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BAUSPLENDIN, A DIMETHYLENEDIOXYFLAVONE FROM *BAUHINIA SPLENDENS**

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Abstract—Wood of *Bauhinia splendens*, an Amazonian creeper, contains bausplendin, 7-methoxy-5,6,3′,4′-dimethylenedioxyflavone, as shown by spectral analysis and synthesis of the isomeric 5-methoxy-7,8,3′,4′-dimethylenedioxyflavone

INTRODUCTION

Bauhinia splendens H B K (Leguminosae–Caesalpinioideae) is a long woody creeper popularly known in the Amazonian region of Brazil as 'cipó escada', 'cipó unha de boi' or 'escada de jabotí' and in Venezuela as 'mororócipó' or 'bejuco de cadena' [2] Its strange flattened, furrowed and entirely ondulated trunk wood was extracted with ethanol Fractionation of the extract gave, in addition to sitosterol, stigmasterol and stearic acid, a flavone designated bausplendin

RESULTS AND DISCUSSION

Mass ($[M]^+$ 340, 100%) and ^{1}H NMR spectra showed bausplendin, $C_{15}H_5O_2$ $OMe(O_2CH_2)_2$, to be a flavonoid One of the methylenedioxy groups must be located at the 3′,4′-positions of ring B in view of the intense RDA-I fragment [3] at *m/z* 146 (98%) and the ABX ^{1}H NMR pattern (at 100 MHz) corresponding to H-2′ (δ7 26, *d*, *J* = 2 Hz), H-5′ (δ6 88, *d*, *J* = 8 Hz) and H-6′ (δ7 40, *dd*, *J* = 8 and 2 Hz) The other methylenedioxy group, together with the methoxyl, must be located on ring A since the two unaccounted protons are represented by singlets, a sharp one at δ6 68 and a broad one at δ6 51 The sharp signal corresponds to H-3 [4] and the broad one must, therefore, correspond to the aromatic proton The methoxyl signal is also broad This seemingly reciprocal broadening indicates long-range coupling [5] and is considered evidence for the vicinality of hydrogen and methoxyl groups as occurs in the alternative structures **1a** and **2a**

The compound corresponding to alternative **1a** was synthesized by a process involving Baker–Venkataraman condensation [6] of 2,4,6-trihydroxyacetophénone with piperonyloyl chloride This gave, in addition to the required flavone **3a**, a trace of **4** and the 2-hydroxy-3-piperonylflavanone, **5** Treatment of the latter with alkali gave a further quantity of **3a** (total yield 60%) The Elbs reaction [7, 8], applied to **3b**, the 7-*O*-benzylated derivative of **3a**, led to the flavone, **1b** (yield relative to consumed **3b**, 10%) The debenzylated derivative, **1c**, was submitted to methylenation to give **1d** (yield 34%), the methylation of which gave **1a** (52%) The end product had all the spectral features, including the value of $\Delta_{OMe} = \delta_{CDCl_3} - \delta_{C_6D_6} = +0\,60$, consistent with an unsubstituted C-6 in 5-methoxyflavones [9] The data, however, are different from the analogous data of bausplendin and this compound, thus, cannot be represented by **1a**

Unfortunately the Δ_{OMe} value for bausplendin is not available In addition, none of the methylenedioxylated derivatives mentioned in reviews published up to 1982 possess the group at the 5,6-position of the flavone skeleton or at biosynthetically equivalent positions of other flavonoid skeletons [10] This lessens the probability that **2a** might represent bausplendin However, the compound possesses two O_2CH_2 groups, a rare feature which it shares only with meliternatin (3,5-dimethoxy-6,7,3′,4′-dimethylenedioxyflavone) [11] and could, thus, very well bear the ring A O_2CH_2 at a singular location Thus, until further data become available, we propose structure **2a** for bausplendin while, nevertheless, considering **2b** as a plausible alternative

EXPERIMENTAL

Isolation of constituents Wood of the creeper, identified by João Murça Pires, Instituto de Pesquisas Agronômicas do Norte (EMBRAPA), Belém, Pará, was air-dried and ground A sample (5 4 kg) was extracted with EtOH in a Soxhlet apparatus The EtOH soln was evaporated and the residue (650 g) washed with $CHCl_3$ The $CHCl_3$ soln was evaporated and the residue (50 g)

*Part 62 in the series "The Chemistry of Brazilian Leguminosae" For Part 61 see ref [1] Taken from the M Sc thesis presented by D O L to Universidade Federal Rural do Rio de Janeiro (1974) and the D Sc thesis presented by G M S to Universidade Federal de Minas Gerais (1984)

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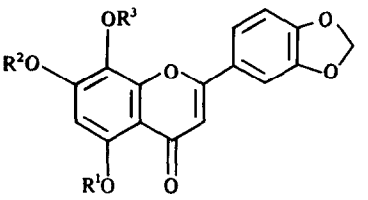
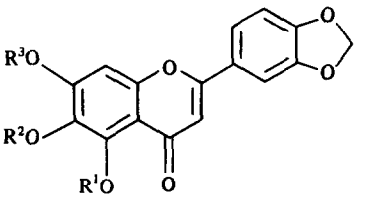
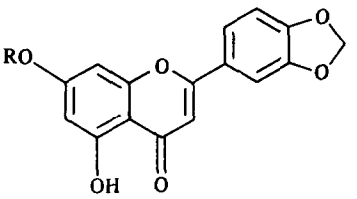


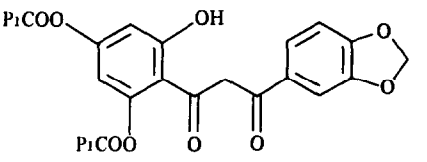
1a R^1 = Me, R^2–R^3 = CH_2
1b R^1 = R^3 = H, R^2 = Bz
1c R^1 = R^2 = R^3 = H
1d R^1 = H, R^2–R^3 = CH_2



2a R^1 = R^2 = CH_2, R^3 = Me
2b R^1 = Me, R^2–R^3 = CH_2



3a R = H
3b R = Bz



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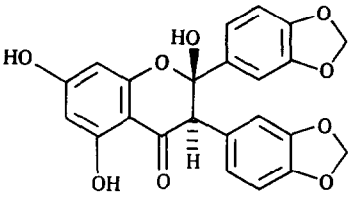

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Bz = benzyl, $C_6H_5CH_2$–
Pi = piperonyl, $CH_2O_2C_6H_3$–

submitted to CC (silica gel, 1 kg) The column was eluted successively with C_6H_6 which gave aliphatic material, C_6H_6–$CHCl_3$ (9 1) which gave a mixture of sitosterol and stigmasterol (880 mg), C_6H_6–$CHCl_3$ (1 4) which gave stearic acid (1345 mg), and C_6H_6–EtOH (49 1) which gave **2a** (8 mg)

Bausplendin (**2a**) Mp 239–241° (EtOH) ([M]$^+$ found *m/z* 340, $C_{18}H_{12}O_4$ requires 340) IR ν_{max}^{KBr} cm^{-1} 1645, 1615, 1500, 1480, 1455, 1440, 1385, 1335, 1300, 1260, 1234, 1210, 1183, 1160, 1143, 1115, 1110, 1087, 1033, 924, 892, 852, 846, 820, 812 UV λ_{max}^{EtOH} nm 245, 278, 332 (ε 12450, 9050, 17000), no shifts in the presence of reagents ^{1}H NMR (100 MHz, $CDCl_3$) δ4 09 (*br s*, OMe), 6 04 (*s*, $2O_2CH_2$), 6 51 (*s*, *br s*, H-8), 6 68 (*s*, H-3), 6 88 (*d*, *J* = 8 Hz, H-5'), 7 26 (*d*, *J* = 2 Hz, H-2'), 7 40 (*dd*, *J* = 8, 2 Hz) MS *m/z* (rel int) 340 (100), 339 (23), 313 (13), 311 (17), 294 (62), 266 (23), 195 (3), 194 (9), 179 (12), 170 (17), 167 (10), 166 (80), 164 (30), 156 (10), 149 (14), 148 (12), 147 (15), 146 (98), 145 (39), 141 (20), 140 (10), 136 (15), 121 (11), 120 (58)

2,4,6-*Tripiperonyloylacetophenone* Phloroacetophenone (73 2 g) and piperonyloyl chloride (241 g) in pyridine (200 ml) were heated at 100° for 30 min The mixture was cooled and poured onto 22 ml conc HCl and ice After 18 hr at 0° the ppt was extracted with EtOAc The EtOAc soln was washed with aq HCl and $NaHCO_3$ The EtOAc soln was dried and concd The ppt was filtered and crystallized from EtOAc to yield the triester (113 g) The EtOAc solns were evaporated and the residue, submitted to chromatography on Al_2O_3 Brockman II, gave an additional quantity of the triester (25 g after crystallization from EtOAc) and the diester (4 g after crystallization from EtOAc)

Triester Mp 148–152° (EtOAc) IR ν_{max}^{KBr} cm^{-1} 1730, 1690, 1610, 1500 UV λ_{max}^{MeOH} nm 274, 307 (ε 30000, 31200). ^{1}H NMR (60 MHz, $CDCl_3$). δ2 47 (*s*, Me), 6 10 (*s*, $3O_2CH_2$), 6 93 (*d*, *J* = 8 Hz, 3H-5'), 7 18 (*s*, H-3, H-5), 7 57 (*d*, *J* = 2 Hz, 2H-2'), 7 80 (*dd*, *J* = 8, 2 Hz, 3H-6') MS *m/z* (rel int) 149 (15), 73 (60), 71 (57), 57 (100), 55 (50), 43 (93)

Diester Mp 160–163° (EtOAc). IR ν_{max}^{KBr} cm^{-1} 3420, 1740, 1640, 1620, 1610, 1570, 1500 UV λ_{max}^{MeOH} nm 272, 308 (ε 13900, 13200), $\lambda_{max}^{MeOH+AlCl_3}$ nm 276, 305, 375 (ε 10600, 14600, 3300) ^{1}H NMR (60 MHz, $CDCl_3$) δ2 55 (*s*, Me), 6 07 (*s*, $2O_2CH_2$), 6 62 (*d*, *J* = 2 Hz, H-3), 6 80, 6 83 and 6 90 (H-5, 2H-5'), 7 55 (*d*, *J* = 2 Hz, 2H-2'), 7 80 (*dd*, *J* = 8, 2 Hz, 2H-6'), 12 60 (*s*, OH-2) MS *m/z* (rel int) 464 [M]$^+$ (1), 149 (67), 121 (8), 92 (8), 91 (14), 58 (100), 43 (99)

5,7-*Dihydroxy-3',4'-methylenedioxyflavone* (**3a**) A mixture of triester (127 g) and KOH (214 g) in dry pyridine (760 ml) was shaken vigorously (room temp, 5 hr) and acidified with HOAc–H_2O (1 1) The solvents were partially removed by

distillation under red pres The ppt was filtered, washed with H_2O and extracted with EtOAc The EtOAc soln was washed with aq $NaHCO_3$ and H_2O and then dried The solvent was evaporated and the residue, submitted to chromatography on silica gel, gave **4** (48 mg after washing with hexane), **3a** (18 g after crystallization from EtOAc) and **5** (41 g after crystallization from EtOAc–C_6H_6) A mixture of **5** (37 g) and KOH (39 g) in EtOH (300 ml) was shaken (room temp, 3 hr), left 18 hr and acidified with HOAc The EtOH and part of the HOAc were removed by distillation under red pres and the residue poured into H_2O The ppt was filtered, washed with H_2O, dried and crystallized from EtOAc–EtOH to yield **3a** (17 g)

Diaroylmethane (**4**) Dark yellow, mp 176–180° IR ν_{max}^{KBr} cm^{-1} 3450, 1615, 1600, 1560 UV λ_{max}^{EtOH} nm 240, 278, 330 inf, 375 (ε 35 500, 11 000, 24 500, 73 400), $\lambda_{max}^{EtOH+AlCl_3}$ nm 245, 278, 340, 388 (ε 31 800, 9800, 20 800, 83 800) ^1H NMR (60 MHz, $CDCl_3$) δ4 47 (*s*, 0 3 CH_2), 6 05 (*s*, 0 7 HC=, $3O_2CH_2$), 6 62 (*s*, H-3, H-5), 6 88 (*d*, *J* = 8 Hz, 2H-5′), 7 43 (*d*, *J* = 2 Hz, 2H-2′), 7 58 (*dd*, *J* = 8, 2 Hz, 2H-6′), 16 9 (*s*, 0 7 OH) MS *m/z* (rel int) 314 $[M]^+$ (3), 313 (20), 312 (99), 311 (34), 191 (16), 149 (100), 123 (8), 122 (51), 121 (35)

Flavone (**3a**) Light yellow, mp 265–268° (EtOAc), lit [12] 263–265° IR ν_{max}^{KBr} cm^{-1} 3350, 1655, 1620, 1605, 1575, 1500 UV λ_{max}^{EtOH} nm 242, 251 inf, 273, 292 inf, 349 (ε 16 500, 15 300, 14 300, 8600, 16 200), $\lambda_{max}^{EtOH+AlCl_3+HCl}$ nm 259, 283, 297 inf, 353, 380 inf (ε 12 100, 1300, 9800, 14 800, 11 000) ^1H NMR [60 MHz, $(CD_3)_2CO$] δ6 17 (*s*, O_2CH_2), 6 28 (*d*, *J* undetermined, H-6), 6 60 (*d*, *J* = 2 Hz, H-8), 6 67 (*s*, H-3), 7 05 (*d*, *J* = 8 Hz, H-5′), 7 60 (*m*, H-2′, H-6′), 12 86 (*s*, OH-5) MS *m/z* (rel int) 298 $[M]^+$ (100), 297 (27), 270 (37), 153 (7), 152 (20), 149 (12), 124 (35), 116 (9)

Hydroxypiperonylflavanone (**5**) Light yellow, 272–274° (EtOAc–C_6H_6) IR ν_{max}^{KBr} cm^{-1} 3480, 3240, 1655, 1640, 1605, 1580, 1505 UV λ_{max}^{EtOH} nm 293, 325 inf (ε 27 800, 11 600), $\lambda_{max}^{EtOH+AlCl_3+HCl}$ nm 312, 370 inf (ε 32 200, 15 100) ^1H NMR [60 MHz, $(CD_3)_2CO$] δ4 05 (*d*, *J* = 3 Hz, H-3 [13]), 6 00, 6 05, 6 17 ($2O_2CH_2$, H-6, H-8), 6 47 (*br s*, OH-2), 6 92 (*d*, *J* = 9 Hz, 2H-5′), 7 30 (*m*, 2H-2′, 2H-6′), 11 93 (*s*, OH-5) MS 20 eV, *m/z* (rel int) 446 $[M]^+$ (3), 301 (1), 300 (13), 299 (86), 298 (100)

7-Benzyloxy-5-hydroxy-3′,4′-methylenedioxyflavone (**3b**). A mixture of **3a** (30 g), benzyl chloride (74 g), dry K_2CO_3 (37 g) and NaI (18 g) in dry Me_2CO (500 ml) was heated under reflux (13 hr) The mixture was cooled and poured into iced H_2O The ppt was filtered, washed with H_2O and cyclohexane, and recrystallized from EtOAc to yield **3b** (33 5 g), light yellow, mp 234–237° IR ν_{max}^{KBr} cm^{-1} 3430, 1665, 1620, 1605, 1570, 1500 UV λ_{max}^{EtOH} nm 258, 275, 350 (ε 7200, 7100, 7100), $\lambda_{max}^{EtOH+AlCl_3+HCl}$ nm 284, 353, 390 (ε 7800, 7500, 5300) ^1H NMR (60 MHz, $CDCl_3$) δ5 12 (*s*, CH_2), 6 05 (*s*, O_2CH_2), 6 40 (*d*, *J* = 2 Hz, H-6), 6 50 (*br s*, H-3, H-8), 6 90 (*d*, *J* = 8 Hz, H-5′) MS *m/z* (rel int) 388 $[M]^+$ (1), 387 (5), 91 (100), 65 (12)

7-Benzyloxy-5,8-dihydroxy-3′,4′-methylenedioxyflavone (**1b**) To a soln of **3b** (33 g) in pyridine (2600 ml) aq KOH (1 43 M, 500 ml) was added The mixture was stirred and aq $K_2S_2O_8$ (0 17 M, 1000 ml) was added over 90 min at 20° After additional stirring (1 hr) and standing (22 hr), the mixture was cooled and acidified with conc HCl The solvents were partially evaporated under red pres The ppt was filtered and purified by chromatography on silica gel to give the starting material, **3b** (27 4 g) The filtered soln was treated with conc HCl (680 ml) and Na_2SO_3 (52 5 g) and heated under reflux (30 min) The soln was cooled and extracted with EtOAc and the EtOAc soln dried and evaporated The residue was submitted to chromatography on silica gel and the fraction eluted with $CHCl_3$–EtOAc (9 1) was recrystallized from Me_2CO to give **1b** (562 mg); yellow, mp 222–228° IR ν_{max}^{KBr} cm^{-1} 3600, 3520, 3420, 1660, 1605, 1585, 1500 UV λ_{max}^{EtOH} nm 258, 286, 346 (ε 11 600, 14 300, 12 000), $\lambda_{max}^{EtOH+AlCl_3+HCl}$ nm. 254 inf, 294, 340 inf, 356, 420 inf (ε 10 900, 13 100, 12 200, 12 700, 5500) ^1H NMR (60 MHz, $CDCl_3$) δ5 18 (*s*, CH_2), 6 05 (*s*, O_2CH_2), 6 50 (*br s*, H-3, H-6), 6 93 (*m*, H-5′), 7 25 (H-2′), 7 42 (H-6′, C_6H_5) MS *m/z* (rel int) 404 $[M]^+$ (16), 314 (21), 313 (100), 285 (15), 167 (9), 146 (6), 145 (6), 139 (28), 111 (6), 91 (95)

5,7,8-Trihydroxy-3′,4′-methylenedioxyflavone (**1c**) A mixture of **1b** (400 mg) and conc HCl (24 ml) in HOAc (24 ml) was heated at 100° (90 min) The mixture was cooled and poured on to ice The ppt was extracted with EtOAc, the EtOAc soln washed with aq $NaHCO_3$ and H_2O, and dried The solvent was evaporated and the residue was washed with hexane to yield **1c** (216 mg), yellow, mp 230° (dec) IR ν_{max}^{KBr} cm^{-1} 3340, 1655, 1650, 1585, 1550, 1500 UV λ_{max}^{MeOH} nm 245 inf, 280, 340 (ε 7100, 6700, 6900), $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm 250 inf, 293, 360, 410 inf (ε 6000, 6000, 7700, 4900) ^1H NMR, [60 MHz, $(CD_3)_2CO$] δ6 15 (*s*, O_2CH_2), 6 32 (*s*, H-6), 6 65 (*s*, H-3), 7 03 (*d*, *J* = 8 Hz, H-5′), 7 73 (*m*, H-2′, H-6′) MS *m/z* (rel int) 314 $[M]^+$ (100), 298 (29), 168 (36), 149 (20), 146 (20), 145 (12), 140 (10)

5-Hydroxy-7,8,3′,4′-dimethylenedioxyflavone (**1d**) A mixture of **1c** (90 mg), CH_2I_2 (92 mg) and Na_2CO_3 (64 mg) in DMSO (0 5 ml) was heated at 50–60° for 8 5 hr under N_2 The mixture was cooled, poured onto ice, neutralized with HCl and extracted with EtOAc The EtOAc soln was washed with H_2O, dried and evaporated The residue was submitted to chromatography on silica gel The fractions, eluted with $CHCl_3$–Me_2CO (17 3 to 7 3), were partially evaporated, and the ppt filtered and washed with hexane–Me_2CO (199 1) to give **1d** (32 mg), yellow, mp 265° (dec) IR ν_{max}^{KBr} cm^{-1} 3450, 1660, 1625, 1600, 1580, 1500 UV λ_{max}^{EtOH} nm 258, 283, 340, 365 inf (ε 6400, 7000, 6700, 4600), $\lambda_{max}^{EtOH+AlCl_3+HCl}$ nm 254, 290, 350, 415 (ε 5800, 5700, 6800, 2400) ^1H NMR (60 MHz, $CDCl_3$) δ6 08 (*s*, $2O_2CH_2$), 6 38 (*s*, H-6), 6 45 (*s*, H-3), 6 88 (*d*, *J* = 8 Hz, H-5′), 7 28 (H-2′), 7 43 (*dd*, *J* = 8, 2 Hz, H-6′), 12 77 (*s*, OH-5) MS *m/z* (rel int) 326 $[M]^+$ (100), 325 (14), 297 (10), 180 (15), 149 (14), 146 (10)

5-Methoxy-7,8,3′,4′-dimethylenedioxyflavone (**1a**) A mixture of **1d** (41 mg), Me_2SO_4 (680 mg) and Na_2CO_3 in dry Me_2CO was heated under reflux with stirring for 17 hr The solvent was evaporated under red pres and the residue taken-up in cold H_2O The mixture was extracted with $CHCl_3$, the $CHCl_3$ soln washed with cold aq NaOH (4%) and H_2O, and dried and evaporated The residue was submitted to chromatography on silica gel The fraction eluted with $CHCl_3$–MeOH (99 1) was concd, the ppt filtered and washed with hexane to give **1a** (22 mg), light yellow, mp 295–297° IR ν_{max}^{KBr} cm^{-1} 1645, 1610, 1500, 1490, 1450, 1400, 1355, 1310, 1255, 1238, 1210, 1095, 1035, 925, 895, 865, 815 UV λ_{max}^{EtOH} nm 255 inf, 278, 335 (ε 5700, 6100, 5500), no shifts in the presence of reagents ^1H NMR (270 MHz, $CDCl_3$) δ3 95 (*s*, OMe), 6 06 (*s*, O_2CH_2), 6 14 (*s*, O_2CH_2), 6 52 (*s*, H-3, H-6), 6 91 (*d*, *J* = 8 Hz, H-5′), 7 32 (*d*, *J* = 2 Hz, H-2′), 7 45 (*dd*, *J* = 8, 2 Hz, H-6′) ^1H NMR (270 MHz, C_6H_6) δ3 35 (*s*, OMe), 5 15 (*s*, O_2CH_2), 5 29 (*s*, O_2CH_2) MS *m/z* (rel int) 340 $[M]^+$ (19), 339 (8), 312 (3), 311 (9), 294 (6), 249 (4), 221 (41), 203 (58), 195 (4), 194 (5), 175 (19), 167 (4), 166 (3), 149 (19), 146 (5), 123 (46), 121 (23), 119 (12), 95 (35), 91 (10)

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