Chemistry of Natural Compounds, Vol. 33, No. 2, 1997

PROANTHOCYANIDINS OF *Ziziphus jujuba**

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UDC 547.972

The catechin and proanthocyanidin compositions of the leaves and bark of Ziziphus jujuba *have been studied over the vegetation periods. This has led to the isolation of 16 compounds, including 8 monomeric catechins – (−)-epiafzelechin, (−)-epicatechin, (−)-epigallocatechin, (−)-epicatechin gallate, (−)-epigal-locatechin gallate, (+)-catechin, (+)-catechin gallate, and (+)-gallocatechin; 4 dimeric proanthocyanidins −(−)-epiafzelechin-(4β-8)-(−)-epicatechin, proanthocyanidin B-2, (−)-epicatechin-(4β-8)-(−)-epigallocatechin, and (−)-epiafzelechin-(4β-8)-(−)-epigallocatechin; and 4 oligomeric proanthocyanidins consisting of epiafzelechin, epigallocatechin, catechin, and epicatechin with different degrees of polymerization. Their structures have been established by a study of PMR and ^{13}C NMR spectra and the products of chemical transformation.*

Among the little-studied medicinal plants in relation to flavan-3-ols, a special position is occupied by common jujube, *Ziziphus jujuba* [1, 2]. The fruit of this low tree has been used since antiquity in the folk medicines of China, the Caucasus, and Central Asia as a diuretic, hypotensive agent, emollient, and expectorant [3, 4]. Jujube leaves contain about 6% and the bark 10-15% of tannins.

Compounds (**1-16**) have been isolated from an aqueous alcoholic extract of jujube leaves and bark by column chromatography on microcrystalline cellulose and gel filtration on Sephadex. These included the monomeric catechins (**1-8**) and dimeric (**9-12**) and oligomeric (**13-16**) proanthocyanidins. From their physicochemical and spectral characteristics, compounds (**1-8**) have been identified as (−)-epiafzelechin (**1**), (−)-epicatechin (**2**), (−)-epigallocatechin (**3**), (−)-epicatechin gallate (**4**), (−)-epigallocatechin gallate (**5**), (+)-catechin (**6**), (+)-catechin gallate (**7**), and (+)-gallocatechin (**8**) [5-8].

On the basis of a study of physicochemical properties (acid hydrolysis, thiolysis, etc.) and spectral characteristics (^1H and ^{13}C NMR), compounds (**9-11**) were identified as (−)-epiafzelechin-(4β-8)-(−)-epicatechin (**9**), proanthocyanidin B-2 (**10**) [6, 7], and (−)-epicatechin-(4β-8)-(−)-epigallocatechin (**11**) [9].

A comparative analysis of the ^{13}C NMR spectra of compounds (**9**) [6, 7] and (**12**), showed the identity of the substituents in rings *A* and *C* and the closeness of their structures. In contrast to the spectrum of compound (**9**), the ^{13}C NMR spectrum of compound (**12**) (Table 1) lacked characteristic signals from the carbon atoms of (−)-epicatechin, while, together with the resonance signals of (−)-epiafzelechin [11, 18], the signals of the carbon atoms of (−)-epigallocatechin [12] were observed. In actual fact, on the acid and thiolytic cleavage of this proanthocyanidin, the "lower" part yielded (−)-epigallocatechin (**3**), and the "upper" part pelargonidin (**17**) and, after catalytic cleavage of the thioether (**18**) with Raney nickel, (−)-epiafzelechin (**1**). Consequently, compound (**12**) was a dimer – (−)-epiafzelechin-(4β-8)-(−)-epigallocatechin.

With vanillin–sulfuric acid, compound (**13**) gave the red coloration characteristic for proanthocyanidins. When (**13**) was subjected to alkaline cleavage in an atomosphere of nitrogen, three aromatic acids were detected: *p*-hydroxybenzoic (**19**), gallic (**20**), and protocatechuic (**21**), which showed the complex composition of this proanthocyanidin.

*The materials of this paper were presented at the Second International Symposium on the Chemistry of Natural Compounds (SCNC, Eskişehir, Turkey, October 22-24, 1996).

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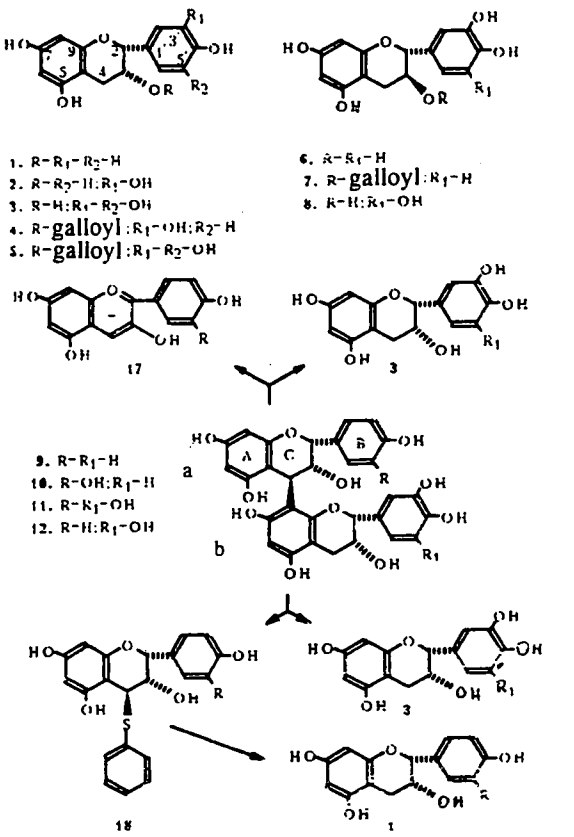
0009-3130/97/3302-0165$18.00


1. R-R1-R2-H
2. R-R2-H;R1-OH
3. R-H;R1-R2-OH
4. R-galloyl;R1-OH;R2-H
5. R-galloyl;R1-R2-OH
6. R-R1-H
7. R-galloyl;R1-H
8. R-H;R1-OH
17
3
9. R-R1-H
10. R-OH;R1-H
11. R-R1-OH
12. R-H;R1-OH
a
b
18
1

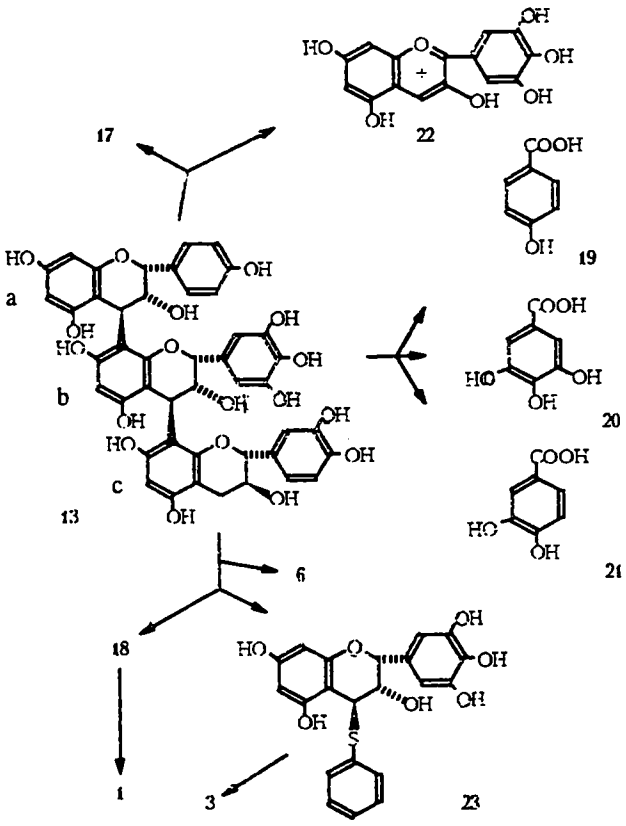
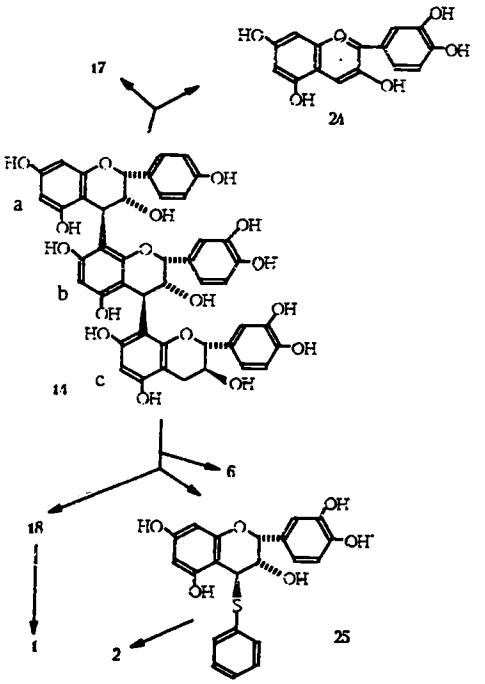

22
17
19
a
b
c
13
20
21
6
18
1
3
23

TABLE 1. Chemical Shifts (ppm) in the ^{13}C NMR Spectrum of Proanthocyan-idin (**12**) in the Mixed Solvent Acetone-d_6 – D_2O

Carbon atoms	Fragments of (12)	
	a	b
C-2	77.2	79.0
C-3	72.6	66.8
C-4	36.5	–*
C-6	97.0[c]	97.0[c]
C-8	96.6[c]	106.6
C-10	103.1	103.1
C-5,7,9	156.4	156.4
C-1′	130.1[a]	131.5[a]
C-2′	129.4	106.6
C-3′	114.4	145.0
C-4′	156.8	133.7
C-5′	114.4	145.0
C-6′	129.4	106.6

*Signals masked by a signal of the solvent. Signals marked with the same letter may be interchanged.



A study of ^{13}C NMR spectrum showed that proanthocyanidin (**13**) was a derivative of several flavan-3-ol systems (Table 2). The signals from C-2 in the fragments of compound (**13**) appeared at 77.1 and 81.7 ppm, which unambiguously showed the presence of both 2,3-*cis*- and 2,3-*trans*-stereochemistries of the flavan-3-ols in this compound [13-16]. A resonance signal at 72.2 ppm related to C-3 of "upper" blocks, the signal of this carbon atom in the "lower" catechin block appearing at 67.7 ppm. The substituted C-4 carbon atoms resonated at 36.8 ppm, and the signal from the corresponding carbon of the "lower" catechin block overlapped with that of the solvent at 29 ppm. A resonance signal at 107.2 ppm related to the C-8 carbon atom of ring *A* forming the interflavan bond, while weak signals at 96.0 and 96.7 ppm related to the C-6 and C-8 carbon atoms not participating in interflavan bonds. The resonance lines at 145.4 and 145.1 ppm relate to C-3′ and C-4′ of ring *B* of catechin and C-3′ and C-5′ of epigallocatechin. The C-4′ carbon atom of epigallocatechin was screened by the two hydroxy groups in the *ortho*-position and resonated at 133.9 ppm. The C-2′, C-5′, and C-6′ carbon atoms of catechin gave

TABLE 2. Chemical Shifts (ppm) in the ^{13}C NMR Spectrum of Proanthocyanidin (**13**) in the Mixed Solvent Acetone-d_6-D_2O

Carbon atoms	Fragments of (13)		
	a	b	c
C-2	77.1	77.1	81.7
C-3	72.2	72.2	67.7
C-4	36.8	36.8	-*
C-6	96.7[e]	96.0[e]	96.0[e]
C-8	96.0[e]	107.2	107.2
C-10	101.7	101.7	101.7
C-5,7,9		153.6–157.8	
C-1′	131.6[a]	130.3[a]	131.6[a]
C-2′	129.8[a]	106.8	115.4[x]
C-3′	114.6[x]	145.4[c]	145.1[c]
C-4′	156.7	133.9	145.1[c]
C-5′	114.6[x]	145.4[c]	116.5
C-6′	129.4[a]	106.8	119.1

*Signals masked by a signal of the solvent. Signals marked with the same letter may be interchanged.

TABLE 3. Chemical Shifts (ppm) in the ^{13}C NMR Spectrum of Proanthocyanidin (**14**) in the Mixed Solvent Acetone-d_6-D_2O

Carbon atoms	Fragments of (14)		
	a	b	c
C-2	77.2[e]	77.0[e]	82.1
C-3	72.5	72.5	67.6
C-4	36.7	36.7	-*
C-6	96.2[a]	96.2[a]	96.2[a]
C-8	96.7[a]	107.8	107.8
C-10	102.0	102.0	102.0
C-5,7,9		154.1–156.9	
C-1′	131.3	131.3	131.3
C-2′	128.9	115.4	115.4
C-3′	114.5	145.4	145.4
C-4′	156.9	145.4	145.4
C-5′	114.5	116.8	116.8
C-6′	128.9	119.9	119.9

*Signals masked by a signal of the solvent. Signals marked with the same letter may be interchanged.

characteristic signals at 115.4, 116.5, and 119.1 ppm, respectively. The presence of signals at 129.8 ppm and also in the 114-115 ppm region and at about 130-131 ppm showed that one of the blocks in compound (**13**) was afzelechin [11, 18].

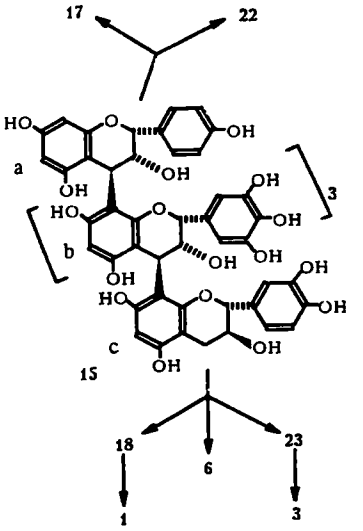
The thiolytic cleavage of (**13**) in the presence of phenyl mercaptan led to (+)-catechin (**6**), occupying the "lower" position, and a mixture of two thioethers (**18**, **23**). As a result of the study of PMR spectra and physicochemical properties of the products of catalytic cleavage of the thioethers it was established that one of the "upper" blocks was (−)-epigallocatechin, while the other block was (−)-epiafzelechin, and, also taking into account the elementary composition of the proanthocyanidin, it is possible to propose a structure of this proanthocyanidin as epiafzelechin-(4β-8)-epigallocatechin-(4β-8)-catechin (**13**).

The physicochemical properties of (**13**) and (**14**) were very close. They differed by the fact that in the ^{13}C NMR spectrum of (**14**) there were the characteristic resonance signals of the carbon atoms of epiafzelechin, epicatechin, and catechin, while the characteristic signals of epigallocatechin were absent (Table 3). After the acid cleavage of (**14**), three compounds were detected in the hydrolysate: pelargonidin (**17**), cyanidin (**24**), and (+)-catechin. Thiolytic cleavage of the substance in the presence of phenyl mercaptan gave three products: two thioethers (**17** and **25**) and (+)-catechin. After degradation of the thioethers, the structures of the "upper" blocks of the proanthocyanidin were established: one of them proved to be

epiafzelechin, and the other epicatechin. A comparison of the characteristics of (**13**) and (**14**) showed that the structure of compound (**14**) corresponded to epiafzelechin-(4β-8)-epicatechin-(4β-8)-catechin.

The ^{13}C NMR spectrum of compound (**15**) showed signals of the carbon atoms of epiafzelechin, epigallocatechin, and catechin. The assignment of the signals is given in Table 4.

A study of the products of alkaline cleavage, acid hydrolysis, and thiolytic degradation of (**15**) confirmed the results obtained by means of ^{13}C NMR spectroscopy. The molecular mass of (**15**) was established by ultracentrifugation and by gel filtration on a calibrated column of Sephadex LH-20, and agreed with the elementary analysis. Thus, it may be assumed that proanthocyanidin (**15**) was a pentamer: epiafzelechin-(4β-8)-[epigallocatechin-(4β-8)-]$_3$-catechin.



The ^{13}C NMR spectra of (**15**) and (**16**) were similar, with the difference that in the spectrum of (**16**) the characteristic resonance signals of epiafzelechin and epigallocatechin gallate appeared (Table 5). A study of its physicochemical characteristics, chemical composition and molecular mass led to the conclusion that (**16**) was a heptamer, i.e., epiafzelechin-(4β-8)-[epigallocatechin gallate-(4β-8)-]$_5$-catechin.

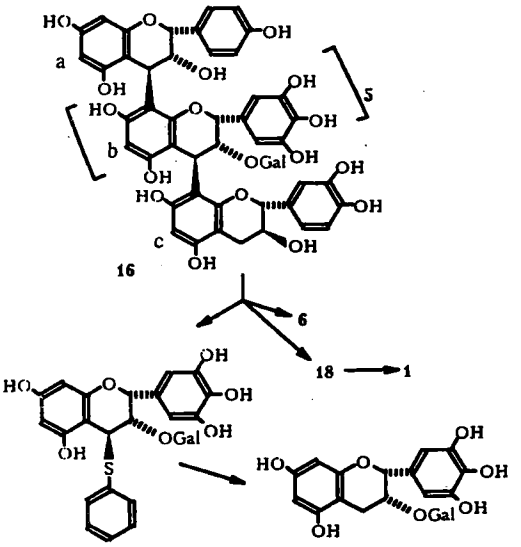


TABLE 4. Chemical Shifts (ppm) in the ^{13}C NMR Spectrum of Proanthocyanidin (**15**) in the Mixed Solvent Acetone-d_6-D_2O

Carbon atoms	Fragments of (15)		
	a	b	c
C-2	77.2	77.2	81.8
C-3	72.1	72.1	67.9
C-4	36.8	36.8	–*
C-6	96.1[e]	96.1e	96.1[e]
C-8	97.0[e]	107.4	107.4
C-10	101.5	101.5	101.5
C-5,7,9		155.1–158.0[g]	
C-1′	131.3[x]	131.3[x]	130.2[x]
C-2′	129.7	107.4	115.5[e]
C-3′	114.5[e]	145.5[m]	145.2[m]
C-4′	157.0[g]	134.0	145.2[m]
C-5′	114.5[e]	145.5	116.9
C-6′	129.7	107.4	119.3

*Signals masked by a signal of the solvent. Signals marked with the same letter may be interchanged.

TABLE 5. Chemical Shifts (ppm) in the^{13}C NMR Spectrum of Proanthocyanidin (**16**) in the Mixed Solvent Acetone-d_6-D_2O

Carbon atoms	Fragments of (16)			
	a	b	c	galloyl
C-2	77.9	76.8	81.3	
C-3	71.3	73.2	68.6	
C-4	37.1	34.4	–*	
C-6	95.8[e]	95.8[e]	95.8[e]	
C-8	96.9[e]	107.5	107.5	
C-10	101.2	101.2	101.2	
C-5,7,9		154.2–157.7		
C-1′	131.1	131.1	131.1	121.3
C-2′	129.6	107.5	115.6[g]	109.9
C-3′	114.4[g]	145.3[p]	145.3[p]	145.5[p]
C-4′	157.3	133.8	145.3[p]	138.9
C-5′	114.4[g]	145.3[p]	116.4	145.5[p]
C-6′	129.6	107.5	119.6	109.9
–COO–				166.3

*Signals masked by a signal of the solvent. Signals marked with the same letter may be interchanged. Underlining indicates galloylating hydroxyl group.

This the first time that the catechin and proanthocyanidin composition of common jujube has been studied in relation to the vegetation phases of the leaves and bark simultaneously. It has been established that in the leaves of the plant during vegetative growth the amount of catechins increases, but by the period of the ripeness of the fruit it decreases sharply. Proanthocyanidins accumulate in the bark. The result of these investigations will be published later.

EXPERIMENTAL

General Information. The UV spectra of the proanthocyanidins and their derivatives were taken in alcoholic solution on a Hitachi EPS-3T instrument, and IR spectra on a Carl Zeiss, Jena, UR-20 instrument, in tablets with potassium bromide. ^1H and ^{13}C NMR spectra were obtained on a Tesla BS-567A/100 MHz (^1H) and 25 MHz (^{13}C) instrument in $(CD_3)_2CO$-D_2O (5:1-1:1) solutions, with HMDS as internal standard for protons, and TMS for carbon (δ-scale). The concentrations of the substances ranged from 15 to 20%. The carbon spectra were obtained under conditions of complete suppression of spin-spin

coupling with protons. Molecular masses were determined on a MOM 3179 ultracentrifuge and by gel filtration on a calibrated column of Sephadex LH-20. In the determination of the optical activities of the substances we employed a JASCO-J-20 instrument. To check the homogeneity of the substances we used PC and TLC on Silufol UV-254 plates [17] with a 1% solution of vanillin in a 5-10% alcoholic solution of sulfuric acid as the revealing agent.

The elementary analyses of all the compounds corresponded to the calculated figures.

Extraction and Isolation of the Proanthocyanidins. Common jujube bark (5.8 kg) was extracted with 80% ethanol six times. The extracts were combined and evaporated in vacuum at 40°C to 2 liters. The concentrated extract was treated successively with diethyl ether, ethyl acetate, and *n*-butanol, giving, respectively, 18.2, 21.1, and 165 g of extractive substances. The aqueous residue yielded a total of 510 g of high-molecular-mass proanthocyanidins.

Separation of the Catechins. The diethyl ether extract (18.2 g) was chromatographed on a column of silica gel (5 × 180 cm), with elution by ethyl acetate–hexane (1:2-4:1). The following compounds were isolated and were identified from their physicochemical constants: (−)-epiafzelechin (**1**) − 0.118 g; (−)-epicatechin (**2**) − 0.222 g; (−)-epigallocatechin (**3**) − 0.308 g; (−)-epicatechin gallate (**4**) − 0.081 g; (−)-epigallocatechin gallate (**5**) − 0.213 g: (+)-catechin (**6**) − 0.096 g; (+)-catechin gallate (**7**) 0.053 g; and (+)-gallocatechin (**8**) − 0.038 g.

Separation of the Dimers. The ethyl acetate fraction (21.1 g) was chromatographed on a column of Sephadex LH-20 (5 × 160 cm), with elution by 80% aqueous methanol. Four dimeric proanthocyanidins were obtained.

(−)-Epiafzelechin-(4β-8)-(−)-epicatechin (9). Amorphous powder with the composition $C_{30}H_{26}O_{11}$, M 562, $[\sigma]_D^{22}$ +28.3° (*c* 1.0; acetone). PMR spectrum: 2.84 (2H, m, H-4′), 4.01(1H, s, H-3), 4.33 (1H, m, H-3′) 4.70 (1H, s, H-4), 4.94 (1H, s, H-2′), 5.15 (1H, s, H-2), 6.00-6.03 (3H, m) − protons of rings A, 6.7-7.2 ppm (7H, m) − protons of rings B.

Proanthocyanidin B-2 (10). Amorphous powder with the composition $C_{30}H_{26}O_{12}$, M 578, $[\alpha]_D^{22}$ +25.1° (*c* 1.0; acetone). PMR spectrum: 2.84 (2H, m, H-4′), 3.99 (1H, s, H-3), 4.32 (1H, m, H-3′), 4.71 (1H, s, H-4), 4.92 (1H, s, H-2′), 5.09 (1H, s, H-2), 6.01-6.08 (3H, m) − protons of rings A, 6.71-7.19 ppm (6H, m) − protons of rings B.

(−)-Epicatechin-(4β-8)-(−)-epigallocatechin (11). Amorphous powder with the composition $C_{30}H_{26}O_{13}$, M 594, $[\alpha]_D^{22}$ +42.3° (*c* 0.78; acetone). PMR spectrum: 2.82 (2H, m, H-4′), 4.03 (1H, br.s, H-3), 4.29 (1H, br.s, H-3′), 4.73 (1H, s, H-4), 4.91 (1H, s, H-2′), 5.07 (1H, s, H-2), 5.80-6.10 (3H, m) − protons of rings A, 6.64 (2H, s), 6.82-6.90 (2H, m), 7.08 ppm (1H, br.s) − protons of rings B.

(−)-Epiafzelechin-(4β-8)-(−)-epigallocatechin (12). Amorphous powder with the composition $C_{30}H_{26}O_{12}$. M 578, $[\alpha]_D^{22}$ +43.4° (*c* 1.2; acetone). PMR spectrum: 2.82 (2H, m, H-4′), 3.98 (1H, s, H-3), 4.29 (1H, br.s, H-3′), 4.75 (1H, s, H-4), 4.94 (1H, s, H-2′), 5.04 (1H, s, H-2), 5.91, 6.08 (3H, H-6, H-8 and H-6′) − protons of rings A, 6.65 (2H, s) − ring B of gallocotechin 6.76 (2H, d, J = 8 Hz, the protons H-3′, H-S′) and 7.28 ppm (2H, d, J = 8 Hz, H-2′, H-6′) − the protons of ring *B* of afzelechin. For the ^{13}C NMR spectrum, see Table 1.

Separation of the Proanthocyanidins. The butanol extract (85 g) was mixed with 85 g of cellulose and transferred to a column of microcrystalline cellulose (800 g). Elution was conducted with chloroform–ethyl acetate (1:10-1:20), ethyl acetate, and acetone, 100-ml fractions being collected, with monitoring by TLC. Eluates 80-196, containing a mixture of relatively low-molecular-mass proanthocyanidins, were combined, evaporated, and rechromatographed (41.9 g) on cellulose with elution by ethyl acetate and ethyl acetate-acetone (10:1-1:1).

Compound (13). The residue from fractions 33-58 (0.881 g) was transferred to a column of Sephadex LH-20 (3 × 130 cm). Elution with 80% ethanol yielded 0.701 g of a light brown amorphous powder with the composition $C_{45}H_{38}O_{18}$, M 866, $[\alpha]_D^{22}$ +58.1° (*c* 1.0; acetone–water (1:1)). For the ^{13}C NMR spectrum, see Table 2.

Compound (14). The residue from fractions 71-94 (1.055 g) was chromatographed on a column of Sephadex LH-20. Elution with 80% ethanol yielded 0.922 g of an amorphous substance with the composition $C_{45}H_{38}O_{18}$, M 866, $[\alpha]_D^{22}$ +51.4° (*c* 1.0; acetone–water (1:1)). For the ^{13}C NMR spectrum, see Table 3.

Compound (15). The residue from fractions 110-123 (1.85 g) was chromatographed on Sephadex LH-20, with elution by 60% ethanol. This led to the isolation of 1.49 g of an amorphous substance with the composition $C_{75}H_{62}O_{32}$. M 1474, $[\alpha]_D^{22}$ +77.8° (*c* 1.0; acetone–water (1:1)). For the ^{13}C NMR spectrum, see Table 4.

Compound (16). The residue (1.380 g) was chromatographed on Sephadex LH-20. Elution by 60% ethanol gave 1.208 g of an amorphous powder with the composition $C_{106}H_{86}O_{46}$, M 2084, $[\alpha]_D^{22}$ +73.6° (*c* 1.0; acetone–water (1:1)). For the ^{13}C NMR spectrum, see Table 5.

Alkaline Cleavage of Compounds (12)-(16). The cleavage of each substance (50 mg) was performed by the procedure described in [18]. The following products were detected and identified: from compounds (**13**), (**15**) and (**16**) − phloroglucinol

and *p*-hydroxybenzoic, protocatechuic, and gallic acids: from compound (**13**) – phloroglucinol and *p*-hydroxybenzoic, and gallic acids; and from compound (**14**) – phloroglucinol and *p*-hydroxybenzoic and protocatechuic acids.

Acid Cleavage of (12). Substance (**12**) (150 mg) was cleaved by the procedure described in [17]. This gave 16 mg of (−)-epigallocatechin, mp 215-216°C, $[\alpha]_D^{22}$ −58°C (*c* 0.11; methanol), λ_{max} 272 (lgε 3.10).

In the hydrolysate, PC showed the presence of pelargonidin, R_f 0.80 (2 N HCl), λ_{max} 518 nm (0.1% HCl in ethanol).

Acid Cleavage of Compounds (13)-(16). In each case, the cleavage of 150 mg of the substance yielded (+)-catechin, mp 178-179°C, $[\alpha]_D^{24}$ +18.3° (*c* 0.9, acetone–water (1:1)) and the corresponding anthocyanidins: pelargonidin, cyanidin, R_f 0.69 (2 N HCl), λ_{max} 252 (0.1% HCl in ethanol), and delphinidin, R_f 0.36 (2 N HCl, λ_{max} 554 (0.1% HCl in ethanol).

Thiolytic Cleavage of (12). A mixture of 300 mg of (**12**) and 4 ml of phenyl mercaptan was treated with 2 ml of acetic acid and 10 ml of ethanol, and the resulting reaction mixture was left at room temperature for 36 h. Then it was concentrated to an oily residue, which was chromatographed on Sephadex LH-20 (1 × 160 cm). Elution with ethanol yielded 22 mg of (−)-epigallocatechin and 63 mg of an amorphous thioether with the composition $C_{21}H_{18}O_5S$, $[\alpha]_D^{25}$ −36.1° (*c* 1.0; methanol), PMR spectrum 4.01 (1H, m, H-3), 4.13 (1H, d, J = 2 Hz, H-4), 5.33 (1H, s, H-2), 5.90 and 6.05 (2H, d, J = 2 Hz, H-6, H-8), 6.81 (2H, d, J = 8 Hz, H-3′, H-5′); 7.33 (2H, d, J = 8 Hz, H-2′, H-6′) – epiafzelechin, 7.12-7.58 (5H, m) – the protons of phenyl mercaptan.

Cleavage of the Thioether (18). The thioether (50 mg) was mixed with 3 ml of ethanol–acetic acid (9:1), the catalyst – Raney nickel – was added to the reaction mixture, and it was kept at 50°C for an hour. Then it was filtered, and the filtrate was concentrated and chromatographed on Sephadex LH-20. Elution with 80% ethanol gave 11 mg of (−)-epiafzelechin (**1**), with mp 249-250°C, $[\alpha]_D^{22}$ −52° (*c* 1.0; acetone).

Thiolytic Cleavage of (13) and (15). The substances (350 and 400 mg) were cleaved, and the reaction products were purified by the method described above. This gave 11 and 8 mg, respectively, of (+)-catechin and 249 and 261 mg of a mixture of thioethers. Catalytic cleavage of the thioethers and purification led to 9 and 6 mg of (−)-epiafzelechin, and 28 and 41 mg of (−)-epigallocatechin.

Thiolytic Cleavage of Compound (14). Compound (**14**) (380 mg) was cleaved, and the reaction products were purified by the method described above. This gave 7 mg of (+)-catechin and 186 mg of a mixture of thioethers. Catalytic cleavage of the thioethers yielded 24 mg of (−)-epiafzelechin and 29 mg of (−)-epicatechin, mp 241-243°C, $[\alpha]_D^{24}$ −69° (*c* 0.5; acetone–water (1:1)).

Thiolytic Cleavage of (16). The reaction was performed by the method described above. The compounds obtained were identified as (+)-catechin, (−)-epiafzelechin, and (−)-epigallocatechin gallate, mp 210-211°C, $[\alpha]_D^{24}$ −195° (*c*, 0.8; water) – the protons of phenyl mercaptan.

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