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SHORT COMMUNICATION

MYRICETIN-7-GLUCOSIDE FROM THE ANDRAECIUM OF THE FLOWERS OF *CALOPHYLLUM INOPHYLLUM*

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Abstract-The andraecium of the flowers of ***Calophyllum inophyllum*** has been found to contain myricetin-7-glucoside, recorded for the first time, along with small quantities of free myricetin and quercetin.

INTRODUCTION

Calophyllum inophyllum L.[1] (Guttiferae) is a moderately sized medicinal tree, found on coastal regions of South India and grown for ornamental purposes. In a preliminary communication,[2] the isolation of a new glycoside of myricetin from the andraecium of its flowers was reported, and the characterization of the glycoside as myricetin-7-glucoside is now given.

RESULTS AND DISCUSSION

The major flavonoid pigment, m.p. 238–240° yielded, on acid hydrolysis, myricetin and glucose in equimolar ratio. The colour reactions* of the glucoside were similar to those of myricetin and different from those of myricetin-3′-glucoside,[3] indicating the presence of a pyrogallol structure in the molecule. The deep yellow colour in the H&hammer-Hansel test indicated a free C-3 hydroxyl, and the positive Wilson boric acid test and the absence of intense UV fluorescence a free C-5-OH. The m.p. and R_f of the pigment (Table 1), were different from all the previously known glycosides of myricetin.[4]

TABLE 1. R_f AND λ_{max} (nm) OF MYRICETIN-7-GLUCOSIDE

	R_f*					λ_{max} (nm) in			
Pigment	HOAc 30%	HOAc 69%	Water satd. phenol	BAW	Forestal	EtOH	EtOH–$AlCl_3$	EtOH–$AlCl_3$ HCl	EtOH–NaOAc
Myricetin-7-glucoside	0.28	0·41	0·35	0.41	0·51	379 260	443	426	390,262
Quercetin-7-glucoside†	0·33	0·50	0.45	0.42	0.61		—	—	— —

* Whatman No. 1, ascending, temperature 28 ± 2°.
† R_f

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[3] A. G. R. NAIR, S. NAGARAJAN and S. S. SUBRAMANIAN, Curr. *Sci.* 33,431 (1964).
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The UV and IR spectra[5] of the glucoside were almost the same as for myricetin (cf. the spectra of myricetin-7-methyl ether and myricetin as well as quercetin-7-glucoside and quercetin). The spectral shifts with NaOMe, NaOAc, $AlCl_3$ and $AlCl_3$/HCl were all in agreement with glycosylation at C-7.[5,6]

Further chemical evidence for the structure of the compound was obtained by complete methylation and hydrolysis. The partial methyl ether (monohydroxypentamethoxyflavone) melted at 250-251" (no Fe^{3+} colour) was different from 3-hydroxy-5,7,3′,4′,5′-pentamethoxyflavone' (m.p. 228-229") and 5-hydroxy-3,7,3′,4′,5′-pentamethoxyflavone[8] (m.p. 144"; alc. Fe^{3+}—deep green). On alkali fission, it yielded 3,4,5-trimethoxybenzoic acid. This established the constitution of the partial methyl ether as 7-hydroxy-3,5,3′,4′,5′-pentamethoxyflavone which showed UV shift (40 nm) with NaOAc, confirming the presence of a free 7-hydroxyl. Thus, the original glucoside was identified, for the first time, as myricetin-7-glucoside.

EXPERIMENTAL*

The fresh andraecium separated from the petals was extracted with hot MeOH and the combined extracts concentrated *in vacuo* with addition of some water towards the end. The aq. concentrate was shaken with petrol (40–60°) and peroxide free ether. The aq. layer kept in an ice-chest for three days deposited a yellow solid which on recrystallization (MeOH–ether) came out as yellow needles, m.p. 238–240° (earlier sintering at 216°), $C_{21}H_{20}O_{13}$, λ_{max} (EtOH) 379, 260 nm. The ether layer contained free myricetin and quercetin, identified by direct comparison with authentic samples.

The glycoside yielded a colourless acetate, m.p. 240-241" (Ac_2O + NaOAc) and methyl ether, m.p. 190-192" (Me_2SO_4 + anhyd. K_2CO_3 in acetone, 40 hr). On acid hydrolysis (7 % H_2SO_4), it yielded myricetin and glucose in equimolar ratio, identified by direct comparison with authentic samples. The methyl ether of the glucoside under the same conditions of hydrolysis-gave 3,5,3′,4′,5′-pentamethylmyricetin, $C_{20}H_{20}O_8$, m.p. 250–251°, λ_{max} (EtOH) 352,274,253 nm. Alkaline fission of the methyl ether gave trimethoxybenzoic acid (m.p. and mixed m.p. 166-168").

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* The compounds recorded above analysed satisfactorily for elements and methoxyl.

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