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PHENYLPROPANOID DERIVATIVES OF CATECHIN, EPICATECHIN AND PHYLLOFLAVAN FROM *PHYLLOCLADUS TRICHOMANOIDES*

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Kew Word Index—*Phyllocladus trichomanoides*; Podacarpaceae; phenylpropanoid-substituted flavan-3-ols; phylloflavan; phylloflavanine.

Abstract—Investigation of the extract of the cladodes of *Phyllocladus trichomanoides* has led to the isolation and identification of (+)-catechin, (−)-epicatechin, phylloflavan and two phenylpropanoid derivatives of epicatechin also known as cinchonains. In addition, three novel compounds identified as the phenylpropanoid derivatives of catechin and phylloflavan have also been isolated. The structures and configurations of these compounds have been established on the basis of chemical and spectroscopic evidence which also has led to a revised assignment of the configuration of the flavan unit in phylloflavan.

INTRODUCTION

In an earlier paper we reported on the structural elucidation of a new flavanoid isolated from *Phyllocladus alpinus* [1]. Since then this compound phylloflavan, so named because it is a major constituent characteristic of *Phyllocladus* species, has been shown to possess some interesting physiological properties [2] and has prompted a more detailed chemical investigation of the extractives of another related species, *Phyllocladus trichomanoides*. *P. trichomanoides* like *P. alpinus* is an evergreen tree which is endemic to New Zealand. The extractives from the cladodes of *P. trichomanoides* when examined on TLC and visualized selectively with vanillin–HCl reagent revealed not only the presence of catechin, epicatechin and phylloflavan, which are common to all *Phyllocladus* species, but also other related compounds. This paper deals with the structural elucidation of these compounds as well as reviewing the chirality of the assymetric centres of the flavan unit and the aliphatic side chain of phylloflavan.

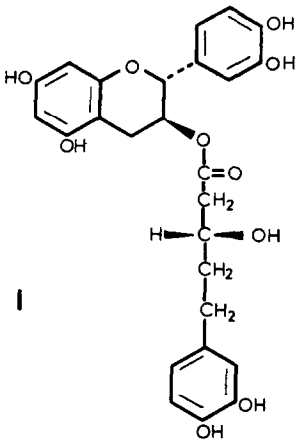
RESULTS AND DISCUSSION

Extraction of the dried twigs or cladodes of *Phyllocladus trichomanoides* with ethyl acetate yielded 11% of/extractives which by repeated chromatography on Sephadex LH-20 using ethanol and ethanol–water as solvents and on MCI-gel using methanol–water as eluant afforded (+)-catechin, (−)-epicatechin, phylloflavan (**1**), cinchonain Ib/(**2**), cinochonian Ia (**3**) and three other new phenylpropanoid-substituted flavanoids **4**, **5** and **6**.

In an earlier report [1] the flavan unit in phylloflavan was assigned the 2,3-*cis*-stereochemistry on the basis of the ^{13}C NMR chemical shift of C-2 (δ78.2), a value characteristic of flavanoids with substituents at C-2 and C-3 in the *cis*-stereochemistry [3]. Since alkaline hydrolysis of phylloflavan yielded (+)-*ent*-epicatechin and (+)-catechin, an observation consistent with epimerization [4], the flavan unit in phylloflavan was assigned the *ent*-epicatechin configuration. However, a recent report on the ^{13}C NMR chemical shifts of a 3-*O*-(1,6-dihydroxy-2-cyclohexene-1-carboxylic acid ester of (+)-catechin [5] shows that the aliphatic substituent induces a large upfield shift of the C-2 resonance of the 2,3-*trans*-flavanoid to the region where the C-2 of the 2,3-*cis*-flavanoids are normally located and hence the position of this chemical shift is no longer diagnostic of the chirality at C-2 and C-3 in 3-*O*-acylated flavans. The assignment of the 2,3-*cis*-configuration to the flavan unit in phylloflavan based on the upfield position of the C-2 chemical shift therefore is ambiguous. To resolve this question, phylloflavan has been hydrolysed without causing epimerization to the flavan unit by mild acid hydrolysis under N_2 to yield (+)-catechin clearly demonstrating that the flavan structure has the normal 2*R* 2,3-*trans*-configuration, rather than the abnormal 2*S* 2,3-*cis*-configuration, as assigned previously [1]. In addition, the magnitude of the H-2 and H-3 coupling constant (J = 5.6 Hz) is more consistent with the *trans*-stereochemistry.

The 3-*O*-substituent in phylloflavan has been determined as β-hydroxy-δ-(3,4-dihydroxyphenyl)-pentanoate, the parent acid, $[\alpha]_D$ + 13.3° (*c*0.1, MeOH) apparently derived biosynthetically from the condensation of caffeic acid and acetyl-S-CoA with subsequent reduction of the double bond. The analogous cinnamic acid condensation product, β-hydroxy-δ-phenylpentanoic acid, has been isolated from the leaves of *Populus balsamifera* [6]. The assignment of the *S* absolute stereochemistry at the chiral centre of the side chain in phylloflavan was made by comparison of its optical rotation with those of β-hydroxy-carboxylic acids of known absolute stereochemistry. These β-hydroxy acids with the *R*-configuration all have negative rotations [7–10]. The absolute configuration of phylloflavan is therefore 2*R*, 3*S*, β*S* as shown in **1**.

Compounds **2** and **3** are closely related structurally as evidenced by the similarity of their ^{13}C NMR and ^{1}H NMR chemical shifts (Table 1). The presence of an epicatechin core in both compounds is also readily apparent with chemical shifts in the region of δ79, 66 and 29 which are associated with the C-2, C-3 and C-4, respectively, of flavans with the 2,3-*cis*-stereochemistry



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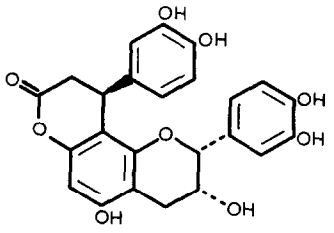

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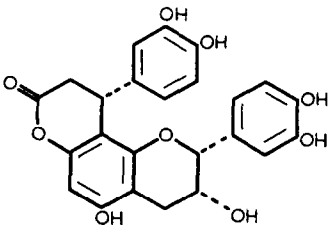

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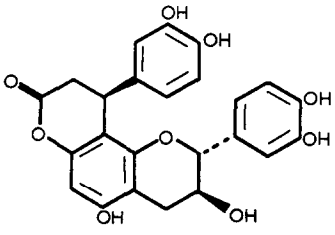

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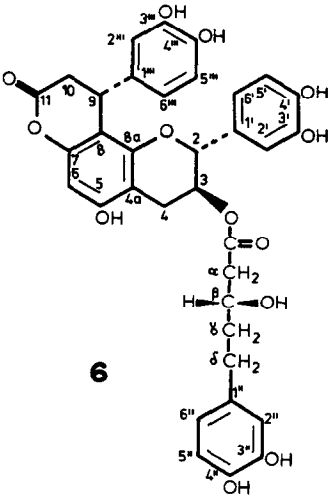

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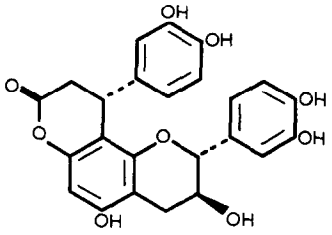

5

[3] as well as the presence of the aromatic chemical shifts identifiable with the phloroglucinol A-ring and the catechol β-ring systems. The observation of only one unsubstituted A-ring carbon at δ96.9 for **2** and 96.8 for **3** and the appearance in both instances of a signal at 106.0 indicate the epicatechin is substituted in the A-ring. In addition to the epicatechin chemical shifts, resonances attributable to a methine carbon (34.2 for **2** and 34.5 for **3**) and a methylene carbon (37.3 for **2** and 38.0 for **3**) together with another aromatic 3,4-dihydroxy substitution system are also observed. The observation of these additional resonances together with the presence of a carbonyl chemical shifts in the region of δ171 suggests a 3,4-dihydroxyphenylpropanoate unit is linked to the A-ring of the epicatechin unit. The IR spectra of both compounds show a strong band at 1747–1750 cm^{-1} which is consistent with a six-membered ring lactone with an unsaturation in the $\alpha\delta$-position [11]. These data may be compared with those of epicatechin-[7,8-bc]-4-(3,4-dihydroxyphenyl)-dihydro-2(3H)-pyranones or cinchonians [12] isolated from the bark of *Cinchona succirubra*. The chemical structures are also consistent with the mass spectrometric data. With the cinchonians, it has been established that in the NMR spectra the position of the C-4a chemical shifts is distinctive for the location of the lactone function in the A-ring, the C-8 location has the C-4a chemical shift more downfield (δ105) than the C-6 regioisomer (~ 100). In compounds **2** and **3**, the C-4a resonances are observed at δ 105.2 and 105.1, respectively, which suggest that the lactone is attached to C-8 in the A-ring in both instances. Compounds **2** and **3** are therefore diastereoisomers with differing configuration of the 3,4-dihydroxyphenyl substituent at C-9 in the lactone ring. The stereochemical assignment of the aromatic substituent at this position

Table 1. ^{1}H NMR (in Me_2CO-d_6) shifts of phylloflavan (1), phylloflananine (6) and the flavanoid-pyrones 2,3,4 and 5

	1	6	2	3	4	5
H-2	4.98 (*d*, *J* = 5.6)	5.10 (*d*, *J* = 5.7)	5.0 (*s*)	4.91 (*s*)	4.73 (*d*, *J* = 7.2)	4.62 (*d*, *J* = 7.6)
H-3	5.28 (*m*)	5.30 (*m*)	4.28 (*m*)	4.30 (*m*)	3.95 (*m*)	4.10 (*m*)
H-4	2.6–2.9 (*m*)	2.80 (*m*)	3.0 (*m*)	2.90 (*m*)	3.01 (*m*)	3.0 (*m*)
H-6	6.05 (*d*, *J* = 2.4)	6.29 (*s*)	6.25 (*s*)	6.24 (*s*)	6.23 (*s*)	6.26 (*s*)
H-8	5.93 (*d*, *J* = 2.4)	—	—	—	—	—
H-9	—	2.8–3.2 (*m*)	2.8–3.1 (*m*)	2.8–3.2 (*m*)	2.5–3.0 (*m*)	2.5–3.1 (*m*)
H-10	—	4.56 (*bd*, *J* = 6)	4.48 (*dd*, *J* = 2, 6)	4.57 (*dd*, *J* = 2, 6)	4.39 (*dd*, *J* = 2, 6)	4.50 (*m*)
H-α	2.38 (*d*, 6.4)	2.40 (*d*, 6.4)	—		—	—
H-β	3.90 (*m*)	3.87 (*m*)	—	—	—	—
H-γ	1.65 (*m*)	1.60 (*m*)	—	—	—	—
H-δ	2.50 (*m*)	2.50 (*m*)	—	—	—	—
ArH	6.4–6.9	6.5–6.9	6.5–7.1	6.4–7.1	6.4–6.8	6.4–6.9

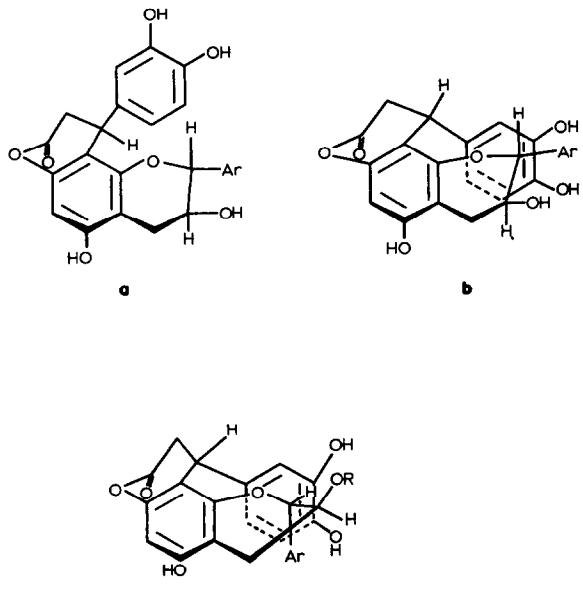

Fig. 1. Conformation of 3,4-dihydroxyphenyl ring relative to the H-2 of flavan unit.

could be established by examination of their ^{1}H NMR spectra and in particular the H-2 chemical shifts of the flavan unit (Table 1). The downfield position of the H-2 resonance (δ5.0) in compound 2 relative to the corresponding epicatechin chemical shift (δ4.88) may be explained by the diamagnetic anisotropic effect of the aromatic substituent on the lactone ring with an a β-configuration (Fig. 1a). Hence 2 is epicatechin-(7,8-bc)-4β-(3,4-dihydroxyphenyl)-dihydro-2(3 H)-pyranone or cinchonian Ia [12]. The chemical shift of H-2 (δ4.91) in 3 in contrast is more upfield and comparable to that of epicatechin indicating that the aromatic substituent in the lactone ring is remote from the H-2 or in the α-configuration as in Fig 1b, hence 3 is epicatechin-(7,8-bc)-4α-(3,4-dihydroxyphenyl)-dihydro-2(3H)-pyranone or cinchonian Ib.

The novel compounds 4 and 5 are similar and analogous to the structural relationship between 2 and 3. The cinchonian-type carbon skeleton of 4 and 5 is also readily apparent from the ^{13}C NMR chemical shifts with the presence of both the flavan and phenylpropanoid carbon chemical shifts, the major difference being the downfield shift of the C-2 resonances (δ81.6 for 4 and 81.9 for 5) observed in both compounds. The flavan unit therefore has the 2,3-*trans*-configuration [3] which is also substantiated by the large H-2, H-3 proton coupling constants (J = 7.1 Hz) [13] observed in their ^{1}H NMR spectra. The lowfield position of the C-4a chemical shifts (δ105.6) in both compounds is indicative of the lactone ring being located on the C-8 of the flavan A-ring and hence 4 and 5 are diastereomeric. The chemical constitution for both compounds is supported by their IR and mass spectra which closely resemble those of the diastereoisomeric pair 2 and 3. Electron impact mass spectral data of these compounds show no, or very weak, molecular ions, but spectral data based on desorption chemical ionization using *iso*-butane or ammonia as the reagent gas provide clear strong MH^+ or $[M+NH_4^+]$ peaks. Compound 4 is assigned the structure with the 3,4-dihydroxyphenyl substituent in the β-conformation in the lactone ring or catechin-(7,8-bc)-4β-(3,4-dihydroxyphenyl)-dihydro-

2(3H)-pyranone and **5** is the α-conformational isomer or catechin-(7,8-bc)-4β-(3,4-dihydroxyphenyl)-dihydro-2(3H)-pyranone on the basis of the relative chemical shift of the H-2 resonances with respect to the effect of the diamagnetic anisotropy of the aromatic substituent discussed earlier for the cinchonians **2** and **3**.

The assignment of the conformation of the 3,4-dihydroxyphenyl substituent on the lactone ring is also supported by CD measurements. It has been established for proanthocyanidins that the strong positive or negative couplets observed in their CD spectra are a result of the interaction of the two aryl chromophores of the upper and lower A-ring [14, 15]. The aryl substituent on the lactone ring in the pyranones is analogous to that in the proanthocyanidins in this respect as it is also positioned in a six-membered heterocyclic ring on the benzylic carbon of the A-ring. In the proanthocyanidins the sign of the large couplet at the low wavelength region in the CD spectrum is associated with the conformation of the aromatic substituent at the interflavanoid bond on the heterocyclic ring. A strong positive couplet is related to proanthocyanidins with the lower A-ring in the β-conformation (above the plane of the upper A-ring) and the negative couplet with the lower A-ring in the α-conformation [14, 15]. Examination of the CD spectra of the pyranones **2–5** shows that the sign of the couplet at 233 nm is similarly related to the conformation of the 3,4-dihydroxyphenyl substituent on the lactone ring with respect to the flavan A-ring, compounds **2** and **4** where the substituents are in the β-configuration have positive couplet and compounds **3** and **5** with the substituents in the α-configuration have negative couplet in line with an earlier observation [12].

Phylloflavanine (**6**) is a new natural product isolated in low yield (0.05%) and its structural relationship to phylloflavan (**1**) and the co-occurring pyranones is readily apparent from its ^{1}H NMR and ^{13}C NMR data (Fig. 2). The large coupling constants (J = 5.7 Hz) observed for the H-2 resonance (δ5.10) indicates that the flavan, like that in phylloflavan, has the 2,3-*trans*-configuration. The presence of the δ-(3,4-dihyroxyphenyl-β-hydroxy-pentanoate side chain at the 3-hydroxyl in addition to the lactone ring is clearly evident in the higher field region of both the ^{1}H NMR and ^{13}C NMR spectra. This chemi-

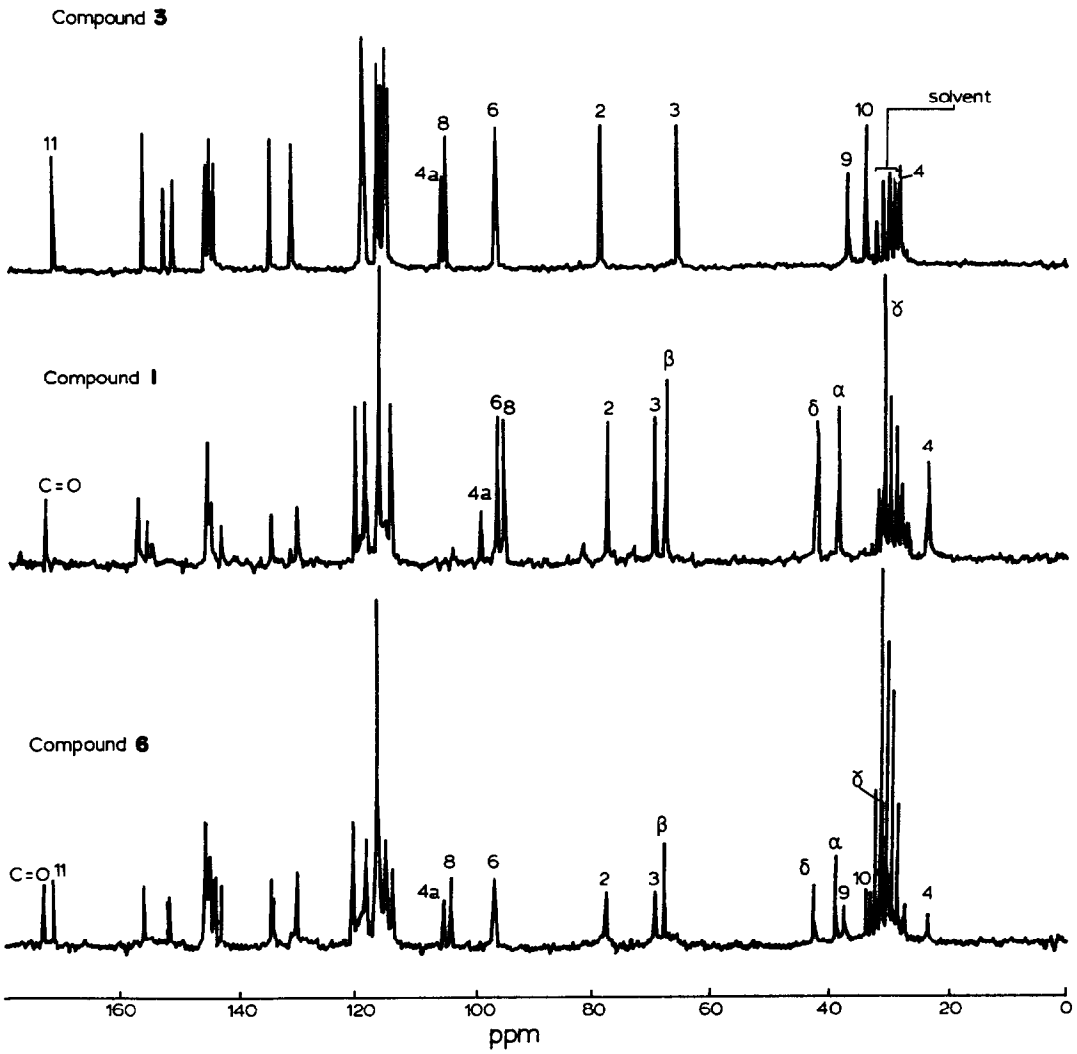

Fig. 2. ^{13}C NMR spectra of compounds **3**, **1** and **6** run in acetone-d_6–H_2O (1:1).

cal constitution ($C_{35}H_{32}O_{13}$) is fully supported by both positive and negative ion FAB mass spectrometry which show strong molecular ions at 661 $(MH)^+$ and 659 $(M-H)^-$, respectively. The downfield positions of the chemical shifts of the C-4a (δ104.5) and the substituted C-8 (105.5), in conjunction with the corresponding normal chemical shift position of the unsubstituted C-6 (96.9) of the A-ring, observed in the ^{13}C NMR spectrum of the compound indicate that the lactone ring is linked to the C-8 position of the flavan A-ring. The 2D ^1H NMR (HOMCOR) spectrum of the compound is fully consistent with the structure and in addition the downfield position of the H-2 resonance (δ5.10) of the flavan moiety relative to the corresponding H-2 of phylloflavan (δ4.98) suggests the proton is influenced by the diamagnetic anisotropy of the 3,4-dihydroxyphenyl group on the lactone ring. The CD spectrum of phylloflavanine shows a strong negative couplet at 233 nm and indicates the 3,4-dihydroxyphenyl on the lactone ring to be in the α-conformation, in apparent contradiction to the ^1H NMR data if the downfield shift of the H-2 is associated with the β-conformation as in compounds **2** and **4**. Studies based on Dreiding models show there is considerable steric interaction between the two bulky di-equatorial substituents at C-2 and C-3 of the flavan with the 2,3-*trans*-configuration and such steric hindrance could be alleviated by simple inversion to the *trans*-di-axial conformation. Indeed Sliwa and co-workers [16, 17] have demonstrated that the β-ring axial conformation is preferred when the flavan possessed a bulky substituent at C-3. Support for this preferred di-axial-conformation, in both phylloflavan (**1**) and phylloflavanine (**6**) is the observed smaller H-2, H-3 coupling constants (J = 5.6 5.7 Hz) for both compounds compared to > 7 Hz for the pyranones **4** and **5** and about 8 Hz for catechin and its methylethers [13]. The smaller coupling constants are consistent with a significant contribution of the *trans*-di-axial-conformation of the bulky C-2 and C-3 substituents [18]. The cause for the observed downfield shift of the H-2 resonance in phylloflavanine compared to phylloflavan becomes more evident because with this aryl substituent at C-2 in the axial conformation, the equatorially orientated proton comes under the influence of the diamagnetic aniosotropy of the α-orientated 3,4-dihydroxyphenyl substituent on the lactone ring (Fig. 1c).

The revised absolute stereochemistry at C-2 of phylloflavan suggests that there is a close biosynthetic relationship of this secondary metabolite to the co-occurring catechin, in contrast to an earlier suggestion [1]. In *Phyllocladus trichomanoides*, elaboration to the flavan-3-ols and phylloflavan structures is observed by further enzymic condensation and cyclization with caffeic acid to produce the 3-hydroxyflavan-[7,8-bc]-4-(3,4-dihydroxyphenyl)-2(3H)-pyranones **2**–**5** and phylloflavanine, respectively. Compounds **1** and **5** are likely intermediates or precursors of phylloflavanine but the observation that the arylpentanoate derivatives are identified with flavan units with the 2,3-*trans*-configuration only, in spite of the fact that the 2,3-*cis*-isomers are more abundant in the cladodes of *P. trichomanoides*, suggests that there is strict enzymic control in the esterification of the C-3 hydroxy group.

EXPERIMENTAL

Optical rotations were measured in Me_2CO and CD spectra were recorded in MeOH. IR spectra were obtained with KBr pellets. ^{13}C NMR and ^1H NMR spectra were performed on Varian FT-80A and XL 200 instruments, respectively. TLC was on Schleicher and Schull cellulose plates using AcOH–H_2O (6:94) as the developing solvent. A voucher specimen of *P. trichomanoides* was lodged in the herbarium, Botany Division, Christchurch, New Zealand (CHR 388244).

Extraction and Isolation. Freeze-dried cladodes or twigs of *Phyllocladus trichomanoides* (500 g) were finely milled and left to soak in Me_2CO–H_2O (1:1) overnight (2 × 1 l). The combined extracts were concentrated to half vol. under red. pres. and to this residue was added an equal vol. of H_2O. The resulting aq. suspension was extracted with EtOAc (4 × 350 ml) and the combined extracts dried over dry Na_2SO_4 and concentrated to yield a solid residue (54 g). The residue was first subjected to CC using Sephadex LH20 with EtOH as eluent to yield a vanillin reactive fraction (27 g) which was again rechromatographed on the same system but with the solvent EtOH–H_2O (15:85) to yield (−)-epicatechin (3.20 g), (+)-catechin (500 mg) and a fraction containing a mixture of flavanoid compounds. Chromatography of this flavanoid fraction on MCl-gel (MeOH–H_2O, 3:7 → 1:1) gave compounds **1**, **2**, **6** and an unresolved fraction. The latter sample was finally fractionated by treatment of the mixture on Sephadex LH20 employing EtOH–H_2O (15:85) to yield compounds **3**, **4** and **5**.

Phylloflavan (**1**) Freeze-dried to yield 1.85 g, $[\alpha]^{578}$–7° (MeOH; *c* 0.04); +5° (Me_2CO, *c* 0.13); R_f 0.20. ^{13}C NMR (Me_2CO-d_6–H_2O): δ23.9 (C4), 31.2 (C-γ), 39.2 (C-α), 42.7 (C-δ), 67.7 (C-β), 69.8 (C-3), 78.2 (C-2), 95.2 (C-8), 96.5 (C-6), 98.6 (C-4a), 114.4, 115.2, 115.6, 115.9, 118.7, 120.1 (unsubstituted catechol ring C), 130.7 (C-1′), 134.7 (C-1″), 143.4, 144.8, 145.3, (oxygenated catechol ring C), 155.7, 156.7, 157.5 (C-5, C-7, C-8a) and 171.3 (C=O). IR ν_{max}^{KBr} cm^{-1}: 820, 1105, 1140, 1285, 144.5, 1515, 1610, 1710, 3200–3500. Negative ion FAB mass spectrum: *m/z* 497 $[M-H]^-$. Compound identical in every respect to that isolated from *P. alpinus* [1]. Hydrolysis of **1** with 2 N HCl at room temp. under N_2 for 24 hr, the mixture neutralized with NaOAc and the product examined by TLC showed that only catechin was produced.

epi*Catechin*-(7,8-*bc*)-4β-(3,4-*dihydroxyphenyl*)-*dihydro*-2(3*H*)-*pyranone* (**2**). Freeze-dried solid, (500 mg), $[\alpha]^{578}$ + 16° (Me_2CO, 0.13; lit. [12] + 12°), R_f 0.20. ^{13}C NMR (Me_2CO-d_6–H_2O): δ28.7 (C-4), 34.2 (C-9), 37.3 (C-10), 66.3 (C-3), 79.2 (C-2), 96.9 (C-6), 105.2 (C-8), 106.0 (C-4a), 115.1, 115.5, 116.4, 117.0, 119.2 (unsubstituted catechol ring C), 131.4 (C-1′) 135.0 (C-1″), 114.4, 114.9, 145.1, 145.6 (oxygenated catechol ring C), 151.2, 152.7 and 156.1 (C-5, C-7, C-8a) and 171.2 (C=0). IR ν_{max}^{KBr} cm^{-1}: 773, 790, 820, 1070, 1115, 1165, 1200, 1290, 1340, 1360, 1450, 1525, 1620, 1747, 3180–3560. MS *m/z* (rel. int.): 434 $[M-H_2O]^+$ (3), 324 (35), 288 (5), 272 (7), 191 (12), 178 (9), 150 (10), 123 (14), 110 (100), CD (MeOH, *c* 3 × 10^{-3}) $\Delta\varepsilon$ + 10.9, λ/mn 233).

epi*Catechin*-(7,8-*bc*)-4α-(3,4-*dihydroxyphenyl*)-*dihydro*-2(3*H*)-*pyranone* (**3**). Obtained as freeze-dried solid (200 mg), R_f 0.52, $[\alpha]^{578}$–192° (Me_2CO, *c* 0.14; lit. [12]–214°). ^{13}C NMR (Me_2CO-d_6–H_2O): δ29.1 (C-4), 34.5 (C-9), 38.0 (C-10), 66.2 (C-3), 79.0 (C-2), 96.8 (C-6), 105.1 (C-8), 106.0 (C-4a), 115.0, 115.3, 116.6, 116.9, 119.1 × 2 (unsubstituted catechol ring C), 131.7 (C-1′), 135.2 (C-1″), 144.4, 144.9, 145.2, 145.7 (oxygenated catechol ring C) 151.4, 152.8, 156.3 (C-5, C-7, C-8a), 171.5 (C=O). IR ν_{max}^{KBr} cm^{-1}: 820, 990, 1070, 1118, 1168, 1200, 1288, 1340, 1360, 1454, 1530, 1623, 1750, 3200–3700. MS *m/z* (rel. int.): 434 $[M-H_2O]^+$ (3), 324 (35), 288 (5), 272 (7), 229 (4), 191 (12), 150 (10), 123 (14), 110 (100). CD (MeOH, *c* 4 × 10^{-4}), $\Delta\varepsilon$ – 37.0 (λ/nm 233).

Catechin-(7,8-*bc*)-4β-(3,4-*dihydroxyphenyl*)-*dihydro*-2(3*H*)-*pyranone* (**4**). Freeze-dried solid (140 mg), R_f 0.35, $[\alpha]^{578}$ + 6.5° (MeOH, *c* 0.15). ^{13}C NMR (Me_2CO-d_6–H_2O): δ27.2 (C-4), 34.4 (C-9), 37.8 (C-10), 67.4 (C-3), 81.6 (C-2), 96.6 (C-6), 105.6 (C-4a),

105.6 (C-8), 115.0, 115.4, 116.4, 116.7, 119.4, 119.4 (unsubstituted catechol ring C), 131.4 (C-1'), 135.0 (C-1''), 144.5, 145.3, 145.3, 145.7 (oxygenated catechol ring C), 151.4, 152.2, 155.9 (C-5, C-7, C-8a), 171.0 (C=O). IR ν_{max}^{KBr} cm^{-1}: 820, 999, 1066, 1117, 1170, 1200, 1287, 1340, 1452, 1527, 1623, 1748, 3200–3550. MS *m/z* (rel. int.): 452 $[M]^+$ (0.5), 434 $[M-H_2O]^+$ (0.6), 288 (2), 272 (1), 191 (4), 178 (3), 152 (5), 150 (3), 123 (24), 110 (100). CD (MeOH, *c* 3 $\times 10^{-3}$) $\Delta\varepsilon + 69$ (λ/nm 233), $\Delta\varepsilon + 4$ (λ/nm 253).

Catechin-(7,8-bc)-4α-(3,4-dihydroxyphenyl)-dihydro-2(3H)-pyranone (**5**). Freeze-dried solid (80 mg), R_f 0.50, $[\alpha]^{578} - 107°$ (Me_2CO, *c*0.10). ^{13}C NMR (Me_2CO-d_6–H_2O): δ28.2 (C-4), 34.0 (C-9), 37.7 (C-10), 67.6 (C-3), 81.9 (C-2), 96.4 (C-6), 105.7 (C-8), 106.0 (C-4a), 115.2, 115.4, 116.6, 116.6, 118.9, 119.9 (unsubstituted catechol ring C), 131.4 (C-1'), 134.5 (C-1''), 144.4, 145.5, 145.5, 145.7 (oxygenated catechol ring C), 151.4, 152.5, 155.9 (C-5, C-7, C-8a), 171.1 (C=O). IR λ_{max}^{KBr} cm^{-1}: 820, 1000, 1062, 1117, 1170, 1200, 1215, 1237, 1340, 1450, 1538, 1620, 1750, 3200–3550. MS *m/z* (rel. int.): 434 $[M-H_2O]^+$ (2), 324 (10), 288 (3), 272 (5), 191 (9), 178 (7), 123 (11), 110 (100), CD (MeOH, *c* 1.4 $\times 10^{-3}$) $\Delta\varepsilon$ 19.0 (λ/nm 233).

Phylloflavanine (**6**). Freeze-dried powder (30 mg), R_f 0.17, $[\alpha]^{578} - 100°$ (MeOH, *c*0.06). ^{13}C NMR (Me_2CO-d_6–H_2O): δ23.8 (C-4), 31.1 (C-γ), 33.9 (C-9), 37.7 (C-10), 39.1 (C-α), 42.9 (C-δ), 68.2 (C-β), 69.8 (C-3), 78.0 (C-2), 96.9 (C-6), 104.5 (C-8), 105.5 (C-4a), 114.3–120 (unsubstituted catechol ring C), 130.4 (C-1'), 134.4, 134.9 (C-1'', C-1'''), 143.3–145.7 (oxygenated catechol/ring C), 151.7, 151.8, 156.0 (C-5, C-7, C-8a), 171.0, 172.6 (C=O). IR ν_{max}^{KBr} cm^{-1}: 820, 1070, 1118, 1165, 1200, 1290, 1450, 1525, 1620, 1725–1745, 3200–3530. FAB-MS *m/z* 661 $[MH]^+$, CD (MeOH, *c*1.56 $\times 10^{-3}$), $\Delta\varepsilon$ 11.9 (λ/nm 233).

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