ALKALOIDS OF THE SAPOTACEAE: *TRANS*-β-METHYLTHIOACRYLATE AND TIGLATE ESTERS OF (−)-ISORETRONECANOL FROM A *PLANCHONELLA* SPECIES*

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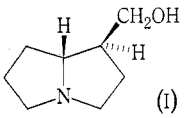
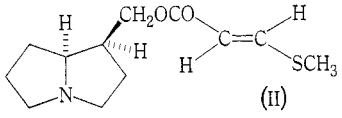
A previous study[1] of the alkaloids of *Planchonella anteridifera* (White & Francis) H. J. Lam. from New Guinea, and *P. thyrsoidea* C. T. White from New Britain, led to the identification of the major alkaloids as *trans*-β-methylthioacrylate, tiglate, and benzoate esters of the pyrrolizidine alcohol laburnine (I). An examination has now been made of the alkaloids from another *Planchonella* species, but this species, which grows in New Guinea in the Ramu Valley, has not been fully identified, and may be a new species. The alkaloids from this species also consist of pyrrolizidine esters, but differ from those previously examined in that they are esters not of laburnine, but of the stereoisomeric alcohol (−)-isoretronecanol. The alkaloids consist essentially of (−)-isoretronecyl *trans*-β-methylthioacrylate (II) together with a smaller proportion of (−)-isoretronecyl tiglate.



(I)



(II)

The mixture of esters of (−)-isoretronecanol proved difficult to separate and a pure sample of ester (II) was reconstituted from (−)-isoretronecanol and *trans*-β-methylthioacrylic acid.

Further evidence of the occurrence of pyrrolizidine alkaloids within the family Sapotaceae has been obtained from preliminary examination of the alkaloids from the bark of the Queensland rain-forest species, *Mimusops elengi* L. Detailed work on this species has not been undertaken because of variability in assays for alkaloids, but a small amount of alkaloid isolated from the bark has been shown to consist largely of a tiglate ester of a base having a mass spectrum identical with that of laburnine and isoretronecanol. As an $[\alpha]_D$ value was not obtained on the small sample isolated by preparative gas chromatography, it is not possible to carry this identification further.

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[1] Hart, N. K., and Lamberton, J. A., *Aust. J. Chem.*, 1966, **19**, 1259.

Experimental

Leaves of a *Planchonella* species were collected near the village of Aiome in the Ramu Valley, Territory of New Guinea, by Mr J. S. Womersley, who recorded a strongly positive field test for alkaloids. Mr Womersley described the species as possibly new and, because of the difficulty in obtaining a complete identification, it is designated only by its reference number NGF24744 at the Herbarium, Lae, New Guinea. The method of isolation of the alkaloids and their spectroscopic and chemical examination were carried out according to the methods already described.[1] Dried leaves (35 kg) extracted in this way afforded a crude alkaloid fraction as a clear brown oil (60 g). When a sample of the crude alkaloids (10 g) was triturated with warm carbon tetrachloride, the soluble portion (7·5–8·0 g) was obtained as a yellowish brown clear liquid, while the insoluble portion consisted of a dark resinous gum, part of which appeared to be non-alkaloidal. Detailed examination was restricted to the material soluble in carbon tetrachloride, which closely resembled in its i.r. and n.m.r. spectra the *Planchonella* alkaloids previously obtained.[1]

(*a*) *Hydrolysis of the Alkaloid*

Hydrolysis of the fraction soluble in carbon tetrachloride was carried out as described previously.[1] A 3·10-g sample of alkaloids yielded a basic fraction (1·65 g) and an acid fraction (1·25 g). The basic fraction from the hydrolysis consisted essentially of a single compound having approximately the same retention time as laburnine on a gas chromatographic column. Distillation of the basic fraction gave isoretronecanol as a colourless oil, $[\alpha]_D$ −65·7° (*c*, 1·88 in ethanol), which readily formed a crystalline picrate, m.p. 190–190·5° (Found: C, 45·7; H, 4·9; N, 15·1. Calc. for $C_8H_{15}NO,C_6H_3N_3O_7$: C, 45·4; H, 4·9; N, 15·1%). There was no depression of melting point when this picrate was mixed with a sample of the picrate of (−)-isoretronecanol of the same melting point, prepared from (−)-isoretronecanol isolated from another source by Culvenor and Smith.[2] For (+)-isoretronecanol $[\alpha]_D$ +79° in ethanol, and for (±)-isoretronecanol picrate m.p. 194°, have been recorded.[3]

The acids from the hydrolysis reaction consisted mainly of *trans*-β-methylthioacrylic acid which was readily purified by crystallization from carbon tetrachloride. The pure acid, m.p. 137–139°, was identified by comparison (i.r., n.m.r. spectra and mixed m.p.) with *trans*-β-methylthioacrylic acid isolated previously.[1] Tiglic acid was not isolated in a pure state but its presence was indicated by the n.m.r. and i.r. spectra of the acids from the hydrolysis and of the original ester alkaloids. Comparison of the relative intensities of the bands attributed to the *trans*-β-methylacrylic acid and tiglic acid moieties of the original alkaloids indicated that the alkaloids consisted of 80% *trans*-β-methylthioacrylate ester and the remainder of tiglate ester.

(*b*) *Isoretronecyl* trans-β-*Methylthioacrylate*

Oxalyl chloride (2 ml) was added to a solution of *trans*-β-methylthioacrylic acid (850 mg) in dry benzene (30 ml), and the mixture heated at reflux temperature for 2 hr under anhydrous conditions. After benzene and excess oxalyl chloride had been removed by distillation under reduced pressure, the residue was dissolved in dry benzene and a solution of isoretronecanol (1·1 g) in dry benzene was added. The mixture was allowed to stand at room temperature for 16 hr and the benzene was then removed under reduced pressure. The residue was taken up in 2% aqueous hydrochloric acid, basified by addition of ammonia, and extracted with chloroform. When the yellow residue (1·21 g) from evaporation of the chloroform extracts was chromatographed on alumina, a pale yellow oil (730 mg) was obtained, and this appeared to be identical with the major constituent of the original mixture of esters. The *trans*-β-methylthioacrylate ester obtained in this way had $[\alpha]_D$ −57·2° (*c*, 1·52 in ethanol) and afforded a picrate which crystallized from ethanol in yellow needles, m.p. 111–113° (Found: C, 46·1; H, 5·1; N, 12·0; S, 6·7. Calc. for $C_{12}H_{19}NO_2S,C_6H_3N_3O_7$: C, 46·0; H, 4·9; N, 11·9; S, 6·8%).

[2] Culvenor, C. C. J., and Smith, L. W., *Aust. J. Chem.*, 1967, **20**, 2499.

[3] Labenskii, A. S., and Men'shikov, G. P., *Zh. obshch. Khim.*, 1948, **18**, 1836 (*Chem. Abstr.*, 1949, **43**, 3827).

(c) *Extraction of the bark of* Mimusops elengi *L.*

Extraction of milled bark (2 kg) collected at Massey Creek, Queensland, gave, by the same process of extraction as above, 1·7 g crude alkaloids. A larger batch of bark from Airlie, northern Queensland, gave a negligible yield of alkaloids. Of the 1·7 g crude alkaloids, approximately 50% was obtained as a mobile oil having an i.r. spectrum typical of a tiglate ester, and comparison by gas chromatography showed that the major component had the same retention time as laburnine tiglate.[1] Hydrolysis of a sample of the alkaloids gave tiglic acid which was isolated in a pure state, and an alcohol having the same retention time on a gas chromatographic column as laburnine and (—)-isoretronecanol. A small sample was collected by preparative gas chromatography and its mass spectrum was found to be identical with that reported for laburnine, but, as the mass spectra of laburnine and (—)-isoretronecanol do not differ, a complete identification cannot be made.

Acknowledgments

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