Phytochemistry, Vol. 20, No. 5, pp. 1167–1168, 1981.
Printed in Great Britain.

0031–9422/81/051167–02 $02.00/0

THE OCCURRENCE OF AURENTIACIN AND FLAVOKAWIN B ON *PITYROGRAMMA TRIANGULARIS* VAR. *PALLIDA* AND *DIDYMOCARPUS* SPECIES

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(*Received* 29 *August* 1980)

Key Word Index—*Pityrogramma triangularis* var. *pallida*; Pteridophyta; frond exudate; *Didymocarpus corchorifolia*; Gesneriaceae; leaf exudate; aurentiacin; flavokawin B; chalcones.

Abstract—The two chalcones, aurentiacin and flavokawin B, were isolated from the frond exudate of *Pityrogramma triangularis* var. *pallida*. In addition, flavokawin B was obtained from the leaf exudate of *Didymocarpus corchorifolia*.

Aurentiacin, 6′-hydroxy-2′,4′-dimethoxy-5′-methylchalcone, is one of five *C*-methylated chalcones known to occur in the free state [1]. It was isolated for the first time from leaves of *Didymocarpus aurantiaca* [2]. We have now detected it as a minor constituent of the farina of *Pityrogramma triangularis* (Kaulf.) Maxon var. *pallida* Weath. Flavokawin B is 6′-hydroxy-2′,4′-dimethoxychalcone. It was first isolated from roots of *Piper methysticum* [3] and later reported from trunk wood of *Aniba riparia* [4]. It has now been identified as an exudate constituent of *P. triangularis* var. *pallida* as well as of *Didymocarpus corchorifolia* Wall.

Two substances, which form orange-yellow crystals, were isolated as minor components of the farina of *P. triangularis* var. *pallida*. This colour indicated that they are chalcones. The UV spectra show a single maximum at 343 nm for both compounds, thus indicating an unsubstituted B-ring [5]. This is corroborated in both cases by the presence of peaks for M − 77 in the MS as well as by the ^{1}H NMR data. These substances appear as dark spots with very high R_f on polyamide and on silica gel (UV 366 nm), turning brown after spraying with 'Naturstoffreagenz A' (β-aminodiethyl ether of diphenylboric acid).

1 has a MW of 298. The ^{1}H NMR signals reveal the presence of one OH group, two OMe groups and one Me group. The OH group is strongly hydrogen-bonded and hence must be placed at C-6′. The two OMe groups can be ascribed to positions 2′ and 4′. Whether the Me is located at C-3′ or C-5′ cannot be decided from the ^{1}H NMR data. The absence of a $AlCl_3$ reaction for the OH at 6′, however, indicates that the Me is at C-5′ and sterically hinders this reaction (cf. [6, 7]). Hence **1** is 6′-hydroxy-2′,4′-dimethoxy-5′-methylchalcone. The identity of **1** with aurentiacin was confirmed by direct comparison with an authentic sample.

The MW of **2** is 14 units lower than that of **1**. The M − 77 peak also is shifted to lower mass by 14 units. According to the ^{1}H NMR data this difference is due to the absence of the Me group. The UV spectra with the usual reagents are almost identical for both compounds, with the exception that $AlCl_3$ causes a bathochromic shift in **2**. Therefore **2** is 6′-hydroxy-2′,4′-dimethoxychalcone. UV spectra and mp are indeed consistent with literature data for flavokawin B [3].

An attempt to find aurentiacin in the leaf exudate of *Didymocarpus* species other than *D. aurentiaca* failed, but led to the discovery of flavokawin B on leaves of *D. corchorifolia*. A small amount of this flavonoid could be isolated by preparative TLC and was shown to be identical with **2**.

The major farina constituents of *P. triangularis* var. *pallida* have been reported previously [6] to be the *C*-methylated flavanones strobopinin, desmethoxymatteucinol and cryptostrobin. With aurentiacin we now record the ninth *C*-methylated flavonoid occurring in *P. triangularis*. This finding underlines once more the outstanding chemistry of this species-complex [7]. Flavokawin B has been found here for the first time as a farina constituent in a gymnogrammoid fern. It may be mentioned that small amounts of pinocembrin also could be detected in the exudate of *P. triangularis* var. *pallida*.

Aurantiacin has been reported earlier as a leaf constituent of *Didymocarpus aurantiaca* [2]. It can be assumed that it is a component of the exudate formed in plants of this genus by glandular trichomes on the lower leaf surface. The benzoquinoid chalcones pedicin, pedicellin, pedicinin and methylpedicinin have been isolated from the 'reddish-brown dust on the underside' of the leaves of *D. pedicellata* [8]. Flavokawin B, however, is reported here for the first time as occurring in the leaf exudate of a *Didymocarpus* species. It is interesting to note that the chalcone pashanone (2′,6′-diOH-4′,5′-diOMe) occurring in roots of *D. pedicellata* [9] also has been found on fertile pinnules of the fern *Onychium siliculosum* [10].

Aurentiacin and flavokawin B have been described as 2′-OH, 4′,6′-diOMe,3′-Me chalcone and 2′-OH,4′,6′-diOMe chalcone, respectively [2–4]. We prefer the enumeration used in the present paper, since it is the 6′-OH, corresponding to 5-OH in flavones and flavonols, that is hydrogen-bonded to the keto group.

EXPERIMENTAL

1 and **2** were isolated from the farina of *Pityrogramma triangularis* var. *pallida* as reported in a previous paper [6]. The material was chromatographed over a column of Si, eluted with toluene and increasing quantities of MeCOEt and MeOH. Both substances were further purified by prep. TLC on Si with a concentrating zone (solvent toluene–MeCOEt, 9:1). They were obtained as orange-yellow crystals from EtOH. Some fractions were rechromatographed over polyamide and purified by prep. TLC on polyamide (solvent: toluene–petrol (bp 100–140°)–MeCOEt–MeOH, 12:3:2:1) to yield pinocembrin, which was identified by direct comparison with an authentic sample.

1 has mp 137–138° (lit. 141° [2]). λ_{max}^{EtOH} nm: 343; + $AlCl_3$: 347; + NaOEt: 340 sh, 260; + NaOAc: 347. MS *m/z* (rel. int.): 298 (M^+, 77), 297 (M − 1, 51), 279 (M − 28, 10), 221 (M − 77, 100), 195 (29). ^{1}H NMR (δ in ppm/TMS): 13.91 (*s*, OH-6′), 8.02–7.41 (*m*, 5 ArH and 2 *trans*-olefinic), 6.29 (*s*, 1 ArH), 3.99 (*s*, 3 H, 1 OMe), 3.93 (*s*, 3 H, 1 OMe), 1.93 (*s*, 3 H, 1 Me).

2 has mp 89–90° (lit. 90–91° [4]). λ_{max}^{EtOH} nm: 343; + $AlCl_3$: 365 (370 after 10 min); + NaOEt 405 sh, 293 sh, 265; + NaOAc: 342. MS *m/z* (rel. int.): 284 (M^+, 20), 283 (M − 1, 16), 256 (M − 28, 6), 20 (M − 77, 29), 181 (11), 43 (100). ^{1}H NMR (δ in ppm/TMS): 13.29 (*s*, OH-6′), 7.70–7.28 (*m*, 5 ArH and 2 H, *trans*-olefinic), 6.15 (*s*, 2ArH), 3.93 (*s*, 3 H, 1 OMe), 3.84 (*s*, 3 H, 1 OMe).

Some plants of *Didymocarpus corchorifolia* were cultivated in a greenhouse at the Botanischer Garten der TH Darmstadt. Freshly collected leaves were rinsed with Me_2CO and the solution was evapd to dryness. The crude exudate material was then chromatographed over a small column of polyamide and the first fractions were further purified by prep. TLC on polyamide. The amount of chalcone isolated was just sufficient to run the UV spectra and for direct TLC comparison with **2**. Thus the identity with flavokawin B was confirmed.

Acknowledgements—We thank Dr. C. D. MacNeill, Mrs. G. Prlaine and J. Lattie (all Oakland, Calif.) for collecting the fern material. Thanks are also due to Dr. G. Schilling (Heidelberg, West Germany) for measuring the ^{1}H NMR spectra, Dr. N. Adityachaudhury (Kalyani, India) for a sample of aurantiacin, and B. L. Burtt and the Regius Keeper of the Royal Botanic Garden at Edinburgh (Scotland) for shoot tips of *Didymocarpus corchorifolia*.

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