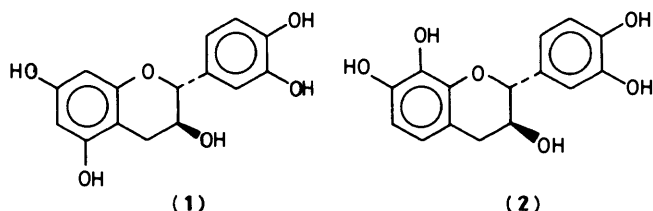


## Synthesis of Condensed Tannins. Part 19. Phenol Oxidative Coupling of (+)-Catechin and (+)-Mesquitol. Conformation of Bis-(+)-Catechins

Desmond A. Young, Esmé Young, David G. Roux, E. Vincent Brandt, and Daneel Ferreira\*  
 Department of Chemistry, University of the Orange Free State, P.O. Box 339, Bloemfontein, 9300 South Africa

Phenol oxidative coupling of (2*R*,3*S*)-2,3-*trans*-3',4',5,7-tetrahydroxyflavan-3-ol[(+)-catechin] generates low yields of ether-{{[3'*O*,8]- and [4'*O*,8]-} and atropisomeric carbon-linked {[2',8]-, [2',6]-, and [6',8]-} bis-(+)-catechins. The isomeric structures were differentiated by nuclear Overhauser effect difference spectroscopy. Extension of condensation of (+)-catechin with (2*R*,3*S*)-2,3-*trans*-3',4',7,8-tetrahydroxyflavan-3-ol[(+)-mesquitol] readily affords the four atropisomeric [5,6:5,8]-bis-[(+)-mesquitol]-(+)-catechins previously encountered in the heartwood of *Prosopis glandulosa* ('Mesquite').

We have recently<sup>1,2</sup> demonstrated the natural occurrence of a new class of condensed tannins in the heartwood of *Prosopis glandulosa* ('Mesquite'). These oligomers, based on bi- and terphenyl type flavan-3-ols, presumably originate from oxidative phenol coupling of the predominant metabolite, (2*R*,3*S*)-2,3-*trans*-3',4',7,8-tetrahydroxyflavan-3-ol[(+)-mesquitol (2)]



to give [5,6]-bis-(+)-mesquitol and similar condensation with (+)-catechin (1) [(2*R*,3*S*)-2,3-*trans*-3',4',5,7-tetrahydroxyflavan-3-ol], leading to atropisomeric [5,8]-(+)-mesquitol-(+)-catechins and [5,6:5,8]-bis-[(+)-mesquitol]-(+)-catechins. Structural elucidation of these analogues and also definition of the conformations of the atropisomeric [5,8]-biphenyl type biflavan-3-ols, were accomplished by nuclear Overhauser effect (n.O.e.) difference spectroscopy (<sup>1</sup>H homonuclear). During the course of structural confirmation of the dimeric homologues by synthesis *via* phenol oxidative coupling, an increased rate of crossed condensations compared with competing self-condensation of either (+)-mesquitol (2) or (+)-catechin (1) was evident. These observations prompted detailed investigation of the oxidative dimerization of (+)-catechin and also extension of 'mixed' coupling with (+)-mesquitol aimed at formation of the [5,6:5,8]-*m*-terphenyl type triflavan-3-ols.

### Results and Discussion

Treatment of (+)-catechin (1) with K<sub>3</sub>[Fe(CN)<sub>6</sub>] in an acetonitrile-glycine buffer<sup>3</sup> over 48 h leads to a low percentage conversion into a complex mixture consisting of C-C- [(3), (5), (7), (9), (11), and (17)] and O-C- [(13) and (15)] bis-(+)-catechins. These different classes of compounds were differentiated by means of 300 MHz <sup>1</sup>H n.m.r. spectroscopy of their methyl ether acetates [e.g. (4)].

The regio-isomeric [2',8]- and [6',8]-C-C linked analogues [(4) and (6), (8), and (10) respectively], obtained as stable atropisomeric pairs in each instance, were readily distinguished by differing <sup>1</sup>H n.m.r. splitting patterns of their residual B-ring

protons [AB-systems each for (4) (δ 6.733 and 6.944, both d, *J* 8.5 Hz) and (6) (δ 6.80 and 7.067, both d, *J* 8.5 Hz) and two singlets each for (8) (δ 6.95 and 6.65), and (10) (δ 6.852 and 6.06)]. Linkage to C-8 of the D-ring followed from chemical-shift values of the respective 6-protons<sup>4,5</sup> [δ 6.183 and 6.177 (each s) for (4) and (6); δ 6.138 and 6.165 (each s) for (8) and (10)]. Allocation of the remaining systems was effected by extensive spin-spin decoupling experiments using the broadened 6'- [(4) and (6)] or 2'- [(8) and (10)] protons as reference signals.

The [2',8]-conformers (4) and (6) gave sharply defined <sup>1</sup>H n.m.r. spectra over the range 25–180 °C. In the case of the [6',8]-atropisomers (8) and (10), however, slow racemization sets in at *ca.* 130 °C reaching an approximate 3:2 equilibrium between *R* and *S* forms (see below) at 180 °C with evidence of exchange from partially broadened resonances. The exceptionally high stabilities of atropisomeric derivatives of the [2',8]- and [6',8]-bis-(+)-catechins must partially be due to rotational restriction imposed by severe steric interactions of the A/C ring system of the 'upper' unit with the E/F portion of the remaining flavanyl moiety. Increased stabilities of the [2',8]-pair (4) and (6) in contrast to those of the [6',8]-analogues (8) and (10), may be attributed to combination of *ortho*-disubstitution on both B- and D-rings relative to the bond, coupled with the 'buttressing effect' of the 4'-methoxy function on 3'-OCH<sub>3</sub> (B-ring). The magnitude of these effects presumably also explains the stabilities of the different non-derivatized conformers (3), (5), (7), and (9) permitting their ready separation in the free phenolic form (*cf.* Experimental section). Such steric effects will presumably cause maximum deviation of co-planarity of rings B and D, thus correlating with absence of an inflection in the 250–260 nm region of the u.v. absorption spectra, characteristic of a degree of biphenyl conjugation,<sup>6,7</sup> of the methyl ether acetates (4), (6), (8), and (10). The presence of a biphenyl moiety is supported by mass spectrometry, the fragment ion *m/z* 315 [27, 62, 36, and 48% for (4), (6), (8), and (10) respectively] representing the B- and D-ring biphenyl 'residue' after two reverse Diels-Alder (RDA) fragmentations followed by the characteristic<sup>8</sup> loss of ketene and the CHO radical.

Conformational analysis (Dreiding models) in conjunction with n.O.e. difference spectroscopy permits assessment of the absolute configuration about the biphenyl bond for both the [2',8]- and [6',8]-bis-(+)-catechin derivatives (4), (6), and (8), (10) respectively. The association of 3'-OMe(B) with 2-H(F) (3.8%) establishes [M]-helicity and a (*R*)-configuration for isomer (4), and indicates a dihedral angle of *ca.* 90° between the planes of the biphenyl B- and D-rings. The corresponding atropisomer (6), where interflavanyl n.O.e. associations were

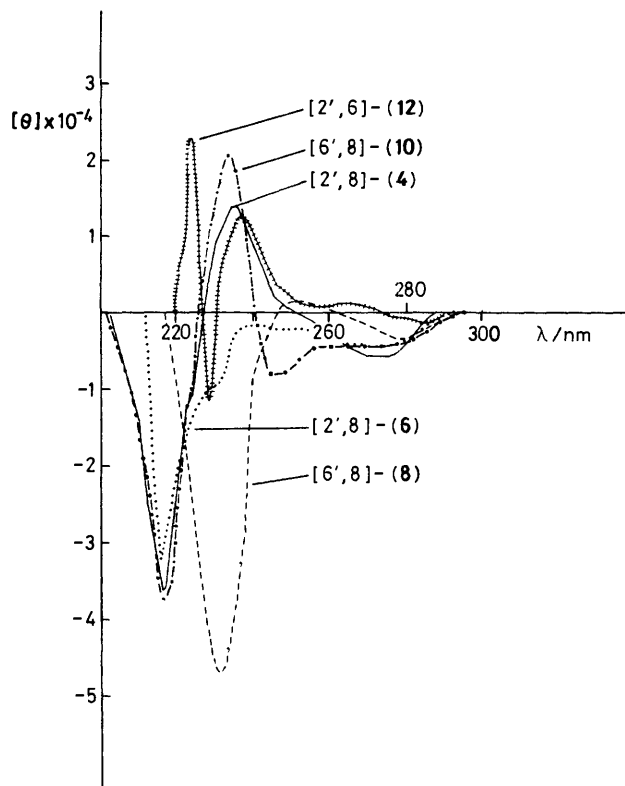
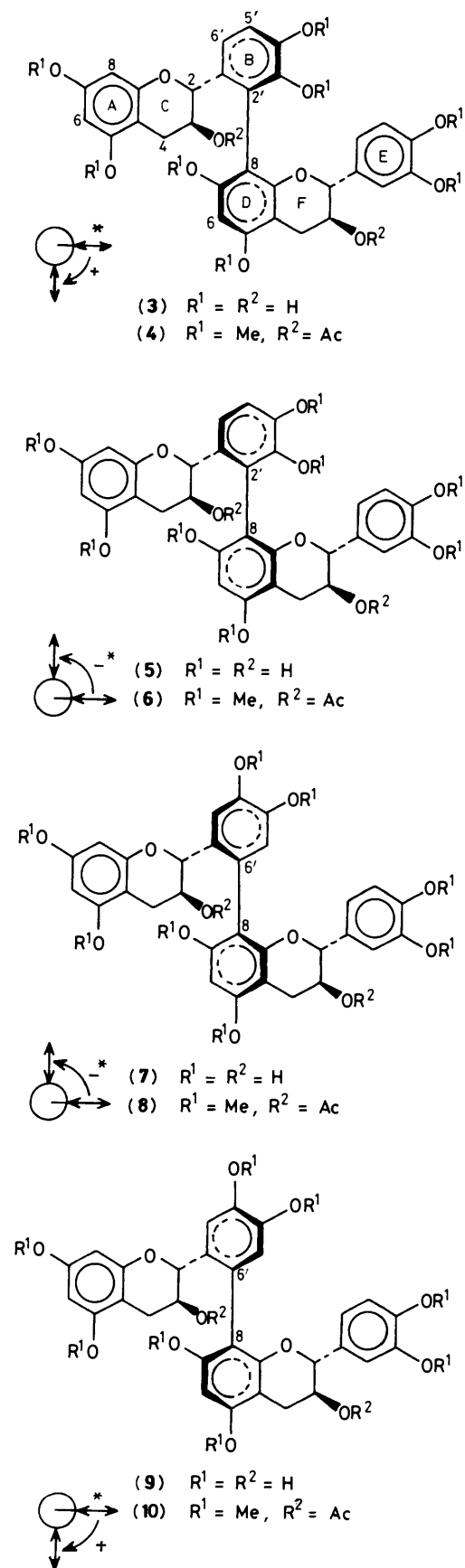


Figure. C.d. spectra of the octamethyl ether diacetates of atropisomeric [2',8]- (4) and (6), [6',8]- (8) and (10) and [2',6] (12) bis-(+)-catechins

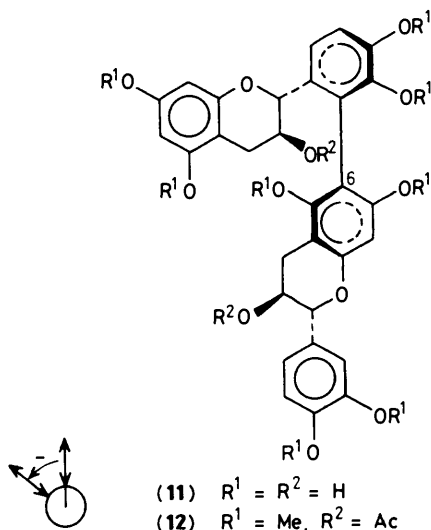
absent, therefore, exhibits [P]-helicity and a (*S*)-conformation. Association of 3-OAc(C)† with 7-OMe(D) (0.6%) and of 3-OAc(F)† with 8-H(A) (1.0%) similarly defines [M]-helicity and a (*R*)-conformation for isomer (8), while [P]-helicity and (*S*)-conformation is consistent with the lack of interflavanyl n.O.e. effects in atropisomer (10).

The u.v. spectra of all four of these derivatives indicate  $^1B_b$  transitions, due to the biphenyl chromophore,<sup>9</sup> in the 225–230 nm region. In the c.d. spectra (Figure) of both the [2',8]-(*R*)-conformer (4) and [6',8]-(*S*)-isomer (10), these transitions exhibit intense sequential positive and negative Cotton effects [ $\lambda_{ext.}$  235 nm,  $\theta +13\,900$  and 222 nm,  $\theta -12\,700$ ,  $A = \theta_1 - \theta_2 = +26\,600$  for (4), and  $\lambda_{ext.}$  233 nm,  $\theta +20\,440$  and 221.5 nm,  $\theta -13\,160$ ,  $A = +33\,600$  for (10)] which presumably indicates exciton interaction<sup>10</sup> between the two chromophores. The positive sign of the A-value in each instance is in agreement with positive chirality (right-handed screwiness) between the two long axes of the flavanyl chromophores, thus confirming (*R*)-absolute configuration for (4) and (*S*) for (10). The c.d. curves (Figure) of the [2',8]-(*S*)- and [6',8]-(*R*)-isomers [(6) and (8) respectively] are characterized by intense negative first Cotton effects [ $\lambda_{ext.}$  230 nm,  $\theta -9\,960$  for (6) and  $\lambda_{ext.}$  231.5 nm,  $\theta -47\,070$  for (8)] at the  $^1B_b$  transition, the second Cotton effect at this transition being obscured by strong competitive effects at low wavelength. Taken in conjunction with results from the n.O.e. experiments, the c.d. data presumably reflect negative chirality (left-handed screwiness) and thus confirm (*S*)-absolute configuration for (6) and (*R*) for (8).

\* Designates exciton chiralities.

† Differentiation between 3-OAc(C) and 3-OAc(F) follows from n.O.e. association of the former with 2-H(B) and of 3-OAc(F) with H-2/6(E).

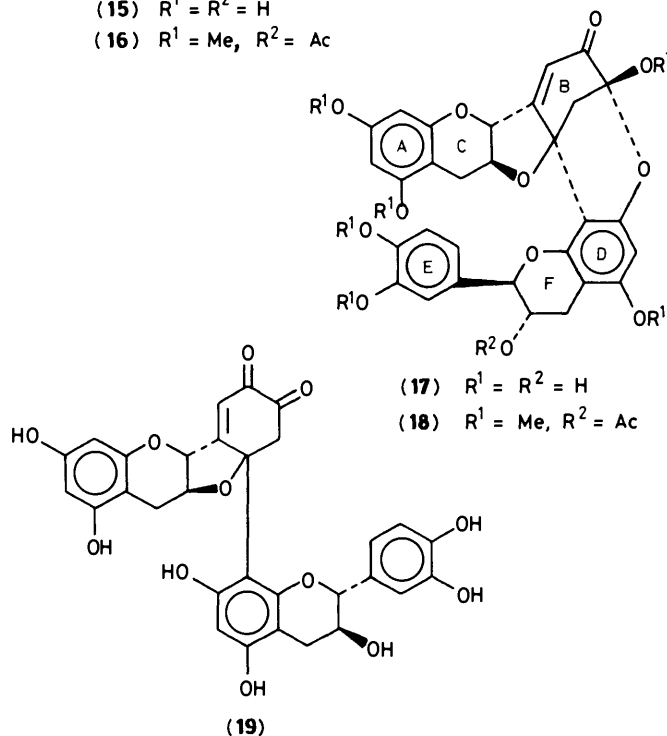
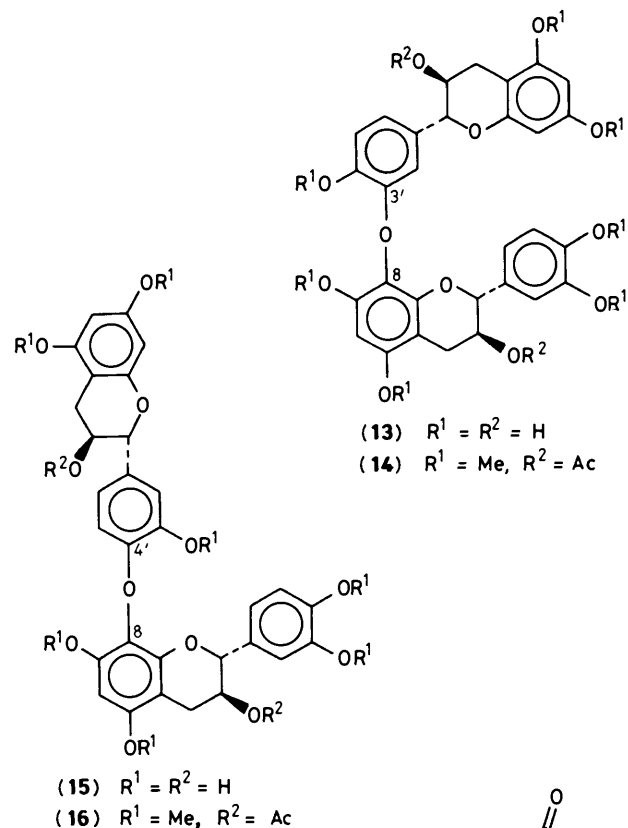
The above C(2'/6')-C(8) linked analogues are accompanied by a single conformer of [2',6]-bis-(+)-catechin (**11**)\* which was identified by means of the chemical-shift value of the 'residual' D-ring proton [ $\delta$  6.383(s)] and the splitting pattern of the B-ring ( $\delta$  7.059 and 6.863, both d,  $J$  9.0 Hz) of its octamethyl ether diacetate (**12**). Steric factors similar to those advanced for the [2',8]-atropisomers (**4**) and (**6**) also govern the stability of (**12**), thus explaining its sharply defined  $^1\text{H}$  n.m.r. spectra, without evidence of racemization over the range 25–180 °C.



The n.o.e. association of 5-OMe(D) with 2-H(C) (2.5%) and of 7-OMe(D) with 3-OAc(C) (0.7%) establishes [P]-helicity and thus (S)-conformation for derivative (**12**). Its c.d. spectrum (Figure) exhibits intense negative first and positive second Cotton effects at the  $^1B_b$  transition,  $\lambda_{\text{ext}}$ , 228 nm,  $\theta$  -11 500 and 223 nm,  $\theta$  22 500,  $A = -34$  000. This presumably indicates negative chirality and thus apparently confirms the (S)-absolute configuration assessed by means of n.o.e. effects.

The  $^1\text{H}$  n.m.r. spectra of the heptamethyl ether diacetates (**14**) and (**16**) of the ether-linked regioisomeric bis-(+)-catechins (**13**) and (**15**) are characterized by spin systems equivalent to two 'intact' tetra-*O*-methyl-3-*O*-acetyl-(+)-catechin moieties except for the absences of a single methoxy resonance and 8-H *m*-doublet. These observations are indicative of intermolecular coupling involving an aromatic hydroxy group and the C-6 or C-8 position of the remaining (+)-catechin unit. Chemical-shift values of the 'residual' D-ring singlets [ $\delta$  6.029, 6.15 for (**14**) and (**16**) respectively] reflect C-8 substitution in both cases. This was confirmed by n.o.e. difference spectroscopy which indicated association of each of these protons with two methoxys for both (**14**) and (**16**). The same technique also enabled definition of coupling through the 3'-hydroxy of the B-ring for (**14**) [association of the 4'-methoxy with the 5'H *o*-doublet ( $\delta$  6.80)] and the 4'-hydroxy for (**16**) [association of the 3'-methoxy with the 2'H *m*-doublet ( $\delta$  6.853)], thus differentiating these isomers as [3',8]- and [4',8]-bis-(+)-catechins (**13**) and (**15**).

The methyl ether acetate (**18**) of the remaining analogue (**17**) exhibited  $^1\text{H}$  n.m.r. spectral properties conspicuously different from those cited above. Major differences include the presence



of a single acetoxy resonance ( $\delta$  1.96), an isolated methylene group ( $\delta$  2.753 and 2.473, each d,  $J$  11.5 Hz), a shielded AB-portion [ $\delta$  3.99, d,  $J$  9.5 Hz;  $\delta$  4.137(*m*)] of a heterocyclic ABXY system, six methoxy resonances only, and a single proton singlet ( $\delta$  6.547) for one of the B-rings. The chemical shift ( $\delta$  6.222) of the highfield aromatic singlet defines the coupling at C-8 (*cf.* ref. 5) of a (+)-catechin moiety. These and other physical data indicate a close structural relationship to the [6',8]-analogue, dehydro-dicatchin A (**19**), obtained by

\* Presumed single conformer since Dreiding models indicate an increased degree of steric constraints on rotation than for the [2',8]-homologues (**3**) and (**5**). The remaining conformer may have been overlooked in the complex phenolic mixture.

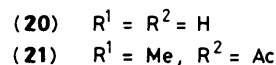
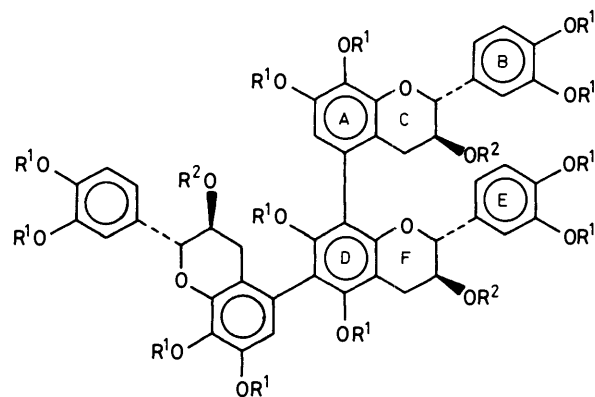
Weinges *et al.*<sup>11,12</sup> via enzymic oxidation of (+)-catechin. The <sup>13</sup>C n.m.r. spectrum of (18), however, exhibits a single carbonyl resonance ( $\delta$  191.68) in addition to that of the 3-O-acetyl ( $\delta$  169.62) of ring F. When taken in conjunction with the presence of a dioxygenated quaternary carbon ( $\delta$  96.25) exhibiting three-bond coupling to 4-OCH<sub>3</sub> (B,  $\delta$  3.628), these data indicate the genesis of (18) from dehydrodicatechin A (19) via formation of a hemiacetal involving 7-OH(D) and the C-4 carbonyl (B).<sup>\*</sup> This requires an orthogonal orientation of the two units adjoined by the newly formed dihydropyranil ring system. Application of n.o.e. difference spectroscopy (<sup>1</sup>H) on the hexamethyl ether acetate (18) showed association of 4-OMe(B) with 3-CH<sub>2</sub>(B) (3.1, 1.1%), 6-H(B) (0.67%), 6-H(D) (0.35%), and *axial* 2-H(C) (0.12%). The last-mentioned effect determines the position of the DEF-moiety to be below the plane of the 'upper' ABC-unit, thus enabling assignment of (*R*)-absolute configuration to both C-2 and C-4 of the B-ring. The close proximity of rings A and E presumably leads to reversal of the chemical-shift values of 8-H(A) ( $\delta$  5.787) and 6-H(A) ( $\delta$  6.017), the latter normally resonating at higher field.

Although oxidative coupling of flavonoids is an established natural phenomenon affecting mainly flavones and flavanones,<sup>13</sup> participation of flavan-3-ols in this mode of condensation is rarely encountered. Prototypes of the latter invariably involve 2'→8 coupling of (+)-catechin via the respective B- and A-rings, thus leading to biphenyl-type dehydrodicatechins.<sup>11</sup> Two different mechanisms were proposed for their formation *i.e.* nucleophilic 1,4-Michael addition of C-8 to an *o*-quinonoid B-ring or, alternatively, coupling of radicals generated at C-2' and C-8. Our present results, however, indicate participation of four possible radical centres on the B-ring of (+)-catechin in the formation of the C-C and O-C coupled bis-(+)-catechins described in the preceding paragraphs.

The nature of the species reacting intermolecularly with the above radicals is not clear. Since we could find no evidence for the formation of bis-(+)-catechins linked exclusively through their A-rings in the oxidative dimerization of (+)-catechin, intermediacy of radicals on its *meta*-oxygenated A-ring appears unlikely.<sup>†</sup> Formation of the C→C-[(3), (5), (7), (9), and (11)] and O→C-[(13) and (15)] coupled analogues may thus be rationalized *via* electrophilic attack (*cf.* ref. 14) of appropriate B-ring radicals on the nucleophilic A-ring. The low concentration of radical species at any given moment, in conjunction with the high nucleophilicity of the (+)-catechin A-ring, may then also explain the absence of bis-(+)-catechins coupled through their respective B-rings.

When a mixture of (+)-catechin (1) and a five-fold excess of (+)-mesquitol (2) was subjected to phenol oxidative coupling under conditions similar to those above, the (+)-catechin was rapidly consumed [2.5 *vs.* 48 h for self-condensation of both (+)-catechin and (+)-mesquitol]. The resulting mixture consisted of biphenyl-type products of both crossed condensation of (+)-mesquitol with (+)-catechin [atropisomeric [5,8]-(+)-mesquitol-(+)-catechins (*cf.* ref. 2)] and, to a lesser degree, of self-condensation of (+)-mesquitol {[5,6]- and [5,5]-bis-

(+)-mesquitol, *cf.* ref. 2}. Under these conditions the sustained excess of (+)-mesquitol allows further oxidative coupling at the remaining nucleophilic centre [6-C(D)] of the rapidly formed [5,8]-(+)-mesquitol-(+)-catechins, thus leading to formation of the four stable atropisomers of the [5,6:5,8]-*m*-terphenyls (20) in yields comparable to those of the dimeric analogues. These bi- and tri-flavan-3-ols were identified as their phenolic methyl ether acetates as were described previously (*cf.* ref. 2).



Notable in the above 'mixed' condensation of (+)-catechin and (+)-mesquitol is the exclusive formation of products of A-ring coupling. Due to its 7,8-*ortho*-dihydroxy functionality, the A-ring of (+)-mesquitol in contrast to its pyrocatechol B-ring, should be highly susceptible to oxidative coupling, thus leading by interaction of the respective C-5 and C-6 radicals, *via* a 'sandwich' transition state<sup>15</sup> (*cf.* also ref. 2), to the dominant [5,6]- and minor [5,5]-bis-(+)-mesquitol. Formation of the atropisomeric [5,8]-(+)-mesquitol-(+)-catechins has similarly been rationalized by pairing of the radicals preferentially<sup>‡</sup> generated at C-5 [(+)-mesquitol] and C-8 [(+)-catechin]. However, when taken in conjunction with observations of electron spin density being restricted to the 3,4-dioxygenated B-ring of a (+)-catechin anion radical (*cf.* results of Kuhnle *et al.*) and our own observations regarding the mechanism of dimerization of the latter, electrophilic attack of the (+)-mesquitol C-5 radical at the nucleophilic C-8 and C-6 positions of the (+)-catechin A-ring, could represent a more plausible rationale for the genesis of the predominant [5,8]- and minor [5,6]-(+)-mesquitol-(+)-catechins.

Observations regarding the relative rate of 'dimerization' of the flavan-3-ols, *i.e.* (+)-catechin-(+)-mesquitol  $\gggg$  (+)-mesquitol-(+)-mesquitol  $>$  (+)-catechin-(+)-catechin, as well as the preference for [5,8]- over [5,6]-coupling in 'mixed' condensations now require comment. The increased rate of crossed coupling of (+)-mesquitol with (+)-catechin relative to mutual coupling of each flavan-3-ol, may be attributed to the combined effect of high nucleophilicity of the A-ring functionality of (+)-catechin and the facile generation of a C-5 radical on the (+)-mesquitol A-ring. Despite the ease of formation of the latter radical, its low concentration and preferential removal *via* electrophilic substitution on the A-ring of (+)-catechin should decrease the probability of radical pairing, thus reducing the rate of formation of bis-(+)-

<sup>\*</sup> Failure of earlier efforts (*cf.* ref. 11) in proving the presence of the  $\alpha$ -diketo B-ring arrangement in (19) was ascribed to the existence of a hemiacetal of type (17) during phenazine formation. Identical melting points (267–268 °C) for the hexamethyl ether acetates of both (17) and (19) strongly suggests that the structure of dehydro-dicatechin A should be altered to (17).

<sup>†</sup> This deduction is substantiated by e.s.r. spectra [*cf.* J. A. Kuhnle, J. J. Windle, and A. C. Waiss, Jr., *J. Chem. Soc. B*, 1969, 313] of (+)-catechin anion radicals where the magnitude of the hyperfine coupling constants indicated that the total electron spin density was located on the B-ring.

<sup>‡</sup> Ascribed to the observation of electron spin density at *para*-positions of phenoxy radicals being twice that at *ortho*-positions (*cf.* ref. 16).

mesquitos. Further reduction in the rate of self-condensation of (+)-catechin may be explained in terms of its pyrocatechol B-ring functionality being less susceptible to oxidation than the substituted pyrogallol A-ring of (+)-mesquitol.

The preference for C-8 substitution of (+)-catechin in condensations with (+)-mesquitol, resembles that for electrophilic substitution of the former in the formation of conventional C(sp<sup>3</sup>)-C(sp<sup>2</sup>) biflavanoids (*cf.* ref. 17) and may be attributed to the combined effect of increased nucleophilicity and a lower degree of steric hindrance at C-8 in comparison to that at C-6. The ease of formation of radical centres on the (+)-mesquitol A-ring in combination with favourable electronic and steric requirements at C-8 of (+)-catechin, may, therefore, account for the natural predominance of [5,8]-(+)-mesquitol-(+)-catechins in *P. glandulosa* and for the exclusive formation of A-A ring coupled analogues in condensations of the aforementioned type.

### Experimental

<sup>1</sup>H and <sup>13</sup>C N.m.r. spectra were recorded on a Bruker AM-300 spectrometer in CDCl<sub>3</sub> and (CD<sub>3</sub>)<sub>2</sub>SO with Me<sub>4</sub>Si as internal standard. Mass spectra were obtained with a Varian CH-5 instrument and c.d. data in methanol on a Jasco J-20 spectropolarimeter. Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. T.l.c. was performed on pre-coated Merck plastic sheets (silica gel 60PF<sub>254</sub>, 0.25 mm) and the plates sprayed with H<sub>2</sub>SO<sub>4</sub>-HCHO (40:1 v/v) after development. Preparative plates (p.l.c.), 20 × 20 cm, Kieselgel PF<sub>254</sub> (1.0 mm) were air-dried and used without prior activation. Separations on Sephadex LH-20 columns (3 × 80 cm) were in ethanol. Fractions (15 ml each) were collected on a rotary fraction collector, starting with introduction of the sample on the column. Methylations were performed with an excess of diazomethane in methanol-diethyl ether over 48 h at -15 °C, while acetylations were in acetic anhydride-pyridine at ambient temperatures. Evaporations were done under reduced pressure at *ca.* 60 °C in a rotary evaporator. N.m.r. spectra at 300 MHz provided criteria of purity of the various bis-(+)-catechins.

*Oxidative Dimerization of (+)-Catechin.*—(+)-2,3-trans-3,3',4',5,7-Pentahydroxyflavan (1) (2.32 g) was dissolved in a solution of acetonitrile-glycine buffer<sup>3</sup> (1:3 v/v, pH 9.0; 10 ml) under N<sub>2</sub>. K<sub>3</sub>Fe(CN)<sub>6</sub> (13.42 g) dissolved in the same buffer (100 ml) at 0 °C was added and the mixture kept under N<sub>2</sub> at ambient temperatures. After 24 h a fresh batch of K<sub>3</sub>[Fe(CN)<sub>6</sub>] (12.42 g) was added and stirring continued for a further 24 h. The mixture was acidified (0.1M HCl) and the solution extracted with EtOAc (5 × 50 ml). The dried (Na<sub>2</sub>SO<sub>4</sub>) solution was evaporated to dryness and the solids subjected to column chromatography on Sephadex LH-20 using ethanol as eluant. The fractions were grouped as follows: 1 (tubes 30–46), 2 (78–102), 3 (110–136), and 4 (140–174).

Fraction 1 (823 mg) consisted of unchanged (+)-catechin. Fraction 2 (47 mg) was methylated and the mixture resolved by p.l.c. in benzene-acetone-methanol (82:16:2, v/v) to give a single fraction at R<sub>F</sub> 0.36 (7.7 mg). The product of acetylation gave two products at R<sub>F</sub> 0.51 (3.4 mg) and 0.43 (3.7 mg) in benzene-acetone (9:1 v/v, × 2).

(S)-{(2R,3S)-2,3-trans-3-Acetoxy-8-[(2R,3S)-2,3-trans-3-acetoxy-3',4',5,7-tetramethoxyflavan-2'-yl]-3',4',5,7-tetramethoxyflavan} (6).—The R<sub>F</sub> 0.51 fraction afforded the octamethyl ether diacetate as a *solid* (Found: C, 65.3; H, 6.2%; M<sup>+</sup>, 774.285 81. C<sub>42</sub>H<sub>46</sub>O<sub>14</sub> requires C, 65.1; H, 6.0%; M<sup>+</sup>, 774.288 76); δ(CDCl<sub>3</sub>, 300 MHz, 25 °C) 7.067 [d, J 8.5 Hz,

6-H(B)], 6.80 [d, J 8.5 Hz, 5-H(B)], 6.747 [dd, J 2.0 and 8.5 Hz, 6-H(E)], 6.712 [d, J 2.0 Hz, 2-H(E)], 6.70 [d, J 8.5 Hz, 5-H(E)], 6.177 [s, 6-H(D)], 6.06 [d, J 2.5 Hz, 8-H(A)], 6.025 [d, J 2.5 Hz, 6-H(A)], 5.27–5.223 [m, 3-H(F)], 5.152 [d, J 4.5 Hz, 2-H(F)], 5.123–5.073 [m, 3-H(C)], 4.925 [d, J 5.0 Hz, 2-H(C)], 3.835, 3.802, 3.794, 3.782, 3.739, 3.733, 3.711, and 3.652 (each s, 8 × OMe), 2.72–2.60 [m, 4-CH<sub>2</sub>(C and F)], and 1.830 and 1.816 (each s, 2 × OAc); c.d. spectrum [θ]<sub>293</sub> 0, [θ]<sub>270</sub> -4 550, [θ]<sub>240</sub> -1 710, [θ]<sub>230</sub> -9 960, [θ]<sub>225</sub> -12 800, [θ]<sub>215</sub> -32 430, and [θ]<sub>212</sub> 0.

(R)-{(2R,3S)-2,3-trans-3-Acetoxy-8-[(2R,3S)-2,3-trans-3-acetoxy-3',4',5,7-tetramethoxyflavan-6'-yl]-3',4',5,7-tetramethoxyflavan} (8).—The R<sub>F</sub> 0.43 band gave the title compound as a *solid* (Found: M<sup>+</sup>, 774.287 35. C<sub>42</sub>H<sub>46</sub>O<sub>14</sub> requires M<sup>+</sup>, 774.288 76); δ(CDCl<sub>3</sub>, 300 MHz, 25 °C), 6.95 [s, 5-H(B)], 6.681–6.705 [m, 2-, 5-, and 6-H(E)], 6.65 [br s, 2-H(B)], 6.138 [s, 6-H(D)], 6.033 [d, J 2.0 Hz, 8-H(A)], 6.022 [d, J 2.0 Hz, 6-H(A)], 5.323–5.726 [m, 3-H(C)], 5.275–5.21 [m, 3-H(F)], 5.189 [br d, J 4.5 Hz, 2-H(C)], 4.935 [d, J 3.5 Hz, 2-H(F)], 3.823, 3.803, 3.797, 3.763, 3.749, 3.713 (× 2), 3.703 (each s, 8 × OMe), 2.853 [dd, J 5.5 and 16.5 Hz, 4-H<sub>eq</sub>(F)], 2.737 [dd, J 4.5 and 17.0 Hz, 4-H<sub>eq</sub>(C)], 2.620 [dd, J 4.5 and 17.0 Hz, 4-H<sub>ax</sub>(C)], 2.506 [dd, J 7.5 and 16.5 Hz, 4-H<sub>ax</sub>(F)], 1.816 [s, 3-OAc(C)], and 1.683 [s, 3-OAc(F)]; c.d. spectrum [θ]<sub>295</sub> 0, [θ]<sub>280</sub> -3 660, [θ]<sub>261.5</sub> 0, [θ]<sub>255</sub> +1 150, [θ]<sub>247</sub> 0, [θ]<sub>231.5</sub> -47 070, and [θ]<sub>217</sub> 0.

Methylation of fraction 3 (161.9 mg) followed by p.l.c. in benzene-acetone-methanol (82:16:2) afforded three bands at R<sub>F</sub> 0.43 (36.2 mg), 0.34 (12.8 mg), and 0.27 (19.4 mg). The R<sub>F</sub> 0.34 fraction was acetylated and the mixture resolved by p.l.c. in benzene-acetone (9:1 v/v) to give two bands at R<sub>F</sub> 0.52 (4.1 mg) and 0.43 (4.1 mg).

(R)-{(2R,3S)-2,3-trans-3-Acetoxy-8-[(2R,3S)-2,3-trans-3-acetoxy-3',4',5,7-tetramethoxyflavan-2'-yl]-3',4',5,7-tetramethoxyflavan} (4).—The R<sub>F</sub> 0.52 fraction afforded the octamethyl ether diacetate as a *solid* (Found: C, 65.1; H, 6.2%; M<sup>+</sup>, 774.288 76; δ(CDCl<sub>3</sub>, 300 MHz, 25 °C) 6.944 [d, J 8.5 Hz, 6-H(B)], 6.884 [d, J 2.0 Hz, 2-H(E)], 6.83 [dd, J 2.0 and 8.5 Hz, 6-H(E)], 6.733 [d, J 8.5 Hz, 5-H(B)], 6.715 [d, J 8.5 Hz, 5-H(E)], 6.183 [s, 6-H(D)], 6.136 [d, J 2.0 Hz, 8-H(A)], 6.027 [d, J 2.0 Hz, 6-H(A)], 5.377 [m, 3-H(F)], 5.329 [m, 3-H(C)], 4.954 [d, J 4.5 Hz, 2-H(C)], 4.797 [d, J 8.0 Hz, 2-H(F)], 3.855, 3.823, 3.81, 3.754, 3.728, 3.707, 3.703, and 3.56 (each s, 8 × OMe), 3.171 [dd, J 6.0 and 16.5 Hz, 4-H<sub>eq</sub>(F)], 2.704 [dd, J 8.0 and 16.5 Hz, 4-H<sub>ax</sub>(F)], 2.606 [dd, J 4.5 and 17.0 Hz, 4-H<sub>eq</sub>(C)], 2.488 [dd, J 4.5 and 17.0 Hz, 4-H<sub>ax</sub>(C)], 1.933 [s, 3-OAc(C)], and 1.613 [s, 3-OAc(F)]; c.d. spectrum [θ]<sub>289</sub> 0, [θ]<sub>270</sub> -5 760, [θ]<sub>250.5</sub> 0, [θ]<sub>235</sub> +13 900, [θ]<sub>227</sub> 0, [θ]<sub>222</sub> -12 700, [θ]<sub>216</sub> -36 300, and [θ]<sub>202</sub> 0.

(S)-{(2R,3S)-2,3-trans-3-Acetoxy-8-[(2R,3S)-2,3-trans-3-acetoxy-3',4',5,7-tetramethoxyflavan-6'-yl]-3',4',5,7-tetramethoxyflavan} (10).—The R<sub>F</sub> 0.43 band gave the title compound as a *solid* (Found: M<sup>+</sup>, 774.285 82. C<sub>42</sub>H<sub>46</sub>O<sub>14</sub> requires M<sup>+</sup>, 774.288 76); δ(CDCl<sub>3</sub>, 300 MHz, 25 °C) 6.852 [s, 2-H(B)], 6.771 [dd, J 2.0 and 8.0 Hz, 6-H(E)], 6.75 [d, J 2.0 Hz, 2-H(E)], 6.716 [d, J 8.0 Hz, 5-H(E)], 6.606 [s, 5-H(B)], 6.165 [s, 6-H(D)], 6.145 [d, J 2.0 Hz, 8-H(A)], 6.027 [d, J 2.0 Hz, 6-H(A)], 5.334 [m, 3-H(C)], 5.303 [m, 3-H(F)], 4.961 [d, J 6.5 Hz, 2-H(C)], 4.920 [d, J 7.0 Hz, 2-H(F)], 3.845, 3.827, 3.765, 3.737, 3.733, 3.722, 3.715, and 3.683 (each s, 8 × OMe), 3.042 [dd, J 5.5 and 16.5 Hz, 4-H<sub>eq</sub>(F)], 2.735 [dd, J 7.0 and 16.5 Hz, 4-H<sub>ax</sub>(F)], 2.775 [dd, J 5.0 and 16.5 Hz, 4-H<sub>eq</sub>(C)], 2.467 [dd, J 6.5 and 16.5 Hz, 4-H<sub>ax</sub>(C)], and 1.933 and 1.613 (each s, 2 × OAc); c.d. spectrum [θ]<sub>295</sub> 0, [θ]<sub>270</sub> -4 700, [θ]<sub>245</sub> -8 220, [θ]<sub>240</sub> 0, [θ]<sub>233</sub> +20 440, [θ]<sub>225</sub> 0, [θ]<sub>221.5</sub> -13 160, [θ]<sub>216</sub> -37 600, and [θ]<sub>201</sub> 0.

Mass fragmentation spectra of the octamethyl ether diacetates (**4**), (**6**), (**8**), and (**10**) were respectively:  $m/z$  774 ( $M^+$  36.4%, 60.0, 39.4, 72.5), 715 (13.0, 53.4, 4.1, 6.8), 714 (30.3, 58.8, 4.4, 15.5), 655 (100, 100, 100, 100), 654 (92.3, 98.1, 40.8, 81.5), 608 (1.9, 4.6, 4.4, 6.5), 548 (5.2, 48.9, 5.1, 14.1), 547 (16.9, 58.1, 18.3, 19.2), 507 (2.1, 14.0, —, 3.1), 506 (5.6, 48.4, 3.2, 7.5), 478 (7.7, 52.4, 8.2, 15.3), 477 (20.6, 50.8, 10.0, 34.4), 387 (5.3, 26.5, —, 4.5), 386 (1.0, 3.6, —, 3.4), 344 (3.9, 27.7, 4.2, 4.7), 327 (23.4, 64.7, 13.6, 15.5), 315 (26.8, 61.9, 35.8, 48.3), 222 (2.8, 12.6, —, 2.8), 221 (1.1, 13.9, —, 1.6), 180 (20.6, 48.5, 11.2, 19.6), 166 (4.8, 29.7, 5.1, 6.7), 165 (20.3, 62.1, 26.1, 20.8), and 151 (51.0, 68.3, 21.7, 49.7).

(2R,3S,8R,10bR,16aS,17aR)-2,3-trans-10b,16a-trans-3-Acetoxy-5,8,13,15-tetramethoxy-2-(3,4-dimethoxyphenyl)-2,3,10b,16a-tetrahydro-8,17a-methano-4H,16H-[1]benzopyrano[2',3':4,5]-furo[2,3-d]oxacino[2,3-h]benzopyran-9(8H)-one (**18**).—Acetylation of the  $R_F$  0.43 fraction afforded the hexamethyl ether acetate as white needles (38 mg), m.p. 267—268 °C (from ethanol) (Found: C, 64.8; H, 5.4%;  $M^+$ , 702.235 06.  $C_{38}H_{38}O_{13}$  requires C, 65.0; H, 5.5%;  $M^+$ , 702.231 24);  $\delta$ (CDCl<sub>3</sub>, 300 MHz, 25 °C) 6.851 [dd,  $J$  2.0 and 9.0 Hz, 6-H(E)], 6.824 [d,  $J$  2.0 Hz, 2-H(E)], 6.81 [d,  $J$  9.0 Hz, 5-H(E)], 6.547 [s, 6-H(B)], 6.222 [s, 6-H(D)], 6.017 [d,  $J$  2.5 Hz, 6-H(A)], 5.787 [d,  $J$  2.5 Hz, 8-H(A)], 5.353 [m, 3-H(F)], 5.15 [d,  $J$  6.9 Hz, 2-H(F)], 4.137 [m, 3-H(C)], 3.99 [d,  $J$  9.5 Hz, 2-H(C)], 3.857, 3.847, 3.817, 3.733, 3.664, 3.628 (each s, 6 × OMe), 3.06 [dd,  $J$  6.0 and 16.0 Hz, 4-H<sub>eq</sub>(C)], 2.927 [dd,  $J$  5.5 and 16.8 Hz, 4-H<sub>eq</sub>(F)], 2.753 [d,  $J$  11.5 Hz, 3-H(B)], 2.677 [dd,  $J$  7.0 and 16.8 Hz, 4-H<sub>ax</sub>(F)], 2.57 [dd,  $J$  10.2 and 16.0 Hz, 4-H<sub>ax</sub>(C)], 2.473 [d,  $J$  11.5 Hz, 3-H(B)], and 1.96 [s, 3-OAc(F)];  $\delta^*$  (<sup>13</sup>C, CDCl<sub>3</sub>, 75.432 MHz, 27 °C) 191.68 [5-CO(B)], 169.82 [3-OCOCH<sub>3</sub>(F)], 166.19 [7-C(D)], 164.28 [5-C(D)], 159.48, 158.47 [5-C, 7-C(A)], 159.23 [1-C(B)], 154.53 [9-C(A)], 152.06 [9-C(D)], 149.01, 148.86 [3-C, 4-C(E)], † 129.01 [1-C(E)], 118.70 [6-C(E)], 115.48 [6-C(B)], 111.14 [5-C(E)], 109.32 [2-C(E)], 105.12 [8-C(D)], 102.29 [10-C(D)], 101.42 [10-C(A)], 96.25 [4-C(B)], 93.29 [6-C(A)], 92.15 [8-C(A)], 88.49 [2-C(B)], 87.00 [6-C(D)], 78.74 [2-C(F)], 78.54 [2-C(C)], 68.35 [3-C(F)], 65.17 [3-C(C)], 56.142, 55.90, 55.46, 55.43 (5 × OCH<sub>3</sub>), 51.67 [4-OCH<sub>3</sub>(B)], 43.14 [3-C(B)], 26.84, 24.12 [4-C(C), 4-C(F)], ‡ and 21.09 [3-OCOCH<sub>3</sub>(F)];  $m/z$  702 ( $M^+$ , 98.9%), 674 (8.6), 673 (18.1), 642 (7.7), 511 (16.3), 510 (26.2), 494 (33.9), 480 (25.3), 479 (5.5), 468 (35.2), 452 (10.7), 449 (4.4), 406 (18.5), 302 (42.6), 301 (69.3), 288 (100), 285 (12.0), 257 (5.5), 255 (16.2), 243 (24.7), 229 (93.1), 222 (26.0), 207 (20.2), 191 (62.5), 180 (65.3), 164 (3.8), and 151 (66.0).

(2R,3S)-2,3-trans-3-Acetoxy-8-[(2R,3S)-2,3-trans-3-acetoxy-3',4',5,7-tetramethoxyflavan-3'-O-y]-3',4',5,7-tetramethoxyflavan (**14**).—Acetylation of the  $R_F$  0.27 fraction afforded the heptamethyl ether diacetate as a solid (20 mg) (Found: C, 64.8; H, 5.8%;  $M^+$ , 760.268 98.  $C_{41}H_{44}O_{14}$  requires C, 64.7; H, 5.8%;  $M^+$ , 760.273 11);  $\delta$ (CDCl<sub>3</sub>, 300 MHz, 25 °C) 6.833 [dd,  $J$  2.0 and 8.5 Hz, 6-H(B)], 6.80 [d,  $J$  8.5 Hz, 5-H(B)], 6.711 [d,  $J$  8.5 Hz, 5-H(E)], 6.694 [d,  $J$  2.0 Hz, 2-H(E)], 6.679 [dd,  $J$  2.0 and 8.5 Hz, 6-H(E)], 6.495 [d,  $J$  2.0 Hz, 2-H(B)], 6.029 [s, 6-H(D)], 6.017 [d,  $J$  2.5 Hz, 8-H(A)], 5.937 [d,  $J$  2.5 Hz, 6-H(A)], 5.223 [dd,  $J$  5.0 and 10.0 Hz, 3-H(C)], 5.187 [m, 3-H(F)], 5.067 [d,  $J$  5.0 Hz, 2-H(C)], 4.808 [d,  $J$  6.5 Hz, 2-H(F)], 3.81, 3.806, 3.803, 3.726, 3.717, 3.65, 3.637 (each s, 7 × OMe), 2.837 [dd,  $J$  5.0 and 17.0 Hz, 4-H<sub>eq</sub>(C)], 2.633 [dd,  $J$  5.0 and 17.0 Hz, 4-H<sub>ax</sub>(C)], 2.627 [dd,  $J$  6.5 and 17.0 Hz, 4-H<sub>eq</sub>(F)], 2.53 [dd,  $J$  5.0 and 17.0 Hz, 4-H<sub>ax</sub>(F)], and 1.937, 1.92 (each s, 2 × OAc).

Fraction 4 was methylated and the mixture subsequently

resolved by p.l.c. in benzene-acetone-methanol (82:16:2 v/v, ×3) into two bands at  $R_F$  0.46 (31 mg) and 0.56 (4.3 mg).

(2R,3S)-2,3-trans-3-Acetoxy-8-[(2R,3S)-2,3-trans-3',4',5,7-tetramethoxyflavan-4'-O-y]-3',4',5,7-tetramethoxyflavan (**16**).—Acetylation of the  $R_F$  0.46 band afforded the heptamethyl ether diacetate as a solid (31 mg) (Found: C, 64.6; H, 5.9%;  $M^+$ , 760.270 48.  $C_{41}H_{44}O_{14}$  requires C, 64.7; H, 5.8%;  $M^+$ , 760.273 11);  $\delta$ (CDCl<sub>3</sub>, 300 MHz, 25 °C) 6.853 [d,  $J$  2.0 Hz, 2-H(B)], 6.723 [dd,  $J$  2.0 and 8.0 Hz, 6-H(B)], 6.70 [d,  $J$  8.5 Hz, 5-H(E)], 6.67 [d,  $J$  3.0 Hz, 2-H(E)], 6.667 [dd,  $J$  3.0 and 8.5 Hz, 6-H(E)], 6.537 [d,  $J$  8.0 Hz, 5-H(B)], 6.15 [s, 6-H(D)], 6.115 [d,  $J$  2.5 Hz, 8-H(A)], 6.057 [d,  $J$  2.5 Hz, 6-H(A)], 5.285 [m, 3-H(C)], 5.227 [m, 3-H(F)], 5.068 [d,  $J$  6.0 Hz, 2-H(F)], 5.007 [d,  $J$  6.5 Hz, 2-H(C)], 3.813, 3.81, 3.796, 3.767, 3.744, 3.74, 3.684 (each s, 7 × OMe), 2.825 [dd,  $J$  5.0 and 17.0 Hz, 4-H<sub>eq</sub>(C)], 2.816 [dd,  $J$  5.0 and 17.0 Hz, 4-H<sub>eq</sub>(F)], 2.70 [dd,  $J$  6.0 and 17.0 Hz, 4-H<sub>ax</sub>(F)], 2.630 [dd,  $J$  6.5 and 17.0 Hz, 4-H<sub>ax</sub>(C)], and 1.943, 1.903 (each s, 2 × OAc).

Mass fragmentation spectra of the heptamethyl ether diacetates (**14**) and (**16**) were respectively:  $m/z$  760 ( $M^+$ , 82.9%, 72.5), 701 (18.8, 15.2), 700 (35.5, 33.1), 642 (28.4, 30.1), 641 (67.8, 37.2), 640 (44.6, 6.3), 594 (2.6, 6.0), 552 (5.5, 3.2), 538 (1.2, 1.7), 534 (20.6, 19.0), 523 (1.7, 1.4), 507 (5.2, 6.1), 478 (15.6, 11.2), 447 (13.8, 14.6), 387 (1.6, 1.9), 373 (7.9, 6.8), 372 (1.7, 4.8), 330 (13.0, 10.4), 327 (27.2, 46.5), 313 (22.7, 20.2), 301 (13.3, 15.4), 299 (20.2, 40.5), 222 (6.6, 4.3), 180 (54.6, 66.7), and 151 (100, 100).

(S)-{(2R,3S)-2,3-trans-3-Acetoxy-6-[(2R,3S)-2,3-trans-3-acetoxy-3',4',5,7-tetramethoxyflavan-2'-y]-3',4',5,7-tetramethoxyflavan} (**12**).—Acetylation of the  $R_F$  0.56 fraction gave the octamethyl ether diacetate as a solid (4.6 mg) (Found:  $M^+$ , 774.287 05.  $C_{42}H_{46}O_{14}$  requires  $M^+$ , 774.288 76);  $\delta$ (CDCl<sub>3</sub>, 300 MHz, 25 °C) 7.059 [d,  $J$  9.0 Hz, 6-H(B)], 6.947 [dd,  $J$  2.0 and 9.0 Hz, 6-H(E)], 6.93 [d,  $J$  2.0 Hz, 2-H(E)], 6.863 [d,  $J$  9.0 Hz, 5-H(B)], 6.823 [d,  $J$  9.0 Hz, 5-H(E)], 6.386 [s, 6-H(D)], 6.071 [d,  $J$  2.0 Hz, 8-H(A)], 6.043 [s,  $J$  2.0 Hz, 6-H(A)], 5.372—5.30 [m, 3-H(F)], 5.22—5.17 [m, 3-H(C)], 4.979 [d,  $J$  8.0 Hz, 2-H(F)], 4.893 [d,  $J$  4.5 Hz, 2-H(C)], 3.864, 3.86, 3.843, 3.733, 3.73, 3.69, 3.676, 3.405 (each s, 8 × OMe), 3.132 [dd,  $J$  5.5 and 16.0 Hz, 4-H<sub>eq</sub>(F)], 2.764 [dd,  $J$  8.0 and 16.0 Hz, 4-H<sub>ax</sub>(F)], 2.70 [dd,  $J$  4.5 and 17.5 Hz, 4-H<sub>eq</sub>(C)], 2.61 [dd,  $J$  5.0 and 17.5 Hz, 4-H<sub>ax</sub>(C)], 1.918 [s, 3-OAc(F)], and 1.888 [s, 3-OAc(C)];  $m/z$  774 ( $M^+$  23.3%), 715 (27.0), 714 (38.4), 655 (37.6), 654 (5.2), 548 (6.8), 547 (9.9), 507 (4.6), 506 (4.4), 505 (12.7), 478 (6.8), 477 (14.2), 387 (6.2), 368 (25.5), 327 (28.3), 315 (10.1), 313 (21.8), 222 (9.5), 180 (31.7), 166 (6.4), 165 (12.6), and 151 (62.0); c.d. spectrum [ $\theta$ ]<sub>290</sub> 0, [ $\theta$ ]<sub>285</sub> -1 350, [ $\theta$ ]<sub>272</sub> 0, [ $\theta$ ]<sub>260</sub> +900, [ $\theta$ ]<sub>250</sub> +1 580, [ $\theta$ ]<sub>237</sub> +12 600, [ $\theta$ ]<sub>230</sub> 0, [ $\theta$ ]<sub>228</sub> -11 480, [ $\theta$ ]<sub>226</sub> 0, [ $\theta$ ]<sub>223</sub> +22 500, and [ $\theta$ ]<sub>219</sub> 0.

*Mutual Condensation of (+)-Catechin and (+)-Mesquitol.*—(+)-Catechin (**1**) (1 g) and (+)-mesquitol (**2**) (5 g) were dissolved in 1:1 (v/v) acetonitrile-glycine buffer (pH 9.0; 50 ml) under N<sub>2</sub>. K<sub>3</sub>[Fe(CN)<sub>6</sub>] (60 g) dissolved in the same buffer (200 ml) was added, and the reaction allowed to proceed at room temperature for 2.5 h. The mixture was acidified (0.1M HCl), extracted with EtOAc (6 × 200 ml), and the combined solution evaporated to dryness. The solids (3.07 g) were resolved on a Sephadex LH-20 column (2.5 × 40 cm) with ethanol as eluant. Fractions (15 ml each) were collected and grouped as follows: 1 (tubes 7—30; 265 mg), 2 (45—63; 486 mg), 3 (64—78; 284 mg), 4 (79—84; 57.6 mg), 5 (85—100; 185.4 mg), and 6 (106—193; 687.3 mg). Fraction 1 consisted of unchanged (+)-mesquitol. Fractions 2—5 were separately methylated and the methyl ether mixtures purified by p.l.c. and subsequently acetylated. These mixtures were accordingly resolved by p.l.c. to give the methyl ether diacetates of the [5,5]- and [5,6]-bis-(+)-

\* Assignments established by 2D C-H heteronuclear shift correlations.

† Assignments may be reversed.

‡ Assignments may be reversed.

mesquitols and the atropisomeric [5,8]-(+)-mesquitol-(+)-catechins. Since these compounds have previously been fully characterized (*cf.* ref. 2), their identification will not be repeated.

Fraction 6 was methylated and a portion (60 mg) of the mixture of methyl ethers purified by p.l.c. on 20 Merck DC-Fertigplatten Kieselgel 60 F<sub>254</sub> in dichloromethane-acetone (8:2 v/v, × 2) to give three bands at  $R_F$  0.29 (9.1 mg), 0.21 (9.4 mg), and 0.12 (5.8 mg). These fractions were separately acetylated and the resultant mixtures resolved by p.l.c. in 1,2-dichloromethane-acetone (96:4 v/v, × 2). Following this treatment the  $R_F$  0.29 fraction afforded the  $R_F$  0.56 (9.0 mg) atropisomer of (2*R*,3*S*)-2,3-*trans*-3-acetoxy-6,8-bis-[2*R*,3*S*]-2,3-*trans*-3',4',7,8-tetramethoxyflavan-5-yl]-3',4',5,7-tetramethoxyflavan (**21**). The  $R_F$  0.21 band similarly gave the  $R_F$  0.60 (3.7 mg) and 0.54 (1.0 mg) atropisomers and the  $R_F$  0.12 fraction the remaining  $R_F$  0.50 (6.1 mg) isomer. These tridecamethyl ether triacetates (**21**) were identical (<sup>1</sup>H n.m.r., m.s. fragmentation, and c.d. data) to the corresponding derivatives of the atropisomeric [5,6:5,8]-*m*-terphenyl type flavan-3-ols previously (*cf.* ref. 2) obtained from the heartwood of *Prosopis glandulosa*.

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