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QUINAZOLINES

X. SYNTHESIS OF 6,6'-METHYLENEBISDEOXYVASICINONE AND ITS HOMOLOGS

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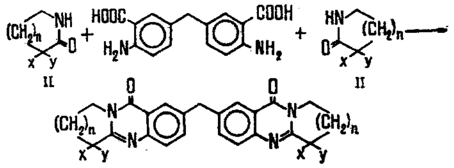
UDC 547.944/945+547.856.1

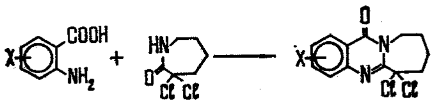
6,6'-Methylenebis(2-methyl-3H-quinazolin-4-one) has been synthesized from methylenebisanthranilic acid [1]. Continuing a study of the chemistry of condensed quinazolines [2-4], in order to synthesize new deoxyvasicinone derivatives we have performed the reaction of methylenebisanthranilic acid (I) with various lactams (γ-butyrolactam, δ-valerolactam, ε-caprolactam, and α-chloro- and α,α-dichloro- ε-caprolactams (IIa-e)). 6,6'-Methylenebisdeoxyvasicinone and its homologs (IIIa-e) were obtained:



a. $x = y = H$, $n = 1$; b. $x = y = H$, $n = 2$; c. $x = y = H$, $n = 3$; d. $x = H$, $y = \mathrm{Cl}$, $n = 3$; e. $x = y = H$, $n = 3$.

The reaction took place smoothly when 1 mole of the acid (I) was heated with 3 moles of a lactam (II) in the presence of phosphorus oxychloride in the water bath (see Table 1).

We have also studied the reaction of anthranilic acid and its derivatives (4-nitro-, 5-bromo-, 5-iodo, and 5-nitroanthranilic acids) (IVa-e) with the lactam (IIe). In this way the quinazolinones (Va-e) were synthesized with yields of 46-59% (see Table 1).



IV IIe Va-e

a. $x = H$; b. $x = 4-\mathrm{NO_2}$; c. $x = 5-\mathrm{Br}$; d. $x = 5-\mathrm{I}$; e. $x = 5-\mathrm{NO_2}$.

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TABLE 1

Initial compound		Reaction product	Yield, %	mp (°C) and solvent	R_f * (Al_2O_3)	mol. wt.	Empirical formula
acid	lactam						
I	IIa	IIIa	84	332–334 (acetic acid + water)	0,63	384	$C_{23}H_{20}O_2N_4$
I	IIb	IIIb	74	244–246 (ethanol)	0,43	—	$C_{25}H_{24}O_2N_4$
I	IIc	IIIc	66	251 - 253 (ethanol)	—	440	$C_{27}H_{28}O_2N_4$
I	IId	IIId	52	153–156 (ethanol)	—	510	$C_{27}H_{26}O_2N_4Cl_2$
I	IIe	IIIe	53	205–206 (butanol)	—	—	$C_{27}H_{24}O_2N_4Cl_4$
IVa	IIe	Va	46	114–115 (hexane)	0,42	284	$C_{13}H_{12}ON_2Cl_2$
IVb	IIe	Vb	55,5	165–166 (butanol)	0,41	—	$C_{13}H_{11}O_3N_3Cl_2$
IVc	IIe	Vc	59	127–127,5 (hexane)	0,78	—	$C_{13}H_{11}ON_2BrCl_2$
IVd	IIe	Vd	52	142 (hexane)	0,74	—	$C_{13}H_{11}ON_2JCl_2$
IVe	IIe	Ve	49,5	176–177 (butanol)	0,43	—	$C_{13}H_{11}O_3N_3Cl_2$

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*The values of R_f were determined in the following solvent systems: for compounds (IVb–e), ether–hexane (1 : 1); for (IIIa), chloroform; for (IIIb), chloroform–ether (1 : 1); and for (Va), ether–petroleum ether (1 : 1).

As can be seen from Table 1, the yield of reaction products depends little on the substituents in the benzene ring of the acids (IVa–e) but an increase in the number of methylene groups in the lactams (IIa–c) or the introduction of substituents into their rings (the lactams IId and e) leads to a decrease in their reactivity with respect to the acid (I). These results are in harmony with the variation in reactivity in condensations of anthranilic acids and lactams which we have suggested previously [3].

The structures of the compounds synthesized were shown on the basis of the results of elementary analysis and IR and mass spectra, and their individualities were checked by chromatography in a thin layer of alumina. The IR spectra of (IIIa–e) each had the absorption bands of a carbonyl group in the 1670–1680 cm^{-1} region. The mass spectrum of (IIIa) was characterized by the presence of the peak of the molecular ion (100%) and also of the peaks of ions with m/e 199 and M − 1; the intensity of the peak of the molecular ion in the case of (IIId) was 25%, and for (Va) 38%. In the spectra of the latter compounds there are fragments corresponding to M − Cl (for (IIId) 15%, and for (Va) 100%). In addition to the fragmentary ions mentioned, the M − 2Cl and M − 2HCl peaks (24% and 14%) are characteristic for the compound (IIId); the strongest peak is that of the ion with m/e 248 (100%).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer, and the mass spectra on a MKh-1303 instrument. The results of elementary analyses corresponded to the calculated figures. Methylenebisanthranilic acid was synthesized by Baumann's method [5], and α,α-dichloro-ε-caprolactam by that of Brenner and Rickenbacher [6].

Synthesis of 6,6'-Methylenebisdeoxyvasicinone (IIIa). To a mixture of 1.43 g (0.005 mole) of methylenebisanthranilic acid (I) and 1.3 g (0.015 mole) of γ-butyrolactam (IIa) was added 4 ml of phosphorus oxychloride. The reaction mixture was heated in the water bath for an hour and was then cooled and poured into water. The resulting solution was made alkaline with 25% ammonia whereupon an oil deposited which crystallized on standing. The crystals were filtered off, carefully washed with water, and dried. The reaction product was purified by precipitation with water from acetic acid solution. This gave 1.62 g (84%) of 6,6'-methylenebisdeoxyvasicinone (IIIa) with mp 332–334°C. IR spectrum: 1680 cm^{-1} (ν_{CO}); mol. wt. 384 (mass spectrometrically).

The condensation of (I) with the lactams (IIb–e) was performed similarly (see Table 1).

Reaction of 4-Nitroanthranilic Acid (IVb) with α,α-Dichloro-ε-caprolactam (IIe). A mixture of 0.45 g (0.0025 mole) of 4-nitroanthranilic acid (IVb), 0.68 g (0.0038 mole) of α,α-dichloro-ε-caprolactam, and 3.5 ml of phosphorus oxychloride was heated in the water bath for an hour, cooled, and decomposed with ice water. The crystals that deposited were filtered off, washed with water to neutrality, and dried. Recrystallization from butanol gave 0.45 g (55.5%) of reaction product (Vb) with mp 165–166°C.

Compounds (Va, c–e) were synthesized similarly.

SUMMARY

6,6'-Methylenebisdeoxyvacisinone and its homologs have been synthesized by the reaction of methylenebisanthranilic acid with lactams (γ-butyrolactam, δ-valerolactam, ε-caprolactam, and α-chloro- and α,α-dichloro-ε-caprolactams). The condensation of anthranilic acid and its derivatives (4-nitro-, 5-bromo-, 5-iodo-, and 5-nitroanthranilic acids) with α,β-dichloro-ε-caprolactam has given seven-membered analogs of deoxyvasicinone containing two chlorine atoms in the polymethylene ring.

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ALKALOIDS OF Papaver Bracteatum

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Papaver bracteatum Lindl. (great scarlet poppy) is a representative of the section Oxytona Bernh., and is a perennial endemic plant of the northern Caucasus [1]. The alkaloids isothebaine, oripavine, bracteine, and bractamine have been isolated previously from this plant collected in Transcaucasia [2]. Cultivated forms of *P. bracteatum* have been studied abroad and more than 15 alkaloids have been isolated [3-7].

We have investigated the epigeal part of *P.bracteatum* collected in the region of Mt. Beshtau (Pyatigorsk) in the end of flowering to beginning of fruit-bearing period. Methanolic extraction yielded 0.6% of combined alkaloids, which were separated into phenolic and nonphenolic fractions. Treatment of the nonphenolic fraction with methanol yielded thebaine [8]. Repeated treatment of the mother solution with ethanol gave thebaine and mecambridine [9].

After the separation of these alkaloids, the mother liquor was chromatographed on a column. Elution with benzene and benzene–methanol yielded isothebaine, oripavine, orientalidine [10], salutaridine [11], alpinigenine [4, 12, 13], floripavidine [11, 14], a base with mp 119-120°C, and two amorphous bases (I) and (II). The alkaloids thebaine, oripavine, salutaridine, and floripavidine were identified by direct comparison with authentic samples, and isothebaine, mecambridine, orientalidine, and alpinigenine by comparison of their properties and spectral characteristics with those given in the literature. The crystalline base with mp 119-120°C was identical in its spectral characteristics with alpinine, which has been found in the amorphous form in *P. alpinum* [12, 13] and has been obtained by the methylation of alpigenine [4]. From the ether-soluble fraction of the combined phenolic alkaloids we isolated isothebaine, oripavine, thebaine and bracteoline, which was identified by comparison with an authentic sample isolated from *Corydalis gortschakovii* [15].

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