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IRYANTHERINS, LIGNOFLAVONOIDS OF NOVEL STRUCTURAL TYPES FROM THE MYRISTICACEAE*

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Key Word Index—*Iryanthera laevis*; *I. ulei*; *I. paraensis*; Myristicaceae; dihydrochalcones; lignoflavonoids; iryantherins, phenol cinnamylation.

Abstract—*Iryanthera laevis*, *I. ulei* and *I. paraensis* contain a series of novel lignoflavonoids the formation of which can be rationalized by the cinnamylation of the phloroglucinol type A-ring of a dihydrochalcone. The lignoid attachments of the flavonoid moieties consist of an arylvinylmethyl group in iryantherin-A, of 1,4-diaryl-2,3-dimethyl-*n*-butyl groups in iryantherins B and C and of 3-aryl-2-cinnamyl-*n*-propyl groups in iryantherins D and E. The construction of iryantherin-F requires oxidative addition of the vinyl unit of an iryantherin-A type compound to the A-ring of a second dihydrochalcone moiety.

INTRODUCTION

Iryanthera laevis Markgr. (Myristicaceae) has been reported to contain the dihydrochalcone **1** in wood [3], fruit [4] and bark [5] accompanied by two ligno-[i.e. $(C_6{\cdot}C_3)_n$-substituted] derivatives of **1** in fruit and bark for which constitutions **2** (now designated iryantherin-A) [4] and **3a** (now designated iryantherin-B [5, 6] have been proposed respectively. The present work describes the occurrence in the same fruit extract of further derivatives of this type, namely **4a** (iryantherin-C), **5a** (iryantherin-D) and **5b** (iryantherin-E). Bark of *I. ulei* Warb. was also found to contain **1**, **3a**, **5a** and **5b**, besides the lignobisdihydrochalcone **6** (iryantherin-F). Bark of a specimen tentatively identified with *I. paraensis* Huber yielded **1** and **6**.

RESULTS

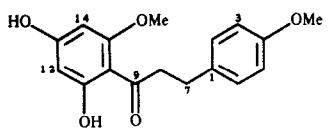
The comparison of the ^{1}H and ^{13}C NMR spectra of all six lignoflavonoids with the analogous spectra of **1** (Tables 1 and 2) provided evidence for the existence of the 4,2′,4′6′- or (in the numbering system adopted in the present paper) 4,11,13,15-tetraoxygenated dihydrochalcone moiety.

The ^{1}H NMR (Tables 1 and 3) and ^{13}C NMR (Tables 2 and 4) spectra for **4a** established the partial formula $C_{35}H_{36}$. The spectra also indicated the presence of two methoxyls, as well as of one carbonyl and the compound gives a tetraacetate (**4b**). The formula can thus be expanded to $C_{32}H_{26}CO(OH)_4(OMe)_2$. The mass spectrum did not show a molecular ion peak, but included two pairs of peaks at *m/z* 477 [M − **a**]/107 (**a**) and *m/z* 421 [M − **c**]/163 (**c**) (**4a**) the *m/z* values of which both add up to 584, the probable M_r of the compound. Hence the molecular formula can be written $C_{35}H_{36}O_8$ or, in expanded form, $C_{32}H_{26}CO{\cdot}O(OH)_4(OMe)_2$. This fact and comparison of the NMR spectra of the iryantherins B (**3a**) and C led to the structural proposal **4a** for the latter compound. All NMR assignments for **4a** were based on ^{1}H–^{1}H and ^{1}H–^{13}C shift correlated 2D spectroscopy (Table 5). This refers inclusively to the doublet at δ3.91 (J = 4.25 Hz) which can only represent H-7′ and correlates with the signals at δ164.71 (obligatorily representing C-11), 159.91 (C-13), as well as 106.64 (C-12) and 115.67 (C-1′). The H-7′/C-11 correlation eliminates the structural alternative in which C-7′ of the lignoid chain is connected to C-14 and the two ether functions of the flavonoid A-ring appear at interchanged positions.

The ^{1}H NMR (Tables 1 and 3) and ^{13}C NMR (Tables 2 and 4) spectra in combination with low resolution mass spectral M_r determinations established formulas $C_{34}H_{32}O_7$ and $C_{35}H_{34}O_7$ respectively for **5a** and **5b**. Iryantherin-D (**5a**) gives a tetraacetate (**5c**) and includes one methoxyl and one carbonyl, while iryantherin-E (**5b**) gives a triacetate (**5d**) and includes two methoxyls and a carbonyl (Tables 1–4). The formulae can thus be expanded to $C_{32}H_{25}CO{\cdot}O(OH)_4OMe$ (**5a**) and $C_{32}H_{25}CO{\cdot}O(OH)_3(OMe)_2$ (**5b**). The mass spectra of both compounds include four pairs of peaks at *m/z* M − **a**/**a**, M − **b**/**b**, M − **c**/**c** and M − **d**/**d** and *m/z* values of which all add up to the respective M_rs 552 (**5a**) and 566 (**5b**). Fragments **a**–**d** stemming from both compounds show identical *m/z* values, in contrast to fragment M − **c** − **d**, *m/z* 165 for **5a** and 179 for **5b**. Thus the additional 14 mass units which characterize **5b** must be associated with the flavonoid A ring. The central evidence for the indi-

Dedicated to Prof. G. B. Marini-Bettòlo on the occasion of his 75th anniversary.

*Part 32 in the series 'The Chemistry of Brazilian Myristicaceae'. For Part 31 see ref. [1]. Part 11 in the series 'The Chemistry of Colombian Myristicaceae'. For Part 10 see ref. [2]. Based in part on the Doctorate thesis presented by L.M.C. to Universidade de São Paulo (1990).



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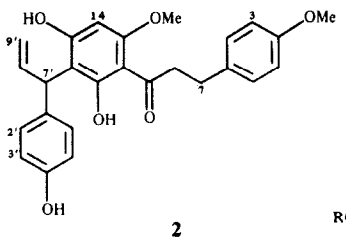

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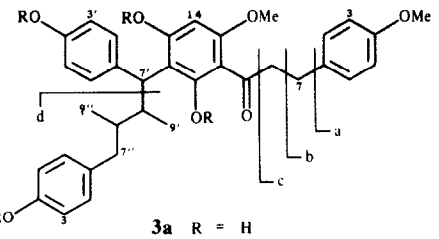
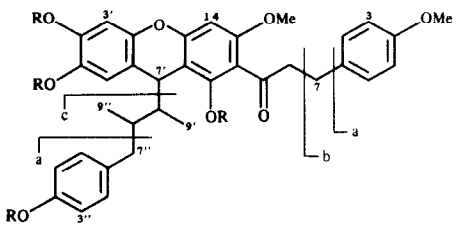
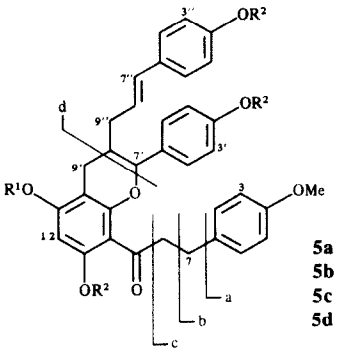


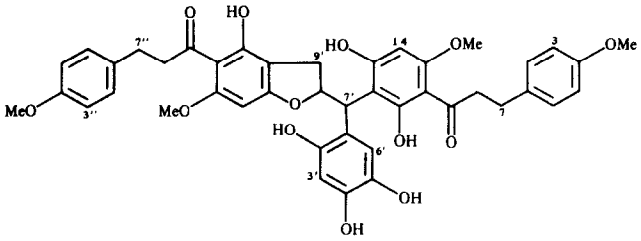
3a R = H
3b R = Ac



4a R = H
4b R = Ac



5a $R^1 = R^2 = H$
5b R^1 = Me, R^2 = H
5c $R^1 = R^2$ = Ac
5d R^1 = Me, R^2 = Ac



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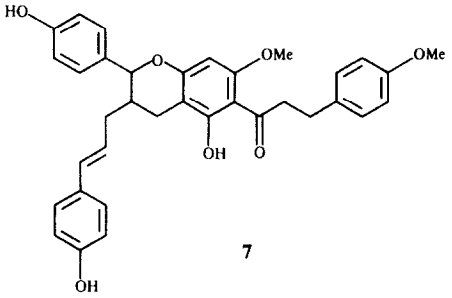

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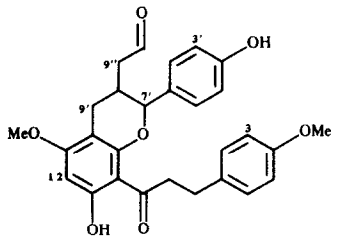

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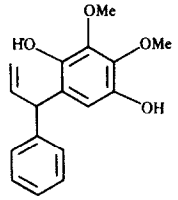

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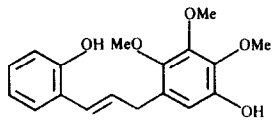

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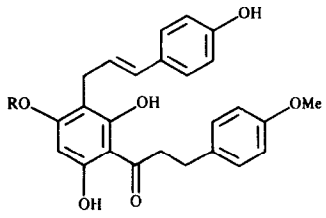
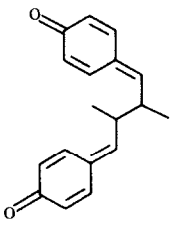


11 R = H or Me



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cated structures comes from the single axial proton at C-8′ (δ2.31). This was correlated with five vicinal protons (Table 6) belonging to a carbinolic-benzylic methine at C-7′ (δ4.81, *d*, $J_{ax\text{-}ax}$ = 9.07 Hz), a benzylic methylene at C-9′ (δ2.41, 2.90) and an allylic methylene at C-9″ (δ2.0, 2.13). The latter feature is included in a 4-hydroxycinnamyl unit (Tables 3 and 4). For **5a** no structural alternatives are admissible as the isolated aromatic proton of the flavonoid ring is flanked by two hydroxyls (C-12, δ96.08) [4]. Besides, it is with this C-12 signal and not with the signal of the C-substituted C-14 (δ101.99) that correlation of the proton signal due to the chelatogenic proton (δ13.78) can be demonstrated (Table 6). Compound **5b** (Tables 1–4 and 7) is represented by a structure in which both methoxyls are flanked by at least one unsubstituted position (δ55.48) and the isolated aromatic proton is flanked by at least one ether group (C-12, δ90.76). Hence the alternative **7** cannot *a priori* be

Table 1. ^{1}H NMR data for flavonoid units of iryantherins (**2**, **4a**, **5a**, **5b**, **6**) and of iryantherin acetates (**3b**, **4b**, **5c**, **5d**)

H	1 [3]	2 [4]	3b	4a	4b	5a	5c	5b	5d	6	
2,6	7.15	7.15	7.3–6.7	7.21	7.16	6.68	6.91	7.17	7.13	7.21	7.15
	d, 9	*d*, 8.6	*m*	*d*, 8.6	*d*, 6.7	*s*	*d*, 8.5	*d*, 8.6	*d*, 8.2	*d*, 8.5	*d*, 8.5
3,5	6.82	6.75	7.3–6.7	6.85	6.84	6.68	6.71	6.83	6.81	6.85	6.83
	d, 9	*d*, 8.6	*m*	*d*, 8.6	*d*, 6.7	*s*	*d*, 8.5	*d*, 8.6	*d*, 8.2	*d*, 8.5	*d*, 8.5
MeO-4	3.74	3.75	3.69	3.76	3.75	3.72	3.75	3.78	3.78	3.76	3.75
	s	*s*	*s*	*s*	*s*	*s*	*s*	*s*	*s*	*s*	*s*
7,7	2.87	3.4–2.6	3.1–2.9	2.92	2.86	2.73	2.78	2.92	3.1–2.9	2.93	2.83
	t, 7	*m*	*m*	*m*	*m*	*m*	*t*, 7.5	*m*	*m*	*t*, 7.5	*t*, 7.5
8,8	3.26	3.4–2.6	3.1–2.9	3.32	3.07	3.11	3.04	3.28	3.1–2.9	3.36	3.19
	t, 7	*m*	*m*	*m*	*m*	*m*	*t*, 7.5	*m*	*m*	*t*, 7.5	*t*, 7.5
HO-11	13.90	14.55	—	14.41	—	13.78	—	14.41	—	13.85	14.68
	s	*s*	—	*s*	—	*s*	—	*s*	—	*s*	*s*
12	5.95	—	—	—	—	5.99	6.52	5.93	6.38	—	—
	d, 2	—	—	—	—	*s*	*s*	*s*	*s*	—	—
14	6.04	6.17	6.46	6.19	6.77	—	—	—	—	6.31	6.06
	d, 2	*s*	*s*	*s*	*s*	—	—	—	—	*s*	*s*
MeO-15	3.88	3.85	3.76	3.95	3.91	—	—	3.78	3.75	3.89	3.99
	s	*s*	*s*	*s*	*s*	—	—	*s*	*s*	*s*	*s*

Table 2. ^{13}C NMR data for flavonoid units of iryantherins (**2**, **3a**, **4a**, **5a**, **5b**, **6**) and of iryantherin acetates (**3b**, **4b**, **5e**, **5d**)

C	1 [3]	2 [4]	3a [6]	3b	4a	4b	5a	5c	5b	5d	6	
1	134.50	134.6	134.53	133.58	134.66	134.19	133.77	134.90	133.78	135.04	134.58	134.32
2,6	130.13	130.1	130.11	129.47	130.21	130.11	129.65	129.19	129.34	129.34	130.11	130.21
3,5	114.46	114.6	114.47	113.83	114.55	114.52	114.22	113.70	113.81	113.83	114.61	114.55
4	158.84	158.9	158.83	157.93	158.88	158.94	158.51	157.73	157.81	157.88	158.97	159.03
MeO-4	55.33	55.4	55.33	55.31	55.40	55.40	55.24	55.22	55.26	55.25	55.42	55.42
7	30.68	30.7	30.68	29.03	30.46	29.79	30.04	28.89	29.98	29.66	30.60	30.51
8	46.87	46.7	46.78	45.43	47.06	46.45	45.84	45.68	46.01	45.98	46.71	46.97
9	205.15	205.0	205.30	201.93	205.91	201.21	205.27	201.09	204.77	201.32	205.33	205.78
10	105.73	105.7	105.63	122.44	107.55	120.73	105.36	120.73	105.26	116.98	106.27	105.95
11	168.26	165.8	166.20		164.71	146.93	165.85	146.40	164.69	147.39	162.95	165.11
12	96.78	114.8	112.10	122.44	106.64	112.91	96.08	109.36	90.76	97.60	110.22	101.31
13	165.52	163.1	163.12		159.91	155.82	159.12	150.05	161.11	157.10	149.91	167.99
14	91.81	91.8	91.70	105.04	91.11	98.72	101.99	113.20	102.65	108.08	91.93	86.50
15	164.46	162.6	162.08	155.70	162.16	157.73	162.97	153.25	160.93	157.10	162.17	159.78
MeO-15	56.11	55.9	55.74	55.92	56.31	56.66	—	—	55.48	56.80	56.45	56.57

dismissed. However, upon acetylation of HO-11 one observes a signal shift towards lower field of 6.84 ppm (90.76→97.60) for the unsubstituted carbon and of 5.43 ppm (102.65→108.08) for the C-substituted carbon (cf. positions 12 and 14 in Table 2) in good agreement with the $\Delta\delta$ values expected for **5b** where the former carbon occupies position 12 (calcd shift 6.2 ppm [7]) and where the latter carbon occupies position 14 (calcd shift 5.6 ppm [7]). In the case of **7** the observed shift values for the unsubstituted and substituted carbons (resp. 6.84 and 5.43 ppm) compare unfavourably with the calculated values (resp. 5.6 and 6.2 ppm).

Ageing of a solution of iryantherin-E (**5b**) in chloroform produced increasing quantities of **8** and of 4-hydroxybenzaldehyde. Spectral comparison of **5b** (Tables 1–4) and of **8** (Experimental) confirmed the structural proposal for the latter compound.

In iryantherin-F (**6**) two dihydrochalcone units (Tables 1 and 2) are connected by a lignoid CH(Ar)·CH(OR)·CH_2-bridge (cf. positions 1′–9′ in Tables 3 and 4). The methylene protons of the latter are represented by two double doublets with large vicinal coupling constants (δ2.78, J = 15, 9.5 Hz; 2.64, J = 15, 7.5 Hz). This demonstrates their rigid positions and hence inclusion, together with the vicinal CHOR (δ5.35, *ddd*, J = 9.5, 7.5, 4 Hz) in a pentacycle. In contrast, the doubly benzylic methine terminal of the bridge (δ4.63, *d*, J = 4 Hz) can escape eclipsation and shows a smaller vicinal coupling constant. The lignoid aryl of this terminal is 2,4,5-trihydroxylated, as evidenced by two aromatic proton singlets (δ6.59 and 6.84) and a UV shift upon addition of H_3BO_3 + NaOAc typical of catechols. The bridge terminals must be inserted into flavonoid A-rings, one (evidently the methylene) into a ring sustaining, besides the methoxyl, an additional ether function. The methoxyl (δ *ca* 56.5) and the ether both must be vicinal to the unsubstituted position, as demonstrated by the relatively low chemical shift (δ87.79) of the corresponding

Table 3. ^{1}H NMR data for lignoid units of iryantherins (**2**, **4a**, **5a**, **5b**, **6**) and of iryantherin acetates (**3b**, **4b**, **5c**, **5d**)

H	**2** [4]	**3b**	**4a**	**4b**	**5a**	**5c**	**5b**	**5d**	**6**
2′,6′	7.20	7.3–6.7	—	—	7.38	7.32	7.15	7.36	—
	d, 8.6	*m*	—	—	*d*, 8.5	*d*, 8.5	*d*, 8.6	*d*, 8.0	—
3′,5′	6.85	7.3–6.7	—	—	6.92	7.12	6.74	7.13	—
	d, 8.5	*m*	—	—	*d*, 8.5	*d*, 8.5	*d*, 8.6	*d*, 8	—
3′	—	—	6.62	6.88	—	—	—	—	6.59
	—	—	*s*	*s*	—	—	—	—	*s*
6′	—	—	6.76	7.02	—	—	—	—	6.84
	—	—	*s*	*s*	—	—	—	—	*s*
7′	5.0–4.9	4.10	3.91	3.80	4.81	4.8	4.72	4.81	4.63
	m	*d*, 4.3	*d*, 4.3	*d*, 7.7	*d*, 9.1	*d*, 8.5	*d*, 8.5	*d*, 8	*d*, 4
8′	6.6–6.0	2.2–1.6	1.83	1.54	2.31	2.2	2.17	2.27	5.35
	m	*m*	*m*	*dq*	*m*	*m*	*m*	*m*	*ddd*
				7.7, 7.4					9.5, 7.5, 4
9′a		—	—	—	2.41	2.40	2.39	2.63	2.78
	5.0–4.9	—	—	—	*m*	*dd*, 16.5, 9.5	*dd*, 16.4, 9.7	*m*	*dd*, 15, 9.5
	m	—	—	—	2.9	2.74	2.85	2.87	2.64
9′b		—	—	—	*m*	*dd*, 16.5, 5.5	*m*	*m*	*dd*, 15, 7.5
Me-9′		0.65	0.92	0.79	—	—	—	—	—
		d, 6.8	*d*, 7.1	*d*, 7.4	—	—	—	—	—
2″,6″	—	7.3–6.7	6.63	6.85	7.20	7.27	7.27	7.28	—
	—	*m*	*d*, 8.5	*d*, 6.2	*d*, 8.6	*d*, 8.5	*d*, 8.4	*d*, 8	—
3″,5″	—	7.3–6.7	6.53	7.18	6.76	7.01	6.86	7.01	—
	—	*m*	*d*, 8.5	*d*, 6.2	*d*, 8.6	*d*, 8.5	*d*, 8.4	*d*, 8	—
7″	—	2.5–2.1	2.23	2.42	6.29	6.30	6.23	6.29	—
	—	*m*	*br d*	*m*	*d*, 15.8	*br d*	*d*, 15.6	*d*, 15.5	—
			7.4			16			
8″	—	2.2–1.6	1.74	2.42	6.0	5.93	5.96	5.94	—
	—	*m*	*m*	*m*	*m*	*ddd*, 16, 8, 6	*m*	*m*	—
9″a	—	—	—	—	2.0	1.99	2.07	2.05	—
	—	—	—	—	*m*	*br dt*	*m*	*m*	—
						14.5, 8.5			—
9″b	—	—	—	—	2.13	2.2	2.17	2.2	—
	—	—	—	—	*m*	*m*	*m*	*m*	—
Me-9″	—	0.84	0.44	0.75	—	—	—	—	—
	—	*d*, 6.6	*d*, 6.8	*d*, 6.9	—	—	—	—	—

Table 4. ^{13}C NMR data for lignoid units of iryantherins (**2**, **3a**, **4a**, **5a**, **5b**, **6**) and of iryantherin acetates (**3b**, **4b**, **5c**, **5d**)

C	**2** [4]	**3a** [6]	**3b**	**4a**	**4b**	**5a**	**5c**	**5b**	**5d**	**6**
1′	135.3	133.21	138.67	115.67	124.19	130.89	136.19	131.46	136.85	107.53
2′	129.3	130.56	129.5	146.17	150.75	129.65	128.04	128.73	128.07	149.91
3′	115.4	115.24*	121.41*	104.15	112.28	116.28	121.84	115.54	121.82	103.84
4′	156.1	155.86	148.86	145.36	142.47	158.51	150.85	155.80	150.78	146.12
5′	115.4	115.24*	121.41*	142.15	138.90	116.28	121.84	115.54	121.82	142.18
6′	129.3	130.56	129.5	116.17	124.59	129.65	128.04	128.73	128.07	117.20
7′	44.1	44.05	43.5	38.06	39.19	84.01	82.39	82.91	82.03	37.20
8′	141.0	36.06	35.31	41.15	42.96	37.59	36.96	37.58	37.21	87.55
9′	111.3	11.79	10.66	12.74	11.39	25.89	25.14	24.18	24.39	27.72
1″	—	133.21	138.67	132.56	138.90	129.98	133.18	130.34	133.64	—
2″,6″	—	130.72	130.36	130.21	130.11	127.98	126.94	127.34	126.92	—
3″,5″	—	115.53*	120.91*	115.39	122.16	116.03	121.63	115.33	121.59	—
4″	—	156.10	149.21	155.91	149.84	157.48	149.84	154.77	149.87	—
7″	—	42.38	41.09	42.72	42.14	132.50	131.86	131.70	131.71	—
8″	—	34.78	32.28	35.03	34.32	124.37	126.22	124.25	126.61	—
9″	—	12.86	14.0	15.96	14.33	36.11	35.28	35.50	35.37	—

Table 5. ^1H–^1H and ^1H–^{13}C 2D NMR correlations for compound **4a**

			Correlated signals	
Signals	H	H	C short range	C long range
14.41	HO-11			164.71, 107.55, 106.64
7.21	2,6	6.85, 2.92	130.21 (114.55)	158.88, 130.21
6.85	3,5	7.21	114.55 (130.21)	134.66, 114.55
6.76	6′		116.17	146.17, 145.36 (142.15, 116.17)
6.63	2″,6″	6.53, 2.23	130.21	155.91, 130.21
6.62	3′		104.15	142.15, 115.67 (146.17, 145.36, 104.15)
6.53	3″,5″	6.63	115.39	132.56, 115.39
6.19	14	3.95	91.11	159.91, 107.55, 91.11 (162.16, 106.64)
3.95	MeO-15	6.19	56.31	162.16, 56.31
3.91	7′	1.83	38.06	164.71, 159.91, 115.67, 106.64
3.76	MeO-4		55.40	158.88, 55.40
3.32	8,8	2.92	47.06	205.91
2.92	7,7	7.21, 3.32	30.46	205.91, 134.66, 130.21
2.23	7″	6.63, 1.74	42.72	132.56, 130.21
1.83	8′	3.91, 0.92	41.15	
1.74	8″	2.23, 0.44	35.03	
0.92	9′	1.83	12.74	38.06
0.44	9″	1.74	15.98	

Table 6. ^1H–^1H and ^1H–^{13}C 2D NMR correlations for compound **5a**

		Correlated signals	
Signals	H	H	C long range
13.78	HO-11		165.89, 105.36, 96,08
7.38	2′,6′	6.92 (4.81)	158.51, 129.65
7.20	2″,6″	6.76 (6.29)	157.48, 127.98
6.92	3′,5′	7.38	130.89, 116.28
6.76	3″,5″	7.20	129.98, 116.03
6.68	2,3,4,5	(2.73)	133.77, 114.22
6.29	7″	(7.20) 6.0	
6.0	8″	6.29, 2.13, 2.0	
5.99	12		105.36, 101.99, 96.08
4.81	7′	2.90, 2.31 (7.38)	
3.72	MeO-4		158.51, 55.24
3.11	8,8	2.73	205.27
2.90	9′b	4.81, 2.41, 2.31	
2.73	7,7	(6.68), 3.11	133.77, 129.65
2.41	9′a	2.90, 2.31	
2.31	8′	4.81, 2.90, 2.41, 2.13, 2.0	
2.13	9″b	6.0, 2.31, 2.0	
2.0	9″a	6.0, 2.31, 2.13	

C-14″. The methine bridge terminal must be inserted between two hydroxyls, since the unsubstituted position cannot be flanked by two such groups (δ91.93). Indeed only one of the hydroxyl groups is chelated and hence vicinal to the carbonyl.

DISCUSSION

More than 20 years ago Ollis and one of us [8] proposed the alkylation of a phenolic unit by a cinnamyl pyrophosphate or its biological equivalent to explain the

Table 7. ^1H–^1H 2D NMR correlations for compound **5b**

Signals	H	Correlated H signals
7.27	2″,6″	6.86 (5.96)
7.17	2,6	6.83
7.15	2′,6′	6.74
6.86	3″,5″	7.27
6.83	3,5	7.17
6.74	3′,5′	7.15
6.23	7″	5.96
5.96	8″	6.23, 2.17, 2.07 (7.27)
4.72	7′	2.17
3.28	8,8	2.92
2.92	7,7	3.28
2.85	9′b	2.39
2.39	9′a	2.85, 2.17
2.17	8′	4.72, 2.39, 2.07
2.07	9″	5.96, 2.17

biosynthesis of neoflavonoids. This then new biogenetic pathway is attractive in that it accounts for the observed natural co-occurrence of dalbergiquinols such as **9** [9] and cinnamylphenols such as **10** [10] in *Dalbergia* and *Machaerium* species (family Fabaceae). Although the mechanistic feasibility of this proposal was later demonstrated by the observation that cinnamyl alcohols condense in aqueous acid solutions to yield both, 3,3-diarylpropenes and cinnamylphenols [11–14], to the best of our knowledge analogously formed pairs of compounds have not since been isolated from natural sources.

Thus the present report constitutes a welcome sequel to the neoflavonoid case. Indeed again the biosynthesis of two co-occurring types of natural products can be explained by the cinnamylation reaction. As in the formation of dalbergiquinols, attack of a phenol (here the phloroglucinol unit of **1**) on C-7 or C-9 of 4-hydroxycinnamyl alcohol would lead respectively to iryantherin-A (**2**) or compound **11**. Although **11** has not yet been found it may well represent the intermediate which, by reaction with C-9 of a second 4-hydroxycinnamyl alcohol unit, leads to a group of compounds such as the iryantherins D (**5a**) and E (**5b**). Oxidative coupling of a precursor of the iryantherin-A type such as **2** and a second dihydrochalcone unit (**1**) would be expected to lead to compounds of the iryantherin-F type such as **6**.

The nucleophilic attack by a phenol on a cinnamyl alcohol, which is the major step in the proposed biosynthetic route to the iryantherins A and F on one hand and to the iryantherins D and E on the other, is mechanistically equivalent to the transformation of cinnamyl alcohols respectively into allylphenols and propenylphenols [8]. Oxidative coupling of propenylphenols is postulated to involve quinonemethide intermediates such as **12**, which then may either lead on to neolignans, the most conspicuous constitutents of Myristicaceae [15] or, after condensation with dihydrochalcones (**1**), to iryantherins B (**3a**) and ultimately C (**4a**).

EXPERIMENTAL

Fruits of Iryanthera laevis. Identification, collection, separation into parts and extraction have been described in detail [4]. The extract from aril labelled A2 (30 g) [4] gave (besides **1**, 15-de-*O*-methyl-**1** and **2** [4]) by repeated silica CC and by prep. TLC (silica, C_6H_{14}–Me_2CO, 4:1, followed by $CHCl_3$–Me_2CO, 4:1) **5b** (9 mg). The extract from mesocarp labelled M2 (25 g) was submitted to CC over silica. Elution with light petrol–EtOAc mixtures of the indicated proportions gave fractions I (17:3, 7 g), composed mainly of triglycerides; II (7:3, 4 g), composed mainly of **1** (3.4 g); III (3:2, 5 g), separated by rechromatography into **1** (1.6 g) and a mixture which gave after repeated CC (silica) and purification by TLC (silica, C_6H_{14}–Me_2CO, 4:1, followed by $CHCl_3$–Me_2CO, 4:1) **5b** (9 mg); IV (3:2, 430 mg) which gave by the same treatment **5a** (10 mg); and V (3:7, 6 g) composed of polar compounds. The extract from kernels labelled K2 (10 g) was treated in the same way. Final TLC (silica, CH_2Cl_2 with a trace of EtOH) gave **4a** (62 mg).

Bark of Iryanthera ulei. Identified by the wood anatomists Arthur Loureiro of Instituto Nacional de Pesquisas da Amazonia, Manaus and Pedro Lisboa of Museu Paraense Emílio Goeldi, Belém. Air-dried powdered bark (660 g) was extracted in a Soxhlet successively with C_6H_{14}, CH_2Cl_2 and EtOH. The solvents were evapd and the residues labelled respectively A (2.7 g), B (11.7 g) and C (7.7 g). A was partitioned between C_6H_{14} and MeOH–H_2O (9:1). The MeOH solution was evapd. The residue (560 mg) was purified by flash chromatography (silica, C_6H_6–EtOAc, 3:2) into **1** (410 mg). B was partitioned between $CHCl_3$ and MeOH–H_2O, 3:2. The ppt. (8.3 g) was removed by

Table 8. Double irradiation ^1H NMR data for compound **6**

Irradiated H		Effect on spectrum					
H	δ	H	δ		H	δ	
2,6	7.21	3,5	6.85	*d*→*s*	7	2.93	Narrowing
7,7	2.93	8,8	3.36	*t*→*s*	2,6	7.21	Narrowing
8,8	3.36	7,7	2.93	*t*→*s*			
14	6.31	HO-11	13.85	NOE			
3′	6.59	HO-11	13.85	NOE	7′	4.63	NOE
7′	4.63	3′	6.59	NOE	14	6.31	NOE
8′	5.35	3′	6.59	NOE	7′	4.63	*d*→*s*
		9′	2.64	*dd*→*d*	9′	2.78	Narrowing
2″,6″	7.15	3″,5″	6.83	*d*→*s*			
7″,7″	2.83	8″,8″	3.19	*t*→*s*	2″,6″	7.15	Narrowing
8″,8″	3.19	7″,7″	2.83	Narrowing			
14″	6.06	3′	6.59	NOE			

filtration, it consisted chiefly of **1**. The $CHCl_3$ solution was evapd. The residue (3.3 g) was submitted to flash chromatography (silica, C_6H_{14}–Me_2CO, 4:1), which gave in order, after purification by TLC (silica C_6H_6–Et_2O, 9:11), **5b** (26 mg) and **6** (6 mg). C was partitioned between $CHCl_3$ and EtOH–H_2O, 3:2. The ppt. (1 g) was removed by filtration. The $CHCl_3$ solution was evapd and the residue (6.4 g) submitted to flash chromatography (silica, CH_2Cl_2). The less polar fractions gave **1** (0.730 g) and the more polar ones gave in order, after purification by TLC (silica, C_6H_6–Et_2O, 6:4), **5a** (21 mg) and **3a** (28 mg).

Bark of Iryanthera paraensis. Identification tentative. Air-dried, powdered material (900 mg), treated as described for *I. ulei*, gave **1** (880 mg) and **6** (3 mg).

Iryantherin-B (**3a**). IR ν_{max}^{KBr} cm^{-1}: 3365, 1610, 1512, 1465, 1446, 1244, 1175, 1033, 826, 756. ^{13}C NMR: Tables 2 and 4.

Iryantherin-B *tetraacetate* (**3b**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1767, 1694, 1608, 1583, 1513. ^1H NMR: Tables 1 and 3. ^{13}C NMR: Tables 2 and 4. MS (70 eV) *m/z* (rel. int.): 738 ([M], 0), 534 ([M−**d**+1], 9), 533 ([M−**d**], 25), 492 ([M−**d**+1−42], 12), 491 ([M−**d**−42], 37), 449 ([M−**d**−84], 37), 407 ([M−**d**−126], 38), 135 ([**c**], 6), 134 ([**c**−1], 11), 121 ([**b**], 100), 107 ([**a**], 50).

Iryantherin-C (**4a**). (Found: C, 72.22; H, 6.08. $C_{35}H_{36}O_8$ requires: C, 71.92; H, 6.16). IR ν_{max}^{film} cm^{-1}: 3390 (OH), 1620 (OH . . . O=C), 1600, 1515, 1450, 1035, 825, 760. ^1H NMR: Tables 1 and 3. ^{13}C NMR: Tables 2 and 4. MS (70 eV) *m/z* (rel. int.); 584 ([M], 0), 477 ([M−**a**], 1.6), 421 ([M−**c**], 100), 163 ([**c**], 1), 121 ([**b**], 50), 107 ([**a**], 22).

Iryantherin-C *tetraacetate* (**4b**). ^1H NMR: Tables 1 and 3. ^{13}C NMR: Tables 2 and 4. MS (70 eV), *m/z* (rel. int.): 752 ([M], 0), 547 ([M−**c**], 34), 505 ([M−**c**−42], 43), 463 ([M−**c**−84], 64), 421 ([M−**c**−126], 43), 121 ([**b**], 100), 107 ([**a**−42], 53).

Iryantherin-D (**5a**). (Found: C, 73.69; H, 5.71. $C_{34}H_{32}O_7$ requires: C, 73.91; H, 5.79). UV λ_{max}^{MeOH} nm: 269, 293 (ε 4200, 4250). IR ν_{max}^{KBr} cm^{-1}: 3354, 1610, 1511, 1228, 1173, 1037, 967, 923, 832. ^1H NMR: Tables 1 and 3. ^{13}C NMR: Tables 2 and 4. MS (70 eV) *m/z* (rel. int.): 552 ([M], 1), 445 ([M−**a**], 3), 431 ([M−**b**], 1), 417 ([M−**c**], 2), 300 ([M−**d**], 2), 252 ([**d**], 45), 165 ([M−**c**−**d**], 7), 153 (43), 145 (50), 135 ([**c**], 8), 134 ([**c**−1], 38), 121 ([**b**], 100), 107 ([**a**], 50).

Iryantherin-D-*tetraacetate* (**5c**). ^1H NMR: Tables 1 and 3. ^{13}C NMR: Tables 2 and 4.

Iryantherin-E (**5b**). (Found: C, 73.92; H, 5.92. $C_{35}H_{34}O_7$ requires: C, 74.20, H, 6.00). UV λ_{max}^{MeOH} nm: 269, 294 (ε 4150, 4100). IR ν_{max}^{KBr} cm^{-1}: 3407, 1614, 1593, 1513, 1450, 1245, 1174, 1033, 967, 916, 829. ^1H NMR: Tables 1 and 3. ^{13}C NMR: Tables 2 and 4. MS (70 eV) *m/z* (rel. int.): 566 ([M], 5), 459 ([M−**a**], 6), 445 ([M−**b**], 2), 431 ([M−**c**], 10), 315 ([M−**d**+1], 10), 252 ([**d**], 7), 251 ([**d**−1], 13), 179 ([M−**c**−**d**], 21), 135 ([**c**], 27), 121 ([**b**], 100), 107 ([**a**], 29).

Iryantherin-E-*triacetate* (**5d**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1771, 1686, 1615, 1582, 1513, 1466, 1246, 1192, 1107, 1037, 969, 913, 829, 756. ^1H NMR: Tables 1 and 3. ^{13}C NMR: Tables 2 and 4.

Degradation product (**8**). ^1H NMR (200 MHz, $CDCl_3$) δ: 7.17 (*d*, *J* = 8.5 Hz, H-2, H-6), 6.85 (*d*, *J* = 8.5 Hz, H-3, H-5), 2.93 (*m*, H-7), 3.3 (*m*, H-8), 5.95 (*s*, H-12), 7.23 (*d*, *J* = 8.6 Hz, H-2′, H-6′), 6.86 (*d*, *J* = 8.6 Hz, H-3′, H-5′), 4.80 (*d*, *J* = 8.8 Hz, H-7′), 2.65 (*m*, H-8′), 2.38 (*m*, H-9′a), 2.90 (*m*, H-9′b), 9.55 (*t*, *J* = 1.25 Hz, H-8″), 2.35 (*m*, H-9″a, H-9″b), 3.80 (*s*, MeO-4, MeO-15), 14.38, (*s*, HO-11). ^{13}C NMR (50 MHz, $CDCl_3$) (DEPT-135) δ: 133.73 (C, C-1), 129.34 (CH, C-2, C-6), 113.84 (CH, C-3, C-5), 157.81 (C, C-4), 29.67 (CH_2, C-7), 46.04 (CH_2, C-8), 204.86 (C, C-9), 105.41 (C, C-10), 164.63 (C, C-11), 90.77 (CH, C-12), 160.87 (C, C-13), 102.03 (C, C-14), 161.45 (C, C-15), 130.55 (C, C-1′), 128.64 (CH, C-2′, C-6′), 115.73 (CH, C-3′, C-5′), 156.11 (C, C-4′), 82.00 (CH, C-7′), 32.82 (CH, C-8′), 24.82 (CH_2, C-9′), 200.04 (C, C-8″), 46.32 (CH_2, C-9″), 55.26 (Me, MeO-4), 55.53 (Me, MeO-15).

Iryantherin-F (**6**). (Found: C, 67.01; H, 5.54. $C_{43}H_{42}O_{13}$ requires: C, 67.36; H, 5.48). UV λ_{max}^{MeOH} nm: 280sh, 294 (ε 10100, 11900); $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm: 286, 327sh (ε 12900, 12000). IR ν_{max}^{KBr} cm^{-1}: 3410, 1614, 1513, 1454, 1245, 1158, 1119, 958, 827, 739. ^1H NMR: Tables 1 and 3. ^{13}C NMR: Tables 2 and 4. MS *m/z* (rel. int.): 766 (M, 0), 179 (7), 167 (38), 166 (4), 151 (7), 135 (12), 121 (100).

Notes to spectral data (Tables 1–8). Spectra were obtained for **1**, **2**, **3a**, **4a**, **4b**, **5a** and **6** in $(CD_3)_2CO$ solutions and for **3b**, **5b**, **5c** and **5d** in $CDCl_3$ solutions. ^1H NMR spectra were registered at 60 (**2**), 80 (**3c**), 200 (**1**, **4a**, **4b**, **5a**, **5b**, **5d**) and 300 (**5c**, **6**) MHz. ^{13}C spectra were registered at 20 MHz (**2**, **3b**, **5c**, **5d**), 50 (**1**, **4a**, **4b**, **5a**, **5b**) and 75 (**3a**, **6**) MHz Additional signals for **3b**: ^1H NMR 2.24 (2AcO), 2.29 (2AcO); ^{13}C NMR 20.72 (Me), 21.09 (3Me), 169.33 (4CO). **4b**: ^1H NMR 2.15, 2.20, 2.27, 2.29 (4AcO); ^{13}C NMR 20.43, 20.49, 20.61, 20.95 (4Me); 168.58, 168.97 (2CO), 169.58 (2CO). **5c**: ^1H NMR 2.14, 2.25, 2.29, 2.32 (4AcO); ^{13}C NMR 20.71, 20.76, 21.10, 21.14 (4Me), 168.21, 169.38 (2CO), 169.01 (2CO). **5d**: ^1H NMR 2.16, 2.29, 2.31 (3AcO); ^{13}C NMR 20.48 (Me), 21.05 (2Me), 168.78, 169.08, 169.33 (3CO). In Table 1 the second of the two columns for **6** refers to H-2″ to H-14″. In Tables 1 and 3 the coupling constants, registered jointly with signal multiplicities, are in Hz. In all ^{13}C NMR spectra the nature of carbon was ascertained by DEPT-135 experiments. In Table 2 the second of the two columns for **6** refers to C-1″ to C-15″ and the attributions for each pair of identically numbered carbons are interchangeable except for C-12 (δ110.98) and C-12″ (δ102.0); C-14 (δ91.93) and C-14″ (δ87.79). In Table 4 asterisked data may be interchanged with other asterisked data of the same column. In Tables 5–7 data in parentheses represent weak correlations. ^1H and ^{13}C NMR data of **1** [3] were thoroughly revised after registry of ^1H–^{13}C (HETCOR) 2D NMR long range correlations. Data assigned to C-11 and C-15 in the original communication on **2** [4] were interchanged according to experience gained during the revisions of spectra of **1**.

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