QUINAZOLINES.

VII. SYNTHESIS OF 6-NITRO-, 6-AMINO-, AND 9,9-DIBROMODEOXYVASICINONE

Kh. M. Shakhidoyatov, A. Irisbaeva, É. Oripov,
and Ch. Sh. Kadyrov

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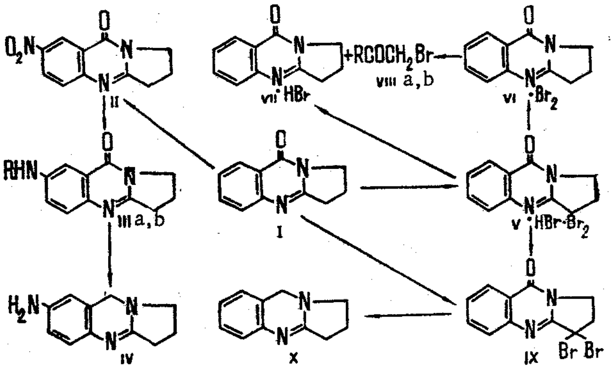
For the synthesis of substituted deoxypeganines and deoxyvasicinines we have studied the electrophilic substitution of deoxyvasicinone. The nitration of deoxyvasicinone (I) with nitrating mixture at temperatures below 5°C gave 6-nitrodeoxyvasicinone (II). The latter was identical with the product synthesized previously from 5-nitroanthranilic acid and γ-butryolactam [1]. The reduction of the nitro group of (II) with iron in glacial acetic acid gave a mixture of 6-amino- and 6-acetylaminodeoxyvasicinones (IIIa, b) with a total yield of 56%, while in the presence of stannous chloride (IIIa) was formed in 90% yield. 6-Aminodeoxypeganine (IV) was obtained from (IIIa) by reduction with zinc in 10% hydrochloric acid.



We then studied the bromination of (I). It was found that the direction of the reaction depends on its conditions. Thus, the reaction of (I) with bromine in chloroform forms a complex (V) which, on standing, loses a molecule of bromine and is converted into deoxyvasicinone hydrobromide (VII). The latter was also obtained from the reaction mixture after the isolation of (V). On treatment with a 5% solution of sodium bicarbonate, (V) lost a molecule of hydrogen bromide and gave a new complex of (I) with bromine (VI). The complexes (VI) and (V) react instantaneously with acetone, forming (VII) and bromoacetone (VIIIa), and similarly with acetophenone, forming (VII) and bromoacetophenone (VIIIb). However, the bromination of (I) in 75% acetic acid with heating gave 9,9-dibromodeoxyvasicinone (IX). There was no formation of 9-monobromodeoxyvasicinone, which has been obtained previously from (I) and N-bromosuccinimide in the presence of benzoyl peroxide [2]. Compound (IX) is also formed when the bromine complex (V) or its mixture with (I) in 75% acetic acid is heated (90-95°C).

The reduction of (IX) with zinc in 10% hydrochloric acid took place with the simultaneous splitting out of bromine atoms and led to deoxypeganine (X).

The yields and physicochemical properties of the compounds obtained are given below. The R_f values were determined for compound (II) in the solvent system chloroform—ethanol (25:1) on silica gel, for compounds (IIIa and b) in chloroform—ethanol (100:1), for compounds (IV) and (X) in chloroform—ether (1:1), and for compound (IX) in ether on alumina:

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Initial compound	Reaction product	Yield, %	mp (solvent for recrystallization (°C)	R_f
I	II	73	187–188 (methanol)	0,75
II	IIIa		248–249 (ethyl acetate)	0,44
	IIIb	56	262–264 (ethanol)	0,28
II	IIIa	90	248–249 (ethyl acetate)	0,44
IIIa	IIIb	95	262–264 (ethanol)	0,28
IIIa	IV	53	183–185 (hexane)	0,12
I	V	75	155–157 (glacial acetic acid)	—
V	VI	62	105–107	—
V	VII	83	304 (ethanol)	—
I	IX	25	188–190 (ethanol)	0,77
V	IX	50	189–191 (ethanol)	0,77
IX	X	37,5	85–87 (hexane)	0,14

LITERATURE CITED

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2. T. Onaka, Tetrahedron Lett., 4387 (1971).

ALKALOIDS OF THREE SPECIES OF *Berberis*

A. Karimov, M. V. Telezhenetskaya, K. L. Lutfullin,
and S. Yu. Yunusov

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Only a few of the numerous publications on *Berberis* alkaloids have been devoted to a study of the leaves (qualitatively, there is no great difference between the alkaloids of the leaves and of the roots [1]). We have studied the leaves of *Berberis oblonga* collected in the Tashkent oblast in the flowering phase in May, 1975.

The combined bases amounted to 0.04%. Extraction was performed successively with chloroform and methanol. Separation of the combined compounds on a column of silica gel yielded two bases which were assigned from their spectral characteristics to the aporphine type and were identified by a direct comparison with authentic samples as thalicmidine and isocorydine. A very small amount of berberine was present in the initial material, as was shown chromatographically.

Thus, in their qualitative composition the alkaloids of the roots [2] and leaves of *B. oblonga* differ sharply: The main alkaloids of the roots are berberine, magnoflorine, and hydroxyacanthine, and the main alkaloids of the leaves is thalicmidine.

The leaves of *B. intergerrima* collected in July, 1974, in the valley of Chon-Kemin (Kirghizia) in the fruit-bearing phase contained 0.18% of total alkaloids. From the nonphenolic fraction of the total four bases were isolated by separation on a column of silica gel. Bases with mp 183-184°C, $[\alpha]_D + 176°$ (c 0.33; CH_3OH) and with mp 191-192°C, $[\alpha]_D + 56°$ (c 0.46; CH_3OH) were identified as isocorydine and thalicmidine, respectively. A third base was obtained in the form of an oil, $[\alpha]_D + 88°$ (c 0.6; CH_3OH), and in its UV spectrum maxima were observed at 282 and 304 nm (log ε 4.34, 4.24), which are characteristic for 9,-10-substituted aporphines [3]. The mass spectrum had the peak of M^+ and of ions with m/e 354, 340, 324, 312, 297, 281. The NMR spectrum ($CDCl_3$, δ scale, ppm) had signals in the form of singlets at 2.49 ($N-CH_3$), 3.59 (OCH_3), and 3.84 ($3OCH_3$), and also three singlets at 6.54, 6.74, and 8.03 from all three aromatic protons.

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