Phytochemistry, 1978, Vol 17, pp 1680–1681 © Pergamon Press Ltd Printed in England 0031–9422/78/0901–1680 $02 00/0

OKANIN 4′-*O*-DIGLUCOSIDE FROM *COREOPSIS PETROPHILOIDES* AND COMMENTS ON ANTHOCHLORS AND EVOLUTION IN *COREOPSIS*

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(*Received* 22 *February* 1978)

Key Word Index—*Coreopsis*; Compositae; anthochlor; new chalcone; okanin 4′-*O*-diglucoside; plant evolution.

Abstract—A new chalcone glycoside, okanin 4′-*O*-diglucoside, is identified from the ray florets of *Coreopsis petrophiloides*. The known distribution of anthochlors in *Coreopsis* indicates that two of the most primitive sections produce in their floral parts complex glucosides of butein (and sulfuretin). The more advanced sections synthesize the monoglucosides of okanin (marein), butein (coreospin) and lanceoletin (lanceolin) and their corresponding aurones. The co-occurrence of marein and lanceolin is thus far restricted to members of sect. *Coreopsis*.

I report the isolation of okanin 4′-*O*-diglucoside from the ray florets of *Coreopsis petrophiloides* collected in Mexico. The compound was similar to marein (isolated from *Coreopsis gigantea* [1] and also present in the ray florets of *C. petrophiloides*) on paper in that it appeared black in UV light and changed to a brownish-orange with NH_3. The R_f values were lower than marein in TBA (0.18 vs 0.34) but higher in 15% HOAc (0.28 vs 0.23) thus suggesting the presence of an additional sugar. Complete acid hydrolysis gave only okanin and glucose. Partial acid hydrolysis gave marein in addition to okanin. Treatment with β-glucosidase produced okanin. The UV spectral properties are essentially identical to those of authentic marein from *Coreopsis gigantea* [1]. These data suggest that the compound is an okanin 4′-*O*-diglucoside, which appears to be a new natural product [2]. Traces of the corresponding aurone (maritimetin 6-*O*-diglucoside) were also detected.

Several comments on anthochlor distribution and systematic relationships in *Coreopsis* are in order. The section of *Coreopsis* viewed as most primitive on the basis of morphology and chromosome number (namely the Mexican sect. *Electra*, which includes *Coreopsis mutica* DC.) consists of plants producing an array of butein and sulphuretin glucosides including acylated glucosides [3, 4]. In addition, the rather primitive section *Anathysana* produces the same array of sulphuretin glucosides as is found in sect. *Electra* [4]. The sect. *PseudoAgarista*, of which *Coreopsis petrophilocides* is a member, is viewed as rather primitive in the genus, but morphological considerations suggest it is not closely related to either sect. *Electra or Anathysana* [3, 5]. Anthochlor chemistry supports this interpretation because sect. *PseudoAgarista* lacks the complex butein-sulphuretin glycosides; instead the flowers contain coreopsin-sulphurein, and in addition marein-maritimein as well as the above-described okanin 4′-*O*-diglucoside. Earlier reports of chalcones and aurones in *Coreopsis* are from species which are considered to be evolutionarily advanced relative to the three sections already mentioned [3] and it is of interest that all are simple monoglucosides [2]. Thus the primitive plants have the more complex glycosylation patterns. The only additional common chalcone in *Coreopsis* is lanceolin, which is the 3′-methyl ether of marein. This chalcone and the corresponding aurone leptosin were reported from *Coreopsis lanceolata* and *C. saxicola* [7]. Recently, Harborne [8] reported the presence of both marein and lanceolin from *Coreopsis nuecensis* Heller, the first report of their co-occurrence in the genus. As part of a current and continuing survey of flavonoids in *Coreopsis* on a worldwide basis, the ray florets of *C. lanceolata* have now been examined and found to contain both marein and lanceolin in large quantities. In the original report on the isolation of anthochlors from *C. lanceolata*, no mention was made of the presence of marein [6]. The report of lanceolin in *C. neucensis* together with its known occurrence in *C. lanceolata*, *C. saxicola* and *C. grandiflora* (the corresponding aurone leptosin was reported for this species, but it is to be expected that lanceolin is also present) is of systematic significance because all four taxa are assigned to sect. *Coreopsis* [3], and lanceolin-leptosin have thus far not been reported in species of other sections. Additional sampling must be done to determine whether this anthochlor pair is restricted to sect. *Coreopsis*.

EXPERIMENTAL

Plant material. Plants were either collected in the field or greenhouse-grown from seed. Voucher specimens are in the herbaria at The University of Iowa and the University of Wyoming. Compounds were isolated by the standard procedures of PC. Marein was identified by comparison of spectral and chromatographic properties with authentic marein from *Coreopsis gigantea*. Lanceolin was identified by spectral and chromatographic properties. All glycosides were acid hydrolyzed, and the sugars recovered and identified by co-chromatography against standards using TLC with Si gel H. The aglycones were analyzed spectrally and run against standards in at least three solvent systems. Glycosides were hydrolyzed with β-glucosidase to okanin and lanceoletin.

Acknowledgements—This research was supported in part by NSF grants GB-20793X, BMS 74-21384 and DEB 77-21727.

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Phytochemistry, 1978, Vol. 17, pp 1681–1682 © Pergamon Press Ltd Printed in England 0031/9422/78/0901-1681 $02 00/0

FLAVONOIDS OF *ALBIZIA ADIANTHIFOLIA*

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(*Received* 30 *January* 1978; *received for publication* 17 *March* 1978)

Key Word Index—*Albizia adianthifolia*; Leguminosae; 3,4,2′,3′,4′-pentahydroxychalcone; 3,7,8,3′,4′-tetrahydroxyflavone; 3,7,8,3′,4′-tetrahydroxyflavanone.

INTRODUCTION

Eleven trees of the *Albizia* genus (Leguminosae) are indigenous to South Africa [1]. Of these *A. adianthifolia* (Schumach) W. F. Wight, with its umbrella-like crown, is characteristic of the Natal coastal bush. The golden-yellow wood is of little industrial importance, while the toxic bark is used by some of the African population in a 'love potion'. It was observed during milling that the wood dust caused considerable respiratory discomfort, a property shared with *A. suluensis* and *A. tanganicensis* [2].

A sample of the wood of *A. adianthifolia* was examined and three flavonoids, 3,4,2′,3′,4′-pentahydroxychalcone (okanin), 3,7,8,3′,4′-tetrahydroxyflavone (melanoxetin) and a dihydroflavonol (**1**), were isolated, the last being in greatest abundance. The properties of **1** were similar in several respects to those of 3,7,8,3′,4′-tetrahydroxyflavanone, originally isolated from *Acacia excelsa* and characterized by Clark-Lewis *et al.* [3, 4]. The reported occurrence of the dihydroflavonol **1** in the heartwood of *Albizia odoratissima* [5] was disputed [4] since its identification was based not upon the isolation of the compound but upon the formation of the pentamethyl ether on methylation of a brown gum. Such methylation of a dihydroflavonol to a 3-methoxyflavanone is without precedent. Under normal methylating conditions dihydroflavonols undergo dehydrogenation and subsequent methylation to give 3-methoxyflavones [6]. This communication reports the results of investigations to establish the identity of **1** and the fact that in our hands one of the products obtained on methylation of the dihydroflavonol **1** was indeed the 3-methoxyflavanone.

RESULTS

From colour tests (violet with either MgHCl or Zn–HCl [7, 8] and a +ve Pacheco reaction [7]) and from the appearance and behaviour of the UV spectrum in various media [9], it was inferred that **1** was a 5-deoxydihydroflavonol. In support of this, the PMR spectrum exhibited 1H signals as doublets at δ(DMSO-d_6) 4.39 and 4.98, J = 11 Hz each, assigned to C-3 and C-2 respectively, and at 6.56 and 7.18, J = 9.0 Hz each, assigned to C-6 and C-5 respectively. A mass ion of m/e 304 (M^+ 16 %) was consistent with $C_{15}H_{12}O_7$. The PMR spectrum of the acetate revealed the presence of 5 × —OCOMe thus defining the degree of hydroxylation in the parent compound. In the same spectrum, 1H signals at $\delta(CDCl_3)$ 5.40 and 5.70, each a doublet with J = 12 Hz, confirmed the reduced state of the C-2, C-3 bond.

Methylation of **1** (DMS–Me_2CO–K_2CO_3) under N_2 on a steam bath for 6 hr, provided a mixture of 5 compounds. Of these, 3 were predominant, each displaying a different colour when sprayed with *p*-anisaldehyde–H_2SO_4 on TLC. Two of these components were isolated by PLC. The most abundant was identified as 3,7,8,3′,4′-tetramethoxyflavanone on the basis of its spectral data (UV, PMR, MS), which agreed closely with published data [10, 11], notwithstanding the marked difference in mp with that published [10, 12] (our value 174°: lit. 166°).

The second methylation product was recovered as colourless needles, mp 149°. Apart from small differences the PMR spectrum was consistent with that reported for 3,7,8,3′,4′-pentamethoxyflavanone [10] obtained as needles mp 138.5° [11]. The UV spectrum (MeOH) displayed inflections at 232, 259 nm and a maximum at 286 nm, while the MS gave a mass ion at m/e 374 (M^+ 18 %) with a base peak at m/e 194.

The third methylation product exhibited TLC properties (R_f and colour) identical with those of the pentamethoxyflavone derived from 3,7,8,3′,4′-tetrahydroxyflavone.

From the above evidence, it is concluded that the dihydroflavonol, **1**, is identical with 3,7,8,3′,4′-tetrahydroxyflavanone. The formation of the pentamethoxy derivative during methylation, was unexpected [4].