# Structural Revision of Some Recently Published Iridoid Glucosides

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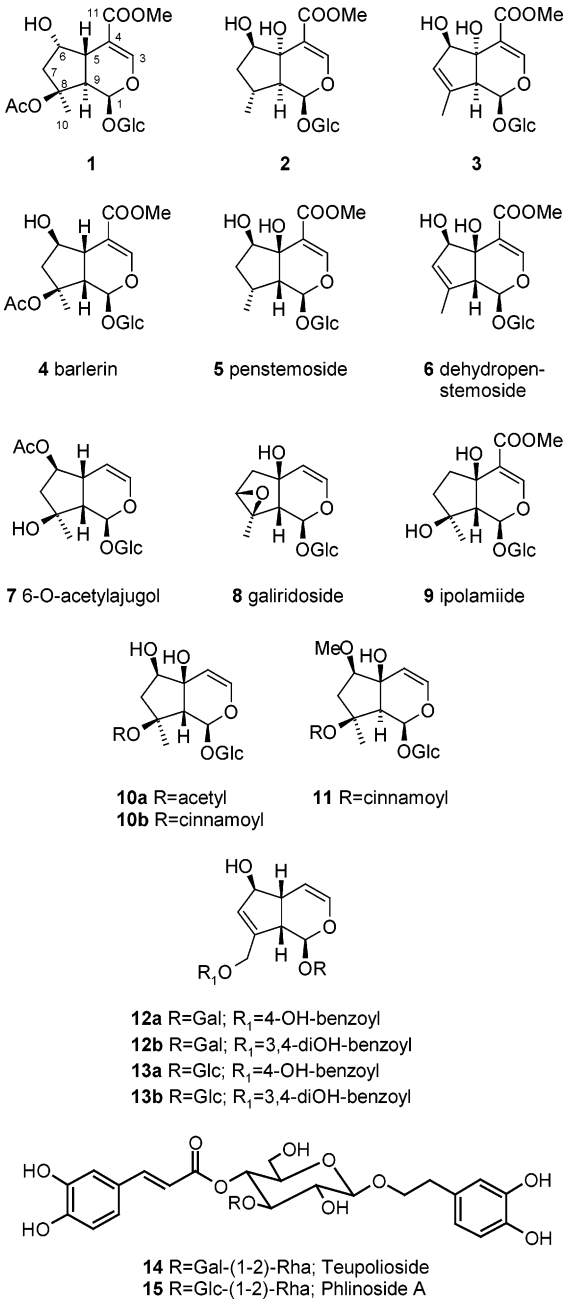
The structures of six different iridoid glucosides have been revised. Three compounds isolated from *Eremostachys glabra* and designated 6,9-*epi*-8-*O*-acetylshanziside (**1**), 5,9-*epi*-penstemoside (**2**), and 5,9-*epi*-7,8-didehydropenstemoside (**3**) have been shown to be identical to the known iridoids barlerin (**4**, 8-*O*-acetylshanziside), penstemoside (**5**), and 7,8-didehydropenstemoside (**6**), respectively. Another compound named harpagoside-B, isolated from *Scrophularia deserti* and proposed to be 9-*epi*-6-*O*-methylharpagoside (**11**), was demonstrated from the spectroscopic data given to be the known harpagoside (**10b**). Finally, two alleged iridoid galactosides from *Buddleja crispa* named buddlejosides A and B (**12a** and **12b**) have been shown to be the corresponding glucosides; the former is identical to agnuside (**13a**), while the latter is 3,4-dihydroxybenzoylaucubin (**13b**), an iridoid glucoside not previously published. This clearly showed that care should be taken with the interpretation of NOEs involving bridgehead protons in iridoid structures because they can be capricious and lead to erroneous structural assignments.

It is a dogma in organic chemistry that if the NMR spectra of two compounds are identical, then the compounds are identical (or enantiomers). That this is indeed the case also for iridoid glucosides has been demonstrated in several papers where it has been shown that epimeric pairs can easily be distinguished, particularly by $^{13}C$ NMR.[1−6] The increasing use of 2D NMR techniques permits a full structure elucidation of many such compounds, rendering chemical correlations almost superfluous. However, the apparent simplicity of these techniques has also given rise to a number of errors in structural assignments mainly due to incorrect data interpretation. Herein, we are demonstrating that this has been the case for six erroneously assigned structures of iridoid glucosides published in recent years.

**Compounds from *Eremostachys glabra.*** Delazar et al.[7] isolated three iridoid glucosides from *E. glabra* (Lamiaceae). The unusual structures 6,9-*epi*-8-*O*-acetylshanziside (**1**), 5,9-*epi*-penstemoside (**2**), and 5,9-*epi*-7,8-didehydropenstemoside (**3**) were assigned to these compounds. A variety of facts make these structures unlikely: (i) The genus *Eremostachys* is closely related to *Phlomis*,[8] a genus from which the three corresponding "normal" iridoids **4**−**6** have been reported. (ii) The relative configuration at C-1, C-5, and C-9 has been the same in all published iridoid structures, except for a few examples with C-5α-substituents in compounds from *Penstemon* species,[5,6,9,10] in one case confirmed by X-ray crystallography,[5] as well as for a single one with a C-9α-hydrogen based on less than convincing evidence[11] (see below). Most important, (iii) the NMR spectra given for the "new" compounds (**1**−**3**) were almost identical to previously published spectra of **4**−**6**, allowing for the different solvents used. We will discuss the evidence for the structures of the three compounds separately.

Regarding compound **1**, Delazar et al.[7] found that "all the $^{1}H$ and $^{13}C$ NMR signals were comparable to those of 8-*O*-acetylshanziside methyl ester" (**4**; the trivial name for this compound is barlerin[12]). However, only a single reference to NMR data for **4** was given,[13] despite the fact that detailed spectra of **4** had been published several times,[14−19] not only with $D_2O$ or DMSO-$d_6$ as solvents but also in $CD_3OD$.[14,16,17] It is apparent from the NMR data reported by Delazar et al.[7] that the spectra were acquired in $CD_3OD$ although $D_2O$ was the solvent specified by the authors. Due to some dissimilarities in the $^{1}H$ NMR spectra compared with the published data (recorded in $D_2O$),[13] it was concluded that the new compound could be different from barlerin. The fact that NOE

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interactions between H-1, H-9, and 10-$CH_3$ as well as between H-5 and H-6 could be observed led Delazar to conclude that the former set of protons was placed on the α-face of the molecule, while the second pair was placed on the *β*-face. Consequently, it was concluded that the structure of the isolated compound was 6,9-*epi*-8-*O*-acetylshanziside methyl ester (**1**). In the discussion, it was ignored that the specific rotation, $[\alpha]_D^{20}$, of **1** was determined as −84, well within the range of that reported for barlerin (**4**), i.e., −75 to −88.[13−16,18,19] In our hands, the $[\alpha]_D^{33}$ value for **4** was determined as −79.

In the case of compound **2**, Delazar et al.[7] concluded that "the spectroscopic data were almost identical to those published for penstemoside" (**5**).[20,21] "However, the $^1$H−$^1$H NOESY spectrum of **2** revealed NOE interactions among the protons leading to the identification of **2** as an epimer of penstemoside." For this compound, the authors again find interactions between H-1, H-9, and 10-$CH_3$ and also between H-6 and 10-$CH_3$, and they conclude that these are all on the α-face of the molecule. Finally, the authors argue from the chemical shift of H-9 that the 5-OH group must be positioned on the α-face in **2**, although it is not entirely clear why this should be the case. The specific rotation for **2** was $[\alpha]_D^{20}$ −91, very similar to that reported for **5**, namely, −100,[20] the other reported value being −171.[21] However, our sample of **5** showed −167.

For compound **3**, Delazar et al.[7] found that the "$^1$H and $^{13}$C NMR data were similar to those published for dehydropenstemoside" (**6**).[22] "However, the $^1$H NMR signal assigned to H-1 ($\delta_H$ 5.83) appeared as a clear doublet ($J$ = 3 Hz) in **3**, as opposed to a singlet in the reported $^1$H NMR data for dehydropenstemoside." The authors then use the NOE interactions found between H-1, H-6, and H-9 to demonstrate that "the compound **3** was actually an epimer of **6**, and the relative stereochemistry at C-1, C-5, C-9, and C-6 was exactly the same as that found in **2**." Also in this case the "deshielded nature of H-9 chemical shift ($\delta_H$ 3.11) confirmed that the OH at C-5 must be on the same face as H-9". Again, it is not clear why this should be the case. The specific rotation for **3** was $[\alpha]_D^{20}$ −93, but in the three previously published papers[22−24] on dehydropenstemoside no specific rotation of the compound was given (however, we have measured the value −94 for compound **6**). In the papers by Yi et al.[23,24] it was demonstrated that the 5- and 6-OH groups of **6** are in a *cis*-relationship via formation of a benzylidene derivative.

The unusual structures reported for the three compounds from *E. glabra* seemed to be unlikely for the reasons listed above, and we decided to investigate this in detail. We had no access to *E. glabra* from Iran, but as an alternative, we were able to isolate barlerin (**4**) and 7,8-dehydropenstemoside (**6**) from *Lamium garganicum*,[25] while penstemoside (**5**) was obtained from a *Peliostomum* sp.[26] The 1D $^1$H and $^{13}$C NMR spectra of these three compounds recorded in $CD_3OD$ (see Tables S1 and S2 in the Supporting Information) proved identical to the data given by Delazar et al.[7] for compounds **1**−**3** and thus demonstrated the identity; furthermore, the specific rotations of **4** and **6** were comparable to the values given for **1** and **3**, while the values for **5** and **2** were dissimilar.

Regarding the interpretation of the NOE data for compound **1**, we reason that Delazar et al.[7] must have overlooked the important interaction between H-5 and H-9. The resonances arising from these two protons are very close in chemical shift ($\delta_H$ 3.05 and 2.99, respectively), and the NOE correlation is thus close to the diagonal, so the interaction may be difficult to observe. However, we are confident that the interaction is present. In addition to this, we also observed the remaining NOE correlations reported by Delazar et al.,[7] including the capricious correlations between H-1, H-9, and 10-$CH_3$ and that between H-5 and H-6. Unfortunately, Delazar et al.[7] take it for granted that these can only be interpreted as *cis*-interactions, with the consequence that H-1, H-9, and 10-$CH_3$ should all be located on the α-face of the iridoid molecule, with H-5 and H-6 on the *β*-face. However, there is substantial evidence that this is not necessarily the case. First, an iridoid glucoside isolated from *Penstemon secundiflorus*[6] was initially assigned the structure 10-hydroxy-8-*epi*-hastatoside due to the presence of an NOE interaction between H-1(α) and 10-$CH_2$(*β*); however, it was later shown by chemical correlation that the structure was the 8-epimer, namely, 10-hydroxyhastatoside,[27] proving that NOE correlations between substituents on the two different faces of the iridoid molecule are possible. Second, during the isolation of iridoids from *Leonurus persicus*,[28] the structure of 6-*O*-acetylajugol (**7**), a compound with major structural similarities to **4**, was discussed. Using 2D NMR spectroscopy, Tasdemir et al.[28] found unexpected interactions similar to those presented for **1**, namely, between H-1/H-9 and H-1/10-$CH_3$, and also between H-5/H-6. Using molecular modeling, it was concluded that in some conformations H-1(α) and H-9(*β*) were close in space and should indeed give rise to such NOEs. The same was found to be the case for H-5(*β*) and H-6(α). In the same report NOE data for the compound galiridoside (**8**) were presented. The crystalline nature of this compound permitted an X-ray crystallographic study. NOE correlations between H-1, H-9, and 10-$CH_3$ and that between H-5 and H-6α were consistent with the interatomic distances obtained from the crystal structure. In the present work, we have obtained an X-ray structure of the crystalline ipolamiide (**9**) (Figure 1), identical to that previously published.[29] Also for this compound clear NOE interactions were evident between H-1/H-9 and H-1/10-$CH_3$ (see Table 1S, Supporting Information). Thus, we have proved that the compound presented as **1** must indeed be barlerin (**4**).

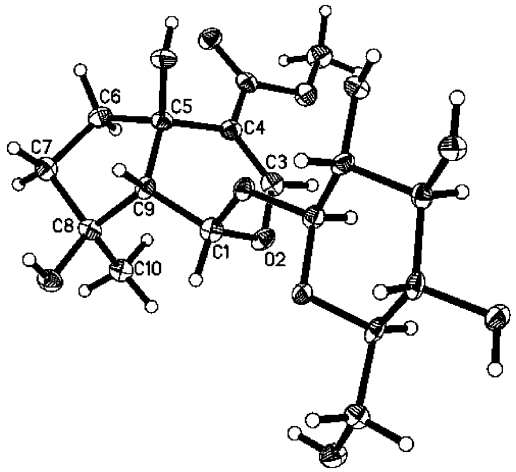


**Figure 1.** X-ray structure of ipolamiide (**9**).

Comparison of the NMR data including the NOE interactions reported[7] for compound **2** with our data for penstemoside (**5**) shows that they are either identical or very similar. We could not discriminate between the NOE interactions arising from H-8(α) and H-9(*β*) with any confidence due to the proximity of the two resonances (0.03 ppm). Thus, the NMR evidence shows that the structure of **2** should be revised to penstemoside (**5**), despite the different specific rotations.

For compound **3** Delazar et al.[7] find NOE correlations between H-6 and H-1, H-9, and H-7. We, however, found that the H-6/H-7 correlation was intense, while the H-1/H-9 correlation was much weaker. Thus, the compound presented as structure **3** is in fact 7,8-dehydropenstemoside (**6**).

**Harpagoside-B from *Scrophularia deserti.*** Together with some other compounds including 8-*O*-acetylharpagide (**10a**) a compound named harpagoside-B (**11**), $[\alpha]_D$ −13.3, was isolated from *S. deserti* (Scrophulariaceae) by Ahmed et al.[11] It was found to have the elemental composition $C_{25}H_{32}O_{11}$ as established by HRMS ($M^+$ 508.5257). A full 1D and 2D NMR data set was recorded (in $CD_3OD$), and sets of $^1$H and $^{13}$C NMR assignments were presented.

**Table 1.** NMR Data for the Sugar Moiety of Buddlejoside A Compared with Model Glycosides

| | buddljeoside A (**12a**)[a] | | teupolioside (**14**)[b] *β*-galactopyranoside | | phlinoside A (**15**)[c] *β*-glucopyranoside | |
|---|---|---|---|---|---|---|
| atom | $^1$H (MeOD) | $^{13}$C (solv?) | $^1$H (MeOD) | $^{13}$C (MeOD) | $^1$H (MeOD) | $^{13}$C (MeOD) |
| | | | Gal | Gal | Glc | Glc |
| 1′ | 4.67/4.80 | 100.1 | 4.36 | 107.5 | 4.43 | 106.8 |
| 2′ | 3.2−3.4 | 74.8 | 3.56 | 72.9 | 3.28 | 75.4 |
| 3′ | 3.2−3.4 | 77.9[d] | 3.48 | 74.9 | 3.39 | 77.9 |
| 4′ | 3.3 t (1.6) | 71.4 | 3.80 | 70.5 | 3.30 | 71.4 |
| 5′ | 3.2−3.4 | 76.2[d] | 3.52 | 77.0 | 3.30 | 78.1 |
| 6a′/6b′ | 3.6/3.8 | 62.7 | 3.72/3.85 | 62.9 | 3.68/3.90 | 62.9 |

[a]Data from ref 35. [b]Data from ref 37. [c]Data from ref 38. [d] Resonances could be interchanged.

The proton chemical shift assignments of **11** were identical with those reported[2] for harpagoside (**10b**). The carbon chemical shifts were within 0.3 ppm, except for a systematic difference of 0.8 ppm due to a TMS standard. The NMR spectra both showed an additional resonance ($\delta_H$ 3.37 and $\delta_C$ 50.4) assigned to the 6-*O*-methyl group in **11**. The unusual structure with a H-9α stereochemistry was deduced from NOE data where correlations between H-1, H-9, and 10-$CH_3$ were observed. The *O*-methyl group should be attached to C-6 since it "exhibited a long-range coupling with C-6 in the HMBC spectrum". Also, "C-6 appeared downfield at $\delta_C$ 78.1, indicating that it was connected to (the) methyl group through an ether linkage".

Considering the data reported, we questioned this structure and have consequently recorded spectra of harpagoside (**10b**). The $^1$H and $^{13}$C NMR (in $CD_3OD$) data given for **11** proved identical to those reported for **10b**, except for the resonance from the methoxy group. We have already discussed the presence of unexpected NOEs above, and this leaves only the character of the methoxy group. The shifts given for the methyl group are almost identical to those found for residual methanol in spectra recorded in $CD_3OD$. The $^{13}$C NMR shift value ($\delta_C$ 50.4) found for the alleged methoxy group is also very different from what would be expected for an *O*-methyl ether. Thus, in 6-*O*-methylaucubin the *O*-methyl group shift has been reported to be much more downfield ($\delta_C$ 56.0 in DMSO-$d_6$),[30] similar to that found for 6-*O*-methylcatalpol ($\delta_C$ 58.0 in $CD_3OD$;[31] see Table 3S, Supporting Information). Also the downfield shift for C-6 ($\delta_C$ 78.1) should be significantly larger than the 2 ppm indicated by Ahmed et al.[11] Thus, in 6-*O*-methylaucubin the shift is $\delta_C$ 89.7 (in DMSO-$d_6$)[30] as compared to that of aucubin ($\delta_C$ 81.6 in $D_2O$), and similarly for 6-*O*-methylcatalpol and catalpol ($\delta_C$ 88.5 vs 79.6 in $CD_3OD$,[31] see Supporting Information). We cannot explain the reported long-range coupling between the *O*-methyl group and C-6. The specific rotation for harpagoside has been reported several times within the limits[32,33] −41 to −60, not close to the value given for **11**. We have no explanation for this discrepancy or for the elemental composition found for **11**, but conclude that the compound isolated from *S. deserti* must be harpagoside (**10b**), an iridoid glucoside that has previously been reported several times from the genus *Scrophularia*.[34]

**Buddlejosides A and B from *Buddleja crispa*.** The two compounds **12a** and **12b** were isolated from the ethyl acetate-soluble extract of *B. crispa* (Scrophulariaceae) by Ahmad et al.[35] The structures were deduced from spectroscopic data including 1D and 2D NMR spectra, but unfortunately, the specific rotations of the compounds were not reported. However, the two compounds were subjected to acid hydrolysis, and the specific rotation of the carbohydrate fraction was found to be close to that of galactose (+80); furthermore, the sugar was identified by comparison of the retention time of the TMS ether with a standard sample.

In our opinion, the $^{13}$C NMR spectra of both compounds (Table 4S in the Supporting Information) indicate that the sugar parts are *β*-glucopyranosyl moieties, although the C-5′ resonances at $\delta_C$ 76.2/76.4 are more upfield (ca. 1.5 ppm) than usual; however, it is within the usual range, and the reported C-3′ and C-5′ signals might need to be interchanged. The authors note that the spectrum of buddlejoside A is closely resembling that published for agnuside;[36] in fact, the spectra are identical within 0.9 ppm, except for the unusually low value given for the C-5′ resonance of the former. The $^1$H NMR spectra also demonstrate that the compounds must be *β*-glucopyranosides. Thus, the H-4′ resonances of the two compounds are found at $\delta$ 3.3, the same value as reported in spectra of *β*-glucopyranosides. Moreover, in *β*-galactosides the proton at C-4′ is equatorial and would be expected to resonate at significantly lower field.

This is evident from evaluation of NMR data for the phenylethanoid glycoside models in Table 1, i.e., for the *β*-galactopyranoside (teupolioside; **14**)[37] and for the corresponding *β*-glucopyranoside (phlinoside A; **15**),[38] where H-4′ of the former resonates at $\delta_H$ 3.80, ca. 0.5 ppm more downfield than in the glucosides. Similar downfield shifts for an equatorial proton in an unsubstituted *β*-glycopyranoside are found in mannopyranosides[39] (H-2′ at $\delta_H$ 3.8) and in allopyranosides[40] (H-3′ at $\delta_H$ 4.0). Finally, the coupling constant reported for the alleged H-4′ (at $\delta$ 3.29) in **12a** and **12b** is reported to be 1.6 Hz. However, this precise shift and the coupling constant appear to be that of the solvent $CD_3OD$.

From the NMR data we have demonstrated that these compounds are not galactosides, but rather glucosides. We cannot explain the discrepancy between these data and the results obtained by acid hydrolysis, but clearly this should be reinvestigated. Tentatively, however, we believe that we can conclude that the compound buddlejoside A is identical to the known agnuside (**13a**). Buddlejoside B (**13b**), however, is a new compound.

## Experimental Section

1D $^1$H and 2D DQF-COSY, gHSQC, gHMBC, and NOESY NMR spectra were recorded at 25 °C on a Varian Unity Inova 500 MHz spectrometer. All compounds were dissolved in $CD_3OD$, and the spectra were referenced according to the solvent peaks ($\delta_H$ 3.31 or $\delta_C$ 49.0), respectively. The mixing time used in the NOESY spectra was 600 ms. Crystal data: **9**·$H_2O$, $M$ = 424.39, orthorhombic, $a$ = 7.8557(2) Å, $b$ = 10.2925(3) Å, $c$ = 24.2085(7) Å, $V$ = 1957.37(9) Å$^3$, $T$ = 120(2) K, space group $P2_12_12_1$, $Z$ = 4, $D_x$ = 1.440 g cm$^{-3}$, crystal size = 0.35 × 0.08 × 0.06 mm$^3$, $\mu$(Cu Kα) = 1.062 mm$^{-1}$, 6898 reflections measured, 2695 unique ($R_{int}$ = 0.03(4)) and 2511 reflections with $I > 2\sigma(I)$, which were used in all calculations. The final $R_1$ was 0.0358 (observed data) and $wR(F^2)$ was 0.0887 (all data). The Flack $x$ parameter is 0.1(2), indicating that this depicts the correct absolute configuration. Measurement: Siemens SMART CCD Platform. Structure determination: SHELXTL, ver. 6.12 (Sheldrick, 2001). (Full X-ray crystallographic data are available as Supporting information.)

Barlerin (**4**; $[\alpha]_D^{33}$ −79 (*c* 0.1, MeOH)) and dehydropenstemoside (**6**; $[\alpha]_D^{33}$ −94 (*c* 0.1, MeOH)) were isolated from *Lamium garganicum*.[25] Penstemoside (**5**; $[\alpha]_D^{22}$ −167 (*c* 0.7, MeOH)) was found in a *Peliostemum* sp.[26] Crystalline ipolamiide (**9**) was obtained from *Lamium eriocephalum*.[41]

**Supporting Information Available:** Table S1 with NMR data of barlerin (**4**) and ipolamiide (**9**); Table S2 with NMR data of penstemoside (**5**) and 7,8-dehydropenstemoside (**6**); table S3 with NMR data for methylcatalpol; Table S4 with NMR data reported for buddlejosides

A and B. This material is available free of charge via the Internet at http://pubs.acs.org.

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