QUINOLINE ALKALOIDS OF Haplophyllum

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The genus Haplophyllum A. Juss. (family Rutaceae) is represented on the world scale by 50 species [1], 32 of which are known in the Soviet Union, including 23 in Central Asia [2], which is a center of species diversity of these plants.

Systematic investigations of alkaloids of the genus Haplophyllum were begun by S. Yu. Yunusov and G. P. Sidyakin in 1948 [3]. Alkaloids were found in all the plants of this species investigated: 12 Central Asian [4, 5], and four Azerbaidzhanian [6]. Abroad, the alkaloids of Haplophyllum hispanicum [7], H. suaveolens [8], and H. tuberculatum [9], which are taxonomically close to the Central Asian plants, have been studied. From these 19 species of Haplophyllum alone, 46 alkaloids have been obtained (see below), including 34 new ones. With the exception of acetylevoxine [7] and 3-dimethylallyl-4-dimethylallyloxy-2-quinolone [9], all the new alkaloids have been isolated from Central Asian plants of the genus Haplophyllum.

Haplophyllum alkaloids belong to the quinoline derivatives and only two of them have proved to be amides [10] (see below). The majority of the alkaloids (furanoquinoline, dihydropyrano-4-quinolone, 2-alkyl- and 2-phenyl-4-quinolone alkaloids, and others) are weak bases, and because of the hydrolysis of their salts they pass into an organic solvent from an acid solution. This enables them to be separated from the stronger bases such as, for example, the dihydrofuroquinoline alkaloids. A number of compounds (pyrano-2-quinolones, some modified furanoquinoline derivatives, and amides) do not exhibit basic properties, and if a phenolic hydroxyl is present they show acidic properties. Consequently, alkaloids can be found not only in the basic but also in the neutral and acidic fractions of a plant extract.

An investigation of plants of the genus Haplophyllum has shown that they contain new representatives of almost all the known varieties of quinoline alkaloids, in which plants of the family Rutaceae are rich [11, 12]. Together with these, in Haplophyllum species peculiar quinoline alkaloids not found in plants of other genera of the family Rutaceae have been discovered: quinoline alkaloids containing a fragment of two isoprene units (Ia, IIa, and XVI), glycoalkaloids of the furanoquinoline series (IXa and IXb) and modified furanoquinine derivatives (XIa, XIb-XIII) (see below).

We have subdivided the quinoline alkaloids isolated up to the present time from plants of the genus Haplophyllum into seven groups. In this review we discuss the characteristic reactions and spectral properties of each group.

Below we give the alkaloids obtained from plants of the genus Haplophyllum (alkaloids isolated previously from other genera of the family Rutaceae are marked with an asterisk):

4-HYDROXY-2-QUINOLONE DERIVATIVES

<table>
<thead>
<tr>
<th>Alkald</th>
<th>Plant</th>
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<tbody>
<tr>
<td>I. Robustinine (edulitine) Ia, R=OCH₃; R₁=H; R₂=H</td>
<td>H. bungei [13], H. foliosum [14]</td>
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<tr>
<td>2. Foliidine, Ib, R=OH; R₁=R₂=CH₃</td>
<td>H. robustum [15]</td>
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<tr>
<td>3. Folimine, Ic, R=OCH₃; R₁=R₂=CH₃</td>
<td>H. dubium [16], H. foliosum [14]</td>
</tr>
<tr>
<td>4. Foliocinnamid, Id, R=OCH₃; R₁=R₂=CH₃</td>
<td>H. foliosum, [17] H. perforatum [18]</td>
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</tbody>
</table>

Alkaloid

4. Foliosidine, Ia, R = OCH₃CH(OH)C(OH)(CH₃)₂; R₁ = R₂ = CH₃
5. Bucharanine, Ib, R = R₂ = H; R₁ = C(CH₃)₂CHCHCH(OH)C(OH)(CH₃)₂
6. Buchardine, IIa, R = R₂ = H
7. 3-Dimethylallyl-4-dimethylallyloxy-2-quinolone, IIb, R = R₁ = C(CH₃)₂

Plant

H. dubium [16], H. foliosum [19], H. perforatum [18]
H. bucharicum [20]
H. bucharicum [21]
H. tuberculatum [9]

PYRANO-2-QUINOLONE DERIVATIVES

Dihydropyrano-4-quinolone derivatives

D-Phenylquinoline and 2-alkyl-4-quinolone derivatives

H. foliosum [25], H. suaveolens [8]
H. bucharicum [14, 20], H. foliosum [14], H. bucharicum [22]
H. dubium [26], H. letifolium [5]
H. foliosum [27], H. perforatum [18]
H. dubium [16, 28], H. foliosum [19]
H. foliosum [29]
H. acutifolium [30]