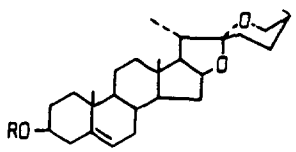
L-rhamnopyranoside and methyl 3,4,6-tri-O-methylgalactopyanoside, and for glycoside D methyl 2,3,4-tri-O-methyl-L-rhamnopyranoside and methyl 3,6-di-O-methyl-D-glucopyranoside. The presence of the dimethylglucose derivative showed branching of the carbohydrate chain. The configurations of the glycosidic centers were determined from molecular rotation differences of the initial glycosides, their progenins, and the aglycon in accordance with Klyne's rule [5].

On the basis of the facts given, the following structures are proposed for tuberosides C and D:



I. Rha $1\xrightarrow{\alpha}2$ Gal $\xrightarrow{\beta}$

II. Rha $1\xrightarrow{\alpha}4$
Rha $1\xrightarrow{\alpha}2$ Glc $1\xrightarrow{\beta}$

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ALKALOIDS OF Liriodendron tulipifera

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UDC 547.944/945

Continuing a systematic study of the alkaloids of the plant Liriodendron tulipifera, L., family Magnoliceae, [1, 2] according to vegetation periods, we have investigated the leaves gathered in the flowering phase in the Botanical Garden of the Uzbek SSR Academy of Sciences (Tashkent).

The dry comminuted raw material was extracted with methanol. The evaporated methanolic extract was treated with chloroform. The total alkaloids (0.30% on the dry weight of the plant) were obtained from the chloroform solution in the usual way, and they were separated into phenolic and nonphenolic fractions. The alkaloids were separated chromatographically on a column of silica gel. Remerine, lirinidine, nornuciferine, nuciferine, and glaucine were isolated from the nonphenolic fraction, and lirinidine, caaverine, isocorypalmine, N-methylcrotsparine, and bases (I) and (II) from the phenolic fraction. All the alkaloids isolated, with the exception of bases (I) and (II), were identified by direct comparison with authentic samples obtained previously from this plant species [1, 2].

Base (I) – $C_{19}H_{21}NO_4$, mp 156-158°C (acetone). Its UV spectrum had an absorption maximum at 286 nm ($\log \varepsilon$ 3.70). The PMR spectrum of (I) (CF_3COOH, δ scale) showed the signals of two methoxy groups (3.52 ppm, s, 3H, and 3.55 ppm, s, 3H) and of four aromatic protons (6.66 ppm, s, 2H; 6.50 ppm, s, 1H; 6.56 ppm, s, 1H). The mass spectrum of the alkaloid contained the following main ion peaks: m/z 327 (M^+), 326 $(M-1)^+$, 296 $(M-31)^+$, 178 (100%), 176, 150, 135. The PMR and mass spectra of (I) are characteristic for tetrahydroprotoberberine alkaloids containing two hydroxy and two methoxy groups [2, 3]. The peak of an ion with m/z 178 showed the presence of a methoxy and a hydroxy group in ring D. The peak of the $(M-OCH_3)^+$ ion with an intensity of 16%, analogous to that in the spectrum of isocorypalmine [2] showed the presence of a methoxy group at C_9. After the partial methylation of

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(I) with diazomethane, isocorypalmine was isolated from the reaction products, which confirmed the presence of a hydroxy group at C_1 and of a methoxyl at C_2. The facts given for compound (I) agree well with literature information for stepholidine from Stephania glabra [4].

The base (II) was isolated in the form of the hydrochloride, mp 254-256°C (acetone–alcohol). Its physicochemical constants and spectral characteristics were close to those of apoglaziovine [5]. In actual fact, when N-methylcrotsparine was heated with 4 N hydrochloric acid (water bath, 2 h) a base was obtained that was identical with the alkaloid (II) that has been isolated (TLC and mass and IR spectra).

Thus, ten bases have been isolated from the leaves of L. tulipifera, and stepholidine and apoglaziovine have been found in this source for the first time.

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N-FORMYL-L-ASPARTIC ACID SYNTHESIS AND CHARACTERIZATION

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UDC 547.475.2

N-Formylamino acids have found use in the synthesis of peptides, which is due to their availability and the relative ease of elimination of the formyl group. Methods are known for obtaining formylamino acids that are based on heating amino acids in concentrated formic acid (I) [1] or the treatment of amino acids with the mixed anhydride of (I) and acetic acid [2, 3]. N-Formyl-L-aspartic acid (II), which has been used for the synthesis of peptides, including aspartame, has not hitherto been described in the pure form, apparently because of the complications caused by the autocatalytic splitting out of the formyl group. Thus, we have found that a preparation of (II) obtained by boiling aspartic acid (III) [sic] contained 15-30% of free (III) after repeated (up to 8 times) evaporation with water.

We have developed a method for obtaining (II) by treating a solution of (III) in (I) with acetic anhydride (IV). In the first stage the anhydride of (II) – (V) – is formed, and in the second stage the ring undergoes hydrolytic opening with the formation of (II). This method of synthesizing (II) differs from that proposed by Zumstein et al. [4] by the fact that, in the first place, we have substantially decreased the amount of (IV) used in the reaction [threefold excess of (IV), calculated on the (III), in place of an eightfold excess].

At 5-10°C, with stirring, 29 ml (0.3 mole) of (IV) was added dropwise to 13.3 g (0.1 mole) of (III) in 30 ml of 99.7% (I), and the reaction mixture was stirred at 20°C until the (IV) had dissolved completely and then for another 1.5 h. If the deposition of a precipitate was observed, the reaction mixture was heated in the water bath (40-45°C). After 1.5 h the solution was evaporated to dryness in vacuum (at a bath temperature not above 50°C). The (V) so formed was treated with 50 ml of water and, after it had dissolved, the solution was reevaporated in vacuum (at a bath temperature not above 50°C) until a transpar-

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