Chemistry of Natural Compounds, Vol. 47, No. 6, January, 2012 [Russian original No. 6, November–December, 2011]

CHEMICAL CONSTITUENTS FROM THE STEMS OF *Liriodendron tulipifera*

Chung-Yi Chen,[1*] Yau-Der Wang,[1] Sun-Wen Juan,[2] and Jin-Cherng Huang[2*]

UDC 547.941+547.918.972

Liriodendron tulipifera is a fast growing hardwood tree species native to the United State, which is used for wood and pulp products [1, 2]. Earlier investigations on the chemical constituents of *L. tulipifera* dealt with several alkaloids and sesquiterpenes [3–11]. These studies have shown the isolated products from the stems of *L. tulipifera*. *L. tulipifera* was chosen for further phytochemical investigation. The MeOH extract of the plant was subjected to solvent partitioning and chromatographic separation to afford 21 pure substances. The chemical constituents in the plants of *L. tulipifera* were separated with column chromatography.

Investigation of the MeOH extract of the plants has led to the isolation of 21 compounds, among which are four alkaloids: liriodenine (**1**) [12], (–)-anonaine (**2**) [13], (–)-norglaucine (**3**), and (–)-glaucine (**4**) [14]; three lignans: (–)-eudesmin (**5**) [15], (+)-syringaresinol (**6**) [16], and (+)-yangambin (**7**) [17]; four steroids: β-sitosterol (**8**), stigmasterol (**9**) [18], β-sitostenone (**10**), and stigmastenone (**11**) [19]; and ten benzenoids: methyl 4-hydroxy-2-methylbenzoate (**12**) [20], methyl β-orcinol carboxylate (**13**), methyl haematommate (**14**) [21], coniferyl aldehyde (**15**) [22], vanillin (**16**) [23], vanillic acid (**17**) [24], methyl vanillate (**18**) [25], *p*-hydroxybenzoic acid (**19**) [26], syringic acid (**20**) [27], and 2,6-dimethoxy-*p*-quinone (**21**) [28]. These compounds were obtained and characterized by the comparison of their physical and spectral data (UV, IR, NMR and MS) with values obtained in the literature. In addition to **5**, all of these compounds were found for the first time from this species.

The specimen of *L. tulipifera* was collected from Chiayi County, Taiwan in December, 2007. A voucher specimen was characterized by Dr. Jin-Cherng Huang of the Department of Forest Products Science and Furniture Engineering, National Chiayi University, Chiayi, Taiwan and deposited in the School of Medical and Health Sciences, Fooyin University, Kaohsiung County, Taiwan. The air-dried stems of *L. tulipifera* (9.0 kg) were extracted with MeOH (80 L × 6) at room temperature, and the MeOH extract (187.5 g) was obtained upon concentration under reduced pressure. The MeOH extract was chromatographed over silica gel using CH_2Cl_2–MeOH as eluent to produce seven fractions. Part of fraction 1 (8.33 g) was subjected to silica gel chromatography by eluting with *n*-hexane–acetone (50:1) to furnish nine fractions (1-1–1-9). Fraction 1-1 (2.12 g) was resubjected to silica gel chromatography by eluting with *n*-hexane–acetone (100:1) and enriched gradually with acetone to obtain five fractions (1-1-1–1-1-5). Fraction 1-1-1 (0.43 g) was further purified by another silica gel column using *n*-hexane–acetone to obtain methyl β-orcinol carboxylate (**13**) (37 mg). Fraction 1-1-2 (0.81 g) eluted with *n*-hexane–acetone (60:1) was further separated using silica gel column chromatography and preparative TLC (*n*-hexane–acetone (50:1)) to yield methyl-haematommate (**14**) (20 mg) and methyl 4-hydroxy-2-methylbenzoate (**12**) (19 mg). Fraction 1-4 (3.90 g) was resubjected to silica gel chromatography by eluting with *n*-hexane–acetone (50:1) and enriched gradually with acetone to obtain four fractions (1-4-1–1-4-4). Fraction 1-4-2 (1.92 g) was eluted with *n*-hexane–acetone (60:1) and further separated using silica gel column chromatography and preparative TLC (*n*-hexane–acetone (40:1)) to give vanillin (**16**) (19 mg) and vanillic acid (**17**) (15 mg). Fraction 1-4-4 (1.22 g) was eluted with *n*-hexane–acetone (40:1) and further separated using silica gel column chromatography and preparative TLC (*n*-hexane–acetone (30:1)) to give a mixture of β-sitostenone (**10**), and stigmastenone (**11**) (0.94 g). Part of fraction 2 (10.26 g) was subjected to silica gel chromatography by eluting with *n*-hexane–acetone (30:1), then enriched with

1) School of Medical and Heath Science, Fooyin University, Ta-Liao, Kaohsiung 831, Taiwan. fax: 886 7 7863667, e-mail: xx377@mail.fy.edu.tw; 2) Department of Forestry and Natural Resources, College of Agriculture, National Chiayi University, Chiayi 600, Taiwan. Published in Khimiya Prirodnykh Soedinenii, No. 6, pp. 898–899, November–December 2011. Original article submitted July 29, 2010.

0009-3130/12/4706-1035

acetone to furnish six fractions (2-1–2-6). Fraction 2-1 (2.06 g) was resubjected to silica gel chromatography by eluting with *n*-hexane–acetone (20:1) and enriched gradually with acetone to give seven fractions (2-1-1–2-1-7). Fraction 2-1-3 (0.26 g) and fraction 2-1-5 (0.33 g) were resubjected to silica gel CC and purified by preparative TLC to yield *p*-hydroxybenzoic acid (**19**) (6 mg) and syringic acid (**20**) (9 mg). Fraction 2-3 (1.25 g) was resubjected to silica gel chromatography by eluting with *n*-hexane–acetone (40:1) and enriched gradually with acetone to obtain five fractions (2-3-1–2-3-5). Fraction 2-3-3 (1.15 g) was eluted with *n*-hexane–acetone (20:1) and further separated using silica gel CC and preparative TLC (*n*-hexane–acetone (30:1)) to give (+)-syringaresinol (**6**) (45 mg) and (+)-yangambin (**7**) (36 mg). Fraction 2-6 (5.21 g) was further purified on a silica gel column (400 g, 230–400 mesh) using CH_2Cl_2–MeOH to obtain a mixture of β-sitosterol (**8**) and stigmasterol (**9**) (1.72 g). Part of fraction 3 (5.91 g) was subjected to silica gel chromatography by eluting with *n*-hexane–acetone (1:1), then enriched with acetone to furnish five fractions (3-1–3-5). Fraction 3-2 (2.47 g) was further purified on a silica gel column using *n*-hexane–acetone system to obtain eudesmin (**5**) (27 mg). Part of fraction 4 (2.66 g) was subjected to silica gel chromatography by eluting with *n*-hexane–acetone (5:1), then enriched with acetone to furnish six fractions (4-1–4-6). Fraction 4-1 (1.03 g) was further purified on a silica gel column using *n*-hexane–acetone to obtain (–)-norglaucine (**3**) (19 mg) and (–)-glaucine (**4**) (24 mg). Fraction 4-2 (1.19 g) was resubjected to silica gel chromatography by eluting with *n*-hexane–acetone (40:1) and enriched gradually with acetone to obtain four fractions (4-2-1–4-2-4). Fraction 4-2-2 (0.53 g) was resubjected to silica gel CC and purified by preparative TLC to yield methyl vanillate (**18**) (9 mg) and coniferyl aldehyde (**15**) (14 mg). Fraction 4-2-4 (0.37 g) was eluted with *n*-hexane–acetone (20:1) and further separated using silica gel CC and preparative TLC (*n*-hexane–acetone (30:1)) to obtain 2,6-dimethoxy-*p*-quinone (**21**) (3 mg). Part of fraction 5 (7.43 g) was subjected to silica gel chromatography by eluting with *n*-hexane–acetone (5:1), then enriched with acetone to furnish six fractions (5-1–5-6). Fraction 5-2 (2.81 g) was further purified on a silica gel column using *n*-hexane–acetone to obtain liriodenine (**1**) (36 mg). (–)-Anonaine (**2**) (14 mg) was further purified on a silica gel column using *n*-hexane–acetone system from fraction 5-3.

ACKNOWLEDGMENT

This investigation was supported by a grant from the National Science Council of the Republic of China (NSC 97-2320-B-242-002-MY3).

REFERENCES

1. S. A. Merkle and H. E. Sommer, In YPS Bajaj, ed, *Biotechnology in Agriculture and Forestry*, trees III, vol. **16**, Springer–Verlag, Berlin, 1991, p. 94.
2. T. W. Kim, Kyo-Hak Publishing Co, Ltd., Seoul, 101 (1995).
3. R. Ziyaev, A. Abdusamatov, and S. Yu. Yunusov, *Chem. Nat. Comp*., **10**, 119 (1974).
4. A. Abdusamatov, R. Ziyaev, and S. Yu. Yunusov, *Chem. Nat. Comp*., **10**, 126 (1974).
5. R. Ziyaev, A. Abdusamatov, and S. Yu. Yunusov, *Chem. Nat. Comp*., **10**, 714 (1974).
6. C. D. Hufford and M. J. Funderburk, *Phytochemistry*, **63**, 1338 (1974).
7. A. Abdusamatov, R. Ziyaev, and S. Yu. Yunusov, *Chem. Nat. Comp*., **11**, 829 (1975).
8. R. W. Doskotch, S. L. Keely, C. D. Hufford, and F. S. el-Feraly, *Phytochemistry*, **14**, 769 (1975).
9. R. Ziyaev, M. S. Yunusov, and S. Yu. Yunusov, *Chem. Nat. Comp*., **13**, 602 (1977).
10. R. Ziyaev, O. N. Arslanova, and A. Abdusamatov, *Chem. Nat. Comp*., **22**, 490 (1986).
11. R. Ziyaev, K. Ikramov, Kh. A. Kadyrov, and A. Abdusamatov, *Chem. Nat. Comp*., **27**, 516 (1991).
12. K. Sawasdee, T. Chaowasku, and K. Likhiwitayawuid, *Molecules*, **15**, 639 (2010).
13. C. Y. Chen, T. Z. Liu, W. C. Tseng, F. J. Lu, R. P. Hung, C. H. Chen, and C. H. Chen, *Food. Chem. Toxicol.*, **46**, 2694 (2008).
14. T. C. Chi, S. S. Lee, and M. J. Su, *Planta Med.*, **72**, 1175 (2006).
15. Z. H. Xu, G. W. Qin, X. Y. Li, and R. S. Xu, *Yao. Xue. Xue. Bao.*, **36**, 669 (2001).
16. B. Yang, G. Chen, X. Song, Z. Chen, X. Song, and J. Wang, *Nat. Prod. Commun.*, **5**, 913 (2010).
17. K. H. Kim, E. Moon, S. Y. Kim, and K. R. Lee, *J. Arg. Food. Chem*., **58**, 4779 (2010).
18. B. Liu, T. Zhang, X. Zhang, W. Ye, and Y. Li, *Zhongguo Zhong Yao Za Zhi*, **35**, 602 (2010).

19. E. M. M. Gaspar and H. J. C. Neves, *Phytochemistry*, **34**, 525 (1993).
20. Y. Z. Piao, Y. J. Kim, Y. A. Kim, H. S. Lee, B. D. Hammock, and Y. T. Lee, *J. Agric. Food. Chem*., **57**, 10004 (2009).
21. I. S. Rojas, B. Lotina-Hennsen, and R. Mata, *J. Nat. Prod.*, **63**, 1396 (2000).
22. H. Shi, H. Wang, M. Wang, and X. Li, *Nat. Prod. Commun.*, **4**, 1565 (2009).
23. C. Zhao, J. Shao and X. Li, *Zhongguo Zhong Yao Za Zhi*, **34**, 2197 (2009).
24. I. J. Lin, W. L. Lo, Y. C. Cha, L. Y. Huang, T. M. Cham, W. S. Tseng, Y. T. Yeh, H. C. Yeh, Y. D. Wang, and C. Y. Chen, *Nat. Prod. Res.*, **24**, 775 (2010).
25. T. Voitl and P. Rudolf von Rohr, *ChemSusChem*, **1**, 763 (2008).
26. R. H. Liu, C. Y. Mei, F. Shao, G. Ren, H. L. Huang, S. S. Chen, and W. L. Yang, *Zhong. Yao. Cai.*, **32**, 1846 (2009).
27. L. Wang, C. F. Zhang, Z. T. Wang, M. Zhang, and L. S. Xu, *J. Asian. Nat. Prod. Res.*, **11**, 903 (2009).
28. M. Antolovich, D. R. Bedgood Jr., A. G. Bishop, D. Jardine, P. D. Prenzler, K. Robards, *J. Agric. Food Chem*., **52**, 962 (2004).