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BIBENZYL DERIVATIVES FROM *FRULLANIA* SPECIES

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Key Word Index—*Frullania bonincola*; *F. davurica*; *F. diversitexta*; *F. ericoides*; *F. parvistipula*; *F. usamiensis*; *F. vethii*; Frullaniaceae; Jungermanniales; Hepaticae; bibenzyls; sesquiterpenoids.

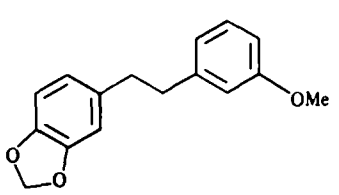
Abstract—Four novel bibenzyl derivatives; 3,4,3′,4′-dimethylenedioxybibenzyl, 3,3′-dimethoxy-4,5-methylenedioxybibenzyl, 3,3′-dimethoxy-4,5-methylenedioxy-4′-hydroxybibenzyl and 3,3′-dihydroxy-4,5,4′,5′-dimethylenedioxybibenzyl were isolated from three *Frullania* species of liverworts and their structures were determined by spectral evidence and synthesis.

INTRODUCTION

Frullania species belonging to the Jungermanniales are rich sources of sesquiterpene lactones and bibenzyl derivatives [1]. In a previous paper [2], we reported the distribution of terpenoids and bibenzyls in 25 *Frullania* species and their chemosystematics. The present paper deals with the isolation of the new bibenzyls from *F. bonincola*, *F. ericoides* and *F. parvistipula* and their structure elucidation and synthesis. We also report the chemical constituents of *F. davurica*, *F. diversitexta*, *F. usamiensis* and *F. vethii*.

RESULTS AND DISCUSSION

Each *Frullania* species collected in Japan was extracted with diethyl ether to give crude extracts which were analysed by TLC, GC and GC/MS equipped with a computer [2]. The extract of *F. ericoides* was chromatographed on silica gel to give two bibenzyl derivatives (**1**) and (**2**), respectively. The former compound has been found in the Australian *F. falciloba* and its structure determined by synthesis [3]. Compound **2**, mp 136–137°, indicated the presence of an aromatic ring (1612, 1580 cm^{-1}), two benzylic methylenes (δ2.76, 4H, *s*), a methylenedioxy group (δ5.83, 2H, *s*), two methoxyl groups (δ3.73, 3.80, each 3H, *s*) and six protons on benzene rings (δ6.13–7.17, *m*). The presence of methylenedioxymethoxybenzyl and methoxybenzyl moieties was confirmed by the mass fragments at *m/z* 165 $[M - 121]^+$. From the above spectral evidence together with biogenetic considerations, **2** appears to be 3,3′-dimethoxy-4,5-methylenedioxybibenzyl. To confirm this assumption, **2** was synthesized as follows: *n*-butyl gallate (**15**) was methylated by methyl iodide in the presence of 5% boric acid to give *n*-butyl 3,4-dihydroxy-5-methoxybenzoate (**16**), which was treated with methylene iodide in the presence of cupric oxide and potassium carbonate to



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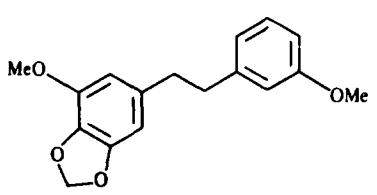

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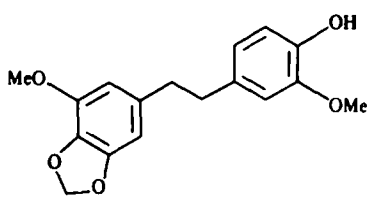

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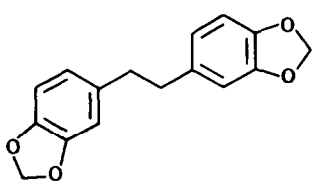

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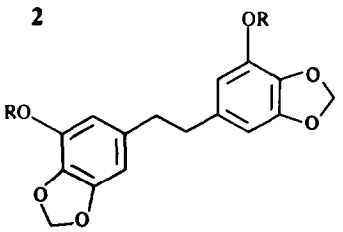

5 R = H
6 R = Me

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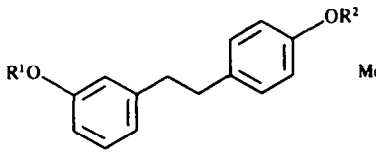
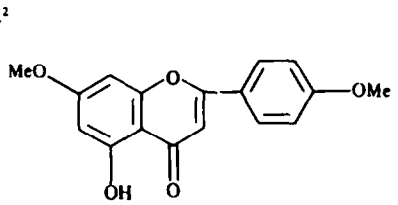


7 R^1 = Me, R^2 = H
8 R^1 = R^2 = Me



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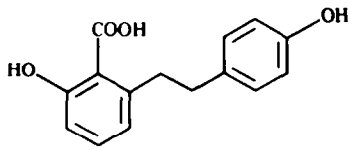

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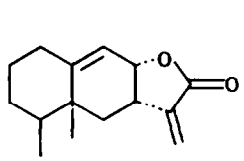

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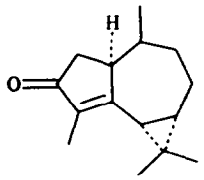

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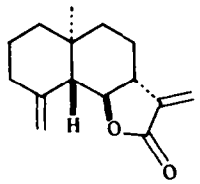

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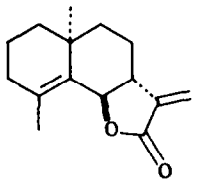

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afford *n*-butyl 3-methoxy-4,5-methylenedioxybenzoate (**17**). Lithium aluminium hydride reduction of **17** gave 3-methoxy-4,5-methylenedioxybenzyl alcohol (**18**) which was brominated by 47% hydrobromic acid to give 3-methoxy-4,5-methylenedioxybenzyl bromide (**19**). The bromide obtained **19** was then treated with triphenylphosphine in dimethylformamide (DMF) to give a phosphonium salt (**20**) which was condensed with 3-methoxybenzaldehyde (**21**) in the presence of sodium ethoxide to furnish the stilbene mixtures (**22**), followed by hydrogenation to afford a pure dihydrostilbene whose physical and spectral data were identical to those of the natural 3,3'-dimethoxy-4,5-methylenedioxybibenzyl (**2**).

The crude extract of *F. bonincola* was chromatographed on silica gel to obtain a new bibenzyl (**3**), mp 62–63°, whose spectral data (Table 1) showed the presence of a methylenedioxyl group, two benzylic methylene groups and five protons on benzene rings, two methoxy groups, a phenolic hydroxyl group (3570 cm^{-1}) and an aromatic ring (1612, 1510 cm^{-1}). The MS spectrum displayed intense fragment ions at *m/z* 165 $[M - 137]^+$ and 137 $[M - 165]^+$ which indicated that hydroxymethoxybenzyl and methylenedioxymethoxybenzyl moieties were present in **3**. The above data and biogenetic considerations suggested that the second new bibenzyl might be 3,3'-dimethoxy-4,5-methylenedioxy-4'-hydroxybibenzyl or 3,4'-dimethoxy-4,5-methylenedioxy-3'-hydroxybibenzyl. To determine its structure, the bibenzyl (**3**) was synthesized as follows. A hydroxyl group of vanillin (**23**) was protected by benzyl bromide to give vanillin benzyl ether (**24**) which was refluxed with 3-methoxy-4,5-methylenedioxybenzylphosphonium bromide (**20**) to afford the stilbene mixtures (**25**), followed by catalytic hydrogenation to furnish a dihydrostilbene whose physical and spectral data, and chromatographic behaviour were identical to those of the natural bibenzyl (**3**).

The crude extract of *F. parvistipula* was treated in the same manner described above to give two new bibenzyls (**4**) and (**5**), together with a sesquiterpene lactone, eremofrullanolide (**11**) [4]. Compound **4**, mp 132–133°, contained the ^1H NMR signals (Table 1) of two methylenedioxyl groups, six protons on benzene rings and two benzylic methylenes. The MS spectrum showed a molecular ion at *m/z* 270 and the base peak at *m/z* 137, indicating the presence of two methylenedioxybenzyl groups in **4**, and 3,4,3',4'-dimethylenedioxybibenzyl was thus suggested for **4**. Condensation of 3,4-methylenedioxybenzylphosphonium bromide (**28**) with 3,4-methylenedioxybenzaldehyde (**29**) gave the stilbene mixtures (**30**), which was hydrogenated as described above to afford a dihydrostilbene which was identical to the natural 3,4,3',4'-dimethylenedioxybibenzyl (**4**) in all respects. The new bibenzyl (**5**) contained the molecular ion at *m/z* 302 and the base peak at 161, suggesting that **5** might possess two hydroxymethylenedioxybenzyl groups. In order to purify it, **5** was methylated with methyl iodide, after confirming the absence of any methoxyl group in the molecule, to give a dimethyl ether (**6**), whose ^1H NMR spectrum (Table 1) indicated the presence of two methylenedioxy groups, two methoxyl groups, two benzylic methylene groups and four protons on benzene rings. On the above evidence along with biogenetic considerations, the structure of **5** was suggested to be 3,3'-dihydroxy-4,5,4',5'-dimethylenedioxybibenzyl. To confirm this assumption, the methyl ether (**6**) and the original bibenzyl (**5**) were synthesized. Wittig reaction of 3-methoxy-4,5-methylenedioxybenzylphosphonium bromide (**20**) with 3-methoxy-4,5-methylenedioxybenzaldehyde (**31**) prepared from 3-methoxy-4,5-methylenedioxybenzyl alcohol (**18**) gave the stilbene mixture (**32**), which was hydrogenated in the same manner described above to afford 3,3'-dimethoxy-4,5,4',5'-dimethylenedioxybibenzyl (**6**) whose physical and spectral data were in good agreement of those of the dimethyl ether (**6**) of the natural bibenzyl (**5**). Demethylation of **6** in the presence of phosphorus tribromide gave **5**, whose chromatographic (TLC, GC) and spectral data were identical to the natural bibenzyl (**5**).

On chromatography of the crude extract of *F. davurica*

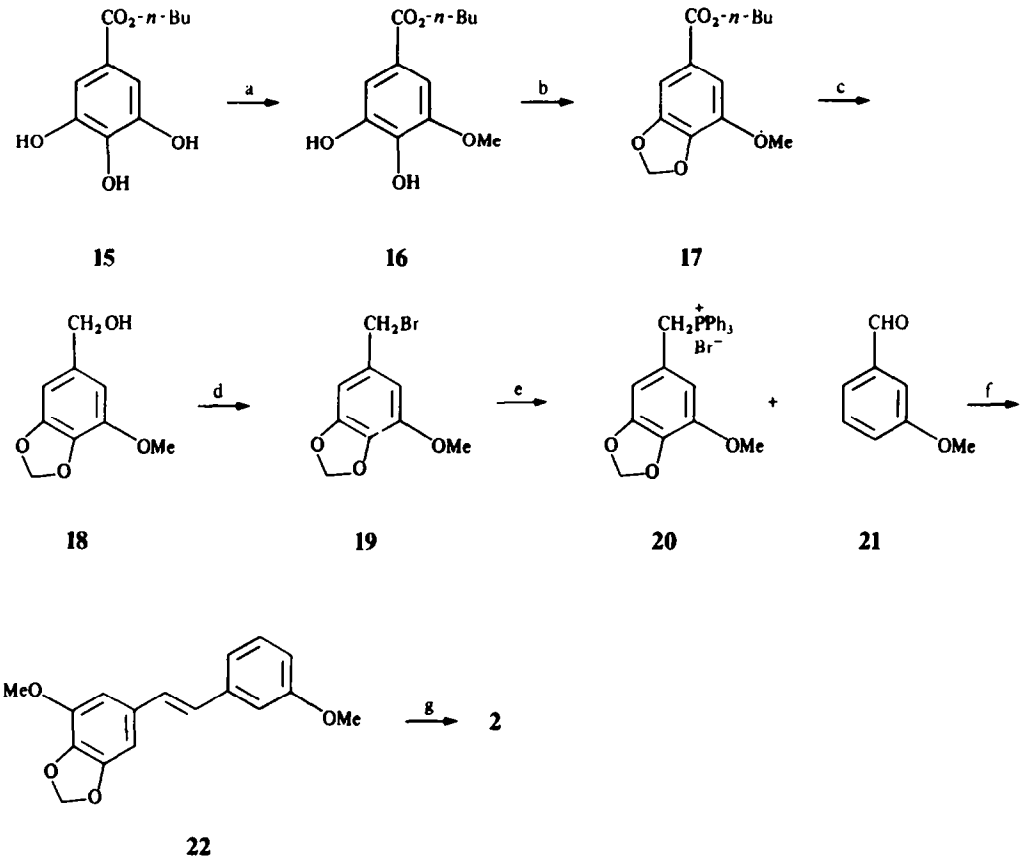


Table 1. ^{1}H NMR data of new bibenzyls

Compounds	2	3	4	6
Ph–$(CH_2)_2$–Ph	2.76 *s*	2.76 *s*	2.78 *s*	2.75 *s*
OMe	3.73 *s*	3.82 *s*		3.83 *s*
	3.80 *s*			
–O–CH_2–O–	5.83 *s*	5.86 *s*	6.00 *s*	5.85 *s*
Ph–	6.13–7.17 *m*	6.20–6.87 *m*	6.60 *m*	6.13–6.30 *m*

the previously known two bibenzyls (**7**) and (**8**) were isolated [5]. The extract of *F. vethii* was treated in the same manner as described above to give 5-hydroxy-7,4'-dimethoxyflavone (**9**) [1]. From the extract of *F. diversitexta*, a sesquiterpene ketone, (+)-cyclocolorenone (**12**), was obtained as major component [1]. The extract of *F. usamiensis* was chromatographed on silica gel to give two sesquiterpene lactones whose physical and spectral data were identical to those of (+)-β-cyclocostunolide (**13**) and (−)-γ-cyclocostunolide (**14**), respectively [4].

Most liverworts contain lunularic acid (**10**) which possess dormancy inducing and plant growth inhibitory activities [6–8]. European *F. dilatata* and *F. tamarisci* also produce **10** [8]. The present isolated bibenzyl derivatives might be derived from **10**.

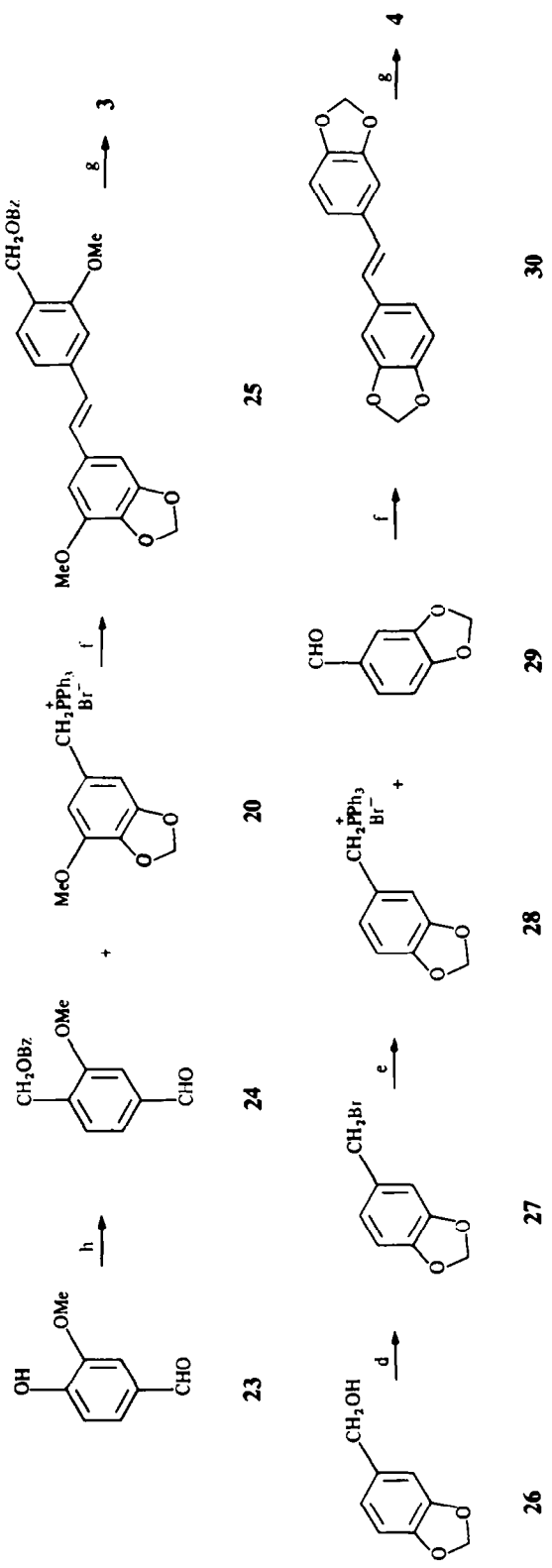
EXPERIMENTAL

TLC, GC and GC/MS were carried out as previously reported [9]. The solvents used for spectral determination were: TMS–$CDCl_3$ [^{1}H NMR 60 MHz)]; EtOH (UV); $CHCl_3$ (IR).

Plant materials. Frullania bonincola Hatt., *F. davurica* Hampe, *F. diversitexta* Steph., *F. ericoides* (Nees) Mont., *F. palvistipula* Steph., *F. usamiensis* Steph. and *F. vethii* Lac. identified by Dr. S. Hattori were deposited at the Herbarium of Institute of Pharmacognosy, Tokushima Bunri University.

Extraction and isolation. The crude extract (280 mg) of *F. ericoides* was chromatographed on silica gel using an *n*-hexane–EtOAc gradients to give 5 fractions. From fraction 2 (5% EtOAc) bibenzyl (**1**) (60 mg) [3] was obtained. Fraction 3 (10% EtOAc) was chromatographed on silica gel using the same solvent system described above to give bibenzyl (**2**) (45 mg): mp 135–137°; $C_{17}H_{18}O_4$; UV λ_{max} nm (log ε): 247 (3.63), 274 (3.51), 279 (3.50); IR ν_{max} cm^{-1}: 3020, 2950, 2850, 1612, 1603, 1588, 1510, 1492, 925, 730; ^{1}H NMR (Table 1); MS *m/z* (rel. int.): 287 $[M+1]^+$ (5), 286 $[M]^+$ (31), 166 (12), 165 (100), 77 (6). All spectral data were identical to those of the synthetic product (**2**) described later.

The crude extract (180 mg) of *F. bonincola* (20.2 g) was treated in the same manner described above to give bibenzyl (**3**) (56 mg):



mp 62–63°; $C_{17}H_{18}O_5$; UV λ_{max} nm (log ε): 226 (3.20), 282 (2.75); IR ν_{max} cm^{-1}: 3570, 3010, 2950, 2850, 2780, 1612, 1510, 1495, 930; ^1H NMR (Table 1); MS *m/z* (rel. int.): 303 $[M+1]^+$ (7), 302 $[M]^+$ (41), 167 (5), 166 (19), 165 (100), 138 (6), 137 (72), 122 (7), 77 (7). The crude extract (320 mg) of *F. parvistipula* (17.6 g) was treated in the same manner as described above to give two bibenzyls (**4**) (12 mg) and (**5**) (65 mg), together with a sesquiterpene lactone, (+)-eremofrullanolide (**11**) (135 mg) [4]. **4**: mp 132–133°, $C_{16}H_{14}O_4$; UV λ_{max} nm (log ε): 212 (3.98), 235 (3.93), 288 (3.90); IR ν_{max} cm^{-1}: 2780, 1610, 1506, 1492, 1445, 940; MS *m/z* (rel. int.): 271 $[M+1]^+$ (7), 270 $[M]^+$ (35), 136 (13), 135 (100), 105 (6), 77 (15), whose physical and spectral data were identical to those of the synthetic product (**4**) (see later). **5**: MS *m/z* (rel. int.): 302 $[M]^+$ (20), 161 (100).

The ether extract (580 mg) from *F. davurica* (48 g) was chromatographed on silica gel using C_6H_6–EtOAc gradient to give two bibenzyls (**7**) (35 mg) and (**8**) (16 mg) whose spectral data were in good agreement with those of authentic 3-methoxy-4′-hydroxybibenzyl and 3,4′-dimethoxybibenzyl, respectively [5].

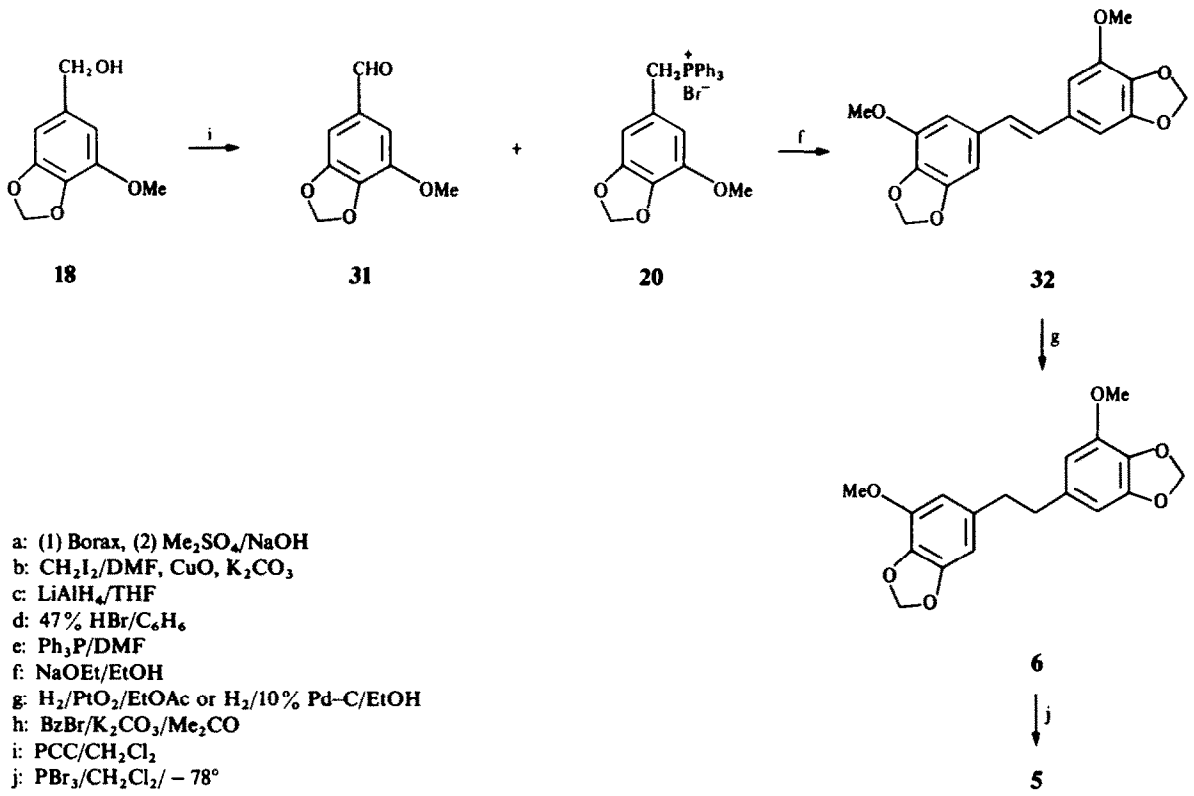
F. diversitexta (28 g) was extracted with Et_2O. On removal of the solvent the crude oil (520 mg), which showed one large spot on TLC, was obtained. Prep. TLC of the extract gave a conjugated ketone (250 mg) whose physical and spectral data were identical to those of authentic cyclocolorenone (**12**) [1].

The extract (1.30 g) of *F. usamiensis* (78 g) was treated in the same manner described above to divide into 15 fractions. Fraction eluted by 20% EtOAc was rechromatographed on silica gel impregnated with $AgNO_3$ (5%) using the same solvent system described above to afford (+)-β-cyclocostunolide (**13**) (20 mg) and (−)-γ-cyclocostunolide (**14**) (70 mg) [4].

F. vethii (120 g) was extracted with Et_2O to give the crude oil (4.30 g), which was chromatographed on silica gel using an *n*-hexane–EtOAc gradient to divide into 22 fractions. From fraction 17, 5-hydroxy-7,4′-dimethoxyflavone (**9**) [1] was obtained.

Synthesis of 3,3′-dimethoxy-4,5-methylenedioxybibenzyl (**2**). To *n*-butyl gallate (**15**) (4.00 g) was added 5% H_3BO_3 (320 ml) and then stirred. To the solution was added dropwise Me_2SO_4 (12 ml) and NaOH (3.2 g/20 ml) and then stirred at room temp. for 1.2 hr and allowed to stand overnight. The solution was acidified by dil. H_2SO_4 and extracted with EtOAc to give *n*-butyl 3,4-dihydroxy-5-methoxybenzoate (**16**) (2.88 g): IR ν_{max} cm^{-1}: 3580, 3350, 2900, 1710, 1620, 1520, 1470, 1190; ^1H NMR: δ0.92 (3H, *t*, *J* = 7.0 Hz), 1.15–1.80 (4H, *m*), 3.80 (3H, *s*), 4.23 (2H, *t*, *J* = 6.0 Hz), 6.30 (2H, *br s*, OH), 7.10 (1H, *d*, *J* = 2.0 Hz), 7.28 (1H, *d*, *J* = 2.0 Hz); MS *m/z* (rel. int.): 240 $[M]^+$ (20), 184 (100).

To DMF (16 ml) was added K_2CO_3 (3 g), CuO (200 mg), CH_2I_2 (1.2 ml) and **16** and stirred at 120–125° for 3 hr in N_2. On removal of the solvent, Et_2O was added to the reaction mixture and the solution was filtered and the solvent was evaporated to give *n*-butyl 3-methoxy-4,5-methylenedioxybenzoate (**17**) (1.90 g): IR ν_{max} cm^{-1}: 3025, 2950, 2880, 1710, 1635, 1610, 1510, 1500, 1465, 1450, 1190, 925; ^1H NMR: δ0.97 (3H, *t*, *J* = 7.0 Hz), 1.17–1.83 (4H, *m*), 3.88 (3H, *s*), 4.28 (2H, *t*, *J* = 4.0 Hz), 5.97 (2H, *s*, $-O-CH_2-O-$), 7.08 (2H, *J* = 2.0 Hz), 7.22 (2H, *d*, *J* = 2.0 Hz); MS *m/z* (rel. int.): 252 $[M]^+$ (10), 196 (100). To $LiAlH_4$ (100 mg) in THF (10 ml) was added dropwise (**17**) (1.36 g) in THF (10 ml) and stirred at room temp. for 2 hr. Work up as usual gave 3-methoxy-4,5-methylenedioxybenzyl alcohol (**18**) (980 mg): IR ν_{max} cm^{-1}: 3600, 3400; ^1H NMR: δ2.87 (1H, *br s*, OH), 3.80 (3H, *s*), 4.40 (2H, *s*), 5.80 (2H, *s*), 6.37 (2H, *s*); MS *m/z* (rel. int.): 182 $[M]^+$ (100), 165 (63). **18** (700 mg) in C_6H_6 (8 ml) was treated with 47% HBr (1 ml) and stirred at room temp. for 2 hr. Work up as usual afforded 3-methoxy-4,5-methylenedioxybenzyl bromide (**19**) (850 mg): IR ν_{max} cm^{-1}: 3000, 2840, 1635, 1610, 1510, 1505, 1495, 1465, 1450, 930, 720, 580; ^1H NMR: δ3.85 (3H, *s*), 4.36 (2H, *s*),



a: (1) Borax, (2) Me_2SO_4/NaOH
b: CH_2I_2/DMF, CuO, K_2CO_3
c: $LiAlH_4$/THF
d: 47% HBr/C_6H_6
e: Ph_3P/DMF
f: NaOEt/EtOH
g: H_2/PtO_2/EtOAc or H_2/10% Pd–C/EtOH
h: BzBr/K_2CO_3/Me_2CO
i: PCC/CH_2Cl_2
j: PBr_3/CH_2Cl_2/ − 78°

5.90 (2H, *s*), 6.33 (2H, *s*); MS *m/z* (rel. int.): 246 $[M]^+$ ($C_9H_9O_3{}^{81}Br$) (10), 244 $[M]^+$ ($C_9H_9O_3{}^{79}Br$) (10), 166 (9), 165 (100), 120 (6), 77 (6). To a solution of **19** (800 mg) in DMF (10 ml) was added triphenylphosphine (1.0 g) and refluxed at 155° for 3 hr to give a phosphonium salt which was recrystallized from Me_2CO to afford 3-methoxy-3,4-methylenedioxybenzylphosphonium bromide (**20**) (1.53 g): ^1H NMR: δ 3.56 (3H, *s*), 5.40 (2H, *d*, *J* = 14.0 Hz, $-CH_2-P$), 5.83 (2H, *s*), 6.20 (1H, *br s*), 6.60 (1H, *br s*), 7.56–7.93 (15H, *m*). A mixture of **20** (700 mg) and 3-methoxybenzaldehyde (**21**) (200 mg) in EtOH (20 ml) was treated with NaOEt to give the stilbene mixtures (**22**): mp 79–81°; IR ν_{max} cm^{-1}: 3010, 2970, 2950, 2780, 1623, 1605, 1598, 1580, 1510, 1493, 1480, 956, 930; ^1H NMR: δ 3.80, 3.90 (each, 3H, *s*), 5.90 (2H, *s*), 6.53–7.06 (8H, *m*); MS *m/z* (rel. int.): 285 $[M + 1]^+$ (25), 284 $[M]^+$ (100), 211 (12), 168 (10), 165 (11), 152 (10), 139 (15). **22** (500 mg) in EtOAc was hydrogenated in the presence of PtO_2 to give 3,3'-dimethoxy-4,5-methylenedioxybibenzyl (**2**) whose physical and spectral data were consistent with those of the natural bibenzyl (**2**).

Synthesis of 3,3'-*dimethoxy*-4-*hydroxy*-4',5'-*methylenedioxybibenzyl* (**3**). Vanillin (**23**) (1.0 g) in Me_2CO was treated with benzyl bromide (1.35 g) in the presence of dry K_2CO_3 to give **24** (1.20 g). Wittig condensation of **24** (50 mg) and **20** (100 mg) in NaOEt–EtOH gave the stilbene mixtures (**25**): mp 82–84°; IR ν_{max} cm^{-1}: 3020, 2940, 2900, 2780, 1605, 1585, 1510, 1495, 930, 725; ^1H NMR: δ 3.63, 3.87 (each, 3H, *s*), 5.04, 5.06 (each 2H, *s*), 5.80, 5.85 (each, 2H, *s*), 6.30, 6.35 (each, 2H, *s*), 6.74–7.30 (10H, *m*); MS *m/z* (rel. int.): 391 $[M + 1]^+$ (6), 390 $[M]^+$ (20), 300 (19), 299 (100), 213 (5), 91 (16). Hydrogenation of **25** (40 mg) in the presence of 10% Pd–C gave 3,3'-dimethoxy-4-hydroxy-4',5'-methylenedioxybibenzyl (**3**) whose physical and spectral data were identical to those of the natural product (**3**).

Synthesis of 3,4,3',4'-*dimethylenedioxybibenzyl* (**4**). To piperonyl alcohol (**26**) (3.20 g) in C_6H_6 was added 47% HBr (2.8 ml) and stirred at room temp. for 2 hr. Work up as usual gave piperonyl bromide (**27**) (3.77 g) which was treated with triphenylphosphine (5.80 g) in DMF and refluxed at 155° for 3 hr to give a phosphonium salt (**28**) (2.85 g). A mixture of **28** (1.20 g) and 3-methoxybenzaldehyde (**29**) (500 mg) was refluxed with NaOEt in EtOH (30 ml). Work up as usual gave the stilbene mixtures (**30**) (1.10 g): mp 164–165°; UV λ_{max} nm (log ε): 220 (4.15), 294 (3.93), 335 (4.03), 350 (3.84); IR ν_{max} cm^{-1}: 2780, 1620, 1505, 1495, 1445, 930, 920; ^1H NMR: δ 5.81 (4H, *s*, $-O-CH_2-O-$ × 2), 6.35 (2H, *s*), 6.51–6.78 (6H, *m*); MS *m/z* (rel. int.): 268 $[M]^+$ (100), 153 (12), 152 (29), 151 (13). **30** (500 mg) in EtOAc (8 ml) was hydrogenated in the presence of PtO_2 (60 mg) to afford 3,4,3'4'-dimethylenedioxybibenzyl (**4**) (420 mg) whose physical and spectral data were identical to those of the natural bibenzyl (**4**).

Synthesis of 3,3'-*dimethoxy*-4,5,4',5'-*dimethylenedioxybibenzyl* (**6**). 3-Methoxy-4,5-methylenedioxybenzyl alcohol (**18**) (150 mg) was oxidized by pyridiniumchlorochromate (PPC) (270 mg) in CH_2Cl_2 (2 ml). Work up as usual gave 3-methoxy-4,5-methylenedioxybenzaldehyde (**31**) (140 mg): ^1H NMR: δ 9.76 (1H, *s*); MS *m/z* (rel. int.): 180 $[M]^+$ (100). Wittig condensation of **31** (80 mg) and **20** (226 mg) in the same manner as described above to give the stilbenes (**32**) (120 mg): UV λ_{max} nm (log ε): 203 (3.83), 223 (3.90), 243 (3.79), 252 (3.66), 335 (3.98), 350 (3.83); IR ν_{max} cm^{-1}: 3000, 2940, 2880, 2780, 1625, 1508, 1495, 928, 720; ^1H NMR: δ 3.88 (6H, *s*), 5.88 (4H, *s*), 6.45–6.71 (6H, *m*); MS *m/z* (rel. int.): 329 $[M + 1]^+$, 328 $[M]^+$ (100), 165 (5), 139 (5), 126 (7). A solution of **32** (120 mg) in EtOH (5 ml) was hydrogenated in the presence of 10% Pd–C to furnish 3,3'-dimethoxy-4,5,4',5'-dimethylenedioxybibenzyl (**6**) (93 mg) whose physical and spectral data were identical to those of the methoxylated stilbene (**6**) derived from

the natural bibenzyl (**5**). **6** (40 mg) in CH_2Cl_2 (2 ml) was treated with PBr_3 at $-78°$ to afford 3,3'-dihydroxy-4,5,4',5'-dimethylenedioxybibenzyl whose chromatographic and MS spectral data were identical to those of the natural bibenzyl (**5**).

Methylation of **5**. The crude bibenzyl (**5**) (50 mg) was methylated by MeI in the presence of dry K_2CO_3 to give a dimethoxyether (**6**), which was identical to the synthetic **6** in all respects.

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