

STRUCTURAL REVISION OF BARLERIN AND ACETYL BARLERIN

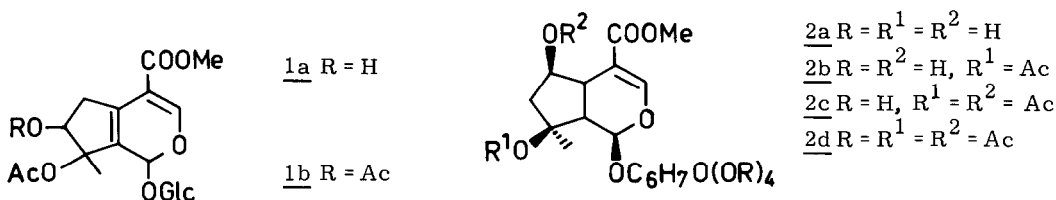
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Summary ^1H - and ^{13}C -NMR data as well as chemical evidence show that the structures of barlerin and acetyl barlerin should be corrected to 8-O-acetyl shanzhiside methylester and 6,8-di-O-acetyl-shanzhiside methylester, respectively.

In 1975 two iridoid glucosides, barlerin and acetyl barlerin, were isolated from *Barleria prionitis* L (Acanthaceae)¹ Both compounds gave the same per-acetate with a melting point of 182°. Based on ^1H -NMR and chemical data the structures were assigned as 1a and 1b. This is so far the only report of carbocyclic iridoids allegedly having a 5,9-double bond. However, in view of the coupling constants reported¹ for the C-1 protons in 1a and 1b (2.0 and 1.5 Hz, respectively) as well as the UV spectra [$\lambda_{\text{max}}^{\text{EtOH}} = 235 \text{ nm}$ ($\log \epsilon = 3.76$)] the structures 1a and 1b seemed unlikely.



In this work we have isolated the iridoids from 13 g of *B. prionitis*. By reversed phase chromatography we isolated 3 iridoids: A (6 mg) with a ^1H -NMR spectrum identical with that of authentic shanzhiside methylester (2a), B (48 mg) amorphous, $[\alpha]_{\text{D}} - 85^\circ$ (c 0.8, MeOH), $\text{C}_{19}\text{H}_{28}\text{O}_{12}$, $\frac{3}{2} \text{H}_2\text{O}$ (combustion), and C (65 mg), amorphous, $[\alpha]_{\text{D}} - 99^\circ$ (c 2.0, MeOH), $\text{C}_{21}\text{H}_{30}\text{O}_{13}$, H_2O (combustion). By acetylation B and C gave the same hexaacetate with melting

points of 179-80° and 180-1°, respectively Exhaustive acetylation of 2a gave 2d with a melting point of 181-2°, $[\alpha]_D -124^\circ$ (c 1.0 CHCl₃), C₂₉H₃₈O₁₇ (combustion) Mixed melting points of 2d with the peracetates of B and C showed no depression Despite the fact that barlerin is reported to be crystalline, we thus conclude, that B and C are barlerin and acetyl barlerin, respectively

The ¹H-NMR data of B and C are virtually identical with those reported for 1a and 1b However, to us they indicated that A and B were 8-O-acetyl-shanzhiside methylester (2b) and 6,8-di-O-acetyl shanzhiside methylester (2c), respectively This was confirmed by the ¹³C NMR data, which are presented in Table 1 The most notable differences between the spectra

Table 1 ¹³C NMR data for 2a, 2b, and 2c. The spectra are recorded in D₂O and have been aligned to C-6' 61.5 ppm (cf ref. 2).

Compound	C-1	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
<u>A</u> (<u>2a</u>)	94.7	152.7	110.6	39.7	76.2	48.6	78.8	50.4	24.2
<u>B</u> (<u>2b</u>)	95.4	153.5	109.2	41.0	75.3	46.7	89.8	48.8	22.5 1 acetyl
<u>C</u> (<u>2c</u>)	95.1	154.3	108.0	38.7	78.8	44.3	89.5	48.9	22.4 2 acetyl

A and B are the downfield shift (11 ppm) of C-8 in B, and the upfield shifts of C-7, C-9, and C-10 (ca 2 ppm) This establishes that B is the 8-O-acetyl derivative of A (cf ref 3) Comparison of the spectra B and C shows a downfield shift (2.5 ppm) of C-6 and upfield shifts of C-5 and C-7 (ca 2 ppm) in C This confirms that C is the 6-O-acetyl derivative of B

Thus we conclude that barlerin and acetyl barlerin are 8-O-acetyl shanzhiside methylester (2b) and 6,8-di-O-acetyl shanzhiside methylester (2c)

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