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DIARYLPROPANES FROM THE WOOD OF *IRYANTHERA GRANDIS*

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Key Word Index—*Iryanthera grandis*; Myristicaceae; trunk wood; flavans; 1,3-diarylpropanes.

Abstract—Trunk wood of *Iryanthera grandis* contains 1-(2'-hydroxy-4',6'-dimethoxyphenyl)-3-(3",4"-methylenedioxyphenyl)-propane and 1-(2'-hydroxy-4',6'-dimethoxyphenyl)-3-(3"-methoxy-4"-hydroxyphenyl)-propane, as well as three additional known diarylpropanes, a new flavan (±)-5,7-dimethoxy-4'-hydroxyflavan and the known (±)-7,4'-dihydroxy-3'-methoxyflavan.

INTRODUCTION

Iryanthera grandis Ducke (Myristicaceae), a tree which may attain a height of 30 m, occurs in the central region of the Amazon [1]. A sample of trunk wood of a specimen, collected near km 135 of the Manaus-Itacoatiara highway (Brazil), yielded besides sitosterol seven flavonoids which were classified by ^{1}H NMR and ^{13}C NMR assignments into 1,3-diarylpropane [2] and flavan [3] types. Tocotrienols, tetralin neolignans and a dihydrochalcone were earlier reported in the fruits of *Iryanthera grandis* [4].

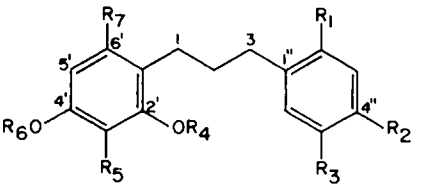
RESULTS AND DISCUSSION

Among the five 1,3-diarylpropanes **1c**, **1d** and **1e** are known compounds, the first two having been isolated from *Iryanthera polyneura* Ducke [5] and **1e** from *Iryanthera coriacea* Ducke [6]. The reisolation of **1e** was an opportunity to determine its ^{13}C NMR spectrum. The assignment of signals was aided by the ^{13}C NMR spectra of related compounds [5].

Compounds **1a** and **1b** belong to the 1,3-diarylpropane class, a flavonoid type [2]. These can be characterized by the discernible $ArCH_2CH_2CH_2Ar$ ^{1}H NMR signals at δ2.08–1.57 (*m*, 2H), 2.80–2.40 (*m*, 4H) and 2.10–1.58 (*m*, 2H), 2.80–2.30 (*m*, 4H) respectively. The two compounds present a common tropylium peak at *m/z* 167 (100%) which imply the presence of a hydroxyl and two methoxyl groups in this moiety. Additionally the mass spectra of these compounds shows important fragment ions at *m/z* 135 (18%) for **1a** (methylenedioxytropylium ion) and at *m/z* 137 (14%) for **1b** (hydroxymethoxytropylium ion).

The ^{1}H NMR spectrum of **1a** includes two multiplets [δ6.20–5.93 (2 ArH) and 6.80–6.50 (3 ArH)], three singlets corresponding to two methoxyl (δ3.78 and 3.75) and a methylenedioxy groups (δ5.86). These data, biogenetic considerations [7], a positive Gibbs test [8] and a paramagnetic shift of the protons on C-3' and C-5' from δ6.20–5.93 to δ6.37 (*d*, J = 2.0 Hz) and 6.20 (*d*, J = 2.0 Hz) in the ^{1}H NMR spectrum upon acetylation, confirmed the structure proposed for **1a**.

In addition to the above mentioned signals, the ^{1}H NMR spectrum of **1b** showed three singlets for methoxyl groups (δ3.78, 3.70 and 3.65), two multiplets at δ6.84–6.47 (3 ArH) and 6.12–5.80 (2 ArH) and a broad singlet at 5.67–5.10 (lost on treatment with D_2O) for two hydroxyl protons. Acetylation of **1b** in the usual way gave a diacetate, *m/z* 402 $[M]^+$ (32%), which presents spectral



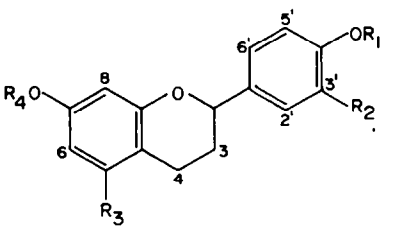
1a $R_1 = R_4 = R_5 = H$, $R_2 - R_3 = OCH_2O$, $R_6 = Me$, $R_7 = OMe$

1b $R_1 = R_4 = R_5 = H$, $R_2 = OH$, $R_6 = Me$, $R_3 = R_7 = OMe$

1c $R_1 = R_4 = R_5 = R_6 = R_7 = H$, $R_2 - R_3 = OCH_2O$

1d $R_4 = R_6 = R_7 = H$, $R_5 = Me$, $R_1 = OMe$, $R_2 - R_3 = OCH_2O$

1e $R_4 = R_5 = R_6 = R_7 = H$, $R_1 = OMe$, $R_2 - R_3 = OCH_2O$



2a $R_1 = R_2 = H$, $R_3 = OMe$, $R_4 = Me$

2b $R_1 = R_3 = R_4 = H$, $R_2 = OMe$

modifications in the ^{1}H NMR (see Experimental) consistent with structure **1b**.

The ^{1}H NMR spectrum of compound **2a**, $C_{15}H_{11}O(OMe)_2OH$, $[\alpha]_D$ 0°, include the typical signals indicative of a cyclic $ArCH(O)CH_2CH_2Ar$ chain and thus it is a flavan. The six aromatic protons form AA'BB' and AB systems which are consistent only with the oxygenation pattern shown in **2a**. The distribution of the substituents around the rings was shown by the retro-Diels–Alder MS fragments at *m/z* 167 (46%) and 120 (6%). Acetylation of **2a** leads to a monoacetate with $[M]^+$ at *m/z* 328 (100%).

The identity of the second flavan **2b** was confirmed by direct comparison with an authentic sample isolated from *Iryanthera elliptica* [9]. The assignments of the ^{13}C NMR signals were made on the basis of literature precedents [10].

EXPERIMENTAL

Isolation of the constituents. Trunk wood of a specimen (voucher herbarium INPA, Manaus, Brazil, 43706) identified by Dr. W. A. Rodrigues, collected near km 135 of the Manaus-Itacoatiara highway, was dried and its powder (4.0 kg) was macerated with EtOH. The extract (151 g) was washed exhaustively with $CHCl_3$. The $CHCl_3$-soluble part (20 g) was chromatographed on a silica column (300 g). Elution with the following solvents: petrol, petrol–EtOAc (19:1, 9:1, 17:3, 4:1), $CHCl_3$, $CHCl_3$–EtOAc (9:1, 17:3) and EtOAc, gave nine fractions which were rechromatographed giving in order aliphatic esters (3132 mg); sitosterol (4952 mg); **1a** (240 mg), **2a** (232 mg); **1d** (284 mg); **1c** (264 mg); **1b** (292 mg); **1e** (4400 mg) and **2b** (320 mg).

1-(*2'-Hydroxy-4', 6'-dimethoxyphenyl*)-3-(*3'', 4''-methylenedioxyphenyl*)-*propane* (**1a**). Oil. UV λ_{max}^{EtOH} nm (ε): 240 (20013), 285 (6320); $\lambda_{max}^{EtOH+EtONa}$ nm (ε): 234 (21066), 290 (7636). IR ν_{max}^{film} cm^{-1}: 3490, 3050, 2990, 2900, 2830, 1615, 1520, 1510, 1480, 1460, 1380, 1350, 1260, 1220, 1160, 1120, 1060, 945, 820, 760. ^{1}H NMR (60 MHz, $CDCl_3$): δ6.80–6.50 (*m*, H-2'', H-5'', H-6''), 6.20–5.93 (*m*, H-3', H-5'), 5.86 (*s*, OCH_2O), 5.13–4.97 (*m*, OH-2'), 3.78 (*s*, OMe), 3.75 (*s*, OMe), 2.80–2.40 (*m*, 2H-1, 2H-3), 2.08–1.57 (*m*, 2H-2). MS *m/z* (rel. int.): 316 (50), 181 (14), 167 (100), 150 (8), 149 (7), 137 (17), 135 (18). Positive Gibbs test [8]. *Acetate of* **1a** (Ac_2O–C_5H_5N, 24 hr room temp.). Oil. IR ν_{max}^{film} cm^{-1}: 3020, 2930, 2860, 2780, 1770, 1620, 1595, 1500, 1460, 1440, 1430, 1370, 1250, 1200, 1150, 1090, 1045, 940, 890, 815. ^{1}H NMR (60 MHz, $CDCl_3$): δ6.78–6.60 (*m*, H-2'', H-5'', H-6''), 6.37 (*d*, *J* = 2.0 Hz, H-3'), 6.20 (*d*, *J* = 2.0 Hz, H-5'), 5.92 (*s*, OCH_2O), 3.80 (*s*, OMe), 3.78 (*s*, OMe), 2.70–2.27 (*m*, 2H-1, 2H-3), 2.17 (*s*, OAc), 1.98–1.50 (*m*, 2H-2). MS *m/z* (rel. int.): 358 (46), 316 (23), 181 (13), 167 (100), 150 (6), 149 (9), 137 (9), 135 (10).

1-(*2'-Hydroxy-4', 6'-dimethoxyphenyl*)-3-(*3''-methoxy-4''-hydroxyphenyl*)-*propane* (**1b**). Oil. UV λ_{max}^{EtOH} nm (ε): 234 (20352), 284 (5088); $\lambda_{max}^{EtOH+EtONa}$ nm (ε): 240 (19080), 292 (6360). IR ν_{max}^{film} cm^{-1}: 3500, 3070, 3000, 2920, 1630, 1540, 1480, 1440, 1380, 1290, 1240, 1170, 1140, 1110, 1080, 1050, 950, 830, 760. ^{1}H NMR (60 MHz, $CDCl_3$): δ6.84–6.47 (*m*, H-2'', H-5'', H-6''), 6.12–5.80 (*m*, H-3', H-5'), 5.67–5.10 (*m*, 2OH), 3.78 (*s*, OMe), 3.70 (*s*, OMe), 3.65 (*s*, OMe), 2.80–2.30 (*m*, 2H-1, 2H-3), 2.10–1.58 (*m*, 2H-2). MS *m/z* (rel. int.): 318 (38), 181 (16), 167 (100), 151 (5), 150 (11), 137 (14). Positive Gibbs test [8]. *Acetate of* **1b**. Crystals, mp 90–92° (EtOAc). IR ν_{max}^{KBr} cm^{-1}: 3010, 2970, 2940, 2860, 1770, 1625, 1590, 1510, 1500, 1470, 1460, 1430, 1420, 1370, 1335, 1280, 1270, 1200, 1160, 1140, 1125, 1090, 1055, 1040, 1030, 910, 880, 830. ^{1}H NMR (60 MHz, $CDCl_3$): δ6.94–6.74 (*m*, H-2'', H-5'', H-6''), 6.36 (*d*, *J* = 2.5 Hz, H-3'), 6.17 (*d*, *J* = 2.5 Hz, H-5'), 3.83 (*s*, OMe), 3.80 (*s*, OMe), 3.78 (*s*, OMe), 2.78–2.27 (*m*, 2H-1, 2H-3), 2.27 (*s*, OAc), 2.10 (*s*, OAc), 2.20–1.78 (*m*, 2H-2). MS *m/z* (rel. int.): 402 (32), 360 (60), 318 (40), 381 (13), 167 (100), 151 (5), 150 (17), 137 (13).

1-(*2',4'-Dihydroxyphenyl*)-3-(*2''-methoxy-4'',5''-methylenedioxyphenyl*)-*propane* (**1e**). ^{13}C NMR (25.2 MHz, $CDCl_3$): δ29.55 (*t*, C-1), 28.76 (*t*, C-2), 30.32 (*t*, C-3), 120.70 (*s*, C-1'), 154.07 (*s*, C-2'), 102.74 (*d*, C-3'), 154.07 (*s*, C-4'), 107.36 (*d*, C-5'), 130.47 (*d*, C-6'), 123.18 (*s*, C-1''), 151.85 (*s*, C-2''), 95.13 (*d*, C-3''), 145.60 (*s*, C-4''), 140.68 (*s*, C-5''), 109.46 (*d*, C-6''), 100.66 (*t*, OCH_2O), 56.66 (*q*, MeO-2''). *Acetate of* **1e**. ^{13}C NMR (25.2 MHz, $CDCl_3$): δ29.71 (*t*, C-1), 29.35 (*t*, C-2), 30.23 (*t*, C-3), 131.61 (*s*, C-1'), 152.08 (*s*, C-2'), 115.70 (*d*, C-3'), 148.78 (*s*, C-4'), 118.84 (*d*, C-5'), 130.06 (*d*, C-6'), 122.37 (*s*, C-1''), 152.08 (*s*, C-2''), 94.61 (*d*, C-3''), 145.88 (*s*, C-4''), 140.57 (*s*, C-5''), 109.46 (*d*, C-6''), 100.72 (*t*, OCH_2O), 168.80 (*s*, MeCOO-2'), 168.70 (*s*, MeCOO-4'), 56.20 (*q*, MeO-2''), 20.58 (*q*, MeCOO-2'), 20.93 (*q*, MeCOO-4').

(±)-5,7-*Dimethoxy-4'-hydroxyflavan* (**2a**). Rose crystals. mp 129–131° (CH_2Cl_2–$CHCl_3$). UV λ_{max}^{EtOH} nm (ε): 230 sh (32604), 277 (2860); $\lambda_{max}^{EtOH+EtONa}$ nm (ε): 247 (26884), 292 (3432). IR ν_{max}^{KBr} cm^{-1}: 3450, 3050, 3000, 2900, 1630, 1530, 1510, 1460, 1380, 1350, 1330, 1280, 1220, 1160, 1120, 1080, 1060, 1020, 980, 960, 900, 830, 760. ^{1}H NMR (60 MHz, Me_2CO-d_6): δ7.17 (*d*, *J* = 8.0 Hz, H-2', H-6'), 6.73 (*d*, *J* = 8.0 Hz, H-3', H-5'), 6.08–5.88 (*m*, H-6, H-8), 4.80 (*dd*, *J* = 8.5, 3.5 Hz, H-2), 3.70 (*s*, OMe), 3.67 (*s*, OMe), 6.08–5.82 (*m*, OH-4'), 2.75–2.43 (*m*, 2H-4), 2.25–1.83 (*m*, 2H-3). MS *m/z* (rel. int.): 286 (100), 179 (6), 167 (46), 154 (6), 120 (6). Negative Gibbs test [8]. *Acetate of* **2a**. Rose crystals, mp 108–110° (C_6H_6). IR ν_{max}^{KBr} cm^{-1}: 3010, 2960, 2940, 2840, 1760, 1625, 1595, 1565, 1510, 1500, 1460, 1440, 1430, 1375, 1350, 1315, 1285, 1230, 1200, 1155, 1115, 1075, 1050, 1020, 950, 920, 860. ^{1}H NMR (60 MHz, $CDCl_3$): δ7.48 (*d*, *J* = 8.0 Hz, H-3', H-5'), 7.10 (*d*, *J* = 8.0 Hz, H-2', H-6'), 6.19–6.00 (*m*, H-6, H-8), 5.00 (*dd*, *J* = 8.5, 3.5 Hz, H-2), 3.81 (*s*, OMe), 3.78 (*s*, OMe), 2.88–2.53 (*m*, 2H-4), 2.30 (*s*, OAc), 2.40–2.00 (*m*, 2H-3). MS *m/z* (rel. int.): 328 (100), 286 (66), 179 (13), 167 (61), 154 (10), 120 (25).

(±)-7,4'-*Dihydroxy-3'-methoxyflavan* (**2b**). ^{13}C NMR (25.2 MHz, $CDCl_3$): δ77.86 (*d*, C-2), 24.58 (*t*, C-3), 30.09 (*t*, C-4), 129.98 (*d*, C-5), 107.82 (*d*, C-6), 154.65 (*s*, C-7), 103.39 (*d*, C-8), 155.69 (*s*, C-9), 119.08 (*s*, C-10), 133.47 (*s*, C-1'), 108.59 (*d*, C-2'), 146.31 (*s*, C-3'), 145.12 (*s*, C-4'), 114.11 (*d*, C-5'), 119.08 (*d*, C-6'), 55.88 (*q*, MeO-3').

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REFERENCES

1. Schultes, R. E. and Holmstedt, B. (1971) *Lloydia* **34**, 61.
2. Lima, R. A. de, Franca, N. C., Díaz, D. P. P. and Gottlieb, O. R. (1975) *Phytochemistry* **14**, 1831.
3. Franca, N. C., Díaz, D. P. P., Gottlieb, O. R. and Paula Rosa, B. de (1974) *Phytochemistry* **13**, 1633.
4. Vieira, P. C., Gottlieb, O. R. and Gottlieb, H. E. (1983) *Phytochemistry* **22**, 2281.
5. De Almeida, M. E. L., Braz Filho, R., von Bülow, M. V., Corrêa, J. J. L., Gottlieb, O. R., Maia, J. G. S. and Da Silva, M. S. (1979) *Phytochemistry* **18**, 1015.
6. Alves de Lima, R., Franca, N. C., Díaz, D. P. P. and Gottlieb,

O. R. (1975) *Phytochemistry* **14**, 1831.
7. Gottlieb, O. R. (1977) *Isr. J. Chem.* **16**, 45.
8. Mesquita, A. A. L., Corrêa, D. de B., Gottlieb, O. R. and Magalhães, M. T. (1968) *Anal. Chim. Acta* **42**, 311.
9. Braz Filho, R., Díaz, D. P. P. and Gottlieb, O. R. (1980) *Phytochemistry* **19**, 455.
10. Ghosal, S., Singh, S. K. and Srivastava, R. S. (1985) *Phytochemistry* **24**, 151.