

The Structures of Four New Taxinine Congeners, and a Photochemical Transannular Reaction

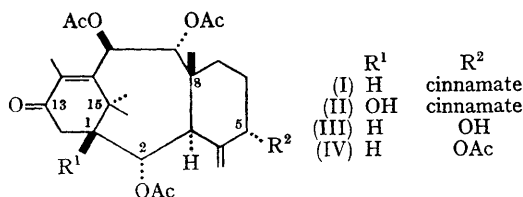
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In addition to taxinine (I)¹⁻³ and *O*-cinnamoyltaxinin-I triacetate (II),² we have isolated the following four new diterpenoids from the leaves of *Taxus cuspidata* Sieb. et Zucc.†

T-A (taxinine A) (III) [m.p. 254—255°, $[\alpha]_D + 106^\circ$ (CHCl₃), C₂₆H₃₆O₈, M⁺ 476, λ_{\max} (MeOH) 270 m μ (ϵ 4,400), ν_{\max} (KBr) 1675 cm.⁻¹‡] shows the 5-H at δ 4.17 in its n.m.r.§ and no signals due to a cinnamate grouping. Treatment of T-A with cinnamic acid-trifluoroacetic anhydride afforded taxinine [δ (5-H) 5.37].⁴

T-H (IV) {m.p. 166—167°, $[\alpha]_D + 96^\circ$ (CHCl₃), C₂₈H₃₆O₉, λ_{\max} (MeOH) 270 m μ (ϵ 4,100), ν_{\max} (KBr) 1673 cm.⁻¹, ‡ n.m.r.: δ (5-H) 5.23, four acetate signals and no signals due to a cinnamate grouping} was also obtained by acetylation of T-A.



T-K (V) [m.p. 167—168°, C₂₆H₃₆O₈, M⁺ 476, ν_{\max} (KBr) 1700 cm.⁻¹‡] and *T-L* (VI) [m.p. 159—160°, C₂₈H₃₆O₉, M⁺ 518, ν_{\max} (KBr) 1695 cm.⁻¹‡] were isolated from the mother-liquors of T-A. The n.m.r. spectrum of T-L in CDCl₃ showed the presence of four acetate methyls and was assigned as indicated in the Figure. In C₆D₆ solution, a multiplet (ddd) at δ 0.90 with splittings of *ca.* 14, 12, and 5 c./sec. becomes apparent. This multiplet must originate from a C-7 proton since irradiation near 0.90 p.p.m. does not affect the H-5 triplet. In conjunction with further double-resonance experiments, this establishes the presence of a C—CH₂—CH₂—CH(OAc)—C grouping and leads to the suggestion of structure (VI) for T-L. The spectrum of T-K is almost identical with that of T-L, with the exception that the 5-H

triplet and the 12-H quartet show at δ 4.42 and δ 3.79, respectively, and only three acetate methyl signals are present; thus T-L corresponds to the 5-acetate of T-K. Irradiation of the 15 α -Me or 8-Me protons caused large increases (15 to 30%)

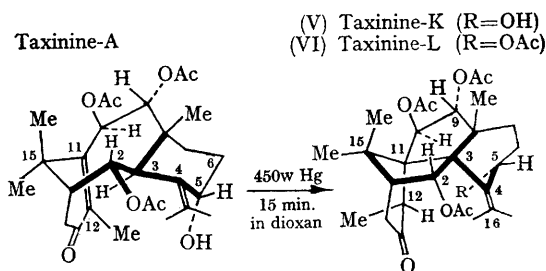


FIGURE. Assignment of 100 Mc./sec. n.m.r. of T-L (CDCl₃): H₁ 2.14 (m), H₂ 6.12 (d), H₅ 5.56 (t), H₆—H₇ 1.2—2.3 (m), H₉ 5.71 (d), H₁₀ 5.65 (d), H₁₂ 3.45 (q), H_{14 α} 2.60 (dd), H_{14 β} 2.44 (dd), H_{15 α} 5.81 (s), H_{15 β} 5.64 (s), 8-Me 1.31 (s), 12-Me 1.24 (d), 15 α -Me 1.68 (s), 15 β -Me 1.21 (s); $J_{1,2} = 5$, $J_{5,6\alpha} = J_{5,6\beta} = 8.5$, $J_{9,10} = 10$, $J_{12-H,12-Me} = 7$, $J_{14\alpha,14\beta} = 20$, $J_{14\alpha,1} = 2.5$, $J_{14\beta,1} = 5$ c./sec.

in the areas of the signals of the 2- and 9-protons. These Overhauser effects⁵ are completely in accord with the structures suggested (*cf.*, Figure). As in taxinine,⁴ double resonance experiments revealed appreciable coupling between the 15 α - and 15 β -methyl groups ($J = ca.$ 0.25 c./sec.).

The structure of T-K was established by the discovery¶ that irradiation of T-A in dioxan for 15 min. with a 450 w high-pressure Hg-lamp produced T-K in more than 50% yield. The ease with which this photo-induced 3→11 transannular bond-formation occurs is not surprising when it is realized that the 3-H is almost directly below the 11,12-double bond in T-A. Mechanistic considerations suggest that the 12-methyl has the β -configuration. The occurrence of this photochemical reaction raises the possibility that T-K and T-L may be artefacts derived from T-A and

† About 250 kg. of dried leaves afforded taxinine (220 g), *O*-cinnamoyltaxinin-I triacetate (200 mg.), T-A (2 g.), T-H (100 mg.), T-K (40 mg.) and T-L (30 mg.); all compounds gave satisfactory analyses.

‡ Only those bands arising from the C(13)=O are given.

§ Except as noted, spectra are for CDCl₃ solutions at 100 Mc./sec.

¶ The photochemistry of taxinine is presently being studied by Dr. M. Kurono of this Department.

T-H, respectively, by the action of sunlight; however, this is thought to be unlikely because the extracts were stored in soda-glass vessels after isolation from the plant.

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¹ M. Shiro, T. Sato, H. Koyama, Y. Maki, K. Nakanishi, and S. Uyeo, *Chem. Comm.*, 1966, 98, and references therein.

² M. Dukes, D. H. Eyre, J. W. Harrison, and B. Lythgoe, *Tetrahedron Letters*, 1965, 4765; D. H. Eyre, J. W. Harrison, and B. Lythgoe, *J. Chem. Soc. (C)*, 1967, 452.

³ For nomenclature and numbering of taxane derivatives see: B. Lythgoe, K. Nakanishi, and S. Uyeo, *Proc. Chem. Soc.*, 1964, 301. The α - and β -configurations for the 15-Me groups are with reference to ring A.

⁴ M. C. Woods, K. Nakanishi, and N. S. Bhacca, *Tetrahedron*, 1966, 22, 243. Although this reference contains an incorrect stereochemistry for taxinine, the n.m.r. assignments are valid.

⁵ F. A. L. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 1965, 87, 5250 and references quoted therein; M. C. Woods, I. Miura, Y. Nakadaira, A. Terahara, M. Maruyama, and K. Nakanishi, *Tetrahedron Letters*, 1967, 321.