XANTHONES OF Alnus glutinosa

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Some species of alder are widely used in scientific and folk medicine [1], but their chemical composition has been studied inadequately. It is known that the leaves and inflorescences (catkins) of Alnus glutinosa (L.) Gaertn. (European alder) contain triterpenes, sterols, and flavonoids. From these organics, together with flavonoids and amino acids [3, 4], we have obtained two substances of xanthone nature which were isolated by the following schem : the aqueous residues of ethanolic extracts of the leaves and catkins were treated with ethyl acetate and the concentrated ethyl acetate extracts were chromatographed on columns of polyamide sorbent with elution by mixtures of water and ethanol containing increasing concentrations of the alcohol.

When chromatographed in Silufol UV-256 plates in the chloroform—ethanol (8:2) solvent system and on FN No. 1 paper in 5% acetic acid, substance (I) had R_f 0.52 and 0.22, and (II) 0.73 and 0.17, respectively. In UV light, both substances appeared on the chromatogram in the form of dark spots the coloration of which did not change after treatment with ammonia vapor or with solutions of aluminum salts. The spectra of both conmpounds in the UV region were characteristic for xanthones [5].

Substance (I) — $C_{15}H_{12}O_6$, mp 192-194°C. UV spectrum ($\lambda_{max}^{C_2H_5OH}$): 358, 276, 261, and 230 nm; with CH_3COONa: 372, 322, 282, and 229 nm (a bathochromic shift by 16 nm of the maximum at 276 nm is characteristic for an OH group in position 3 or 6 [5]); with CH_3COONa and H_3BO_3: 370, 300, 274, and 231 nm; with C_2H_5ONa: 388, 284, 265, and 229 nm (the maximum did not disappear, which showed the absence of vicinally located OH groups); with $AlCl_3$: 369, 298, 275, and 229 nm (the absence of a considerably bathochromic shift of the maximum at 261 nm indicated that the substance had no OH groups in positions 1 and 8). The IR spectrum of substance (I) showed the following absorption bands (cm^{-1}): 3585 (—OH), 3100 (—OCH_3), 1690 (C=O of a γ-pyrone), 1620, 1513 (aromatic double bonds).

The following signals were observed in the PMR spectrum [δ scale, ppm, $(CD_3)_2CO$]: doublet at 7.57 (J = 2 Hz) — H-5; quartet at 7.48 (J_1 = 2 Hz, J_2 = 6.5 Hz) — H-7; doublet at 7.05 (J = 6.5 Hz) — H-8; singlet at 6.70 — H-2; at 11.42 — OH at C-6; and a broadened signal of a C-4 OH group at 6.24. The singlets of methoxy groups in positions 1 and 3 were located at 3.90 and 3.83 ppm, respectively. The assignment of the signals that have been given was confirmed in the PMR spectrum of the acetate of substance (I) (in $CDCl_3$): quartet at 7.70 (J_1 = 2.5 Hz, J_2 = 6.5 Hz) — H-7; doublets at 7.45 (J = 2.5 Hz) — H-5, and at 6.95 (J = 6.5 Hz) — H-8; singlet at 6.65 — H-2. Three-proton singlets of OCH_3 groups in positions 1 and 3 gave signals at 3.60 and 3.50 ppm. Signals of aromatic acetyl groups at C-6 and C-4 appeared at 2.37 and 2.31 ppm, respectively. From the facts given, the structure of substance (I) can be represented as 4,6-dihydroxy-1,3-dimethoxyxanthone.

Substance (II) — $C_{16}H_{14}O_7$, mp 176-179°C. UV spectrum ($\lambda_{max}^{C_2H_5OH}$, nm): 337, 280, 225; with CH_3COONa: 336, 300 sh, 280, and 225 (no bathochromic shift of the maximum at 337 was observed, i.e., there is no free OH group in position 3 or 6); with C_2H_5ONa: 345, 282, 225 (the maxima did not disappear which indicates the absence of vicinally located OH groups); with $AlCl_3$: 347, 290, 239 (a bathochromic shift of the maximum at 225 nm is characteristic for the free OH group in position 1 and 8).

The IR spectrum showed absorption bands at (cm^{-1}): 3570 (—OH), 3080, 2960 (—OCH_3), 1700 (γ-pyrone C=O), 1618, 1525 (aromatic double bonds). The PMR spectrum contained the following signals (ppm): singlet at 6.91 — H-3; doublets at 7.34 and 8.16 (J = 8 Hz) — H-7 and H-8. An OH group at C-4 was represented by a broadened signal at 6.02 ppm, and an OH

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group at C-1 bound by a strong intramolecular hydrogen bond by one at 13.89 ppm. Methoxy groups at C-2, C-5, and C-6 appeared in the form of three-proton singlets in the 4.10-3.90 ppm region. The experimental results obtained indicate that substance (II) was 1,4-dihydroxy-2,5,6-trimethoxyxanthone.

It must be mentioned that this is the first time that substances of xanthone nature have been detected in plants of the family Betulaceae, and that they are new natural compounds.

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NATURE OF THE TANNINS OF SOME SUBTROPICAL PLANTS

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We have studied the nature of the condensed tannins of the flowers and leaves of mimosa (*Acacia dealbata* Link), the common pomegranate (*Punica granatum* L.) and the leaves of kaki persimmon (*Diospyros kaki* L.), European blackberry (*Rubus fruticosus*), the common quince (*Cydonia vulgaris*), and common tea (*Thea sinensis* L.). It was established that the condensed tannins are formed in the oxidative polymerization of flavan-3-ols and of flavan-3,4-diols [1, 2].

The phenolic compounds of extracts of the above-mentioned plant materials were fractionated on polyamide. The elution of the polyamide was carried out in the following way. Fraction I — water; fraction (II) — methanol with an increase in its concentration up to 70% (V); fraction (III) — 100% methanol, with KOH followed by neutralization with HCl; and fraction (IV) — dimethylformamide. Fraction (IV) which contained polymers, was subjected to complete acid hydrolysis. A pink coloration formed, which was due to the hydrolysis on condensed flavan-3,4-diols and their conversion into anthocyanins. Extraction was carried out with n-amyl alcohol [4]. The products of hydrolysis of fraction (IV) were studied by the PC method in the solvent systems 1) BAW; 2) Forestal's solvent; 3) FCW—formic acid—conc. HCl—water (5:2:3) [3, 4]. Catechins of tea leaves and aglycons of the anthocyanins of the fruit of the egg plant and blackberry were used as markers [1, 4].

The products from the hydrolysis of the tannins of *Diospyros kaki*, *Rubus fruticosus*, and *Cydonia vulgaris* formed a single compound (I) with a pink color. R_f 0.65, 0.50, and 0.23 in systems 1-3, respectively, λ_{max}^{MeOH}: 277, 535 nm, $\lambda_{440}/\lambda_{max}$ = 18%, bathochromic shift due to a 5% solution of $AlCl_3$, $\Delta\lambda = 15$. Substance (I) was identified as cyanidin.

The products of the hydrolysis of the tannin from *Punica granatum* consisted of two substances, one of which was substance (I). Substance (II) had a pink color, R_f 0.41, 0.32, 0.13 in systems 1-3, respectively, λ_{max}^{MeOH}: 276, 545 nm, $\lambda_{440}/\lambda_{max}$ = 18%, bathochromic shift due to a 5% solution of $AlCl_3$, $\Delta\lambda = 15$. Substance (II) was identified as delphinidin.

The products of the hydrolysis of the tannin from *Thea sinensis* consisted of a single colorless substance (III) with R_f in system 1 of 0.56, λ_{max}^{MeOH} 276 nm, reacting with the vanillin reagent. It was identified as epicatechin.

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