

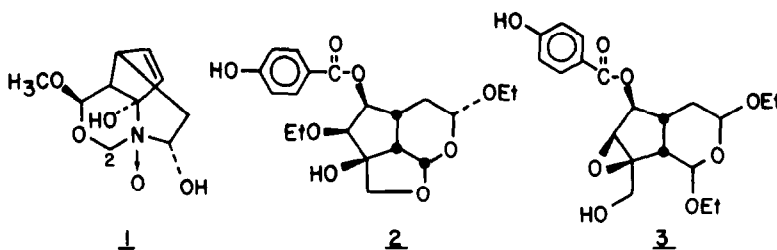
REAPPRAISAL OF THE STRUCTURE FOR THE ALKALOID  
BUDDAMIN FROM BUDDLEYA DAVIDII

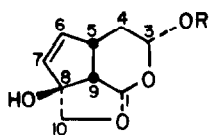
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**Summary:** The structure of the alkaloid buddamin, isolated from Buddleya davidii cannot be correct, based upon the reported spectral data. An alternate structure is proposed, which also suggests that buddamin is an artifact of the isolation procedure.

Structure 1 was recently proposed<sup>1</sup> for buddamin, an isolate obtained from a methanol Soxhlet extraction of Buddleya davidii Franchet, followed by differential pH separation (NH<sub>3</sub> basification) and low pressure column chromatography. The molecular formula C<sub>10</sub>H<sub>15</sub>NO<sub>5</sub> was proposed based on an M<sup>+</sup> ion at m/z 229 (0.21% relative intensity). The mass spectrum also showed an m/z 197 (2.8%) and all other fragments were interpreted<sup>1</sup> as arising from this unit. Ir spectral data were assigned as 3460 and 3410 cm<sup>-1</sup> (OH), 1625 cm<sup>-1</sup> (C=C) and N-oxide. Also reported were <sup>13</sup>C and <sup>1</sup>H nmr spectra. The assignment of a 1625 cm<sup>-1</sup> band to an N-oxide, the assignment of a <sup>13</sup>C nmr chemical shift of 74.64 ppm to C-2, and the rare juxtaposition of aminoalcohol functional groups in 1 led us to search for a simpler interpretation of the data.

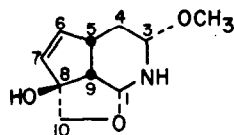
Analogies were seen between part of the reported data and that for the recently synthesized<sup>2</sup> compound 2. Such a structure was originally suggested<sup>3</sup> for specionin, but the synthetic 2 and specionin were not identical and the new structure 3 is now proposed<sup>2</sup> for specionin. Closer analogs, however, are represented by 4, which is the acid-catalyzed rearrangement product from treatment<sup>4</sup> of aucubigenin (the aucubin aglycone) and the synthetic<sup>2</sup> 5. The reported<sup>1</sup> <sup>13</sup>C and <sup>1</sup>H nmr data for buddamin are completely consistent with its formulation as 6, with the spectral comparisons for 4, 5, and 6 given in Table 1.





4: R=H

5: R=Et

 $^{13}\text{C}$ 6 $^1\text{H}$ 

Carbon No.	4	6	4	5	6
1	90.1	96.49	5.70d	5.59d	5.58d
3	102.2	100.41	5.11dd	4.80dd	4.70dd
4	31.4	30.30	1.5-2.2m	1.92 + 1.77ddd	1.81dd
5	48.3	50.11	3.45brs	3.34m	3.28m
6	133.8	134.13	5.81dd	5.77dd	5.82m
7	140.5	139.41	6.00dd	5.86dd	5.82m
8	95.4	93.90			
9	40.1	38.84	2.66dd	not reported	2.58dd
10	70.1	74.64	3.80, 4.00dd	3.78, 3.98dd	3.79, 4.00dd
OMe	-	55.57	-	-	3.43s

(The data for **4** is taken from Ref. 4, that for **5** from Ref. 2, and that for **6** from Ref. 1. We have reversed the carbon assignments for C-5 and C-9 given in Ref. 4.)

Our proposed structure **6** has the molecular formula  $\text{C}_{10}\text{H}_{15}\text{NO}_3$  (MW 197) rather than  $\text{C}_{10}\text{H}_{15}\text{NO}_5$  (MW 229) as proposed for buddamin, but the intensity (0.21%) of the  $m/z$  229 peak and the presence of an  $m/z$  197 ion from which the entire fragmentation scheme derives<sup>1</sup> is consistent with our formulation rather than **1**.

Since aucubin is a constituent of *Buddleia* species,<sup>5</sup> it seems likely that buddamin is an aucubin-derived artifact as specionin appears to be a catalpol-derived artifact.<sup>2,3</sup> The general mechanism proposed<sup>4</sup> for formation of **4**, suffices to explain **6** as well.

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#### References

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