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# CONSTITUENTS OF NAUCLEA DIDERRICHII. PART V. A GLYCOSIDIC ALKALOID

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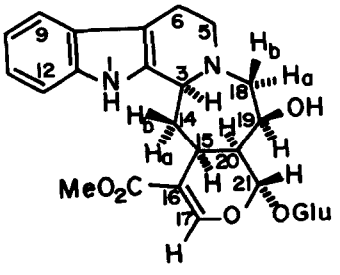
The report on the structure of rubenine by Brown and Charalambides[1] prompts us to report the current state of our investigation of the N. diderrichii constituent that we described previousl as an amorphous alkaloidal glycoside[2]. Although the routine mass spectra did not show a parent ion, the spectra of the alkaloid and its acetylated derivative obtained with a field desorption mass spectrometer[3] are in accord with the formula $C_{27}H_{34}N_2O_{10}$ for the alkaloid. The acetylated derivative was not obtained crystalline, but tlc purification provided a sample the microanalysis of which was in accord with the formula for a pentaacetate, supporting the above mass spectral evidence. The alkaloid showed ir absorption at 2.92 (sh), 3.05 (br), 5.93, 6.12 μ and uv absorption at 225 (log ε 4.44), 278 (log ε 3.80)mμ; the ir values for the pentaacetate were 2.89 (sh), 3.02 (br), 5.73 (br, strong), 5.92, 6.10 μ.

The 220 MHz nmr spectra[4] of the alkaloid (in DMSO-$d_6$) and its pentaacetate (in $CDCl_3$), shown in condensed form in the Table, provide a wealth of information concerning the chemical environment and relationship to neighboring protons of essentially all of the structurally significant protons, and we propose that all of the spectroscopic data available are in accord with structure I for the




I

TABLE

The 220 MHz n.m.r. spectra of alkaloid I and its pentaacetate. Protons are identified by the labelling scheme shown for the structures. Integrated signal areas are in accord with the number of protons assigned to them. Coupling constants derived from observed signal multiplicities are reported.

| | ALKALOID I (in DMSO-$d_6$) | | | PENTAACETATE II (in $CDCl_3$) | |
|---|---|---|---|---|---|
| Proton | Chem. Shift (τ) (Multiplicity) | Coupling Constants (Hz) | Proton | Chem. Shift (τ) (Multiplicity) | Coupling Constants (Hz) |
| Tryptamine-derived portion | | | | | |
| 1 | - | - | 1 | ∿2.0 (br) | - |
| 5,6 | (6.4-7.5)† | - | 5,6 | (6.75-7.45)† | - |
| 9 | 2.66 (d) | $J_{9,10}$=7.8 | 9 | 2.50-2.98 (m) | - |
| 10 | 3.04 (dd) | $J_{9,10}$=$J_{10,11}$=7.8 | 10 | | |
| 11 | 2.95 (dd) | $J_{10,11}$=$J_{11,12}$=7.8 | 11 | | |
| 12 | 2.71 (d) | $J_{11,12}$=7.8 | 12 | | |
| Glucose-derived portion | | | | | |
| 1' | 5.33 (d) | $J^*_{1',2'}$=7.3 | 1' | 5.11 (d) | $J_{1',2'}$=8 |
| 2' | 6.81 (m) | $J^*_{1',2'}$=7.3 | 2' | 4.97 (dd) | $J_{1',2'}$=8; $J_{2',3'}$=9 |
| 3' | (6.4-7.5) | | 3' | 4.75 (dd) | $J_{2',3'}$=9=$J_{3',4'}$ |
| 4' | | | 4' | 4.89 (dd) | $J_{3',4'}$=9=$J^*_{4',5'}$ |
| 5' | | | 5' | 6.29 (m) | $J^*_{4',5'}$=9; $J_{5',6a'}$=4.5; $J_{5',6b'}$=1 |
| 6a' | | | 6a' | 5.70 (dd) | $J_{5',6a'}$=4.5; $J_{6a',6b'}$=12.5 |
| 6b' | | | 6b' | 5.88 (dd) | $J_{5,6b'}$=1; $J_{6a',6b'}$=12.5 |
| R(H) | 5.0-5.23 (3H); 5.54 (1H); other H may be in 6.4-7.5 envelope | | R(Ac) | singlets observed at 8.03 (6H), 7.99 (3H), 7.97 (3H), 7.91 (3H). | |

| | | | | | |
|---|---|---|---|---|---|
| 3 | 6.14 (m) | $J_{3,14a} \sim 1$; $J^{*}_{3,14b} = 10$ | 3 | 5.97 (m) | $J_{3,14a} \sim 1$; $J^{*}_{3,14b} = 10$ |
| 14a | 7.55 (m) | $J_{3,14a} \sim 1$; $J_{14a,14b} = 13.5$; $J_{14a,15} \sim 1$ | 14a | ? | - |
| 14b | 8.26 (m) | $J^{*}_{3,14b} = 10$; $J_{14a,14b} = 13.5$; $J^{*}_{14b,15} = 9.5$ | 14b | 8.15 (m) | $J^{*}_{3,14b} = 10$; $J_{14a,14b} = 13$; $J^{*}_{14b,15} = 10$ |
| 15 | 6.97 (m) | $J_{14a,15} \sim 1$; $J^{*}_{14b,15} = 9.5$; $J_{15,20} = 6$ | 15 | 7.36 (m) | $J^{*}_{14b,15} = 10$ |
| 20 | 7.93 (m) | $J_{15,20} = 6$; $J^{*}_{19,20} = 3.5$; $J^{*}_{20,21} = 8.5$ | 20 | 7.24 (m) | $J^{*}_{19,20} \sim 1.5$; $J^{*}_{20,21} = 5$ |
| 19 | 5.80 (m) | $J_{18a,19} = 2$; $J_{18b,19} = 5$; $J^{*}_{19,20} = 3.5$ | 19 | 4.60 (m) | $J^{*}_{18a,19} = 5$; $J^{*}_{18b,19} = 6$; $J^{*}_{19,20} = 1.5$ |
| 18a | (6.4-7.5)† | | 18a | 7.04 (dd) | $J^{*}_{18a,19} = 5$; $J_{18a,18b} = 13$ |
| 18b | | | 18b | 6.77 (dd) | $J^{*}_{18b,19} = 6$; $J_{18a,18b} = 13$ |
| 21 | 4.38 (d) | $J^{*}_{20,21} = 8.5$ | 21 | 4.50 (d) | $J^{*}_{20,21} = 5$ |
| 17 | 2.55 (s) | - | 17 | 2.61 (s) | - |
| $CO_2Me$ | 6.30 (s) | - | $CO_2Me$ | 6.24 (s) | - |

*These couplings have been confirmed by decoupling experiments.

†These protons are assumed to form part of the complex multiplet in the range indicated in the brackets.

alkaloid. The tryptamine-derived portion can readily be recognized in the nmr, and signals can be assigned to the glycosidic unit, particularly in the penta-acetate, that indicate that it is a β-glucoside[5]. The terpenoid-derived portion is the heart of the structural problem, and here we note first that ir, uv and nmr data indicate the presence of the methyl β-alkoxyacrylate moiety of ring E. Chemical shift evidence and explicit decoupling experiments demonstrate the structural features and stereochemistry assigned to the centres that form the continuous chains 3, 14, 15 and 18, 19, 20, 21; the relationship at the 15, 20 linkage was deduced from the observed splitting of corresponding proton signals, but confirmation by a decoupling experiment could not be made because of the closeness of their chemical shifts. The main structural novelty of I lies in the seven-membered ring D, a feature reported previously for rubenine[1] and naucle-chine[6], another N. diderrichii alkaloid.

After we prepared this report we learnt from Dr. R. T. Brown that he has assigned structure I to 3α-dihydrocadambine, an alkaloid of Anthocephalus cadamba. Direct comparison by ir, nmr, and tlc of his crystalline pentaacetate with our material demonstrates that they are chemically identical, and it is appropriate to use the name 3α-dihydrocadambine for the alkaloid. The data presented by the two laboratories consequently corroborate the independent conclusions of each. We are grateful to Dr. Brown for delaying publication of his report[7] in order to allow simultaneous publication of ours.

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3. We are deeply grateful to Professor G. W. Wood, University of Windsor, for carrying out these determinations for us.
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