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ON THE OCCURRENCE OF ACYLATED FLAVONOID AGLYCONES

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Abstract—The known acylated flavonoid aglycones are reviewed. Their substitution patterns and their distribution in plants are discussed briefly. A new pair of flavonol esters is reported in *Notholaena candida* var. *candida*, the acetate and butyrate of isognaphalin.

INTRODUCTION

Acylated flavonoid *O*-glycosides occur scattered within angiosperms, gymnosperms and ferns, and an increasing number of such compounds are being reported [1]. The acyl substituents found in flavone and flavonol glycosides include aliphatic acids, such as acetic, malonic and succinic acids, as well as aromatic acids, such as benzoic, gallic, *p*-coumaric, caffeic and ferulic acids [1]. A series of acylated *C*-glycosides are also known [2]. In both types of glycoside, acylation takes place at the sugar moiety. Compounds acylated at the flavonoid nucleus itself are rare.

RESULTS AND DISCUSSION

The first free aglycone to be found in acylated form was the 3-acetate of pinobanksin 7-methyl ether (alpinone) from seeds of *Alpinia japonica* (Zingiberaceae) [3]. Only 20 years later the next flavanonol acetate was reported, namely the 3-acetate of pinobanksin itself. This compound ('P-20') was found in bud excretion of some 15 species and hybrids of *Populus* (Salicaceae) [4, 5]. Consequently, it may be present also in propolis [Weigel, H. and Wollenweber, E., unpublished results]. Recently we found this same acetyl flavanonol in the leaf gland excretion of *Comptonia peregrina* (Myricaceae) [6]. Aromadendrin 3-acetate was tentatively identified in aerial parts of *Ageratina espinosara* (Asteraceae [7] and later it was isolated from seeds of *Aframomum pruinosum* (Zingiberaceae) along with the 3-acetate of aromadendrin 7-methyl ether [8]. Naringenin 3-acetate and eriodictyol 3-acetate were found in aerial parts of *Baccharis varians* (Asteraceae) [9] and the 8-acetate of isowogonin (5,8-dihydroxy-7-methoxyflavanone) was isolated from the frond exudate of the fern *Notholaena neglecta* [10]. This was, by the way, the first report of the natural occurrence of this synthetically long known [11] flavanone. One acetylated isoflavone is also known: 7-hydroxy-2-*C*-methyl-8-acetoxyisoflavone was isolated from roots of *Glycyrrhiza glabra* (Leguminosae) [12].

Acylated 7,4′-dimethylherbacetin, isolated from the farinose frond exudate of the fern *Notholaena affinis* [13], was the first acylated flavonol and also the first natural butyryl flavonoid to be described. The corresponding acetyl derivative was detected only in trace amounts in this material [14]. In further species of *Notholaena*, acetates and butyrates of flavonols were also found jointly, in varying proportions, appearing as twin spots on chromatograms [15]. The flavonols involved are 8-hydroxygalangin 7-methyl ether (in NG—1/2), herbacetin 7-methyl ether (in NAS—1/2), herbacetin 7,4′-dimethyl ether (in NA—1/2), gossypetin 7,4′-dimethyl ether (NA—3/4) [16], gossypetin 3,7,3′-trimethyl ether (NAS—4) and 5,8-dihydroxy-3,7,2′,3′,4′-pentamethoxyflavone (NAS—5) [17]. We found a new twin pair of esters, namely the acetate and butyrate of isognaphalin (5,8-dihydroxy-3,7-dimethoxyflavone) in the farinose frond exudate of a distinct population of *Notholaena candida* var. *candida* (see Experimental). Unusual flavonol esters were reported from aerial parts of *Gutierrezia dracunculoides* (Asteraceae) [18]. They are the 4′-*O*-methylbutyrate and the 4′-*O*-isovalerate of quercetin 3,3′-dimethyl ether.

This survey on acylated flavonoid aglycones is probably incomplete. However, there are clearly two trends in their natural distribution. There is one group of compounds formed by the 3-*O*-acetates of flavanones and dihydroflavonols, occurring scattered in higher plants, and there is a group of flavonols which, until today, appear to be restricted to the fern genus *Notholaena*. These latter all are 8-hydroxyflavonols, methylated in position 7 and esterified with either acetic or butyric acid in position 8. There is a 7-methoxy-8-acetoxyflavanone from *Notholaena* that forms a kind of link between both groups. The isoflavone from *Glycyrrhiza* also appears related formally to the first group by its 8-acetoxy substitution, while only the two esters of dimethylquercetin from *Gutierrezia* seem to be 'outsiders'. It is striking that, among the acylated flavonoid aglycones known to date, there is none with an aromatic acid as acyl moiety and no acylated flavone has yet been found. However, most of the acylated flavonoid aglycones now known were reported very recently, so it can be assumed that more new types will soon be found.

EXPERIMENTAL

Notholaena candida var. *candida* was collected on Highway 135, SE. of Tehuacan, Mexico (Edo Oaxaca) on 8 May 1983 It is rather abundant at this site on dry rocky limestone slopes. Fronds were clipped from the plants and air-dried in a paper bag. Vouchers (Yatskievych and Wollenweber 83–156) are kept at Bloomington, Indiana and at Darmstadt. The farinose exudate was recovered by dipping the fronds in Me_2CO for a short time. Fern fronds (360 g) yielded 9 g exudate material (2.5 % dry wt). A relatively large amount of the flavonol galangin 3-methyl ether crystallized from the concd soln and was filtered off The remainder was subjected to CC on Si eluted with toluene and increasing amounts of MeCOEt and MeOH. Galangin and kaempferol 3-methyl ether were then identified in polar fractions and more galangin 3-methyl ether was isolated. Several fractions also contained terpenoids which have, as yet, not been studied further. Some of the non-polar fractions yielded light yellow crystals that on TLC showed two spots of similar R_f [Polyamide DC-11, toluene–petrol (100–140)–MeCOEt–MeOH (30:90:2:1.5): **1** at 0.78, **2** at 0.69; Si, toluene–MeCOEt (9:1): **1** at 0.72, **2** at 0.67] and identical colour behaviour (dark in UV_{366}, brownish with NA). The two components were separated by prep. TLC on Si. Compound **1** mp 181–182°; **2**, mp 244–246° (from EtOH). The UV spectra of both products are identical (λ_{max}^{MeOH} nm: 351, 271; $\lambda_{max}^{AlCl_3}$ nm: 408, 331, 282, $\lambda_{max}^{AlCl_3+HCl}$ nm: 405, 326, 281; λ_{max}^{NaOH} nm: 385, 283; λ_{max}^{NaOAc} nm: 350, 270). In the MS, **1** exhibits $[M]^+$ at m/z 384 and **2** at m/z 356, while for both products the fragmentation at lower m/z values is identical (m/z 313, 295, 271, 241, 181, 153, 115, 105, 89, 77, 69). This indicates that these compounds are the butyrate (**1**) and the acetate (**2**) of the same flavonoid. As a matter of fact, hydrolysis (HCl, boiling HOAc) yields a known flavonol, which is identified by co-TLC with an authentic marker as well as by its UV and MS to the 3,7-dimethyl ether of 8-hydroxygalangin (isognaphalin) [19].

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