

Investigations on *Hoya species*.

VIII*. Leaf Flavonols and Di-C-glycosylflavones

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Nine *Hoya* species were investigated for their leaf flavonoids. Four species contained flavonols identified as the 3-diglycosides of kaempferol and/or isorhamnetin, in some species acylated with ferulic and/or *p*-cumaric acid. Five species had no flavonols but were rich in flavones. Identified were: schaftoside, isoschaftoside, di-C-arabinosylapigenin and vicenin 2.

Introduction

Relatively little is known of the leaf phenolics of the Asclepiadaceae [1]. In an investigation of thirty Asclepiadaceae Kozjek *et al.* [2] found them rich in flavonols, with kaempferol and quercetin derivatives as main constituents. Tri-hydroxylated phenolics and C-glycosylflavones were not found. In Utrecht investigations on Asclepiadaceae are restricted to the genus *Hoya* [3–5]. Surprisingly, only in a few species flavonols could be detected, in most species only flavones were found [5, 6]. From a systematic point of view *Hoya* is a rather difficult genus. A reliable systematic monograph of the genus does not exist; quite a number of species are cultivated for ornamental purposes, very often under incorrect names. Phytochemistry may be very helpful in distinguishing *Hoya* species and it has been shown that the latex triterpenes are very promising in this connection [5]. Flavonoids may at least be used for a sub-classification in the genus, based on the presence of respectively apigenin mono- and di-C-glycosides, apigenin-O-glycosides and flavonols [5]. The present investigation is meant to obtain insight in the variation within the group of flavonol, respectively di-C-glycosylflavone-containing species.

Materials and Methods

Fresh leaves were used, obtained from plants cultivated in the greenhouses of the Botanical Laboratory of the University of Utrecht. Most of them are cuttings originating from the Botanic Gardens of Heidelberg, Utrecht, Frankfurt, Gent and München. The nine species, *Hoya bandaensis* Schlechter, *H. bella* Hook., *H. gonoloboides* Regel, *H. imperialis* Lindl., *H. lacunosa* Blume, *H. minima* Cost, *H. motoskeii* Teysm., *H. multiflora* Blume, and *H. polyneura* Hook., were kept under the name attached to them when they were obtained. Specimens were deposited in the Herbarium of the University of Utrecht.

The leaves were extracted with acetone. After filtration and addition of water, lipophilic compounds were removed by extraction with ligroin. The acetone-water extract was concentrated, acidified to pH 2–3 and extracted with butanol. The butanol extract was evaporated to dryness and the residue was taken up in methanol and further purified by band-chromatography on paper with 15% acetic acid and tert. butanol-acetic acid-water 3:1:1, sometimes followed by further purification in other solvent systems. Isolated compounds were classified and/or identified by colour, R_f values, UV spectrum inclusive shifts, often by comparison with the authentic substance, and by analysis of their acid and/or alkaline hydrolysis products. The di-C-glycosylflavones were compared both as such and after permethylation (Si gel TLC with chloroform-ethyl acetate-acetone 5:4:1) with the authentic referent. Mass spectra were taken of most of the permethylated glycosylflavones [7].

Results and Discussion

In a previous investigation [5] it was shown that only four *Hoya* species (out of twenty-five) contained flavonols in their leaves, *H. bandaensis*, *H. bella*, *H. imperialis*, and *H. multiflora*. From *H. bandaensis* leaves the 3-rutinosides of kaempferol and isorhamnetin were now isolated in addition to apigenin-7-rutinoside. The last component is the main flavone of several other *Hoya* species. Previously, in *H. bella* leaves kaempferol-3-arabinosylglucoside and the ferulyl derivatives of kaempferol- and isorhamnetin-3-(di)glycosides were found [8]. *H. imperialis* leaves possessed one main flavonoid

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which was identified as kaempferol-3-diglucoside. In *H. multiflora* flavonoids were almost absent, the traces present consisted of the ferulyl- and *p*-cumaryl derivatives of kaempferol-3-rutinoside.

Of the di-C-glycosylflavones 6-C-glucosyl-8-C-arabinosylapigenin (schaftoside) and 6-C-arabinosyl-8-C-glucosylapigenin (isoschaftoside) were generally present like in *H. lacunosa* (in addition to 6,8-di-C-arabinosylapigenin and a C-hexosyl-C-pentosylluteolin derivative) [9], *H. minima* (in addition to vicianin 2 (= 6,8-di-C-glucosylapigenin)), and *H. motoskeii*. *H. gonoloboides* leaves contained isoschaftoside and an O-methyl ether of a 6,8-di-C-pentosylluteolin. Vicianin 2 was isolated from *H. polyneura*.

Based on their flavonoids alone the species within the flavonol group appear rather similar. *H. bandaen-*

sis seems to take an intermediate position between the flavonol group and that with apigenin-O-glycosides. Apigenin-7-O-rutinoside (and mainly also the 7-O-glucoside) was also isolated from *H. australis* R. Br. ex Traill. [4], *H. coronaria* Blume, *H. globulosa* Hook. and *H. ovalifolia* Wight & Arn. Also, in the group of species with di-C-glycosylflavones the variation appears rather small, with schaftoside and isoschaftoside as common constituents. It thus seems that the flavonoids of *Hoya* species are well suited for a sub-classification in the genus, but not for identification on the species level.

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