

Phytochemical Studies<sup>1</sup>

## The Structure of Taiwanin A

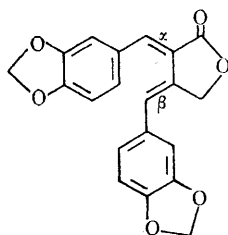
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SOME years ago four crystalline products were isolated from an acetone extract of the heartwood of *Taiwania cryptomerioides* Hayata (Family Taxodiaceae, tribe *Athrotaxae*, genus *Taiwania*, monotypic) grown in the University Forest, Shi-tou, Taiwan.<sup>2</sup> Recently, taiwanins B and D were shown to be identical with the known compounds savinin and hinokiol.<sup>3</sup> On the basis of data reported here, taiwanin A is now assigned structure (Ia).



(Ia) Taiwanin A

(Ib) Savinin [  $\beta$ -double bond saturated ](Ic) Hinokinin [  $\alpha$ - and  $\beta$ -double bonds saturated ]

The tentative molecular formula  $C_{20}H_{14}O_6$  was confirmed by the mass spectrum (parent ion,  $m/e$  350). Optical activity was not observed on this material in a variety of solvents. The infrared spectrum in potassium bromide revealed strong absorptions at  $1753\text{ cm}^{-1}$  ( $\alpha\beta$ -unsaturated- $\gamma$ -lactone)  $1630$  and  $1615\text{ cm}^{-1}$  (conjugated diene),  $1587$  and  $1485\text{ cm}^{-1}$  (phenyl),  $925\text{ cm}^{-1}$  (methylenedioxy), and  $805\text{ cm}^{-1}$  (1,2,4-trisubstituted benzene derivative). Ultraviolet maxima in methanol were seen at  $268\text{ m}\mu$  ( $\log \epsilon$  4.44) and  $365\text{ m}\mu$  ( $\log \epsilon$  4.00). The former band may be attributed to a partial styrene system, whilst the latter is in

accord with a chromophore extending over an oxygenated phenyl ring, double bond, and lactonic functions. The 60 Mc./sec. nuclear magnetic resonance spectrum, recorded in perdeuterodimethyl sulphoxide with tetramethylsilane as an internal standard, possessed signals at 7.47 and 6.68 p.p.m. (two vinyl protons), 6.82 and 6.44 p.p.m. (two aromatic protons with both *ortho*- and *meta*-coupling), 6.64 and 6.54 p.p.m. (two aromatic protons with *ortho*-coupling only), 6.37 and 6.18 p.p.m. (two aromatic protons with *meta*-coupling only), 5.92 and 5.84 p.p.m. (four methylenedioxyprotons), and 5.04 p.p.m. (doublet, two methylene protons). An n.m.r. measurement at 100 Mc./sec. revealed an allylic coupling of 1.6 c./sec. between the two alicyclic protons and the upfield vinyl proton. The aromatic ABX pattern located at 6.54, 6.44, and 6.18 p.p.m. is indicative of a shielding effect due to the proximity of the second aromatic ring, with signals at 6.82, 6.64, and 6.37 p.p.m. These data are compatible with a *cis*, *trans*-configuration for taiwanin A as shown in structure (Ia).

With the aid of platinum oxide catalyst and the use of glacial acetic acid as the solvent, taiwanin A consumed 2.50 equivalents of hydrogen gas. It was assumed that the diene system was initially reduced, followed by possible hydrogenolysis of the lactone system. The presence of the lactone functional group was supported by a potentiometric titration (355). Further chemical proof of structure (Ia) was obtained by manganese dioxide oxidation of the allylic hydroxy-acid, derived from the titration experiment, to an aldehydo-acid. Re-oxidation of this latter compound by basic silver nitrate solution gave a diacid, identical with  $\alpha\alpha'$ -dipiperonylidene succinic acid.

Lignans have not been characterized hitherto in the Taxodiaceae, but are widely distributed in the related Families Cupressaceae, Pinaceae, and Podocarpaceae.<sup>4,5</sup> Taiwanin A is seen to be

<sup>1</sup> For the previous paper in this series, see: K.-T. Wang and B. Weinstein, *Experientia*, 1963, 19, 519.<sup>2</sup> Y.-T. Lin, T.-B. Lo, and E.-H. Shih, *J. Chinese Chem. Soc. (Formosa)*, 1955, 2, 87.<sup>3</sup> Y.-T. Lin, Y.-S. Lin, and T.-B. Lo, *J. Chinese Chem. Soc. (Formosa)*, 1963, 10, 163.<sup>4</sup> R. Hegnauer, "Chemotaxonomie Der Pflanzen", Birkhäuser Verlag, Basle, 1962, Vol. 1, pp. 335—337, 353—355, 378—380, 414—415.<sup>5</sup> F. M. Dean, "Naturally Occurring Oxygen Ring Compounds", Butterworths, London, 1963, p. 39.

allied with both savinin (hibalactone) (Ib) (previously obtained from *Juniperus sabina*,<sup>6,7</sup> *Chamecypris obtusa* var. *breviramea*,<sup>8</sup> *C. obtusa*, and *C. pisifera*<sup>9</sup>) and hinokinin (cubebinolide) (Ic) (similarly found in *C. obtusa*<sup>10</sup>). These three compounds form a homologous series of lignan

derivatives, which is highly suggestive of an internal phytochemical correlation.<sup>11</sup>

Synthetic confirmation of formula (Ia) is now in progress.

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<sup>9</sup> M. Masumura and F. S. Okumura, *J. Amer. Chem. Soc.*, 1955, **77**, 1906.

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