

and 337 nm (inflection), and the mass spectrum had peaks of ions with  $m/z$  399 ( $M^+$ ), 356, and 340. The spectral characteristics agreed with those given in the literature for  $\beta$ -lumicolchicine [8].

Of the bases identified, this is the first time that colchamine, 2-demethylcolchicine, cornigerine, and  $\beta$ -lumicolchicine have been isolated from this plant.

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#### FORMATION OF DIISOEUGENOL IN THE SYNTHESIS OF ETHYLBIS(4-HYDROXY-3-METHOXYPHENYL)METHANE

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In order to widen the assortment of dimeric models of lignin, we attempted to synthesize ethylbis(4-hydroxy-3-methoxyphenyl)methane from guaiacylpropan-1-ol and guaiacol by the procedure of [1]. Compound (I) with mp 176-177°C (by reprecipitation in hexane from ethereal solution) was obtained in a yield of 44%. According to its mass spectrum, its molecular mass was 328.16817, composition  $C_{20}H_{24}O_4$  (MKh 1310, resolving power 10,000, reference substance perfluorokerosene), which did not correspond to ethylbis(4-hydroxy-3-methoxyphenyl)methane ( $M = 288$ ,  $C_{17}H_{20}O_4$ ).

It is known from the literature that (1-hydroxyalkyl)phenols are capable of condensing, with the splitting out of water, in acid and alkaline media, giving dimers and trimers [2-4]. Judging from the molecular mass and composition of the product obtained, dimerization of the initial guaiacylpropan-1-ol had taken place in the acid medium. To check this hypothesis, we performed a reaction under the same conditions but taking only guaiacylpropan-1-ol. As a result, we isolated a substance identical with that obtained previously (I). PMR spectrum of this substance ( $\delta$ , ppm): 0.78-1.0 (5H, q, 2  $CH_3$ ), 1.25-1.75 (2.2 H, m,  $-CH_2-$ ), 2.15-2.5 (1 H, q,  $-CH-$  of a five-membered ring), 2.67-3.00 (0.8 H, q,  $-CH-$  of a five-membered ring), 3.5-3.87 (6.9 H, m, two intense  $OCH_3$  signals superposed on a 1 H multiplet of a five-membered ring), 5.25-5.5 (2.1 H, d, 2 OH), 6.28-6.8 (4.6 H, m, arom. H). The "value" of one proton was calculated on the basis of the assumption that the total integral corresponded to 24 protons. The spectrum was taken in  $CDCl_3$ , 0 - HMDS, on a BS 567 A instrument (Tesla, Czechoslovakia) at 100 MHz. The spectrum proved to be identical with that of authentic diisoeugenol [5] also taken at 100 MHz.

We then performed the condensation of guaiacylpropan-1-ol in an acid medium without heating, at room temperature (18-20°C), taking samples for thin-layer chromatography on Silufol plates after predetermined intervals of time. The solvent system was diethyl ether-hexane (4:1 by volume) and the revealing agent was iodine. Without heating, the spot of diisoeugenol appeared on the plate 2 h after the beginning of the reaction. The reaction

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took place slowly and was not complete after two days. On heating (80°C) the diisoeugenol spot appeared on the plate immediately, and the reaction was complete in 40 min.

Consequently, in the presence or in the absence of guaiacol, on heating or at room temperature, guaiacylpropan-1-ol undergoes dimerization in an acid medium with the splitting out of water and the formation of diisoeugenol.

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#### PRODUCTION OF WATER-SOLUBLE PHYTOMELANINS

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Phytomelanins (PMs) possess a unique combination of physicochemical properties (anti-oxidant, semiconducting, electron- and ion-exchange, chelating, catalytic) and a many-sided biological activity (antitumoral, radioprotective, lysis-preventing, growth-activating, bacteriostatic) [1, 3]. They belong to a promising class of physiologically active compounds that permit the creation of combined drugs with a prolonged effect [2]. However, the possibilities of using PMs are limited by the absence of cheap sources of their production. Another serious factor complicating the structural-functional study of PMs and their practical application is the insolubility of PMs in organic solvents and in water. Furthermore, the necessity has arisen in acute form for the development of a series of unified methods of obtaining various types of melanins in which all the conditions of their isolation are standardized. Such an approach is necessary since, in view of the polymeric nature of the pigments, it will permit melanins with reproducible properties to be obtained.

In continuation of investigations pursued earlier [3], we have developed a general principle for the isolation of PMs from diverse natural raw materials which ensures the production of the water-soluble  $\text{NH}_4$  salt of the substance (solubility about 20%) with a yield of 0.6-0.9%. As raw materials we have used valves from the cotton plant *Gossypium hirsutum*, bagasse from sugar-beet *Beta vulgaris*, pomace from the grape *Vitis vinifera*, and seed husks from the sunflower, *Helianthus annuus*, i.e., wastes from the corresponding industries that may be considered as promising raw materials for obtaining PMs.

The production of the PMs comprised: 1) extraction with 5%  $\text{NH}_4\text{OH}$  at a liquor ratio of 1:8-1:10, 25°C; for raw material containing more than 3-5% of pectin we used 5%  $\text{NaOH}$  as extractant, at a liquor ratio of 1:10-1:15; 2) precipitation with dilute  $\text{HCl}$  (1:1) at pH 3.0-3.5; 3) washing with  $\text{H}_2\text{O}$  to pH 6.0-6.5; 4) extraction with 1%  $\text{NH}_4\text{OH}$ ; 5) reprecipitation with  $\text{HCl}$  (1:1); 6) reextraction with 1%  $\text{NH}_4\text{OH}$ ; 7) fractional precipitation with  $\text{C}_2\text{H}_5\text{OH}$  from ammoniacal solutions at pH 8.5-9 (a fraction was collected at a ratio of the volume of the precipitant to the volume of the solvent of 9:1); 8) dissolution in  $\text{H}_2\text{O}$ ; 9) gel filtration on Sephadex G-25 (eluent 0.001%  $\text{NH}_4\text{OH}$ , pH 9.8). The eluate was concentrated in a rotary evaporator.

In the  $\text{NAD}\cdot\text{H}_2$  ( $0.72\cdot 10^{-4}$  M)–( $\text{K}_3\text{Fe}(\text{CN})_6$ ) ( $3.65\cdot 10^{-4}$  M) system the purified preparations of PMs (0.25 mg) in phosphate buffer (pH 7.2) accelerated electron transfer by a factor of 2.5-3.0. The process of reducing  $\text{Fe}^{3+}$  is described by the following equation, with the

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