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ISOQUINOLINE ALKALOIDS. IV.[1] A SIMPLE ENTRY TO OXOAPORPHINE ALKALOIDS: CORUNNINE AND GLAUVINE

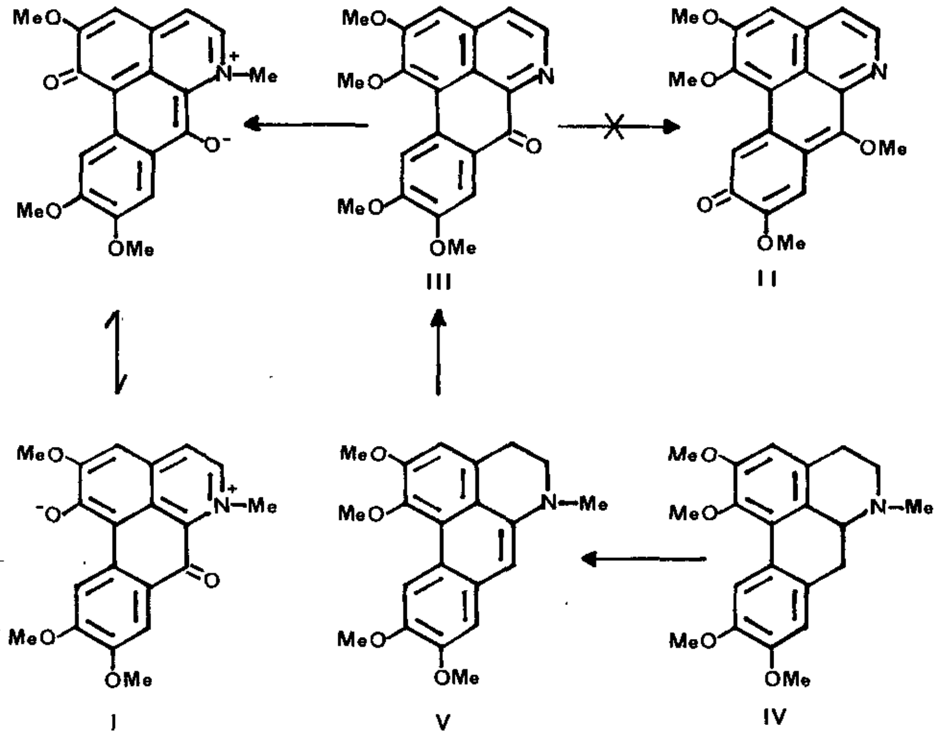
Luis Castedo,* Rafael Suau, and Antonio Mouriño

Departamento de Química Orgánica de la Facultad de Ciencias.
Bilbao (Spain)

An efficient lead tetraacetate oxidation of glaucine (IV) to O-methylatheroline (III) is described. Simple heating of III afforded corunnine (I) instead of glauvine (II) as it had been previously reported.[2]

Two green alkaloids, corunnine [3] and glauvine,[2] with very similar UV and NMR spectra, have been isolated from two different species of Glaucium flavum and were ascribed structures (I) and (II), respectively. The structure of corunnine (I) has been unambiguously confirmed by two different syntheses.[1,4] As glauvine was not available to us and Yakhontova and col. reported[2] that it can be obtained from O-methylatheroline (III), we decided to study this conversion.

Since O-methylatheroline (III) is a minor alkaloid in plants probably derived by oxidation of co-ocurring glaucine (IV) [5],we were interested in finding an easy route to III from the common alkaloid glaucine (IV)[6]. Although a good deal of attention has



been paid to the oxidation of aporphine alkaloids [7], no simple and synthetically useful conversion for non-phenolic aporphines to oxoaporphines has been reported to the best of our knowledge.

Treatment of glaucine (IV) with lead tetraacetate (1:3 molar ratio) in glacial acetic acid at room temperature for twelve hours led to the isolation of O-methylatheroline (III) [8] (69 % yield) together with a variable amount of dehydroglaucine (V) (7 to 10 % yield) which could be easily separated by column chromatography on basic alumina. When dehydroglaucine (V) was treated with lead tetraacetate, as above, O-methylatheroline (III) was obtained in an almost quantitative yield. On this basis dehydroglaucine (V) appears to be the first stage in the oxidation process of IV to III.

After heating O-methylatheroline (III) at 150 °C (bath temperature) for 32 hours a 1:2 mixture of starting material and a green compound was obtained in about 75 % yield, which was resolved by column chromatography on basic alumina. The green compound, m.p., 254-56 °C (from ethanol), was identified as corunnine (I) by direct comparison (IR, t.l.c., UV, NMR and mixed m.p.) with authentic material. Higher reaction temperatures gave analogous results in much shorter periods of time (1 hour at 200 °C).[9]

These last results strongly suggest that corunnine and glauvine might be identical and should have structure (I).

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8 The identity of all compounds was proved by direct comparison with authentic specimens.

9 No green alkaloid was isolated when the reaction was carried out in a sealed tube, using DMSO or DMF as solvent.

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