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PROANTHOCYANIDINS OF *Polygonum corarium*. II

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Eight proanthocyanidins have been isolated from the roots of Polygonum coriarum. *The structures of two dimers, two trimers, including an acylglycosylated one, a tetramer, and three oligomers have been determined. All the compounds isolated were polymers and copolymers of (−)epigallocatechin, (−)epigallocatechin gallate and (−)epicatechin with C-4β→C-8 interflavan bonds.*

As reported previously [1], we have isolated a number of proanthocyanidins from *Polygonum coriarum* Grig. In the present communication we give the results of a study of the physicochemical properties of the isolated compounds (**1**)-(**8**) and the determination of their structures.

The UV spectrum of compound (**1**) had absorption maxima at 220 and 278 nm with a shoulder at 245 nm and an absorption minimum at 256 nm. In the IR spectrum of (**1**) a strong broad band in the 3500-3200 cm^{-1} region was due to the stretching vibrations of hydroxy groups. Absorption in the 1625, 1545, 1510, and 1435 cm^{-1} regions related to an aromatic ring. In addition, the spectrum contained bands at 2935 and 1495 cm^{-1} (−CH− and $-CH_2-$), 1320 and 1200 cm^{-1} (O−H and C−O), and 1270 and 1040 cm^{-1} (C−O−C).

The UV and IR spectra of substance (**1**) showed that it was a proanthocyanidin. In actual fact its cleavage with a fivefold amount of caustic soda in a nitrogen atmosphere led to the formation of a phenol and a phenolic acid, which were identified by direct comparison with authentic specimens as phloroglucinol (**9**) and gallic acid (**10**). Under the action of

Scheme 1

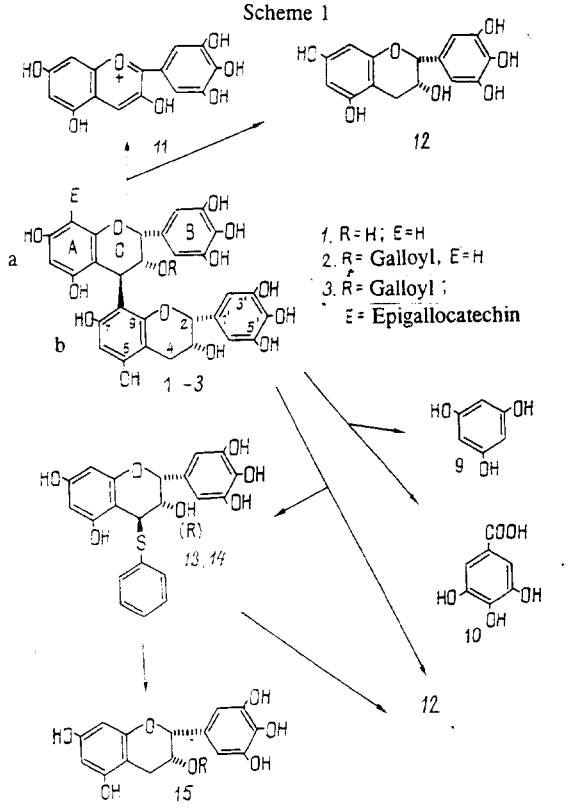

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TABLE 1. Parameters of the PMR Spectra of Compounds (1)-(3)

Fragments	Protons					Galloyl
	H-2	H-3	H-4	H-6, 8	H-2′, 6′	H-2″, 6″
1a	4.81 c	4.19	4.16 s	5.93 s	6.34	
1b	4.92 c	3.88 s	*	5.93 s	6.52	
2a	5.42	5.37	4.84	5.92	6.34	6.92
2b	4.84	4.1—4.2	*	5.92	6.52	
3a	4.96	4.06—4.22	4.79	5.93	6.54	
3b	5.24	5.39	4.79	5.93	6.66	6.93
3c	4.96	4.06—4.22	*	6.03	6.70	—

*The signal was masked by a signal of the solvent.

TABLE 2. Parameters of the ^{13}C NMR Spectrum of Compound (4)

Carbon atoms	Fragments of tarachin (4)			
	a	b	c	galloyl
2	76.8	74.8	79.2	
3	73.1	74.8	66.7	
4	36.8	34.8	*	
5, 7, 9	156.0	156.0	156.0	
6	97.6	97.6	97.6	
8	97.6	106.9	106.9	
10	101.3	101.3	100.7	
1′	131.6	131.6	131.6	122.2
2′	106.9	106.9	114.6	110.3
3′	146.1	146.1	115.8	146.1
4′	132.9	132.9	146.1	139.2
5′	146.1	146.9	146.1	146.1
6′	106.9	106.9	120.8	110.3
--COO--				167.4

*The signal was masked by a signal of the solvent.

hydrochloric acid, a dilute aqueous solution of the substance assumed an intense red color, which showed the formation of the anthocyanidin (**11**), and then the red-brown color of a flabofen [compound not known — Translator.] appeared.

According to its PMR spectrum (Table 1), compound (**1**) was a dimeric proanthocyanidin and consisted of two (−)epigallocatechin units [2, 3]. Thus, at 5.93 ppm a three-proton singlet appeared that related to H-8 ands H-6 of the "upper" and H-6 of the "lower" block. Resonance signals relating to the H-2′ and H-6′ protons of rings *B* appeared in the 6.34 and 6.52 regions in the form of two-proton singlets. Broadened singlets at 3.88 and 4.19 ppm related, respectively to H-3 of the "lower" and H-3 of the "upper" block [4]. The H-2 proton of the "upper" block appeared in the form of a singlet at 4.81 ppm and that of the "lower" block at 4.92 ppm, while the proton at the substituted C-4 carbon gave a broadened singlet at 4.61 ppm.

On the thiolytic cleavage of the dimer in the presence of thiophenol, identical catechins were obtained from the "lower" and "upper" blocks (**13**), and these were identified as (−)-epigallocatechin (**12**, Scheme 1).

Thus, compound (**1**) was prodelphinidin B-2 — (−)epigallocatechin-(4β→8)-(−)-epigallocatechin.

The UV, IR, and PMR spectra of compound (**2**) contained the characteristic signals of proanthocyanidins. Its physicochemical and spectral properties were very close to those of dimer (**1**). As compared with the latter, however, the PMR spectrum of (**2**) showed paramagnetic shifts of the signals of the H-2, H-3, and H-4 protons (5.42, 5.37, and 4.84 ppm, respectively) [2]. In the light of the facts given above and also of the presence of a two-proton singlet at 6.92 ppm, which is characteristic for gallic acid, it can be stated unambiguouly the the "upper" block was galloylated (Table 1).

The thiolytic cleavage of dimer (**2**) (Scheme 1) led to the thioether (**14**) and (−)-epigallocatechin (**12**), which was identified by its physicochemical properties in comparison with an authentic specimen. Catalytic cleavage of the thioether (**14**) gave a substance identified as (−)-epigallocatechin gallate (**15**).

Thus, substance (**2**) was (−)epigallocatechin gallate)-(4β→8)-(−)epigallocatechin.

TABLE 3. Parameters of the ^{13}C NMR Spectrum of Compound (5)

Carbon atoms	Tarachisin fragments (5) 3)				
	a	b	c	glucose	galloyl
2	75.0	75.0	78.3		
3	71.3	71.3	65.1		
4	36.0	36.0	*		
5, 7, 9	154.8	154.8	156.1		
6	95.1	95.1	95.1		
8	95.1	106.0	106.0		
10	101.0	101.0	101.0		
1′	130.5	130.5	130.5	101.0	121.7
2′	106.0	106.0	106.0	75.0	109.1
3′	144.9	144.9	144.9	78.3	144.9
4′	132.3	132.3	132.3	69.2	140.0
5′	144.9	144.9	144.9	75.0	144.9
6′	106.0	106.0	106.0	63.1	109.1
–COO–					

*The signal was masked by a signal of the solvent.

It must be mentioned that this is the first time that (−)epigallocatechin (4β→8)-(−)-epigallocatechin (the dimer B-2) and (−)-epigallocatechin gallate)-(4β→8)-(−)epigallocatechin (the dimer B′-2) have been isolated from *Polygonum coriarum* and characterized.

According to its UV and IR spectra, compound (3), which has been called taraninin was also a condensed catechin, i.e., a proanthocyanidin.

The PMR spectrum of taraninin (Table 1) showed the signals of protons belonging to galloylated and nongalloylated epigallocatechins [4-6]. The protons of rings *A* of the "upper" epigallocatechins appeared in the 5.93 ppm region in the form of a three-proton singlet (H-8 and H-6 of the "top" and H-6 of one of the "lower" blocks, but precisely which it does not appear possible to determine), and the signal at 6.03 ppm may therefore relate to H-6 of the "middle" or of the "lower" block.

The resonance signals relating to the protons of rings *B* of the catechin blocks (H-2′ and H-6′) appeared in the form of two-proton singlets in the 6.54, 6,66, and 6.70 ppm regions, respectively. Analysis of the spectrum showed that the "lower" block was ungalloylated (4.96, br. s, H-2; 4.19, br. m, H-3) [4]. The paramagnetic shifts of the signals of the protons (H-2, H-3, and H-4) unambiguously showed that one of the "upper" blocks was acylatd. A two-proton singlet at 6.93 ppm, which is characteristic for gallic acid, indicated that this block was acylated by gallic acid.

On the thiolytic hydrolysis of taraninin (Scheme 1), epigallocatechin was formed from the "lower" part, and two thioethers from the "upper" part. Catalytic cleavage of the thioethers led to epigallocatechin and epigallocatechin gallate. Consequently, taraninin has the structure and relative configuration (3) — (−)-epigallocatechin-(4β→8)-[(−)epigallocatechin gallate]-(4β→8)-(−)-epigallocatechin.

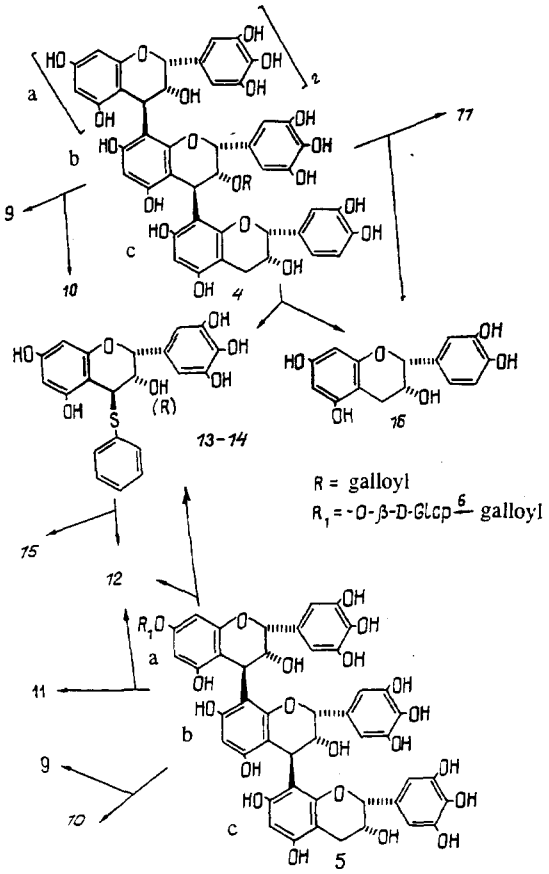
On the basis of spectral and chemical methods of investigation, compound (4) was assigned to the proanthocyanidins and was named tarachin. In the ^{13}C NMR spectrum of compound (4) (Table 2) obtained under conditions of complete suppression of spin-spin coupling with protons, signals characteristic for epigallocatechin, epicatechin, and a gallic acid residue [7-9] appeared.

Analysis of the chemical shifts of the carbon atoms C-2, C-3, and C-4 showed that some of the epigallocatechin blocks of the chain were galloylated [3, 10]. In the spectrum, together with the resonance signals of the carbon atoms of the gallic acid residue, a paramagnetic shift of the signal of the C-3 carbon atom and a diamagnetic shift of the signal of the C-4 carbon atom of one of the "upper" epigallocatechins were observed.

Resonance signals from the C-5, C-7, and C-9 carbon atoms of the phloroglucinol nuclei appeared in the form of a broadened signal at 156.0-156.3 ppm. An intense signal at 146.1 ppm related to C-3′ and C-5′ of rings *B* of the epigallocatechins and to C-3′ and C-4′ of the epicatechin [11, 12]. The C-4′ carbon atoms of the epigallocatechins were screened and, as the result of a diamagnetic shift, resonated in the 132.9 ppm region [13]. Signals from the C-2′ and C-6′ carbon atoms of rings *B* and of the substituted C-8 carbon atoms of the phloroglucinol nuclei coincided and gave a relatively intense signal at 106.9 ppm [14]. The resonance signals from the C-2′, C-5′, and C-6′ atoms of ring *B* of the epicatechin appeared at 114.6, 115.8, ands 120.8 ppm, respectively [11].

The chemical shift of the C-10 carbon atoms of the "upper" proanthocyanidin blocks, with a value of 101.3 ppm showed that the interflavan bond was of the C-4→C-8 type [15]. The thiolytic cleavage of (**4**) led to two thioethers and epicatechin, which was identified by comparison with an authentic specimen. The catalytic cleavage of the thioethers gave epigallocatechin and epigallocatechin gallate. Consequently, tarachin is a copolymer having the structure and relative configuration (**4**) - [(−)-epigallocatechin]$_2$-(4β→8)-[(−)-epigallocatechin gallate]-(4β→8)-(−)-epicatechin.

Scheme 2



In contrast to tarachin, in the ^{13}C NMR spectrum of tarachisin (**5**) together with the signals of a gallic acid residue there were the signals of glucose and the characteristic signals of prodelphinidins (Table 3).

Signals belonging to C-2, C-3, and C-4 of the "upper" and "middle" blocks appeared at 75.0, 71.3, and 36.0 ppm, respectively, and signals relating to the C-2 and C-3 carbon atoms of the "lower" block at 78.0 and 65.1 ppm, respectively. The appearance of the C-3 signal at 65.1 ppm and the absence of a shifted C-4 signal at about 26-27 ppm (the corresponding signal was masked by a signal from the solvent in the 29 ppm region) permits the unambiguous conclusion that the "lower" epigallocatechin was not esterified [16].

The chemical shifts of C-1, C-3, and C-5 of glucose showed that the anomeric center had the β- configuration. Most of the signals of the sugar moiety were masked by the signals of the carbon atoms of rings *C* of the epigallocatechins. The paramagnetic shift of the signal of C-6 of the sugar residue in tarachisin (63.1 ppm) was close to the chemical shift of the sixth carbon atom of glucose with an acylated hydroxy group [17, 18].

The enzymatic cleavage with β-glucosidase and the acid hydrolysis of tarachisin showed that the sugar residue consisted of one *D*-glucose molecule galloylated at C-6 and linked to the aglycon by a β-bond [19].

The results of the mild thiolytic cleavage of (**5**) (scheme 2) showed the absence of a sugar residue in the "lower" epigallocatechin block; consequently, if the stereochemical hindrance in the molecule is taken into acount, it may be assumed that the "upper" epigallocatechin block was glycosylated in the C-7 position.

On the basis of the results obtained, for tarachisin we propose the structure and configuration (**5**) — [7-O-(6-O-galloyl-β-*D*-glucopyranosyl)-(−)-epigallocatechin]-(4β→8)-(−)-epigallocatechin-(4β→8)-(−)-epigallocatechin.

The absorption maximum in the UV spectrum and the features of the IR spectrum showed that tarantannin A (**6**) was a high-molecular-mass acylated proanthocyanidin. Table 4 gives the results of the assignment of the resonance signals in the ^{13}C NMR spectrum of (**6**).

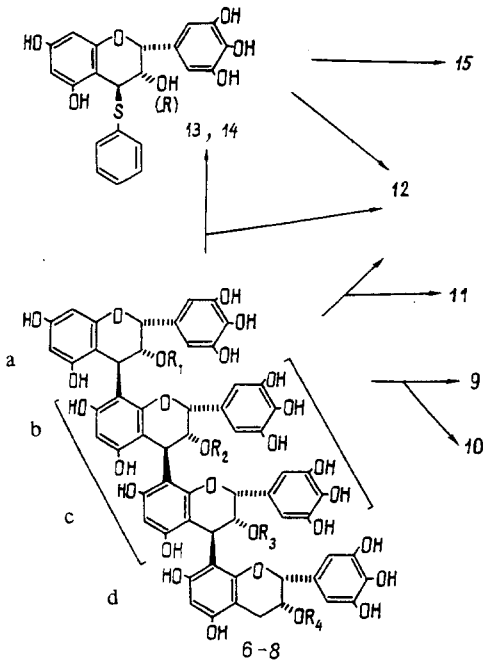
The resonance signals at 155.0-156.7 ppm relate to the C-5, C-7, and C-9 carbon atoms of the phloroglucinol nuclei. The signals of the C-3′ and C-5′ carbon atoms of rings *B* appeared in the form of an intense resonance at at 145.9 ppm, and the screened C-4′ atom resonated in the 132.9 ppm region. Resonance signals at 130.9 ppm related to C-1′ and at 107.1, to C-2′ and C-6′ of rings *B*. An intense resonance at 106.8 ppm related to the substituted the substituted C-8 carbon atoms of rings *A*, and signals at 95.7-95.9 ppm to the unsubstituted C-6 and C-8 atoms.

The resonance signals at 100.0-101.9 ppm relating to the C-10 carbon atoms adjacent to the substituted C-4 carbons determined the interflavan bond as C-4→C-8.

Signals of the C-2 atoms of the "lower" and "upper" blocks appeared at 78.3 ppm. Resonance signals at 72.1 and 74.5 ppm related to the C-3's of the "upper" blocks, and a signal at 65.5 ppm to the C-3 atom of the "lower" block. The substituted C-4 carbon atoms of the unesterified "top" blocks resonated at 36.6 ppm, those of the esterified blocks at 34.2 ppm, and C-4 of the unesterified "bottom" block at 29.0 ppm. The resonance of the C-2 atom at 76-78 ppm and the absence of a signal in the range above 80 ppm showed the *cis*- orientation of the substituents at C-2 and C-3 in the heterocyclic ring of the prodelphinidin units.

Analysis of the chemical shifts of the carbon atoms in the ^{13}C NMR spectrum of the proanthocyanidin (**6**) showed that it was a copolymer of epigallocatechin and epigallocatechin gallate, as was confirmed by the presence of resonance signals characteristic for a gallic acid residue: 121.0, 110.1, 145.9, 139.0, and 170.3 ppm (C-1, C-2′, C-6′, C-3′, C-5′, C-4′, and C=O, respectively [sic]). The thiolytic cleavage of (**6**) and a study of the degradation products (Scheme 3) confirmed what has been said above. The ratio of epigallocatechin and epigallocatechin gallate in the copymer was approximately 75:25.

Scheme 3



6. $R_1 = R_4 = H$; R_2: R_3 = galloyl — a, (b:c), d = 75 : 25
7. $R_1 = R_4 = H$; R_2: R_3 = galloyl — a, (b:c), d = 50 : 50
8. $R_1 = R_2 = R_3 = R_4$ = galloyl — a, b, c, d = 100

TABLE 4. Parameters of the ^{13}C NM Spectrum of Compound (6)

Carbon atoms	Fragments of tarantannin A (6)				
	a	b	c	d	galloyl
2	78.3	78.3	78.3	78.3	
3	72.1	72.1	74.5	65.5	
4	36.6	36.6	34.2	29.0	
5, 7, 9		155.0 — 156.7			
6		95.7 — 95.7			
8	95.7	106.8	106.8	106.8	
10		100.0 — 101.9			
1	130.9	130.9	130.9	130.9	121.0
2', 6'	107.1	107.1	107.1	107.1	110.1
3', 5'	145.9	145.9	145.9	145.9	145.6
4'	132.9	132.9	132.9	132.9	139.0
–COO–					170.3

Thus, tarantannin A is epigallocatechin-(4β→8)-[epigallocatechin-(4β→8)-epigallocatechin gallate]$_9$-(4β→8)-epigallocatechin (**6**).

The UV and IR spectra of tarantannin B (**7**) were almost identical with those of tarantannin A. These proanthocyanidins differ by the fact that the latter, besides having a higher molecular mass, also has a greater number of esterified epigallocatechins in its molecule than the former.

A comparison of the ^{13}C NMR spectra (Table 5) and a study of the ratios of the resonance signals of the degradation products on the thiolytic cleavage of tarantannin B permitted the conclusion that it was also a copolymer of epigallocatechin and epigallocatechin gallate in a ratio of approximtely 50:50 and, consequently was epigallocatechin-(4β→8)-[epigallocatechin-(4β→8)-(epigallocatechin gallate)]$_9$-(4β→8)-epigallocatechin (**7**).

Taranicin (**8**) is a yellow-brown amorphous powder showing in its IR spectrum absorption bands at (cm^{-1}) 3500 (OH), 1690 (−COO−), 1620, 1545 and 1450 (arom. ring), 1320 (−C−OH) and 1250 and 1045 (−C−O−C), which are characteristic for galloylated proanthocyanidins.

The ^{13}C NMR spectrum of taranicin (**8**) revealed signals relating to epigallocatechin blocks and gallic acid residues. An analysis of the chemical shifts of the signals of the C-2, C-3 and C-4 carbon atoms (73.6, 73.6 and 35.4 ppm for the "upper" blocks, and 76.0, 69.8,and 26.9 ppm for the "lower" block, respectively showed that all the epigallocatechin blocks in the taranicin molecule were galloylated (Table 6).

The chemical shifts of the C-10 carbons of the "upper" blocks are characteristic (102.8 ppm) for proanthocyanidins with a C-4→C-8 interflavan bond.

On the thiolytic cleavage of taracinin in the presence of thiophenol and acetic acid, two compounds were obtained. (−)-Epigallocatechin gallate was formed from the lower part of the molecule, this being identified by its melting point and IR and PMR spectra. Only a catechin thioether was formed from the upper blocks, and this was cleaved catalytically with Raney nickel. The resulting catechin was identified from its physicochemical and spectral characteristics as epigallocatechin gallate.

On the basis of the results obtained we propose for taranicin the structure and relative configuration (**8**) — (epigallocatechin gallate)-(4β→8)-[epigallocatechin gallate)-(4β→8)-(epigallocatechin gallate)]$_8$-(4β→8)-epigallocatechin gallate.

EXPERIMENTAL

For general information, see [1]. PMR and ^{13}C NMR spectra were taken on BS 567 A 25 MHz TESLA (Czechoslovakia) and Bruker WN-200 SY ν_C = 50.3 MHz (FRG) instruments in deuteroacetone or deuteroacetone−deuterowater (1:1 and 1:2) solutions, with TMS and HMDS as internal standards (δ scale). The concentrations of the substances ranged between 15 and 30%.

TABLE 5. Parameters of the ^{13}C NMR Spectra of Compound (7)

Carbon atoms	Fragments of tarantannin B (7)				
	a	b	c	d	galloyl
2	76.6	76.6	76.6	76.6	
3	72.1	72.1	74.5	65.5	
4	37.0	37.0	34.9	29.0	
5, 7, 9	155.9	155.9	155.9	155.9	
6	97.9	97.9	97.9	97.9	
8	97.9	107.2	107.2	107.2	
10		100.6 — 102.6			
1′	131.5	131.5	131.5	131.5	121.2
2′, 6′	107.5	107.5	107.5	107.5	110.2
3′, 5′	146.4	146.4	146.4	146.4	146.1
4′	133.1	133.1	133.1	133.1	139.4
–COO–					166.0

TABLE 6. Parameters of the ^{13}C NMR Spectrum of Compound (8)

Carbon atoms	Fragments of taracinin (8)			
	a	b	c	galloyl
2	73.6	73.6	76.0	
3	73.6	73.6	69.8	
4	35.4	35.4	26.9	
5, 7, 9	157.0	157.0	157.0	
6	96.9	96.9	96.9	
8	96.9	108.3	108.3	
10	102.8	102.8	102.8	
1′	131.2	131.2	131.2	121.2
2′, 6′	108.3	108.3	108.3	110.4
3′, 5′	145.8	145.8	145.8	145.8
4′				138.6
–COO–				162.4

The proanthocyanidins were separated by column chromatography on a powder of crystalline cellulose, brand LK for column chromatography (Czechoslovakia), and on Sephadex LH-20 (Sweden). To identify and check the individuality of the substances we used PC and TLC on Silufol 254 plates. Solvent systems: 1) BAW (4:1:5), 2) BAW (40:12:28), 3) chloroform – methanol – water – acetic acid (9:3:0.5:0.5), 4) chloroform – *n*-butanol – acetone – formic acid – water (3.5:13:10:10:8).

The analyses of all the componds were close to the calculated figures.

Isolation of the Proanthocyanidins. The methods of extracting the proanthocyanidins from the raw material have been given in [1].

Separation of the Proanthocyanidins. The total proanthocyanidins of the ethyl acetate fraction (10 g) were deposited on a column of specal construction containing Sephadex LH-20 (5 and 160 cm, 450 g), and were eluted with 80% aqueous

ethanol, 10-20-ml fractions being collected. Identical fractions containing individual compounds were combined, and the solvent was evaporated off.

Prodelphinidin B-2 (1). The evaporation of fractions with the appropriate identical compositions yielded 0.557 g of an amorphous powder with the composition $C_{30}H_{26}O_{14}$, M 610, decomp. at 290-300°C, $[\alpha]_D^{24}$ + 146.2° (s 0.26; acetone), R_f 0.20 (system 3). IR spectrum: ν_{max} 3500, 2935, 1625, 1545, 1510, 1435, 1320, 1200, 1040, 830, 770, 730 cm^{-1}.

Prodelphinidin B-2′ (2). The appropriate identical fractions gave 0.432 g of an amorphous substance $C_{37}H_{30}O_{18}$, M 760, $[\alpha]_D^{24}$ + 142.1° (s 0.38; acetone), R_f 0.28 (system 3). IR spectrum: ν_{max} 3500, 2930, 1675, 1620, 1545, 1516, 1435, 1320, 1260, 1200, 1040, 830, 774, 733 cm^{-1}.

Taraninin (3). When the appropriate homogeneous fractions were evaporated 0.724 g of a residue was obtained, by the rechromatography of which a compound (0.683 g) was isolated with the composition $C_{52}H_{42}O_{23}$, M 1064, $[\alpha]_D^{24}$ + 63.6° (s 0.21; acetone), R_f 0.10 (system 3). UV spectrum: λ_{max} 220, 245, 278, 310 nm. λ_{min} 258 nm. IR spectrum: ν_{max} 3500, 2930, 16693, 1615, 1540, 1515, 1445, 1330, 1250, 1200, 1045, 830, 805, 774, 7730 cm^{-1}.

Tarachin (4). The appropriate identical fractions yielded 0.937 g of residue. Rechromatography gave 0.787 g of a substance $C_{67}H_{44}O_{32}$, M 13660, $[\alpha]_D^{24}$ + 48.7° (s 0.32; methanol), R_f 0.46 (system 4). IR spectrum: ν_{max} 3400, 1695, 16618, 1550, 1450, 1320, 1250, 1120, 1040, 830, 810, 775, 7443 cm^{-1}.

Tarachisin (5). Fractions with the appropriate identical composition gave 1.211 g of residue, which was rechromatographed, with the isolation of a compound $C_{58}H_{52}O_{30}$, M 1228, $[\alpha]_D^{24}$ + 72.8° (s 0.22; ethanol), R_f 0.33 (system 4). IR spectrum: ν_{max} 3400, 1692, 1622, 1550, 14660, 1330, 1250, 1111, 1038, 860, 830, 804, 770. 7443 cm^{-1}.

The butanolic extract (50 g) was mixed with 50 g of cellulose and transferred to a column of cellulose (450 g). Elution was conducted with chloroform–ethyl acetate (1:10), ethyl acetate, and acetone, 100-ml fractions being collected [1]. Eluate fractions 265-480, containing a mixture of three substances, were combined, evaporated, and rechromatographed (19.7 g) on cellulose (450 g) with elution by acetone and acetone–water (99:1-95:5). Fractions with a volume of 25-50 ml were collected.

Tarantannin A (6). The residue from fractions 85-107 (4.81 g) was chromatographed on Sephadex LH-20 (3 × 130 cm), with elution by 80% ethanol. This gave 3.09 g of an amorphous substance with M^+ 6600, decomposing at 290-300°C, $[\alpha]_D^{22}$ + 58° (s 0.31; ethanol). IR spectrum: ν_{max} 3410, 2940, 1695, 1610, 1540, 1425, 1325, 1240, 1200, 1150, 1100, 1040, 840, 800, 770, 740 cm^{-1}.

Tarantannin B (7). The residue from fractions 119-143 (7.31 g) was deposited on a column of Sephadex LH-20 and was eluted with 80% ethanol. This gave 6.01 of a substance with M 7500, $[\alpha]_D^{22}$ + 100° (s 0.28; ethanol). IR spectrum: ν_{max} 3440, 1695, 1620, 1540, 1450, 1330, 1240, 1195, 1115, 1030, 970, 830, 805, 775, 740 cm^{-1}.

Taranicin (8). The residue from fractions 160-180 (3.67 g) was chromatographed on a column of Sephadex LH-20, with the isolation of 2.23 g of an amorphous substance, M^+ 8400, decomposing at 290-300°C., $[\alpha]_D^{22}$ + 70° (s 0.29; ethanol). IR spectrum: ν_{max} 3500, 1695, 1615, 1540, 1515, 1450, 1320, 1250, 1200, 1045, 830, 805, 774, 730 cm^{-1}.

Alkaline Cleavage of Substances (1)-(8). With the passage of a slow current of nitrogen, a mixture of 50 mg of substance and 5 ml of 50% KOH was immersed in a bath with a temperature of 155-160°C, and then the temperature was raised over 5 min to 230°C. The reaction mixture was rapidly cooled, acidified, diluted with water, and extracted with ethyl acetate. The extract was dried, the solvent was distilled off, and the residue was chromatographed on polyamide. This gave two compounds: $C_6H_6O_3$, M^+ 126, mp 218-219°C, and $C_7H_6O_5$, M^+ 170, mp 220°C, decomp., which were identified as phloroglucinol and gallic acid, respectively.

Acid Cleavage of Compounds (1)-(4) and (6)-(8). A solution of 100 mg of substance in 4 ml of ethanol was treated with 5 ml of 2 N HCl, an the mixture was heated on the water bath under reflux in a current of nitrogen for 2 h. The course of the reaction was monitored by TLC every 20 min. The reaction mixture was diluted with water and extracted with ethyl acetate (4 × 3 ml). The extract was washed and dried, and the solvent was distilled off. The residue was chromatographed on Sephadex LH-20, with elution by 80% ethanol. This gave epigallocatechin, $C_{15}H_{14}O_7$, mp 215-216°C, $[\alpha]_D^{21}$ — 56° (s 0.41; methanol), λ_{max} 272 (logε 3.10), R_f 0.42 (system 1). Delphinidin was detected by in the hydrolsate by paper chromatography, R_f 0.36 (2 N HCl), λ_{max} 554 (0.1% HCl in ethanol).

Acid Cleavage of (5). The substance (72 mg) was cleaved by the method described above. The residue was chromatographed on a column of Sephadex LH-20, with elution by 60% ethanol. This gave (−)-epigallocatechin and monogalloylglucose, M^+ 332, mp 135-137°C, $[\alpha]_D^{22}$ + 26° (s 0.18; acetone), PMR (acetone-d_6): 3.00-5.3 (7H, m) 7.14 (2H, s). Delphinidin was detected in the hydrolysate by paper chromatography.

Enzymatic Hydrolysis of (5). A solution of 120 mg of the glycoside in 5 ml of water was treated with the enzyme β-glucosidase. The reaction mixture was placed in a thermostat and was kept at 30°C for 6 h and was then chromatographed on Sephadex LH-20. This gave a galloylated glucose identified as 6-O-galloyl-D-glucose.

Thiolytic Cleavage of Compounds (1) and (5). A mixture of 100 mg of substance with 2 ml of phenyl mercaptan and 1 ml of acetic acid in 10 ml of ethanol was left at room temperature for 36 h. During the first 10 h, the course of the reaction was monitored by TLC every hour. The reaction mixture was concentrated, and the oily residue was chromatographed on Sephadex with elution by ethanol. This gave (-)-epigallocatechin and an amorphous thioether.

Cleavage of the Thioethers from (1) and (5). Each thioether was mixed with 2 ml of ethanol–acetic acid (9:1). Then a catalyst — Raney nickel — was added to to the reaction mixture and it was kept at 50°C for for 1 h. It was filtered, and the filtrate was concentrated and was chromatographed on Sephadex LH-20. The substance was eluted with 80% ethanol. (−)-Epigallocatechin was obtained.

Thiolytic Cleavage of Compounds (2)-(4) and (6)-(8). The reaction was performed by the method described above. In all cases other than (4) three compounds were obtained: (−)-epigallocatechin and a mixture of two thioethers. Compound (4) gave epicatechin $C_{15}H_{14}O_6$, M 290, mp 241-243°C, $[\alpha]_D^{22}$ −69° (s 0.48; acetone–water (1:1), λ_{max} 283 nm (log ε 3.28) R_f 0.57 (system 2).

The cleavage of the thioethers from (2)-(4) and (6)-(8) was carried out by the method described above. The compounds obtained were identified as (−)-epigallocatechin and epigallocatechin gallate: $C_{21}H_{18}O_{11}$, mp 210-211°C, $[\alpha]_D^{22}$ −136° (s 0.40; methanol–water), λ_{max} 278 nm (log ε 3.91), R_f 0.64 (system 2).

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