Pergamon 0031-9422(95)00030-3 Phytochemistry, Vol. 41, No. 3, pp. 801–802, 1996

0031-9422/96 $15.00 + 0.00

HOMOERYTHRINA ALKALOIDS FROM SILVER PINE, *LAGAROSTROBOS COLENSOI*

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(*Received* 16 *June* 1995)

Key Word Index—*Lagarostrobos colensoi*; Podocarpaceae; silver pine; dyshomerythrine; homoerythrina alkaloids; insecticide.

Abstract—A group of homoerythrina alkaloids with dyshomerythrine as the major component have been isolated from extracts of *Lagarostrobos colensoi*. This is the first time these alkaloids have been isolated from Podocarpaceae.

INTRODUCTION

During an investigation of New Zealand plants for various biological activities we have examined a number of extracts for the presence of insecticidal activity. This paper reports the results of studies of the observed activity of foliage from the conifer *Lagarostrobos colensoi* (Hook.) Quinn (formerly *Dacrydium colensoi* Hook.) or silver pine.

Previously, studies on the chemistry of *L. colensoi* have focused on the terpenoid and phenolic constituents [1–5]. A survey of insecticidal activity of foliage from New Zealand conifers showed this species had some activity, but the active constituents were not isolated [6]. No alkaloids were detected when foliage extracts from this tree were screened during a phytochemical survey [1], so we were somewhat surprised to find the major activity of our extract to be associated with an alkaloidal fraction.

RESULTS AND DISCUSSION

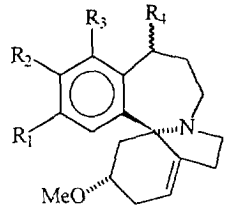
Florisil column chromatography of the crude alkaloidal fraction followed by reversed-phase HPLC yielded six known alkaloids in sufficient quantity for structural determination. The major compound was shown to be dyshomerythrine (3-epi-schelhammericine) (**1**), a homoerythrina alkaloid, and as for an earlier isolation was contaminated with minor amounts of the 18-methoxyl analogue [7]. Four of the other compounds were closely related compounds varying only in substitution pattern on the aromatic ring: comosivine (**2**), 2,7-dihydrohomoerysotrine (**3**) and holidinine (**4**); or in the seven-membered ring; 3-epi-12-hydroxyschelhammericine (**5**). The sixth compound was determined to be the degraded homoerythrina alkaloid, lenticellarine (**6**). The compounds were identified from comparison of their mass spectrals ^1H and ^{13}C NMR data with those reported in the literature [8–10].

All of these compounds showed some insecticidal activity against agricultural pests (e.g. *Heliothis virescens*).

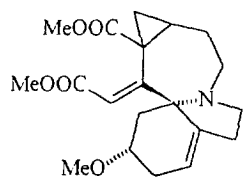
Homoerythrina alkaloids have a restricted distribution, occurring so far only in southeast Asian species of apparently unrelated families; Liliaceae (*Schelhammera Kunthera*), Phellinaceae (*Phelline*), Meliaceae (*Dysoxylum*) and the conifer genera *Cephalotaxus* (Cephalotaxaceae) and *Athrotaxis* (Taxodiaceae) (*Schelhammera* and *Kuntheria* are now placed in the family Convallariaceae) [11]. To our knowledge this is the first report of the occurrence of alkaloids in a Podocarpaceae species. The taxonomic status of *L. colensoi* has been the subject of continued debate [12]. Chemotaxonomic studies based on biflavones and flavonoids raise serious doubts about the placement of this species in *Lagarostrobos* [3, 4]. The work reported here may represent further chemical evidence for revision of the genus; however, conclusive results must await a systematic alkaloid screening of related genera.

EXPERIMENTAL

Foliage from a single young tree at the Scientific Reserve at Taita, Wellington, New Zealand, was sampled in November 1989 and December 1991. A voucher specimen from the earlier collection is deposited at the Landcare Research Herbarium, Lincoln, New Zealand (CHR465054). The plant material from the second collection (1.66 kg fr. wt) was dried, shredded and extracted with EtOH (95%, 3 × 12 hr). The extract was defatted by partitioning with hexanes. The dried extract (91 g) was taken up in 1 N HCl and partitioned with $CHCl_3$. The pH of the aq. layer was adjusted to pH 9–10 and the alkaloids extracted with $CHCl_3$. The alkaloid fr. was subjected to Florisil CC eluting with a $CHCl_3$ through to MeOH gradient. The alkaloids were further purified by prep. RP HPLC (pH stable C-18, 25 × 250 mm) eluting



		R_1	R_2	R_3	R_4
1	Dyshomoerythrine	CH_2	CH_2	OMe	H
2	Comosivine	OMe	OMe	OMe	H
3	2,7-Dihydrohomoerysotrine	OMe	OMe	H	H
4	Holidinine	OH	OMe	OMe	H
5	3-Epi-12-hydroxyschelhammericine	CH_2	CH_2	H	H



6 Lenticellarine

with H_2O–MeOH–Et_2NH (35: 65: 0.1) to yield dyshomerythrine (200 mg), 3-epi-12-hydroxy-schelhammericine (4 mg), comosivine (2 mg), holidinine (5 mg), 2,7-dihydrohomoerysotrine (2 mg) and lenticellarine (30 mg).

Acknowledgements—We thank Tony Druce for assistance with plant collection and identification. Funds for S.J.B. were provided by the NZ Foundation for Research, Science and Technology under Contract CO8322.

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