TABLE 1. Coordinates of the Atoms ($\times 10^3$) of the Molecule of (I)

Atom	x	y	z	Atom	x	y	z
C(1)	182(3)	274(2)	85(1)	C(9)	312(4)	521(2)	−129(1)
C(2)	184(3)	203(3)	176(2)	C(10)	202(3)	626(2)	−99(1)
C(3)	344(3)	148(2)	200(2)	C(11)	259(3)	654(2)	1(2)
N(4)	474(2)	240(1)	199(1)	N(12)	239(2)	549(1)	58(1)
C(5)	452(2)	331(2)	148(2)	C(13)	600(3)	224(2)	255(2)
C(6)	341(2)	353(2)	85(1)	O(14)	608(2)	127(2)	296(1)
C(7)	340(2)	450(1)	22(1)	C(15)	720(3)	317(2)	264(2)
C(8)	277(3)	417(2)	−71(1)	I	−179	529	54

preted by the direct method using the Rentgen-75 program [4] and was refined by the method of least squares, initially in the isotropic (R = 0.19) and then in the anisotropic approximation (R = 0.113). The coordinates of the nonhydrogen atoms are given in Table 1.

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CHANGE IN PHYTIN UNDER THE INFLUENCE OF VARIOUS FACTORS

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Depending on the quality of rice flour, its phytin content ranges from 4.5 to 7%. Under the action of a high temperature in roasting, a considerable amount of the phytin is converted into phosphate and, consequently, the phytin content in cooked rice flour has fallen considerably.

Continuing investigations to determine the reasons for the formation of phosphate in the preparation of phytin from uncooked rice flour [1], we have directed our attention to the fact that freshly precipitated paste-like moist phytin (sample 1) and phytin dried at room temperature (sample 2) differ somewhat in color after they have been dried in the drying chest at 100-105°C for 5-6 h. Neither of the dried phytin samples gave the qualitative reaction for phosphate [2]. At the same time, if they were dissolved in 1% nitric acid and the solutions were neutralized with ammonia to pH 8.0-9.0, the precipitates that deposited were not uniformly amorphous but contained microcrystalline inclusions and this was more pronounced in sample 1. Both precipitates, after being dried at room temperature, gave the yellow coloration characteristic for phosphate with an aqueous solution of silver nitrate.

Earlier, on heating phytin at 160-200°C for three hours, we likewise observed no formation of phosphate, which led us to an erroneous conclusion [1]. It was found that this sample of phytin also contained phosphate but, for unknown reasons, this was not directly detected qualitatively but only after the reprecipitation of the phytin. The reason for this phenomenon can perhaps be explained after the structure of the phosphate has been established.

It must be mentioned that in sample 1 the amount of phosphate formed was considerably greater than in sample 2. At a high temperature, apparently, the presence of a certain amount of moisture leads to an easier cleavage of the phosphate—magnesium and phosphate—calcium bonds of the phytin molecule.

We observed a similar phenomenon when phytin was boiled with 10% sulfuric acid for 6-7 h. Under these conditions, the phytin was converted quantitatively into phosphate, and a crystalline precipitate of CaSO₄ deposited from the acid solution. When the acid solution was neutralized with 25% ammonia to pH 8.0-9.0, a microcrystalline precipitate of phosphate (AgNO₃) deposited. The IR spectra of the phosphate obtained on the cooking of rice flour [1], on the drying of phytin, and on the treatment of phytin with sulfuric acid were identical. The phosphate was an organic compound of inositol with phosphoric acid.

We may note that the experimental results that we have obtained on phytin are evidence in favor of Neuberg's structure [3].

Thus, in the process of drying moist phytin at high temperatures, a considerable amount of it is lost. In order to prevent the formation of phosphate in part, the roasting of rice flour and the drying of the phytin must be carried out at a low temperature.

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DESTRUCTION OF LIGNIN ON PHOTOELECTROCHEMICAL REDUCTION

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The electrochemical reduction of lignin in nonaqueous media leads to a change in its molecular mass, the degree of degradation depending on the type of solvent and the potential of the cathode [1]. It has been shown [2, 3] that the photolysis of solution of lignin likewise leads to a degradation of the substance. Furthermore, it has been established that on irradiation the lignin fragments pass into an excited state, which causes a qualitative change in their redox properties [4].

We assumed that a combination of the methods of preparative photolysis and electrolysis could give lignin preparations with physicochemical — in particular, molecular-mass — characteristics different from those of the initial lignin.

The process of photolysis, electrolysis, and photoelectrolysis were carried out in hexametapol–methanol (67 mole-% of ethanol) saturated with LiCl for 5 h at a concentration of lignin of 0.5-5 g/liter. After the end of the process, the solution was diluted with dimethylformamide and passed through a column of Sephadex LH-20 calibrated with respect to monomers, dimers, and the polymer. The degradation of the polymer component of the lignin was calculated from the normalized gel-filtration curves of the lignins, taking the ratio of the integral absorption of the elution zone of the polymer fraction of the reduced substrate to the analogous magnitude for the initial preparation.

According to the results of gel filtration, the electrolysis of lignin at a copper cathode using a potential of −4.0 V relative to a silver comparison electrode in the solvent system mentioned led to only slight degradation of the polymeric part of the substance (12%). The photolysis of a solution of hydrolysis lignin in the system mentioned was likewise accompanied by slight cleavage (18%). In the combination of photochemical and electrochemical actions, however, the polymeric component of the molecule of the hydrolysis lignin underwent 73% degradation, i.e., the cleavage processes were not simply summed but enhanced one another. The observed effect was characteristic for various lignin preparations: nitrolignin [5] was 66% cleaved on photoelectrolysis, pine dioxane lignin was 87% cleaved, and pine soda lignin 89% cleaved (Fig. 1).

Thus, a combination of the methods of preparative photolysis and electrolysis of lignin preparations in organic solvents greatly intensifies the processes of degradation of lignin to low-molecular-weight components.