Tetrahedron Letters No. 37, pp.3425 - 3428, 1971. Pergamon Press. Printed in Great Britain.

THE ABSOLUTE CONFIGURATION OF THE ISOPAVINE ALKALOIDS[1]

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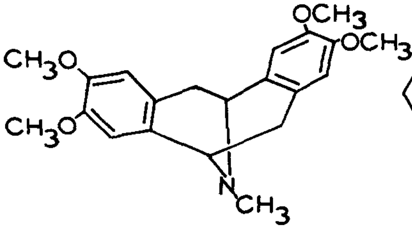
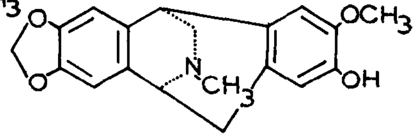
(Received in USA 22 July 1971; received in UK for publication 6 August 1971)

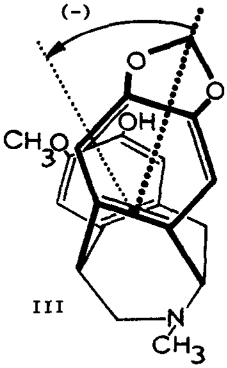
The absolute configuration of the pavine alkaloid (-)-argemonine (I) was firmly determined by chemical degradation,[2] and through a non-empirical analysis of the cd spectrum.[3] The results of an empirical ord study were also interpreted as leading to the absolute configuration depicted.[4]



I



II



III

In an effort to establish the absolute configuration of the related isopavine base (-)-amurensine (II),[5] its cd spectrum was determined in ethanol at room temperature. Application of the aromatic chirality method[6] to amurensine leads to the absolute configuration denoted in II and III. The first of the two pairs of split cd curves centered around 285 nm can be correlated to the $^{1}L_{b}$ band (Fig.). The fact that the first Cotton effect at longer wavelength is negative shows that the chirality of the corresponding benzene transitions is also negative, or left-handed, as shown in expression III. Similarly, the second pair of Cotton effects centered around 240 nm, which are assignable to interactions between $^{1}L_{a}$

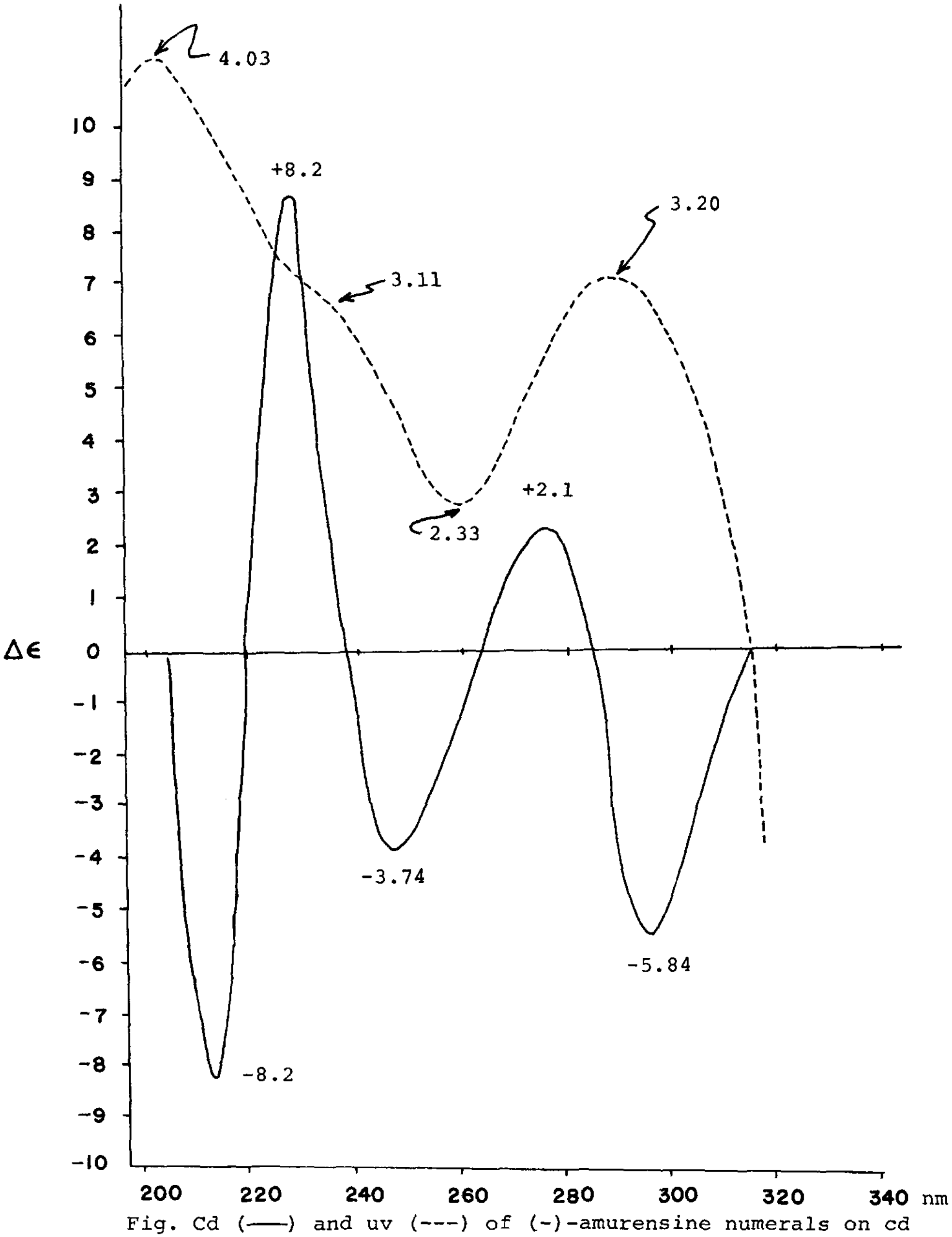
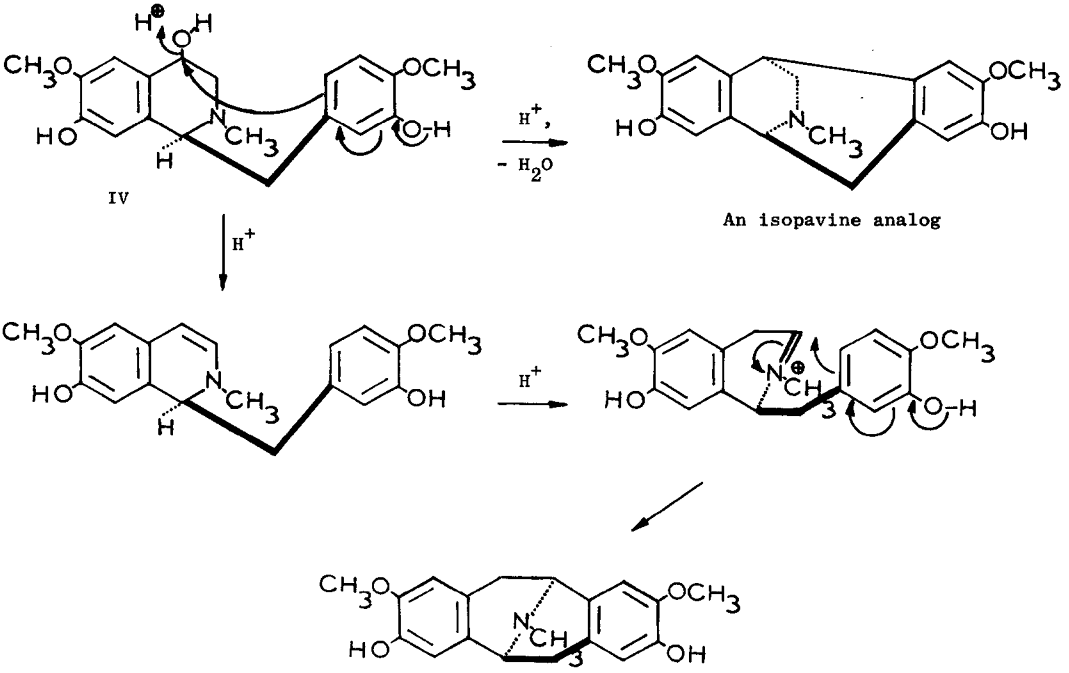


Fig. Cd (——) and uv (---) of (-)-amurensine numerals on cd curve are Δε and those on uv curve are log ε values.

transitions, and hence perpendicular to ^1L_b transitions, leads to the assignment of the same absolute configuration. The negative Cotton effect at 215 nm is due to ^1B transitions (long-axis) but the shorter wavelength portion below 205 nm is not clear, presumably because of instrumental limitations.

The method as applied in the present case is basically very similar to the treatment of Mason and coworkers.[3,7] The difference lies in the fact that the mutual phases of the two interacting benzene transitions need not be considered under the present treatment.[6] Snatzke, et al., have also developed a useful treatment of some of the isoquinoline alkaloids in which the cd curves resulting from benzenoid transitions are interpreted on the basis of a sector rule.[8]

In argemonine (I) or amurensine (II or III), the nitrogen bridge is situated below the V-plane of these molecules. This conclusion can be extended to all known pavine and isopavine alkaloids which possess in common with argemonine and amurensine negative specific rotations at the D line.[9]



IV

An isopavine analog

(−)-Bisnorargemonine,
a pavine alkaloid

The fact that the pavine and isopavine alkaloids have the identical absolute configuration points to the possibility of a common biogenetic precursor such as the 4-hydroxyreticuline IV which, depending upon the plant family or genus, can cyclize directly to an isopavine species as shown above, or alternatively can undergo dehydration, double bond isomerization and intramolecular cyclization to a pavine analog.[10,11,12]

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