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Two glycosides from the stem bark of *Tetracentron sinense*

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Abstract

Two glycosides, tetracentronsides A and B, were isolated from the stem bark of *Tetracentron sinense* Oliv., along with ten known compounds, β-sitosterol, lupeol, betulinic acid, oleanolic acid, vanillic aldehyde, vanillic acid, maslinic acid, huazhongilexin, daucosterol and catechin. On the basis of spectral and chemical evidence, tetracentronside A and B were identified as 3,4,5-trimethoxyphenyl-*O*-6′-*O*-vanilloyl-β-D-glucopyranoside and (8R, 8′R) 9-β-D-glucopyranosyl dihydrocubebin, respectively. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Tetracentron sinense Oliv. is the only representative of the genus *Tetracentron* (Magnoliaceae) (How, Wu, Ko & Chen, 1982). The chemical constituents of this plant have never been reported. In this investigation, two new compounds, named tetracentronsides A (**1**) and B (**2**), as well as ten known compounds, β-sitosterol (**3**), lupeol (**4**), betulinic acid (**5**), oleanolic acid (**6**), vanillic aldehyde (**7**), vanillic acid (**8**), maslinic acid (**9**), huazhongilexin (**10**), daucosterol (**11**) and catechin (**12**) were isolated from the stem bark of *T. sinense* and characterized by spectral and chemical methods.

2. Results and discussion

Tetracentronside A (**1**), isolated as white needles, had the molecular formula $C_{23}H_{28}O_{12}$ as shown by HR-EIMS (*m*/*z* 496.1578). It gave a positive colouration with ferric chloride and Molish reagent, indicating that **1** is a glycoside with phenolic hydroxy groups. The UV spectrum showed $\lambda_{\max}$ at 271 and 239 nm. The IR spectrum suggested the presence of hydroxyl groups (*br*, 3364 cm^{-1}), carbonyl groups (1732 cm^{-1}) and aromatic rings (1612, 1520 cm^{-1}). After hydrolysis of **1** in 10% methanolic HCl solution, D-glucose and vanillic acid were detected by co-TLC with authentic samples.

The β-D-glucopyranosyl moiety of **1** was recognized from a ^{1}H-NMR signal at δ 4.86 (*d*, J = 7.5 Hz, H-1′) and the evidence mentioned above. The vanilloyl moiety was identified by the mass spectral fragments at *m*/*z* 329 $[\text{M-vanilloyl}]^+$ and 151 $[\text{vanilloyl}]^+$, and by comparing its ^{1}H- and ^{13}C-NMR spectral data with those of vanillic acid (**8**). The presence of a trimethoxyphenyl moiety was inferred based on the above data and further supported by the mass spectral fragments at *m*/*z* 313 $[\text{M-}C_9H_{11}O_4]^+$ and 184 $[C_9H_{11}O_4 + H]^+$. In the HMBC experiment of **1**, cross peaks were observed between H-1′ and C-1, and H-6′ and $\rangle C{=}O$. (Fig. 1). Therefore, **1** was determined to be 3,4,5-trimethoxyphenyl-*O*-6′-*O*-vanilloyl-β-D-glucopyranoside.

Tetracentronside B (**2**) was obtained as white plates, and had the molecular formula $C_{26}H_{32}O_{11}$ as determined by HR-EIMS (*m*/*z* 520.1994). The UV spectrum showed $\lambda_{\max}$ at 287 and 234 nm. Hydrolysis of **2** in 7% methanolic HCl solution yielded D-glucose, as detected by co-TLC, in addition to (−)dehydroxycube-

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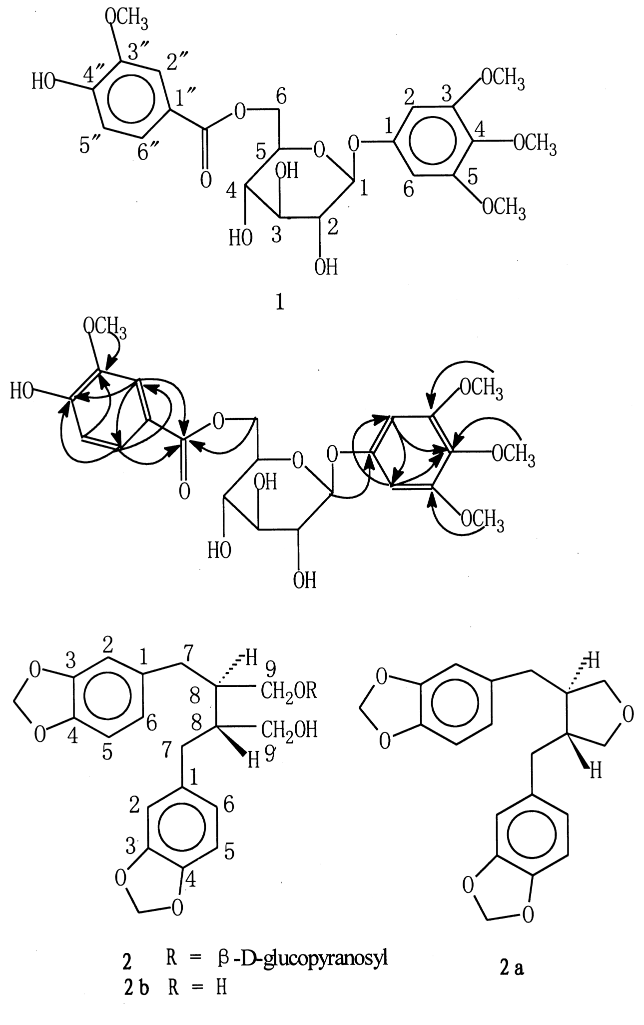
bin (**2**a) and (−)dihydrocubebin (**2**b), obtained by CC and whose mp, $[\alpha]_D$ and spectral data were identical to those reported (Carvalho, Yoshida, Gottlieb & Gottlieb, 1987; Anjaneyulu, Atcuta, Ramachandra & Venkateshwarlu, 1981; Koul, Taneija, Pushpangadan & Dhar, 1988). The β-D-glucopyranosyl moiety of **2** was recognized from the ^{1}H-NMR signal at δ 4.17 (*d*, J = 7.8 Hz, H-1″) and the mass spectral fragment at *m*/*z* 358 [M-Glc]$^+$ in the EIMS. The aglycone, a dihydrocubebin moiety, was identified by comparing its ^{1}H- and ^{13}C-NMR spectral with those of **2**b, and based on the evidence mentioned above. Thus, **2** was determined to be (8*R*, 8′*R*) 9-β-D-glucopyranosyl dihydrocubebin.

3. Experimental

3.1. General

Mps: uncorr. UV: in MeOH; IR: KBr discs; NMR: 500 MHz for ^{1}H and 125 MHz for ^{13}C, TMS as internal standard; CC: silica gel, 200–300 mesh. Optical rotations were measured on a PE-241 Polarimeter. TLC was carried out on silica gel (10–40 μ) plates. Spots were detected by spraying with 5% ethanolic phosphomolybdic acid solution followed by heating.



1

2 R = β-D-glucopyranosyl
2b R = H

2a

Fig. 1. Structures of **1**, **2**, **2**a and **2**b (HMBC correlations).

3.2. Plant material

Stem bark of *T. sinense* Oliv. was collected at Nanchuan, Chongqing, China, in August 1995 and identified by Prof. G. M. Shu (Sichuan Institute of Chinese Materia Medica), where a voucher specimen is kept.

3.3. Extraction and separation

The dried and powdered bark (2 kg) was extracted with 95% EtOH (8 l × 3). After removing solvent under reduced pressure, 98 g of residue was obtained. This was divided into six frs. by CC with $CHCl_3$–MeOH (10 : 0–3). Fr. 1 was subjected to further CC eluted with a gradient of petroleum ether (bp 60–90°C): EtOAc (10 : 1–3) to yield **3** (98 mg), **4** (16 mg), **5** (45 mg), **6** (20 mg) and **7** (8 mg). From fr. 2, **8** (10 mg) and **9** (22 mg) were obtained by CC ($CHCl_3$: EtOAc : MeOH, 10 : 10 : 2). **10** was obtained by recrystallization of fr. 3 from EtOAc. Fr. 4 was separated by CC ($CHCl_3$: MeOH, 10 : 1) to yield **11** (80 mg), **1** (25 mg) and **2** (580 mg). **12** (32 mg) was isolated by purification of fr. 6 by CC ($CHCl_3$: MeOH : H_2O, 13 : 5 : 2 lower layer).

3.4. Identification of known compounds

Compounds **3**, **4** (Sholichin, Yamasaki, Kasai & Tanaka, 1980), **5** (Sholichin et al., 1980), **6**, **7**, **8** (Wang, Zhang & Chen, 1991), **9** (Kojima & Ogura, 1986), **10** (Lin, Qin & Xu, 1995), **11**, and **12** (Porter, Newman, Foo, Wong & Hemingway, 1982; Yu, Shen, Shen, Chen & Xiao, 1989) were identified by co-TLC with authentic samples and by comparison of their spectral data with those reported.

3.5. Tetracentronside A (*1*)

White needles. mp 125–126°C. $[\alpha]_D^{25} = -43.6°$ (c = 0.234, MeOH). UV λ_{max} (nm): 271, 239; IR ν_{max} cm^{-1}: 3364 (OH), 1732 (C=O), 1612, 1520 (aromatic rings), 1462, 1369, 1215, 1119, 1042, 833, 664. ^{1}H-NMR spectral data (CD_3OD): δ 6.39 (2H, *s*, 2/6-H), 3.65 (6H, *s*, 3/5-OMe), 3.67 (3H, *s*, 4-OMe), 4.87 (1H, *d*, J = 7.5 Hz, 1′-H), 4.72 (1H, *dd*, J = 12/2 Hz, 6′α-H), 4.38 (1H, *dd*, J = 12/7 Hz, 6′ß-H), 7.52 (1H, *d*, J = 1 Hz, 2″-H), 6.83 (1H, *d*, J = 8 Hz, 5″-H), 7.53 (1H, *dd*, J = 8/1 Hz, 6″-H), 3.84 (3H, *s*, 3″-OMe). ^{13}C-NMR spectral data (CD_3OD): δ 155.7 (1-C), 96.8 (2/6-C), 154.8 (3/5-C), 135.0 (4-C), 58.6 (3/5-OMe), 61.2 (4-OMe), 103.1 (1′-C), 74.9 (2′-C), 77.8 (3′-C), 72.0 (4′-C), 75.8 (5′-C), 65.3 (6′-C), 122.5 (1″-C), 113.9 (2″-C), 148.8 (3″-C), 153.1 (4″-C), 116.0 (5″-C), 125.2 (6″-C), 167.9 (C=O), 58.5 (3″-OMe). FABMS (*m/z*): 497 [M + 1]$^+$, 329 [M-vanilloyl]$^+$, 313, 295, 184, 169, 151. HR-EIMS (*m/z*): 496.1578 (M^+, $C_{23}H_{28}O_{12}$, calc. 496.1581).

3.6. Hydrolysis of tetracentronside A (*1*)

Tetracentronside A (10 mg) was dissolved in 10% HCl–MeOH solution and heated at 80°C for 2 h. In the reaction mixture, vanillic acid was identified by TLC on silca gel $60F_{254}$ ($CHCl_3$: MeOH, 10 : 0.3); glucose was detected on silica gel G [lower phase of $CHCl_3$: MeOH : H_2O, 15 : 6 : 2-HOAc (9 : 1)].

3.7. Tetrecentronside B (*2*)

White plates, mp 156–157°C, $[\alpha]_D^{25} = -12.1°$ (c = 0.280, MeOH). UV λ_{max} (nm): 287, 234. IR ν_{max} cm^{-1}: 3460, 3348 (OH), 1501, 1447, 1393, 1254, 1038, 926, 810, 700. ^{1}H-NMR spectral data (CD_3OD): δ 6.61 (2H, *d*, $J < 1.0$ Hz, 2/2′-H), 6.66 (2H, *d*, $J = 7.8$ Hz, 5/5′-H), 6.59 (2H, *dd*, $J = 7.8/ < 1.0$ Hz, 6/6′-H), 2.50–2.70 (4H, *m*, 7/7′-H), 2.05 (1H, *m*, 8-H), 1.89 (1H, *m*, 8′-H), 3.87 (2H, *m*, 9α/9′α-H), 3.50–3.70 (2H, *m*, 9ß/9′ß-H), 5.87 (4H, *s*, $O_2CH_2 \times 2$), 4.17 (1H, *d*, J = 7.8 Hz, 1″-H). ^{13}C-NMR spectral data (CD_3OD): δ 137.1 (1/1′-C), 109.6 (2/2′-C), 149.7 (3/3′-C), 147.9 (4/4′-C), 111.2 (5/5′-C), 123.9 (6/6′-C), 36.4 (7/7′-C), 45.1 (8-C), 42.6 (8′-C), 71.1 (9-C), 63.6 (9′-C), 102.8 (O_2CH_2), 105.4 (1″-C), 72.5 (2″-C), 78.9 (3″-C), 75.9 (4″-C), 78.8 (5″-C), 63.3 (6″-C). HR-EIMS (*m/z*): 520.1994 (M^+, $C_{26}H_{32}O_{11}$, calc. 520.1945), 358 [M-Glc]$^+$, 340, 217, 204, 192, 161, 135.

3.8. Hydrolysis of tetracentronside B (*2*)

A solution of tetracentronside B (80 mg) in 7% HCl–MeOH (8 ml) and CH_2Cl_2 (2 ml) was refluxed at 60°C for 10 h. The reaction mixture was subjected to CC ($CHCl_3$: MeOH, 10 : 0.3) to yield (−)dehydroxycubebin (**2**a) and (−)dihydrocubebin (**2**b), whose mp, $[\alpha]_D$ and other spectral data were identical to those reported (Anjaneyulu et al., 1981; Carvalho et al., 1987; Koul et al., 1988).

References

Anjaneyulu, A. S. R., Atchuta, R. P., Ramachandra, R. L., & Venkateswarlu, R. (1981). *Tetrahedron*, *37*, 3641.

Carvalho, M. G., Yoshida, M., Gottlieb, O. R., & Gottlieb, H. E. (1987). *Phytochemistry*, *26*, 265.

How, F. C., Wu, T. L., Ko, W. C., & Chen, T. C. (1982). In *A dictionary of the families and genera of chinese seed plants* (p. 483). Beijing: Science Press.

Kojima, H., & Ogura, H. (1986). *Phytochemistry*, *25*, 729.

Koul, S. K., Taneija, S. C., Pushpangadan, P., & Dhar, K. L. (1988). *Phytochemistry*, *27*, 1479.

Lin, L. D., Qin, G. W., & Xu, R. S. (1995). *Yaoxue Xuebao*, *53*, 98.

Porter, L. J., Newman, R. H., Foo, L. Y., Wong, H., & Hemingway, R. W. (1982). *J. Chem. Soc. Perkin Trans I*, *5*, 1217.

Sholichin, M., Yamasaki, K., Kasai, R., & Tanaka, O. (1980). *Chem. Pharm. Bull*, *28*, 1006.

Wang, M. A., Zhang, H. D., & Chen, Y. Z. (1991). *Journal of Lanzhou University (Natural Sciences)*, *27*(2), 93.

Yu, Q. Z., Shen, Z. B., Shen, H. Y., Chen, Q., & Xiao, Z. Y. (1989). *Journal of Chengdu University of Science and Technology*, *2*, 101.