ANOMALOUS MASS SPECTRA OF SOME APORPHINE METHIODIDES

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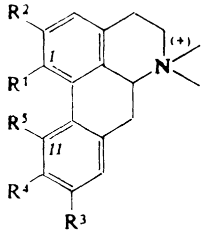
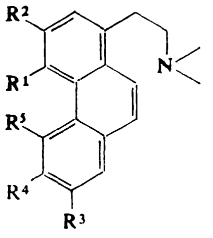
Methiodides of corydine, isocorydine and isothebaine are O-demethylated in the ionic source of the mass spectrometer by hydrogen iodide formed on pyrolysis of the sample. The reaction is common in aporphine methiodides substituted in positions 1 and 11 by one hydroxyl and one methoxyl group. The behaviour can be explained by the combined action of the hydrogen bridge and steric strain.

The mass spectra of quaternary aporphines have been described several times without mention of any anomalies[1-4]. During the measurement of the mass spectra of nonvolatile quaternary methiodides of aporphine alkaloids (*I*), pyrolysis of the sample occurs in the ionic source of the mass spectrometer. Elimination of hydrogen iodide gives rise predominantly to a methine of the phenanthrene type (*II*), splitting off of methyl iodide leads to the tertiary aporphine base *III*. The molecular ions of both products differ by 14 mass units, the presence of the peak of the tertiary base enables the differentiation of quaternary aporphine alkaloids from genuine phenanthrene alkaloids with the methine structure. The molecular ion of the methine usually predominates over the peak of the tertiary base. The ratio of the abundances of both ions often depends on the mode of heating the sample. The base peak of the spectrum belongs always to the ion $CH_2{=}\overset{(+)}{N}{-}CH_3$ (m/z 58) formed by fragmentation of the methine. A complementary ion $M - 58$ is sometimes observed. In some cases, the molecular peak of compound *IV* points to the pyrolytic fission of the methine[5].

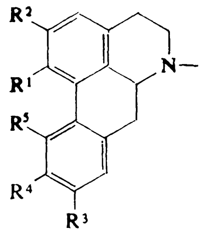
The results presented below show that the complexity of behaviour is further enhanced in some quaternary aporphines by a O-demethylation reaction. The mass spectra of corydine methiodide (*Ia*) and isocorydine methiodide (*Ib*) exhibit three molecular ions of m/z 355, 341 and 327, even with highly purified samples. The first one belongs to the normal methine *IIa* or *IIb*. The most abundant peak of mass 341 represents the tertiary base *IIIa* and *IIIb*, resp., only partially, since it does not reveal fully the fragmentation pattern expected for corydine or isocorydine. Labelling the samples with [O^2H]-ethanol in the ionic source shows the presence of one active hydrogen in the ion of mass 355, but two acidic hydrogens are found in the ionic species of mass 341 and 327. The mass spectra of both methiodides are similar and bear also a good resemblance to that of magnoflorine iodide (*Ic*). These facts prove that hydrolysis of a methoxyl group takes place during the evaporation of the sample.



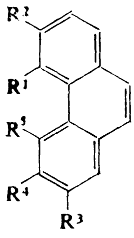
I



II



III



IV

a: $R^1 = OH$, $R^2 = R^4 = R^5 = OCH_3$, $R^3 = H$
b: $R^1 = R^2 = R^4 = OCH_3$, $R^3 = H$, $R^5 = OH$
c: $R^1 = R^5 = OH$, $R^2 = R^4 = OCH_3$, $R^3 = H$
d: $R^1 = OH$, $R^2 = R^5 = OCH_3$, $R^3 = R^4 = H$
e: $R^1 + R^2 = OCH_2O$, $R^3 = H$, $R^4 = OCH_3$, $R^5 = OH$
f: $R^1 = OH$, $R^2 = OCH_3$, $R^3 + R^4 = OCH_2O$, $R^5 = H$
g: $R^1 = R^2 = R^4 = R^5 = OCH_3$, $R^3 = H$

Out of the methiodides studied, that of isothebaine (*Id*, *m/z* 325, 311, 297) undergoes the demethylation. No loss of methyl is, however, observed with methiodides of bulbocapnine (*Ie*, *m/z* 339, 325), domesticine (*If*, *m/z* 339, 325) and O,O-dimethylcorytuberine (*Ig*, *m/z* 369, 355) or with magnoflorine iodide (*Ie*, *m/z* 341, 327). The masses of the molecular ions found are given in parenthesis. From the behaviour of the derivatives *Ia*–*Ig*, the conclusions can be drawn that in the ionic source of the mass spectrometer the methiodides of those aporphine alkaloids are demethylated which bear in the inner positions 1 and 11 one hydroxyl and one methoxyl group. The hydrolysing agent is hydrogen iodide set free by pyrolysis of the unvolatile salt. A strong hydrogen bridge between both substituents in these positions weakens the CH_3—O bond and enables the access and reaction of the iodide anion. The hydrogen bridge between hydroxyl and methoxyl group in other vicinal positions (*cf*. *Ie* and *If*) does not suffice to evoke the reaction. The process is positively influenced by release of steric strain. The stability of O,O-dimethylcorytuberine methiodide (*Ig*) to demethylation shows, however, that the driving force of the reaction cannot be attributed to the steric strain of the inner 1,11-substituents alone. The tendency to undergo demethylation of an inner substituent was also observed in classical chemistry. Isocorydine methiodide (*Ib*) when treated at 160–10°C with 2-aminoethanol suffered a Hofmann elimination accompanied by hydrolysis of the 1-methoxy function[6].

EXPERIMENTAL

The mass spectra were measured on a AEI-MS902 spectrometer with direct inlet probe at ion source temperature 180–210°C.

Corydine methiodide (Ia): 355(3), 341(28), 327(16), 326(7, 5), 312(13), 310(9), 298(6), 296(10), 284(9), 283(12), 270(35), 255(20), 142, 127, 58 (out of scale).

Isocorydine methiodide (Ib): 355(19), 341(90), 327(35), 326(31), 312(25), 310(24), 298(9), 297(13), 296(14), 284(25), 283(24), 270(67), 255(36), 142, 127, 58 (out of scale).

Magnoflorine iodide (Ic): 341(32), 327(12), 326(5), 313(2,3), 312(8, 5), 310(5), 297(3, 2), 296(3, 8), 284(6), 293(11), 282(4), 270(4), 269(3), 268(5), 165(6), 152(7), 142, 128, 127, 58 (out of scale).

Isothebaine methiodide (Id): 325(3), 311(15), 297(10), 296(7), 294(4), 280(9), 254(14), 240(31), 226(6), 225(15), 207(10), 197(9), 142, 127, 58 (out of scale).

Bulbocapnine methiodide (Ie): 339(4), 325(14), 324(10), 311(4), 310(17), 295(3), 282(6), 280(6), 266(2, 5), 264(3), 252(3, 5), 224(4), 142, 127, 58 (out of scale).

Domesticine methiodide (If): 339(15), 325(3), 324(3), 311(0, 4), 310(2), 308(1, 2), 294(1, 4), 282(5), 281(8), 268(1, 8), 267(2, 4), 266(2, 7), 238(2, 7), 165(6, 5), 152(10) 142, 128, 127, 58 (out of scale).

O,O-*Dimethylcorytuberine methiodide* (Ig): 369(7), 355(17), 341(7), 340(29), 324(35), 311(3), 310(3), 309(4), 308(6), 294(5), 282(3), 281(2, 5), 280(2), 279(2), 266(4), 265(3), 142, 127, 58 (out of scale).

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