THE DYNAMICS OF THE ACCUMULATION OF THE ALKALOIDS OF THE GENUS Ungernia

A. Abdusamatov, S. A. Khamidkhodzhaev, and S. Yu. Yunusov

UDC 547.944/945

Plants of the genus Ungernia, comprising seven species – U. victoris Vved., U. tadshicorum Vved., U. ferganica Vved., U. severtzovii B. Fedtsch., U. spiralis, U. trisphaera Bge., and U. minor Vved. – are distributed in various regions of Central Asia [1-3].

The investigation of the alkaloids of the Ungernia was begun by Orekhov and Norkina, who isolated the alkaloid tazettine from the bulbs of U. severtzovii in 1936 [4]. In 1938, Yurashevskii isolated lycorine from the bulbs of U. tadshicorum [5].

Our systematic investigations, performed since 1949, show that the plants of the genus Ungernia contain bases [6-13] belonging to various groups of amaryllis alkaloids. By studying the dynamics of the accumulation of the latter [14], it is possible to gain an idea of the formation, mutual transitions, and roles of the alkaloids in the process of the development of the plant.

A study of the dynamics with respect to the vegetation periods of the accumulation of galanthamine in the leaves of U. victoris collected on the R. Shargun' in the Katta-Khovar gorge and of lycorine in the leaves of U. trisphaera collected in the Ashkhabad region of the Turkmen SSR (Table 1) showed that the maximum accumulation of alkaloids, including galanthamine and lycorine, is found in the early vegetation period; and in the period of the dying-off of the epigeal part the amount of combined alkaloids, and of galanthamine and lycorine, diminishes sharply [9, 14, 15].

In the period of complete withering, the epigeal part contains no alkaloids, and they accumulate in the bulbs and roots (Table 2) [16].

We have determined the influence of the growth site on the qualitative and quantitative content of alkaloids in the leaves of U. victoris. The leaves were collected from various growth sites (Table 3). The amount of combined alkaloids, including galanthamine, varied markedly according to the growth site of the plant [9, 14]. Obviously the effects of various soil and climatic conditions are involved here.

TABLE 1

Date of collection of leaves of U. victoris (1960)	Percentage of wt. of the dry leaves		Date of collection of leaves of U. trisphaera (1964)	Percentage of wt. of the dry leaves	
	combined alkaloids	galanthamine		combined alkaloids	galanthamine
5.III	1,0	0,21	25.III	1,3	0,61
9.IV	0,54	0,17	8.IV	1,25	0,55
16.IV	0,52	0,15	15.IV	1,09	0,52
20.IV	0,51	0,14	21.IV	1,0	0,5
25.IV	0,5	0,13	5.V	0,77	0,45
9.V	0,45	0,09	15.V	0,30	0,1
25.V	0,43	0,06	5.VI	0,15	0,02
2.VI	0,33	0,05			

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 60-64, January, 1971. Original article submitted November 9, 1970.

TABLE 2

Collection date (1962)	Plant organs	Percentage of the dry plant: combined alkaloids	galantham.	lycorine
	U. victoris			
8.IV	Leaves	0,53	0,14	0,052
	Bulbs	0,75	0,20	0,25
	Roots	1,67	0,28	0,69
5.VII	Leaves (dried naturally)	None	—	—
	Bulbs	0,96	0,21	0,28
	Roots	2,02	0,42	0,92
	U. tadshicorum			
17.III	Leaves	0,12	0,0014	0,01
	Bulbs	0,31	0,03	0,14
	Roots	1,54	0,052	0,8
27.VII	Leaves (dried naturally)	None	—	—
	Bulbs	0,47	0,04	0,208
	Roots	1,93	0,058	1,05

TABLE 3

Collection site	Collection date (1960)	Total alkaloids (% wt. of dry plant)	Galanthamine (% wt. of dry plant)	Collection date (1962)	Total alkaloids (% wt. of dry plant)	Galanthamine (% wt. of dry plant)	Collection date (1970)	Total alkaloids (% wt. of dry plant)	Galanthamine (% wt. of dry plant)
Shargun'	25.IV	0,5	0,13	8.IV	0,53	0,14	23.IV	0,41	0,1
Amanalsai	29.IV	0,4	0,08	8.IV	0,5	0,11	24.IV	0,39	0,075
Sangardak	11.V	0,27	0,025	8.IV	0,41	0,08	24.IV	0,32	0,036
Obizarang	11.V	0,33	0,088	9.IV	0,49	0,12	23.IV	0,36	0,082
Guliob	12.V	0,46	0,068	9.IV	0,54	0,09	23.IV	0,38	0,071
Shirkent	15.V	0,36	0,041	10.IV	0,43	0,085	24.IV	0,33	0,065
Sina	27.V	0,16	traces	10.IV	0,35	0,04	—	—	—

TABLE 4

Site and date of collection	Plant organ	Total alkaloids	Lycorine	Hippeastrine	Galanthamine	Narwedine	Pancratine	Hordenine	Ungminorine	Tazettine
		percentage of weight of the dry plant								
U. tadshicorum Tadzhik SSR, Lenin region, Tulyanazar section, 13.IV 1963	Leaves	0,27	0,047	0,077	0,0086	—	—	—	—	0,037
	Bulbs	0,52	0,23	—	0,056	—	—	—	—	0,098
	Roots	1,67	0,73	—	0,068	—	—	—	—	0,37
U. ferganica Osh oblast, village of Dmitrievka 10. V 1963	Leaves	0,095	0,0067	0,0015	0,0015	—	—	0,016	0,004	—
	Bulbs	0,6	0,26	—	—	—	0,04	—	—	0,14
	Roots	3,28	2,25	—	—	—	0,03	—	—	0,51
U. Severtzovii Tashkent oblast, Karzhantau, 1962	Leaves	0,75	0,46	0,008	0,01	0,005	0,12	—	0,005	0,004
	Bulbs	1,32	0,38	—	0,033	0,01	0,12	—	0,074	0,005
	Roots	2,15	0,8	—	—	—	0,022	—	0,48	0,006
U. trisphaera Turkmen SSR, Kaakhkinskii region 26.IV 1962	Leaves	0,48	0,10	0,24	—	—	—	—	—	—
	Bulbs	0,92	0,33	—	—	—	—	—	—	—

From the epigeal parts of U. tadshicorum, U. ferganica [13], U. severtzovii [12], and U. trisphaera [10], in addition to other alkaloids, we isolated the alkaloid hippeastrine, which is absent from the subterranean organs of these plants (Table 4). The absence of hippeastrine from the subterranean organs and the increase in the amount of lycorine make it possible to assume that hippeastrine is converted into lycorine.

The results of the investigation of the dynamics of the accumulation of the alkaloids in the leaves of U. victoris are given in Table 5. The amount of combined alkaloids and also of galanthamine, narwedine, hordenine, and lycorine in the leaves gradually decreases as the plant develops, and in the bulbs and roots

TABLE 5

Plant organs	Collection date (1964)	Combined alkaloids	Galanthamine	Narwedine	Hordenine	Lycorine
		percentage of wt. of dry plant				
Leaves	25.III	0,61	0,15	0,055	0,067	0,059
	4.IV	0,49	0,135	0,054	0,049	0,056
	12.IV	0,46	0,12	0,041	0,038	0,042
	20.IV	0,41	0,10	0,035	0,031	0,019
	28.IV	0,37	0,08	0,025	0,021	0,010
Bulbs	4.IV	0,76	0,18	—	—	0,23
	28.IV	0,85	0,24	—	—	0,31
Roots with tip	4.IV	1,65	0,32	—	—	0,74
	28.IV	1,78	0,38	—	—	0,85

the amount of galanthamine and lycorine increases while narwedine and hordenine are absent. These facts permit the assumption that in the leaves galanthamine is partially converted to narwedine and in the bulbs narwedine is converted into galanthamine. These alkaloids possibly take part in redox processes occurring in the plants.

Hordenine is a derivative of ethylphenylamine, and therefore it is probably synthesized from the tyrosine present in the plant.

The decrease in the amount of hordenine as the plant develops and its absence from the subterranean organs are explained by the possibility of its decomposition.

EXPERIMENTAL

The comminuted leaves of U. victoris (1000 g, collected in the Katta-Khovar gorge on March 25, 1964) were moistened with 5% ammonia, placed in a continuous-circulation extractor, and extracted with chloroform. The final chloroform extract was treated with 10% sulfuric acid until the alkaloids had been removed completely. The sulfuric acid extracts were filtered and, with cooling, made alkaline with 25% ammonia. The alkaloids were exhaustively extracted first with ether and then with chloroform. The yield of combined ethereal alkaloids was 4.35 g and of chloroform alkaloids 1.75 g.

When 4.35 g of the combined ethereal alkaloids was treated with 20 ml of acetone, 0.35 g of narwedine with mp 184-185°C was obtained. With cooling, conc. hydrobromic acid was added to the acetone mother solution until it was faintly acid, whereupon 1.96 g of crystalline galanthamine hydrobromide with mp 246-248°C (decomp.) deposited. From the acidic acetone solution, the alkaloids were transferred in the form of the free bases into ether. Yield 2.05 g. The combined ethereal alkaloids (2.05 g) were dissolved in 10 ml of acetone, giving 0.2 g of narwedine. The acetone mother solution was treated with conc. oxalic acid solution to a feebly acid reaction. The yield of hordenine oxalate with mp 227-228°C was 1.035 g. The combined chloroformic alkaloids (1.75 g) were treated with 25 ml of acetone, giving 0.592 g of lycorine with mp 247-249°C (decomp.).

Bulbs of U. victoris (500 g, collected in the Katta-Khovar gorge on April 4, 1964) freed from skin, dried, and ground were wetted with 5% ammonia solution and extracted with chloroform. The alkaloids were extracted from the latter with 10% sulfuric acid, and 620 ml of the acid solution was made alkaline with 25% ammonia solution, giving a precipitate of 0.75 g of lycorine. Then the alkaloids were extracted with ether and chloroform. After concentration, 2.35 g of ethereal and 0.7 g of chloroformic alkaloids were obtained. The ethereal alkaloids (2.35 g) were dissolved in 30 ml of acetone and, with cooling, the solution was made weakly acid with conc. HBr. This led to the separation of 1.15 g of technical galanthamine hydrobromide. The chloroform alkaloids (0.7 g) were treated with acetone, giving 0.4 g of lycorine.

The comminuted roots with tips of U. victoris (300 g, collected in the Katta-Khovar gorge on April 4, 1964) were wetted with 8% ammonia solution (1 : 1) and extracted with chloroform. The chloroform solution was concentrated to 600 ml, whereupon 1.2 g of lycorine deposited. After the separation of the lycorine, the alkaloids were extracted with 10% sulfuric acid. The acid solution was made alkaline, giving 0.72 g of lycorine. From the alkaline solution the alkaloids were extracted with ether and chloroform. On concentration, 2.4 g of ethereal and 0.63 g of chloroformic alkaloids were obtained. The ethereal fraction (2.4 g) was dissolved in 35 ml of acetone, and acidification of the solution with conc. HBr gave 1.23 g of technical galanthamine hydrobromide. The chloroform fraction (0.63 g) was treated with acetone, giving 0.3 g of lycorine.

The methods mentioned were adopted, respectively, for the leaves, bulbs, and roots collected at different vegetation periods of the plant.

SUMMARY

A study of U. victoris, U. tadshicorum, and U. trisphaera with respect to the vegetation periods and growth sites has shown that the maximum accumulation of alkaloids takes place in the early vegetation period and that naturally dried leaves do not contain alkaloids. The alkaloid content also depends on the growth site.

In the period of the vigorous development of the epigeal part, some alkaloids are possibly converted into one another (hippeastrine into lycorine, galanthamine into narwedine, and narwedine into galanthamine).

LITERATURE CITED

1. Flora of the USSR, Vol. 4 [in Russian], (1935), p. 488.
2. E. E. Korotkova, Dokl. Akad. Nauk UzSSR, 1961, No. 11, 24.
3. S. A. Khamidkhodzhaev and E. E. Korotkova, Dokl. Akad. Nauk UzSSR, 1966, No. 7, 39.
4. S. S. Norkina and A. P. Orekhov, Zh. Obshch. Khim., 7, 902 (1937).
5. N. K. Urashchevskii, Zh. Obshch. Khim., 8, 949 (1938).
6. S. Yu. Yunusov and Kh. A. Abduazimov, Dokl. Akad. Nauk UzSSR, 1953, No. 6, 44.
7. Kh. A. Abduazimov and S. Yu. Yunusov, Dokl. Akad. Nauk UzSSR, 1956, No. 4, 7.
8. S. Yu. Yunusov and Kh. A. Abduazimov, Zh. Obshch. Khim., 29, 1724 (1959).
9. A. Abdusamatov, Kh. A. Abduazimov, and S. Yu. Yunusov, Uzb. Khim. Zh., 1962, No. 1, 46.
10. Kh. Allayarov, Kh. A. Abduazimov, and S. Yu. Yunusov, Uzb. Khim. Zh., 1964, No. 2, 46.
11. M. Normatov, Kh. A. Abduazimov, and S. Yu. Yunusov, Uzb. Khim. Zh., 1965, No. 2, 25.
12. L. S. Smirnova, Kh. A. Abduazimov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 322 (1965).
13. I. Israilov, Kh. A. Abduazimov, and S. Yu. Yunusov, Dokl. Akad. Nauk UzSSR, 1965, No. 3, 18.
14. S. Yu. Yunusov, Izv. Akad. Nauk UzSSR, 1948, No. 4, 11.
15. A. Abdusamatov, Kh. Allayarov, Kh. A. Abduazimov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 459 (1969).
16. A. Abdusamatov, Kh. A. Abduazimov, and S. Yu. Yunusov, Dokl. Akad. Nauk UzSSR, 1963, No. 1, 18.