Prodelphinidin Polymers: Definition of Structural Units

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The two basic structural units of condensed prodelphinidin polymers have been defined by generation of the C-4 carbocations, corresponding in stereochemistry to (+)-gallocatechin (1) and (−)-epigallocatechin (2), and trapping them as their phloroglucinol adducts (4) and (7). Two naturally occurring dimeric prodelphinidins with stereochemistry based on that of gallocatechin have also been isolated.

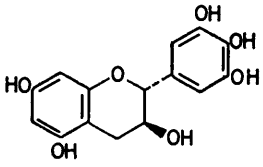
THE chemistry of the procyanidins, a widely distributed class of phenolic secondary plant products, is now well understood. The structure and distribution of the singly linked B-type procyanidin dimers has been studied [1-3] and the anomalous ^{1}H n.m.r. spectra of their acetate and methyl ether derivatives have been explained on the basis of rotational isomerism.[4,5] Additionally, the structure of the doubly linked A-type dimers has been successfully assigned by ^{13}C n.m.r. spectroscopy [6-8] and the distribution of this class of procyanidins in the plant kingdom has also been studied.[9]

In contrast, little is known of the chemistry of the prodelphinidins apart from the fact that a wide range of woody plants yield delphinidin when methanolic extracts of their fruit or leaves are heated with butanol and hydrochloric acid.[9] The flavan-3-ols corresponding to this group of phenolic polymers, (+)-gallocatechin (1) and (−)-epigallocatechin (2) are well known natural products

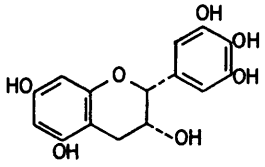
[1] K. Weinges, W. Kaltenhauser, H.-D. Marx, E. Nader, F. Nader, J. Perner, and D. Seiler, *Annalen*, 1968, **711**, 184.
[2] R. S. Thompson, D. Jacques, E. Haslam, and R. J. N. Tanner, *J.C.S. Perkin I*, 1972, 1387.
[3] F. Delle Monache, F. Ferrari, and G. B. Marini Bettolo, *Gazzetta*, 1971, **101**, 387.
[4] A. C. Fletcher, L. J. Porter, and E. Haslam, *J.C.S. Chem. Comm.*, 1976, 627.
[5] A. C. Fletcher, L. J. Porter, E. Haslam, and R. K. Gupta, *J.C.S. Perkin I*, 1977, 1628.
[6] D. Jacques, E. Haslam, G. R. Bedford, and D. Greatbanks, *J.C.S. Chem. Comm.*, 1973, 518.
[7] D. Jacques, E. Haslam, G. R. Bedford, and D. Greatbanks, *J.C.S. Perkin I*, 1974, 2663.
[8] G. Schilling, K. Weinges, O. Müller, and W. Mayer, *Annalen*, 1973, 1471.
[9] E. C. Bate-Smith, *Phytochemistry*, 1975, **14**, 1107.

and were isolated and characterised long ago.[10,11] However, although at least four ' leucodelphinidins ' have been reported with flavan-3,4-diol structures assigned,[12] their proposed formulations have not been supported by compelling evidence. In view of the failure so far either to isolate [13] or to demonstrate the existence [14] of flavan-3,4-diols in plant material containing proanthocyanidins possessing a 5,7-dihydroxylated ring A, it seems probable that the above ' leucodelphinidins ' possess structures analogous to the B-type procyanidin series.[1]

The isolation of proanthocyanidin polymers from

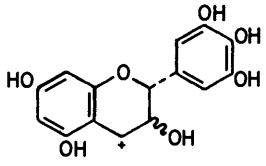


(1)



(2)

vegetative tissue may now be achieved under very mild conditions which apparently cause little degradation.[15] The structure of the constituent monomer units of these polymers may readily be determined by capture by



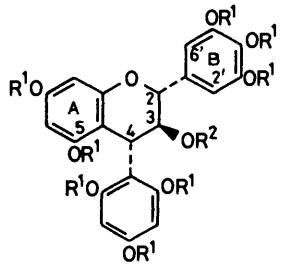
(3)

phloroglucinol of the carbocation (3) generated from the polymer under mild acid conditions.[5]

RESULTS AND DISCUSSION

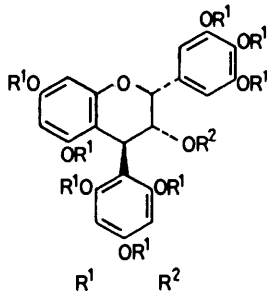
Two proanthocyanidin polymers were isolated from the leaves of crown vetch (*Coronilla varia* L.) and flowering currant (*Ribes sanguineum* Pursh.). Each polymer is a rich source of prodelphinidin units, as shown by the delphinidin : cyanidin ratios of 2.5 : 1 and 6.8 : 1 respectively, determined by degradation with hot butanol and hydrochloric acid. These ratios are close to previously determined values.[9,15]

Treatment of each polymer with phloroglucinol under acid conditions and separation of the products by chromatography yielded the prodelphinidin–phloroglucinol adducts. The *Ribes sanguineum* polymer yielded the phloroglucinol adduct (4) with a flavan unit of stereochemistry corresponding to that of (+)-gallocatechin. The structure of the adduct was readily determined by the spectral properties of the phenol (4), nona-acetate (5), and octamethyl ether (6). The ^{1}H n.m.r. spectra of (4)—(6) were all identical with those of the corresponding derivatives of the phloroglucinol adduct of the carbocation possessing the (+)-catechin stereochemistry [5] except for the H-2 and H-6 absorptions. The spectra of (5) and (6) showed large couplings in the heterocyclic ring, which defines the 2,3-*trans*-3,4-*trans*-stereochemistry; the sharp two-proton singlet, δ 7.33 (acetate derivative) arises from the 2′- and 6′-protons, and thus defines the ring B oxidation pattern.

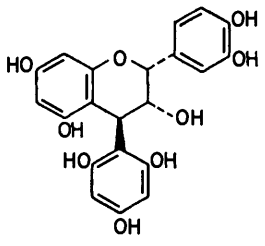


	R^1	R^2
(4)	H	H
(5)	Ac	Ac
(6)	Me	H

The *Coronilla varia* polymer yielded the (−)-epigallocatechin–phloroglucinol adduct (7) which was accompanied by the (−)-epicatechin–phloroglucinol adduct (9), previously synthesised from *Butea frondosa* gum.[5] The structure of (7) was established by the close correspondence of the ^{1}H n.m.r. spectrum of its nona-acetate (8) with that of the octa-acetate derived from (9).[5]



	R^1	R^2
(7)	H	H
(8)	Ac	Ac



(9)

The $[\alpha]_D$ values for (5), (6), and (8) corresponded both in sign and in relative magnitude to those for the corresponding procyanidin structures,[5] thereby establishing that the prodelphinidin adducts possess the same absolute configuration.

The lower molecular weight flavonoids of the *Ribes sanguineum* leaves extract were separated from the polymer by ethyl acetate extraction. Two-dimensional paper chromatography revealed that this extract contained at least eight flavonoids and flavonoid glycosides, in addition to eight components reactive to vanillin

[10] D. G. Roux, *Nature*, 1957, **179**, 158.
[11] M. Tsujimura, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1929, **10**, 253.
[12] K. Weinges, W. Bahr, W. Ebert, K. Goritz, and H.-D. Marx, *Fortschr. Chem. org. Naturstoffe*, 1969, **27**, 158.
[13] E. Haslam in ' The Flavonoids,' eds. T. J. Mabry, H. Mabry, and J. B. Harborne, Chapman and Hall, London, 1975, p. 505.
[14] D. Jacques, C. T. Opie, L. J. Porter, and E. Haslam, *J.C.S. Perkin I*, 1977, 1637.
[15] W. T. Jones, R. B. Broadhurst, and J. W. Lyttleton, *Phytochemistry*, 1976, **15**, 1407.

(flavans; see Table 1). The flavans included a major component, number 5, with a mobility characteristic of a proanthocyanidin dimer.[5]

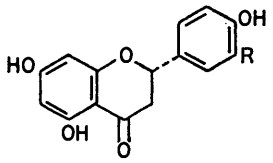
TABLE 1

Paper-chromatographic R_F values of the major flavans of *Ribes sanguineum* leaves

Component no.	R_F *a*	R_F *b*	Structure
1 [c]	0.59	0.52	Epicatechin [d]
2	0.45	0.43	Gallocatechin
3 [c]	0.37	0.45	Epigallocatechin
4	0.29	0.58	
5 [c]	0.27	0.34	Prodelphinidin B-4
6	0.19	0.48	
7	0.10	0.31	
8 [c]	0.09	0.45	

[a] t-Butyl alcohol–acetic acid–water (3 : 1 : 1 v/v). [b] 15% Acetic acid. [c] Major components. [d] On the basis of R_F data alone.

The ethyl acetate soluble fraction was separated into a number of fractions containing monomeric flavanoids, and finally an homogeneous sample of the major prodelphinidin (Table 1, number 5). The earlier fractions containing mixtures of lower molecular weight flavonoids were acetylated and separated by preparative t.l.c. This yielded the acetates of the major flavan-3-ol, (−)-epigallocatechin (2), and a small amount of (+)-gallocatechin (1). Other flavonoids isolated were the

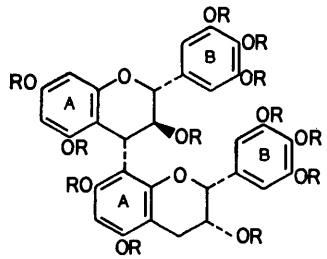


(10) R = H
(11) R = OH

acetates of naringenin (10), eriodictyol (11), and two unidentified flavonoid acetates.

The major prodelphinidin was treated with phenylmethanethiol and acetic acid in ethanol.[2] Paper chromatography revealed that it was rapidly cleaved to yield epigallocatechin plus a more mobile flavan. Treatment of the prodelphinidin with diazomethane yielded a decamethyl ether, $M^{+\cdot}$ 750, confirming its molecular constitution. The major prodelphinidin also yielded a dodeca-acetate (12). The ^{1}H n.m.r. spectrum of this derivative established the 2,3-*trans*-3,4-*trans*-stereochemistry of the upper flavan unit ($J_{2,3}$ 9.6, $J_{3,4}$ 10.0 Hz). The 2,3-*cis*-stereochemistry of the lower flavan unit was established by the existence of distinct signals for H-2 and H-3 and the rather narrow envelope of signals for the C-4 methylene protons. This is in contrast to the presence of a lower flavan unit with 2,3-*trans*-stereochemistry, where the H-2 and H-3 signals are coincident and those of H-4 are very broad. The presence of trihydroxylated B-rings was confirmed by the presence of two sharp, approximately two-proton singlets at δ 6.87 and 7.00, corresponding to the major rotational isomer, and a minor pair at δ 7.31 and 7.33.

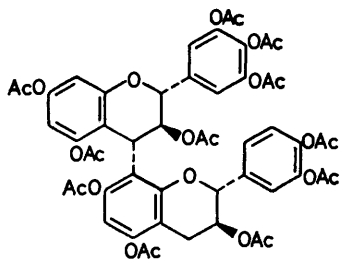
The structure of the major prodelphinidin acetate therefore corresponds to (12) and by analogy with the procyanidins this prodelphinidin may be referred to as B-4 (13). The ^{1}H n.m.r. spectrum of (12) is in fact very similar to the published [1] spectrum of procyanidin B-4 deca-acetate apart from differences in the aromatic region.



(12) R = Ac
(13) R = H

The occurrence of a dominant proanthocyanidin with opposite stereochemistry for the upper and lower flavan units parallels procyanidin synthesis in *Rubus* species, where procyanidin B-4 dominates and is accompanied by (−)-epicatechin (2).[2,5] Similarly *Ribes sanguineum* contains an almost homogeneous prodelphinidin polymer containing gallocatechin units, and prodelphinidin B-4 (13) is accompanied by (−)-epigallocatechin (2) as the dominant monomeric flavan-3-ol. This implies that prodelphinidin biosynthesis is probably under the same control as procyanidin biosynthesis, where a flav-3-en-3-ol has been implicated as the key biosynthetic intermediate.[14,16]

A further prodelphinidin containing a mixed ring B oxidation pattern was isolated from *Salix caprea*. The isolation of procyanidin B-6 from this source [2] resulted in a fraction being obtained where B-6 was contaminated



(14)

with two other proanthocyanidins. Acetylation yielded the acetate of B-6 plus an homogeneous sample of the acetate of the major proanthocyanidin contaminant. The mass spectrum of the acetate revealed a molecular ion at *m/e* 1 056, and this and subsequent fragmentations were consistent with a proanthocyanidin containing eleven hydroxy-groups.

This was confirmed by the analytical figures and ^{1}H

[16] E. Haslam, C. T. Opie, and L. J. Porter, *Phytochemistry*, 1977, **16**, 99.

n.m.r. spectrum, which was identical with that of procyanidin B-3 deca-acetate apart from a higher proton integration in the acetate region and a different appearance of the aromatic region, δ 6.9—7.2. The outstanding feature was a sharp, approximately two-proton singlet at δ 6.94, confirming the presence of a trihydroxylated ring B. However, two structural alternatives remained, *viz.* that the extra hydroxy-group could reside in either the upper *or* the lower flavan unit. This was resolved by the observation (see Experimental section) that the acetate functions are rapidly hydrolysed under the conditions of pigment generation from proanthocyanidins [Bu^{n}OH–5% HCl (4 : 1); 100 °C; 2 h] and the acetate derivative yields the phenolic anthocyanidin. In fact the anthocyanidin may be generated from the phenol or the acetate with equal facility. This confirmed that the *Salix caprea* proanthocyanidin was a prodelphinidin and the acetate must possess structure (14).

The occurrence of proanthocyanidins with flavan units of different ring B oxidation patterns is not novel. Apart from the considerable number of compounds isolated from *Acacia* species containing 5-deoxyflavan units, two other more pertinent examples exist. A proanthocyanidin with (−)-epiafzelechin linked through C-4 to (−)-4′-*O*-methylepigallocatechin has been isolated from *Ouratea*, *Prionostemma*, and *Maytenus* species [17] and a procyanidin with (+)-catechin linked through C-4 to (−)-epiafzelechin was isolated from the fruit of *Wistaria sinensis*.[18]

The above results almost certainly imply that in addition to the two 'normal' series of B-type procyanidins and prodelphinidins possessing homogeneous oxidation patterns in the rings B of both the upper and lower units, two further series must exist with 'crossed' oxidation patterns. These series, added to the rarer propelargonidins and the corresponding flavan-3-ols (+)-afzelechin and (−)-epiafzelechin, imply that at least 72 B-series proanthocyanidins possessing 5,7-dihydroxylated rings A exist in nature.

[17] F. Delle Monache, M. Pomponi, G. B. Marini-Bettolo, I. L. d'Albuquerque, and O. G. de Lima, *Phytochemistry*, 1976, **15**, 573.

EXPERIMENTAL

Mass spectra were measured on an A.E.I. MS30 instrument and ^{1}H n.m.r. spectra were obtained at 60 MHz with a Varian EM 360 spectrometer. Sephadex LH-20 chromatography with ethanol was carried out as described by Haslam and his co-workers.[2] Paper chromatography was carried out in 6% acetic acid (solvent A) and butan-2-ol–acetic acid–water (14 : 1 : 5 v/v) (solvent B). Anthocyanidins were generated from the proanthocyanidins as described by Bate-Smith.[19] Under the conditions of this reaction (butan-1-ol–5% HCl; 100 °C; 2 h) the anthocyanidin pigment was generated with equal facility from both proanthocyanidins *and* their acetate derivatives. The reaction was tested for several procyanidins and prodelphinidins, and their acetates.

Extraction of Prodelphinidin Polymers.—The leaves of *Ribes sanguineum* (2 200 g) were extracted in four batches with acetone–water (7 : 3 v/v) according to the method of Jones *et al.*,[15] with an additional six-fold ethyl acetate extraction after the light petroleum extraction. This procedure yielded 15 g of ethyl acetate-soluble flavonoids plus 40 g of crude freeze-dried prodelphinidin polymer. The *Coronilla varia* prodelphinidin polymer was isolated in a similar way.[15]

TABLE 2

^{1}H N.m.r. data for flavan derivatives (δ [*J*/Hz]; $SiMe_4$ internal standard; $CDCl_3$ solvent, unless otherwise specified)

Compound	Ring A H-6, H-8	Ring B H-2′, H-6′	Phloroglucinol ring-protons	2-H	3-H	4-H	2′-H	3′-H	4′-H_2	Acetates
Gallocatechin hexa-acetate	6.66, 6.70 [2.0]	7.16(s)					5.17(br s)	5.17(m)	2.8—3.0(m)	2.16, 2.26
Epigallocatechin hexa-acetate	6.56, 6.66 [2.3]	7.20(s)					5.06(s)	5.40(m)	2.8—3.0(m)	2.16, 2.26
(4) [a]	5.95(s)	6.65(s)	6.04(br s)	4.54 [b]	4.54 [b]	4.54 [b]				
(5)	6.62, 6.79 [2.2]	7.33(s)	7.02(s)	5.00(d) [10.0]	5.78(t) [9.6]	4.70(d) [9.4]				1.76, 2.00, 2.04, 2.33, 2.40
(6) [c]	6.02, 6.20 [2.2]	6.69(s)	6.18(s)	4.62(d) [9.0]	4.28(t) [9.0]	4.68(d) [9.0]				3.40br, 3.42 3.75, 3.80 3.87, 3.92 [c]
(8)	6.64, 6.78 [2.0]	7.20(s)	6.84, 7.00 [2.4]	5.48(s)	5.14(dd)	4.48(d) [2.5]				1.86, 1.93 2.04, 2.17 2.27, 2.34
(9), acetate	6.60, 6.77 [2.4]	7.22, 7.33	6.84, 6.93 [2.5]	5.47(s)	5.16(dd)	4.48(d) [2.4]				1.87, 1.92, 2.04, 2.18, 2.30, 2.34
Prodelphinidin B-4 acetate (12) [d]	6.59, 6.77 AB quartet	6.87(s), 7.00(s) 7.31(s), 7.33(s)	6.67(s) *[e]	4.90(d) [9.6]	5.79(t) [9.6]	4.63(d) [10.0]	5.10(s)	5.31(m)	2.8—3.9	1.7—2.3
Salix prodelphinidin acetate (14) [f]	6.48(br s)	6.94(s) 6.9—7.2	6.62(s) [e]	4.49(d) [9.4]	5.60(t) [9.7]	4.76 [10.0]	5.06(br s)	5.06(m)	2.4—3.0	1.68, 1.93, 1.96, 2.24, 2.25, 2.32

[a] Solvent [^{2}H$_6$] acetone. [b] Heterocyclic ring-proton chemical shifts are virtually coincident for both the procyanidin and prodelphinidin adducts; signal appears as a broad singlet. [c] A methyl ether; peaks in acetate column refers to methoxy resonances. [d] Apart from the ring B resonances, the shifts for the major rotamer only could be assigned. [e] For lower flavan unit. [f] Major rotamer only.

(2R,3S,4S)-4-(2,4,6-*Trihydroxyphenyl*)*flavan*-3,3′,4′,5,5′,-7-*hexaol*.—The *Ribes sanguineum* polymer (20.0 g) and phloroglucinol hydrate (40.0 g) were stirred in ethyl acetate–0.1M-HCl (1 : 4; 1 000 ml) at 20 °C for 16 h. The aqueous phase was extracted with ethyl acetate (6 × 150 ml) to yield 25 g of crude product. The bulk of the phloroglucinol was removed by crystallisation from ethanol, and the remaining ethanol solution was chromatographed on Sephadex LH-20 (5 × 40 cm) in ethanol.[2] The eluate was collected as 15 ml fractions and these were combined to yield the crude adduct. Rechromatography in the same system on a smaller column yielded a chromatographically homogeneous sample of the *product* as a light tan powder (1.1 g), R_F(A) 0.40, R_F(B) 0.39. Reaction with butan-1-ol–HCl yielded delphinidin chloride and phloroglucinol.

Acetylation of the phenol (acetic anhydride–pyridine) and purification by preparative t.l.c. [silica; benzene–

[18] K. Weinges, K. Goritz, and F. Nader, *Annalen*, 1968, **715**, 164.

[19] E. C. Bate-Smith, *Phytochemistry*, 1973, **12**, 907.

acetone (4 : 1 v/v)] gave a single product, R_F 0.40, and precipitation from methanol–water yielded an amorphous *nona-acetate* (Found: C, 57.9; H, 4.4. $C_{39}H_{36}O_{19}$ requires C, 57.9; H, 4.5%); $M^{+\cdot}$ 808; $[\alpha]_{589}^{25}$ − 38.3° (*c* 0.2, $CHCl_3$).

Methylation (diazomethane in ether–methanol) yielded a major methyl ether from preparative t.l.c. [silica; ethyl acetate–light petroleum (b.p. 40—60 °C) (6 : 4 v/v)], R_F 0.58, and crystallisation from methanol yielded the *octamethyl ether*, plates, m.p. 149—151 °C (Found: C, 64.4; H, 6.15. $C_{29}H_{34}O_{10}$ requires C, 64.2; H, 6.3%); *m/e* 542 $(M)^{+\cdot}$, 333, 301 (100%), 181, and 167; $[\alpha]_{589}^{25}$ − 141° (*c* 0.25, $CHCl_3$).

(2R,3R,4R)-4-(2,4,6-*Trihydroxyphenyl*)*flavan*-3,3′,4′,5,5′,7-*hexaol*.—The polymer from *Coronilla varia* (7.4 g) was treated with phloroglucinol hydrate (15 g) and the products were worked up and separated as described above. Chromatography effected satisfactory separation from the accompanying procyanidin adduct, but the *product* (0.60 g) [R_F(A) 0.39, R_F(B) 0.38] could not be separated from procyanidin oligomers. The crude phenol (0.47 g) was therefore acetylated (acetic anhydride–pyridine). Purification by preparative t.l.c. [silica; benzene–acetone (4 : 1 v/v)] gave a major product with R_F 0.49 and precipitation from methanol–water yielded the amorphous *nona-acetate* (Found: C, 57.6; H, 4.6. $C_{39}H_{36}O_{19}$ requires C, 57.9; H, 4.5%); $M^{+\cdot}$ 808; $[\alpha]_{589}^{25}$ + 83.3° (*c*. 0.2, $CHCl_3$).

(2R,3R,4R)-4-(2,4,6-*Trihydroxyphenyl*)*flavan*-3,3′,4′,5,7-*pentaol*.—The prodelphinidin adduct was accompanied by the corresponding procyanidin adduct, which was obtained as a tan solid (0.17 g), R_F(A) 0.57, R_F(B) 0.52. The phenol was acetylated to yield the octa-acetate, isolated and purified as above, R_F 0.59 [silica; benzene–acetone (4 : 1 v/v], and crystallised from methanol; m.p. 154—155 °C, (lit.,[5] 148—150 °C) (Found: C, 59.15; H, 4.7. Calc. for $C_{37}H_{34}O_{18}$: C, 59.2; H, 4.6%); $M^{+\cdot}$ 750.

Separation of Ribes *Flavanoids*.—The ethyl acetate fraction (15 g) from the prodelphinidin polymer preparation was chromatographed on Sephadex LH-20 (5 × 40 cm) and the eluate was collected as 15 ml fractions.

Prodelphinidin B-4. Fractions 275—400 yielded an almost homogeneous sample of the major prodelphinidin (0.53 g), R_F(A) 0.38, R_F(B) 0.28. Reaction with phenylmethanethiol in acetic acid and ethanol [2] yielded (−)-epigallocatechin, R_F(A) 0.29, R_F(B) 0.37, co-chromatographed with authentic material isolated from earlier fractions, plus two more mobile products, R_F(A) 0.19, R_F(B) 0.80, and R_F(A) 0.22, R_F(B) 0.86, presumably corresponding to the benzylthio-derivatives of the gallocatechin carbocation.[2]

A homogeneous sample of the *dodeca-acetate* was obtained by reaction of the prodelphinidin with acetic anhydride–pyridine to yield a major product, R_F 0.25 [silica; benzene–acetone (4 : 1 v/v)], m.p. 154—156 °C (methanol) (Found: C, 57.9; H, 4.4. $C_{54}H_{50}O_{26}$ requires C, 58.2; H, 4.5%); $[\alpha]_{589}^{25}$ −77.0° (*c* 0.2, $CHCl_3$).

The prodelphinidin also yielded a deca-methyl ether (diazomethane in ether–methanol), *m/e* 750 $(M^{+\cdot})$, 541, 509, 331, 299, 210, and 181 (100%).

Other Flavonoids.—The remaining fractions from the chromatography of the ethyl acetate-soluble fraction all contained complex mixtures of flavonoids. The components were separated by acetylation (acetic anhydride–pyridine) of the mixtures and separation by preparative t.l.c. [silica; benzene–acetone (4 : 1 v/v)]. Major flavonoids found in each fraction were as follows.

(1) Fractions 150—275 yielded eriodictyol, a dark u.v.-absorbent spot on paper, R_F(A) 0.24, R_F(B) 0.85. The tetra-acetate had R_F 0.62, *m/e* 456 $(M^{+\cdot})$, 414, 372, 330, 288, 153, and 136. The ^{1}H n.m.r. spectrum revealed the characteristic ABX system for the heterocyclic ring protons,[20] δ($CDCl_3$) H-2 5.50, H-3*ax* 3.02, and H-3*eq* 2.79 ($J_{2,3(ax.)}$ 13.2, $J_{2,3(eq.)}$ 3.1, $J_{3(eq.),3(ax.)}$ 20.6 Hz). Eriodictyol was accompanied by a small amount of naringenin, R_F 0.70, recognised from the mass spectrum of its triacetate, *m/e* 398 (M^{+}), 356, 314, 272, 153, and 120, and its ^{1}H n.m.r. spectrum.

(2) Fractions 75—125 contained a number of flavonoid glycosides and the major flavan-3-ol component, (−)-epigallocatechin, R_F(A) 0.29, R_F(B) 0.37, isolated as its hexa-acetate, R_F 0.50; *m/e* 558 $(M^{+\cdot})$, 516, 498, 456, 432, 414, 390, 372, 348, 330, and 288; $[\alpha]_{589}^{25}$ −27.0° (*c* 0.24, $CHCl_3$); the ^{1}H n.m.r. spectrum ($CDCl_3$) was identical to that of authentic (−)-epicatechin penta-acetate apart from the appearance of H-2′ and H-6′ signals as a two-proton singlet, δ 7.22. The fractions also contained a small amount of gallocatechin, R_F(A) 0.38, R_F(B) 0.46, which yielded a hexa-acetate, R_F 0.60, with a mass spectrum identical with that of epigallocatechin hexa-acetate, and ^{1}H n.m.r. spectrum ($CDCl_3$) the same as that of authentic (+)-catechin penta-acetate apart from the H-2′ and H-6′ signals appearing as a two-proton singlet at δ 7.25.

Prodelphinidin from Salix caprea *Catkins*.—During studies on the procyanidin polymer from *Salix caprea* [5] a collection was obtained where the polymer contained significant amounts of prodelphinidin units. The ethyl acetate extract contained procyanidins B-3 and B-6 and other lower-mobility proanthocyanidins. Sephadex chromatography yielded a sample of procyanidin B-6 mixed with three other proanthocyanidins, the major component of which was a prodelphinidin, R_F(A) 0.43, R_F(B) 0.34. The mixture could not be separated by further chromatography, and was acetylated; the products were separated [preparative t.l.c. on silica in benzene–acetone (4 : 1 v/v)] to yield procyanidin B-6 hexa-acetate,[5] R_F 0.46, plus the major *prodelphinidin undeca-acetate*, R_F 0.32, as an amorphous solid purified by precipitation from methanol–water (Found: C, 58.7; H, 4.8. $C_{52}H_{48}O_{24}$ requires C, 59.1; H, 4.6%); $M^{+\cdot}$ 1 056, $[\alpha]_{589}^{20}$ − 68.8° (*c* 0.61, $CHCl_3$). Reaction with butan-1-ol–5% HCl (4 : 1 v/v) at 100 °C produced delphinidin chloride.

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