Proanthocyanidins from Stem Bark of Pavetta owariensis, 3. Nmr Study of Acetylated Trimeric Proanthocyanidins Possessing a Doubly-Linked Structure

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PROANTHOCYANIDINS FROM STEM BARK OF *PAVETTA OWARIENSIS*, 3.[1] NMR STUDY OF ACETYLATED TRIMERIC PROANTHOCYANIDINS POSSESSING A DOUBLY-LINKED STRUCTURE[2]

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ABSTRACT.—The ^{1}H- and ^{13}C-nmr chemical shifts of the acetylated trimeric proanthocyanidins of *Pavetta owariensis*, possessing a doubly-linked structure, have been assigned by 2D and proton decoupling nmr experiments. Pavetannin B4, a new trimer, has been identified as epicatechin-(4β→6, 2β→*O*→7)-*ent*-epicatechin-(4β→8)-epicatechin [**5**] by spectroscopic analysis of its acetate.

Proanthocyanidins have been studied extensively because of their important biological activities and their interesting chemical structures. The variety of biological activities (including antitumor, antiviral, antioxidative, molluscicidal, and anthelmintic properties) is related to their ability to form complexes with proteins, which is largely dependent on the actual structure of the proanthocyanidin (1–9). During the past few years, modern spectroscopic techniques, including fabms and nmr spectroscopy, have played a major role in the structural elucidation of these complex molecules. ^{13}C-nmr spectroscopy has proven to be the most generally useful technique for the study of the free phenolic proanthocyanidins, whereas the application of ^{1}H-nmr spectroscopy requires suitable derivatization to, e.g., methyl ethers, methyl ether acetates, or full acetates. However, the signal multiplicity associated with rotational isomerism complicates the interpretation of both ^{1}H- and ^{13}C-nmr spectra of these derivatives at ambient temperature.

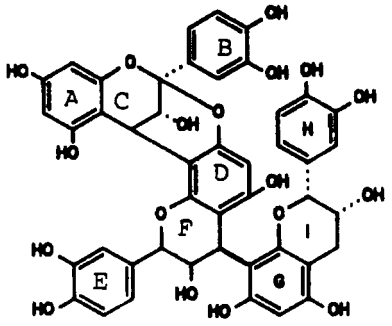
In previous papers, we have reported the isolation, from stem bark of *Pavetta owariensis* P. Beauv. (Rubiaceae), and the characterization of a series of dimeric and trimeric proanthocyanidins possessing a doubly-linked structure (10,11).

This communication presents the ^{1}H- and ^{13}C-nmr assignments of the acetates of cinnamtannin B1 [**1**], pavetannin B1 [**2**], pavetannin B3 [**3**], pavetannin B5 [**4**], all isolated and identified before (11), and a new trimeric proanthocyanidin, pavetannin B4 [**5**].

Reexamination of the ^{13}C-nmr spectral data of these trimeric compounds indicated that all compounds had a C-4 terminal flavanyl substituent in a quasi-equatorial position, as concluded from the absence of the diagnostic γ-effect [i.e., the chemical shift of C-2 of the middle unit was almost identical to that of the parent flavan-3-ol derivatives (12)]. The relative 3,4-*cis* configuration (F ring) of **1** and **2** was indicated by the fact that

[1]For Part 2 see Baldé *et al.* (11).

[2]Dedicated to the memory of our colleague Staf Van Driessen.



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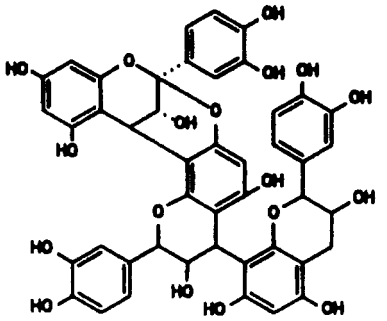

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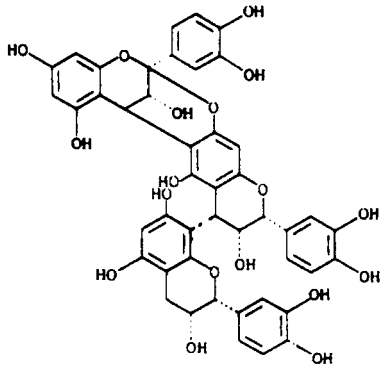

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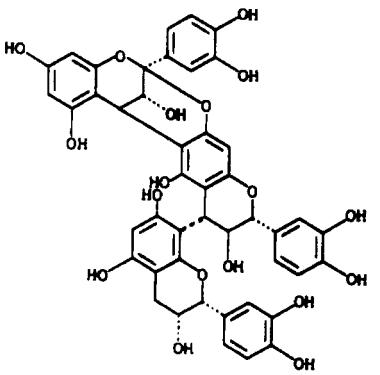

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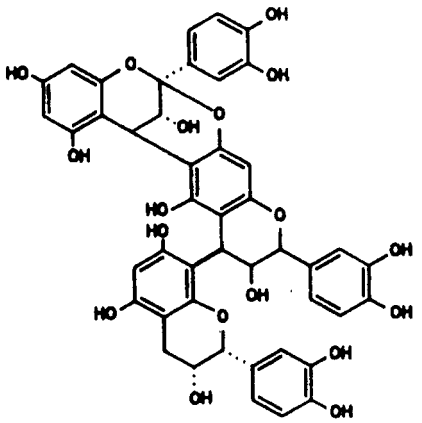

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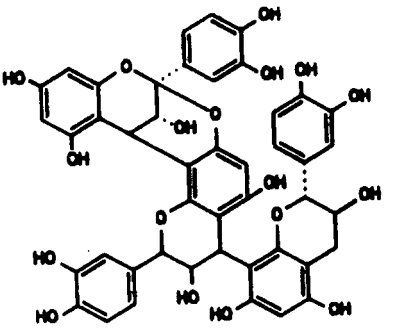

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the heterocyclic proton coupling constants ($J_{3,4}$=4.0 Hz) (13), were not observable in the ^{1}H-nmr spectra of the free phenols. Owing to the fact that the sign of the Cotton effect(s) of triflavanoids, contributed by the aryl chromophores at C-4, is (are) often dominated by the interaction between the upper and middle units, the cd features do not necessarily permit unambiguous conclusions regarding the stereochemical orientation (α or β) of the C-4 flavanyl substituent at both interflavanoid linkages. On this basis, the structures of cinnamtannin B1 [**1**], pavetannin B3 [**3**], pavetannin B5 [**4**], and pavetannin B6 [**6**] (11) had to be revised as shown in this paper.

In addition, with regard to the graphical representation of oligomeric proanthocyanidins, the α or β denomination of the stereochemistry at C-4 must always

be related to the normal, conventional orientation of the parent molecule. It must be retained, even if for graphical reasons this parent unit would be rotated and represented in a non-conventional orientation (IUPAC rule F-6.2). Overlooking this rule has caused a lot of confusion and errors throughout the existing literature (14). It appears, therefore, appropriate to recapitulate some of the A-type proanthocyanidins isolated and identified from *P. owariensis* as follows: pavetannin A1 (10) is *ent*-epicatechin-(4α↦8, 2α↦*O*↦7)-*ent*-catechin, pavetannin A2 (11) is *ent*-epicatechin-(4α↦8, 2α↦*O*↦7)-catechin, cinnamtannin B1 [**1**] is epicatechin-(4β↦8, 2β↦*O*↦7)-epicatechin-(4α↦8)-epicatechin, pavetannin B1 [**2**] is epicatechin-(4β↦8, 2β↦*O*↦7)-epicatechin-(4α↦8)-*ent*-epicatechin, pavetannin B3 [**3**] is epicatechin-(4β↦6, 2β↦*O*↦7)-epicatechin-(4α↦8)-epicatechin, pavetannin B5 [**4**] is epicatechin-(4β↦6, 2β↦*O*↦7)-catechin-(4α↦8)-epicatechin, and pavetannin B6 [**6**] is epicatechin-(4β↦8, 2β↦*O*↦7)-epicatechin-(4α↦8)-catechin.

RESULTS AND DISCUSSION

Acetylation of cinnamtannin B1 [**1**] and pavetannin B1 [**2**] with Ac_2O/pyridine at room temperature followed by cc and preparative tlc on Si gel yielded the peracetates. In the ir spectra, the complete acetylation was reflected by the absence of an OH absorption in the region 3100–3700 cm^{-1} and the presence of an intense band at 1771 cm^{-1} (C=O). Fabms at medium resolution (2500) showed the $[M+Na]^+$ ion at *m/z* 1475 and the $[M+H]^+$ ion at *m/z* 1453. Other prominent ions were observed at *m/z* 1411, 1393, 1351, 1333, 1309, 1307, and 1291, due to losses of $CH_2=C=O$, HOAc, and CO_2 fragments. The lower mass region showed abundant ions at *m/z* 497, 455, 413, 371, 329, and 287, which are diagnostic for the "upper" doubly-linked flavan unit. The ion at *m/z* 497 can be explained by cleavage of the C-C and C-O bonds with loss of an H atom, probably H-3, whereas the remaining fragments are due to further fragmentation of the parent ion at *m/z* 497, following successive elimination of ketene fragments.

The 199 MHz ^{1}H-nmr spectra of peracetylated **1** and **2** at ambient temperature, plagued by the adverse effects of dynamic rotational isomerism, were almost identical. Similarly, their 50.10 MHz ^{13}C-nmr spectra revealed a close structural relationship, while conformational isomerism again caused a doubling of many of the ^{13}C nmr signals. Unambiguous assignments of ^{1}H and ^{13}C resonances have been achieved by 2D nmr techniques, including homo-(COSY) and heteronuclear (HETCOR) shift correlation experiments, and spin-echo Fourier transform (SEFT) experiments. Owing to the close structural resemblance of peracetylated **1** and **2**, detailed structural analysis is presented for the acetate of **2**.

In the 2D ^{1}H-detected ^{1}H-^{13}C heteronuclear one-bond correlation experiment (HETCOR) of acetylated **2**, the C-4 signals at δ 26.17 and 26.31 (I ring), δ 27.41, 27.41, 33.44, and 33.64 (C and F rings) showed a correlation with H-4 signals at δ 2.90 and 3.00 (I ring), 4.31 (2H, C and/or F rings), and 4.62 (2H, C and/or F rings), respectively. The C-2 methine signals (F and I rings) at δ 75.36, 75.53, 76.62, and 76.72 were correlated with the H-2 signals at δ 5.71, 5.42, 5.20, and 4.79, respectively, while the C-3 signals at δ 66.37, 66.37, 66.72, 67.92, 69.79, and 70.48 were correlated with the H-3 signals at δ 5.53, 5.20, 4.99, 5.00, 5.20, and 5.37, respectively. Differentiation of rotameric signals was effected by ^{1}H-^{1}H and long-range ^{1}H detected ^{1}H-^{13}C correlation spectra.

The ^{1}H-^{1}H COSY spectrum, recorded at 600 MHz, clearly defined the signals of the I ring protons H-4 (δ 2.90 and 3.00) and H-3 (δ 5.53 and 5.20) of the two predominant conformational isomers. Unambiguous assignment of the duplicated H-2 (I) signals was permitted only for the resonance at δ 5.20 through its correlation with H-3 (I, δ 5.53), the second H-2 (I) rotameric signal occurring either at δ 5.42 or 4.79 (Figure 1).

However, the long-range HETCOR spectrum (Figure 2) showed well resolved C-3 signals at δ 66.37, 66.37 (I-ring), δ 66.72 and 67.92 (C-ring), and δ 69.79 and 70.48 (F-ring), facilitating the unambiguous location of both H-2 (I) signals. A connectivity between the C-3 (I) resonance and the H-2 (I) signals at δ 5.20 and 4.79 was indicated by the corresponding two-bond correlations. This assignment was also supported by the one-bond heteronuclear correlation between C-2 (I) at δ 76.72 and both rotameric H-2 (I) signals. The duplicated resonances of C-2 (F and C) were assigned at δ 75.36, 75.53 and δ 97.82 and 98.28, respectively, based on their long range correlation with H-4 at δ 4.30, 4.63 (F) and 4.31, 4.62 (C). Absence of any one-bond correlation with H-2 signals provided further evidence for the chemical shifts of the C-2 ketal carbons (C ring) of both rotamers. Subsequently the two sets of heterocyclic ^{1}H and ^{13}C signals were not only unambiguously distinguished from each other but were also correlated in the above 2D *nmr* experiments.

In the high field aromatic region (phloroglucinol moiety), the signals of H-6 and H-8 (A ring) showed direct correlation with the ^{13}C resonances at δ 109.73 and 109.80 [C-

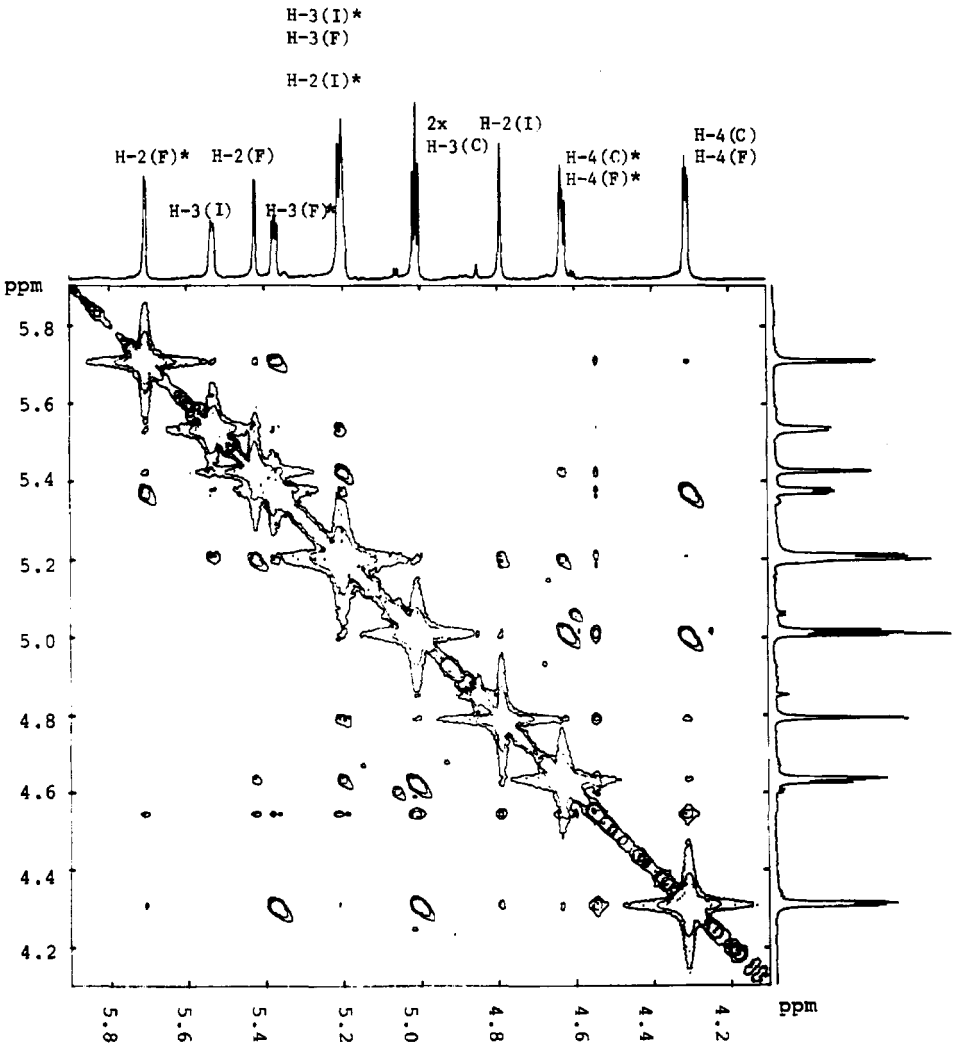

FIGURE 1. $^{1}H,^{1}H$-COSY spectrum of acetylated **2** (heterocyclic part). *Indicates rotameric signals.

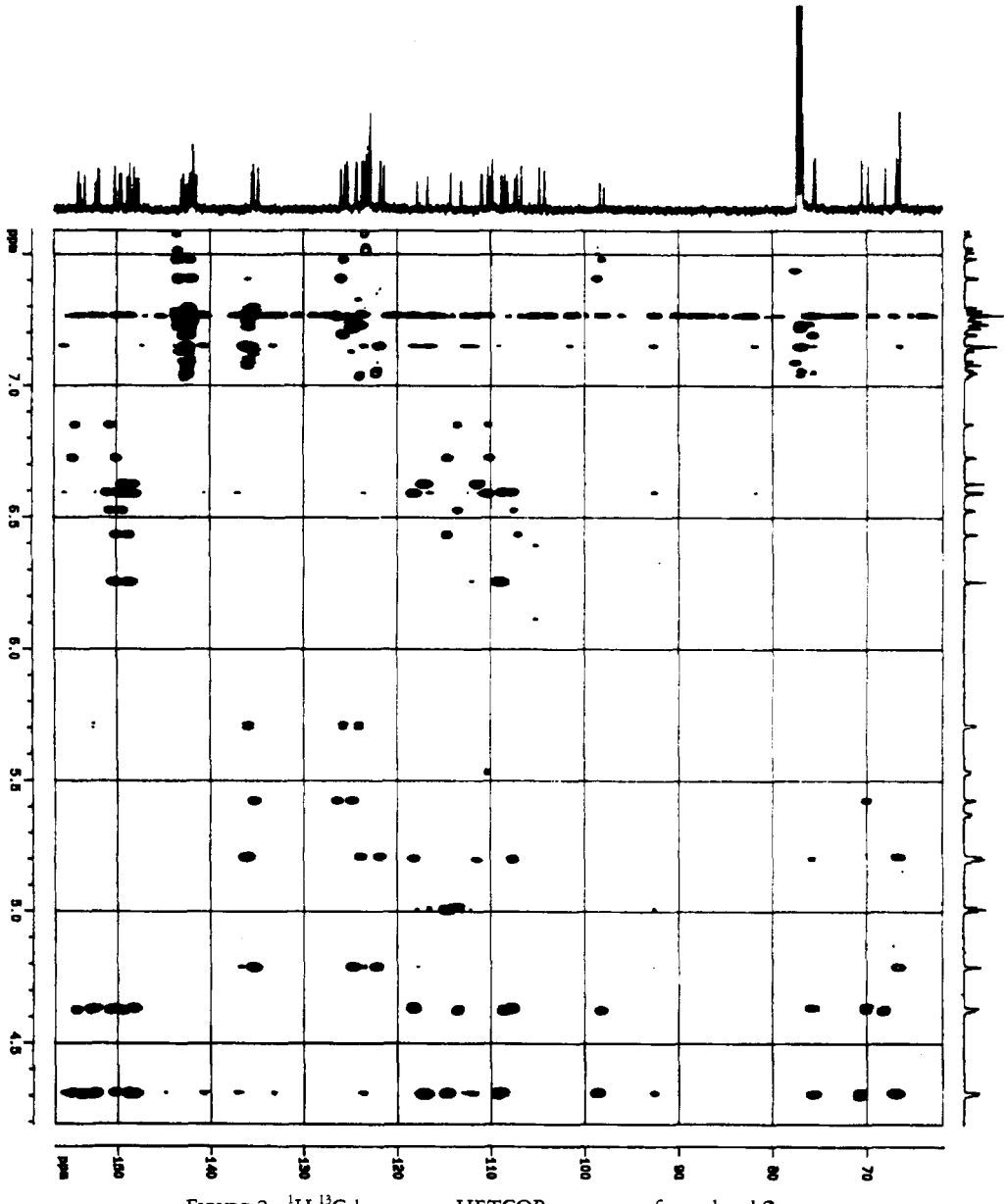

FIGURE 2. $^{1}H,^{13}C$-long range HETCOR spectrum of acetylated **2**.

6(A)], 106.69 and 107.14 [C-8(A)]. This was confirmed by the long-range correlation for H-6/C-8 (A) and H-8/C-6 (A). In addition these aromatic protons showed cross peaks with the carbon signals at δ 113.09 and 114.21 in the ^{1}H-^{13}C long-range HETCOR spectrum, which were thus assigned to C-4a(A) in the predominating rotameric forms. Independent support for the assignment of C-4a(A) was evident from the correlation with H-3 (C). Similarly, the ^{13}C resonances at δ 116.69 and 117.79 were assigned to C-4a(D), based on their two- and three-bond correlation with the signals attributed to H-3 and H-4(F), respectively. On the other hand, the C-4a (D) carbon signals also showed cross peaks with the aromatic proton resonances at δ 6.62 and 6.59, which were thus readily assignable to H-6 (D). The remaining proton signals in the high field aromatic

region (δ 6.25 and 6.58) were consequently attributed to H-6 (G) of both conformers. Based on detailed ^{1}H-^{13}C shift correlation spectral examinations, the carbon signals at δ 104.18 and 104.76 were assigned to C-6 of the G ring, and those resonating at δ 110.27 and 110.84 to C-6 of the D ring. The assignments for 4a (G) signals at δ 109.95 and 110.98 were confirmed by their long-range correlation with H-6 (G) and H-4 and H-3 (I). Next, with the chemical shifts of the heterocyclic proton resonances and those at the 6 position beyond doubt (see above), the chemical shifts at δ 107.33, 108.17 and δ 108.45, 108.75 could be assigned to C-8 (D) and C-8 (G), respectively, by observed long-range correlations between C-8(D)/H-4(C) and H-6 (D) on the one hand, and C-8(G)/H-3(F), H-4 (F) and H-6(G) on the other. No long-range correlations were observed between C-8(D) and H-3 (C), and between C-2(C) and H-3 (C), H-6(B) or H-2 (B). The correlations between H-4 and the phloroglucinol C-8a of constituent units were clearly seen through three-bond couplings, thus permitting the assignment of the ^{13}C resonances of C-8a in each instance (A ring δ 154.11 and 153.87; D ring δ 151.93 and 150.20; G ring δ 153.38 and 152.21). Assessment of the remaining quaternary aromatic carbons C-5 and C-7 (A, D, and G) was rather tentative as chemical shift differences were small. No long-range correlation was observed between C-1(B) and H-6(B).

The downfield aromatic region (catechol region) of acylated **2** showed complex ^{1}H-^{1}H and ^{1}H-^{13}C correlations, preventing unambiguous assignments, except for the following signals. Based on their long-range correlations with the rotameric signals of C-2(C) ketal carbon, the dual resonances of the H-2(B) protons were assigned at δ 7.41 and 7.48 (J=2 Hz). Since the catechol H-6 and H-2 protons have the same aromatic ring, the rotameric signals of H-6(B) were unambiguously assigned at δ 7.51 and 7.57 (dd, J=2 Hz, J=8 Hz). In addition, the chemical shift values of the H-5(B) signals (δ 7.26, 7.23; broad singlets) and the C-4 (B) resonances at δ 143.04 and 142.83 clearly followed from ^{1}H-^{1}H COSY and long-range ^{1}H-^{13}C correlation experiments, respectively. HETCOR data also revealed C-6 of the catechol ring located to lower fields as compared to the analogous C-2. Similarly, the assignment of the signals of C-6(E) (δ 125.96, 125.26), C-2 (H) (δ 121.75, 122.81), and H-2(H) (δ 7.19, 7.22) could be established by 2D nmr methods. Due to the complexity of the ^{1}H-nmr spectrum in the region δ 7.0–7.3 and small ^{13}C nmr chemical shift differences of the remaining tertiary and quaternary carbons (B, E, and H), these ^{13}C-nmr assignments were rather tentative. A summary of the ^{1}H- and ^{13}C-nmr assignments for compounds **1** and **2** is shown in Tables 1 and 2, respectively.

The ^{1}H- and ^{13}C-nmr assignments of a mixture (compounds **3** and **4**), the acetates of pavetannin B-3 and B-5, respectively, also listed in Tables 1 and 2, were made by comparison with the assignments for the acetylated **1** and **2**.

Although efforts to separate a mixture have hitherto failed, the components were tentatively identified as the acetates of cinnamtannin B 1 [**1**] and the novel epicatechin-(4β↦6, 2β↦*O*↦7)-*ent*-epicatechin (4β↦8)-epicatechin [**5**], designated as pavetannin B4. Whereas the ^{1}H-nmr spectrum of the mixture was too complex to permit spectral interpretation, the presence of two closely related condensed tannins was evident from the fabms and SEFT-^{13}C-nmr spectrum. Owing to unequal intensities (relative ratio 5:1), the signals arising from each compound could be allocated, thus establishing the structure of the major compound **1** by comparison of the ^{13}C-nmr data. The signals arising from the minor compound **5** were reminiscent of those of the acetate of pavetannin B3 [epicatechin-(4β↦6, 2β↦*O*↦7)-epicatechin-(4α↦8)-epicatechin]. However, notable differences were observed for the F-flavan C-3 carbons in **5** relative to **3**, suggesting an *ent*-epicatechin configuration of the middle unit in **5**. As shown in Table 1, the H-8(D) signals also revealed a close structural relationship between **3**, **4**, and **5**, suggesting a (4↦6)-interflavanyl linkage for **5**. Therefore, compound **5** was identified

TABLE 1. ^{1}H-nmr Data of Peracetylated Compounds **1–5**[a] ($CDCl_3$, δ values, *J* in Hz).

Ring/Proton	Compound			
	1	**2**	**3** and **4**	**5**
C H-3	4.99 (1H, d, *J*=4)	4.99 (1H, d, *J*=4)	4.86, 4.89	5.00 (1H, m)
	4.99 (1H, d, *J*=4)	5.00 (1H, d, *J*=4)	5.16	5.00 (1H, m)
H-4[b]	4.29 (1H, d, *J*=4)	4.31 (1H, d, *J*=4)	4.19, 4.45	4.29 (1H, d, *J*=4)
	4.62 (1H, d, *J*=4)	4.62 (1H, d, *J*=4)	4.38, 4.53	4.62 (1H, m)
F H-2	5.43 (1H, s)	5.42 (1H, s)	5.51, 5.51	5.40 (1H, m)
	5.71 (1H, d, *J*=2)	5.71 (1H, d, *J*=2)	5.69, 5.69	5.70 (1H, brs)
H-3	5.20 (1H, s)	5.20 (1H, m)	5.20, 5.33	5.21 (1H, s)
	5.37 (1H, m)	5.37 (dd, *J*=2;4)	5.30, 5.41	5.39 (1H, brs)
H-4[b]	4.31 (1H, d, *J*=4)	4.30 (1H, d, *J*=4)	4.19, 4.45	4.31 (1H, d, *J*=4)
	4.62 (1H, d, *J*=4)	4.63 (1H, d, *J*=4)	4.38, 4.57	4.62 (1H, m)
I H-2	4.79 (1H, s)	4.79 (1H, s)	4.77, 4.66	4.79 (1H, s)
	5.20 (1H, s)	5.20 (1H, m)	5.20, 5.33	
H-3	5.20 (1H, s)	5.20 (1, m)	5.20, 5.20	5.21 (1H, s)
	5.54 (1H, m)	5.53 (1H, m)	5.51, 5.51	5.52 (1H, m)
H-4	2.90 (2H, brs)	2.90 (2H, brs)	2.90–3.07	2.92 (2H, m)
	3.01 (2H, m)	2.95–3.04 (2H)	2.90–3.07	3.00 (2H, m)
A H-6	6.43 (1H, d, *J*=2)	6.43 (1H, d, *J*=2)	6.40, 6.40	6.42 (1H, d, *J*=2)
	6.52 (1H, d, *J*=2)	6.52 (1H, d, *J*=2)	6.51, 6.48	6.52 (1H, d, *J*=2)
H-8	6.72 (1H, d, *J*=2)	6.72 (1H, d, *J*=2)	6.73, 6.73	6.73 (1H, d, *J*=2)
	6.84 (1H, d, *J*=2)	6.85 (1H, d, *J*=2)	6.81, 6.81	6.85 (1H, d, *J*=2)
D H-6	6.59 (1H, s)	6.59 (1H, s)		
	6.62 (1H, s)	6.62 (1H, s)		
H-8			6.57, 6.64	6.67 (1H, s)
			6.88, 6.88	6.80 (1H, s)
G H-6	6.26 (1H, s)	6.25 (1H, s)	6.28, 6.33	6.24 (1H, s)
	6.59 (1H, s)	6.58 (1H, s)	6.57, 6.57	6.59 (1H, s)
B H-2	7.40 (1H, d, *J*=2)	7.41 (1H, d, *J*=2)	7.03–7.53	7.41
	7.48 (1H, d, *J*=2)	7.48 (1H, d, *J*=2)		7.48
H-6	7.53 (1H, m)	7.51 (dd, *J*=2;8)		7.51
	7.60 (1H, m)	7.57 (dd, *J*=2;8)		7.63
B,E,H	7.02–7.29	7.03–7.29		7.03–7.29

[a]Data for **2** were recorded at 600 MHz; for the other compounds, at 200 MHz.
[b]Assignments may be interchanged.

as epicatechin-(4β↦6, 2β↦*O*↦7)-*ent*-epicatechin-(4β↦8)-epicatechin (pavetannin B4).

Based on careful examination of COSY and HETCOR spectra, most of the resonances of acetylated trimeric proanthocyanidins possessing a doubly-linked structure may be unequivocally assigned as exemplified above. In contrast to previous papers dealing with nona-acetate A-type procyanidins (10,15), the signal for the C-2 ketal carbon (C ring) is clearly shown to resonate at δ 97, whereas the resonance at δ 105–106 corresponds to C-4a (A ring). This confirms recent results regarding the assignment of C-2 and C-4a of an A-type unit (16).

EXPERIMENTAL

PLANT MATERIAL AND ISOLATION OF **1–5**.—Stem bark of *P. owariensis* (white variety) was collected in Sérédou, Guinea. The plant was taxonomically identified at the Department of Botany of the Research Center of Medicinal Plants in Sérédou, where a voucher specimen is deposited. Proanthocyanidins **1–5** were isolated and purified, as described before, by dccc, repetitive cc on Sephadex LH-20, and preparative tlc on Si gel (10,11).

TABLE 2. ^{13}C-nmr ($CDCl_3$) Chemical Shifts of Peracetylated Compounds **1–5**.[a]

Ring	Carbon	Compound				
		1	**2**	**3**	**4**	**5**
C	C-2	98.22	98.28	98.12	97.89	98.13
		97.75	97.82	97.33	97.32	97.62
	C-3	67.85	67.92	67.93	67.98	66.99
		66.63	66.72	66.46	66.49	66.93
	C-4	33.57	33.64	33.66	33.66	33.75
		33.40	33.44	33.42	33.42	33.66
F	C-2	[b]	75.53	[b]	75.57	75.68
		[b]	75.36	[b]	75.40	75.49
	C-3	70.42	70.48	70.32	70.46	70.86
		69.73	69.79	69.70	69.76	68.03
	C-4	27.33	27.41	27.15	27.37	27.37
		27.33	27.41	27.00	27.22	27.19
I	C-2	[b]	76.72	[b]	76.75	76.75
		[b]	76.72	[b]	76.75	76.75
	C-3	66.29	66.37	66.30	66.29	66.29
		66.29	66.37	66.30	66.29	66.29
	C-4	26.16	26.31	26.22	26.22	26.34
		29.60	26.17	29.71	29.69	29.71
A	C-4a	114.10	114.21	—		
		112.99	113.09			
	C-5	147.58	147.88	113.19		
		147.74	147.81	147.76		
	C-6	109.67	109.80	109.64		
		109.67	109.73	109.41		
	C-7	149.55	149.68	149.55		
		149.55	149.63	149.55		
	C-8	107.04	107.14	107.24		
		106.57	106.69	107.24		
	C-8a	153.99	154.11	153.84		
		153.76	153.87	153.76		
D	C-4a	117.73	117.79	—		
		116.62	116.69	—		
	C-5	148.50	148.60	148.50		
		148.03	148.12	148.01		
	C-6	110.72	110.84	108.17		
		110.19	110.27	107.23		
	C-7	149.55	149.49	149.57		
		148.73	148.79	148.62		
	C-8	108.09	108.17	110.88		
		107.22	107.33	110.00		
	C-8a	151.83	151.93	151.91		
		150.08	150.20	150.18		
G	C-4a	110.89	110.98	110.89		
		109.84	109.95	109.88		
	C-5	148.50	148.12	148.58		
		148.03	147.65	147.84		
	C-6	104.70	104.76	104.70		
		104.12	104.18	104.14		
	C-7	148.73	148.60	148.70		
		148.50	148.15	147.84		
	C-8	108.68	108.75	108.97		
		108.38	108.46	108.23		
	C-8a	153.29	153.38	153.76		
		152.12	152.21	152.00		

TABLE 2. Continued.

Ring	Carbon	Compound				
		1	2	3	4	5
B	C-1[c]	134.72	135.29	134.70		
		135.31	135.37	135.51		
	C-2	123.16	123.22	123.09		
		123.57	123.31	123.24		
	C-3[c]	141.67	141.48	141.72		
		141.67	141.68	141.68		
	C-4	142.96	143.04	142.00		
		142.72	142.83	142.90		
	C-6	125.85	125.54	125.80		
		125.44	125.31	125.35		
E	C-1[c]	134.72	134.85	134.74		
		135.31	134.79	135.51		
	C-2	124.21	124.34	124.34		
		123.57	123.66	123.77		
	C-3[c]	141.67	141.76	141.74		
		142.02	141.80	141.98		
	C-4[c]	142.43	142.49	142.44		
		142.02	142.16	142.19		
	C-6	125.85	125.96	125.51		
		125.20	125.26	125.07		
H	C-1[c]	135.31	135.48	135.51		
		134.72	135.39	134.74		
	C-2	123.16	123.04	123.19		
		122.93	123.00	123.00		
	C-3[c]	141.67	141.76	141.70		
		141.67	141.68	141.70		
	C-4[c]	142.02	142.08	142.06		
		141.67	141.92	141.70		
	C-6	124.21	124.26	124.34		
		123.16	123.62	123.67		
B-E-H	C-5	121.29	121.36	121.33		
		121.64	121.75	121.73		
		121.75	122.81	121.79		
		122.75	122.81	122.79		
		122.93	122.85	122.86		
		122.93	122.85	122.86		
MeCOO-		19.38	19.47	19.54		
		19.85	19.92	19.96		
			19.98	20.05		
		20.08	20.14	20.12		
			20.35	20.39		
			20.38			
			20.42			
			20.48			
			20.52			
		20.55	20.61	20.64		
		20.72	20.66	20.70		
			20.77	20.72		
			20.87	20.80		
			20.94	20.94		
		21.08	21.11			
			21.18	21.19		
MeOCO-			167.80	167.72		
		167.83	167.87	167.79		

TABLE 2. Continued.

Ring	Carbon	Compound				
		1	**2**	**3**	**4**	**5**
			167.92	167.92		
			168.04	168.00		
			168.15	168.07		
			168.26	168.20		
		168.30	168.42	168.43		
			168.45	168.47		
			168.59	168.61		
			168.61	168.71		
		168.94	169.05	169.10		
			169.08			
		169.17	169.36	169.31		
		169.70	169.78	169.70		
			169.84	169.80		
			170.06	170.06		
			170.21			
		170.52	170.49			

[a]Data for **2** were recorded at 150 MHz; for the other compounds at 50.10 MHz.
[b]Overlapped with the solvent signals.
[c]Assignments may be interchanged in the same column.

GENERAL EXPERIMENTAL PROCEDURES.—Acetylations were performed in Ac_2O/pyridine at room temperature. Ir spectra were measured on a Beckman Acculab 4 or a Brucker IFS48 FT-ir spectrometer. The fabms was recorded on a VG 70-SEQ hybrid mass spectrometer with glycerol and *m*-nitrobenzyl alcohol as matrix. The nmr spectra of acetylated compounds were recorded in $CDCl_3$ on Jeol FX 200 NMR (^1H 199.5 MHz, ^{13}C 50.1 MHz), Bruker WP 250 (^1H 250 MHz, ^{13}C 62.8 MHz), and Bruker AM 600 (^1H 600.1 MHz, ^{13}C 150 MHz) instruments. Chemical shifts are reported in δ values downfield from internal TMS. All 1D and 2D spectra were recorded using standard instrumental software packages. The 2D COSY and ^1H-detected one-bond and multiple-bond ^{13}C multiple-quantum coherence spectra were recorded on the Bruker AM 600 spectrometer using the conditions reported previously (17).

Pavetannin B4 [**5**].—Compound **5** [epicatechin-(4β↦6, 2β↦*O*↦7)-*ent*-epicatechin-(4β↦8)-epicatechin] was obtained in a yield of 0.013%. Tlc [Si gel, EtOAc-HCOOH-HOAc-H_2O (140:2:1:59)] R_f 0.28; fabms *m/z* $[M+Na]^+$ 887, $[M+H]^+$ 865; ^1H nmr see Table 1; ^{13}C nmr see Table 2.

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