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IODINE OXIDATION OF HOMOPROAPORPHINE ALKALOID REGLAMINE

Abstract: The article presents a method for the synthesis of a homoproporphine alkaloid from various homoproporphine alkaloid with iodine oxidation [11]. The identity of the synthesized substance has been proved by modern spectral methods and the structure of the new substance has been established. And also their composition was determined by chemical transformation.

Key words: alkaloid, regelamine, oxidation, chromatography, IR spectroscopy.

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Introduction

Partial syntheses of dehydro and oxo homoproporphine alkaloids. In the last decade, from a large number of plants producing homoaporphine alkaloids, their dehydro derivatives containing double bonds and oxy groups in various positions have been isolated. The most numerous of them are 6a, 7 dehydroaporphins (dehydroglaucon 15 and analogs), 7 oxoaporphins (ateroline 16 and analogs) and their quaternary bases (corunnin 17 and analogs). Their syntheses have also been carried out [2].

In recent years, many methods have been used to synthesize new compounds by oxidizing iodine. N-aryl glycine esters were converted into cyclic form under the action of light, and the synthesis of quinolines in high yield was carried out using iodine.

The advantage of this method is that no catalysts or metal-containing intermediates are used [10].

Homologues of oxytocin were synthesized synthetically from existing alkaloids by oxidation of the natural alkaloid cytisine with iodine. During oxidation with iodine, the amino group in the ring is protected by a butoxycarbonyl group [6].

Homoaporphine alkaloids are isolated from various plants. The most common of these are colchicine and colchamine, and effective methods have been developed to extract and purify them from various plant organs. Usually the product has a complex composition, and different alkaloids are distributed depending on the type of plant and the place of growth. Methods have also been developed

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for the chemical synthesis of other members of the group from these alkaloids [3].

Homoaporphine alkaloids are of great interest for synthesis because of their strong biological action. In addition to active chemical synthesis, physicochemical methods for the synthesis of new alkaloids from natural alkaloids are being studied. One such method is the synthesis of a homoaporphine ring during arylation using Pd in the presence of Pd. This method is used in the synthesis of homonantein [4].

Kava et al. [7] converted them into 6a, 7-dehydro and 7-oxoaporphins by oxidation of non-phenolic aporphins with iodine. The oxidation of phenolic aporphins with iodine led to completely different compounds [5].

So, when isotebain is oxidized with iodine, a green compound is released.

Previously, only two alkaloids of the dehydroporaporphine (6,6a-didehydro-noraporphine) series, dehydronorglaucin and dehydronorlaurelin, were known in the literature. In recent years, from plants of this. Annonaceae, a number of 6, 6a dehydronoraporphins have been isolated, but containing substituents at the C-7 position in the form of methyl and hydroxyl groups [8].

Therefore, the partial synthesis of dehydro and oxo-homoproporphine alkaloids and the search for their presence in colchicum is of certain interest. There are only two known dehydrohomoproporphine alkaloids - regecolin and isorehekolin, isolated from the columbus Kesselring. In addition, only two 7-oxo-homoproporphine bases, regelinone and isoregelinone, were isolated from the same plant. Dehydro and oxo derivatives of other homoproporphine alkaloids in plants have not yet been identified, despite the high probability of their presence. The reason for this may be the low extractability in chloroform from aqueous solutions due to the strong polarity and low content. In order to partially synthesize them and identify them in mother liquors, we studied the reactions of iodine oxidation of the homoproporphine alkaloid regelamine [1].

The iodine oxidation of regelamine yielded a mixture of two compounds - with Rf 0.19 and 0.31 (main). In the PMR spectrum of the main reaction product, there is only one three-proton singlet, which by value (3.56 ppm) [3] corresponds to the quaternary N-methyl group. The signal of the oxymethyl group of

the starting regelamine (3.73 ppm) [6] is absent in the spectrum. This indicates that, as in luteidin, elimination of the C2 methyl group, the base position, took place. Based on this, the structure of the US was assumed for the dehydrogenation product. This structure was confirmed by its identification with 12-demethylrehekoline, a regecolin hydrolysis product.

Synthesis method.

Oxidation of regelamine with iodine. 0.15 g of Regelamine was dissolved in 8 ml of dioxane, 0.15 g of freshly melted sodium acetate was added. Next, 0.12 g of iodine in 6 ml of dioxane was added to the boiling solution over 2 hours until the reaction solution turned dark orange.

Experimental part.

Using different solubility of the reaction products in dioxane, acetone and a mixture of acetone and methanol and chromatography on alumina, it was possible to isolate 3 compounds: with Rf 0.41; 0.47 (minor) and 0.64 (yolanthamine with Rf 0.52) according to system 4.

We studied the PMR spectra of two compounds with Rf 0.41 and 0.64 (in C2D5OD): compound 2, Rf 0.41 (ppm): 6.63 (1H, s, H-3), 3.56 (3H, s, N + -CH3) and 3.52 (3H, s, ol. OCH3). compound 3, Rf 0.64 (ppm): 5.76; 5.83 and 5.88 (H-13, H-4, H-5), 3.55 (3H, s, ol. OCH3), 2.40 (3H, s, N - CH3).

It was not possible to separate the mixture into individual compounds.

Oxidation of regelamine with iodine, both in the presence of sodium acetate and without it, leads to a mixture of substances, the main of which 12-demethylrehekoline has been isolated and studied. A similar oxidation of regelamine (1, Scheme 1) leads to the isolation of two new compounds from the mixture, which, according to spectral data, suggest structures 2 and 3.

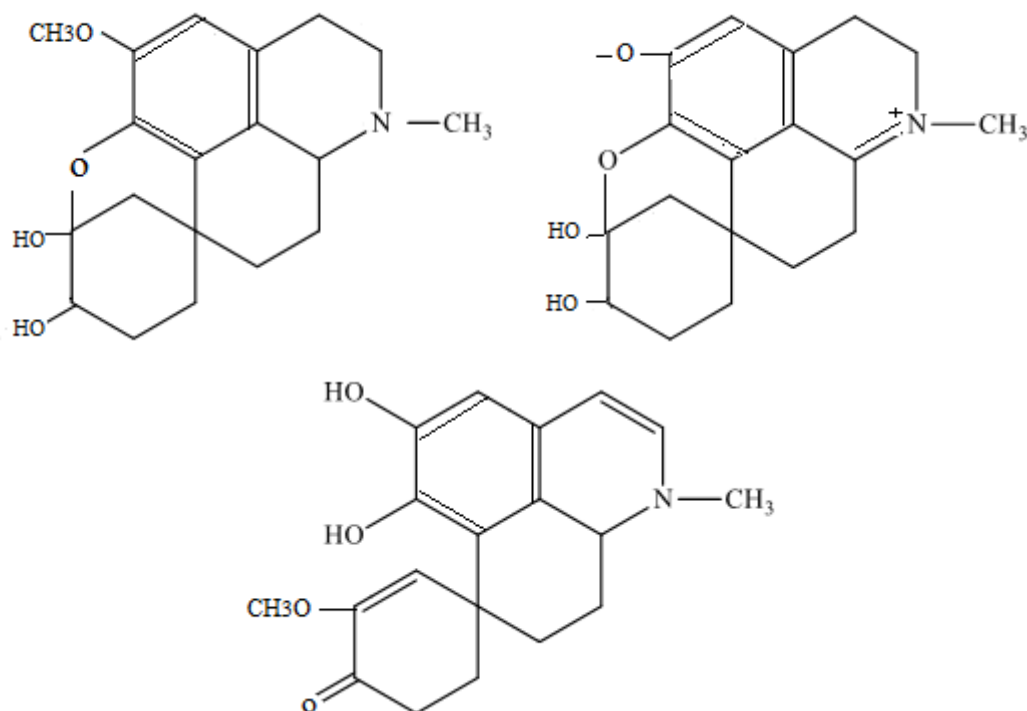
It should be noted that the elimination of the methyl group from the C-2 position of the benzene ring during oxidation with iodine was also observed by some authors in aporphine alkaloids. At the same time, it should be noted that the oxidation of both phenolic and non-phenolic homoproporphins with iodine results in the formation of quaternary dehydro derivatives with a double bond at 6.6a, while aporphins form 6a, 7-dehydro derivatives [9].

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Scheme 1. Oxidation reaction of regelamine with iodine

In addition to oxidation with iodine, we obtained regecolin and regelinone from kesselringin by a photochemical reaction. Regecolin was obtained by irradiation of an aqueous solution of kesselringin with sunlight after the displacement of air with nitrogen. When oxygen is displaced from the air solution and irradiated, kesselringin forms a mixture of products

reactions containing a significant amount of regelinone. The yield is 26%.

Conclusions.

The products obtained were identified by chromatographic and spectroscopic methods.

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