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DIARYLPROPANES FROM *IRYANTHERA CORIACEA**

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Key Word Index—*Iryanthera coriacea*; Myristicaceae; 1,3-diarylpropanes.

Abstract—The trunk wood of *Iryanthera coriacea* Ducke (Myristicaceae) contains six compounds which belong to the recently discovered 1,3-diarylpropane type of flavonoids: 1-(2-hydroxy-4-methoxyphenyl)-3-(3,4-methylenedioxyphenyl)-propane, 1-(2,4-dihydroxyphenyl)-3-(3,4-methylenedioxyphenyl)-propane, 1-(4-methoxyphenyl)-3-(2-hydroxy-4,5-methylenedioxyphenyl)-propane, 1-(4-hydroxy-2-methoxyphenyl)-3-(4-hydroxy-3-methoxyphenyl)-propane, 1-(2,4-dihydroxyphenyl)-3-(2-methoxy-4,5-methylenedioxyphenyl)-propane, 1-(2,4-dihydroxy-3,5-methylphenyl)-3-(2-hydroxy-4,5-methylenedioxyphenyl)-propane.

The trunk wood of *Iryanthera coriacea* Ducke contains besides the previously described (±)-3′,4′-dihydroxy-5,7-dimethoxyflavan [2], sitosterol and virolane (**1a**) [3], five additional 1,3-diarylpropanes. These were recognized as such on grounds of their PMR spectra which, with respect to the signals associated with the trimethylene chain, were all identical to the spectrum reported for **1a** [3]. Other features of these spectra, in combination with the spectra of the derived acetates or methyl ethers, allowed recognition of nature and number of the substituents. Once the distribution of these substituents among the aryl groups became known through MS (Table 1), only their relative location on each ring remained to be determined. This was achieved by analysis of the PMR signals produced by the aromatic protons.

Initially, with respect to the B-rings, a broad 3H singlet at τ 3·3 revealed the 3′,4′-disubstitution for compounds **1a**, **1c** and **1g**. While this indicated immediately that **1c**, as indeed the known **1a**, have piperonyl units, the formulation of a guaiacyl unit for **1g** was based additionally on a negative Gibbs test. Two 1H singlets at τ 3·3 and 3·5 revealed the 2′,4′,5′-trisubstitution for compounds **1e**, **1i** and **1k**, settling the structure of their B-rings.

With respect to the A-rings, an AA′BB′ pattern in the spectrum of **1e** located the OMe, only group whose position remains to be defined, at the 4-position. The multiplicity of the 3 1H signals (*d*, *J* 2 Hz; *dd*, *J* 8, 2Hz; *d*, *J* 8Hz) located the two substituents of **1a**, **1c**, **1g** and **1i** at C-2 and C-4. While this evidence led to completion of structural proposals for **1c** and **1i**, two alternative formulae could still be written for the remaining compounds. Since, however, this problem had already been solved for **1a** through a positive Gibbs test and a strong MS peak at *m/e* 136 (**2a**) [3], a negative Gibbs test and absence of the 136-peak are compatible only with **1g**. The *meta*-relation of 2 hydroxyls and 1 aromatic H, evident from the relatively small shift of the PMR singlet from τ 3·10 to

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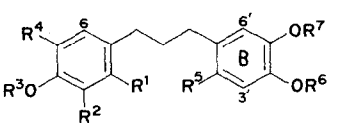
Table 1. MS and distribution of substituents among natural 1,3-diarylpropanes

	(1c)	(1a)	(1e)	(1g)	(1i)	(1k)
$M^{+\cdot}$	272 (73)	286 (62)	286 (25)	288 (60)	302 (60)	316 (50)
$ArCH_2CH_2^+$	137 (18)	151 (20)	135 (19)		137 (10)	
				151 (32)		165 (32)
$Ar'CH_2CH_2^+$	149 (43)	149 (18)	165 (42)		179 (10)	
$ArCH_2^+$	123 (38)	137 (100)	121 (4)	137 (100)	123 (26)	151 (100)
$Ar'CH_2^+$	135 (100)	135 (33)	151 (100)		165 (100)	
(2)		136 (72)				150 (30)
(3)			150 (8)			
Ar	2OH	OH, OMe	OMe	OH, OMe	2OH	2OH, 2Me
Ar'	O_2CH_2	O_2CH_2	OH,O_2CH_2	OH, OMe	OMe, O_2CH_2	OH,O_2CH_2

3·05 upon acetylation, is compatible with two structures for **1k**. The symmetrical alternative, however, must be discarded, since in the PMR spectrum of the triacetate (**1l**) the two aromatic methyl resonances occur at different frequencies.



(**1a**) $R^1=OH$, $R^2=R^4=R^5=H$, $R^3=Me$, $R^6-R^7=CH_2$
(**1b**) $R^1=OAc$, $R^2=R^4=R^5=H$, $R^3=Me$, $R^6-R^7=CH_2$
(**1c**) $R^1=OH$, $R^2=R^3=R^4=R^5=H$, $R^6-R^7=CH_2$
(**1d**) $R^1=OAc$, $R^2=R^4=R^5=H$, $R^3=Ac$, $R^6-R^7=CH_2$
(**1e**) $R^1=R^2=R^4=H$, $R^3=Me$, $R^5=OH$, $R^6-R^7=CH_2$
(**1f**) $R^1=R^2=R^4=H$, $R^3=Me$, $R^5=OAc$, $R^6-R^7=CH_2$
(**1g**) $R^1=OMe$, $R^2=R^3=R^4=R^5=R^6=H$, $R^7=Me$
(**1h**) $R^1=OMe$, $R^2=R^4=R^5=H$, $R^3=R^6=Ac$, $R^7=Me$
(**1i**) $R^1=OH$, $R^2=R^3=R^4=H$, $R^5=OMe$, $R^6-R^7=CH_2$
(**1j**) $R^1=OAc$, $R^2=R^4=H$, $R^3=Ac$, $R^5=OMe$, $R^6-R^7=CH_2$
(**1k**) $R^1=R^5=OH$, $R^2=R^4=Me$, $R^3=H$, $R^6-R^7=CH_2$
(**1l**) $R^1=R^5=OAc$, $R^2=R^4=Me$, $R^3=Ac$, $R^6-R^7=CH_2$
(**1m**) $R^1=R^5=OMe$, $R^2=R^4=Me$, $R^3=Me$, $R^6-R^7=CH_2$

(**2a**) $R^2=R^4=H$, $R^3=Me$
(**2k**) $R^2=R^4=Me$, $R^3=H$

(**3e**) $R^6-R^7=CH_2$

EXPERIMENTAL

Isolation of the constituents of Iryanthera coriacea. A specimen from the vicinity of Manaus, Amazonas, classified by the botanist W. Rodrigues (Herbaria INPA, Manaus: Chem. 40/72; Bot. 35391) gave a trunk wood sample (4 kg) which was powdered and extracted with EtOH. The C_6H_6–$CHCl_3$ 1:1 soluble portion (25 g) of this extract (215 g), upon chromatography on a silica (300 g) column, was separated into the following fractions with the indicated eluants: A_1 ($CHCl_3$), A_2 ($CHCl_3$–MeOH 99·5:0·5), A_3 ($CHCl_3$–MeOH 95:5). A_1 (0·3 g) was composed of aliphatic esters. A_2 (11 g) was crystallized from C_6H_6 to give (±)-3′,4′-dihydroxy-5,7-dimethoxyflavan [2] (8·5 g). The mother-liquor, upon chromatography on a florisil (80 g) column, was separated into the following fractions with indicated eluants: B_1 (light petrol-Et_2O 94:6), B_2 (light petrol–Et_2O 8:2). B_1 (0·1 g) was crystallized C_6H_{14} giving **1a** (80 mg). B_2 (1·2 g) was crystallized from MeOH giving sitosterol (0·8 g). The mother liquor was purified by preparative TLC (SiO_2, $CHCl_3$–MeOH 95:5) giving **1g** (0·12 g). A_3 (4 g) crystallized from C_6H_6 giving **1k** (0·35 g). The mother liquor, upon chromatography on a SiO_2 (50 g) column, was separated into the following fractions with the indicated eluants: C_1 (C_6H_6–AcOEt 95:5), C_2(C_6H_6–AcOEt 9:1), C_3 (C_6H_6–AcOEt 8:2). C_1 (30 mg) and C_2 (40 mg), respectively **1e** and **1i**, were chromatographically pure oils. C_3 (0·15 g) was shown by TLC to contain 2 components. The mixture was acetylated and the components isolated as the acetates **1j** and **1d** (0·6 g) by preparative TLC (SiO_2, $CHCl_3$–MeOH 8:2).

The six 1,3-diarylpropanes were characterized as follows. (**1a**), identified with **1a** and, after acetylation, **1b** by direct comparison with authentic samples [3].

1-(2,4-*Dihydroxyphenyl*)-3-(3,4-*methylenedioxyphenyl*)-*propane* (**1c**) isolated as the *diacetate* (**1d**), oil (Found: M 356·1255, $C_{20}H_{20}O_6$ requires: M 356·1260). ν_{max}^{film} (cm^{-1}): 2950, 1760, 1600, 1495, 1440, 1370, 1250, 1200, 1135, 1100, 1040, 1010, 970, 810. PMR ($CDCl_3$, τ): 2·80 (*d*, *J* 8·0 Hz, H-6), 3·06 (*dd*, *J* 8·0, 2·0 Hz, H-5), 3·16 (*d*, *J* 2·0 Hz H-3), 3·32 (*s*, H-2′, 5′, 6′), 4·08 (*s*, O_2CH_2), 7·3–7·6 (*m*, $2ArCH_2$), 7·73 (*s*, COMe), 7·85 (*s*, COMe), 7·9–8·3 (*m*, $CH_2CH_2CH_2$). MS (*m/e*): 356 (75%) M, 314 (51), 272 (73), 149 (43), 137 (18), 136 (100), 135 (42), 123 (38).

1-(4-*Methoxyphenyl*)-3-(2-*hydroxy*-4,5-*methoxyphenyl*)-*propane* (**1e**) oil (Found: M 286·1208, $C_{17}H_{18}O_4$ requires: M 286·1205). λ_{max}^{EtOH} (nm): 285, 295 (ε 3250, 3350); $\lambda_{max}^{EtOH+NaOH}$ (nm): 295 (ε 5200). Gibbs test: negative. ν_{max}^{film} (cm^{-1}): 3450, 2940, 1615, 1510, 1490, 1465, 1300, 1250, 1100, 1075, 1050. PMR ($CDCl_3$, τ): 3·10 and 3·70 (AA′BB′ system, *J* ~ 8·0 Hz, H-2, 6 and 3, 5), 3·38 (*s*, H-6′), 3·50 (*s*, H-3′), 4·15 (*s*, O_2CH_2), 5·10 (*br s*, OH), 6·30 (*s*, OMe), 7·43 (*t*, *J* 8·0 Hz, $2ArCH_2$), 7·8–8·4 (*m*, $CH_2CH_2CH_2$). *Acetate* (**1f**), oil. ν_{max}^{film} (cm^{-1}): 2940, 1760, 1500, 1480, 1460, 1370, 1200, 1160, 1070, 1040.

1-(4-*Hydroxy*-2-*methoxyphenyl*)-3-(4-*hydroxy*-3-*methoxyphenyl*)-*propane* (**1g**), oil (Found: M 288·1354, $C_{17}H_{20}O_4$ requires: M 288·1362). λ_{max}^{EtOH} (nm): 225, 280 (ε 13350, 4800); $\lambda_{max}^{EtOH+NaOH}$ (nm): 245, 295 (ε 15740, 5850); no H_3BO_3 + NaOAc shift. Gibbs test: negative. ν_{max}^{film} (cm^{-1}): 3390, 2940, 1600, 1510, 1460, 1270, 1185, 1150, 1125, 1040. PMR ($CDCl_3$, τ): 3·07 (*d*, *J* 8 Hz, H-6), 3·2–3·3 (*m*, H-2′, 5′, 6′), 3·50–3·78 (*m*, H-3, 5), 4·55 (*s*, 2OH), 6·13 (*s*, OMe), 6·23 (*s*, OMe), 7·43 (*t*, *J* 7·0 Hz, $2ArCH_2$), 7·8–8·3 (*m*, $CH_2CH_2CH_2$). *Diacetate* (**1h**), oil. ν_{max}^{film} (cm^{-1}): 2940, 1760, 1600, 1505, 1465, 1420, 1370, 1270, 1205, 1150, 1120, 1040, 1020. PMR ($CDCl_3$, τ) 2·98–3·45 (*m*, H-3, 5, 6, 2′, 5′,

6'), 6·21 (*s*, OMe), 6·23 (*s*, OMe), 7·41 (*t*, *J* 7·0 Hz, $2ArCH_2$), 7·80 (*s*, 2COMe), 7·8–8·3 (*m*, $CH_2C\underline{H}_2CH_2$).

1-(2,4-*Dihydroxyphenyl*)-3-(2-*methoxy*-4,5-*methylenedioxyphenyl*)-*propane* (**1i**), oil (found: M 302·1161, $C_{17}H_{18}O_5$ requires: 302·1154). λ_{max}^{EtOH} (nm): 225, 290, 298 (ε 12600, 5700, 5940). $\lambda_{max}^{EtOH+NaOH}$ (nm): 235, 298 (ε 12450, 8600). Gibbs test positive. ν_{max}^{film} (cm^{-1}): 3390, 1615, 1500, 1485, 1470, 1190, 1160, 1100, 1040. PMR ($CDCl_3$, τ): 3·05 (*d*, *J* 8 Hz, H-6), 3·40 (*s*, H-6'), 3·46 (*s*, H-3'), 3·60–3·80 (*m*, H-3, 5), 4·12 (*s*, O_2CH_2), 5·23 (*br s*, 2OH), 6·26 (*s*, OMe), 7·3–7·6 (*m*, $2ArCH_2$), 7·8–8·3 (*m*, $CH_2C\underline{H}_2CH_2$). *Diacetate* (**1j**), oil. ν_{max}^{film} (cm^{-1}): 1760, 1500, 1480, 1420, 1370, 1200, 1100, 1015. PMR ($CDCl_3$, τ): 2·73 (*d*, *J* 8·0 Hz, H-6), 3·10 (*dd*, *J* 8·0, 2·0 Hz, H-5), 3·16 (*d*, *J* 2·0 Hz, H-3), 3·36 (*s*, H-6'), 3·50 (*s*, H-3'), 413 (*s*, O_2CH_2), 6·26 (*s*, OMe), 7·3–7·6 (*m*, $2ArCH_2$), 7·75 (*s*, COMe), 7·80 (*s*, COMe), 7·8–8·3 (m, $CH_2C\underline{H}_2CH_2$).

1-(2,4-*Dihydroxy*-3,5-*dimethylphenyl*-3-(2-*hydroxy*-4,5-*methylenedioxyphenyl*)-*propane* (**1k**), crystals, mp 129–131° (C_6H_6) (Found: C, 68·36; H, 6·32. $C_{18}H_{20}O_5$ requires: C, 68·35, H, 6·32%). λ_{max}^{EtOH} (nm): 280, 300 (ε 9100, 7750); $\lambda_{max}^{EtOH+NaOH}$ (nm): 322 (ε 3800). Gibbs test negative. ν_{max}^{KBr} (cm^{-1}): 3500, 2940, 1620, 1505, 1490, 1440, 1180, 1105, 1040, 940, 860. PMR [$(CD_3)_2CO$, τ]: 2·27 (*s*, OH), 3·24 (*s*, OH), 3·27 (*s*, OH), 3·33 (*s*, H-6), 3·40 (*s*, H-6'), 3·57 (*s*, H-3'). 4·17 (*s*, O_2CH_2), 7·37 (*t*, *J* 7 Hz, $2ArCH_2$), 7·84 (*s*, 2ArMe), 7·8–8·3 (*m*, $CH_2C\underline{H}_2CH_2$). *Triacetate* (**1l**), crystals, mp 114–115° (EtOH). ν_{max}^{KBr} (cm^{-1}): 3070, 1780, 1625, 1600, 1510, 1440, 1380, 1190, 1140, 1100, 820. PMR ($CDCl_3$, τ): 3·07 (*s*, H-6), 3·32 (*s*, H-5'), 3·46 (*s*, H-3'), 4·08 (*s*, O_2CH_2), 7·3–7·8 (*m*, $2ArCH_2$), 7·70 (*s*, COMe), 7·75 (*s*, COMe), 7·80 (*s*, COMe), 7·8–8·3 (*m*, $CH_2C\underline{H}_2CH_2$), 7·89 (*s*, ArMe), 8·07 (*s*, ArMe). MS (*m/e*): 443 (8%) M + 1, 442 (26) M, 401 (32), 400 (100), 359 (22), 358 (100), 317 (16), 316 (76), 165 (25), 164 (56), 152 (23), 151 (100), 150 (7), 43 (55). *Trimethyl ether* (**1m**) (**1k**, Me_2SO_4, Me_2CO, K_2CO_3, reflux, 16 h) oil. ν_{max}^{film} (cm^{-1}): 2940, 1500, 1480, 1420, 1240, 1190, 1160, 1110, 1040, 1020, 940. PMR ($CDCl_3$, τ): 3·16 (*s*, *H*-6), 3·33 (*s*, H-6'), 3·50 (*s*, H-3'), 4·13 (*s*, O_2CH_2), 6·26 (*s*, OMe), 6·31 (*s*, OMe), 6·33 (*s*, OMe), 7·40 (*t*, *J* 7·0 Hz, $2ArCH_2$), 7·80 (*s*, 2ArMe), 7·8–8·3 (*m*, $CH_2C\underline{H}_2CH_2$). MS (*m/e*): 358 (28%) M, 193 (11), 192 (16), 179 (35), 166 (17), 165 (100), 149 (25), 135 (8).

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