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MASS-SPECTROMETRIC STUDY OF THE STRUCTURE OF ROBUSTINE AND DUBAMINE

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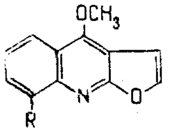
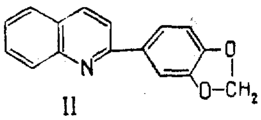
The study of the mass spectra of quinoline and its derivatives and of dictamnine and five of its dimethoxy and methylenedioxy analogs has been reported previously [1, 2].

We have studied the quinoline alkaloids of various plants of the genus Haplophyllum. Robustine (I), with the structure of 8-hydroxydictamnine, was isolated from H. robustum Bge., dubamine (II), with the structure of α-piperonylquinoline [3, 4] from H. dubium, and dictamnine from H. ramosissimum [2, 5]:



I R = OH
III R = OCH₃
IV R = H



II

As was to be expected of these aromatic systems, in the mass spectra of robustine (I), dubamine (II), and γ-fagarine (III) (figure), the peaks of the molecular ions had the maximum intensities.

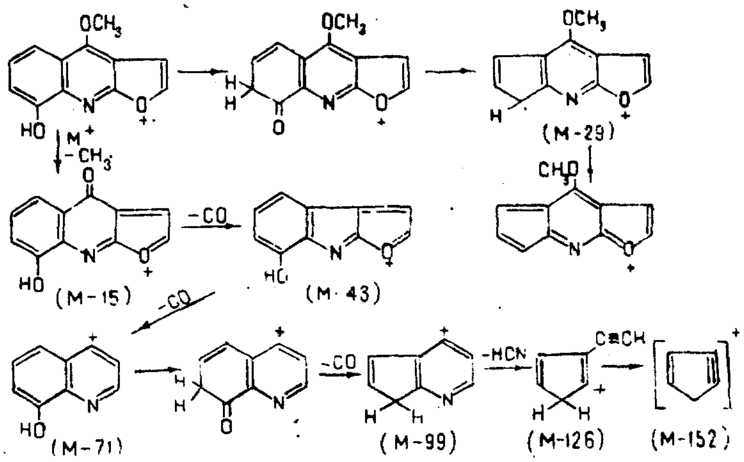
γ-Fagarine gives intense peaks of ions with m/e 228 (M-1) and 200 (M-29). This behavior is typical for 8-methoxyfuranoquinolines and 8-methoxyquinolines [2]. The results of a study of the mass spectra of the furanoquinoline alkaloids containing a methoxy group at C-8 enables the formation of all the other ions to be explained.

In contrast to the mass spectra of phenols [1] and hydroxyquinolines [2], where the peak of the (M-28) ion is generally greater than that of the (M-29) ion, the mass spectrum of I has an intense peak of an ion with m/e 186 (27% of the maximum peak) and a low-intensity peak of ions with m/e 187 (4%). The (M-29) ion in substance I apparently arises by the splitting out of the group of atoms CHO because of the hydroxy group at C-8, since the peak corresponding to this ion is not found in the mass spectrum of dictamnine. A cyclopentadienyl ring is formed.

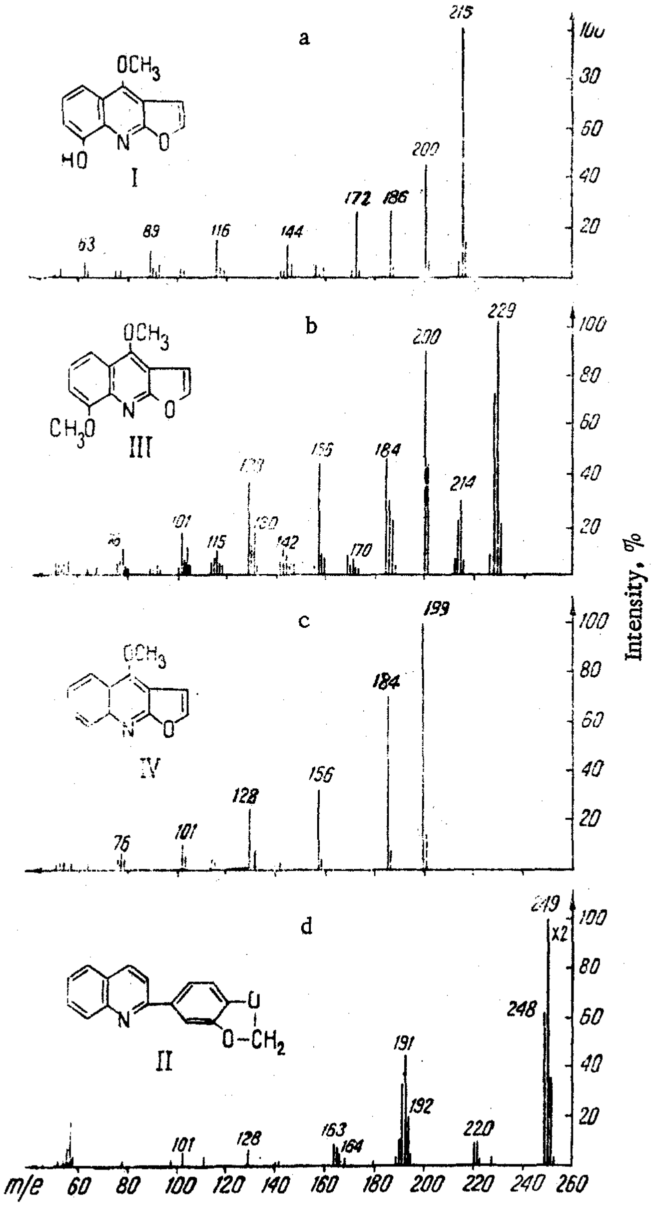
On the subsequent splitting out of a methyl radical, 3 CO molecules (which affects C-4, the furan ring, and the phenol group), a molecule of HCN, and, finally, acetylene, the (M-152) ion with m/e 63 is obtained, this apparently being a cyclopentenynyl ion radical. The transitions (M-15) → (M-43) → (M-71) are confirmed by metastable peaks.

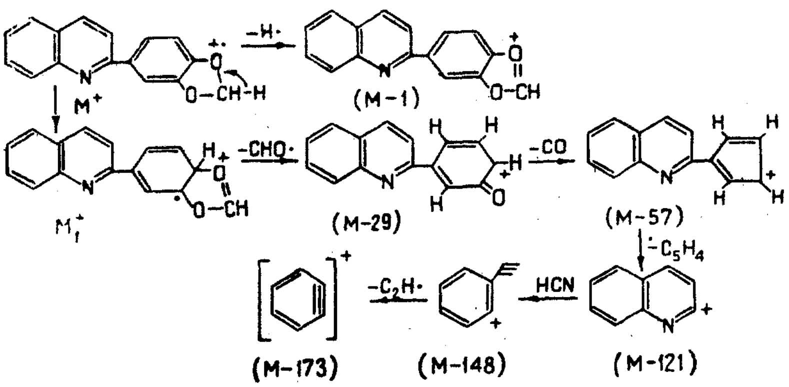
$m^* = 148$, for 200 → 172 calculated 148.

$m^* = 120.5$, for 172 → 144 calculated 120.5.



Dubamine (II) is the first phenylquinoline alkaloid studied by mass spectrometry. The molecular ion with m/e 249 undergoes α-rupture with the elimination of one of the hydrogen atoms of the methylenedioxy group, which leads to a stable onium ion with m/e 248.


a
OCH3
HO
N
O
I
63
89
116
144
172
186
200
215
b
OCH3
CH3O
N
O
III
76
101
115
128
130
142
156
170
184
200
214
229
c
OCH3
N
O
IV
76
101
128
156
184
199
d
N
O
O–CH2
II
101
128
163
164
191
192
220
248
249
x2
20
40
60
80
100
Intensity, %
m/e
60
80
100
120
140
160
180
200
220
240
260


M+
–H·
(M–1)
M1+
–CHO·
(M–29)
–CO
(M–57)
–C5H4
(M–121)
HCN
(M–148)
–C2H·
(M–173)

The molecular ion (M^+) can rearrange into ($\overset{+}{M}_1$). The splitting out of a formyl radical from the latter gives an ion with m/e 220 which, on losing a molecule of CO, gives an ion with m/e 192. Then the cyclopentadienyl ring is detached (probably in the form of cyclopentenyne) and an ion with m/e 128 is formed. This ion first splits off a molecule of HCN and then a C_2H radical, which leads to the ion radical of dehydrobenzene. The ions with m/e 219, 191, and 164 possibly arise by the successive loss by the molecular ion of molecules of formaldehyde, CO, and HCN.

Experimental

The mass spectra were taken on a MKh-1303 mass spectrometer with ionizing electrons having an energy of 34 eV and an ionizing current of 150 μa at 150° C for II and III and at 175° C for I. The maximum peak in the spectrum was taken as 100%, and the spectra show only peaks having an intensity equal to or greater than 2%.

Summary

The results of a study of the mass spectra of robustine and dubamine have enabled a probable scheme of their fragmentation to be given.

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