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A tannin of the condensed series has been isolated previously from the roots of *Hibiscus cannabinus* (kenaf) growing in the Tashkent province [1].

The aim of the present work was to study the roots of kenaf cultivated in Vietnam, which have not previously been investigated chemically.

The bulk of the roots of the industrial variety of kenaf collected in the harvesting period (environs of Hanoi) was extracted with benzene, chloroform, methanol, and aqueous methanol. The concentrated methanolic extracts were treated with ether and ethyl acetate. From the ethereal fraction by partition chromatography in columns of silica gel using elution with moist ether four catechins were isolated — K_1 , K_2 , K_3 , and K_4 . The amount of K_1 was very small. By one- and two-dimensional chromatography in system 1 [butan-1-ol-acetic acid-water (40:12:28)] and system 2 (2% acetic acid) using the method of intensifying the spots with authentic samples of standard substances isolated from the catechin complex of tea and the roots of the cotton plant [2], K_1 was identified as (–)-epicatechin gallate.

Substance K_2 consisted of colorless crystals with the composition $C_{15}H_{14}O_6$, mp 176–177°C (hot water), $[\alpha]_D^{20} +16.0^\circ$ (c 0.80; acetone + water), λ_{\max} 278 nm (ethanol), mp of the acetyl derivative 130–131°C (chloroform), $[\alpha]_D^{20} +32.0^\circ$ (c 0.60; chloroform).

On fusion with caustic soda, phloroglucinol and protocathechuic acid were formed. By comparison with an authentic sample K_2 was identified as (+)-catechin.

Substance K_3 had the composition $C_{22}H_{20}O_{11}$, mp 210–213°C, $[\alpha]_D^{20} -182^\circ$ [c 0.31; ethanol-acetone (1:1)]; mp of the acetyl derivative 157–160°C. On alkaline degradation, phloroglucinol and gallic acid were formed. On the basis of its chemical composition and UV, IR, and NMR spectra, K_3 was identified as (–)-epigallocatechin gallate.

Substance K_4 had the composition $C_{15}H_{14}O_6$, mp 231–232°C, $[\alpha]_D^{20} -59.0^\circ$ [c 0.32; acetone-water (1:1)]; mp of the acetyl derivative 150–152°C, $[\alpha]_D^{20} +16.0^\circ$ (c 0.75; chloroform). A mixture with an authentic sample of (–)-epicatechin gave no depression of the melting point.

By chromatograph on polyamide using chloroform and a chloroform-ethanol gradient, the ethyl acetate extract yielded two more compounds — K_5 and K_6 . Qualitative reactions with specific reagents and chromatographic analysis in systems 1 and 2 showed that these compounds were flavans [3].

Substance K_5 formed a cream-colored amorphous material which rapidly began to darken on storage and had no clear melting point; $[\alpha]_D^{20} +57.4^\circ$ (c 0.32; ethanol); its acetyl derivative had the composition $C_{50}H_{46}O_{22}$, mp 167–169°C, R_f 0.18 in system 3 [benzene-acetone (8:2)]. When K_5 was heated with 2 N HCl, an anthocyanidin dye was formed which was identified as cyanidin by comparison with an authentic sample and by the results of UV spectroscopy.

Under the action of 0.01% HCl, K_5 hydrolyzed with the formation of (–)-epicatechin and (+)-catechin. The action of thioglycolic acid gave (–)-epicatechin and a (+)-thioester which, after reduction over Raney nickel was converted into (+)-catechin.

On the basis of the chemical transformations performed, K_5 was assigned to the dimeric proanthocyanidins the "lower" halves of which have the configuration of (–)-epicatechin and the "upper" halves that of (+)-catechin.

The methylation of K_5 with diazomethane gave an octamethyl ether, and subsequent acetylation a diacetyloctamethyl derivative showing that the hydroxy groups of the proanthocyanidin

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do not participate in the formation of the interflavan bond. Analysis of the NMR spectrum of the acetyl derivative of K₅ showed that the interflavan bond is located in the C₄-C₈ (C₆) positions of the "upper" and "lower" halves of the molecule.

Thus, it has been established that K₅ is a dimeric proanthocyanidin and has the structure of 8-(3,3',4',5,7-pentahydroxyflavan-4-yl)-3,3',4',5,7-pentahydroxyflavan [4].

LITERATURE CITED

1. B. Makhsudova, Fam Van Tkhin', and O. S. Otroshchenko, Khim. Prir. Soedin., 233 (1979).
2. A. K. Karimdshanov, A. I. Ismailov, and A. S. Sadykov, Tr. Tashkent. Gos. Univ., No. 341, 63 (1968).
3. K. Weinges, W. Kaltenhäuser, H. D. Marx, E. Nader, F. Nader, J. Perner, and D. Seiler, Ann. Chem. No. 711, 184 (1968).
4. L. T. Pashinina, T. K. Chumbalov, V. I. Sheichenko, and R. Zh. Shukenova, Khim. Prir. Soedin., 205 (1978).

ESSENTIAL OILS OF THE GENUS *Ledum*

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The essential oils for analysis were obtained, by the method of distillation with water, from four species of *ledum* - *Ledum palustre* L. var. *vulgare* Ledb. (crystal tea *ledum*, common form), *Ledum palustre* L. var. *dilatatum* Wahlbg. (crystal tea *ledum*, broad-leaved form), *Ledum palustre* L. var. *angustum* E. Busch. (crystal tea *ledum*, narrow-leaved form, collected on the territory of the Tomsk province; *Ledum hypoleucum* Kom. (subwhite *ledum*), *Ledum decumbens* (Ait) Small. (sprawling *ledum*), and *Ledum macrophyllum* Tolm. (large-leaved *ledum*) collected in the Far East. The oils consisted of yellow or greenish-yellow clear liquids with a burning taste and a sharp characteristic odor. The yields of the oils from the air-dry war materials and their physicochemical constants are given in Table 1.

The amounts of acids and phenols isolated from the essential oils by treatment with a 5% aqueous solution of sodium hydrogen carbonate and with caustic soda [1] were very low (Table 1).

The acids were investigated by descending paper chromatography (LS paper) in butan-1-ol saturated with 25% ammonia solution [2]. A 0.1% ethanolic solution of bromothymol blue was

TABLE 1. Yields and Physicochemical Constants of the Essential Oils of the Genus *Ledum* L.

Species of ledum	Amount, %			n_{20}^{20}	d_{20}^{20}	Acid No.	Ester No.
	essen- tial oil	in the essen- tial oil					
		acids	phe- nols				
Ledum palustre L. var. vulgare Ledb.	1.62	1.23	2.13	1.4856	0.9732	0.75	10.21
Ledum palustre L. var. dila- tatum Wahlbg.	1.23	1.31	2.83	1.4975	0.9621	0.70	11.45
Ledum palustre L. var. angus- tum E. Busch.	1.52	0.88	2.15	1.4998	0.9352	0.69	10.55
Ledum hypoleucum Kom.	0.54	3.94	3.38	1.4850	0.9397	7.95	24.99
Ledum decumbens (Ait) Small.	1.10	1.68	2.99	1.4835	0.9399	1.45	7.95
Ledum macrophyllum Tolm.	2.32	0.12	0.85	1.4822	0.8753	1.47	12.59

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