

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.

#### LITERATURE CITED

1. A. D. Turova, Medicinal Plants of the USSR and their Use [in Russian], Moscow (1974), p. 334.
2. O. P. Khvorost, A. G. Serbin, and N. F. Komissarenko, Rast. Res., 20, No. 3, 430 (1984).
3. O. P. Khvorost and A. G. Serbin, New Drugs from Plants of Siberia and the Far East [in Russian], Tomsk (1986), p. 160.
4. O. P. Khvorost, O. F. Narozhna, and A. G. Serbin, Farm. Zh., 5, 73 (1986).
5. V. I. Glyzin, G. G. Nikolaeva, and T. D. Dargaeva, Natural Xanthonenes [in Russian], Nauka (Siberian division) (1986), p. 3.

#### NATURE OF THE TANNINS OF SOME SUBTROPICAL PLANTS

V. V. Kirillova and Z. T. Kondzhariya

UDC 547.192

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,  $\lambda_{\max}^{\text{MeOH}}$ : 277, 535 nm,  $\lambda_{440}/\lambda_{\max} = 18\%$ , bathochromic shift due to a 5% solution of  $\text{AlCl}_3$ ,  $\Delta\lambda = 15$ . 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,  $\lambda_{\max}^{\text{MeOH}}$ : 276, 545 nm,  $\lambda_{440}/\lambda_{\max} = 18\%$ , bathochromic shift due to a 5% solution of  $\text{AlCl}_3$ ,  $\Delta\lambda = 15$ . 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,  $\lambda_{\max}^{\text{MeOH}}$  276 nm, reacting with the vanillin reagent. It was identified as epicatechin.

---

Sukumi Zonal Experimental Station of Subtropical Crops, N. O. Vavilov All-Union Scientific-Research Institute of Plant Growing. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 602-603, July-August, 1987. Original article submitted December 17, 1986.

The products of the hydrolysis of the tannins from Acacia dealbata consisted of three substances (I-III).

It was established that the tannins of Diospyros kaki, Rubus fruticosus, and Cydonia vulgaris were formed by the polymerization of leukocyanidin, that of Thea sinensis from catechin, those of Punica granatum from leukocyanidin and leukodelphinidin, and those of Acacia dealbata from catechin, leukocyanidin, and leukodelphinidin. A direct relationship was observed between the amount of free catechins and the possibility of the formation of tannins of catechin nature.

#### LITERATURE CITED

1. J. B. Harborne, The Biochemistry of Phenolic Compounds, Academic Press, London (1964) [Russian translation, Mir, Moscow (1968), p. 85].
2. D. G. Roux and E. Paulus, Biochem. J., **78**, 120 (1961).
3. S. S. Tanchev, Anthocyanins in Fruit and Vegetables [in Russian], Pishchevaya Promyshlennost', Moscow (1980), p. 82.
4. J. B. Lowry, "Relative evolutionary significance of anthocyanins in flowers and fruit," in: PAC International Symposium on Chemistry in Evolution and Systematics (1972).

#### BROMINATED DIPHENYL ETHERS FROM THE MARINE SPONGE Dysidea fragilis

N. K. Utkina, M. V. Kazantseva, and V. A. Denisenko

UDC 547.562.4:562.1+593.4

Sponges of the family Dysideidae contain a large number of brominated diphenyl ethers [1-3]. We have investigated the sponge Dysidea fragilis gathered on the littoral of Mozambique during the 19th voyage of the Scientific Research Vessel Bogorov. Chromatography on silica gel of a chloroform extract of the freeze-dried sponge (195 g) yielded three fractions. Crystallization of the first fraction from hexane gave a new diphenyl ether (I) with the composition  $C_{12}H_4O_2Br_6$ , mp 151-153°C, yield 1.18% (on the dry weight of the sponge). The mass spectrum ( $M^+$  654, 656, 660, 662, 664, 666) and the PMR spectrum [ $(CDCl_3, \delta)$  7.79 (d,  $J = 2$  Hz, H-6), 7.29 (dd,  $J = 8$  Hz, 2 Hz, H-4), 6.42 (d,  $J = 8$  Hz, H-3, and 6.01 (br s, OH)] showed the presence in compound (I) of six bromine atoms, a hydroxy group and three interacting aromatic protons.

The positions of the substituents were determined with the aid of double heteronuclear resonance, details of the  $^{13}C$  NMR spectra being given in Table 1. The methylation of (I) with MeI gave a monomethyl ether, mp 118-120°C (hexane), PMR spectrum ( $CDCl_3$ ): 7.79 (d,

TABLE 1. Chemical Shifts and  $^{13}C$ - $^1H$  Spin-Spin Coupling Constants ( $\delta$ , DMSO- $d_6$ )

Carbon atoms	I		III	
	$\delta$	$J_{C-H}$ , Hz	$\delta$	$J_{C-H}$ , Hz
1	112.1	d 11.1	151.5	br.s
2	152.0	m	137.7	t 7.4
3	116.1	d 164.6	117.5	br.s
4	131.3	d 169.2; d 6.5	125.0	d 174.8; d 6.5
5	114.3	d 11.1	118.4	t 5.5
6	135.0	d 172.9; d 6.5	119.6	d 165.5; d 8.3
1'	148.8	br.s	144.8	m
2'	139.8	br.s	159.8	br.s
3'	117.2	br.s	116.3	d 168.3; d 6.5
4'	125.2	br.s	115.5	t 4.0
5'	119.8	br.s	127.8	d 172.9; d 6.5
6'	115.8	br.s	118.1	br.s
OMe			60.4	q 146.1

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center, USSR Academy of Sciences, Vladivostok. Translated from Khimiya Prirodnikh Soedinenii, No. 4, pp. 603-605, July-August, 1987. Original article submitted January 28, 1987.