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STRUCTURAL CONFIRMATION OF SPIROELLIPTIN FROM *IRYANTHERA ELLIPTICA* BY SYNTHESIS*

ANSELMO A. MORAIS, RAIMUNDO BRAZ FO and OTTO R. GOTTLIEB†

Instituto de Ciências Exatas, Universidade Federal Rural do Rio de Janeiro, 23460 Seropédica, RJ, Brazil; †Instituto de Química, Universidade de São Paulo, 05508 São Paulo, SP, Brazil

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Key Word Index—*Iryanthera elliptica*; Myristicaceae; spiroelliptin; spiro-cyclohexadienone-1,1′-tetralins; synthesis; reduction of chalcones.

Abstract—Spiroelliptin, a spiro[cyclohexadienone-1,1′-tetralin] from *Iryanthera elliptica*, was synthesized by a novel process which involved the catalytic hydrogenation of the appropriate chalcone. This and other spiro[methoxycyclohexadienone-1,1′-tetralin] derivatives, obtained by the same process or by the oxidative coupling of the appropriate 1,3-diarylpropanes, were used as models in the compilation of ^1H and ^{13}C NMR data allowing the recognition of three such naturally occurring structural types.

INTRODUCTION

When spiroelliptin (**1**) was isolated from *Iryanthera elliptica* Ducke [2] it was immediately supposed that this substance might be a natural oxidation product of **2a**. Indeed several 1,3-diarylpropanes not only occur in Myristicaceae [3], but had also been used as starting materials in the synthesis of other spiro[cyclohexadienone-1,1′-tetralin] derivatives [4–6].

Interpretation of the ^1H NMR spectrum of spiroelliptin had initially led to the alternative formulations **1**, **3a** and **4a**. A decision in favour of **1** was subsequently reached mainly in view of the spectrum of a rearranged methylation product, the dibenzocycloheptane **5a**. Hence it was deemed necessary to confirm the structural proposal **1** by synthesis.

RESULTS

The obvious route to **1** was thought to involve first the base catalysed condensation of the appropriate acetophenone and benzaldehyde, next the catalytic hydrogenation of the resulting chalcone **6a** to the 1,3-diarylpropane **2a**. This contains a catechol which would have to suffer selective protection in order to stabilize the substrate towards the oxidative condition in the cyclization reaction. Such protection, however, turned out to be superfluous, because the spiro-cyclohexadienone can also be obtained by a reductive sequence. This surprising fact was discovered by chance upon catalytic hydrogenation of the chalcone **6a**. The resulting reaction mixture contained not only the 1,3-diarylpropane **2a**, but also the spiro-derivative **1**. Its identity with spiroelliptin was ascertained by spectral means.

The analogous catalytic hydrogenation of the isomeric chalcone **6b** led to the 1,3-diarylpropane **2b**, the spiro-derivative **3a** and the flavan **7**. The hypothetical intermediates **8a** and **8b** may be precursors of the 1,3-diarylpropanes, respectively **2a** and **2b**. Alternatively **9a** and **9b**, putative precursors of the spiro-derivatives **1** and **3a**, could also lead to **2a** and **2b**.

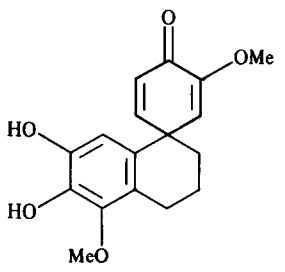
Although at this stage the original objective had already been reached, it was nevertheless decided to prepare spiro-derivatives of type **4** in order to complete the series of models. Comparison of the NMR data of representatives of the three series of spiro-cyclohexadienones should lead to a spectral method for the identification of types **1**, **3** and **4**. The reaction sequences again started by preparation of the appropriate chalcones (**6c**, **6d**, **6e**). These were catalytically hydrogenated to the corresponding 1,3-diarylpropanes (**2c**, **2d**, **2e**) which, upon oxidation with $Fe(DMF)_3Cl_2$–$FeCl_4$ [4], gave the corresponding spiro-cyclohexadienones (**4b**, **4c**, **4d**). An additional model compound of type **3** was prepared analogously by the sequence **6f** → **2f** → **3b**.

DISCUSSION

The ^1H and ^{13}C NMR spectra of the spiro-cyclohexadienones obtained are sufficiently diagnostic to provide a classification of such compounds according to structural type. Indeed, comparison of the NMR data of **3a**, **3b** and spirobroussonin A (**3c**), as well as of **4b**, **4c**, **4d** and spirobroussonin B (**4e**) (Tables 1 and 2), confirm the structural proposals for these recently described phytoalexins of *Broussonetia papyrifera* (Moraceae) [7].

Rearrangement of the spiro-cyclohexadienone-1,1′-tetralins into dibenzocycloheptanes remains an additional valid method of structural elucidation. It occurs in acid medium (**1** → **5b**) and, as was observed previously [2], may proceed with concomitant methylation (**1** → **5a**). Such dibenzocycloheptanes should be easily oxidizable into diphenic acids, valuable synthons for the preparation of compounds containing symmetric or asymmetric bi-

*Part XXVIII in the series "The Chemistry of Brazilian Myristicaceae". For Part XXVII see ref. [1]. Taken from part of the Doctorate thesis presented by A.A.M. to the Universidade de São Paulo (1983).



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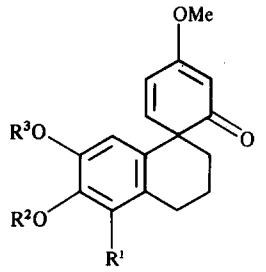
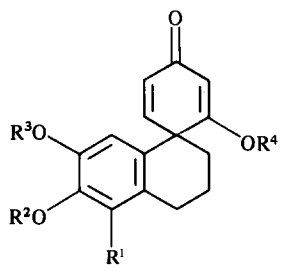
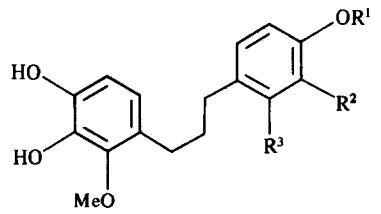


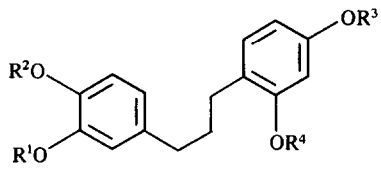
3a R^1 = OMe, R^2 = R^3 = H
3b R^1 = R^3 = H, R^2 = Me
3c R^1 = R^2 = R^3 = H



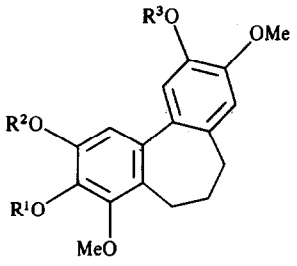
4a R^1 = OMe, R^2 = R^3 = H, R^4 = Me
4b R^1 = R^2 = H, R^3 = R^4 = Me
4c R^1 = R^3 = H, R^2 = R^4 = Me
4d R^1 = R^4 = H, R^2——R^3 = CH_2
4e R^1 = R^2 = R^3 = H, R^4 = Me



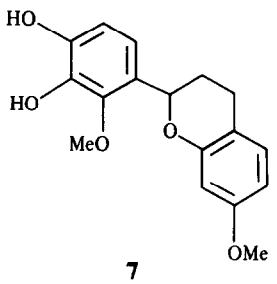
2a R^1 = R^3 = H, R^2 = OMe
2b R^1 = Me, R^2 = H, R^3 = OH



2c R^1 = R^3 = H, R^2 = R^4 = Me
2d R^1 = R^4 = Me, R^2 = R^3 = H
2e R^1——R^2 = CH_2, R^3 = R^4 = H
2f R^1 = R^3 = Me, R^2 = R^4 = H



5a R^1 = R^2 = R^3 = Me
5b R^1 = R^2 = R^3 = H



7

phenyl units, such as e.g. the schizandrin type neolignans [8] and lignans [9].

EXPERIMENTAL

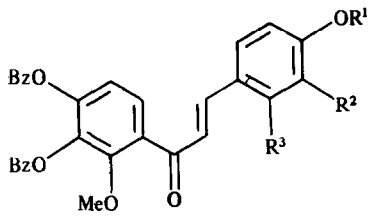
Preparation of the chalcones. Appropriately substituted acetophenones and benzaldehydes gave by aldol condensation according to ref. [10] **6a** (yield 71%), **6b** (80%), **6e** (77%) and according to ref. [11] **6c** (81%), **6d** (82%), **6f** (17%).

Hydrogenation of the chalcones. A soln of the chalcone (1 g) in $CHCl_3$ (5 ml) and EtOH (40 ml) in a Parr apparatus was flushed with N_2. Catalyst (0.5 g, 10% Pd–C) and AcOH (10 ml) was added, vacuum applied and H_2 was admitted under pressure (50 psi, 4 hr). The usual work-up, followed by silica gel chromatography of the crude reaction mixture gave from **6a** → **2a** (77%) + **1** (11%) and from **6b** → **2b** (27%) + **7** (45%) + **3a** (18%). The usual work-up, followed by crystallization from appropriate solvents of the crude reaction mixture, gave from **6c** → **2c** (60%), from **6d** → **2d** (35%), from **6e** → **2e** (80%) and from **6f** → **2f** (80%).

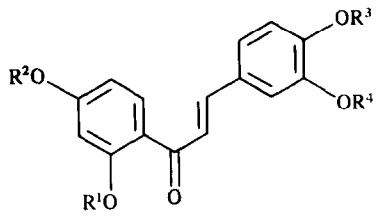
Oxidation of the 1,3-*diarylpropanes.* This was performed as described [4], followed by chromatographic (silica gel) purification of the crude reaction mixture, and gave from **2c** → **4b** (70%), from **2d** → **4c** (65%), from **2e** → **4d** (60%) and from **2f** → **3b** (70%).

4,3′,4′-*Tribenzyloxy*-3,2′-*dimethoxychalcone* (**6a**). Yellow oil. IR ν_{max}^{film} cm^{-1}: 1660, 1615, 1575, 1510, 1470, 1260, 1150, 930, 905, 865, 810. ^1H NMR (100 MHz, $CDCl_3$): δ 3.90, 3.92 (2*s*, 2OMe), 5.10, 5.15, 5.18 (3*s*, $3CH_2Ph$), 6.80 (*d*, *J* = 8 Hz, H-5′), 6.90 (*d*, *J* = 8 Hz, H-5), 7.1–7.5 (*m*, H-2, H-6), 7.18 (*d*, *J* = 16 Hz, H-α), 7.40 (*s*, 3Ph), 7.45 (*d*, *J* = 8 Hz, H-6′), 7.63 (*d*, *J* = 16 Hz, H-β). MS *m/z* (rel. int.): 586 $[M]^+$ (0), 347 (1), 319 (1), 267 (2), 91 (100).

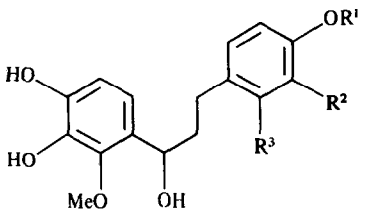
2,3′,4′-*Tribenzyloxy*-4,2′-*dimethoxychalcone* (**6b**). Yellow oil. IR ν_{max}^{film} cm^{-1}: 1660, 1600, 1615, 1580, 1500, 1460, 1380, 1260,



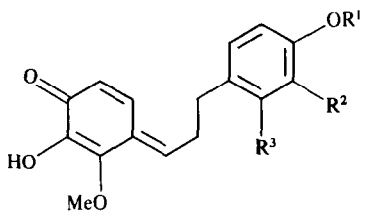
6a R^1 = Bz, R^2 = OMe, R^3 = H
6b R^1 = Me, R^2 = H, R^3 = OBz



6c $R^1 = R^3$ = Me, $R^2 = R^4$ = Bz
6d $R^1 = R^4$ = Me, $R^2 = R^3$ = Bz
6e R^1 = H, R^2 = Bz, R^3—R^4 = CH_2
6f R^1 = H, $R^2 = R^4$ = Me, R^3 = Bz



8a $R^1 = R^3$ = H, R^2 = OMe
8b R^1 = Me, R^2 = H, R^3 = OH



9a $R^1 = R^3$ = H, R^2 = OMe
9b R^1 = Me, R^2 = H, R^3 = OH

Table 1. ^{1}H NMR chemical shifts of spiro[methoxycyclohexadienone-1,1′-tetralin] derivatives: **1**, **3a**, **3b**, **4b**, **4c**, **4d** in $CDCl_3$; **3c**, **4e** [7] in DMSO-d_6 (60 MHz, TMS as internal standard)*

	1	**3a**	**3b**	**3c**	**4b**	**4c**	**4d**	**4e**
H-2	*d* (2)							
	5.95							
H-3		*d* (2)						*d* (1.5)
		5.50	5.50	5.43	5.70	5.70	5.70	5.65
H-5	*d* (10)	*dd* (10, 2)						*dd* (10, 1.5)
	6.22	6.10	6.10	6.12	6.18	6.10	6.10	5.94
H-6	*dd* (10, 2)	*d* (10)						
	7.00	6.60	6.56	6.59	6.88	6.86	6.72	6.89
4H-2′, 3′	*m*							
	1.9–2.1	1.7–2.2	1.6–2	1.8–2.1	1.6–2.1	1.8–2.2	1.96	1.8–2
2H-4′	*m*						*t* (7)	
	2.7–2.9	2.6–3	2.7–3	2.56	2.7–3	2.7–3	2.76	2.61
H-5′			*s*					
			6.62	6.45	6.72	6.68	6.58	6.48
H-8′	*s*							
	6.30	6.08	6.36	6.05	6.31	6.35	6.46	6.17
MeO	*s*							
	3.86	3.85	3.86	3.81	3.74	3.84		3.63
MeO	*s*							
	3.62	3.85	3.84		3.70	3.70		
CH_2O_2							*s*	
							5.84	

*Multiplicities and coupling constants (Hz, in parentheses) are valid for all entries from left to right.

Table 2. ^{13}C NMR chemical shifts of spiro[methoxycyclo-hexadienone-1,1'-tetralin] derivatives: **1**, **3a**, **4b**, **4c** in $CDCl_3$; **3c**, **4e** [7] in DMSO-d_6 (25 MHz, TMS as internal standard)*

	1	3a	3c	4b	4c	4e
C-1	44.3 *s*	53.3	52.2	46.7	46.6	45.9
C-2	124.7 *d*		202.3 *s*	180.4	180.2	179.9
C-3	146.1 *s*	98.8 *d*	98.5	102.2	102.4	101.9
C-4	180.1 *s*	171.3	170.5	188.2	188.2	186.9
C-5	125.0 *d*	117.7	115.8	123.6	123.8	122.9
C-6	156.7 *d*	149.4	149.4	151.6	151.3	151.8
C-2'	34.4 *t*	34.2	33.4	33.7	33.7	33.1
C-3'	18.6 *t*	18.3	18.0	19.4	19.6	19.0
C-4'	22.7 *t*	23.0	28.2	28.8	29.2	28.2
C-4'a	120.8 *s*	122.4	126.1	130.0	128.7	127.7
C-5'	144.4 *s*	144.7	117.1 *d*	116.0	113.2	116.1
C-6'	137.6 *s*	137.6	143.4	145.8	146.1	144.5
C-7'	148.1 *s*	148.0	144.3	146.3	144.3	143.7
C-8'	109.8 *d*	110.7	114.2	109.8	111.6	113.6
C-8'a	124.1 *s*	126.9	127.5	124.0	126.3	123.9
MeO-3	54.4 *q*					
MeO-5'	59.2 *q*	59.7				
MeO-4		56.0 *q*	56.0			
MeO-2				55.8 *q*	55.8 *q*	55.8
MeO-6'						
MeO-7'				55.7 *q*		

*Multiplicities are valid for all entries from left to right.

1110, 1075, 910, 840, 810. ^{1}H NMR (100 MHz, $CDCl_3$): δ3.82, 3.88 (2*s*, 2OMe), 5.02 (*s*, CH_2Ph), 5.18 (*s*, 2CH_2Ph), 6.54 (*d*, *J* = 2 Hz, H-3), 6.60 (*dd*, *J* = 2, 8 Hz, H-5), 6.80 (*d*, *J* = 8 Hz, H-5'), 7.48 (*s*, 3Ph), 7.2–7.6 (*m*, H-α, H-6), 7.64 (*d*, *J* = 8 Hz, H-6'). 8.07 (*d*, *J* = 16 Hz, H-β). MS *m/z* (rel. int.): 586 $[M]^+$ (0), 347 (2), 319 (1), 91 (100).

3,4'-*Dibenzyloxy*-4,2'-*dimethoxychalcone* (**6c**). Yellow, mp 141–143° (EtOH). IR ν_{max}^{KBr} cm^{-1}: 1640, 1600, 1500, 1450, 1370, 1240, 1150, 1010, 990, 975, 840, 815. ^{1}H NMR (60 MHz, $CDCl_3$): δ3.82, 3.94 (2*s*, 2OMe), 5.50, 5.80 (2*s*, 2CH_2Ph), 6.58 (*d*, *J* = 2 Hz, H-3'), 6.60 (*dd*, *J* = 2, 8 Hz, H-5'), 6.84 (*s*, *J* = 8 Hz, H-5), 7.15 (*d*, *J* = 2 Hz, H-2), 7.2–7.25 (*m*, H-α, H-6), 7.40 (*s*, 2Ph), 7.70 (*d*, *J* = 8 Hz, H-6'), 7.60 (*d*, *J* = 16 Hz, H-β). MS *m/z* (rel. int.): 480 $[M]^+$ (0), 267 (1), 213 (1), 91 (100).

4,4'-*Dibenzyloxy*-3,2'-*dimethoxychalcone* (**6d**). Yellow, mp 135–136° (EtOH). IR ν_{max}^{KBr} cm^{-1}: 1640, 1600, 1500, 1460, 1380, 1255, 1130, 975, 920, 830, 800. ^{1}H NMR (100 MHz, $CDCl_3$): δ 3.84, 3.90 (2*s*, 2OMe), 5.18, 5.20 (2*s*, 2CH_2Ph), 6.58 (*d*, *J* = 2 Hz, H-3'), 6.64 (*dd*, *J* = 2, 8 Hz, H-5'), 6.87 (*d*, *J* = 8 Hz, H-5), 7.12 (*dd*, *J* = 2, 8 Hz, H-6), 7.16 (*d*, *J* = 2 Hz, H-2), 7.24 (*d*, *J* = 16 Hz, H-α), 7.42 (*s*, 2Ph), 7.62 (*d*, *J* = 16 Hz, H-β), 7.70 (*d*, *J* = 8 Hz, H-6'). MS *m/z* (rel. int.): 480 $[M]^+$ (5), 267 (1), 241 (7), 213 (2), 91 (100).

4'-*Benzyloxy*-2'-*hydroxy*-3,4-*methylenedioxychalcone* (**6e**). Yellow, mp 113–116° (EtOH). IR ν_{max}^{KBr} cm^{-1}: 1635, 1600, 1540, 1470, 1385, 1245, 1150, 980, 920, 850, 810. ^{1}H NMR (100 MHz, $CDCl_3$): δ5.12 (*s*, CH_2Ph), 6.02 (*s*, O_2CH_2), 6.58 (*d*, *J* = 2 Hz, H-3'), 6.60 (*dd*, *J* = 2, 8 Hz, H-5'), 6.85 (*d*, *J* = 8 Hz, H-5), 7.15 (*dd*, *J* = 2, 8 Hz, H-6), 7.19 (*d*, *J* = 2 Hz, H-2), 7.40 (*s*, Ph), 7.40 (*d*, *J* = 12 Hz, H-α), 7.84 (*d*, *J* = 12 Hz, H-β), 7.84 (*d*, *J* = 8 Hz, H-6'), 13.45 (*s*, OH). MS *m/z* (rel. int.): 374 $[M]^+$ (15), 227 (1), 175 (2), 148 (10), 91 (100).

4-*Benzyloxy*-2'-*hydroxy*-3,4'-*dimethoxychalcone* (**6f**). Yellow, mp 115–117° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 1630, 1600, 1560, 1455, 1370, 1250, 1020, 975, 955, 840, 795. ^{1}H NMR (100 MHz, $CDCl_3$): δ3.98 (2*s*, 2OMe), 5.22 (*s*, CH_2Ph), 6.48 (*d*, *J* = 2 Hz, H-3'), 6.50 (*dd*, *J* = 2, 8 Hz, H-5'), 6.90 (*d*, *J* = 8 Hz, H-5), 7.22 (*dd*, *J* = 2, 8 Hz, H-6), 7.28 (*d*, *J* = 16 Hz, H-α), 7.3–7.55 (*m*, H-2), 7.40 (*s*, Ph), 7.82 (*d*, *J* = 8 Hz, H-6'), 7.85 (*d*, *J* = 16 Hz, H-β). MS *m/z* (rel. int.): 390 $[M]^+$ (8), 299 (4), 151 (15), 91 (100).

1-(3',4'-*Dihydroxy*-2'-*methoxyphenyl*)-3-(4''-*hydroxy*-3''-*methoxyphenyl*)-*propane* (**2a**). Mp 74–76° (C_6H_6). IR ν_{max}^{KBr} cm^{-1}: 3420, 3240, 1620, 1500, 1440, 1370, 1265, 1150, 1045, 955, 910, 845, 800. ^{1}H NMR (60 MHz, $CDCl_3 + CCl_4$): δ1.7–2.2 (*m*, CH_2), 2.58 (*t*, *J* = 7 Hz, 2ArCH_2), 3.78, 3.80 (2*s*, 2OMe), 5.7 (*s*, OH), 6.3 (*s*, 2OH), 6.60 (*s*, H-2'', H-5'', H-6''), 6.66 (*d*, *J* = 8 Hz, H-5'), 6.82 (*d*, *J* = 8 Hz, H-6'). MS *m/z* (rel. int.): 304 $[M]^+$ (98), 167 (30), 154 (73), 153 (87), 138 (98), 137 (100), 123 (26), 107 (25).

1-(3',4'-*Dihydroxy*-2'-*methoxyphenyl*)-3-(2''-*hydroxy*-4''-*methoxyphenyl*)-*propane* (**2b**). Oil. IR ν_{max}^{film} cm^{-1}: 3400, 1620, 1500, 1490, 1235, 1165, 1150, 1040, 960, 935, 840, 810. ^{1}H NMR (60 MHz, $CDCl_3 + CCl_4$): δ1.7–2.1 (*m*, CH_2), 2.56 (*t*, *J* = 7 Hz, 2ArCH_2), 3.74 (*s*, OMe), 5.4–5.6 (*br s*, 3OH), 6.42 (*d*, *J* = 2 Hz, H-3''), 6.46 (*dd*, *J* = 2, 8 Hz, H-5''), 6.86 (*s*, H-5', H-6'), 7.08 (*d*, *J* = 8 Hz, H-6''). MS *m/z* (rel. int.): 304 $[M]^+$ (40), 154 (23), 153 (27), 151 (25), 138 (20), 137 (100).

1-(4'-*Hydroxy*-2'-*methoxyphenyl*)-3-(4''-*hydroxy*-3''-*methoxyphenyl*)-*propane* (**2c**). Mp 76–78° (C_6H_6). IR ν_{max}^{KBr} cm^{-1}: 3450, 1620, 1520, 1440, 1250, 1030, 960, 930, 850, 810. UV λ_{max}^{EtOH} nm: 225, 280 (ε14950, 7850); $\lambda_{max}^{EtOH+NaOH}$ nm: 242, 292 (ε19000, 10600). ^{1}H NMR (100 MHz, $CDCl_3$): δ 1.7–2.2 (*m*, CH_2), 2.60 (*t*, *J* = 7 Hz, 2ArCH_2), 3.76, 3.86 (2*s*, 2OMe), 5.1 (*s*, OH), 5.64 (*s*, OH), 6.35 (*dd*, *J* = 2, 8 Hz, H-5'), 6.40 (*d*, *J* = 2 Hz, H-3'), 6.68 (*dd*, *J* = 2, 8 Hz, H-6''), 6.78 (*d*, *J* = 8 Hz, H-5''), 6.82 (*d*, *J* = 2 Hz, H-2''), 6.95 (*d*, *J* = 8 Hz, H-6'). MS *m/z* (rel. int.): 288 $[M]^+$ (28), 138 (53), 137 (100), 107 (26). *Diacetate*, mp 85–86°. IR ν_{max}^{KBr} cm^{-1}: 1760, 1610, 1470, 1360, 1265, 1150, 1030, 960, 900, 820. ^{1}H NMR (100 MHz, $CDCl_3$): δ1.7–2.1 (*m*, CH_2), 2.4–2.75 (*m*, 2ArCH_2), 2.28, 2.30 (*s*, 2OAc), 3.79, 3.82 (2*s*, 2OMe), 6.56 (*d*, *J* = 2 Hz, H-3'),

6.60 (*dd*, $J = 2$, 8 Hz, H-5'), 6.84 (*d*, $J = 8$ Hz, H-5''), 6.88 (*d*, $J = 2$ Hz, H-2''), 6.93 (*dd*, $J = 2$, 8 Hz, H-6''), 7.06 (*d*, $J = 8$ Hz, H-6'). MS *m/z* (rel. int.): 372 $[M]^+$ (10), 330 (55), 288 (61), 138 (80), 137 (100).

1-(4'-*Hydroxy*-2'-*methoxyphenyl*)-3-(3''-*hydroxy*-4''-*methoxyphenyl*)-*propane* (**2d**). Oil. IR ν_{max}^{film} cm^{-1}: 3540, 1620, 1510, 1460, 1370, 1225, 1150, 1040, 955, 930, 840, 820. UV λ_{max}^{EtOH} nm: 228, 280 (ε13 650, 5850); $\lambda_{max}^{EtOH+NaOH}$ nm: 245, 290 (ε17 500, 7600). ^1H NMR (60 MHz, $CDCl_3$): δ1.7–2.2 (*m*, CH_2), 2.57 (*t*, $J = 7$ Hz, $2ArCH_2$), 3.72, 3.87 (2*s*, 2OMe), 5.75 (*s*, 2OH), 6.40 (*dd*, $J = 2$, 8 Hz, H-5'), 6.46 (*d*, $J = 2$ Hz, H-3'), 6.7–6.8 (*m*, H-2'', H-5'', H-6'), 6.93 (*d*, $J = 8$ Hz, H-6'). MS *m/z* (rel. int.): 288 $[M]^+$ (49), 151 (27), 138 (48), 137 (100), 107 (30). *Diacetate*, oil. IR λ_{max}^{film} cm^{-1}: 1760, 1600, 1510, 1465, 1370, 1205, 1150, 1030, 950, 895, 835. ^1H NMR (60 MHz, CCl_4): δ1.7–2.2 (*m*, CH_2), 2.20 (*s*, 2OAc), 2.59 (*t*, $J = 7$ Hz, $ArCH_2$), 3.79 (*s*, 2OMe), 6.55–7 (*m*, H-3', H-5', H-2'', H-5'', H-6''), 7.02 (*d*, $J = 8$ Hz, H-6''). MS *m/z* (rel. int.): 372 $[M]^+$ (10), 330 (55), 288 (61), 138 (80), 137 (100).

1-(2',4'-*Dihydroxyphenyl*)-3-(3'',4''-*methylenedioxyphenyl*)-*propane* (**2e**). Mp 78–80° (C_6H_6–C_6H_{14}). IR ν_{max}^{KBr} cm^{-1}: 3440, 1625, 1500, 1450, 1240, 1135, 1035, 930, 860, 815. UV λ_{max}^{EtOH} nm: 225, 284 (ε7400, 4900); $\lambda_{max}^{EtOH+NaOH}$ nm: 236, 290 (ε8050, 5200). ^1H NMR (100 MHz, $CDCl_3 + Me_2CO$-d_6): δ1.7–2.1 (*m*, CH_2), 2.56 (*t*, $J = 7$ Hz, $2ArCH_2$), 5.90 (*s*, O_2CH_2), 6.34 (*dd*, $J = 2$, 8 Hz, H-5'), 6.48 (*d*, $J = 2$ Hz, H-3'), 6.64 (*s*, H-2'', H-5'', H-6''), 6.88 (*d*, $J = 8$ Hz, H-6'), 8.04 (*s*, OH), 8.12 (*s*, OH). MS *m/z* (rel. int.): 272 $[M]^+$ (85), 149 (18), 137 (26), 136 (100), 135 (64), 123 (72), 109 (10). *Diacetate*, oil. IR ν_{max}^{film} cm^{-1}: 1760, 1600, 1490, 1440, 1360, 1240, 1125, 1030, 970, 915, 815. ^1H NMR (60 MHz, $CDCl_3 + CCl_4$): δ1.7–2.1 (*m*, CH_2), 2.18, 2.22 (2*s*, 2OAc), 2.4–2.7 (*m*, $ArCH_2$), 5.92 (*s*, O_2CH_2), 6.68 (*m*, H-2'', H-5'', H-6''), 6.86 (*d*, $J = 2$Hz, H-3'), 6.92 (*d*, $J = 2$, 8 Hz, H-5'), 7.20 (*d*, $J = 8$ Hz, H-6'). MS *m/z* (rel. int.): 356 $[M]^+$ (44), 272 (63), 148 (25), 137 (28), 136 (100), 135 (50), 123 (44).

1-(2'-*Hydroxy*-4'-*methoxyphenyl*)-3-(4''-*hydroxy*-3''-*methoxyphenyl*)-*propane* (**2f**). Mp 72–74° (C_6H_6). IR ν_{max}^{KBr} cm^{-1}: 3500, 1610, 1520, 1460, 1365, 1250, 1155, 1030, 940, 920, 865, 805.UV λ_{max}^{EtOH} nm: 232, 280 (ε9900, 7600); $\lambda_{max}^{EtOH+NaOH}$ nm: 248, 294 (ε11 500, 10 000). ^1H NMR (100 MHz, $CDCl_3$): δ1.7–2.1 (*m*, CH_2), 2.5–2.75 (*m*, $2ArCH_2$), 3.75, 3.88 (2*s*, 2OMe), 5 (*s*, OH), 5.5 (*s*, OH), 6.40 (*d*, $J = 2$ Hz, H-3'), 6.44 (*dd*, $J = 2$, 8 Hz, H-5'), 6.70 (*dd*, $J = 2$, 8 Hz, H-6''), 6.74 (*d*, $J = 2$ Hz, H-2''), 6.84 (*d*, $J = 8$ Hz, H-5''), 7.03 (*d*, $J = 8$ Hz, H-6'). MS *m/z* (rel. int.): 288 $[M]^+$ (34), 151 (20), 150 (20), 138 (43), 137 (100). *Diacetate*, oil. IR ν_{max}^{film} cm^{-1}: 1770, 1620, 1510, 1450, 1370, 1260, 1140, 1030, 900, 850, 820. ^1H NMR (100 MHz, $CDCl_3$): δ1.7–2.1 (*m*, CH_2), 2.22, 2.32 (2*s*, 2OAc), 2.4–2.8 (*m*, $2ArCH_2$), 3.80, 3.84 (2*s*, 2OMe), 6.65 (*d*, $J = 2$ Hz, H-3'), 6.7–6.9 (*m*, H-2'', H-5'', H-6''), 6.80 (*dd*, $J = 2$, 8 Hz, H-5'), 7.22 (*d*, $J = 8$ Hz, H-6'). MS *m/z* (rel. int.): 372 $[M]^+$, (18), 330 (60), 288 (79), 138 (56), 137 (100).

Spiro[3-*methoxy*-4-*oxo*-2,5-*cyclohexadiene*-1,1'-6',7'-*dihydroxy*-5'-*methoxy*-1',2',3',4'-*tetrahydronaphthalene*] (**1**). Mp 148–150° (EtOAc). IR ν_{max}^{KBr} cm^{-1}: 3540, 3480, 1660, 1590, 1500, 1450, 1380, 1245, 1160, 1040, 940, 895, 860, 835. UV λ_{max}^{EtOH} nm: 242, 275 (ε11 100, 5050); $\lambda_{max}^{EtOH+NaOH}$ nm: 245, 293 (ε10 850, 5550). ^1H and ^{13}C NMR: Tables 1 and 2. MS *m/z* (rel. int.): 302 $[M]^+$ (100), 301 (15), 287 (11), 274 (21), 259 (29). *Diacetate*, mp 61–63° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 1770, 1660, 1600, 1480, 1410, 1365, 1075, 970, 905, 845, 825. ^1H NMR (60 MHz, CCl_4): δ1.85–2.1 (*m*, CH_2CH_2), 2.16, 2.28 (2*s*, 2OAc), 2.7–3 (*m*, $ArCH_2$), 3.64, 3.80 (2*s*, 2OMe), 5.90 (*d*, $J = 2$ Hz, H-2), 6.18 (*d*, $J = 9$ Hz, H-5), 6.56 (*s*, H-8'), 6.94 (*dd*, $J = 2$, 9 Hz, H-6). MS *m/z* (rel. int.): 386 $[M]^+$ (5), 344 (35), 302 (100), 301 (6), 287 (4), 274 (16), 259 (13).

Spiro[3-*methoxy*-4-*oxo*-2,5-*cyclohexadiene*-1,1'-6',7'-*dihydroxy*-5'-*methoxy*-1',2',3',4'-*tetrahydronaphthalene*] (**3a**). Mp 165–167° (EtOAc). IR ν_{max}^{KBr} cm^{-1}: 3600–3100, 1660, 1600, 1460, 1340, 1230, 1160, 1070, 950, 915, 865, 800. UV λ_{max}^{EtOH} nm: 235, 287, 315i (ε11 350, 7500, 4450); $\lambda_{max}^{EtOH+NaOH}$ nm: 248, 298, 312i (ε11 100, 9300, 6650). ^1H and ^{13}C NMR: Tables 1 and 2. MS *m/z* (rel. int.): 302 $[M]^+$ (100), 301 (5), 287 (11), 273 (17), 259 (10). *Diacetate*, mp 63–65° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 1770, 1650, 1570, 1480, 1370, 1240, 1010, 950, 910, 845, 800. ^1H NMR (60 MHz, CCl_4): δ1.7–2.2 (*m*, CH_2CH_2), 2.14, 2.25 (2*s*, 2OAc), 2.6–3 (*m*, $ArCH_2$), 3.82 (*s*, 2OMe), 5.34 (*d*, $J = 2$ Hz, H-3), 6.36 (*s*, H-8'), 6.54 (*d*, $J = 10$ Hz, H-6), 6.10 (*dd*, $J = 2$, 10 Hz, H-5). MS *m/z* (rel. int.): 386 $[M]^+$ (21), 344 (34), 302 (100), 287 (19), 273 (19), 259 (8).

Spiro[4-*methoxy*-2-*oxo*-3,5-*cyclohexadiene*-1,1'-7'-*hydroxy*-6'-*methoxy*-1',2',3',4'-*tetrahydronaphthalene*] (**3b**). Mp 146–148°. IR ν_{max}^{KBr} cm^{-1}: 3500–3100, 1670, 1620, 1520, 1450, 1250, 1050, 850, 810. ^1H amd ^{13}C NMR: Tables 1 and 2. MS *m/z* (rel. int.): 286 $[M]^+$ (100), 285 (12), 271 (30), 269 (20), 257 (18), 243 (17). *Acetate*, mp 56–58°. IR ν_{max}^{KBr} cm^{-1}: 1760, 1630, 1500, 1460, 1365, 1260, 1155, 955, 905, 865, 820. ^1H NMR (100 MHz, $CDCl_3$): δ1.7–2.1 (*m*, CH_2CH_2), 2.18 (*s*, OAc), 2.6–2.9 (*m*, $ArCH_2$), 3.78, 3.80 (2*s*, 2OMe), 5.42 (*d*, $J = 2$ Hz, H-3), 6.05 (*dd*, $J = 2$, 9 Hz, H-5), 6.38 (*s*, H-8), 6.50 (*d*, $J = 9$ Hz, H-6), 6.65 (*s*, H-5'). MS *m/z* (rel. int.): 328 (50) $[M]^+$, 286 (100), 285 (32), 271 (42), 257 (24), 243 (21), 227 (11).

Spiro[2-*methoxy*-4-*oxo*-2,5-*cyclohexadiene*-1,1'-7'-*hydroxy*-6'-*methoxy*-1',2',3',4'-*tetrahydronaphthalene*] (**4b**). Mp 175–178°. IR ν_{max}^{KBr} cm^{-1}: 3500–3100, 2950, 2860, 1660, 1620, 1580, 1520, 1460, 1365, 1270, 1240, 1180, 1120, 1030, 990, 860, 820, 810, 700. UV λ_{max}^{EtOH} nm: 236, 280 (ε9300, 5850); $\lambda_{max}^{EtOH+NaOH}$ nm: 230, 260, 293, (ε9850, 8500, 5050). ^1H and ^{13}C NMR: Tables 1 and 2. MS *m/z* (rel. int.): 286 $[M]^+$ (100), 271 (62), 258 (62), 257 (10), 243 (68), 215 (65). *Acetate*, oil, IR ν_{max}^{film} cm^{-1}: 1770, 1660, 1600, 1510, 1460, 1365, 1270, 1035, 910, 860, 820. ^1H NMR (100 MHz, $CDCl_3$): δ1.8–2.2 (*m*, CH_2CH_2), 2.30 (*s*), 2.7–3 (*m*, $ArCH_2$), 3.70, 3.84 (2*s*, 2OMe), 5.70 (*d*, $J = 2$ Hz, H-3), 6.10 (*dd*, $J = 2$, 10 Hz, H-5), 6.52 (*s*, H-8'), 6.74 (*s*, H-5'), 6.84 (*d*, $J = 10$ Hz, H-6). MS *m/z* (rel. int.): 330 $[M]^+$ (24), 286 (100), 271 (7), 257 (10), 243 (15), 215 (7). *Dimethyl ether*, oil. ^1H NMR (60 MHz, CCl_4): δ1.8–2.2 (*m*, CH_2CH_2), 2.6–3 (*m*, $ArCH_2$), 3.68 (*s*, 2OMe), 3.66 (*s*, OMe), 5.62 (*d*, $J = 2$ Hz, H-3), 6.10 (*dd*, $J = 2$, 10 Hz, H-5), 6.28 (*s*, H-8'), 6.60 (*s*, H-5'), 6.80 (*d*, $J = 10$ Hz, H-6). MS *m/z* (rel. int.): 330 $[M]^+$ (100), 285 (6), 257 (11), 272 (5), 241 (9).

Spiro[2-*methoxy*-4-*oxo*-2,5-*cyclohexadiene*-1,1'-6'-*hydroxy*-7'-*methoxy*-1',2',3',4'-*tetrahydronaphthalene*] (**4c**). Mp 158–160°. IR ν_{max}^{KBr} cm^{-1}: 3500–3100, 1670, 1630, 1600, 1500, 1460, 1240, 1030, 980, 850, 800. ^1H and ^{13}C NMR: Tables 1 and 2. MS *m/z* (rel. int.): 286 $[M]^+$ (100), 271 (3), 258 (9), 243 (17), 215 (8). *Acetate*, IR ν_{max}^{KBr} 1770, 1660, 1600, 1460, 1370, 1270, 1035, 915, 875, 820. ^1H NMR (60 MHz, CCl_4): δ1.8–2.1 (*m*, CH_2CH_2), 2.30 (*s*, OAc), 2.7–3 (*m*, $ArCH_2$), 3.60, 3.64 (2*s*, 2OMe), 5.70 (*d*, $J = 2$ Hz, H-3), 6.10 (*dd*, $J = 2$, 10 Hz, H-5), 6.40 (*s*, H-8'), 6.80 (*s*, H-8), 6.78 (*d*, $J = 10$ Hz, H-6), MS *m/z* (rel. int.): 328 $[M]^+$ (9), 286 (100), 271 (4), 258 (6), 243 (9), 257 (4). *Methyl ether*, oil. IR ν_{max}^{film} cm^{-1}: 1660, 1590, 1500. 1465, 1360, 1255, 1030, 985, 920, 860, 850. ^1H NMR (60 MHz, $CDCl_3$): δ1.8–2.2 (*m*, CH_2CH_2), 2.6–3 (*m*, ArOMe), 3.64, 3.66, 3.84 (3*s*, 3OMe), 5.75 (*d*, $J = 2$ Hz, H-3), 6.15 (*dd*, $J = 2$, 10 Hz, H-5), 6.34 (*s*, H-8'), 6.66 (*s*, H-5), 6.86 (*d*, $J = 10$ Hz, H-6). MS *m/z* (rel. int.): 300 $[M]^+$ (100), 275 (13), 257 (23), 253 (5).

Spiro[2-*hydroxy*-4-*oxo*-3,5-*cyclohexadiene*-1,1'-6',7'-*methylenedioxy*-1',2',3',4'-*tetrahydronaphthalene*] (**4d**). Mp 221–223° (C_6H_6). IR ν_{max}^{KBr} cm^{-1}: 3400, 1635, 1590, 1500, 1470, 1390, 1230, 1035, 930, 860, 820. ^1H and ^{13}C NMR: Tables 1 and 2. MS *m/z* (rel. int.): 270 $[M]^+$ (100), 242 (66), 229 (87), 199 (26), 170 (43), 141 (37), 115 (35).

4',5',5''-*Trihydroxy*-3',4''-*dimethoxy*-1,2:2',1'-3,4:1'',2''-*dibenzo*-1,3-*cycloheptadiene* (**5b**). Mp 144–146° (MeOH). ^1H NMR (60 MHz,

$CDCl_3$): δ1.9–2.6 (*m*, $CH_2CH_2CH_2$), 3.84, 3.92 (2*s*, 2OMe), 5.4 (*s*, 3OH), 6.70 (*s*, H-6), 6.90 (*s*, H-3'), 6.74 (*s*, H-3).

3',4'-Dihydroxy-7,2'-dimethoxyflavan (7). Mp 142–145°. IR ν_{max}^{KBr} cm^{-1}: 3400, 1620, 1500, 1360, 1255, 1150, 980, 930, 855, 800. ^1H NMR (100 MHz, $CDCl_3$): δ2–2.3 (*m*, CH_2), 2.7–3 (*m*, $ArCH_2$), 3.80, 3.88 (2*s*, 2OMe), 5.25 (*dd*, *J* = 4, 8 Hz, CH), 5.4, 5.5 (2*s*, 2OH), 6.46 (*d*, *J* = 2 Hz, H-8), 6.50 (*dd*, *J* = 2, 8 Hz, H-6), 6.75 (*d*, *J* = 8 Hz, H-5'), 6.95 (*d*, *J* = 8 Hz, H-6'), 7.00 (*d*, *J* = 8 Hz, H-5). MS *m/z* (rel. int.): 302 $[M]^+$ (45), 166 (18), 150 (39), 137 (100), 133 (20). *Acetate*, oil. ^1H NMR (60 MHz, $CDCl_3 + CCl_4$): δ2–2.3 (*m*, CH_2), 2.20, 2.30 (2*s*, 2OAc), 2.7–3 (*m*, $ArCH_2$), 3.72, 3.82 (2*s*, 2OMe), 5.25 (*dd*, *J* = 4, 8 Hz, CH), 6.36 (*d*, *J* = 2 Hz, H-6), 6.40 (*dd*, *J* = 2, 8 Hz, H-6), 6.98 (*d*, *J* = 8 Hz, H-5'), 7.38 (*d*, *J* = 8 Hz, H-6').

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