THE TECHNOLOGY OF THE ISOLATION OF THE ALKALOIDS DUBINIDINE AND HAPLOPHYLIDINE

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The dihydrofuranoquinoline alkaloid dubinidine has been isolated from Haplophyllum foliosum and Haplophyllum dubium [1]. It possesses valuable pharmacological properties [2] and is in the stage of introduction into medical practice.

We have carried out the isolation and separation of the alkaloids from yhe epigeal part of H. foliosum under semiindustrial conditions. Various organic solvents have been tested, as well as aqueous and acid extractions using a number of cation-exchangers.

Of organic solvents, the best yield of total alkaloids was given by chloroform (1.1-1.2% of the dry weight of the raw material).

Extraction with water formed very dilute diffusion liquors, but 0.5-0.7% hydrochloric acid gave unstable results.

The alkaloids were absorbed completely from the acid extract by KU-1 cation-exchanger, and desorption was carried out with a 1.5% solution of ammonia in 85% ethyl alcohol with subsequent elimination of the solvent by distillation in a vacuum apparatus. The yield of total alkaloids was 1.1%; from the mixture dubinidine was obtained in the form of the hydrochloride (yield 0.11% of the weight of the plant). We have treated more than 1 ton of raw material by this method.

The furanoquinoline alkaloid halophylidine has been isolated from the seeds of H. perforatum [3]. It also possesses valuable pharmacological properties and is in the stage of introduction into medical practice [4].

We have developed a method of obtaining haplophylidine by the continuous extraction of the seeds with extraction gasoline. The alkaloids were extracted from the gasoline solution with 10% sulfuric acid and technical haplophylidine was precipitated with 25% ammonia. The yield of haplophylidine was 0.22-0.24% of the weight of the seeds.

An industrial process of obtaining dubinidine and haplophylidine has been developed on the basis of the investigation carried out.

The technology of isolating the other alkaloids is being developed at the present time.

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THE POSSIBILITY OF PHENOL-DIENONE REARRANGEMENTS IN LIGNIN

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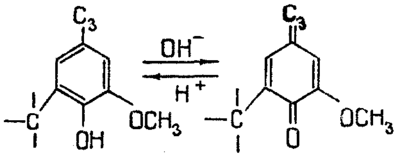
When the thiolignin isolated from spent chips from the sulfate digestion of wood of coniferous species [1] is heated for 1 hr in 0.1 N caustic soda in an inert gas atmosphere, a marked reduction in the content of weakly acidic groups with pK values of 13-14 takes place. The same effect is observed (table) with a specially prepared fraction of thiolignin with a high content of these groups and also with lignins isolated under mild conditions by extracting spruce sawdust with dioxane [2] and digesting the latter in dimethyl sulfoxide [3].

Sample	Content of acid groups with pK 13–14, mg-eq/g	
	before heating	after heating
Thiolignin	0.85	0.18
Thiolignin fraction insoluble in hot alcohol	2.47	0.65
Dioxane lignin	0.44	0.10
Dimethyl sulfoxide lignin	0.88	0.14

According to literature data [4], and also to the experimental material that we have accumulated, the groups with pK values of 13–14 in lignin are so-called "condensed" [5] phenolic units of type I, which, in our opinion, may be regarded as sterically hindered phenols [6] containing bulky substituents generally in positions, 2, 4, and 6 of the aromatic nucleus and capable of phenol-dienone rearrangements as follows



The rearrangements mentioned also, apparently, explain the disappearance of the groups with pK 13–14 in lignins when they are heated in alkali.

It must be noted that the possibility of phenyl-dienone rearrangements in "condensed" lignin units is not taken into account in any theory relating to the processes of delignification of wood in the preparation of cellulose. A consideration of this fact will permit a completely new approach to the study of the mechanism of the majority of the reactions of lignin, particularly in industrial processes for the chemical treatment of wood.

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