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FLAVONOID AND OTHER CONSTITUENTS OF *BAUHINIA MANCA**

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Key Word Index—*Bauhinia manca*; Leguminosae; 5,5-dimethoxylariciresinol; 4-*O*-methylisoliquiritigenin; 4'-*O*-methylliquiritigenin; 7,3'-dimethoxy-4-hydroxyflavan; 3',4'-dihydroxy-7-methoxyflavan; 2,4'-dihydroxy-4-methoxydihydrochalcone; antimicrobial activity.

Abstract—Phytochemical analysis of the stem of *Bauhinia manca* yielded 63 compounds, among them six new natural products. Major constitutents were found to be 3-*O*-galloylepicatechin, gallic acid, cinnamic acid, β-sitosterol and its β-D-glucoside. The two new flavans possess significant antifungal activity.

INTRODUCTION

The genus *Bauhinia* comprises about 300 species growing in tropical areas around the globe [1]. Some *Bauhinia* species are used as remedies against various diseases in folk medicines of Africa, Asia, Middle and South America [2–5]. Up to now, only about 10 *Bauhinia* species have been investigated phytochemically [1, 6].

Bauhinia manca Standley is a climber found in forests of Costa Rica and Panama [5]. An infusion from its stems (and leaves) is used as an antidiabetic, astringent and diuretic agent [7, 8]. Stems of *B. manca* are also reported to have antirheumatic properties [9]. Pharmacological studies demonstrated the hypoglycaemic activity of stem extracts in animal tests [9–11]. Since nothing is known on the constituents of this plant, we started a phytochemical analysis of the stem.

RESULTS

Extracts from stems of *Bauhinia manca* were partitioned between organic solvents and water followed by chromatographic separation and structure determination of pure substances. As the result, 63 compounds were obtained, among them a series of 10 *p*-coumaric acid and 7 ferulic acid esters with long chain alcohols, which have already been reported in a preceding communication [12].

The other constituents are compiled in Table 1. Main constituent of the stem of *B. manca* is 3-*O*-galloylepicatechin (**20**); major components are gallic acid, cinnamic acid, β-sitosterol and its β-D-glucoside. All other compounds have been found in low concentrations only. No alkaloids could be detected.

The structure determinations are mainly based on spectroscopic studies of the isolated compounds and suitable derivatives. In some cases synthetic studies were performed to furnish final proof of structures. Absolute configurations were deduced from CD measurements.

Antifungal tests demonstrate significant antibiotic activity of some of the isolated compounds against various fungi (Table 2). Maximum effects were observed for **14** and **17**.

DISCUSSION

The flavonoids **8**, **13**, **16** and **17**, the dihyrochalcone **10** and the lignan **3** are hitherto unknown natural products. The flavonoids **6** and **11** can be considered characteristic constituents of the Leguminosae [13]. **9** and **10** belong to the so-called 'retro-chalcones' [14], which are of special interest from a biogenetic point of view. Up to now, retro-chalcones had only been described in *Glycyrrhiza* species, and **10** is the first dihydro-compound in this group. Some of the antifungal components isolated from *B. manca* are already known as phytoalexins in the literature [15, 16]. From a pharmacological point of view the glucoside of β-sitosterol might be responsible for antidiabetic activity [17–20], whereas the high content of gallic acid and gallic acid derivatives explains the use of the plant as an astringent.

EXPERIMENTAL

General procedures. Mps are uncorr. TLC was performed on precoated plates (Nano plates Sil-20 UV, Macherey-Nagel); detection: UV and anisaldehyde [21] followed by heating. UV/Vis and CD were recorded in MeOH solution, IR spectra in KBr or $CHCl_3$. Unless otherwise stated, ^1H NMR spectra were recorded at 90 MHz, ^{13}C NMR spectra at 22.5 MHz with TMS as internal standard. MS were obtained by EI at 70 eV.

Plant material according to [12]. Collection was done in Moravia de Siquirres, Provincia Limón, Costa Rica, in January 1982. The plant material was compared by M. A. Constenla with the herbarium specimen held under no. 7634 (Tonduz, 1983) no. 61784 (1976) no. 74347 (1951) no. 59536 (1975) and no. 87969 (1981) in the herbarium of the Museo Nacional de Costa Rica, San José, and in addition identified by R. A. Ocampo.

*Part 31 in the series 'Constituents of Tropical Medicinal Plants'. For Part 30 see Torrenegra, R., Pedrozo P., J.A., Achenbach, H. and Bauereiß, P. (1988) *Phytochemistry* **27**, 1843–48.

Table 1. Constituents of *B. manca*

Structural class	Compound	Isolated from	Concentrations† (ca)
Sterols	β-Sitosterol	P	230
	β-Sitosterol-3-*O*-β-D-glucoside	T	170
	Stigmast-4-en-3-one	P	19
	Stigmast-4-en-3,6-dione	T	3.5
Acetogenins	Alkanols [$Me(CH_2)_nCH_2OH$] $n=20\rightarrow26$	T	10
	Hexadecanoic acid	D	0.03
Shikimates	Cinnamic acid	D	110
	Cinnamoyl-β-D-glucose	E	0.7
	(E)-4-Hydroxycinnamic acid methyl ester*	D	2
	(E)-4-Hydroxy-3-methoxycinnamic acid methyl ester*	D	0.7
	Gallic acid	E	340
	Gallic acid methyl ester*	E	460
	4-Hydroxy-2-methoxybenzoic acid methyl ester*	D	1.5
	4-Hydroxy-3-methoxybenzoic acid methyl ester*	D	0.7
	3,4-Dihydroxybenzoic acid methyl ester*	D	14
	ω-Hydroxypropioguaiacone (**1**)	D	4
	Syringaresinol (**2**)	D	20
	(7*S*,8*R*,8′*R*)-5,5′-Dimethoxylariciresinol (**3**)	D	3
Flavonoids	Apigenin	D	0.4
	Chrysoeriol (**4**)	D	0.7
	Luteolin 5,3′-dimethyl ether (**5**)	D	0.7
	Kaempferol	D	1.5
	Isoliquiritigenin (**6**)	D	20
	Isoliquiritigenin 2′-methyl ether (**7**)	D	3
	Isoliquiritigenin 4-methyl ether (**8**)	D	1.5
	Echinatin (**9**)	D	0.4
	2,4′-Dihydroxy-4-methoxydihydrochalcone (**10**)	D	1
	(2*S*)-Naringenin	D	14
	(2*S*)-Eriodictyol	D	6
	(2*S*)-Liquiritigenin (**11**)	D	7
	(2*S*)-Liquiritigenin 7-methyl ether (**12**)	D	0.7
	(2*S*)-Liquiritigenin 4′-methyl ether (**13**)	D	0.4
	(2*S*)-7,4′-Dihydroxyflavan (**14**)	D	3
	(2*S*)-4′-Hydroxy-7-methoxyflavan (**15**)	T	70
	(2*S*)-7,3′-Dimethoxy-4′-hydroxyflavan (**16**)	T	3.5
	(2*S*)-3′,4′-Dihydroxy-7-methoxyflavan (**17**)	D	3
	(2*S*)-7,4′-Dihydroxy-3′-methoxyflavan (**18**)	D	0.3
	Obtustyrene (**19**)	T	0.7
(Others)	5,7-Dihydroxychromone	D	1
	(2*R*,3*R*)-3-*O*-Galloylepicatechin (**20**)	E	570

(P: petrol extract; T: CCl_4 extract; D: dichloromethane extract; E: ether extract).
*Might (partly) be artefacts.
†Concentrations are given in $\%\cdot10^{-3}$ (total MeOH extract = 100%).

Extraction and chromatography. After exhaustive extraction with petrol [12] the ground woody parts of the plant (5 kg) were extracted with 15 l of MeOH for 160 hr in a Soxhlet under reduced pressure (60°, 200 mbar). The solvent was removed yielding 370 g residue, which was dissolved in a mixture of MeOH and H_2O and extracted successively with CCl_4, CH_2Cl_2 and Et_2O. These extracts were concd to yield 12 g residue from CCl_4, 5 g from CH_2Cl_2 and 8 g from Et_2O. The individual extracts were repeatedly subjected to CC using silica gel, Sephadex LH-20, Fractogel PVA 500 or Fractogel TSK HW-40 (S), respectively, and various eluents. The following compounds were isolated: **15**, **16**, **19** from the CCl_4 extract, **1**–**14**, **17**, **18** from the CH_2Cl_2 extract and **20** from the Et_2O extract.

General procedure for methylation. The sample (0.0005–0.05 mmol) was dissolved in dry acetone (1–10 ml), MeI (0.1–2.5 ml) and K_2CO_3 (10–250 mg) were added, and the reaction mixture was stirred for 12 hr at room temp. After filtration and evapn the product was dissolved in $CHCl_3$ and purified by CC over silica gel.

General procedure for acetylation. The sample (0.005–0.2 mmol) was dissolved in a mixture of pyridine p.a. and Ac_2O (1:1, 0.5–5 ml) and stirred for 24 hr at room temp. After removal of the reaction mixture the product was purified by CC over silica gel.

ω-Hydroxypropioguaiacone (**1**). Colourless crystals (10 mg), mp 93–95°; TLC (cyclohexane–acetone 7:3): R_f 0.10, orange-

Table 2. Antifungal activities of some isolated compounds against various fungi

Compound	*Botrytis cinerea*	*Claviceps viridis*	*Coprinus cinereus*	*Rhizoctonia solani*	*Saprolegnia asterophora*
6	(+)	—	—	—	+
7	(+)	—	—	—	(+)
8	—	○	○	○	—
9	+	○	○	○	+
14	(+)	+	++	+	++
15	(+)	—	+	(+)	(+)
16	(+)	+	—	+	(+)
17	+	+	+	+	++
18	(+)	(+)	(+)	(+)	+
19	+	+	(+)	+	+

++ = high activity, + = low activity, (+) = very low activity, − = inactive, ○ = not tested.

brown with anisaldehyde; UV λ_{max} nm (log ε): 229 (4.13), 276 (3.99), 304 (3.92); +NaOH: 248 (3.96), 290 (3.72, sh), 345 (4.26); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530 (OH), 1665 (C=O), 1600 (C=C); ^1H NMR ($CDCl_3$): δ2.04 (1H, *br*, $CH_2\underline{OH}$), 3.18 (2H, *t*, *J* = 5.5 Hz, H_2-2), 3.96 (3H, *s*, OMe), 4.02 (2H, *t*, *J* = 5.5 Hz, H_2-3), 6.19 (1H, *br*, Ar-O<u>H</u>), 6.95 (1H, *d*, *J* = 8.5 Hz, H-5'), 7.53 (1H, *d*, *J* = 2 Hz, H-2'), 7.55 (1H, *dd*, J_1 = 8.5, J_2 = 2 Hz, H-6'); ^{13}C NMR (acetone-d_6): δ41.6 (C-2), 56.5 (OMe), 58.8 (C-3), 111.9 (C-2'), 115.4 (C-5'), 124.0 (C-6'), 131.0 (C-1'), 148.4 (C-4'), 152.4 (C-3'), 198.2 (C-1); MS *m/z* (rel. int.): 196 (24, $[M]^+$), 151 (100), 123 (8), 43 (14).

ω-Hydroxypropioguaiacone diacetate. **1** (2 mg) was acetylated; CC (cyclohexane-EtOAc 4:1) yielded 2 mg colourless crystals, mp 56–58°; TLC (cyclohexane–EtOAc 4:1): R_f 0.10, brownish-yellow with anisaldehyde; UV λ_{max} nm (log ε): 254 (3.92), 302 (3.53); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1765, 1735, 1685 (C=O), 1600 (C=C); ^1H NMR ($CDCl_3$): δ2.04 (3H, *s*, $CH_2O\underline{Ac}$), 2.34 (3H, *s*, Ar-O<u>Ac</u>), 3.29 (2H, *t*, *J* = 6 Hz, H_2-2), 3.90 (3H, *s*, OMe), 4.51 (2H, *t*, *J* = 6 Hz, H_2-3), 7.13 (1H, *d*, *J* = 8.5 Hz, H-5'), 7.56 (1H, *dd*, J_1 = 8.5, J_2 = 2 Hz, H-6'), 7.61 (1H, *d*, *J* = 2 Hz, H-2'); MS *m/z* (rel. int.): 280 (1, $[M]^+$), 238 (34), 178 (11), 151 (100), 43 (30).

(7S,8R,8'R)-5,5'-Dimethoxylariciresinol (**3**). Colourless crystals (5 mg), mp 124–126°; TLC (CCl_4–MeOH 4:1); R_f 0.34, violet with anisaldehyde; $[\alpha]_D^{21}$ +5° (MeOH; *c* 0.27); CD nm (Δε): 247 (−0.7); UV λ_{max} nm (log ε): 235 (4.08, sh), 272 (3.64), 280 (3.60, sh); +NaOH: 256 (4.15), 285 (4.07, sh); IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1610, 1520 (C=C); ^1H NMR (400 MHz, acetone-d_6) [22]: δ2.32 (1H, *dddd*, $J_1 \approx J_2 \approx J_3 \approx J_4 \approx$ 7 Hz, H-8), 2.53 (1H, *dd*, J_1 = 13.5, J_2 = 11 Hz, H_A-7'), 2.71 (1H, *m*, H-8'), 2.95 (1H, *dd*, J_1 = 13.5, J_2 = 5 Hz, H_B-7'), 3.69 (1H, *dd*, J_1 = 8, J_2 = 7 Hz, H_A-9'), 3.81 (12H, *s*, OMe), 3.85 (2H, *m*, H_2-9), 3.94 (1H, *dd*, J_1 = 8, J_2 = 6.5 Hz, H_B-9'), 4.80 (1H, *d*, *J* = 7 Hz, H-7), 6.53 (2H, *s*, H-2', H-6'), 6.66 (2H, *s*, H-2, H-6); ^{13}C NMR (CD_3OD) [23]; δ34.0 (C-7'), 43.8 (C-8'), 54.1 (C-8), 56.9 (OMe), 60.6 (C-9), 73.6 (C-9'), 84.3 (C-7), 104.6 (C-2, C-6), 107.3 (C-2', C-6'), 132.9 (C-1, C-1'?), 135.2 (C-4, C-4'), 149.4 (C-3, C-3', C-5, C-5'); MS *m/z* (rel. int.): 420 (73, $[M]^+$), 235 (10), 181 (31), 168 (43), 167 (100), 151 (35), 137 (30), 43 (20).

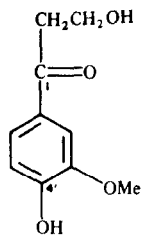
(7S,8R,8'R)-5,5'-*Dimethoxylariciresinol triacetate.* **3** (1 mg) was acetylated to yield the triacetate (without further purification); TLC (cyclohexane–acetone 1:1): R_f 0.49, violet with anisaldehyde; UV λ_{max} nm (log ε): 270 (4.25), 278 (4.20, sh); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1740 (C=O), 1605 (C=C), 1370 (<u>Me</u>CO), 1140 (C-O); ^1H NMR (400 MHz, $CDCl_3$): δ2.06 (3H, *s*, CH_2OAc), 2.33 (6H, *s*, Ar-OAc), 2.58 (1H, *dd*, J_1 = 13.5, J_2 = 10.5 Hz, H_A-7'), 2.60 (1H, *m*, H-8), 2.73 (1H, *m*, H-8'), 2.87 (1H, *dd*, J_1 = 13.5, J_2 = 4.5 Hz, H_B-7'), 3.77 (1H, *dd*, J_1 = 8.5, J_2 = 7.5 Hz, H_A-9'), 3.81 (6H, *s*, OMe), 3.83 (6H, *s*, OMe), 4.13 (1H, *dd*, J_1 = 8.5, J_2 = 6.5 Hz, H_B-9'), 4.24 (1H, *dd*, J_1 = 11.5, J_2 = 7.5 Hz, H_A-9), 4.42 (1H, *dd*, J_1 = 11.5, J_2 = 6.5 Hz, H_B-9), 4.85 (1H, *d*, *J* = 6 Hz, H-7), 6.41 (2H, *s*, H-2', H-6'), 6.58 (2H, *s*, H-2, H-6); MS *m/z* (rel. int.): 546 (9, $[M]^+$), 505 (10), 504 (31), 463 (10), 462 (39), 402 (7), 249 (11), 235 (27), 231 (14), 194 (12), 182 (13), 181 (40), 168 (40), 167 (100), 43 (62).

Racemic **3** *by hydrogenation of (racemic)* **2**. **2** (5 mg) was hydrogenated with Pd/C in EtOAc (room temp., 2 hr). The mixture was filtered, evapd and chromatographed (CC; silica gel, CCl_4–MeOH 9:1); among the products: racemic **3** (0.8 mg).

Luteolin 5-3'-dimethyl ether (**5**). Yellow crystals (1.7 mg), mp 290–292°; TLC ($CHCl_3$–MeOH 9:1): R_f 0.41, yellow with anisaldehyde; UV/Vis λ_{max} nm (log ε): 240 (4.15), 265 (4.09), 288 (3.95, sh), 337 (4.18); +NaOH: 230 (4.21, sh), 259 (4.21), 267 (4.18, sh), 320 (3.91, sh), 393 (4.26); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1640 (C=O), 1600 (C=C); ^1H NMR (400 MHz, CD_3OD): δ3.88 (3H, *s*, OMe), 3.96 (3H, *s*, OMe), 6.37 (1H, *d*, *J* = 2 Hz, H-6), 6.51 (1H, *d*, *J* = 2 Hz, H-8), 6.53 (1H, *s*, H-3), 6.92 (1H, *d*, *J* = 8.5 Hz, H-5'), 7.42 (1H, *d*, *J* = 2 Hz, H-2'), 7.47 (1H, *dd*, J_1 = 8.5, J_2 = 2 Hz, H-6'); MS *m/z* (rel. int.): 314 (100, $[M]^+$), 313 (29), 285 (19), 268 (28), 151 (27), 137 (21).

Luteolin 5,3'-dimethyl ether diacetate. **5** (1 mg) on acetylation and CC (CCl_4–MeOH 19:1) yielded 1 mg crystals, mp 195–198°; TLC (CCl_4–MeOH 19:1): R_f 0.18, yellow with anisaldehyde; UV/Vis λ_{max} nm (log ε): 237 (4.13), 266 (4.19), 320 (4.08); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770, 1645 (C=O), 1610 (C=C); ^1H NMR ($CDCl_3$): δ2.34 (3H, *s*, OAc), 2.36 (3H, *s*, OAc), 3.92 (3H, *s*, OMe), 3.99 (3H, *s*, OMe), 6.60 (1H, *d*, *J* = 2 Hz, H-6), 6.69 (1H, *s*, H-3), 7.00 (1H, *d*, *J* = 2 Hz, H-8), 7.17 (1H, *d*, *J* = 8.5 Hz, H-5'), 7.43 (1H, *d*, *J* = 2 Hz, H-2'), 7.48 (1H, *dd*, J_1 = 8.5, J_2 = 2 Hz, H-6'); MS *m/z* (rel. int.): 398 (39, $[M]^+$), 356 (27), 314 (32), 313 (19), 285 (10), 268 (7), 43 (100).

Isoliquiritigenin 2'-methyl ether (**7**). Yellow crystals (7 mg), mp 213–214.5°; TLC (cyclohexane–EtOAc 1:1): R_f 0.24, orange with anisaldehyde; UV/Vis λ_{max} nm (log ε): 237 (4.04), 350 (4.35); +NaOH: 258 (4.06), 318 (3.86, sh), 419 (4.48); IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1620 (C=O), 1600 (C=C); ^1H NMR (400 MHz, acetone-d_6): δ3.92 (3H, *s*, OMe), 6.53 (1H, *dd*, J_1 = 8.5, J_2 = 2 Hz, H-5'), 6.58 (1H, *d*, *J* = 2 Hz, H-3'), 6.90 (2H, <u>AA'</u>BB', H-3, H-5), 7.48 (1H, *d*, *J* = 16 Hz, H-α), 7.56 (1H, *d*, *J* = 16 Hz, H-β), 7.59 (2H, AA'<u>BB'</u>, H-2, H-6), 7.61 (1H, *d*, *J* = 8.5 Hz, H-6'), 8.88 (1H, *s*, OH), 9.08 (1H, *s*, OH); ^{13}C NMR (acetone-d_6): δ56.2 (OMe), 100.3 (C-3'), 108.8 (C-5'), 116.8 (C-3, C-5), 122.6 (C-1'), 125.7 (C-



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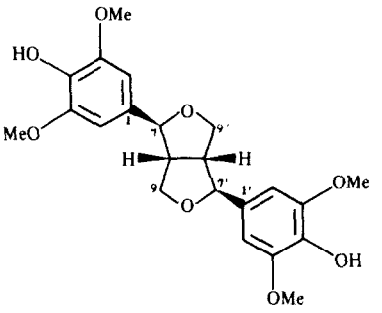

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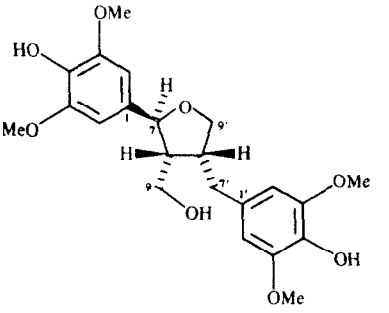

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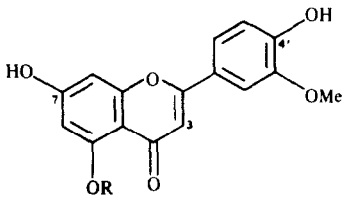

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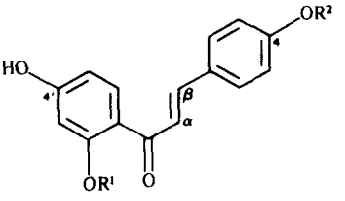

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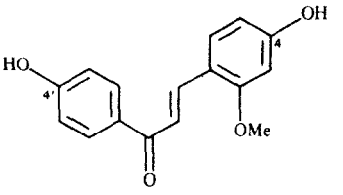

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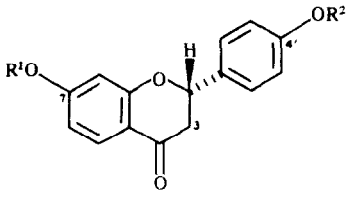

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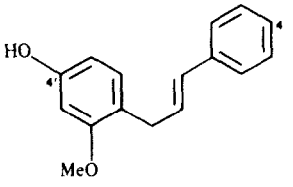

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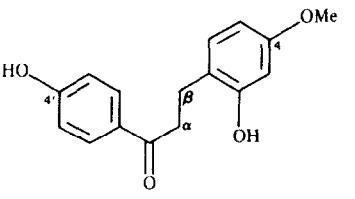

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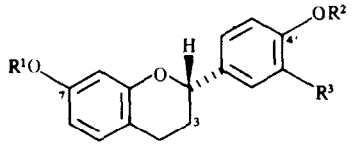

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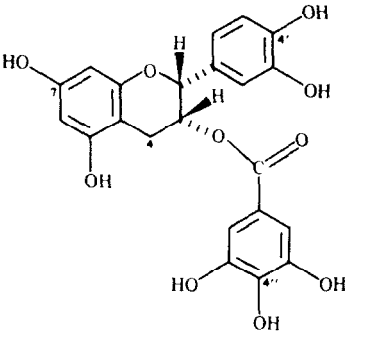
18 R^1 = H, R^2 = H, R^3 = OMe



20

1), 128.3 (C-α), 130.9 (C-2, C-6), 133.4 (C-6'), 142.0 (C-β), 160.3 (C-4), 161.8, 163.2 (C-2', C-4'), 190.0 (C=O); MS *m/z* (rel. int.): 270 (100, $[M]^+$), 269 (18), 255 (30), 253 (12), 242 (18), 199 (11), 164 (70), 163 (24), 151 (84), 147 (33), 137 (25), 121 (26), 120 (16), 119 (17), 118 (8), 108 (19), 107 (31), 91 (21), 65 (22), 43 (19).

Synthesis of **7**. 4'-Hydroxy-2'-methoxyacetophenone [160 mg (1 mmol)] and 4-hydroxybenzaldehyde [120 mg (1 mmol)] were dissolved in 0.5 ml EtOH; 1.9 g KOH (60%) were added and the mixture stirred for 24 hr at room temp. After dilution with 10 ml H_2O and acidification with acetic acid the mixture was extracted with $CHCl_3$ and purified by CC (silica gel, $CHCl_3$–MeOH 19:1) to yield **7** (80 mg).

Isoliquiritigenin 4-methyl ether (**8**). Yellow crystals (3 mg), mp 170–172°; TLC ($CHCl_3$–MeOH 19:1): R_f 0.64, yellow with

anisaldehyde; UV/Vis λ_{max} nm (log ε): 239 (3.89, sh), 309 (4.05, sh), 365 (4.18); +NaOH: 233 (4.01, sh), 279 (3.87), 330 (4.00), 395 (4.19); IR ν_{max}^{KBr} cm^{-1}: 3380 *br* (OH), 1630 (C=O), 1600 (C=C); ^1H NMR (acetone-d_6): δ3.87 (3H, *s*, OMe), 6.38 (1H, *d*, J = 2.5 Hz, H-3'), 6.48 (1H, *dd*, J_1 = 8.5, J_2 = 2.5 Hz, H-5'), 7.01 (2H, AA'BB', H-3, H-5), 7.82 (2H, AA'BB', H-2, H-6), 7.83 (2H, *s*, H-α, H-β), 8.12 (1H, *d*, J = 8.5 Hz, H-6'), 9.45 (1H, *s*, OH), 13.57 (1H, *s*, OH); MS *m/z* (rel. int.): 270 (86, $[M]^+$), 269 (48), 163 (21), 137 (30), 134 (100), 121 (93), 119 (10), 108 (17).

Isoliquiritigenin 4-methyl ether diacetate. **8** (1.5 mg) after acetylation and purification by CC (petrol–acetone 4:1) yielded 1.5 mg oily product; TLC ($CHCl_3$–MeOH 95:5): R_f 0.69, brown with anisaldehyde; UV/Vis λ_{max} nm (log ε): 232 (4.44), 337 (4.58); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770, 1660, 1640 (C=O), 1600 (C=C); ^1H NMR (400 MHz, acetone-d_6): δ 2.20 (3H, *s*, OAc), 2.31 (3H, *s*, OAc), 3.87 (3H, *s*, OMe), 7.03 (2H, AA'BB', H-3, H-5), 7.09 (1H, *d*, J = 2.5 Hz, H-3'), 7.21 (1H, *dd*, J_1 = 8.5, J_2 = 2.5 Hz, H-5'), 7.27 (1H, *d*, J = 16 Hz, H-α), 7.56 (1H, *d*, J = 16 Hz, H-β), 7.74, (2H, AA'BB', H-2, H-6), 7.88 (1H, *d*, J = 8.5 Hz, H-6'); MS *m/z* (rel. int.): 354 (20, $[M]^+$), 312 (24), 311 (19), 295 (7), 270 (40), 269 (45), 253 (11), 241 (12), 213, (10), 163 (23), 161 (12), 151 (12), 137 (25), 134 (81), 133 (11), 121 (100), 108 (18), 43 (53).

Isoliquiritigenin trimethyl ether from **6**, **7** *or* **8**. 3 mg **6** (respectively 1.5 mg **7** or 1 mg **8**) were methylated and purified by CC (petrol–acetone 9:1) to yield the trimethyl ether, mp 87–90°; TLC (petrol–acetone 9:1): R_f 0.10, red-violet with anisaldehyde; UV/Vis λ_{max} nm (log ε): 227 (3.80), 340 (3.91); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650 (C=O), 1600 (C=C); ^1H NMR (400 MHz, $CDCl_3$): δ3.86 (3H, *s*, OMe)3.92 (3H, *s*, OMe), 3.95 (3H, *s*, OMe), 6.50 (1H, *d*, J = 2 Hz, H-3'), 6.56 (1H, *dd*, J_1 = 8.5, J_2 = 2 Hz, H-5'), 6.92 (2H, AA'BB', H-3, H-5), 7.39 (1H, *d*, J = 15.5 Hz, H-α), 7.55 (2H, AA'BB', H-2, H-6), 7.65 (1H, *d*, J = 15.5 Hz, H-β), 7.74 (1H, *d*, J = 8.5 Hz, H-6'); MS *m/z* (rel. int.): 298 (100, $[M]^+$), 297 (11), 283 (41), 281 (11), 270 (25), 165 (48), 161 (19), 135 (36), 122 (19), 121 (80), 77 (17), 63 (10).

Echinatin (**9**). Yellow crystals (1 mg), mp 209–211°; TLC ($CHCl_3$–MeOH 95:5): R_f 0.26, orange with anisaldehyde; UV/vis λ_{max} nm (log ε): 235 (3.74), 312 (3.87), 367 (4.14); +NaOH: 248 (3.90), 270 (3.88, sh), 433 (4.37); IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1640 (C=O), 1600, 1550 (C=C); ^1H NMR (400 MHz, acetone-d_6): δ3.93 (3H, *s*, OMe), 6.50 (1H, *dd*, J_1 = 9, J_2 = 2.5 Hz, H-5), 6.55 (1H, *d*, J = 2.5 Hz, H-3), 6.95 (2H, AA'BB', H-3', H-5'), 7.68 (1H, *d*, J = 16 Hz, H-α), 7.73 (1H, *d*, J = 9 Hz, H-6), 8.05 (2H, AA'BB', H-2', H-6'), 8.07 (1H, *d*, J = 16 Hz, H-β), 9.00 (2H, *br*, OH); MS *m/z* (rel. int.): 270 (14, $[M]^+$), 240 (14), 239 (100), 121 (21).

Synthesis of **9**. 4'-Hydroxyacetophenone [55 mg (0.40 mmol)] and 4-hydroxy-2-methoxybenzaldehyde [50 mg (0.33 mmol)] were dissolved in 1 ml KOH (50%) and heated at 100° for 15 min. The mixture was poured on ice-water (3 g) and neutralized with HCl. The product crystallized while standing overnight; final purification by CC (silica gel, $CHCl_3$–MeOH 97:3) yielded 20 mg, which proved to be identical with **9**. ^{13}C NMR (acetone-d_6): δ56.1 (OMe), 100.3 (C-3), 109.1 (C-5), 116.2 (C-3', C-5'), 117.1, 120.2 (C-1, C-1'), 131.2, 132.1 (C-α, C-6), 131.6 (C-2', C-6'), 139.5 (C-β), 161.6, 162.1, 162.4 (C-2, C-4, C-4'), 188.8 (C=O).

2,4'-Dihydroxy-4-methoxychalcone. The compound was synthesized from 4'-hydroxyacetophenone (55 mg) and 2-hydroxy-4-methoxybenzaldehyde (50 mg) analogous to the synthesis of **9**. Purification by CC (silica gel, $CHCl_3$–MeOH 98:2) yielded 45 mg yellow crystals, mp 90–92°. TLC ($CHCl_3$–MeOH 19:1): R_f 0.31, yellow with anisaldehyde; UV/Vis λ_{max} nm (log ε): 230 (3.92, sh), 313 (4.00, sh), 367 (4.26); +NaOH: 247 (3.98), 350 (3.99, sh), 430 (4.31); IR ν_{max}^{KBr} cm^{-1}: 3220 *br* (OH), 1630 (C=O), 1600 (C=C); ^1H NMR (acetone-d_6): δ3.80 (3H, *s*, OMe), 6.53 (1H, *dd*, J_1 = 9, J_2 = 2.5 Hz, H-5), 6.57 (1H, *d*, J = 2.5 Hz, H-3), 6.96 (2H, AA'BB', H-3', H-5'), 7.70 (1H, *d*, J = 9 Hz, H-6), 7.74 (1H, *d*, J = 16 Hz, H-α), 8.03 (2H, AA'BB', H-2', H-6'), 8.10 (1H, *d*, J = 16 Hz, H-β); ^{13}C NMR (acetone-d_6): δ55.8 (OMe), 102.6 (C-3), 107.4 (C-5), 116.2 (C-3', C-5'), 116.7, 120.4 (C-1, C-1'), 131.2, 131.9 (C-α, C-6), 131.6 (C-2', C-6'), 139.9 (C-β), 159.5, 162.6, 163.8 (C-2, C-4, C-4'), 189.1 (C=O); MS *m/z* (rel. int.): 270 (23, $[M]^+$), 254 (50), 253 (100), 252 (40), 224 (32), 152 (14), 121 (61).

2,4'-Dihydroxy-4-methoxydihydrochalcone (**10**). Colourless oil (2 mg). TLC ($CHCl_3$–MeOH 95:5): R_f 0.40, yellow with anisaldehyde; UV λ_{max} nm (log ε): 218 (4.06, sh), 280 (4.02); +NaOH: 235 (3.91, sh), 324 (4.14); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1710, 1660, 1620, 1600, 1585; ^1H NMR (acetone-d_6): δ2.90 (2H, *m*, H-β), 3.23 (2H, *m*, H-α), 3.70 (3H, *s*, OMe), 6.37 (1H, *dd*, J_1 = 8.5, J_2 = 2.5 Hz, H-5), 6.43 (1H, *d*, J = 2.5 Hz, H-3), 6.91 (2H, AA'BB', H-3', H-5'), 7.05 (1H, *d*, J = 8.5 Hz, H-6), 7.94 (2H, AA'BB', H-2', H-6'), 8.40 (1H, *br*, OH), 9.15 (1H, *br*, OH); MS *m/z* (rel. int.): 272 (64, $[M]^+$), 137 (100), 124 (26), 121 (53).

Synthesis of **10**. 2,4'-Dihydroxy-4-methoxychalcone (10 mg) and Zn powder (200 mg) were refluxed in 3 ml HOAc for 20 min. After cooling the reaction mixture was filtered; the filtrate was evaporated and the residue purified by CC (silica gel, cyclohexane–acetone 75:25) to yield 2.5 mg of a compound identical with **10**.

4,4'-Dihydroxy-2-methoxydihydrochalcone. This compound was synthesized from **9** (10 mg), as for the synthesis of **10**. Purification by CC (silica gel, $CHCl_3$–MeOH 97:3) gave 5 mg of a colourless oil. TLC ($CHCl_3$–MeOH 19:1): R_f 0.29, orange with anisaldehyde; UV λ_{max} nm (log ε): 220 (4.29), 280 (4.29); +NaOH: 238 (4.22), 325 (4.42); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590 (OH), 1710, 1670, 1600; ^1H NMR (acetone-d_6): δ2.85 (2H, *m*, H-β), 3.10 (2H, *m*, H-α), 3.79 (3H, *s*, OMe), 6.34 (1H, *dd*, J_1 = 8, J_2 = 2.5 Hz, H-5), 6.45 (1H, *d*, J = 2.5 Hz, H-3), 6.91 (2H, AA'BB', H-3', H-5'), 6.99 (1H, *d*, J = 8 Hz, H-6), 7.91 (2H, AA'BB', H-2', H-6'), 8.13 (1H, *br*, OH), 9.08 (1H, *br*, OH); MS *m/z* (rel. int.): 272 (73, $[M]^+$), 151 (18), 137 (100), 124 (31), 121 (68), 107 (18), 65 (12).

(2S)-Liquiritigenin 7-methyl ether (**12**). Colourless crystals (2 mg), mp 150–152°; TLC ($CHCl_3$–MeOH 95:5): R_f 0.53, orange with anisaldehyde; $[\alpha]_D^{21}$ −33° (MeOH; *c* 0.10); CD nm ($\Delta\varepsilon$): 329 (+3.7), 302 (−8.9), 233 (+3.8); UV λ_{max} nm (log ε): 217 (4.37), 231 (4.32), 273 (4.18), 313 (3.85); +NaOH: 240 (4.37), 273 (4.13), 315 (3.92, sh); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590 (OH), 1675 (C=O), 1605 (C=C); ^1H NMR (acetone-d_6): δ2.70 (1H, *dd*, J_1 = 16.5, J_2 = 3.5 Hz, H-3_{eq}), 3.05 (1H, *dd*, J_1 = 16.5, J_2 = 12.5 Hz, H-3_{ax}), 3.87 (3H, *s*, OMe), 5.48 (1H, *dd*, J_1 = 12.5, J_2 = 3.5 Hz, H-2), 6.53 (1H, *d*, J = 2.5 Hz, H-8), 6.64 (1H, *dd*, J_1 = 8.5, J_2 = 2.5 Hz, H-6), 6.90 (2H, AA'BB', H-3', H-5'), 7.41 (2H, AA'BB', H-2', H-6'), 7.77 (1H, *d* J = 8.5 Hz, H-5), 8.49 (1H, *s*, OH); MS *m/z* (rel. int.): 270 (89, $[M]^+$), 269 (40), 177 (18), 164 (15), 151 (100), 122 (14), 120 (50), 119 (15), 107 (23), 91 (24), 79 (14), 43 (55).

(2S)-Liquiritigenin 4'-methyl ether (**13**). Colourless crystals (1 mg), mp 175–178°; TLC (CCl_4–MeOH 9:1): R_f 0.35, orange with anisaldehyde; $[\alpha]_D^{21}$ −29° (MeOH; *c* 0.07); CD nm ($\Delta\varepsilon$): 330 (+2.2), 303 (−3.8), 235 (+3.0); UV λ_{max} nm (log ε): 217 (4.37, sh), 231 (4.30), 274 (4.16), 312 (3.86); +NaOH: 253 (4.01), 335 (4.38); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1675 (C=O), 1605 (C=O); ^1H NMR (acetone-d_6): δ2.75 (1H, *dd*, J_1 = 16.5, J_2 = 3.5 Hz, H-3_{eq}), 3.06 (1H, *dd*, J_1 = 16.5, J_2 = 12.5 Hz, H-3_{ax}), 3.83 (3H, *s*, OMe), 5.50 (1H, *dd*, J_1 = 12.5, J_2 = 3.5 Hz, H-2), 6.43 (1H, *d*, J = 2 Hz, H-8), 6.58 (1H, *dd*, J_1 = 8.5, J_2 = 2 Hz, H-6), 6.99 (2H, AA'BB', H-3', H-5'), 7.49 (2H, AA'BB', H-2', H-6'), 7.73 (1H, *d*, J = 8.5 Hz, H-5), 9.42 (1H, *s*, OH); MS *m/z* (rel. int.): 270 (47, $[M]^+$), 269 (19), 163 (9), 135 (12), 134 (100), 121 (41), 119 (19), 108 (13), 91 (16).

(2S)-7,4'-Dihydroxyflavan (**14**). Colourless crystals (6 mg), mp 193–195°; TLC ($CHCl_3$–MeOH 19:1): R_f 0.36, violet with anisaldehyde; $[\alpha]_D^{21}$ −23° (MeOH; *c* 0.40); CD nm ($\Delta\varepsilon$): 278 (−0.8), 234 (+0.7), 220 (−3.4); UV λ_{max} nm (log ε): 224 (4.28),

283 (3.76), 290 (3.61, sh); +NaOH: 243 (4.29), 290 (3.86); IR ν_{max}^{KBr} cm^{-1}: 3470, 3400 (OH), 1615, 1595 (C=C); ^1H NMR (acetone-d_6): δ2.06 (2H, *m*, H-3), 2.75 (2H, *m*, H-4), 4.95 (1H, *dd*, J_1 = 9, J_2 = 3.5 Hz, H-2), 6.31 (1H, *br d*, J = 2.5 Hz, H-8), 6.36 (1H, *dd*, J_1 = 8, J_2 = 2.5 Hz, H-6), 6.84 (2H, AA'BB', H-3', *H*-5'), 6.88 (1H, *d*, J = 8 Hz, H-5), 7.27 (2H, AA'BB', H-2', H-6'), 8.10 (2H, *br*, OH); ^{13}C NMR (acetone-d_6): see Table 3; MS *m/z* (rel. int.): 242 (100, $[M]^+$), 241 (8), 225 (7), 147 (8), 136 (17), 133 (12), 123 (44), 121 (11), 120 (80), 119 (15), 107 (24), 91 (15).

(2S)-4'-*Hydroxy*-7-*methoxyflavan* (**15**). Colourless crystals (140 mg), mp 153.5–154.5°; TLC (petrol–acetone 4:1): R_f 0.19, brownish-yellow with anisaldehyde; $[\alpha]_D^{21}$ −16.7° (MeOH; *c* 0.70); CD nm ($\Delta\varepsilon$): 273 (−1.2), 234 (+0.5), 220 (−3.8); UV λ_{max} nm (log ε): 224 (4.33), 283 (3.77), 288 (3.67, sh); +NaOH: 244 (4.25), 283 (3.77), 288 (3.77); IR ν_{max}^{KBr} cm^{-1}: 3390 (OH), 1610, 1590 (C=C); ^1H NMR (acetone-d_6): δ2.10 (2H, *m*, H-3), 2.78 (2H, *m*, H-4), 3.72 (3H, *s*, OMe), 4.95 (1H, *dd*, J_1 = 9, J_2 = 3.5 Hz, H-2), 6.36 (1H, *d*, J = 2.5 Hz, H-8), 6.42 (1H, *dd*, J_1 = 8.5, J_2 = 2.5 Hz, H-6), 6.85 (2H, AA'BB', H-3', H-5'), 6.93 (1H, *d*, J = 8.5 Hz, H-5), 7.26 (2H, AA'BB', H-2', H-6'), 8.32 (1H, *s*, OH); ^{13}C NMR (acetone-d_6): see Table 3; MS *m/z* (rel. int.): 256 (81, $[M]^+$), 150 (31), 149 (18), 137 (100), 133 (18), 132 (11), 131 (10), 121 (12), 120 (49), 119 (11), 107 (16), 91 (13), 77 (10).

(2S)-7,3'-*Dimethoxy*-4'-*hydroxyflavan* (**16**). Colourless crystals (7 mg), mp 107.5–108.5°; TLC ($CHCl_3$–MeOH 199:1): R_f 0.55, violet with anisaldehyde; $[\alpha]_D^{21}$ −26° (MeOH; *c* 0.13); CD nm ($\Delta\varepsilon$): 288 (−1.1), 240 (+0.3), 225 (−1.2); UV λ_{max} nm (log ε): 227 (4.38), 281 (4.13), 288 (4.08, sh); +NaOH: 249 (4.34), 285 (4.20), 289 (4.21); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540 (OH), 1615, 1580 (C=C); ^1H NMR (400 MHz, acetone-d_6): δ2.04 (1H, *m*, H_A-3), 2.16 (1H, *m*, H_B-3), 2.73 (1H, *m*, H_A-4), 2.90 (1H, *m*, H_B-4), 3.74 (3H, *s*, OMe), 3.86 (3H, *s*, OMe), 4.96 (1H, *dd*, J_1 = 9, J_2 = 3.5 Hz, H-2), 6.38 (1H, *d*, J = 2.5 Hz, H-8), 6.45 (1H, *dd*, J_1 = 8.5, J_2 = 2.5 Hz, H-6), 6.82 (1H, *d*, J = 8 Hz, H-5'), 6.91 (1H, *dd*, J_1 = 8, J_2 = 2 Hz, H-6'), 6.95 (1H, *d*, J = 8.5 Hz, H-5), 7.06 (1H, *d*, J = 2 Hz, H-2'), 7.45 (1H, *s*, OH); ^{13}C NMR (acetone-d_6): see Table 3; MS *m/z* (rel. int.): 286 (100, $[M]^+$), 163 (11), 150 (91), 138 (11), 137 (88), 135 (18).

(2S)-4'-*Acetoxy*-7,3'-*dimethoxyflavan*. **16** (2 mg) was acetylated and the product purified by CC (petrol–acetone, 17:3): 2 mg oily product; TLC (petrol–acetone 17:3): R_f 0.16, reddish-brown with anisaldehyde; $[\alpha]_D^{21}$ −23° ($CHCl_3$; *c* 0.2); UV λ_{max} nm (log ε): 220 (4.42, sh), 274 (3.87, sh), 279 (3.92), 289 (3.70); +NaOH: 249 (4.20), 284 (3.99), 289 (3.99), 300 (3.73, sh); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1765 (C=O), 1620, 1585 (C=C); ^1H NMR (400 MHz, acetone-d_6): δ2.06 (1H, *m*, H_A-3), 2.23 (1H, *m*, H_B-3), 2.23 (3H, *s*, OAc), 2.73 (1H, *m*, H_A-4), 2.90 (1H, *m*, H_B-4), 3.75 (3H, *s*, OMe), 3.85 (3H, *s*, OMe), 5.08 (1H, *dd*, J_1 = 10, J_2 = 2.5 Hz, H-2), 6.42 (1H, *d*, J = 2.5 Hz, H-8), 6.48 (1H, *dd*, J_1 = 8.5, J_2 = 2.5 Hz, H-6), 6.97 (1H, *d*, J = 8.5 Hz, H-5), 7.05 (1H, *dd*, J_1 = 8, J_2 = 1.5 Hz, H-6'), 7.08 (1H, *d*, J = 8 Hz, H-5'), 7.23 (1H, *d*, J = 1.5 Hz, H-2'); MS *m/z* (rel. int.): 328 (40, $[M]^+$), 287 (15), 286 (81), 163 (11), 162 (10), 161 (10), 151 (11), 150 (100), 149 (11), 138 (11), 137 (87), 135 (17), 77 (12), 43 (21).

(2S)-3',4'-*Dihydroxy*-7-*methoxyflavan* (**17**). Amorphous powder (6 mg); TLC ($CHCl_3$–MeOH 19:1): R_f 0.42, violet with anisaldehyde; $[\alpha]_D^{21}$ −19° (MeOH; *c* 0.40); CD nm ($\Delta\varepsilon$): 288 (−0.9), 220 (−2.8); UV λ_{max} nm (log ε): 222 (4.02, sh), 283 (3.72), 288 (3.67, sh); +NaOH: 242 (3.84, sh), 284 (3.74, sh), 289 (3.78); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3560 (OH), 1620, 1585 (C=C); ^1H NMR (400 MHz, acetone-d_6): δ1.98 (1H, *m*, H_A-3), 2.09 (1H, *m*, H_B-3), 2.68 (1H, *m*, H_A-4), 2.88 (1H, *m*, H_B-4), 3.73 (3H, *s*, OMe), 4.92 (1H, *dd*, J_1 = 9, J_2 = 3.5 Hz, H-2), 6.36 (1H, *d*, J = 2.5 Hz, H-8), 6.42 (1H, *dd*, J_1 = 8.5, J_2 = 2.5 Hz, H-6), 6.77 (1H, *dd*, J_1 = 8, J_2 = 2 Hz, H-6'), 6.83 (1H, *d*, J = 8 Hz, H-5'), 6.92 (1H, *d*, J = 2 Hz, H-2'), 6.95 (1H, *d*, J = 8.5 Hz, H-5), 8.00 (2H, *br*, OH); ^{13}C NMR (acetone-d_6): see Table 3; MS *m/z* (rel. int.): 272 (83, $[M]^+$), 150 (50), 149 (25), 148 (32), 137 (100), 136 (57), 123 (12), 108 (10), 89 (16), 79 (13), 78 (16), 77 (27), 65 (21), 51 (15), 43 (20).

(2S)-7,4'-*Dihydroxy*-3'-*methoxyflavan* (**18**). Amorphous powder (0.7 mg); TLC (CCl_4–MeOH 9:1): R_f 0.25, violet with anisaldehyde; $[\alpha]_D^{21}$ not measurable; CD nm ($\Delta\varepsilon$): 284 (−0.6), 227 (−1.0); UV λ_{max} nm (log ε): 226 (4.19, sh), 282 (3.87); +NaOH: 246 (4.19), 292 (3.95); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3550 (OH), 1615, 1600 (C=C); ^1H NMR (400 MHz, acetone-d_6): δ2.01 (1H, *m*, H_A-3), 2.12 (1H, *m*, H_B-3), 2.68 (1H, *m*, H_A-4), 2.86 (1H, *m*, H_B-4), 3.86 (3H, *s*, OMe), 4.94 (1H, *dd*, J_1 = 10, J_2 = 2 Hz, H-2), 6.30 (1H, *d*, J = 2.5 Hz, H-8), 6.37 (1H, *dd*, J_1 = 8, J_2 = 2.5 Hz, H-6), 6.82 (1H, *d*, J = 8 Hz, H-5'), 6.88 (1H, *d*, J = 8 Hz, H-5), 6.90 (1H, *dd*, J_1 = 8, J_2 = 2 Hz, H-6'), 7.05 (1H, *d*, J = 2 Hz, H-2'), 7.54 (1H, *s*, OH), 8.09 (1H, *s*, OH); MS *m/z* (rel. int.): 272 (83, $[M]^+$), 151 (11), 150 (100), 147 (10), 137 (34), 136 (13), 135 (28), 123 (19), 107 (12).

Synthesis of racemic **18**. 4'-Hydroxy-3'-methoxyacetophenone [55 mg (0.33 mmol)] and 2,4-dihydroxybenzaldehyde [46 mg (0.33 mmol)] were dissolved at 1° in EtOAc (4 ml, saturated with HCl gas). The mixture was kept for 3 days at 1°, then poured into dry Et_2O (30 ml). The red-coloured crystalline flavylium salt (50 mg) was collected and air-dried. TLC ($CHCl_3$–MeOH 9:1): R_f 0.41; UV/Vis λ_{max} nm (log ε): 238 (3.99, sh), 276 (3.95), 289 (3.84, sh), 309 (3.54), 375 (3.39), 505 (4.01), 535 (3.93, sh); +NaOH: 235 (4.05, sh), 271 (4.04), 308 (3.61), 330 (3.62), 400 (3.29), 585 (4.61); ^1H NMR (CD_3OD): δ4.08 (3H, *s*, OMe), 7.17 (1H, *d*, J = 8.5 Hz, H-5'), 7.48 (1H, *dd*, J_1 = 8.5, J_2 = 2.5 Hz, H-6), 7.62 (1H, *d*, J = 2.5 Hz, H-8), 8.02 (1H, *d*, J = 2.5 Hz, H-2'), 8.22 (1H, *dd*, J_1 = 8.5, J_2 = 2.5 Hz, H-6'), 8.22 (1H, *d*, J = 8.5 Hz, H-5), 8.40 (1H, *d*, J = 8.5 Hz, H-3), 9.10 (1H, *d*, J = 8.5 Hz, H-4); MS *m/z* (rel. int.): 269 (15, $[M]^+$), 268 (100), 240 (31), 44 (5), 43 (7). The flavylium salt (40 mg) dissolved in HOAc (5 ml) was hydrogenated on PtO_2. After decolourization the soln was filtered, evapd and the residue separated by CC (silica gel, CCl_4–MeOH 47:3) to yield 3.5 mg racemic **18**, 152–155°.

(2S)-7,3',4'-*Trimethoxyflavan*. 1.5 mg **16** (respectively 1.5 mg **17**, 2 mg racemic **18**) were methylated; purification by CC (cyclohexane–acetone 9:1) yielded the trimethoxyflavan (oily product, 0.8 mg from **16**, 1 mg from **17**, 1 mg racemate from synthetic (±)-**18**); TLC (petrol-acetone 9:1): R_f 0.19, dark-brown with anisaldehyde; CD nm ($\Delta\varepsilon$): 288 (−0.6), 225 (−0.7); UV λ_{max} nm (log ε): 226 (3.95), 279 (3.51), 283 (3.51), 288 (3.40, sh);

Table 3. ^{13}C NMR data of the flavans **14**–**17**

C	**14**	**15**	**16**	**17**
2	78.2	78.3	78.7	78.4
3	25.0	25.0	25.2	24.9
4	30.8	30.8	30.9	30.7
5	130.6	130.7	130.8	130.7
6	108.8	107.7	107.9	107.6
7	156.8	160.1	160.3	160.0
8	103.9	102.4	102.5	102.3
9	157.5	157.0	157.1	156.9
10	113.6	114.8	115.0	115.0
1'	133.7	133.8	134.5	134.4
2'	128.1	128.1	111.0	114.1
3'	115.9	115.9	148.4	145.4
4'	157.9	157.8	147.3	145.8
5'	115.9	115.9	115.7	115.8
6'	128.1	128.1	119.9	118.3
OMe		55.5	55.6	55.5
OMe			56.5	

IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620, 1590 (C=C); ^1H NMR (acetone-d_6): δ2.1 (2H, *m*, H-3), 2.8 (2H, *m*, H-4), 3.74 (3H, *s*, OMe), 3.81 (3H, *s*, OMe), 3.82 (3H, *s*, OMe), 4.99 (1H, *dd*, $J_1 = 8.5$, $J_2 = 3.5$ Hz, H-2), 6.38 (1H, *d*, $J = 2$ Hz, H-8), 6.43 (1H, *dd*, $J_1 = 9$, $J_2 = 2$ Hz, H-6), 6.8–7.2 (4H, *m*, H-2′, H-5, H-5′, H-6′); MS *m/z* (rel. int.): 300 (100, $[M]^+$,), 167 (14), 165 (13), 164 (82), 151 (25), 149 (57), 136 (10), 57 (16).

Obtustyrene (**19**). Colourless oil (1.3 mg). TLC (CH_2Cl_2–MeOH 99:1): R_f 0.33, ruby-coloured with anisaldehyde; UV λ_{max} nm (log ε): 217 (4.11, sh), 251 (4.10), 285 (3.66, sh), 293 (3.45, sh); +NaOH: 249 (4.17), 285 (3.76), 293 (3.70, sh); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1600 (C=C); ^1H NMR (acetone-d_6): δ3.40 (2H, *d*, $J = 5$ Hz, C$\underline{H}_2$–CH=CH), 3.80 (3H, *s*, OMe), 6.4 (4H, *m*, H-3′, H-5′, CH_2-C$\underline{H}$=C$\underline{H}$), 6.96 (1H, *d*, $J = 8$ Hz, H-6′), 7.30 (5H, *m*, H-2, H-3, H-4, H-5, H-6), 8.17 (1H, *s*, OH); ^1H NMR (400 MHz, acetone-d_6): δ3.40 (2H, *d*, $J = 5$ Hz, C$\underline{H}_2$–CH=CH), 3.80 (3H, *s*, OMe), 6.38 (1H, *dd*, $J_1 = 8$, $J_2 = 2$ Hz, H-5′), 6.40 (2H, m, CH_2–C$\underline{H}$=C$\underline{H}$), 6.48 (1H, *d*, $J = 2$ Hz, H-3′), 6.96 (1H, *d*, $J = 8$ Hz, H-6′), 7.19 (1H, *m*, H-4), 7.29 (2H, *m*, H-3, H-5), 7.39 (2H, *m*, H-2, H-6), 8.17 (1H, *s*, OH); MS *m/z* (rel. int.): 240 (100, $[M]^+$), 239 (21), 225 (17), 209 (23), 137 (13), 116 (10), 115 (27), 91 (15).

Synthesis of **19**. **19** was synthesized from 4′-hydroxy-2′-methoxyacetophenone (160 mg) and benzaldehyde (104 mg) analogous to **7**. Purification by CC (silica gel, $CHCl_3$–MeOH 99:1) yielded 140 mg 4′-hydroxy-2′-methoxychalcone [24], mp 146–149°. TLC (cyclohexane–EtOAc 7:3): R_f 0.15, yellow with anisaldehyde; MS *m/z* (rel. int.): 254 (100, $[M]^+$), 253 (60), 239 (14), 237 (13), 226 (34), 165 (16), 163 (18), 152 (12), 151 (92), 137 (14), 136 (25), 131 (14), 122 (11), 108 (17), 105 (12), 103 (19), 77 (18). 40 mg of the chalcone were dissolved in Et_2O abs. (2 ml) and $LiAlH_4$ (17 mg) were added. The mixture was refluxed for 30 min, then 125 mg $AlCl_3$ suspended in Et_2O were added and the mixture further heated (30 min). Work-up with H_2O, acidification, and extraction with Et_2O. Evaporation and purification by CC (silica gel, CH_2Cl_2) gave an oily product (14 mg) identical with **19**.

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