (MeOH),易溶于水,有甜味。与对照品蔗糖纸层析, Rf值相同。薄层酸水解[5]检出葡萄糖和果糖,推断化合物VI为蔗糖。

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参考文献:

[1] 中国科学院植物志编辑委员会. 中国植物志. 第四十三卷,第三分册 [M].北京: 科学出版社, 1997.

[2] 丛浦珠,苏克曼. 分析化学手册. 第九分册. 第二版 [M].北京: 化学工业出版社, 2000.

[3] 于德泉,杨峻山. 分析化学手册. 第七分册. 第二版 [M].北京: 化学工业出版社, 2000.

[4] Lemuel D W, Judith A P. Effect of certain compounds on solubility of cholesterol in coconut oil [J]. Proc Soc Exptl Biol Med, 1964, 115: 497-504.

[5] 赵萍萍,李宝明,何丽一. 苷中结合糖测定方法的研究 [J].药学学报, 1987, 22(1): 70-74.

# Studies on chemical constituents of root of *Polygala tenuifolia* (Yuanzhi) Ⅰ

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**Abstract** **Object** To study the chemical constituents of the root of traditional Chinese medicine "Yuanzhi" (*Polygala tenuifolia* Willd.). **Methods** Seperation and purification were performed on silica gel, Sephadex LH-20 and ODS CC. Their structures were established on the basis of physicochemical and spectral analysis. **Results** Five compounds were isolated and identified as tenuifoliside B (Ⅰ), methyl 3, 4, 5-trimethoxycinnamate (Ⅱ), polygalaxanthone Ⅲ (Ⅲ), 7-*O*-methylmangiferin (Ⅳ) and lancerin (Ⅴ), respectively. **Conclusion** Compounds Ⅱ and Ⅳ were isolated from the plant of *Polygala* L. for the first time and compound Ⅴ was isolated from *P. tenuifolia* for the first time.

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**Key words** *Polygala tenuifolia* Willd; sucrose esters; xanthone glycosides

# 远志的化学成分研究(Ⅰ)

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摘 要:目的 研究中药远志 *Polygala tenuifolia* 根中的化学成分。方法 采用硅胶、Sephadex LH-20及 ODS柱层析进行分离纯化,通过理化性质和光谱分析鉴定结构。结果 从中分离得到了 5个化合物,分别鉴定为 tenuifoliside B(Ⅰ),3,4,5-三甲氧基肉桂酸甲酯(Ⅱ),polygalaxanthoneⅢ(Ⅲ),7-*O*-methylmangiferin(Ⅳ)和 lancerin(Ⅴ)。结论 化合物Ⅱ和Ⅳ为首次从远志属植物中分离得到,化合物Ⅴ为首次从远志植物中分离得到。

关键词:远志;蔗糖酯;吡酮苷

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The root of *Polygala temuifolia* Willd., "Yuanzhi" is a well-known traditional Chinese medicine used as an expectorant, tonic, sedative and dementia preventing agent[1]. It was reviewed that various xanthones, saponins and oligosaccharide esters had existed in this plant[2]. But the precise mechanisms of the therapeutic effects, especially of dementia preventing effect of *P. tenuifolia*, were not completely understood. In order to determine the active components in this plant, a systematic chemical study was made on the root of *P. tenuifolia* from the main production area, Shanxi Province. In previous paper, the structure elucidation of two new xanthone *O*-glycosides[3] was reported. In this paper, another five compounds isolated from the roots of *P. tenuifolia* were continuously reported, they are: tenuifoliside B (Ⅰ), methyl 3, 4, 5-trimethoxycinnamate (Ⅱ), polygalaxanthone (Ⅲ), 7-*O*-methylmangiferin (Ⅳ), and lancerin (Ⅴ). Among them, compounds Ⅱ and Ⅳ were isolated from the plants of *Polygala* for the first time and compound Ⅴ was obtained from *P. tenuifolia* L. for the first time.

## 1 Instruments and materials

Mps uncorr. were carried out using a XT4A melting point apparatus. UV spectra were recorded on a TU-1901 spectrophotometer, whereas IR spectra were obtained on an AVATER-360 spectrophotometer. ESI-MS spectra were performed at a QSTAR spectrometer, while FAB-MS were obtained on a KYKY-ZHP-5# mass spectrometer. $^{1}$HNMR and $^{13}$CNMR spectra were measured on a JEOL JNM-A300 spectrometer, while COSY, HMQC and HMBC spectra were performed on Bruker AM-500. D101 resin (Tianjin Chemical Co.). CC: silica gel (200-300 mesh, Qingdao Marine Chemical Factory).

The root of *P. tenuifolia* was bought from Taiyuan Chinese Medicinal Materials Co., Shanxi Province. The plant was identified by Professor TU Peng-fei, from School of Pharmaceutical Sciences, Peking University Health Sciences Center.

## 2 Extraction and isolation

The air-dried roots of *P. tenuifolia* (11 kg) were ground and refluxed with 95% EtOH for three times. The extract was combined and evaporated *in vacuo* to yield 4.9 kg of residue, a portion (2 kg) of which was suspended in water and extracted successively with petroleum, $CHCl_3$ and *n*-BuOH. Parts of the *n*-BuOH extract were subjected to a macroporous resin D101 colum (11.5 cm×85.5 cm), and eluted with $H_2O$, 20%, 50%, 70%, and 95% EtOH. The 20% EtOH eluate (19.8 g) was chromatographed on a silica gel CC, eluting with $CHCl_3$-MeOH-$H_2O$ from the ratio of 6∶1∶0 to 7∶3∶0.5. Fr. 17-19, were rechromatographed on a reduced pressure silica gel CC, eluted with $CHCl_3$-MeOH-$H_2O$ (80∶20∶5 lower phase) gave Ⅰ (247.2 mg). Fr. 20-39 were performed on a reduced pressure silica gel CC, with $CHCl_3$-MeOH-$H_2O$ (80∶20∶5 lower phase) as eluent to afford 22 fractions. Among them, Fr. 5-11 purified by ODS and Sephadex LH-20 furnish Ⅱ (57.4 mg), Fr. 12-22 were recrystallized with

MeOH to give Ⅳ (56.7 mg), Fr. 40-49 were firstly chromato-graphed on silica gel, then purified with Sephadex LH-20 and ODS to give Ⅴ (13.3 mg). Fr. 60-91 were recrystallized with MeOH to give Ⅲ (17.6 mg).

**3 Structure elucidation**

Compound Ⅰ: Yellow amorphous powder. IR $\nu_{max}^{KBr}$ ($cm^{-1}$) 3 403 (OH), 1 700 (C= O), 1 631 (C= C), 1 607, 1 516, 1 459 (aromatic ring). FAB-MS m/z 667 $[M-H]^-$, 689 $[M+Na-2H]^-$. $^1$HNMR ($CD_3OD$, 300 MHz): δ 7.90 (2H, d, J= 9.0 Hz, H-2, 6″′), 7.70 (1H, d, J= 15.9 Hz, H-7″), 6.92 (2H, s, H-2″, 6″), 6.81 (2H, d, J= 8.7 Hz, H-3″′, 5″′), 6.45 (1H, d, J= 15.9 Hz, H-8″), 5.49 (1H, d, J= 3.9 Hz, H-1′), 5.47 (1H, d, J= 8.4 Hz, H-3), 3.86 (6H, s, H-3″, 5″-OMe), 4.8-3.4 (H of sugars). $^{13}$CNMR ($CD_3OD$, 300 MHz): 168.2 (C-7″′, 9″), 163.6 (C-4″′), 149.4 (C-3″, 5″), 148.0 (C-7″), 139.6 (C-4″), 133.0 (C-2″′, 6″′), 126.6 (C-1″), 122.1 (C-1‴), 116.2 (C-3″′, 5″′), 115.4 (C-8″), 107.0 (C-2″, 6″), 104.9 (C-2), 93.1 (C-1′), 84.1 (C-5), 79.5 (C-3), 74.9 (C-3′), 74.0 (C-4), 73.1 (C-2′), 72.5 (C-5′), 71.6 (C-4′), 65.6 (C-1), 65.1 (C-6′), 63.4 (C-6), 56.9 (3″, 5″-OMe). Comparing with the reported data[4], the structure of compound Ⅰ was identified as β-*D*-(3-*O*-sinapoylfrucotofu-ranosyl-α-*D*-[6-*O*-(*p*-hydroxybenzoyl)]-glucopyranoside, *i.e.* tenuifoliside B.

Compound Ⅱ: White needle (methanol/$H_2O$), mp 92℃-94℃. $^1$HNMR (DMSO-$d_6$, 300 MHz): 7.59 (1H, d, J= 15.9 Hz, H-7), 6.33 (1H, d, J= 15.9 Hz, H-8), 6.73 (2H, s, H-2, 6), 3.86 (6H, s, 3, 5-OMe), 3.85 (3H, s, 4-OMe), 3.78 (3H, s, -COOMe). Comparing the $^1$HNMR data with those of 3, 4, 5-trimethoxy-cinnammic acid[5], an additional methyl signal appeared and the active hydrogen signal of -COOH disappeared. $^{13}$CNMR (DMSO-$d_6$, 300 MHz): 167.4 (C-9), 153.4 (C-3, 5), 144.8 (C-7), 140.2 (C-4), 129.8 (C-1), 117.0 (C-8), 105.2 (C-2, 6), 60.9 (4-OMe), 56.1 (3, 5-OMe), 51.7 (-COOMe). ESI-MS m/z 253 $[M+H]^+$, 221 $[M-OCH_3]^+$. Thus, compound Ⅱ was elucidated to be methyl 3, 4, 5-trimethoxycinnamate.

Compound Ⅲ: Yellow powder, mp 204℃-206℃. UV $\lambda_{max}^{MeOH}$ nm: 363, 316, 258, 241. $^1$HNMR (DMSO-$d_6$, 300 MHz): 13.74 (1H, s, C-1-OH), 7.45 (1H, s, H-8), 6.91 (1H, s, H-5), 6.40 (1H, s, H-4), 4.70 (1H, d, J= 3 Hz, H-1 of Api), 4.58 (1H, d, J= 9.9 Hz, H-1 of Glu), 4.05 (1H, t, H-2 of Glu), 3.89 (3H, s, OMe), 3.85 (1H, d, J= 9.3 Hz, H-5 of Api), 3.74 (1H, br s, H-2 of Api), 3.57 (1H, d, J= 9.3 Hz, H-5 of Api), 3.5-3.2 (overlapped, H-6, 3 of Glu, H-4 of Api), 3.19 (1H, dd, H-4 of Glu), 3.08 (1H, m, H-5 of Glu). $^{13}$CNMR (DMSO-$d_6$, 300 MHz): 180.0 (C-9), 163.9 (C-3), 161.8 (C-1), 156.2 (C-4a), 154.7 (C-6), 151.7 (C-4b), 146.1 (C-7), 111.4 (C-8a), 109.1 (C-1 of Api), 107.7 (C-2), 104.8 (C-8), 102.7 (C-5), 101.3 (C-8b), 93.5 (C-4), 79.9 (C-5 of Glu), 78.9 (C-3 of Glu), 78.8 (C-3 of Api), 75.6 (C-2 of Api), 73.2 (C-1 of Glu), 73.0 (C-4 of Api), 70.7 (C-4 of Glu), 68.5 (C-6 of Glu), 62.9 (C-5 of Api), 55.9 (OMe). FAB-MS m/z 568 $[M]^+$. All of these data were in good agreement with those reported data of 2-*C*-[β-*D*-apifuranosyl-(1→6)-β-*D*-glucopyranosyl]-1, 3, 6-trihydroxy-7-methoxyxanthone[6]. So compound Ⅲ was identified as 2-*C*-[β-*D*-apifuranosyl-(1→6)-β-*D*-glucopyranosyl]-1, 3, 6-trihydroxy-7-methoxyxanthone, *i.e.* polygalaxanthone Ⅲ.

Compound Ⅳ: Yellow powder, mp 249℃-250℃. UV $\lambda_{max}^{MeOH}$ nm: 359, 316, 258, 241. IR $\nu_{max}^{KBr}$ ($cm^{-1}$): 3 431 (OH), 1 648 (chelated C= O), 1 618, 1 588, 1 481 (aromatic ring). $^1$HNMR (DMSO-$d_6$, 300 MHz): 13.74 (1H, s, C-1-OH), 10.89, 10.69 (2H, br s, -OH×2), 7.45 (1H, s, H-8), 6.92 (1H, s, H-5), 6.40 (1H, s, H-2), 4.59 (1H, d, J= 9.9 Hz, H-1 of Glu), 4.07 (1H, br s, H-2 of Glu), 3.89 (3H, s, OMe), 3.68 (1H, dd, H-4 of Glu), 3.5-3.2 (overlapped, H-3, 5, 6 of Glu). $^{13}$CNMR (DMSO-$d_6$, 300 MHz): 179.0 (C-9), 164.0 (C-3), 161.8 (C-1), 156.2 (C-4a), 154.6 (C-6), 151.7 (C-4b), 146.0 (C-7), 111.4 (C-8a), 107.9 (C-2), 104.8 (C-8), 102.8 (C-5), 101.3 (C-8b), 93.4 (C-4), 81.7

(C-5 of Glu), 79.0 (C-3 of Glu), 73.1 (C-1 of Glu), 70.7 (C-4 of Glu), 70.1 (C-2 of Glu), 61.6 (C-6 of Glu), 55.9 (OMe). FAB-MS m/z 453 [M - H]$^+$. Furthermore, comparing the data with the reported values[7], the structure of Ⅳ was characterized as 2-*C*-β-*D*-glucopyranosyl-1, 3, 6-trihydroxy-7-methoxy-xanthone, *i. e.* 7-*O*-methylmangiferin.

Compound Ⅴ: Yellow powder, mp 203 ℃ - 204 ℃. UV $\lambda_{max}^{MeOH}$ nm: 378, 313, 261, 231. IR $\nu_{max}^{KBr}$ (cm$^{-1}$): 3 378 (OH), 1 648 (chelated C=O), 1 613, 1 475(aromatic ring). $^1$HNMR (DMSO-$d_6$, 300 MHz): 13.08 (1H, s, C-1-OH), 10.00 (1H, s, OH), 7.40 (1H, overlapped, H-5), 7.39 (1H, d, J= 2.7 Hz, H-8), 7.30 (1H, dd, J= 2.7, 9 Hz, H-6), 6.26 (1H, s, H-2), 4.02 (1H, m, H-2 of Glu), 3.70 (1H, br d, J= 12 Hz, H-6 of Glu), 3.36 (1H, overlapped, H-6 of Glu), 3.23 (3H, m, H-2, 3, 5 of Glu). $^{13}$CNMR (DMSO-$d_6$, 300 MHz): 179.9 (C-9), 161.8 (C-1), 153.9 (C-7), 148.9 (C-4b), 124.5 (C-6), 120.1 (C-8a), 119.1 (C-5), 107.8 (C-8), 104.4 (C-4), 101.8 (C-8b), 97.9 (C-2), 81.6 (C-5 of Glu), 78.8 (C-3 of Glu), 73.3 (C-1 of Glu), 70.9 (C-4 of Glu), 70.8 (C-2 of Glu), 61.7 (C-6 of Glu). FAB-MS m/z 405 [M - H]$^+$. In HMBC spectra, the signal of δ4.71 (1H, d, J= 9.9 Hz, H-1 of Glu) was correlated with δ 104.4 (C-4), 156.2 (C-4a) and 165.4 (C-3), so compound Ⅴ was determined to be 4-*C*-β-*D*-glucopyranosyl-1, 3-dihydroxy-7-methoxy-xanthone, *i. e.* lancerin[6].

**References:**


[1] ChP [S]. 2000. Part Ⅰ.

[2] Jiang Y, Tu P F. Progress of studying on *Polygala tenuifolia* [J]. Chin Tradit Herb Drugs, 2001, 32(8): 759-761.

[3] Jiang Y, Tu P F. Two new xanthone glycosides from *Polygala tenuifolia* [J]. Chin Chem Lett, 2002, 13(4): 335-336.

[4] Ikeya Y, Sugama K, Okada M, *et al*. Four new phenolic glycosides from *Polygala tenuifolia* [J]. Chem Pharm Bull, 1994, 42(11): 2305-2308.

[5] Ito H, Taniguchi H, Kita T, *et al*. Xanthones and a cinnamic acid derivatives from *Polygala tenuifolia* [J]. Chem Pharm Bull, 1977, 16 1614-1616.

[6] Miyase T, Noguchi H, Chen X M. Sucrose esters and xanthone C-glycosides from the roots of *Polygala sibrica* [J]. J Nat Prod, 1999, 62(7): 993-996.

[7] Fujita M, Inoue T. Studies on the constituents of *Iris florentina* L. Ⅱ. C-glucosides of xanthones and flavanones from the leaves [J]. Chem Pharm Bull, 1982, 30(7): 2342-2348.


# 香椿假种皮的二萜类成分


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摘 要: 目的 研究香椿假种皮二萜类成分。方法 采用低压柱层析、中压柱层析等色谱技术对香椿假种皮的二氯甲烷萃取部分进行分离, 用$^1$HNMR $^{13}$CNMR EI-MS IR鉴定化学结构。结果 得到了 5个二萜化合物, 分别为香椿酯(Ⅰ)、18-氧弥罗松酚(Ⅱ)、18-羟基弥罗松酚(Ⅲ)、花柏酚(Ⅳ)、4-epiagathadial(Ⅴ)。结论 化合物Ⅱ ~ Ⅴ为首次从该植物中分离得到。



关键词: 香椿; 二萜; 红豆杉科

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## Diterpenoids from aril of *Torreya grandis* cv. *merrilli*


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**Abstract** **Object** To study the diterpenoids from the aril of *Torreya grandis* cv. *merrilli*. **Methods**



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