

云南铁杉中的木脂素成分

赵友兴, 罗晓东, 周俊*

(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, 云南昆明 650204)

摘要: 从云南铁杉 (*Tsuga dumosa*) 心材中提取分离得到 8 个木脂素, 采用波谱方法鉴定了它们的结构。其中化合物 1 (4, 8-dihydroxyepipinoresinol) 为新化合物, 2~8 为首次从该种植物中分离得到。

关键词: 云南铁杉; 木脂素; 4, 8-dihydroxyepipinoresinol

中图分类号: Q 946 **文献标识码:** A **文章编号:** 0253-2700(2004)02-0229-05

Lignans from *Tsuga dumosa*

ZHAO You-Xing, LUO Xiao-Dong, ZHOU Jun*

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

Abstract: A new lignan, named 4, 8-dihydroxyepipinoresinol (1), was isolated from the methanol extract of the heartwoods of *Tsuga dumosa*, together with seven known lignans (2-8). Their structures were elucidated on the basis of spectroscopic evidence. It is first time that compounds 2-8 were isolated from this plant.

Key words: *Tsuga dumosa*; Lignan; Epipinoresinol

Tsuga dumosa is an economically important conifer indigenous to the Yunnan Province of China (Southwest College of Forestry, Yunnan Forestry Administration, 1988). Sesquilignans and lignans from this genus have been reported previously (Kawamura *et al.*, 1997). Chemical investigation of the heartwoods of *T. dumosa* collected from the northern part of Yunnan province, led to the isolation of a new lignan 4, 8-dihydroxyepipinoresinol (1), as well as seven known lignans, α -conidendrin (2), (+)-lariciresinol (3), (threo) 3, 3'-dimethoxy-4, 8'-oxyneoligna-9, 4', 7', 9'-tetraol (4), (threo) 3, 3'-dimethoxy-4, 8'-oxyneoligna-9, 4', 7', 9'-tetraol-7 (8)-ene (5), 8-hydroxy- α -conidendric acid methyl ester (6), (-)-nortrachelogenin (7) and vladinol D (8) (Fig. 1). Their structures were determined by spectral methods.

Compound 1 was obtained as amorphous powder, possessing a molecular formula $C_{20}H_{22}O_8$ on the basis of EIMS (m/z 390, $[M]^+$) and HRESIMS ($[M + Na]$ found: m/z 413.1219, calcd:

* 通讯联系人 Corresponding author

收稿日期: 2003-12-29, 2004-03-11 接受发表

作者简介: 赵友兴 (1974-) 男, 在读博士, 主要从事植物化学研究。

413.1212). Its IR spectrum showed a broad absorption at 3413 cm^{-1} for hydroxyl groups and strong absorptions at 1615 , 1519 and 1457 cm^{-1} for phenyl groups. ^1H NMR spectrum showed two tri-substituted aromatic groups according to the signals at δ 7.15 (d, $J = 2.0\text{ Hz}$), 6.88 (dd, $J = 2.0$, 8.1 Hz), 6.76 (d, $J = 8.1\text{ Hz}$) and δ 6.96 (d, $J = 1.8\text{ Hz}$), 6.84 (dd, $J = 1.8$, 8.1 Hz), 6.80 (d, $J = 8.1\text{ Hz}$) and two methoxyls at δ_{H} 3.85 and 3.84 (each 3H, s). The ^{13}C NMR and DEPT spectrum revealed the presence of 20 carbon atoms including two methoxyls and two $\text{C}_6 - \text{C}_3$ units, indicating the typical structures of lignans. Compound **1** contained two rings beside two phenyl groups based on a calculation of unsaturation degree ($n = 10$), suggesting that **1** can best be accommodated in the structure of 2, 6-diaryl-3, 7-dioxabicyclo [3, 3, 0] octane in which the chemical shifts of C - 1', 1'', C - 1, 5 and C - 2, 6 are sensitive to its stereochemistry (Chiba *et al*, 1980; Pelter *et al*, 1976). The similar ^{13}C NMR spectral data with epipinoresinol (Rahman *et al*, 1990) except for the signals at δ_{C} 101.70 and 101.91 indicated that **1** has the same skeleton as epipinoresinol with C - 1' of the axial aryl group and C - 1'' of the equatorial one but not the symmetrical 4, 8-dihydroxypinoresinol (Pelter *et al*, 1982). This assumption was confirmed by the different chemical shifts of C - 2 (δ_{C} 81.0) with C - 6 (δ_{C} 86.6), C - 1 (δ_{C} 56.8) with C - 5 (δ_{C} 61.6) and C - 1' (δ_{C} 131.0) with C - 1'' (δ_{C} 135.5) in ^{13}C NMR spectrum.

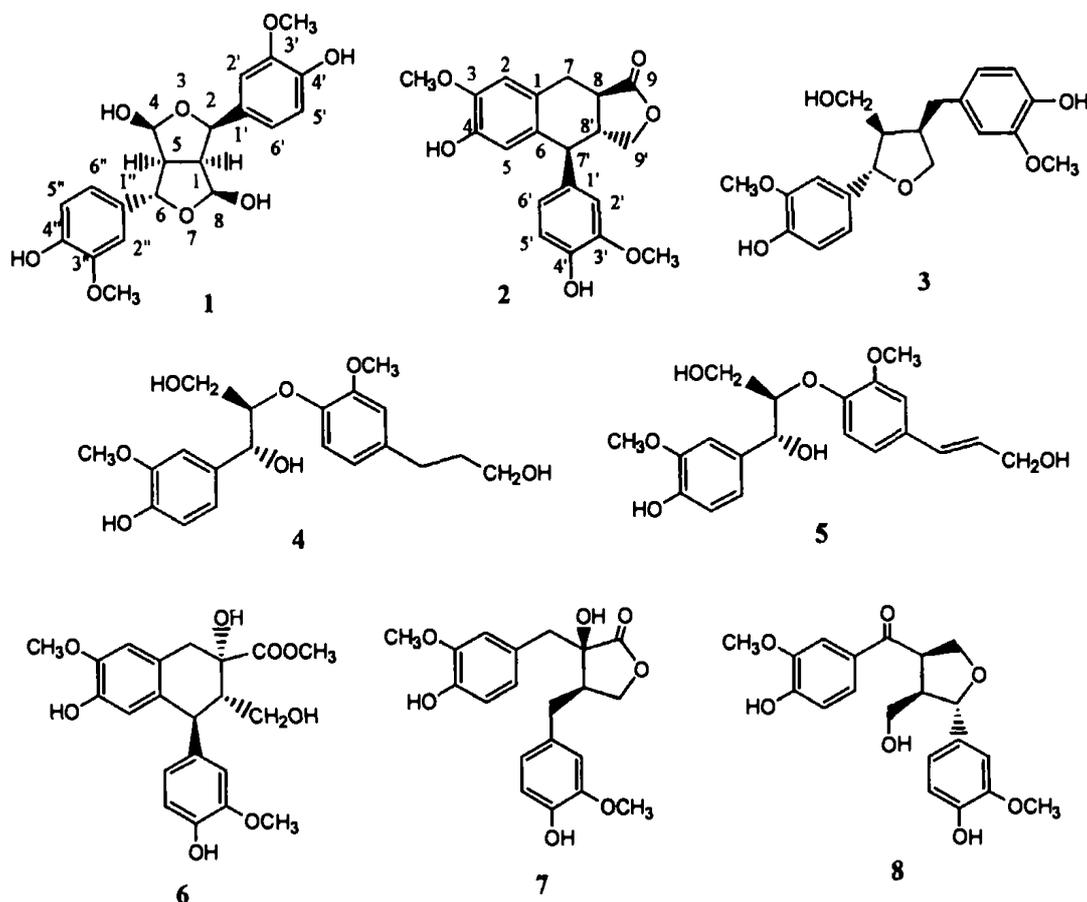


Fig. 1 Structures of compounds 1 - 8

The signals at δ_C 101.7 and 101.9 for two carbons both attached to two oxygen atoms were assigned to be at C-8 and C-4 by HMQC and $^1\text{H}-^1\text{H}$ COSY spectrum revealing correlations of H-4/H-5 and H-8/H-1. The structure of 2, 6-diaryl-3, 7-dioxabicyclo [3, 3, 0] octane in **1** was supported by HMBC spectrum (Fig. 2) exhibiting correlations from H-2'' (δ_H 7.15) and H-6'' (δ_H 6.88) to C-6 (δ_C 86.6), H-2' (δ_H 6.96) and H-6' (δ_H 6.84) to C-1 (δ_C 56.8), H-4 (δ_H 4.79) to C-2 (δ_C 81.0) and H-8 (δ_H 5.53) to C-6 (δ_C 86.6). The HMBC correlations of the methoxy protons at δ_H 3.84 with C-3'' (δ_C 149.1) and δ_H 3.85 with C-3' (δ_C 148.9) indicated the linkage of two methoxyl to positions C-3'' and C-3' respectively. Two equatorial hydroxyls at positions C-8 and C-4 were proposed by ROESY spectrum (Fig. 2) showing important correlations of H-1/H-4 and H-5/H-8. Based on above spectral evidence, **1** was elucidated to be 4, 8-dihydroxyepipinoresinol.

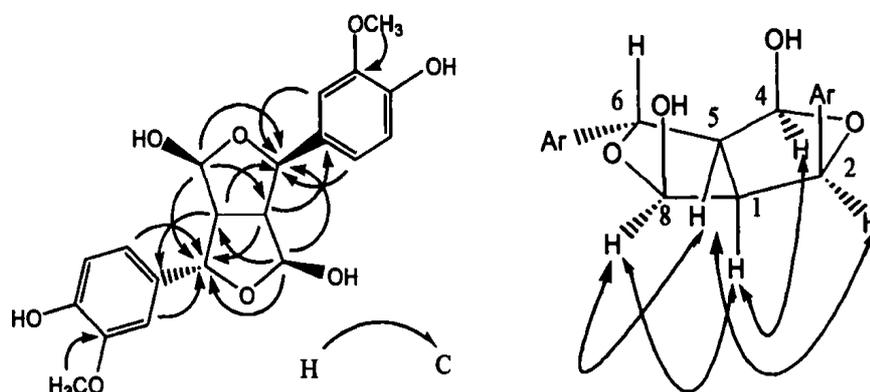


Fig. 2 Key HMBC and ROESY correlations of compound **1**

Experimental

General Experimental Procedures Melting point was measured on a XRC-1 micro-melting point apparatus and was uncorrected. Optical rotation was determined on a JASCO-20 polarimeter. IR spectra were obtained on KBr pellets using a Bio-Rad FTS-135 spectrometer. UV spectra were recorded on a UV 210A spectrometer. MS spectra were carried out on a VG Auto Spec-3000 spectrometer. The 1D and 2D NMR spectra were obtained on BRUKER AM-400 and DRX-500 spectrometers. TLC was carried on silica gel G pre-coated plates. Separation and purification were performed by column chromatography on silica gel (200-300 mesh).

Plant Material The heartwoods of *Tsuga dumosa* were collected in the Dayao of Yunnan province, in July 2002 and identified by Prof. Jun Zhou of Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen was deposited in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation The air-dried heartwoods of *T. dumosa* (5.0 kg) were extracted with 15 L EtOH (90% \times 3) at 60°C for 4 h each time. The EtOH extraction was evaporated in vacuo. The residue (365 g) was subjected to column chromatography on silica gel (200-300 mesh), eluted with gradient chloroform-methanol-water (12:1:0.1) to yield 5 fractions. Fraction 3 was further separated over Sephadex LH-20 and Si-gel column developed with chloroform/methanol (1:1) to afford compound **1** (15 mg). Fraction 2 was purified by repeated silica gel column chromatography eluted with petroleum ether/acetone/EtOAc (3:2:1) and CHCl_3 /EtOAc (1:1) to yield **2** (7.8 g), **3** (70 mg), **6**

(90 mg), **7** (1.68 g) and **8** (85 mg), and fraction 4 chromatographed with petroleum ether / acetone / CHCl₃ (1:1:1 and 1:2:1) to give **4** (28 mg) and **5** (10 mg), respectively.

4, 8-Dihydroxyepipinoresinol (1) C₂₀H₂₂O₈, amorphous powder; mp: 128–130°C; [α]_D²⁷ +36.8 (c 0.29, MeOH); UV_{max} (MeOH): 206.4, 229.8, 280.6 nm; IR bands (KBr): 3413, 2920, 1615, 1519, 1457, 1436, 1361, 1276, 1152 and 1026 cm⁻¹; ¹H NMR (500 MHz, CD₃OD) δ 7.15 (1H, d, J=2.0 Hz, H-2''), 6.96 (1H, d, J=1.8 Hz, H-2'), 6.88 (1H, dd, J=2.0, 8.1 Hz, H-6''), 6.84 (1H, dd, J=1.8, 8.1 Hz, H-6'), 6.80 (1H, d, J=8.1 Hz, H-5'), 6.76 (1H, d, J=8.1 Hz, H-5''), 5.53 (1H, s, H-8), 5.44 (1H, d, J=8.0 Hz, H-2), 4.79 (1H, d, J=2.4 Hz, H-4), 4.73 (1H, d, J=6.7 Hz, H-6), 3.85, 3.84 (each 3H, s, 2OCH₃), 3.17 (1H, m, H-1), 2.95 (1H, s, H-5); ¹³C NMR (125 MHz, CD₃OD) δ 56.8 (d, C-1), 81.0 (d, C-2), 101.9 (d, C-4), 131.0 (s, C-1'), 111.3 (d, C-2'), 148.9 (s, C-3'), 146.9 (s, C-4'), 115.9 (d, C-5'), 120.3 (d, C-6'), 56.4 (q, 2×OCH₃), 61.6 (d, C-5), 86.6 (d, C-6), 101.7 (d, C-8), 135.5 (s, C-1''), 111.2 (d, C-2''), 149.1 (s, C-3''), 147.1 (s, C-4''), 116.0 (d, C-5''), 120.2 (d, C-6''). HRESIMS *m/z*: 413.1219 [M (C₂₀H₂₂O₈) + Na], calcd. 413.1212; EIMS *m/z*: 390 [M]⁺ (6), 362 (3), 340 (3), 326 (10), 298 (4), 238 (3), 228 (8), 192 (7), 161 (6), 152 (97), 151 (100), 137 (30), 109 (23), 81 (34).

α-Conidendrin (2) C₂₀H₂₀O₆, white amorphous powder; FAB⁺ MS *m/z*: 357 [M+H]⁺; ¹H NMR data were consistent with those in the literature (Dhal *et al.*, 1986); ¹³C NMR (100 MHz, CD₃OD) δ 178.0 (s, C-9), 147.4 (s, C-3'), 145.9 (s, C-3), 145.4 (s, C-4), 144.1 (s, C-4'), 133.6 (s, C-1'), 131.3 (s, C-6), 125.4 (s, C-1), 120.8 (d, C-6'), 115.3 (d, C-5, 5'), 114.7 (d, C-2), 111.4 (d, C-2'), 71.9 (t, C-9'), 55.3, 55.2 (q, 2ArOCH₃), 49.2 (d, C-7'), 47.0 (d, C-8'), 41.5 (d, C-8), 28.6 (t, C-7).

(+)-Lariciresinol (3) C₂₀H₂₄O₆, white amorphous powder; FAB⁺ MS *m/z*: 361 [M+H]⁺; ¹H NMR data were similar to those in the literature (Sugiyama *et al.*, 1993); ¹³C NMR (100 MHz, CD₃OD) δ 149.0 (s, C-3), 148.9 (s, C-3'), 147.1 (s, C-4'), 145.8 (s, C-4), 134.9 (s, C-1), 133.2 (s, C-1'), 122.3 (d, C-6), 120.2 (d, C-6'), 116.3 (d, C-5), 116.1 (d, C-5'), 113.4 (d, C-2), 111.0 (d, C-2'), 85.1 (d, C-7), 73.9 (t, C-9'), 62.1 (t, C-9), 56.6 (d, C-8), 56.3 (q, 2×OCH₃), 45.1 (d, C-8'), 39.8 (t, C-7').

(threo) 3, 3'-Dimethoxy-4, 8'-oxyneoligna-9, 4', 7', 9'-tetraol (4) C₂₀H₂₆O₇, white amorphous powder; EI-MS *m/z*: 378 [M]⁺; ¹H and ¹³C NMR data were consistent with those in the literature (Miyase *et al.*, 1987).

(threo) 3, 3'-Dimethoxy-4, 8'-oxyneoligna-9, 4', 7', 9'-tetraol-7 (8)-ene (5) C₂₀H₂₄O₇, white amorphous powder; EI-MS *m/z*: 376 [M]⁺; ¹H NMR data were consistent with those in the literature (Miki *et al.*, 1980); ¹³C NMR (100 MHz, CD₃OD) δ 151.8 (s, C-3), 149.3 (s, C-3'), 148.8 (s, C-4), 147.2 (s, C-4'), 133.8 (s, C-1'), 133.2 (s, C-1), 131.4 (d, C-8), 128.6 (d, C-7), 120.8 (d, C-6, 6'), 118.9 (d, C-5), 115.7 (d, C-5'), 111.8 (d, C-2), 111.3 (d, C-2'), 87.2 (d, C-8'), 74.1 (d, C-7'), 63.7 (t, C-9), 61.9 (t, C-9'), 56.6 (q, 3-OCH₃), 56.4 (q, 3'-OCH₃).

8-Hydroxy-α-conidendric acid methyl ester (6) C₂₁H₂₄O₈, amorphous powder; EI-MS *m/z*: 404 [M]⁺; ¹H and ¹³C NMR data were consistent with those in the literature (Kawamura *et al.*, 1997).

(-)-Nortrachelogenin (7) C₂₀H₂₂O₇, amorphous powder; EI-MS *m/z*: 374 [M]⁺; ¹H and ¹³C NMR data were consistent with those in the literature (Achenbach *et al.*, 1983).

Vladinol D (8) C₂₀H₂₂O₇, white amorphous powder; EI-MS *m/z*: 374 [M]⁺; ¹H NMR data were consistent

with those in the literature (Tan *et al.*, 1990); ^{13}C NMR (100 MHz, CD_3OD) δ 200.3 (s, C-7), 153.5 (s, C-4), 149.2 (s, C-3), 149.1 (s, C-4'), 147.5 (s, C-3'), 133.5 (s, C-1'), 130.1 (s, C-1), 125.0 (d, C-6), 121.0 (d, C-6'), 115.9 (d, C-5), 115.8 (d, C-5'), 112.4 (d, C-2), 111.4 (d, C-2'), 85.3 (d, C-7'), 71.8 (t, C-9), 61.2 (t, C-9'), 56.4, 56.3 (q, 2ArOCH_3), 54.6 (d, C-8'), 50.2 (d, C-8).

Acknowledgements: All spectra were recorded by the analytical group of the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

References:

- Achenbach H, Waibel R, Ivan AM, 1983. Lignans and other constituents from *Carissa edulis* [J]. *Phytochemistry*, **22** (3): 749—753
- Chiba M, Hisada S, Nishibe S, *et al.*, 1980. ^{13}C NMR analysis of symplocosin and (+)-epipinoresinol glucoside [J]. *Phytochemistry*, **19** (2): 335—336
- Dhal R, Nabi Y, Brown E, 1986. 7-Syntheses totales des (\pm)- α -et- β -conidendrines et des methyl (\pm)- α -et- β -conidendrals [J]. *Tetrahedron*, **42** (7): 2005—2016
- Kawamura F, Kawai S, Ohashi H, 1997. Sesquiligans and lignans from *Tsuga heterophylla* [J]. *Phytochemistry*, **44** (7): 1351—1357
- Miyase T, Ueno A, Takizawa N, *et al.*, 1987. Studies on the glycosides of *Epimedium grandiflorum* Morr. var. *thunbergianum* (Miq.) Nakal [J]. *Chem Pharm Bull*, **35** (9): 3713—3719
- Miki K, Takehara T, Sasaya T, *et al.*, 1980. Lignans of *Larix leptolepis* [J]. *Phytochemistry*, **19** (3): 449—453
- Pelter A, Ward RS, Watson DJ, *et al.*, 1982. Synthesis of 2, 6-diaryl-4, 8-dihydroxy-3, 7-dioxabicyclo [3.3.0] octanes [J]. *J Chem Soc Perkin I*, **1**: 175—181
- Pelter A, Ward RS, Rao EV, *et al.*, 1976. Revised structures for pluviatilol, methyl pluviatilol and xanthoxylol [J]. *Tetrahedron*, **32** (22): 2783—2788
- Rahman MMA, Dewick PM, Jackson DE, *et al.*, 1990. Lignans of *Forsythia intermedia* [J]. *Phytochemistry*, **29** (6): 1971—1980
- Southwest College of Forestry, Yunnan Forestry Administration, 1988. *Iconographia Arbororum Yunnanicorum*. Tomus I [M]. Kunming: Yunnan Science and Technology Press, 67
- Sugiyama M, Kikuchi M, 1993. Characterization of lariciresinol glucosides from *Osmanthus asiaticus* [J]. *Heterocycles*, **36** (1): 117—121
- Tan RX, Jakupovic J, Jia ZJ, 1990. Aromatic constituents from *Vladimiria souliei* [J]. *Planta Med*, **56** (5): 475—477