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STRUCTURES OF TWO NEW IRIDOIDS FROM
BARLERIA PRIONITIS LINN

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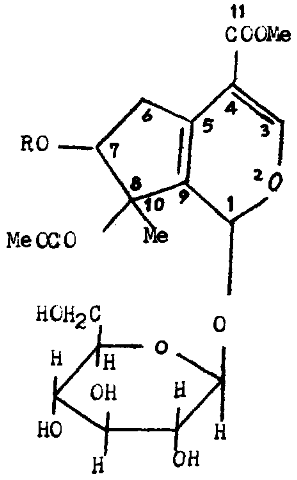
The chromatographic examination of the alcoholic extract of the leaves and stems of Barleria prionitis Linn (Acanthaceae), revealed the presence of five iridoids. Two of these have been isolated and purified over silica gel through various chromatographic manipulations. Their structures have been assigned and they were named as Acetyl Barlerin (A) and Barlerin (B).

To our knowledge, this is the first report on the occurrence of iridoids in the family Acanthaceae, hitherto unknown for these compounds. Although the order Tubiflorae is quite prominent for iridoids; their presence is restricted only to a few families (1,2).

The less polar of the two, A is a hygroscopic amorphous powder with a molecular formula $C_{21}H_{28}O_{13}$. B was crystallised from ethyl acetate to white needles mp 180°C, $[\alpha]_{D}^{20}$ -102°(CH_3OH), and has the molecular formula as $C_{19}H_{26}O_{12}$. It differs from A by the loss of one acetyl group.

Like other naturally occurring members of this class, A and B, on mild acid hydrolysis initially developed a blue colour and then converted into glucose and an insoluble black polymeric product due to the decomposition of the aglycone (3).

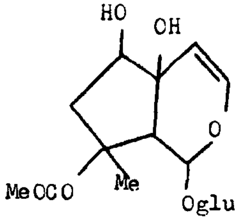
The structures for A and B, based upon the chemical and spectroscopic data and analogy to other known iridoids, are represented as I and II



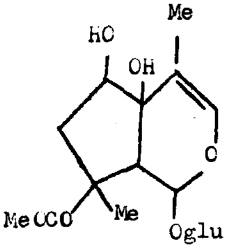
(I) A: R = $-COCH_3$

(II) B: R = H

The glucose is attached to the hemiacetalic - OH at C-1 by analogy to other glucosides of this class. Spectroscopic evidence of this location is given by the low field resonance signals of the anomeric proton at C-1 (δ5.90, 1H(d) J = 2.0 cps and δ5.98, 1H(d) J = 1.5 cps) in the nmr spectra of A and B respectively. The position of the signal of this proton compares well with C-1 proton in acetyl harpagide, III (4) and lamioside, IV (5) (δ6.11, 1H(d) J = 0.8 cps and δ5.96, 1H(d) J≈0.8 cps respectively). That the glucose is in β-configuration, is shown by the signal of the anomeric proton at C'-1 (δ4.70, 1H(d), J = 7 cps) (6).



Acetyl harpagide (III)

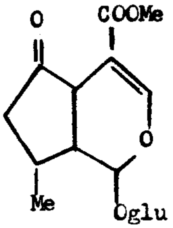


Lamioside (IV)

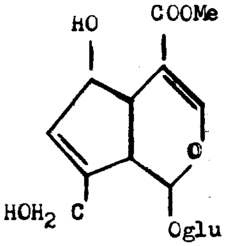
A resonance signal at δ3.72, 3H(s) is assigned to a -COOMe group in the aglycones of A and B. Another signal at δ7.61, 1H(s) is assigned to the olefinic proton at C-3. In their uv spectra in ethanol, a strong absorption was observed at 235 nm (log ϵ 3.76). In the ir spectra also, strong absorption bands at 1695 cm^{-1}

and 1640 cm^{-1} further support the presence of a conjugated carbonyl system.

A comparison of chemical shifts of C-3 proton and carbomethoxy protons of A and B, with those of verbenalin, V (3) and daphylloside, VI (7) substantiates the above frame work.



Verbenalin (V)



Daphylloside (VI)

Compound	δ(-$COOCH_3$)	δ(C_3-H)
Verbenalin	3.78	7.58 (d), J=1.5 cps
Daphylloside	3.80	7.58 (d), J=1.0 cps
A	3.72	7.61
B	3.72	7.61

The nmr of A displays resonance signals corresponding to two acetyl groups (3H(s) at δ 2.05 and δ 2.10), while in B, only one signal for acetyl group (3H(s) at δ 2.00) was observed. When A was acetylated in presence of pyridine and acetic anhydride, an acetate was obtained. It was crystallised from methanol, mp 182°C, $[\alpha]_D^{20}$ - 96° ($CHCl_3$), and has the molecular formula as $C_{29}H_{36}O_{17}$. The nmr integral curve of the acetate corresponded to six acetyl groups in the aglycone of A. Acetylation of B under similar conditions, resulted in the formation of the same acetate. Evidently A is the monoacetyl derivative of B, which has one acetylable hydroxyl group in its aglycone.

In the nmr spectra of A and B, the signal at δ1.50, 3H(s), indicated the presence of a methyl group, attached to a carbon devoid of protons, similar to the methyl group of acetyl harpagide III (4) (δ 1.45, 3H(s)) and lamioside, IV (5) (δ 1.42, 3H(s)). The observed small paramagnetic shift can be assigned to neighbouring double bond in A and B, absent in acetyl harpagide and lamioside. Therefore by analogy the methyl group could be located at C-8 in A and B where an acetyl group is already present. This is further supported by the fact that when B is hydrogenated in presence of Pt/C under mild conditions, a dihydroderivative was obtained, the nmr of which does not exhibit any significant paramagnetic shift for the methyl group, thereby, indicating that it is not present on an unsaturated carbon.

The dihydroderivative of B still exhibits a signal for the olefinic proton (δ 7.58, 1H(s)) which indicates that the double bond between C-3 and C-4 in six membered pyran ring is intact. Therefore two double bonds are present in A and B. One of these is in the six membered ring and the other in the five membered ring. One hydroxyl group (acetyl group in A) should also be present in B at C-6 and C-7 owing to its easy acetylability.

Spectroscopic evidences supported the location of other double bond between C-5 and C-9 as the most plausible one. In the nmr spectra of dihydro B and its acetate, a signal at δ 2.75, 1H(m) is assigned to C-9 proton (δ 2.88, 1H(m) in acetyl harpagide (4) and δ2.80, 1H(m) in lamioside (5)). This signal is absent in A and B due to the presence of a double bond between C-5 and C-9.

The position of -OR is located at C-7, which can be explained as follows. In the nmr spectra of A and its acetate, a signal at δ 5.20, 1H(m) is due to the proton of -C<u>H</u>OAc at C-7. The position of -OR at C-6 can be discarded safely, as it would have given a comparatively low field signal (ca δ 5.75 (7)) due to the presence of a neighbouring double bond, and which should have shifted to a lower field in the nmr of its dihydroderivative; which was not observed, however.

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