Investigations on Hoya Species.  
III. Leaf Phenolics and Latex Lipids of Hoya lacunosa Bl. * 

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Hoya lacunosa, Asclepiadaceae, C-Glycosylflavonoids, Latex, Triterpenoids, 4-α-Methylsterols  

Hoya lacunosa leaves contain some main C-glycosylflavonoids, which were identified as: 6-C- 
arabinosyl 8-C-glucoisopyllogigenin (isoschaftoside), 6-C-glucosyl 8-C-arabinosylapigenigenin (schaftosi- 
de) and 6,8-di-C-arabinosylapigenigen. In the latex triterpenols were found, often both free and in 
ester form, of which β-amyrin, α-amyrin, lupeol, 24-methylene cycloartenol, obtusifoliol and cyco- 
eucalenol were identified in the free alcohol fraction. The esters, forming the major part of the to- 
tal lipid fraction, were solely acetates of some of the above mentioned alcohols.  

Introduction  

A number of Asclepiadaceae have been investigat- 
ed for their chemical constituents, but comparative- 
ly little is known of the genus Hoya [1, 2]. The only 
species investigated in some detail are H. australis 
and H. bella. H. australis has been analysed for latex 
lipids and wax components [3 — 5]. In the latex both 
free triterpenols and their esters were present. The 
main free alcohols are β-amyrin, α-amyrin, cycloar- 
tenol and 24-methylene cycloartenol, whereas esteri- 
fication occurs mainly with cinnamic acid and to a 
lesser extent with acetic acid. H. bella latex differs in 
its composition, not only in the presence of the free 
alcohols lupeol and isobaureno, found in addition 
to β-amyrin and cycloartenol, but also by the occur- 
rence of propionate acids and isovaleroates of these triter- 
penols [2]. Less is known of the leaf phenolics of the 
two species; H. australis contains large amounts of 
chlorogenic acid [3], some other phenolic depsides 
and apigenin and luteolin derivatives (O-glycosids) [16]. H. bella is rich in acetylated flavonol glycosides 
esterified with ferulic acid, the latter also was found 
in free form in young leaves [2].  

Chlorogenic acid has previously been found in 
leaves of H. bandanensis [6]. In a general screening for 
flavonoids in Asclepiadaceae Kozjek et al. [7] indi- 
cate the presence of leucocyaninid and the possible 
ocurrence of quercetin and kaempferol in H. carno- 
sa leaves. In their discussion they emphasize the ab-

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Fig. 1. HPLC analysis of *Hoya lacunosa* leaf phenolics. V = referent vitexin, 1. 2 and 8 are unknown, 3 = a C-hexosyl C-pentosyllumetolin, 4 = schaftoside mixed with a phenolic depside, 5 = the glucose ester of ferulic acid, 6 = 6,8-di-C-arabinopyranosylapigenin and 7 = isoschaftoside.

Fig. 2. Gas-chromatogram of the unsaponified total lipid fraction of *Hoya lacunosa* latex on a 3% SE 30 column, temperature-programmed at 2 ° min from 200 – 300 °C. Internal standard 5-z-cholestanone. 1. 2 and 3 are unknown homologues, 6 = obtusifoliol, 7 = z-amyrin, 8 = a mixture of cy­cloeucalenol, z-amyrin and lupeol, 9 = 24-methylenecycloar­tanol + z-amyrin acetate, 10 = a mixture of z-amyrin acetate and lupeol acetate. Other peaks were not identified. See also Table I.

### Table I. Identification of triterpenoids from *Hoya lacunosa* latex.

<table>
<thead>
<tr>
<th>Total lipid peak</th>
<th>M+</th>
<th>Fractions obtained after Al2O3 and TLC separation main fragments</th>
<th>base peak</th>
<th>identity</th>
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<tr>
<td>No.</td>
<td>RT [240 °]</td>
<td>%</td>
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<td></td>
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<tr>
<td>1</td>
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<td>0.4</td>
<td>378</td>
<td>378 350 281</td>
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<tr>
<td>2</td>
<td>1.19</td>
<td>0.7</td>
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<td>3</td>
<td>1.62</td>
<td>0.1</td>
<td>434</td>
<td>434 280 354 221 210 250</td>
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<tr>
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<td>386</td>
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<tr>
<td>5</td>
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<td>tr</td>
<td>426</td>
<td>218 203 424 189 190 426 217 219 205</td>
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<tr>
<td>6</td>
<td>2.67</td>
<td>tr</td>
<td>426</td>
<td>411 426 245 410 201 233 327 227 393</td>
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<tr>
<td>7</td>
<td>2.83</td>
<td>tr</td>
<td>426</td>
<td>218 203 219 189 426 190</td>
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<tr>
<td>8</td>
<td>3.05</td>
<td>17</td>
<td>426</td>
<td>408 393 175 411 189 300 426 409 301</td>
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<td>9</td>
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<td>22</td>
<td>440</td>
<td>422 300 407 440 175 203 216 379</td>
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<td>10</td>
<td>4.15</td>
<td>52</td>
<td>468</td>
<td>218 203 242 217 406 391 189 191</td>
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<tr>
<td>12</td>
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<td>3.3</td>
<td>482</td>
<td>273 175 408 285 393 409 203 365</td>
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<td>tr</td>
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<td>494 74 87 75 143 495 199</td>
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<tr>
<td>15</td>
<td>sh.</td>
<td>tr</td>
<td>494</td>
<td>494 74 87 75 143 495 199</td>
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</table>

*Except for peak 14, above m/e 170, in order of decreasing intensity.*
Results and Discussion

From a first PC screening of its butanol extract H. lacunosa appeared quite different from the previously investigated species H. bella and H. australis, but rather similar to H. multiflora Bl. With most solvents the two species (H. l. and H. m.) showed two distinct flavonoid spots and one major phenolic depside. On further analysis the flavonoids of H. lacunosa appeared mainly of the di-C-glycosylapigenin type, identified as: schaftoside (6-C-glucosyl 8-C-arabinosylapigenin) [14], 6,8-di-C-arabinopyranosylapigenin [15], and isoschaftoside (6-C-arabinosyl 8-C-glucosylapigenin). More flavonoids were present, but finally their concentration was too low for complete identification. Evidence was obtained, however, for the occurrence of C-hexosyl C-pentosyl luteolin derivatives.

A good HPLC separation of the mixture was not obtained (see Fig. 1), partly because the phenolic depsides elute in the same area as the C-glycosides. Of the eight phenolics indicated, 1, 2 and 8 remained unidentified, 3 = a C-hexosyl C-pentosylluteolin derivative, 4 = schaftoside which co-chromatographs with a phenolic depside, 5 = a glucose ester of ferulic acid, 6 = 6,8-di-C-arabinopyranosylapigenin and 7 = isoschaftoside.

Compared with H. australis and H. bella, H. lacunosa shows a comparatively simple latex composition of which a gas chromatogram of the total lipid extract is given in Fig. 2. Mass spectral data, obtained after further separation by Al₂O₃ and TLC, are summarized in Table I. A surprising lack of esters other than acetates, exists, although, like in other Hoya species, esters form the major part (about 80%) of the total latex lipid (compare: H. australis 74% esters, of which, however, 57.7% cinnamates). On further analysis β-amyrin, α-amyrin, lupeol and 24-methylencycloartanol were identified from the free triterpenol fraction (9.5%). The ester fraction contained the acetates of the first three triterpenols. Sterols could not be detected, but 4-α-methylsterols (7.5%) were present, two of which were identified as obtusifoliol and cycloeucalenol.

It thus seems that both in its latex composition and in the phenolic leaf composition H. lacunosa again is fundamentally different from the previously investigated Hoya species. In the phenolic region it is quite distinct from H. bella with its acylated flavonol glycosides. H. australis is more difficult to evaluate because high concentrations of chlorogenic acid tend to mask the low concentrations of flavonoids present. Most of its flavonoids are O-glycosides [16] contrary to the C-glycosides of H. lacunosa. The occurrence of C-glycoflavones also contradicts the concept of Kozjek et al. [7] of a special place of the Asclepiadaceae within the Contortales based on among others the absence of those compounds. For its latex a marked distinction of H. lacunosa is found in the simple esters composition, the triterpenols found belong to the common, rather ubiquitous type, although generally lupeol and α-amyrin were not found together in Hoya species.

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