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Berberis ALKALOIDS

XIV. DYNAMICS OF THE ACCUMULATION OF ALKALOIDS IN *Berberis oblonga*

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UDC 547.944/945

The study of plants of the genus *Berberis* (Berberidaceae) is due to the presence in them of the alkaloid berberine, which, in the form of the bisulfate, is used as a cholagogue [1, 2]. The level of berberine in different species of barberry ranges from 0.3 to 1% [3].

The roots of *B. oblonga* gathered in Kazakhstan at the stage of unripe fruit yielded 0.30% of berberine [3]. We have previously isolated a number of isoquinoline alkaloids in a study of various organs of this plant [4].

We have now studied the dynamics of the accumulation of alkaloids in the roots, young stems, and leaves of *B. oblonga* growing on the bank of the Chilisai in the Navkat region of Osh province. Results on the determination of the total alkaloids and the amounts of the main alkaloids are given in Table 1. The total alkaloids from each sample were separated by methods described in the literature [5, 6]. The total amount of alkaloids in the roots proved to be highest at the end of vegetation, while in the young shoots and leaves it was during the mass flowering period. The level of alkaloids in the epigeal part decreased sharply towards the end of vegetation, while in the roots an increase in their total amount was observed, which is in harmony with the laws established by S. Yu. Yunusov [7]. The main alkaloids in the roots and young shoots were berberine, magnoflorine, and oxyacanthine, while in the leaves the main alkaloid was glaucine.

TABLE 1. Dynamics of the Accumulation of Alkaloids in Various Organs of *B. oblonga* during the Phases of Vegetation

Phase of development of the plant	Plant organ	Total amount of alkaloids, %	Quaternary bases, %	Tertiary bases, %	Levels of the main alkaloids			
					berberine iodide	oxyacanthine	magnoflorine iodide	glaucine
Mass-flowering period, May 18, 1989	Roots	4.3	2.2	2.1	0.66	0.45	0.61	—
	Young shoots	1.40	0.50	0.90	0.30	0.35	0.11	—
	Leaves	0.39	0.15	0.24	0.05	0.05	—	0.16
Fruit-ripening period, August 25, 1989	Roots	5.20	2.90	2.30	1.05	0.55	0.01	—
	Young shoots	1.1	0.3	0.08	0.22	0.24	0.03	—
	Leaves	0.28	0.08	0.20	0.04	0.04	—	0.13
End of vegetation, October 23, 1989	Roots	6.6	4.15	2.45	1.22	1.01	1.11	—
	Young shoots	0.54	0.31	0.23	0.14	0.21	0.05	—
	Leaves	0.03	0.03	0.03	0.01	0.02	—	0.02

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Thus, it may be concluded that for the production of berberine it is desirable to gather the roots at the end of vegetation and the young shoots and leaves during the period of mass flowering.

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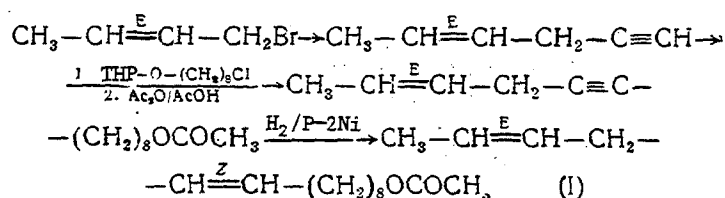
SYNTHESIS OF THE PHERMONE OF *Ephestia kuehniella*

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UDC 547.3+632.7

The Mediterranean flour moth is one of the main pests of stored cereals. The pheromone of the Mediterranean flour moth is tetradeca-9Z,12E-dienol acetate (I). The presence of a methylene-separated diene system complicates the performance of a stereospecific synthesis. In the synthesis of aliphatic dienic pheromones the main methods are the elongation of the chain of an unsaturated fragment already having a double bond with the required configuration or a double and a triple bond, or the coupling of synthons each of which has an unsaturated bond (for example, [1-4]), but syntheses by the elongation of a fragment containing a 1,4-nonconjugated system are encountered considerably more rarely. In particular, we may mention the work of Bac and Langlois [5], who obtained 1-dimethylaminohepta-2Z,5E-diene by the stereoselective fragmentation of 1,2,3,6-tetrahydropyridine methiodide with cesium fluoride. Subsequently, these authors performed chain elongation with 1-chloro-7-(tetrahydropyran-2-yloxy)-heptane.

In the scheme for the synthesis of pheromone (I) that we propose, the main synthon - the enyne (2) - was obtained by the ethynylation of crotyl bromide:



Ethynylation was carried out in three ways: 1) by the interaction of the lithium acetylide-ethylenediamine complex with crotyl bromide in DMSO for 15 h; 2) by the interaction of crotyl bromide with lithium acetylide obtained by the dropwise addition of butyllithium (0.6 mole) to a saturated solution of acetylene in THF, with cooling (+5°C); and 3) via the Iotsich complex obtained in the following way: with cooling to -20°C, ethylmagnesium bromide was added to a saturated solution of acetylene in THF, and, after the addition of the whole amount, the mixture was stirred for 1 h while the temperature was allowed to rise to 0°C, and crotyl bromide was added, and then the reaction mixture was heated at 60°C for 1 h. In all cases, the reaction was stopped by the addition of water or ammonium chloride solution, the substance was extracted with ether, the extract was dried, the ether was evaporated off, and the residue was distilled in vacuum, bp 43-45°C/30 mm,

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