DYNAMICS OF THE ACCUMULATION OF THE ALKALOIDS OF *Reseda luteola* STRUCTURE OF LUTINE AND LUTININE

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In the vegetable kingdom, the family Resedaceae numbers 65 species (six genera). Only one genus — *Reseda* — grows in the USSR; it includes 10 species, five of which are found in Central Asia [1] and four in all regions of Uzbekistan [2]. *R. luteola* L. is a biannual herbaceous plant found in the form of individual thickets on hills, mountain slopes, and close to field crops. It has been shown previously that the plant contains alkaloids [3]. The present paper gives information on a study of the quantitative and qualitative changes in the composition of the total bases during the vegetation periods. We have considered the dynamics of the accumulation of alkaloids in the plant collected in the Samarkand oblast (Urgut region, Ittifak kolkhoz [collective farm]) on the northern slopes of the Zarafshan range. The procedure for isolating and separating the combined alkaloids and their main representatives has been described previously [3]. The results of the investigation are given in Table 1.

It can be seen from Table 1 that the greatest amount of alkaloids is contained in the epigeal part and the roots of the plant in the period of vigorous growth and flowering. The quantitative ratios between the alkaloids also change as a function of the phase of development. Thus, while in the period of vigorous growth the greatest amount of resedine is found in the epigeal part and in the roots, in the period of the withering of the epigeal part its amount here is very low. The amount of resedine in the epigeal part increases during the flowering period, and as the plant develops the amounts of phenyl-β-naphthylamine and of β-hydroxyphenylethylamine fall. The facts given are in complete agreement with laws revealed previously [4].

On studying the dynamics of the accumulation of alkaloids, in the separation of the combined ether-soluble alkaloids from the epigeal part of the plant collected in the period of vigorous growth we isolated another three bases. The spectral characeeristics and some physicochemical constants of one of them coincide with those for cinnamamide.

The base (II), $C_{16}H_{11}NO_2$, with mp 185-186°C (chloroform), which we have called lutine, forms cherry-red crystals. Its UV spectrum has absorption maxima at 216, 222, and 274 nm (log ε 4.45, 4.37, and 4.50). The IR spectrum contains absorption bands at 3320 cm^{-1} (active hydrogen), 1670 cm^{-1} (C=O), 710 and 770 cm^{-1} (monosubstituted benzene ring), and 750 cm^{-1} (ortho-disubstituted benzene ring). The molecular ion of compound (II) appears in the form of an intense peak with m/e 249 (100%) (the composition was determined from the high-resolu-

TABLE 1.

Date of collection (1975)	Phase of development	Plant organ	Combined alkaloids	Amounts of the main alkaloids, % of the total			
				resedine	resedinine	phenyl-β-naphthylamine	β-hydroxyphenylethylamine
25.IV	Early period (vigorous growth)	Epigeal part	0,12	52,06	13,01	0,5	1,62
		Roots	0,11	45,02	9,03	0,6	1,58
25.V	Flowering	Epigeal part	0,11	30,1	17,5	0,45	0,92
		Roots	0,07	5,7	1,5	0,2	0,5
10.VI	Massive fruit-bearing	Epigeal part	0,05	14,07	10,02	0,37	0,72
5.VII	End of vegetation (withering of the epigeal part)	Epigeal part	0,01	3,1	0,01	0,1	0,3
		Roots	0,06	19,2	3,8	—	—

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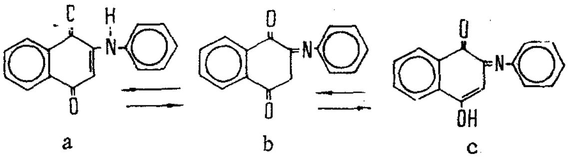
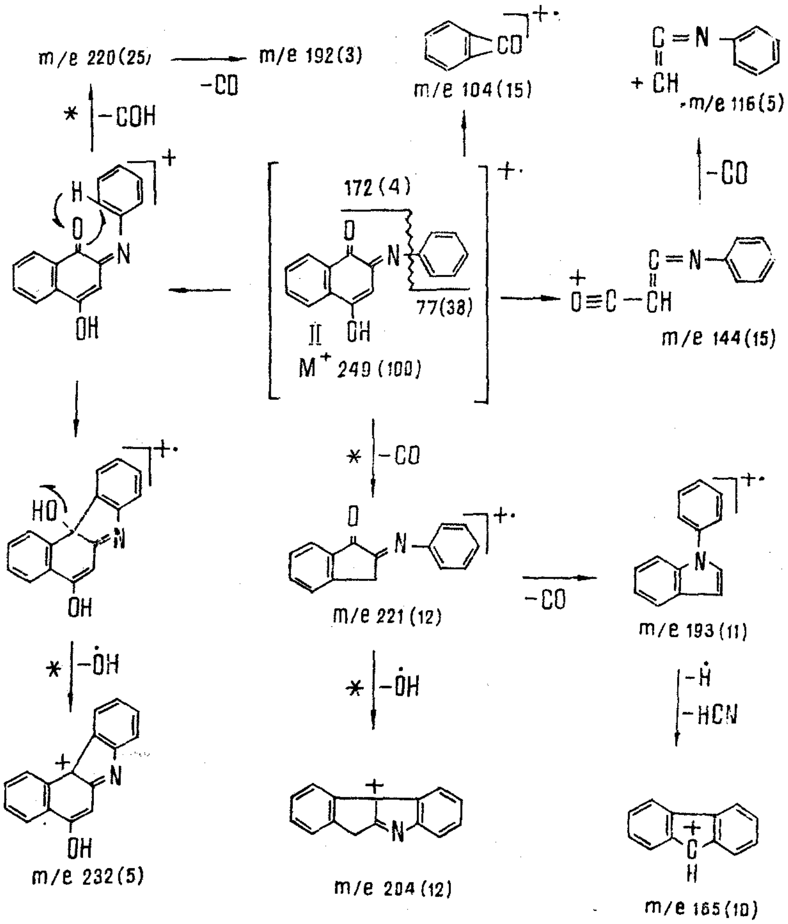
tion mass spectrum) and by a number of pairs of fragmentary ions totalling 249 amu; 172 + 77 and 105 + 144. Ions with m/e 77, 104, and 105 are characteristic of benzene derivatives [5].

The composition, melting point, and color of the (II) were identical with those of 2-anilino-1,4-naphthoquinone [6]. The authors concerned [6] assumed that this compound can exist in one of three tautomeric forms: *a*, b, and c (Scheme 1). However, they did not show a predominant tautomeric state in the native form. To answer this question, we have analyzed the IR and mass spectra of (II).



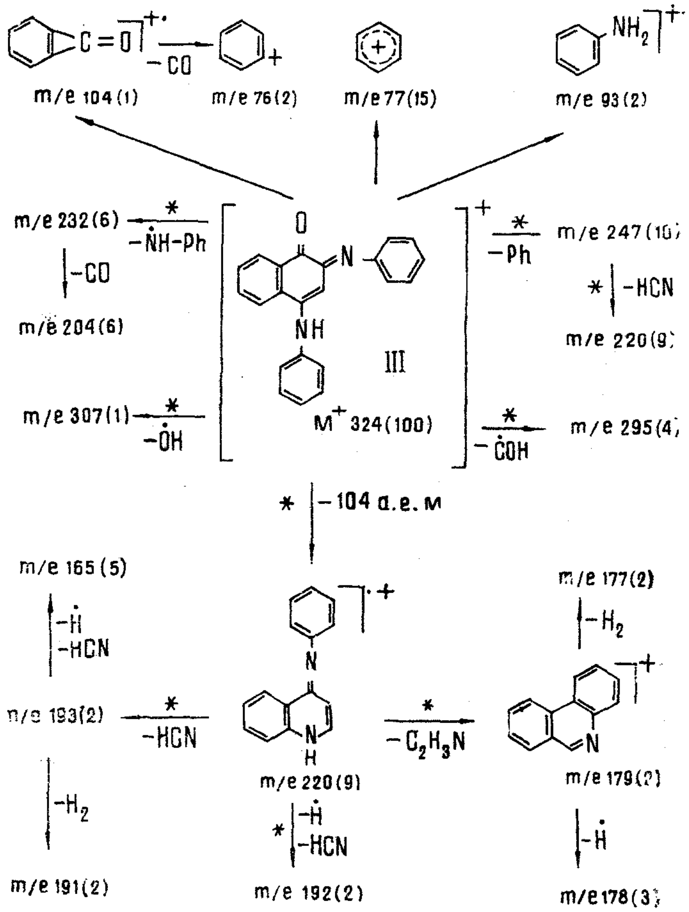
Scheme 1

The results of a study of the fragmentation and of the determination of the elementary compositions of key ions confirmed that we were dealing with 2-anilino-1,4-naphthoquinone. The shift of the M^+ peak by 1 amu in the spectrum of the D analog of (II), and also the presence of an absorption band at 3320 cm^{-1} (ν_{OH} or ν_{NH}) excludes tautomeric form b. The absence from the mass spectrum of an aniline fragment with m/e 93 excludes form *a*. Thus, in the crystalline state, in solution, and in the form of a vapor compound (II) exists in form c.



Scheme 2

In the mass spectrum of (II) fragments with m/e 221 and 220 are formed through the loss by the molecular ion of a CO molecule and a ĊOH radical, and then both ions, eliminating a second CO molecule, are converted into ions with m/e 193 and 192, respectively. The subsequent decomposition of these ions leads to a fluorenyl ion with m/e 165 (Scheme 2). The shift of the peaks of ions with m/e 220 and 192 to the same extent as the M^+ peak in the spectrum of the D analog of (II) shows that the ion with m/e 220 is obtained by the ejection of C_1—OH and not of C_4—OH. The peak of the ion with m/e 232 corresponds to the ejection from M^+ of an OH radical, and such a radical is also eliminated by the (M — CO)$^+$ ion, which leads to an ion with m/e 204. In the spectrum of the D analog, the ions with m/e 232 and 204 are shifted by 1 amu, which indicates a complex rearrangement nature of the elimination of OH (see Scheme 2).



Scheme 3

Base (III) with mp 177-179°C (chloroform), which we have called lutinine, forms dark red crystals. The mass spectrum of the compound [m/e 324 M^+ (100%), 295, 247, 232, 220, 204, 178, 165, 105, 104, 93, 77] has some similarity with the spectra of lutine and of phenyl-β-naphthylamine [7] and is characterized by the maximum peak of the molecular ion with m/e 324. The even-numbered mass of the M^+ ion, and also the presence of a fragment with m/e 93 suggest that this compound may be an aniline derivative of form IIc (see Scheme 1). The melting point and the color of base (III) coincide with those of 4-anilino-2-phenylinino-1,2-dihydronaphthalen-1-one [6], and the nature of the fragmentation of compound (III) also agrees with this structure.

The decomposition of the molecule of (III) under electron impact takes place through the cleavage of ordinary bonds and also through a complex multistage rearrangement mechanism (Scheme 3). Thus, lutine and lutinine are new bases consisting of naphthoquinone derivatives and we are the first to have found them in nature.

EXPERIMENTAL

The UV spectra were taken on a Hitachi spectrometer, the IR spectra on a UR-20 instrument (tablets with KBr), and the mass spectra on an MKh-1303 instrument with a system for the direct introduction of the sample at 90-100°C and at an ionizing voltage of 40 V. The accurate masses of the ions were measured on a Varian MAT-311 mass spectrometer.

Isolation and Separation of the Combined Alkaloids. The combined ether-soluble alkaloids [3] were chromatographed on a column of silica gel (1:20). Elution of the alkaloids with petroleum ether yielded 75 mg of phenyl-β-naphthylamine and a red mixture of two bases. A benzene—chloroform (1:1) eluate yielded 0.16 g of cinnamamide. The mixture of two bases was separated by preparative TLC on a fixed layer of silica gel in the benzene—chloroform (5:3) system, giving 16 mg of (II) with mp 185-186°C and 13 mg of (III) with mp 177-179°C.

SUMMARY

The qualitative and quantitative changes in the composition of the combined bases in *Reseda luteola* during the vegetation periods have been studied. From the epigeal part of the plant we have isolated cinnamamide and two new alkaloids: lutine and lutinine. A study of the spectral characteristics and the mechanism of fragmentation has shown that lutine has the structure of 2-anilino-1,4-naphthoquinone and lutidine that of 4-anilino-2-phenylamino-1,2-dihydronaphthalen-1-one.

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THE ELECTROCHEMICAL EXTRACTION OF ALKALOIDS OF THE PYRROLIZIDINE SERIES FROM PLANT RAW MATERIAL. I

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The alkaloids of the pyrrolizidine series — platyphylline, seneciphylline, and their N-oxide forms — consist of complex cyclic diesters of the bicyclic base heliotridane and dicarboxylic acids and are widely represented in various species of Cruciferae [1].

As pharmacological and clinical investigations have shown, platyphylline possesses valuable atropine-like properties, and it is used as a spasmolytic and hypotensive agent. Seneciphylline can be used for the synthesis of curaremimetic compounds [2].

A characteristic feature of alkaloids of the pyrrolizidine series is the presence in the plant raw material of the N-oxide forms, the amounts of which in different species of *Senecio* depend on the growth site and the date of collection and range between 80 and 93% [3]. The isolation of the N-oxide alkaloids and their conversion into the reduced form is an important step in the production of the alkaloids, since this considerably raises the yield of the main product.

At the present time, the optimum conditions for the isolation of the N-oxide alkaloids of *Senecio* are connected with the process of their extraction by dichloroethane in the presence of glucose and with the process of the reduction of a sulfuric acid or hydrochloric acid

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