Pergamon

0031-9422(95)00118-2

Phytochemistry, Vol. 39, No. 4, pp. 935–936, 1995

0031 9422/95 $9.50 + 0.00

A TAXANE FROM THE HIMALAYAN YEW, *TAXUS WALLICHIANA*

SUNIL K. CHATTOPADHYAY* and RAM P. SHARMA

Central Institute of Medicinal and Aromatic Plants, P.O. CIMAP, Lucknow 226015, India

(*Received in revised form* 19 *December* 1994)

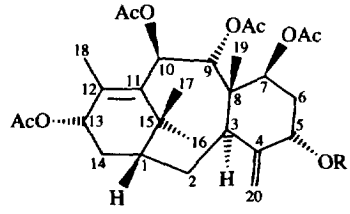
Key Word Index—*Taxus wallichiana*; Taxaceae; taxanes; diterpenoids.

Abstract—The stem bark of *Taxus wallichiana* gave the new taxane 2-deacetoxydecinnamoyl taxinine J, whose structure was established by spectroscopic data.

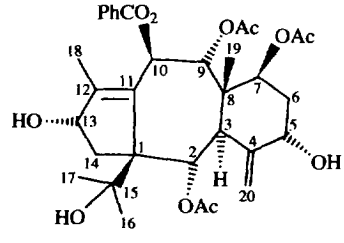
INTRODUCTION

The Himalayan Yew (*Taxus wallichiana* [Zucc] = *T. baccata* ssp. *wallichiana* Zucc Pilg.) is a small medium-sized evergreen tree growing in the temperate Himalayas at altitudes of 1800–3300 m and in the Khasia hills at altitudes of 1500 m. The plant is used in the Ayurvedic system of medicine [1], and its needles can be a good source of 10-deacetyl baccatin III [2], the starting material for the synthesis of the important anticancer drugs paclitaxel and docetaxel. Several other taxanes and rearranged taxane [3–5] and apocarotenoid [6] have also been isolated from the Himalayan Yew. As part of ongoing studies on this plant, we report the isolation of a new taxane (2-deacetoxydecinnamoyl taxinine J) (**1**) from the stem bark. Two other compounds, 2-deacetoxytaxinine J (**2**) [7] and 2α-acetoxy brevifoliol (**3**) [8], have also been isolated from this plant. These compounds are known, but had not been isolated before, from the Himalayan Yew.

Compound **1** was isolated as a crystalline material in 0.02% yield (on dried plant material) from the 2-deacetoxytaxinine J (**2**) fraction by repeated column chromatography of a bark extract. The ^{1}H NMR spectrum of **1** showed the presence of four methyls, a C-4 (20) exo-methylene group, four acetates and one secondary hydroxyl. The spectrum was very similar to that of **2**, the main difference being the absence of one cinnamoyl group and the upfield shift of H-5 $\Delta\delta$ (− 1.22 ppm). Full assignment of the ^{1}H and ^{13}C NMR spectra by 1D and 2D techniques (H–H COSY, ^1J- and $^3J^1$H–^{13}C correlations) was achieved at room temperature. The C-5 hydroxyl is non-esterified; thus **1** is 2-deacetoxydecinnamoyl taxinine J. The large value of $J_{9,10}$ (10.8 Hz) shows that the B-ring adopts the chair–boat conformation [4]. Since a β-orientation of H-13 was evident from the ROESY spectrum (cross-peaks between H-13, H-17 methyl), the observed splitting pattern of H-13 (*ddq*, J = 10.7, 4.7, 1.4 Hz) suggests that the conformation of ring A is within the twist–boat pseudorotational domain [4].



1 R = H
2 R = COCH = CHPh



3

EXPERIMENTAL

Plant material was collected in Himachal Pradesh, India. A voucher specimen is kept at the herbarium of CIMAP.

Extraction and isolation. The dried and powdered bark (0.4 kg) was extracted with MeOH (4 × 2 l) at room temp. The combined extracts were concd (final vol. 100 ml), suspended in H_2O and extracted with $CHCl_3$

*Author to whom correspondence should be addressed.
CIMAP Communication No. 94-41J.

(3 × 0.5 l). Evapn of the $CHCl_3$ phase left a residue (11 g) that was separated by CC (110 g silica gel, hexane containing increasing amounts of EtOAc as eluant). Hexane–EtOAc (80:20) and hexane–EtOAc (1:1) yielded 2-deacetoxytaxinine J (**2**) (800 mg) and **1** (80 mg), respectively.

Dried, powdered needles (5 kg) were likewise extracted and fractionated. The $CHCl_3$ fr. on CC over silica gel and elution with $CHCl_3$–MeOH (49:1) gave 2α-acetoxy brevifoliol (**3**).

2-Deacetoxydecinnamoyl taxinine J (**1**). Crystals, mp. 188–190°, $[\alpha]_D^{25}$ + 114° (MeOH; *c* 1.0). UV λ_{max}^{MeOH} nm: 216. IR ν_{max}^{KBr} cm^{-1}: 3548, 2937, 1714, 1680, 1443, 1340, 1220, 1136, 975, 759. FAB-MS *m/z*: 543 $[M + Na]^+$ $[C_{28}H_{40}O_9 + Na]^+$, 461 $[MH - HOAc]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ1.78 (1H, *m*, H-1), 1.72 (1H, *m*, H-2α), 1.88 (1H, *m*, H-2β), 3.20 (1H, *d*, *J* = 5.4 Hz, H-3), 4.28 (1H, *d*, *J* = 3.0 Hz, H-5), 1.95 (1H, *m*, H-6α), 1.65 (1H, *m*, H-6β), 5.67 (1H, *dd*, *J* = 11.6, 5.4 Hz, H-7), 5.81 (1H, *d*, *J* = 10.8 Hz, H-9), 6.25 (1H, *d*, *J* = 10.8 Hz, H-10), 5.72 (1H, *ddq*, *J* = 10.7, 4.7, 1.4 Hz, H-13), 1.08 (1H, *dd*, *J* = 15.2, 4.7 Hz, H-14α), 2.77 (1H, *ddd*, *J* = 15.2, 10.7, 8.5 Hz, H-14β), 1.55 (3H, *s*, H-16), 0.98 (3H, *s*, H-17), 2.18 (3H, *s*, H-18), 0.79 (3H, *s*, H-19), 5.15 (1H, *d*, *J* = 1.2 Hz, H-20a), 4.83 (1H, *d*, *J* = 1.6 Hz, H-20b), 2.05, 2.04, 2.01, 1.96 (4 × 3H, *s*, OAc). ^{13}C NMR (75 MHz, $CDCl_3$): δ39.6 (*d*, C-1), 26.9 (*t*, C-2), 35.5 (*d*, C-3), 151.4 (*s*, C-4), 73.3 (*d*, C-5), 36.0 (*t*, C-6), 69.8 (*d*, C-7), 46.7 (*s*, C-8), 76.6 (*d*, C-9), 72.1 (*d*, C-10), 135.9 (*s*, C-11), 137.7 (*s*, C-12), 70.0 (*d*, C-13), 32.3 (*t*, C-14), 38.9 (*s*, C-15), 26.2 (*q*, C-16), 32.1 (*q*, C-17), 15.9 (*q*, C-18), 12.6 (*q*, C-19), 112.6 (*t*, C-20), 170.3, 170.0, 169.6, 169.2 (*s*, OAc), 21.4, 21.0, 20.9, 20.8 (*q*, OAc).

Acknowledgements—We are grateful to Dr G. Appendino (University of Torino, Italy) and Prof. P. Gariboldi (University of Camerino, Italy) for helpful suggestions and for the identification of 2α-acetoxy brevifoliol and 2-deacetoxytaxinine J. We also thank the Director, CIMAP, for providing necessary facilities.

REFERENCES

1. Kapoor, L. D. (1990) in *Hand Book of Ayurvedic Medicinal Plants*, p.317. CRC Press, Inc., Boca Raton, FL.
2. Appendino, G., Gariboldi, P., Gabeta, B., Pace, R., Bombardelli, E. and Viterbo, D. (1992) *J. Chem. Soc. Perkin Trans I* 2925.
3. Appendino, G., Ozen, H. C., Gariboldi, P., Torregiani, E., Gabetta, B., Nizzola, R and Bombardelli, E. (1993) *J. Chem. Soc. Perkin Trans I* 1563.
4. Barboni, L., Garboldi, P., Torregiani, E., Appendino, G., Gabetta, B. and Bombardelli, E. (1993) *Phytochemistry* **33**, 145.
5. Chattopadhyay, S. K., Sharma, R. P., Appendino, G., Garboldi, P. and Schenk, H. (1994) *Phytochemistry* (in press).
6. Appendino, G., Ozen, H. C., Enriu, R., Barbni, L., Gabetta, B. and Zini, G. F. (1993) *Fitoterapia* **64**, 396.
7. Jigyu, L., Zhida, M. and Niwa, M. (1988) *Acta Chim. Sin.* **46**, 1053.
8. Appendino, G., Barboni, L., Gariboldi, P., Bombardelli, E., Gabetta, B and Viterbo, D. (1993) *J. Chem. Soc. Chem. Commun.* 1587.