Tannins and Related Compounds. Part 26.[1] Isolation and Structures of Stenophyllanins A, B, and C, Novel Tannins from *Quercus stenophylla*

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Together with four known ellagitannins (casuarinin, casuariin, castalagin, and castalin) containing the core of an open-chain form of D-glucose, three unusual and closely related tannins, stenophyllanins A, B, and C, have been isolated from the bark of *Quercus stenophylla*. Degradative and synthetic studies, in conjunction with ^{1}H n.m.r., ^{13}C n.m.r., and mass spectrometry, have led to the unequivocal assignments of the structures in which an ellagitannin (casuarinin or casuariin) moiety is attached through a carbon–carbon linkage to the A-ring (C-8 or C-6) of a flavan-3-ol [(+)-catechin] unit.

Systematic chemical investigations of the bark of *Quercus stenophylla* Makino (Fagaceae) have hitherto revealed the presence of an exceptionally complex mixture of more than sixty phenolic metabolites including both condensed and hydrolysable tannins. Of these compounds, (+)-catechin,[2] which is one of the component units of condensed tannins, as well as hydrolysable tannins based upon a variety of polyalcohol cores, *i.e.*, D-glucose,[3] *proto*-quercitol,[4] quinic acid,[5] and *p*-hydroxyphenethyl alcohol 1-*O*-β-D-glucopyranoside (salidroside),[2,6] has been found to predominate in the ethyl acetate-soluble portion of the bark extract. We now report the isolation from the water-soluble portion, and characterization of a new type of tannin, designated as stenophyllanins A (2), B (1), and C (3), together with four known ellagitannins containing the core of an open-chain form of D-glucose.

Results and Discussion

The chromatographic techniques outlined previously[7] were used to separate individual tannins occurring in the aqueous layer remaining after the ethyl acetate extraction. Three novel tannins, stereophyllanins A, B, and C, were obtained together with four ellagitannins, which were identified as casuarinin (4),[4] casuariin (5),[8] castalagin (6),[9] and castalin (7)[10] by comparisons of their physical and spectral data with those of authentic samples.

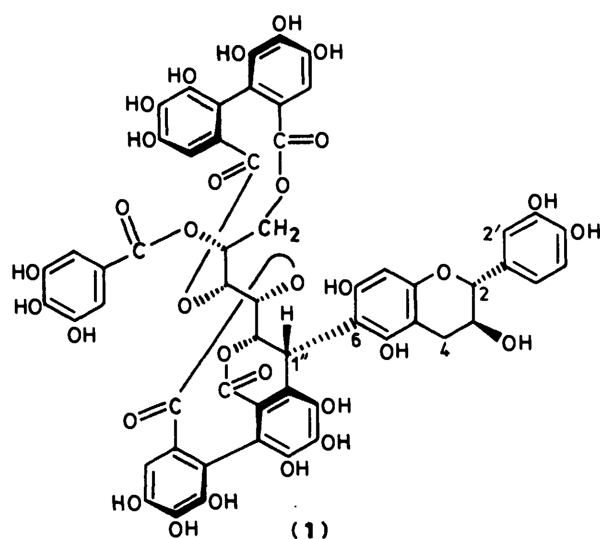
Stenophyllanin B (1).—The first novel tannin was obtained as an off-white, amorphous powder, showed an $[M + H]^+$ ion peak at *m/z* 1 209 in the fast atom bombardment mass spectrum. It gave a pink colouration on treatment with the anisaldehyde–sulphuric acid reagent [7a] confirming the presence of a phloroglucinol nucleus in the molecule, while the reaction with nitrous acid (to give a purple colouration)[11] was consistent with an ellagitannin. The ^{1}H n.m.r. spectrum showed three sharp singlets at δ 6.58, 6.59, and 6.93, each corresponding to one proton. These uncoupled aromatic signals were attributed to the protons of hexahydroxydiphenoyl groups, and thus at least two such groups were shown to be present in the molecule. In addition, the appearance of a two-proton singlet at δ 7.15 indicated the presence of a gallic acid ester group. Other aromatic signals comprised a high field singlet signal at δ 5.95, assigned to the proton on a phloroglucinol ring, and an ABX system at δ 6.69 (dd, *J* 2, 8 Hz), 6.77 (d, *J* 8 Hz), and 6.88 (d, *J* 2 Hz), suggesting the presence of a 1,3,4-trisubstituted aromatic (pyrocatechol-type) ring. In the aliphatic proton region, a doublet at δ 4.50 (*J* 8 Hz) and a pair of double doublets at δ 2.50 (*J* 8, 16 Hz) and 2.90 (*J* 6, 16 Hz), due to a methine bearing an oxygen function and a benzylic methylene, respectively, were observed, which were closely analogous to those of the respective 2- and 4-H of a flavan-3-ol derivative with 2,3-*trans* stereochemistry. The presence of a 2,3-*trans* flavan-3-ol moiety in the molecule was further substantiated by ^{13}C n.m.r. spectroscopy which showed, among others, three aliphatic carbon signals at δ 82.0, 68.2, and 31.6 p.p.m. similar to those due to the C-ring carbons of (+)-catechin (8).[12] Low field aromatic carbon signals at δ 155.0, 155.2, and 155.9 p.p.m., attributable to the carbons bearing an oxygen function on the phloroglucinol ring, were similar to those of C-5, C-7, and C-8a of (+)-catechin. However, the ^{13}C n.m.r. spectrum differed from that of (+)-catechin (8) in showing one high field phloroglucinol ring signal at δ 96.3 p.p.m. which appeared as a doublet in the off-resonance spectrum. This fact, combined with the above-mentioned ^{1}H n.m.r. observation, indicated the presence of a substituent at C-6 or C-8 of the flavan-3-ol moiety. Examination of the ^{13}C n.m.r. spectrum revealed, in addition to flavan C-ring signals, the presence of six sp^3 carbons, five of which bear an oxygen atom (δ 81.2, 74.9, 73.3, 71.3, and 64.5 p.p.m.). The remaining carbon signal appearing significantly for upfield (δ 38.3 p.p.m.) was attributed to a benzylic methine. These ^{13}C n.m.r. spectral data suggested that a C_6-polyalcohol unit, probably some sort of carbohydrate, was connected to the flavan-3-ol moiety through a carbon–carbon linkage.

First, in order to clarify the structure of the flavan-3-ol moiety, the acid-catalysed degradation * of stenophyllanin B (1) was attempted. Refluxing of compound (1) in ethanol containing acetic acid (20%), followed by repeated chromatography over Sephadex LH-20 and MCI-gel CHP-20P, yielded, among many uncharacterized compounds, a crystalline compound {m.p. 171 °C, $[\alpha]_D$ +13.7° (acetone)} that was shown to be identical with (+)-catechin (8).

The polyalcohol moiety was defined by oxidative degradation of stenophyllanin B (1) with iron(III) chloride; this afforded glucose and arabinose, thus confirming that the polyalcohol carbons, except for the C-1 atom, have the same configuration as those of glucose.

Upon enzymatic hydrolysis with tannase, stenophyllanin B (1) liberated gallic acid and an amorphous compound (9), whose molecular mass [*m/z* 1 057 $(M + H)^+$, fast atom bombardment] confirmed its desgalloyl structure (Scheme 1). The ^{13}C n.m.r. spectrum of compound (9) showed a downfield shift (Δ δ +2.4) of the methylene carbon (C-6) signal in the polyalcohol moiety compared with that of stenophyllanin B (δ 64.5 p.p.m.). This observation was in good agreement with casuarinin (4) which lacks a galloyl group at the C-5 position.

* Based on the observation that proanthocyanidins consisting of chains of flavan-3-ol units linked through carbon–carbon linkages at C-(4)–C(8) or C(4)–C(6) are degraded to monomeric flavan-3-ols in acid medium.[12]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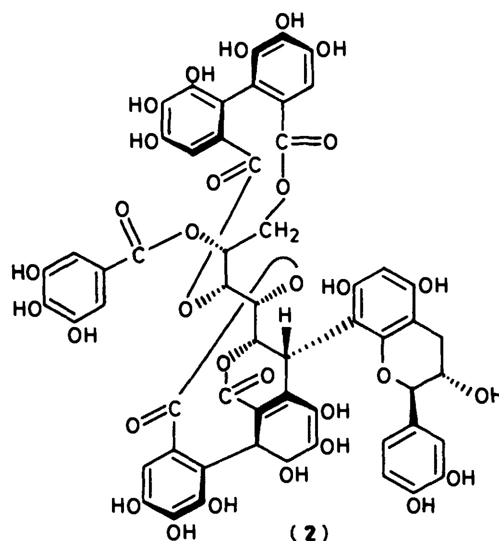
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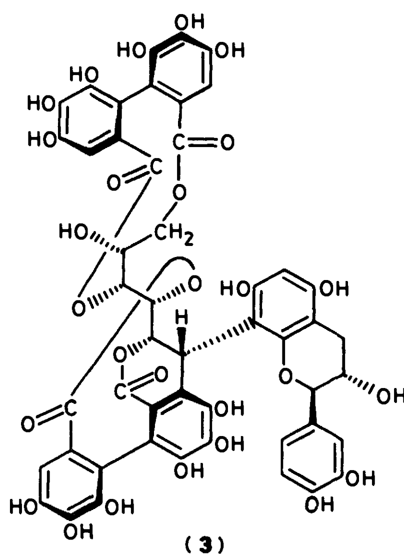
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The absence of the galloyl group at the C-5 position in the hydrolysate (9) was further confirmed by analysis of the ^{1}H n.m.r. spectrum which showed an upfield shift† of the C-5 proton signal, as compared with that of stenophyllanin B (1) (δ 5.60).

The hexahydroxydiphenoyl groups occurring in stenophyllanin B (1) resisted tannase hydrolysis. In order to elucidate the nature of the hexahydroxydiphenoyl groups, the following reactions were carried out. Methylation of stenophyllanin B (1) with dimethyl sulphate and anhydrous potassium carbonate in dry acetone gave the nonadecamethyl ether (10) (m/z 1 474 M^+, field desorption), which was subsequently subjected to methanolysis with methanolic sodium methoxide to yield methyl tri-*O*-methylgallate, dimethyl 4,4',5,5',6,6'-hexamethoxybiphenyl-2,2'-dicarboxylate (11) and a crystalline hydrolysate (12), m/z 927 [$(M + H)^+$, field desorption]. The specific optical rotation [$-27.8°$ ($CHCl_3$)] of compound (11) indicated the chirality to be in the *S*-series.[13] The presence of another hexamethoxydiphenoyl group in the hydrolysate (12) was evident from examination of the ^{13}C n.m.r. spectrum which showed signals at δ 163.6 and 167.2 p.p.m. due to two carboxy carbons, together with twelve aromatic carbon signals similar to those of compound (11). The ^{1}H n.m.r. spectrum of compound (12) exhibited two low field signals at δ 5.04 (d, J 4 Hz) and 4.63 (dd, J 4, 7 Hz) attributable to 1-H and 2-H of the polyalcohol, respectively. Since the ^{13}C n.m.r. chemical shift (δ 31.3 p.p.m.) for C-1 of the polyalcohol in compound (12) indicated the absence of an oxygen function at this position, one of two ester groups was considered to be still located at the C-2 position. Several attempts to hydrolyse this ester group, even at elevated temperatures or in high concentrations of alkali, were unsuccessful. On periodic acid oxidation, followed by reduction with sodium borohydride, compound (12) yielded a degradation product (13), m/z 836 (M^+, electron impact). The circular dichroism spectrum of compound (13) exhibited positive plain curves at 267 nm ($\theta = +0.21 \times 10^5$) and 313 nm ($\theta = +0.36 \times 10^5$), and a negative one at 287 nm ($\theta = -0.11 \times 10^5$), similar to those of compound (11), thus showing the chirality of the remaining hexahydroxydiphenoyl group to be *S*.[14]

The ^{1}H n.m.r. spectrum of stenophyllanin B (1) exhibited a singlet at δ 4.68 due to 1-H of the polyalcohol, suggesting that the dihedral angle between 1- and 2-H is *ca.* 85°.* On the other hand, 1-H appeared as a doublet (J 4 Hz) in the ^{1}H n.m.r. spectra of compounds (12) and (13) (δ 5.04 and 4.95, respectively). These facts implied that the dihedral angle between 1- and 2-H is changed by hydrolysis of the ester group. Inspection of the Dreiding model clearly revealed that

† In fact, the C-5 proton signal was overlapped by an H_2O or HOD signal which lies in the range δ 3.6—4.2.

* This value was estimated from the Karplus correlation.

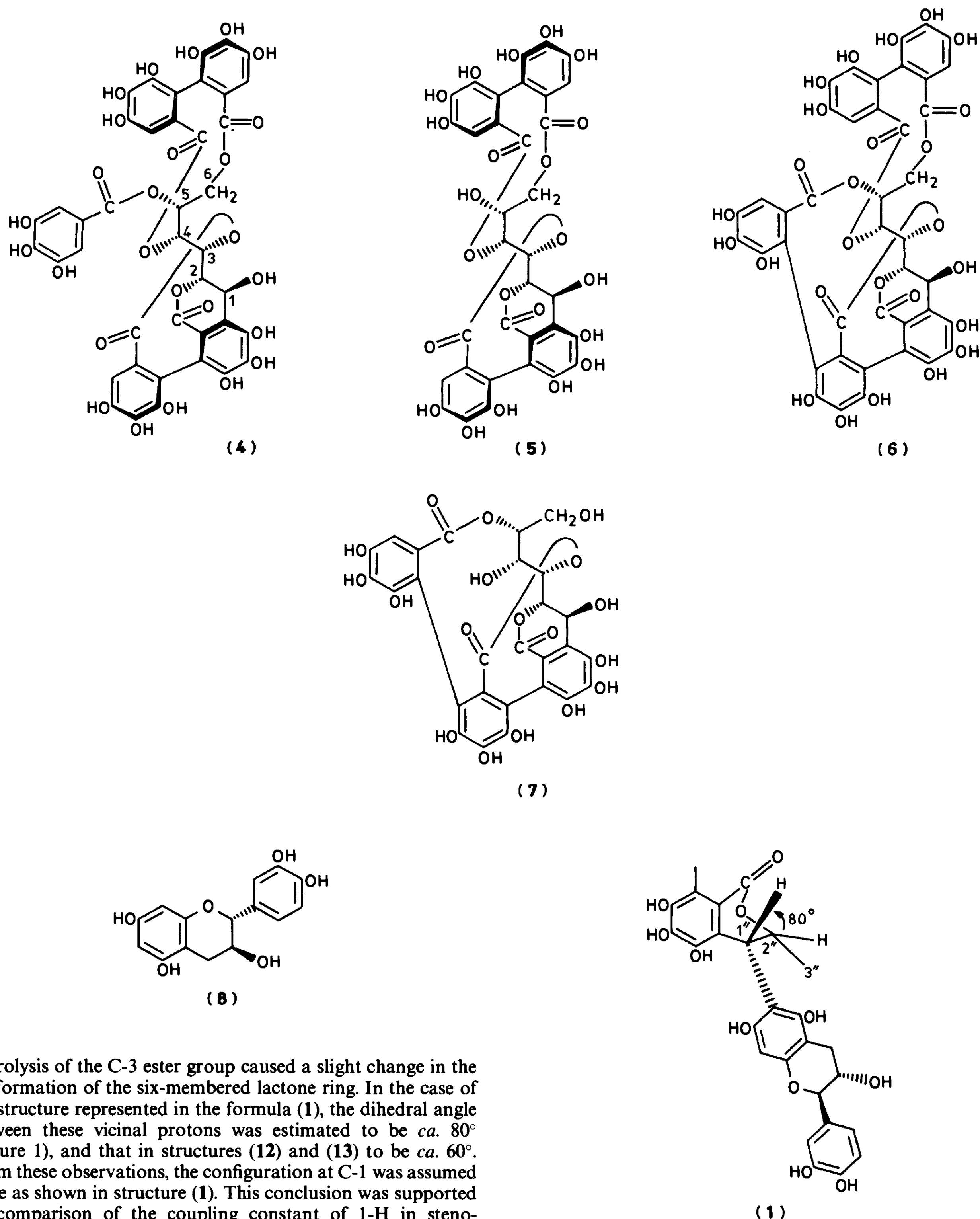
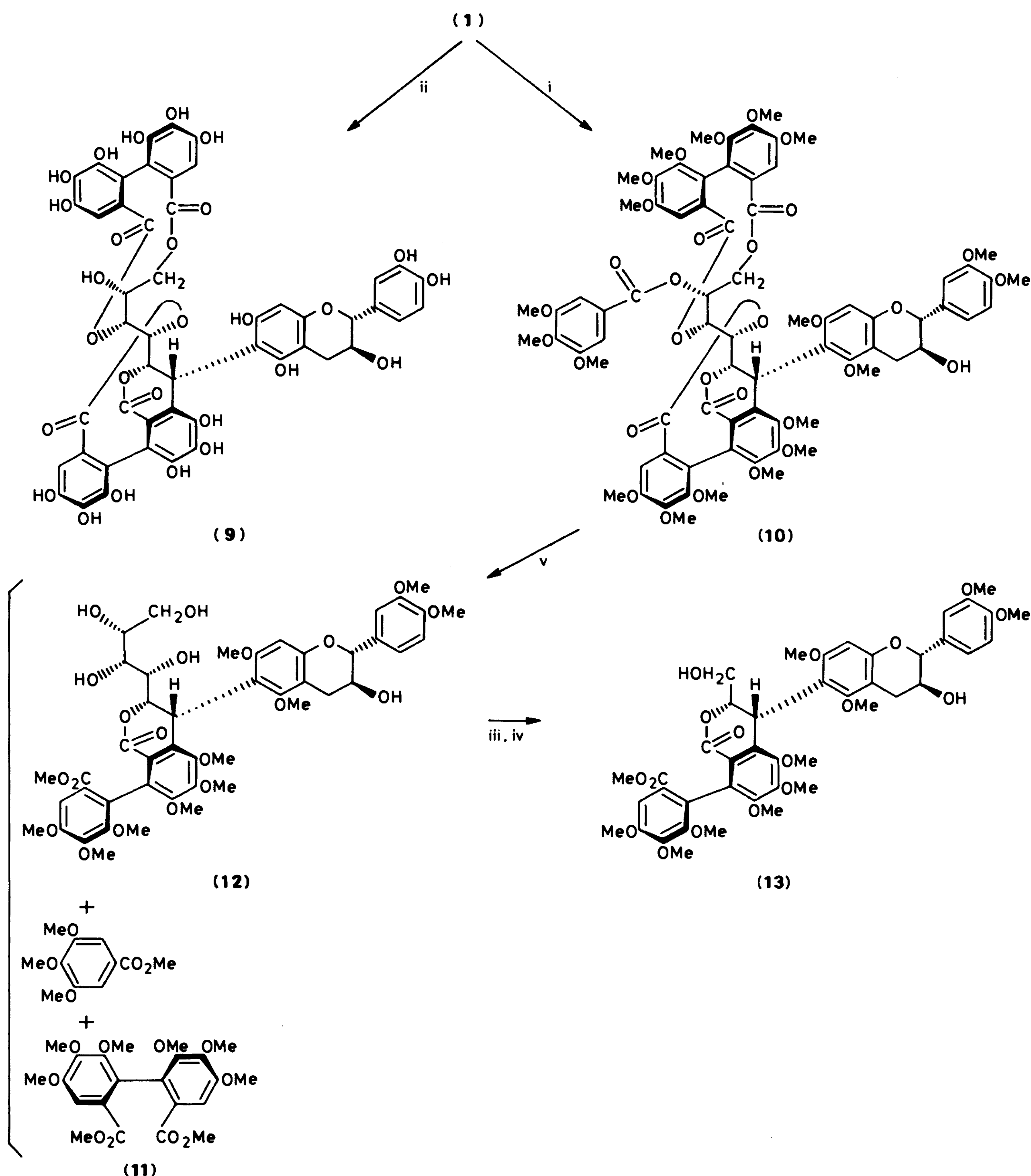


Figure 1. The conformation of stenophyllanin B (1)

hydrolysis of the C-3 ester group caused a slight change in the conformation of the six-membered lactone ring. In the case of the structure represented in the formula (1), the dihedral angle between these vicinal protons was estimated to be *ca.* 80° (Figure 1), and that in structures (12) and (13) to be *ca.* 60°. From these observations, the configuration at C-1 was assumed to be as shown in structure (1). This conclusion was supported by comparison of the coupling constant of 1-H in stenophyllanin B (1) with those of casuarinin (4) and its C-1 epimer, stachyurin (14), whose configurations at C-1 had already been established;[8] the coupling constant in stenophyllanin B (1) was compatible with that of stachyurin (14) (*J* 1.5 Hz) rather than that of casuarinin (4) (*J* 4 Hz), indicating that stenophyllanin B has the same configuration as stachyurin (14).

Previously, we demonstrated that in the methyl ethers of C-6 or C-8 substituted catechin derivatives there are ^{13}C n.m.r. chemical shift differences in the A-ring carbons, especially those of C-8, C-4a, and C-6, which make it possible to distinguish between C-6 and C-8 substitution.[7b] In the ^{13}C n.m.r. spectrum of compound (13), signals due to C-8, C-4a, and C-6 were observed at δ 96.4, 106.4, and 115.7 p.p.m., respectively, consistent with C-6 substitution [(for example, gambiriin A-3 nonamethyl ether (15):[15] C-8, δ 96.1; C-4a, 108.4; C-6, 117.7 p.p.m., see Figure 2]. Furthermore, the chemical shift (δ 4.50) for 2-H of the catechin moiety in the ^1H n.m.r. spectrum of

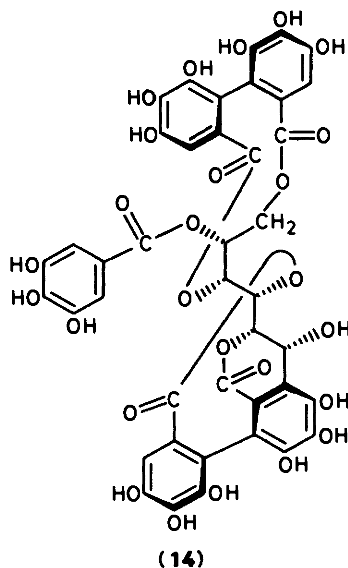


Scheme 1. *Reagents:* i, Me_2SO_4, K_2CO_3; ii, tannase; iii, $NaIO_4$; iv, $NaBH_4$; v, NaOMe, MeOH

stenophyllanin B (**1**) was almost identical with that of (+)-catechin (**8**) (δ 4.56), indicating that the substituent did not affect 2-H.[16,17] Based on these observations, the polyalcohol moiety was concluded to be attached at the C-6 position of the catechin moiety.

One of the hexahydroxydiphenoyl groups was presumed to be located at the C-4 and C-6 positions in the polyalcohol moiety (as mentioned above, the galloyl group occupied the polyalcohol C-5 position), since the chemical shifts for 3-, 4-, 5-, and 6-H of the polyalcohol were similar to those found in stachyurin (**14**) (this is discussed in detail later in this paper.)

Stenophyllanin A (**2**).—The second novel tannin, stenophyllanin A (**2**), obtained as an off-white, amorphous powder, showed chromatographic properties and colour reactions similar to those of stenophyllanin B (**1**). The fast atom bombardment mass spectrum, with the same $(M + H)^+$ ion peak at m/z 1 209 as that of stenophyllanin B (**1**), confirmed its



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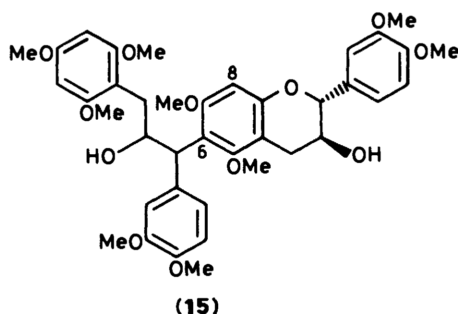

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molecular weight. The ^{1}H n.m.r. spectrum, measured at room temperature, did not give information on the structure, because of the broadening of signals, presumably due to dynamic rotational isomerism.[12] Examination of the ^{13}C n.m.r. spectrum, however, permitted the characterization of the functional groups, showing the presence of catechin and polyalcohol moieties together with a galloyl and two hexahydroxydiphenoyl groups. The chemical shifts for the polyalcohol carbons were in agreement with those of stenophyllanin B (1) and implied the occurrence of a similar substitution pattern in the polyalcohol moiety. The appearance of a signal due to C-1 of the polyalcohol at high field (δ 38.3 p.p.m.) indicated the absence of an oxygen function at this position, thus confirming its '*C*-glycosidic' nature. When methylated in the same way as described above, stenophyllanin A (2) formed the nonadecamethyl ether (16), *m/z* 1 474 (M^+, field desorption), which was subsequently treated with sodium methoxide in methanol to yield a hydrolysate (17), *m/z* 926 (M^+, field desorption), together with methyl tri-*O*-methylgallate and dimethyl (*S*)-4,4′,5,5′,6,6′-hexamethoxybiphenyl-2,2′-dicarboxylate (11). The one-proton aromatic singlet at δ 7.32 and two ester carbon signals at δ 167.3 and 163.6 p.p.m. in the ^{1}H and ^{13}C n.m.r. spectra, respectively, of the hydrolysate (17) clearly indicated the presence of another hexamethoxydiphenoyl group in compound (17); by comparison of the circular dichroism data with those of the degradation product (13) obtained from stenophyllanin B (1), the chirality of this hexamethoxydiphenoyl group was established as *S*. The ^{13}C n.m.r. spectrum of compound (17) was almost identical with that of the hydrolysate (12) derived from stenophyllanin B (1), except for the chemical shifts for C-6, C-4a, and C-8 in the catechin moiety. These carbon resonances appeared at δ 89.3, 101.5, and 111.3 p.p.m., respectively, the chemical shifts being in close agreement with those found in a C-8 substituted catechin derivative, gambiriin A-1 nonamethyl ether (18)[15] (C-6, δ 88.6; C-4a, 102.5; and C-8, 112.2 p.p.m.). These observations thus suggested that the polyalcohol is attached to the C-8 position of the catechin moiety. In the ^{1}H n.m.r. spectrum of compound (17). The signals due to 2-H of the catechin skeleton were at lower field [δ 5.03 (d, *J* 7 Hz)] than that of compound (12) [δ 4.70 (d, *J* 8 Hz)], indicating that in compound (17) the substituent is situated close to C-2.[16] Moreover, the relative difference in the chemical shift for the catechin A-ring proton in compounds (17) [δ 6.01 (s)] and (12) [δ 6.29 (s)] was consistent with the observation that 8-H resonates at higher field than the alternative possibility 6-H.[18] On the basis of these findings, the polyalcohol was concluded to be located at the C-8 position of the catechin moiety.

In order to confirm the allocation of the galloyl and hexahydroxydiphenoyl groups in the polyalcohol chain and also to elucidate the absolute configurations at C-2 and C-3 in the catechin moiety, an attempt was made to prepare stenophyllanins by the acid-catalysed condensation of (+)-catechin (8) and casuarinin (4) whose structures have been unequivocally established. Treatment of a mixture of (+)-catechin (8) and casuarinin (4) with a catalytic amount of toluene-*p*-sulphonic acid in dry dioxane, and subsequent separation by repeated chromatography over Sephadex LH-20 and MCI-gel CHP-20P with a variety of solvent systems, afforded stenophyllanin A (2) in *ca.* 4% yield, together with a large quantity of unchanged starting material (4). The alternative C-6 substituted isomer, stenophyllanin B (1), could not be obtained, presumably because C-6 is more sterically hindered than C-8.[19]

The configuration at C-1 of the polyalchohol in stenophyllanin A (2) was concluded to be the same as that in stenophyllanin B (1) as it is similar to the coupling constant of the 1-H signal (singlet at δ 4.41) in the 100 MHz ^{1}H n.m.r. spectrum of stenophyllanin A (1).

Stenophyllanins A (2) and B (1) were accompanied by the structurally related tannin, stenophyllanin C (3), isolated as an off-white, amorphous powder. The fast atom bombardment mass spectrum showed an intense $(M + H)^+$ ion peak at *m/z* 1 057 which corresponded to the loss of one galloyl group from the molecular mass of stenophyllanin B (1) or A (2). The absence of a two-proton aromatic singlet and seven carbon resonances due to the galloyl group in the ^{1}H and ^{13}C n.m.r. spectra, respectively, agreed with the mass spectral data. On methylation with dimethyl sulphate and potassium carbonate in acetone, stenophyllanin C (3) yielded a hexadecamethyl ether (19), *m/z* 1 280 (M^+, field desorption). The ^{1}H n.m.r. spectrum of the methyl ether (19) exhibited a signal at δ 6.00 attributable to the catechin A-ring proton, the chemical shift of which was in good accord with that of the nonadecamethyl ether (16) of stenophyllanin A (δ 6.00) rather than that of the stenophyllanin B methyl ether (10) (δ 6.18); this suggests that a substituent is located at C-8 of the catechin moiety. The methyl ether (19) formed, on acetylation with acetic anhydride and pyridine, an acetate (20), *m/z* 1 364 (M^+, field desorption), which exhibited proton resonances due to two aliphatic acetoxy groups at δ 1.85 and 2.01. One of the acetoxy groups was attributed to that in the catechin moiety (at C-3), while the other was presumed to be located at C-5 in the polyalcohol chain. From these chemical and spectroscopic data, stenophyllanin C (3) was shown to be desgalloyl stenophyllanin A. Final structural confirmation was obtained by the partial hydrolysis of stenophyllanin A (2) with tannase, which afforded a hydrolysate, shown to be identical with stenophyllanin C (3).

Stenophyllanins A, B, and C represent a new class of tannins in which a flavan-3-ol (catechin) unit, one of the component

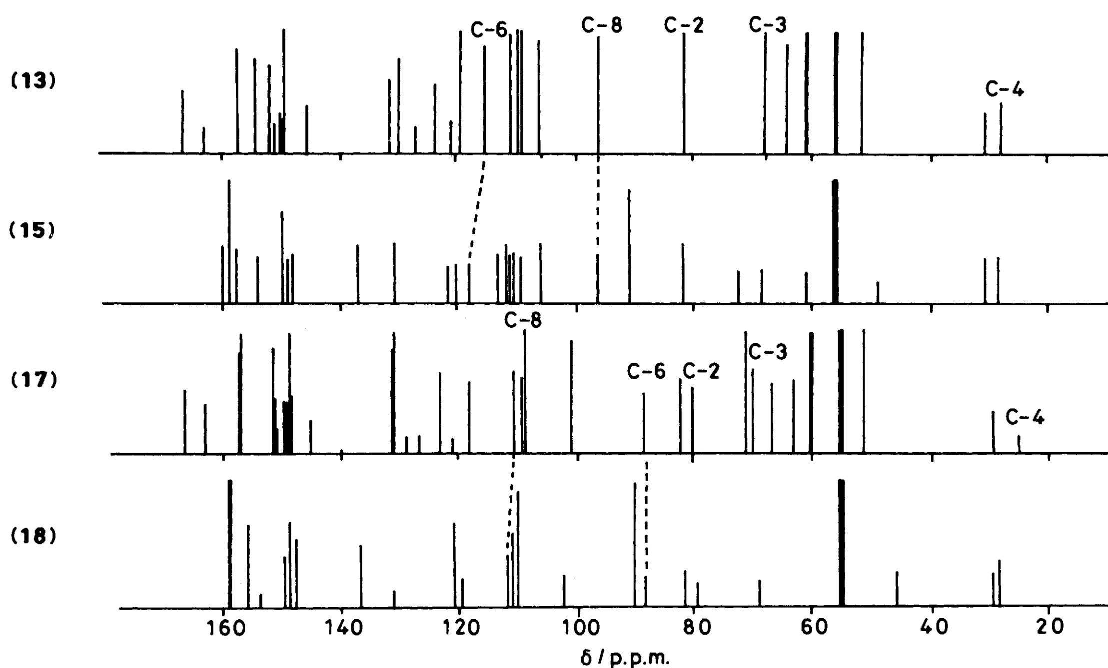
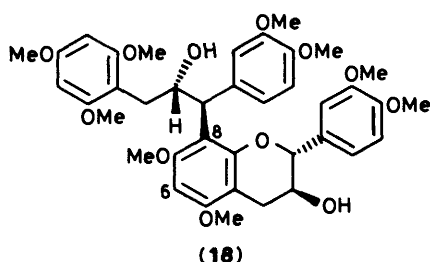


Figure 2. ^{13}C N.m.r. spectra of compound (**13**), gambiriin A-3 nonamethyl ether (**15**), compound (**17**), and gambiriin A-1 nonamethyl ether (**18**) (solvent $CDCl_3$; tetramethylsilane as internal standard)

Scheme 2. *Reagents:* i, Me_2SO_4, K_2CO_3; ii, NaOMe, MeOH; iii, $NaIO_4$; iv, $NaBH_4$



(18)

units of condensed tannins, is connected to a hydrolysable tannin moiety through a carbon–carbon linkage.

Experimental

M.p.s were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter. I.r. spectra were recorded on a JASCO DS-301 spectrophotometer. Electron impact (EI) mass spectra were measured with a JEOL JMS D-300 spectrometer equipped with a direct inlet system, while field desorption and fast atom bombardment mass spectra were taken with a JEOL JMS DX-300 instrument. ^1H (100 MHz) and ^{13}C (25.05 MHz) N.m.r. spectra were recorded on JEOL PS-100 and JEOL FX-100 spectrometers, respectively (the JEOL FX-100 instrument was also used for ^1H n.m.r. measurements), using tetramethylsilane as the internal reference. Circular dichroism curves were determined on a JASCO J-20 apparatus for solutions in methanol. Column chromatography was performed using Sephadex LH-20 (25—100 μm; Pharmacia Fine Chemicals), MCI-gel CHP-20P (75—150 μm; Mitsubishi Chemical Industries Ltd.) previously designated as Diaion HP-20P,[7b] Avicel micro-crystalline cellulose (Funakoshi), Bondapak C_{18}/Porasil B (Waters Associates), and Kieselgel 60 (70—230 mesh; Merck). T.l.c. was conducted on precoated Kieselgel 60 F_{254} plates (0.20 mm; Merck) in the solvent systems (A) benzene–ethyl formate–formic acid (1:7:1, v/v); (B) benzene–ethyl formate–formic acid (1:5:2, v/v); and (C) benzene–ethanol (4:1, v/v), or on precoated cellulose F_{254} plates (0.10 mm; Merck) using the solvent systems (D) 2% acetic acid and (E) the upper layer of butan-1-ol–acetic acid–water (4:1:5, v/v). Spots on t.l.c. were detected by their blue fluorescence under u.v. light, and with iron(III) chloride or *p*-anisaldehyde–sulphuric acid spray. H.p.l.c. was carried out on a Toyo Soda apparatus equipped with an SP 8700 solvent delivery system and a UV-8 model II spectrophotometer using an LS-410 column (5 μm; 300 × 4 mm) (solvent: acetonitrile–50 × 10^{-3}M-sodium phosphate–water, 3:17 v/v). Analytical g.l.c. for sugars was conducted over 1.5% SE-30 (2 m × 4 mm) with nitrogen as the carrier gas. Ether refers to diethyl ether.

Isolation of the Tannins.—The air-dried bark (4.74 kg) of *Quercus stenophylla* was chopped into small pieces and extracted at room temperature with acetone–water (4:1, v/v). Concentration of the extract under reduced pressure (*ca.* 40 °C) gave an aqueous solution, which deposited resinous precipitates which were unaffected by the iron(III) chloride reagent. After removal of the precipitates, the filtrate was extracted successively with ether and ethyl acetate. The ethyl acetate layer, after concentration, was applied to a column (9.0 cm i.d. × 83 cm) of Sephadex LH-20. Elution with a solvent system of ethanol–water–acetone[7c] gave six fractions: I (95 g), II (26 g), III (6 g), IV (9 g), V (4 g), and VI (4 g), the first three containing lower-molecular-weight phenolic compounds. Fractions IV and V were separately chromatographed over Sephades LH-20 (4.0 cm i.d. × 41 cm) using a solvent system of methanol–water (2:3, v/v), followed by purification on an MCI-gel CHP-20P column (2.0 cm i.d. × 22 cm) with methanol–water (3:7, v/v), to yield casuariin (5) (56 mg) and castalagin (6) (32 mg), respectively. Chromatography of fraction VI over cellulose (3.6 cm i.d. × 28 cm) with 2% acetic acid and then over Sephadex LH-20 (7.5 cm i.d. × 30 cm) with ethanol gave casuarinin (4) (170 mg). The aqueous layer remaining after the ethyl acetate extraction was mixed with Celite-545 (1.2 kg), and the solvent was evaporated off under reduced pressure (*ca.* 40 °C). A brown powder thus obtained was packed in a glass column. Elution with acetone and evaporation of the solvent gave a dark brown gum, which was chromatographed over Sephadex LH-20 (11 cm i.d. × 55 cm) using water with increasing amounts of methanol. On monitoring with t.l.c. and h.p.l.c., the eluates were divided into six fractions: I′ (296 g), II′ (122 g), III′ (198 g), IV′ (41 g), V′ (138 g), and VI′ (68 g). Fraction I′ was successively chromatographed over MCI-gel CHP-20P (4.5 cm i.d. × 53 cm) with water, Sephadex LH-20 (2.2 cm i.d. × 55 cm) with water, and Bondapak C_{18}/Porasil B (2.5 cm i.d. × 28 cm) with methanol–water (19:1) to give castalin (7) (24 mg). Rechromatography of fraction III′ over MCI-gel CHP-20P (4.5 cm i.d. × 53 cm) using water with increasing amounts of methanol furnished stenophyllanin C (3) (1.5 g). Repeated chromatography of fraction V′ over Sephadex LH-20 (2.3 cm i.d. × 58 cm) with methanol–water (4:1, v/v) and cellulose (4.6 cm i.d. × 40 cm) with 2% acetic acid gave stenophyllanin A (2) (3.1 g) and an additional crop of casuarinin (4) (4.6 g). Fraction VI′ containing stenophyllanin B (2) as the major tannin was separated by chromatography over MCI-gel CHP-20P (4.5 cm i.d. × 53 cm) with methanol–water (3:2, v/v) and then over Sephadex LH-20 (3.6 cm i.d. × 55 cm) with a solvent system of ethanol–water–acetone (54:36:10, v/v) to yield pure stenophyllanin B (1) (3.7 g).

Stenophyllanin B (1). This *compound* was obtained as an off-white, amorphous powder, $[\alpha]_D^{20}$ +93.6° (c 0.97 in methanol) (Found: C, 52.6; H, 4.1. $C_{56}H_{40}O_{31}$·$4H_2O$ requires C, 52.5; H, 3.8%); R_F (B) 0.57, R_F (D) 0.41; *m/z* 1 209 [$(M + H)^+$, 13%, fast atom bombardment (FAB)], 1231 [$(M + Na)^+$, 5], 1 190 (10), 1 039 (6), 752 (7), 734 (11), and 304 (34); δ_H(CD_3COCD_3) 2.50 (1 H, dd, *J* 8 and 16 Hz, 4-H), 2.90 (1 H, dd, *J* 6 and 16 Hz, 4-H), 4.07 (1 H, d, *J* 12 Hz, 6″-H), 4.50 (1 H, d, *J* 8 Hz, 2-H), 4.68 (1 H, s, 1″-H), 4.79 (1 H, br s, 2″-H), 4.95 (1 H, dd, *J* 12 and 3 Hz, 6″-H), 5.21 (1 H, t, *J* 2 Hz, 3″-H), 5.60 (1 H, dd, *J* 8 and 3 Hz, 5″-H), 5.78 (1 H, dd, *J* 8 and 2 Hz, 4″-H), 5.95 (1 H, s, 8-H), 6.58, 6.59, 6.93 (each 1 H, s, H of HHDP*), 6.72 (1 H, d, *J* 8 Hz, 5′-H), 6.80 (1 H, dd, *J* 8 and 2 Hz, 6′-H), 6.91 (1 H, d, *J* 2 Hz, 2′-H), and 7.15 (2 H, s, galloyl H); δ_C(CD_3COCD_3) 31.6 (t, C-4), 38.3 (d, C-1″), 64.5 (t, C-6″), 68.2 (d, C-3), 71.3, 73.3, 74.9, 81.2 (each d, C-2″, C-3″, C-4″, and C-5″), 82.0 (d, C-2), 96.3 (d, C-8), 101.0 (s, C-4a), 107.5 (s, C-6), 105.9, 107.1, 108.8 (d, HHDP C-3 and C-3′), 110.1 (d, galloyl C-2 and C-6), 115.1, 115.5 (d, C-2′ and C-5′), 115.7, 116.0, 116.8 (s, HHDP C-1 and C-1′), 120.0 (d, C-6′), 120.9 (s, galloyl C-1), 122.3, 124.0, 125.1, 127.0, 128.0 (each s, HHDP C-2 and C-2′), 131.9 (s, C-1′), 135.1, 136.2, 136.8, 137.6 (each s, HHDP C-5 and C-5′), 139.4 (s, galloyl C-4), 143.0, 144.4, 145.3, 145.7, 146.1 (each s, HHDP C-4, C-4′, C-6 and C-6′, and C-3′, C-4′), 155.0, 155.2, 155.9 (each s, C-5, C-7 and C-8a), and 165.9, 167.1, 168.3, 169.0, 169.7 p.p.m. (CO_2).

Oxidative Degradation with Iron(III) *Chloride.*—Stenophyllanin B (1) (10 mg) was heated for 80 h under reflux in aqueous 10% iron(III) chloride (1.5 ml). The mixture was diluted with water and neutralized with Amberlite MB-3. The almost colourless solution was concentrated to dryness and the residue

* HHDP = Hexahydroxydiphenoyl.

was trimethylsilylated with a few drops of *N*-trimethylsilylimidazole. G.l.c. analysis showed peaks (R_t 13.6, 20.4 min; column temp. 150 °C; flow rate 50 ml min^{-1} and R_t 9.0, 10.2 min; column temp. 130 °C; flow rate 50 ml min^{-1}) corresponding to the trimethylsilyl derivatives of glucose and arabinose, respectively.

Acid-catalysed Degradation.—Stenophyllanin B (**1**) (200 mg) was refluxed for 90 h in ethanol containing acetic acid (3 ml). Evaporation of the solvent gave a pale brown powder, which was applied to a column of Sephadex LH-20. Elution with methanol–water (4:1, v/v) yielded relatively non-polar compounds, which were separated by chromatography over MCI-gel CHP-20P using methanol–water (3:7, v/v) to yield (+)-catechin (**8**) (9 mg) as colourless needles (from water), m.p. 171 °C, $[\alpha]_D^{24}$ +13.7° (*c* 0.12 in acetone), identified by i.r. and t.l.c. comparisons with an authentic sample.

Enzymatic Hydrolysis with Tannase.—To a solution of stenophyllanin B (**1**) (100 mg) in water (20 ml) was dropwise added (at 37 °C) tannase dissolved in 0.1M-acetate buffer (pH 5.4; 100 ml) and the mixture was further incubated at 37 °C for 50 min. Evaporation of the solvent afforded a gum, which was treated with methanol. The methanol-soluble portion was applied to an MCI-gel CHP-20P column in methanol–water (1:4, v/v) to give gallic acid (9 mg) and *5″-desgalloylstenophyllanin B* (**9**) (20 mg) as an off-white, amorphous powder, $[\alpha]_D^{24}$ +108.1° (*c* 0.69 in methanol) (Found: C, 52.8; H, 4.0. $C_{49}H_{36}O_{27}\cdot 3H_2O$ requires C, 53.0; H, 3.8%); R_F(E) 0.18; *m/z* 1 057 [(*M* + H)$^+$, 11%, FAB], 1 079 (5), and 1 038 (2); $\delta_H(CD_3COCD_3)$ 2.50 (1 H, dd, *J* 8 and 16 Hz, 4-H), 2.90 (1 H, dd, *J* 6 and 16 Hz, 4-H), 4.50 (1 H, d, *J* 8 Hz, 2-H), 4.69 (1 H, s, 1″-H), 4.80 (1 H, br s, 2″-H), 5.26 (1 H, br s, 3″-H), 5.50 (1 H, br d, *J* 8 Hz, 4″-H), 5.95 (1 H, s, 8-H), 6.49, 6.56, 6.83 (each 1 H, s, H of HHDP), and 6.7—6.9 (3 H, m, H of catechin B-ring); $\delta_C(CD_3COCD_3)$ 31.8 (C-4), 37.9 (C-1″), 67.9 (C-5″ and C-6″), 68.4 (C-3), 75.8, 76.3, 81.6, (C-2″, C-3″ and C-4″), 81.9 (C-2), 96.1 (C-8), 100.8 (C-4a), 105.7 (C-6), 107.2, 108.8 (HHDP C-3 and C-3′), 115.4, 115.9 (C-2′ and C-5′), 115.9, 116.8 (HHDP C-1 and C-1′), 120.0 (C-6′), 122.4, 123.8, 125.3, 127.1, 127.8 (HHDP C-2 and C-2′), 131.4 (C-1′), 135.1, 135.8, 136.5, 137.8 (HHDP C-5 and C-5′), 143.2, 144.4, 145.1, 145.4, 145.5, 145.7 (HHDP C-4, C-4′, C-6 and C-6′, and C-3′, C-4′), 154.7, 155.9 (C-5, C-7 and C-8a), and 168.6, 169.9, 170.8 p.p.m. (CO_2).

Nona-O-methylstenophyllanin B (**10**).—A mixture of stenophyllanin B (**1**) (1.2 g), anhydrous potassium carbonate (8.0 g), and dimethyl sulphate (5 ml) in dry acetone (40 ml) was refluxed for 4 h with stirring. After the removal of inorganic salts, the filtrate was concentrated to a syrup, which was chromatographed over silica gel. Elution with benzene–acetone (17:3, v/v) gave the *nonadeca-O-methyl ether* (**10**) as a pale yellow amorphous powder, $[\alpha]_D^{23}$ +47.9° (*c* 0.41 in chloroform) (Found: C, 60.4; H, 5.3. $C_{75}H_{78}O_{31}\cdot H_2O$ requires C, 60.3; H, 5.4%); *m/z* 1 474 [M^+, 100%, field desorption (FD)]; $\delta_H(CDCl_3)$ 2.5—3.3 (2 H, m, 4-H), 3.37—4.08 (OMe), 4.24 (1 H, d, *J* 14 Hz, 6″-H), 4.48 (1 H, s, 1″-H), 4.62 (1 H, d, *J* 8 Hz, 2-H), 4.73 (1 H, br s, 2″-H), 4.9—5.1 (2 H, m, 3″-H and 6″-H), 5.42 (1 H, dd, *J* 8 and 2 Hz, 5″-H), 5.75 (1 H, dd, *J* 8 and 2 Hz, 4″-H), 6.18 (1 H, s, 8-H), 6.56, 6.70, 7.12 (each 1 H, s, H of HMDP*), 6.9—7.1 (3 H, H of catechin B-ring), and 7.31 (2 H, s, galloyl H).

The *monoacetate* (prepared with acetic anhydride and pyridine) was obtained as a white amorphous powder, $[\alpha]_D^{24}$ + 59.8° (*c* 0.19 in chloroform) (Found: C, 61.5; H, 5.5. $C_{77}H_{80}O_{32}$ requires C, 61.0; H, 5.3%); R_F(C) 0.72; *m/z* 1 516 (M^+, 100%, FD), 1 474 (3), and 1 456 (2); $\delta_H(CDCl_3)$ 1.91 (3 H, s, OAc), 2.6—3.3 (2 H, m, 4-H), 3.4—4.1 (OMe), and 6.24 (1 H, s, 8-H).

Methanolysis of the Methyl Ether (**10**) *with Methanolic Sodium Methoxide.*—The nonadecamethyl ether (**10**) (180 mg) was stirred at room temperature in methanol (30 ml) containing sodium methoxide (600 mg). After 85 h, the mixture was neutralized with Dowex 50W-X8 (H^+ form) resins, and the solution was concentrated to a syrup, which was chromatographed over silica gel. Elution with benzene–ethanol (9:1, v/v) yielded methyl tri-*O*-methylgallate as colourless prisms (from methanol) (25 mg), m.p. 81—83 °C, and dimethyl (*S*)-4,4′,5,5′,6,6′-hexamethoxybiphenyl-2,2′-dicarboxylate (**11**) as a colourless syrup (50 mg), $[\alpha]_D^{24}$ −27.8° (*c* 1.3 in chloroform), identified by t.l.c. and i.r. comparisons with authentic samples. Subsequent elution with benzene–ethanol (4:1, v/v) gave the *hydrolysate* (**12**) as colourless prisms (from methanol) (55 mg), m.p. 156—157 °C, $[\alpha]_D^{23}$ +107.3° (*c* 0.67 in chloroform) (Found: C, 59.0; H, 6.1. $C_{56}H_{64}O_{25}$ requires C, 59.2; H, 5.7%); R_F(C) 0.42; *m/z* 927 [(*M* + H)$^+$, 100%, FD]; $\delta_H(CDCl_3)$ 2.5—3.0 (2 H, m, 4-H), 3.5—3.9 (OMe), 4.63 (1 H, dd, *J* 4 and 7 Hz, 2″-H), 4.70 (1 H, d, *J* 8 Hz, 2-H), 5.04 (1 H, d, *J* 4 Hz, 1″-H), 6.29 (1 H, s, 8-H), 6.87 (1 H, d, *J* 8 Hz, 5′-H), 6.93 (1 H, d, *J* 2 Hz, 2′-H), 6.97 (1 H, dd, *J* 8 and 2 Hz, 6′-H), and 7.36 (1 H, s, H of HMDP); $\delta_C(CDCl_3)$ 31.1 (C-4), 52.1, 55.7, 56.0, 60.2, 60.5, 60.7, 60.8 (OMe), 63.6 (C-6″), 67.6 (C-3), 70.9, 71.7, 83.5 (C-2″, C-3″, C-4″ and C-5″), 81.5 (C-2), 96.6 (C-8), 106.3 (C-4a), 115.4 (C-6), 157.2, 157.4, 157.5 (C-5, C-7, and C-8a), and 163.6, 167.2 p.p.m. (CO_2).

The *penta-acetate* of the hydrolysate (**12**) was obtained as a white amorphous powder, $[\alpha]_D^{26}$ +104.5° (*c* 0.29 in chloroform) (Found: C, 59.0; H, 6.1. $C_{56}H_{64}O_{35}$ requires C, 59.2; H, 5.7%); R_F(C) 0.69; *m/z* 1 136 (M^+, 100%, FD), 1 076 (1.5), and 1 051 (1); $\delta_H(CDCl_3)$ 1.97, 2.02, 2.04 (each 3 H, s, OAc), 2.00 (6 H, s, 2 × OAc), 2.5—3.0 (2 H, m, 4-H), 3.5—4.0 (OMe), 6.34 (1 H, s, 8-H), 6.81 (1 H, d, *J* 8 Hz, 5′-H), 6.87 (1 H, d, *J* 2 Hz, 2′-H), 6.93 (1 H, dd, *J* 8 and 2 Hz, 6′-H), and 7.37 (1 H, s, H of HMDP).

Oxidation of the Methanolysate (**12**) *with Sodium Periodate, followed by Reduction with Sodium Borohydride.*—The methanolysate (**12**) (62 mg) was kept at room temperature in methanol (5 ml) and water (0.5 ml) containing sodium periodate (50 mg). After 22 h, the mixture was poured into water, and the resulting white precipitates were collected by filtration. Purification on a silica gel column using benzene–ethanol (9:1, v/v) yielded an aldehyde as a white amorphous powder, $[\alpha]_D^{26}$ +139.6° (*c* 0.43 in chloroform); *m/z* 834 (M^+, 22%, EI), 806 (29), 627 (28), 346 (20), and 180 (39); $\delta_H(CDCl_3)$ 2.76 (1 H, dd, *J* 16 and 8 Hz, 4-H), 3.15 (1 H, dd, *J* 16 and 4 Hz, 4-H), 4.72 (1 H, d, *J* 8 Hz, 2-H), 4.73 (1 H, d, *J* 1 Hz, 2″-H), 5.36 (1 H, d, *J* 1 Hz, 1″-H), 6.28 (1 H, s, 8-H), 6.89 (1 H, d, *J* 8 Hz, 5′-H), 6.96 (1 H, d, *J* 2 Hz, 2′-H), 7.00 (1 H, dd, *J* 8 and 2 Hz, 6′-H), 7.35 (1 H, s, H of HMDP), and 9.75 (1 H, s, 3″-H); $\delta_C(CDCl_3)$ 28.2 (C-4), 30.7 (C-1″), 51.8, 55.6, 55.9, 59.8, 60.7 (OMe), 67.6 (C-3), 81.7 (C-2), 85.8 (C-2″), 96.4 (C-8), 106.4 (C-4a), 119.8 (C-6), 166.6 (CO_2), and 199.9 p.p.m. (CHO).

The aldehyde (46 mg) in methanol (2 ml) was treated with sodium borohydride (20 mg) at room temperature. After 20 min, the excess of reagent was decomposed by adding acetic acid and the solution was concentrated to a syrup, which was chromatographed over silica gel. Elution with benzene–acetone (3:1, v/v) and crystallisation of the eluate from methanol furnished the *alcohol* (**13**) (44 mg) as colourless prisms, m.p. 167—168 °C, $[\alpha]_D^{26}$ +124.0° (*c* 0.52 in chloroform) (Found: C, 60.0; H, 6.0. $C_{43}H_{48}O_{17}\cdot 1.5H_2O$ requires C, 59.8; H, 6.0%); R_F(C) 0.62; *m/z* 836 (M^+, 3%, EI), 657 (20), 625 (11), 359 (6), and 180 (48); $\delta_H(CDCl_3)$ 2.07 (1 H, d, *J* 4 Hz, OH, disappeared on addition of D_2O), 2.6—3.4 (2 H, m, 4-H), 3.5—3.95 (OMe), 4.62 (1 H, dd, *J* 4 and 10 Hz, 2″-H), 4.72 (1 H, d, *J* 8 Hz, 2-H), 4.95 (1 H, d, *J* 4 Hz, 1″-H), 6.29 (1 H, s, 8-H), 6.88 (1 H, d, *J* 8 Hz, 5′-H),

* HMDP = Hexamethoxydiphenoyl.

6.95 (1 H, d, *J* 2 Hz, 2'-H), 7.00 (1 H, dd, *J* 8 and 2 Hz, 6'-H), and 7.36 (1 H, s, H of HMDP); $\delta_C(CDCl_3)$ 28.4 (C-4), 31.1 (C-1''), 51.8, 55.5, 56.0, 60.4, 60.5, 60.8 (OMe), 64.1 (C-3''), 67.9 (C-3), 81.8 (C-2 and C-2''), 96.4 (C-8), 106.4 (C-4a), 109.2 (C-5'), 109.9 (HMDP C-3), 111.3 (C-2'), 115.7 (C-6), 119.9 (C-6'), 130.2 (C-1'), and 163.2, 166.8 p.p.m. (CO_2); c.d. (*c* 1.1 × 10^{-5} in methanol) $[\theta]_{225}$ +1.34 × 10^5, $[\theta]_{267}$ +0.21 × 10^5, $[\theta]_{287}$ −0.11 × 10^5, and $[\theta]_{313}$ +0.36 × 10^5.

Stenophyllanin A (**2**).—This compound was obtained as an off-white, amorphous powder, $[\alpha]_D^{28}$ +48.1° (*c* 1.2 in methanol) (Found: C, 54.5; H, 3.7. $C_{56}H_{40}O_{31}\cdot1.5\ H_2O$ requires C, 54.4; H, 3.5%); R_F(B) 0.61, R_F(D) 0.37; *m/z* 1 209 [$(M + H)^+$, 71%, FAB], 1 190 (13), 1 057 (12), and 1 039 (9); $\delta_H(CD_3COCD_3)$ 2.3—3.2 (2 H, m, 4-H), 4.41 (1 H, br s, 1''-H), 5.92 (1 H, br s, 6-H), and 6.5—7.1 (aromatic H); $\delta_C(CD_3COCD_3)$ 31.6 (C-4), 38.3 (C-1''), 64.8 (C-6''), 67.7 (C-3), 69.8, 73.1, 74.2, 81.4 (C-2'', C-3'', C-4'', and C-5''), 82.4 (C-2), 96.5 (C-6), 101.0 (C-4a), 105.1, 105.7, 108.8 (HHDP C-3 and C-3'), 107.6 (C-6), 110.0 (galloyl C-2 and C-6), 114.8, 115.7 (C-2' and C-5'), 116.4, 116.8 (HHDP C-1 and C-1'), 120.5 (C-6' and galloyl C-1), 123.3, 125.2, 126.8, 127.7 (HHDP C-2 and C-2'), 131.5 (C-1'), 135.1, 116.4, 116.8 (HHDP C-1 and C-1'), 120.5 (C-6' and galloyl C-1), 123.3, 125.2, 126.8, 127.7 (HHDP C-2 and C-2'), 131.5 (C-1'), 135.1, 136.2, 136.6, 137.7 (HHDP C-5 and C-5'), 139.5 (galloyl C-4), 142.9, 144.1, 144.4, 144.5, 145.3, 145.7, 145.8 (C-3' and C-4', and HHDP C-4, C-4', C-6 and C-6'), 153.8, 155.3, 156.3 (C-5, C-7, and C-8a), and 166.4, 168.0, 168.6, 169.3 p.p.m. (2 × C) (CO_2).

Oxidative Degradation with Iron(III) *Chloride.*—Stenophyllanin A (**2**) (20 mg) was refluxed for 80 h with 10% iron(III) chloride in water (2 ml). Work-up as above gave sugars which were analysed as their trimethylsilyl ethers by g.l.c. (glucose R_t 19.4, 31.9 min; column temp. 150 °C; flow rate 40 ml min^{-1}, and arabinose R_t 12.5, 14.2 min; column temp. 130 °C; flow rate 40 ml min^{-1}).

Enzymatic Hydrolysis with Tannase.—Stenophyllanin A (**2**) (400 mg) in water (40 ml) was treated with tannase in the same way as described for stenophyllanin B (**1**), and the reaction mixture was worked up similarly to give gallic acid (56 mg) and stenophyllanin C (3) (145 mg), the latter being identified by n.m.r. spectroscopy (see below).

*Nonadeca-*O*-methylstenophyllanin A* (**16**).—A mixture of stenophyllanin A (**2**) (200 mg), dimethyl sulphate (1 ml), and anhydrous potassium carbonate (1.5 g) in dry acetone (20 ml) was heated under reflux for 3.5 h, and the reaction mixture was treated in the same way as described above to give the *nonadeca-*O*-methyl ether* (**16**) as a pale yellow amorphous powder, $[\alpha]_D^{28}$ −17.5° (*c* 1.3 in chloroform) (Found: C, 60.4; H, 5.5. $C_{75}H_{78}O_{31}\cdot H_2O$ requires C, 60.3; H, 5.4%); *m/z* 1 474 (M^+, 100%, FD); $\delta_H(CDCl_3)$ 2.5—2.8 (2 H, m, 4-H), 3.44—4.10 (OMe), 4.67 (1 H, s, 1''-H), 4.72 (1 H, d, *J* 8 Hz, 2-H), 5.30 (1 H, dd, *J* 2 and 8 Hz, 5''-H), 5.56 (1 H, dd, *J* 4 and 8 Hz, 4''-H), 6.00 (1 H, s, 6-H), and 6.5—7.15 (8 H, m, aromatic H).

The *monoacetate* was obtained as a white amorphous powder, $[\alpha]_D^{17}$ −6.0° (*c* 0.63 in chloroform) (Found: C, 60.8; H, 5.5. $C_{77}H_{80}O_{32}$ requires C, 61.0; H, 5.3%); R_F(C) 0.72; *m/z* 1 516 (M^+, 100%, FD); $\delta_H(CDCl_3)$ 1.86 (3 H, s, OAc), 2.5—2.8 (2 H, m, 4-H), 3.6—4.1 (OMe), 4.24 (1 H, dd, *J* 4 and 14 Hz, 6''-H), 4.64 (1 H, s, 1''-H), 6.00 (1 H, s, 6-H), and 6.6—7.35 (8 H, m, aromatic H).

Methanolysis of the Methyl Ether (**16**) *with Methanolic Sodium Methoxide.*—The nonadecamethyl ether (**16**) (230 mg) was treated with sodium methoxide (400 mg) in methanol (20 ml) at room temperature for 80 h, and the reaction mixture was worked up as before to give methyl tri-*O*-methylgallate (27 mg) and dimethyl (*S*)-4,4',5,5',6,6'-hexamethoxybiphenyl-2,2'-dicarboxylate (**11**) (58 mg), $[\alpha]_D^{24}$ −27.3° (*c* 0.36 in chloroform). The *methanolysate* (**17**) was obtained from the fraction eluted later as a white amorphous powder, $[\alpha]_D^{24}$ +105.3° (*c* 0.87 in chloroform) (Found: C, 57.1; H, 5.8. $C_{46}H_{54}O_{20}\cdot2H_2O$ requires C, 57.4; H, 6.1%); R_F(C) 0.42; *m/z* 926 (M^+, 100%, FD); $\delta_H(CDCl_3)$ 4.60 (1 H, dd, *J* 3 and 7 Hz, 2''-H), 5.03 (1 H, d, *J* 7 Hz, 2-H), 5.12 (1 H, d, *J* 3 Hz, 1''-H), 6.01 (1 H, s, 6-H), 6.84 (1 H, d, *J* 8 Hz, 5'-H), 6.99 (1 H, dd, *J* 2 and 8 Hz, 6'H), 7.02 (1 H, d, *J* 2 Hz, 2'-H), and 7.32 (1 H, s, H of HMDP); $\delta_C(CDCl_3)$ 25.5 (C-4), 30.1 (C-1''), 52.1, 55.3, 55.7, 56.0, 60.5, 60.7, 60.8 (OMe), 63.7 (C-6''), 67.2 (C-3), 70.4, 71.6 (2 × C), 83.0 (C-2'', C-3'', C-4'' and C-5''), 80.8 (C-2), 89.3 (C-6), 101.5 (C-4a), 109.1 (2 × C), 109.6 (C-2', C-5' and HMDP C-3), 111.3 (C-8), 118.8 (C-6'), and 163.6, 167.3 p.p.m. (CO_2); c.d. (*c* 1.1 × 10^{-5} in methanol) $[\theta]_{225}$ +1.72 × 10^5, $[\theta]_{265}$ +0.31 × 10^5, $[\theta]_{287}$ −0.94 × 10^5, and $[\theta]_{315}$ +0.24 × 10^5.

The *penta-acetate* of the methanolysate (**17**) was obtained as a white amorphous powder, $[\alpha]_D^{24}$ +108.5° (*c* 0.22 in chloroform) (Found: C, 58.9; H, 5.8. $C_{56}H_{64}O_{25}$ requires C, 59.2; H, 5.7%); R_F(C) 0.70; *m/z* 1 136 (M^+, 100%, FD), 1 076 (4), 1 051 (2), and 1 007 (2); $\delta_H(CDCl_3)$ 1.87, 2.00 (each 3 H, s, OAc), 1.95 (9 H, s, 3 × OAc), 2.5—2.8 (2 H, m, 4-H), 4.42—4.96 (OMe), 4.09 (1 H, d, *J* 16 Hz, 6''-H), 5.38 (1 H, dd, *J* 8 and 3 Hz, 4''-H), 6.09 (1 H, s, 6-H), 6.8—7.1 (3 H, m, catechin B-ring proton), and 7.38 (1 H, s, H of HMDP).

Oxidation of the Methanolysate (**17**) *with Sodium Periodate, followed by Reduction with Sodium Borohydride.*—The methanolysate (**17**) (80 mg) in methanol (2 ml) and water (1 ml) was stirred at room temperature with sodium periodate (45 mg) for 13 h. The mixture was diluted with water and resulting white precipitates were collected by filtration. Reduction of the aldehyde with sodium borohydride (40 mg) in methanol (5 ml) and water (1 ml) at room temperature for 5 h, and chromatography over silica gel using benzene–acetone (3:1, v/v) furnished an *alcohol* as a white amorphous powder (47 mg), $[\alpha]_D^{24}$ +110.1° (*c* 0.14 in chloroform) (Found: C, 59.0; H, 5.7. $C_{43}H_{48}O_{17}\cdot2H_2O$ requires C, 59.2; H, 6.0%); R_F(C) 0.63; *m/z* 836 (M^+, 100%, EI), 818 (19), 787 (17), 657 (36), 625 (46), 359 (5), and 180 (25); $\delta_H(CDCl_3)$ 2.61 (1 H, dd, *J* 16 and 8 Hz, 4-H), 2.98 (1 H, dd, *J* 16 and 6 Hz, 4-H), 3.5—3.9 (OMe), 4.66 (1 H, dd, *J* 5 and 10 Hz, 2''-H), 4.77 (1 H, d, *J* 7 Hz, 2-H), 5.04 (1 H, d, *J* 5 Hz, 1''-H), 6.08 (1 H, s, 6-H), 6.8—7.0 (3 H, m, catechin B-ring proton), and 7.34 (1 H, s, H of HMDP).

Condensation of Casuarinin (**4**) *with* (+)*-Catechin* (**8**).—A mixture of casuarinin (**4**) (1.98 g) and (+)-catechin (**8**) (0.64 g) in dry dioxane containing toluene-*p*-sulphonic acid (0.2 g) was heated under reflux for 6 h. The solvent was evaporated under reduced pressure, and the residue was chromatographed over Sephadex LH-20 using methanol–water (4:1, v/v). Rechromatography over Sephadex LH-20 using water with increasing amounts of ethanol (up to 40%), and purification on an MCI-gel CHP-20P column with methanol–water (1:3, v/v) gave, together with unchanged casuarinin (**4**) (1.2 g), stenophyllanin A (**2**) (102 mg), identified by h.p.l.c., t.l.c. and ^1H n.m.r. comparison.

Stenophyllanin C (**3**).—This compound was obtained as an off-white, amorphous powder, $[\alpha]_D^{21}$ +80.7° (*c* 1.30 in methanol) (Found: C, 53,4; H, 3.8. $C_{49}H_{36}O_{27}\cdot2.5H_2O$ requires C, 53.4; H, 3.8%); R_F(B) 0.54; R_F(E) 0.17; *m/z* 1 057 [$(M + H)^+$, 17%, FAB], 1 038 (3), and 905 (5); $\delta_H(CD_3COCD_3)$ 2.54 (1 H, dd, *J* 6 and 16 Hz, 4-H), 2.89 (1 H, dd, *J* 4 and 16 Hz, 4-H), 5.96 (1 H, s, 6-H), and 6.28—7.02 (6 H, m, aromatic H); $\delta_C(CD_3COCD_3\text{–}D_2O)$ 38.1 (C-1''), 67.7, 68.8, 76.1 (2 × C), 80.9

(C-2″, C-3″, C-4″, C-5″ and C-6″), 81.8 (C-2), 96.6 (C-6), 100.4 (C-4a), 105.4, 105.5, 108.8 (HHDP C-3 and C-3′), 107.4 (C-8), 114.8, 116.0 (C-2′ and C-5′), 120.5 (C-6′), 122.9, 125.5, 127.2, 127.9 (HHDP C-2 and C-2′), 131.6 (C-1′), 135.1, 135.9, 136.5, 137.7 (HHDP C-5 and C-5′), 143.0, 144.3, 145.2, 145.6 (C-3′ and C-4′, and HHDP C-4, C-4′, C-6 and C-6′), 153.4, 155.3, 156.0 (C-5, C-7, and C-8a), and 168.1, 168.4, 169.7, 170.6 p.p.m. (CO_2).

Hexadeca-O-methylstenophyllanin C (**19**).—Stenophyllanin C (**3**) was methylated in the same way as described above to yielded the *hexadeca-O-methyl ether* (**19**) as a white amorphous powder, $[\alpha]_D^{20}$ $-20.6°$ (*c* 1.25 in chloroform) (Found: C, 60.1; H, 5.3. $C_{65}H_{68}O_{27}\cdot H_2O$ requires C, 60.1; H, 5.4%); *m/z* 1 280 (M^+, 100%, FD); $\delta_H(CDCl_3)$ 2.5—2.8 (2 H, m, 4-H), 3.44—4.08 (OMe), 4.64 (1 H, s, 1″-H), 6.00 (1 H, s, 6-H), and 6.53—6.94 (6 H, m, aromatic H).

The *diacetate* was obtained as a white amorphous powder, $[\alpha]_D^{20}$ $-10.5°$ (*c* 0.75 in chloroform) (Found: C, 60.3; H, 5.4. $C_{69}H_{72}O_{29}$ requires C, 60.7; H, 5.3%); $\delta_H(CDCl_3)$ 1.85, 2.01 (each 3 H, s, OAc), 2.5—2.9 (2 H, m, 4-H), 3.42—4.09 (OMe), 6.00 (1 H, s, 6-H), and 6.55—7.24 (6 H, m, aromatic H).

Casuarinin (**4**).—This compound was obtained as an off-white, amorphous powder, $[\alpha]_D^{18}$ $+45.4°$ (*c* 0.57 in methanol); R_F(D) 0.32, R_F(E) 0.18; $\delta_H(CD_3COCD_3)$ 4.07 (1 H, d, *J* 14 Hz, 6-H), 4.66 (1 H, d, *J* 4 Hz, 2-H), 4.88 (1 H, dd, *J* 14 and 3 Hz, 6-H), 5.14 (1 H, dd, *J* 8 and 3 Hz, 5-H), 5.46 (2 H, m, 3- and 4-H), 5.62 (1 H, d, *J* 4 Hz, 1-H), 6.49, 6.55, 6.77 (each 1 H, s, H of HHDP), and 7.10 (2 H, s, galloyl H); $\delta_C(CD_3COCD_3-D_2O)$ 165.3, 166.0, 168.4, 168.9, and 169.3 p.p.m. (CO_2). The ^1H and ^{13}C n.m.r. spectra were identical with those reported before.[8]

Hydrolysis with tannase gave casuariin (**5**) (see below) and gallic acid.

Methylation in the same way as described above yielded the pentadeca-*O*-methyl ether as a pale yellow amorphous powder, $[\alpha]_D^{23}$ $-39.6°$ (*c* 1.73 in chloroform) $\delta_H(CDCl_3)$ 3.42—4.00 (OMe), 4.21 (1 H, d, *J* 14 Hz, 6-H), 4.44 (1 H, s, 1-H), 5.00 (1 H, dd, *J* 3 and 14 Hz, 6-H), 5.32 (1 H, t, *J* 2 Hz, 3-H), 5.48 (1 H, dd, *J* 8 and 3 Hz, 5-H), 5.71 (1 H, dd, *J* 8 and 3 Hz, 4-H), 6.53, 6.72, 7.09 (each 1 H, s, H of HHDP), and 7.37 (2 H, s, galloyl H).

Casuariin (**5**).—This compound was obtained as an off-white, amorphous powder, $[\alpha]_D^{21}$ $+149.7°$ (*c* 1.1 in methanol); R_F(B) 0.47; $\delta_H(CD_3COCD_3)$ 3.91 (1 H, d, *J* 12 Hz, 6-H), 4.15 (1 H, dd, *J* 8 and 3 Hz, 5-H), 4.69 (1 H, dd, *J* 12, 3 Hz, 6-H), 4.76 (1 H, dd, *J* 5 and 3 Hz, 2-H), 5.10 (1 H, dd, *J* 8 and 3 Hz, 4-H), 5.50 (1 H, t, *J* 3 Hz, 3-H), 5.68 (1 H, d, *J* 5 Hz, 1-H), and 6.44, 6.54, 6.76 (each 1 H, s, H of HHDP); $\delta_C(CD_3COCD_3)$ 165.0, 168.7, 169.5, and 170.4 p.p.m. (CO_2). The spectral characteristics coincided with those reported previously.[8]

Castalagin (**6**).—This compound was obtained as an off-white, amorphous powder, $[\alpha]_D^{26}$ —99.9° (*c* 0.52 in methanol); R_F(D) 0.53; $\delta_H(CD_3OD-C_6D_6)$ 3.92 (1 H, d, *J* 12 Hz, 6-H), 5.08 (1 H, d, *J* 6 Hz, 2-H), 4.08—5.18 (2 H, 6-and 3-H), 5.23 (1 H, t, *J* 6 Hz, 4-H), 5.57 (1 H, d, *J* 4 Hz, 1-H), 5.5—5.7 (1 H, m, 5-H), and 6.58, 6.82, 6.85 (each 1 H, s, H of HHDP); $\delta_C(CD_3COCD_3)$ 164.3, 165.3, 166.3, 166.8, and 168.8 p.p.m. (CO_2). The ^1H n.m.r. spectrum was identical with that described in the literature.[9]

Castalin (**7**).—This compound was obtained as an off-white, amorphous powder, $[\alpha]_D^{17}$ $+14.4°$ (*c* 0.46 in water) R_F(E) 0.11; *m/z* 633 [$(M + H)^+$, 19%, FAB], 655 [$(M + Na)^+$, 2%]; $\delta_H(CD_3COCD_3-D_2O)$ 4.98 (1 H, dd, *J* 2 and 6 Hz, 3-H), 5.16 (1 H, m, 5-H), 5.18 (1 H, dd, *J* 5 and 2 Hz, 2-H), 5.62 (1 H, d, *J* 5 Hz, 1-H), and 6.79 (1 H, s, H of HHDP); $\delta_C(CD_3COCD_3-D_2O)$ 165.3, 166.3, and 168.1 p.p.m. (CO_2). The ^1H n.m.r. spectrum was identical with that described in the literature.[10]

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