ticularly in derived horticultural varieties of *E. carnea* and *E. melanthera*.

Comparison of the *Erica* pigments with those previously identified in a related family, the Epacridaceae [1] is shown in Table 2. Several significant comparisons are readily apparent. Glucose was detected in floral anthocyanins of only 2/54 Epacridaceae species (*Trochocarpa gunnii* and *T. cunninghamii*) [1]. Methylated anthocyanins (peonidin and malvidin) are relatively abundant in *Erica* species (25/39), but are infrequent in the Epacridaceae (1/54). Delphinidin anthocyanins also occur more commonly in the genus *Erica*, their presence in the Epacridaceae being confined mainly to fruits [1].

Table 2. Comparison of floral anthocyanins of *Erica* with those of the Epacridaceae

| Species examined (no.) | | *Erica* 39 | Epacridaceae 54 |
|---|---|---|---|
| Dp | glc | 23 | 6 (gal) |
| | ara | 11 | 4 |
| Cy | glc | 41 | 52 (gal) 2 (glc) |
| | ara | 39 | 50 |
| Mv | glc | 23 | 1 (gal) |
| | ara | 16 | 1 |
| Pn | glc | 9 | 0 |
| | ara | 1 | 0 |
| Pg | glc | 4 | 1 (gal) |
| | ara | 1 | 2 |
| Biosides present | | 8(21%) | 19 (28%) |
| Methylated anthocyanins present | | 25 | 1 |

3-Biosides are present in species from both families, but are found in higher concentration in the Epacridaceae, particularly in fruits of species from the subfamily Stypheliae [1]. The quantity of 3-biosides in extracts of *Erica* species was usually too low to permit absolute identification by isolation and degradative procedures. However, from PC data, the principal bioside appears to be rutinose (cf. robinobiose in Epacridaceae [1]. Anthocyanins with 5-glycosylation were not observed in either group. However, in other genera of the Ericaceae, e.g. *Rhododendron* [2,3], 3, 5-diglycosides occur frequently.

## EXPERIMENTAL

Fresh plant material was collected from Kew and Shinfield Gardens, UK, and from Kirstenbosch Gardens and in the field, S. Africa. Voucher specimens are lodged in the herbarium, Botany Department, University of Tasmania. Laboratory procedures for extraction, isolation and identification of anthocyanins were as previously described [1]. Relative aglycone concn was extimated visually. For all major pigments, the anthocyanidin and sugar present was determined unambiguously, following acid hydrolysis.

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# FLAVONOIDS OF *ELAEOCARPUS LANCEOFOLIUS*

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**Key Word Index**—*Elaeocarpus lanceofolius*; Elaeocarpaceae; 4′-methylmyricetin; myricetin; myricetin-3-*O*-rhamnoside.

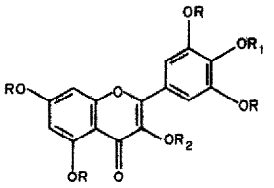
**Abstract**—4′-Methylmyricetin has been isolated from the leaves of *Elaeocarpus lanceofolius* together with myricetin and its 3-*O*-rhamnoside. This is the second report of the natural occurrence of a 4′-methyl ether of myricetin and the first in the family, Elaeocarpaceae.

## INTRODUCTION

In continuation of the work done on the phenolic constituents of *Elaeocarpus* species [1] in our laboratory, we now report on the flavonoid constituents of *Elaeocarpus lanceofolius* Roxb., a large tree growing in the eastern Himalayas and hills of Assam up to 8000 ft [2].

## RESULTS AND DISCUSSION

Preliminary fractionation of the ethanolic extract of the plant material and subsequent chromatography of individual fractions gave three crystalline flavonoids two of which were readily identified as myricetin (**1**) and myricetin-3-*O*-rhamnoside (**2**) by spectroscopic and chroma-



(1) R = $R_1$ = $R_2$ = H
(2) R = $R_1$ = H, $R_2$ = rhamnose
(3) R = $R_2$ = H, $R_1$ = Me
(4) R = $R_2$ = Et, $R_1$ = Me

tographic comparison with authentic samples. The third flavonoid, $C_{16}H_{12}O_8$, mp 264°, $\lambda_{max}$ 265, 368 nm, was characterized as 4′-methylmyricetin (3) on the following evidence: (i) its MW derived from MS is 332 which corresponds to that required for a monomethylether of myricetin; (ii) on methylation with $CH_2N_2$ it gave a penta Me ether, $M^+$ 402, mp 152°, identical in all respects with hexamethylmyricetin; (iii) acetylation with $Ac_2O$–$Et_3N$ yielded a pentaacetate, mp 180°, the PMR spectrum of which showed signals for five acetoxy, one methoxy, a pair of *m*-coupled and another pair of equivalent aromatic protons; (iv) its UV spectrum remained unaltered in borate buffer indicating the absence of a catechol system in the molecule; (v) alkaline hydrolysis of the pentaethylether (4) of the compound gave a phenol and an acid which were characterized as 6-hydroxy-ω,2,4-triethoxy-acetophenone and 3,5-diethyl-4-methylgallic acid respectively from detailed spectral analysis and direct comparisons.

4′-Methylmyricetin is relatively rare in nature [3] and there is one other instance of its isolation and that too is as a rhamnoside, mearnsitrin [4] from the leaves of *Acacia mearnsii*. 4′-Methylmyricetin (mearnsetin), obtained from mearnsitrin, was reported amorphous and its acetyl derivative was described crystalline without any mention of its mp. This is the first report of the isolation of 4′-methylmyricetin in a crystalline state and from a plant of the family, Elaeocarpaceae.

## EXPERIMENTAL

Mp's were determined in open capillaries and are uncorrected. UV spectra were recorded in EtOH. PMR were taken in $CDCl_3$. PC solvents used were, BAW (BuOH–HOAc–$H_2O$, 4:1:5), Forestal (conc HCl–HOAc–$H_2O$, 3:30:10).

*Isolation of flavonoids.* Dried and pulverized leaves of *Elaeocarpus lanceofolius* were defatted and then extracted with EtOH (95%). The extract was concentrated to a syrup under red. pres., taken up in $H_2O$ and extracted successively with $CHCl_3$, $Et_2O$ and EtOAc. The $Et_2O$ extract on concentration and repeated crystallization from MeOH yielded myricetin and the EtOAc extract on concentration and chromatography on cellulose furnished myricetin-3-*O*-rhamnoside.

*4′-Methylmyricetin* (3). The mother liquors from the isolation of myricetin after chromatography on Si gel and elution with $C_6H_6$–EtOAc (9:1) gave a pale yellow solid which crystallized from MeOH as fine needles, mp 264°; $R_f$ 0.77 (BAW), 0.58 (Forestal); UV; $\lambda_{max}$ 265, 368 nm; $\lambda_{max}^{alc, NaOMe}$ 275, 408 nm, $\lambda_{max}^{alc, NaOAc, H_3BO_3}$ 264, 368 nm; MS; $M^+$ 332. Methylation of the compound gave a pentamethylether, $M^+$ 402, mp 152°, mp remained undepressed on admixture with hexamethylmyricetin. Acetylation with $Ac_2O$–$Et_3N$ gave a pentaacetate, $M^+$ 542, mp 180°, PMR; δ, 2.30 (12 H, *s*, 4-OAc), 2.40 (3 H, *s*, 1-OAc), 3.73 (3 H, *s*, Ar-OMe), 7.50 (2 H, *s*, Ar-H), 6.86 and 7.36 (2 H, *dd*, *J* 2.5 Hz, *m*-coupled Ar-H).

*Ethylation and alkaline hydrolysis of 4′-methylmyricetin.* Treatment with $Et_2SO_4$–$K_2CO_3$ in refluxing $Me_2CO$ gave a pentaethylether, mp 160°. It was hydrolysed with ethanolic alkali (5 N) and the reaction product fractionated into phenolic and acidic constituents by usual procedures. The phenol, mp 96°; UV; $\lambda_{max}$ 213, 225 *sh*, 288 nm, $\lambda_{max}^{alc, NaOH}$ 240 *sh*, 287, 342 nm; PMR; δ, 1.40 (9 H, three overlapped triplets, *J* 7 Hz), 3.66 (2 H, *q*, *J* 7 Hz), 4.08 (4 H, two overlapped quartets, *J* 7 Hz), 4.66 (2 H, *s*), 5.86 and 6.05 (2 H, *dd*, *J* 2.5 Hz); MS; *m/e* 268 ($M^+$, 20%), 224 (6), 209 (100), 181 (20), 153 (44) and m*, 187.2 (268 → 224), 156.8 (209 → 181), 129.3 (181 → 153), was found to be identical with that obtained by similar treatment of myricetin. The acid, mp 114°, PMR; δ, 1.43 (6 H, *t*, *J* 7 Hz), 4.12 (4 H, *q*, *J* 7 Hz), 3.9 (3 H, *s*), 7.37 (2 H, *s*), 10.63 (1 H), was identical (mmp, co-TLC) with 3,5-diethyl-4-methylgallic acid obtained by synthesis (see below).

*3,5-Diethyl-4-methyl gallic acid.* Gallic acid was selectively methylated [5] by refluxing in $Me_2CO$ with $Me_2SO_4$ and $NaHCO_3$ for 6 hr. The reaction product on usual work-up furnished a mixture of two compounds identical with the mixture of gallic acid and 4-methyl gallic acid, kindly supplied by Dr. Shipchandler [cf. Ref. 6]. 4-Methylgallic acid, mp 246°, separated from this mixture by chromatography on Si gel and elution with $C_6H_6$–$CHCl_3$ (1:1), was ethylated and crystallized from $H_2O$ as needles of 3,5-diethyl-4-methyl gallic acid, mp 114°.

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