

$\Delta^{\alpha\beta}$ -DIHYDROWASANINE, A NEW ALKALOID FROM PIPER GUINEENSE

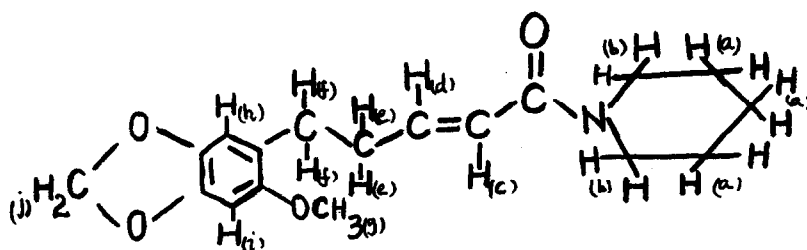
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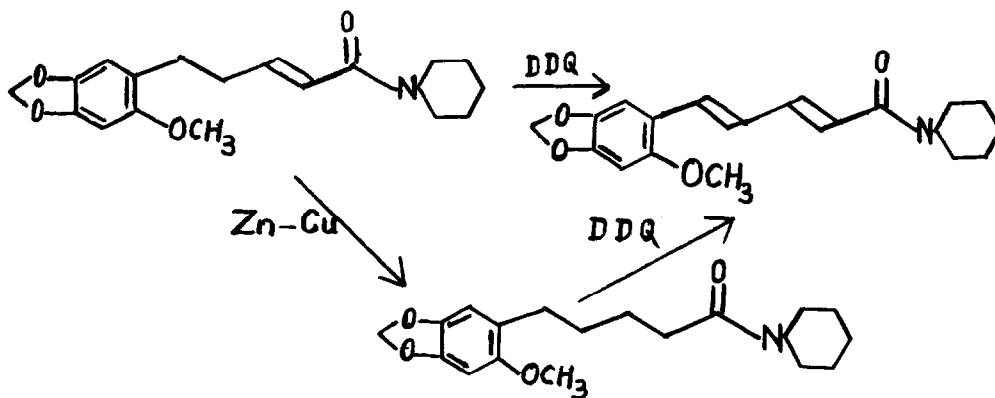
As a result of a recent report in this journal of wasanine¹, a piperine-type amide from the roots of Piper guineense, we are prompted to immediately report our work on the same plant. In our investigation we have isolated wasanine, $\Delta^{\alpha\beta}$ -dihydrowasanine and some minor alkaloids from the seeds of Piper guineense. We wish to report the isolation and structure elucidation of $\Delta^{\alpha\beta}$ -dihydrowasanine (1).

The hexane extract of the air dried finely powdered seeds of Piper guineense (collected from Buea) on chromatography over alumina yielded a fraction in hexane eluates mp 99-100° (C₆H₆-C₆H₁₂). The compound was analysed as C₁₈H₂₃NO₄, m/e M⁺ 317, 205, 175, 166, 135. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ) 302 (3.839), 206 (4.481). The IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹ 2850 (-OCH₃), 1650 (tert. amide C=O), 1610 (trans conjugated -CH=CH-), 1255, 1035, and 925 (O-CH₂-O). The NMR, mass fragmentation pattern and elemental analysis were in agreement with the proposed structure. Reduction of the new alkaloid with Zn-Cu couple indicated that the olefinic double bond was conjugated with the carbonyl group of the amide²⁻³. The reduction product was identical with that obtained from the catalytic reduction of the alkaloid. Attempts to oxidise this new compound to known products in order to establish the position of methoxy group were unsuccessful and an indirect method was therefore used. Dehydrogenation of the new alkaloid with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) afforded a compound mp 176-178°, identical (NMR, MS, IR, mp, mmp) with wasanine. A similar dehydrogenation of the catalytic and Zn-Cu couple reduction product afforded wasanine (Scheme 1). Oxidation of the dehydrogenation product with neutral KMnO₄ gave 2-methoxy-3,4-methylenedioxybenzaldehyde mp 110° (Lit⁴ 111.5-112°). Further oxidation of the aldehyde gave the corresponding acid mp 146-147° (Lit⁴ 148-149°) thus confirming that the methoxy group is at the 2-position.



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| (a) δ 1.65 (6H, s) | (e) & (f) δ 2.20 - 2.80 (4H, m) |
| (b) δ 3.53 (4H, broad s) | (g) δ 3.83 (3H, s) |
| (c) δ 6.23 (1H, d, J 16Hz) | (h) δ 6.68 (1H, s) |
| (d) δ 6.88 (1H, m, J 16Hz) | (i) δ 6.57 (1H, s) |
| | (j) δ 5.93 (2H, s) |



Scheme 1.

The proposed structure of the alkaloid has also been confirmed through the synthesis of the dehydrogenation product⁵ starting with 2-methoxypiperic acid. Treatment of piperidine in dry benzene with the acid chloride of 2-methoxypiperic acid gave a compound identical (IR, MS, NMR, mp, mmp) with wasanine.

REFERENCES AND NOTES

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2. B.L. Sondengam, Ph. D. Thesis, University of Ibadan, 1973.
3. D.E.U. Ekong, J.I. Okogun and B.L. Sondengam, *J.Chem.Soc.*; 2118 (1975).
4. K.N. Campbell, P.F. Hopper and B.K. Campbell *J.Org.Chem* 16 (1951) 1736.
5. Details will be published in a full paper dealing with dihydro-wasanine and other constituents of the seeds of *Piper guineense*.