Phytochemistry. 1974. Vol. 13, pp. 1953 to 1955. Pergamon Press. Printed in England.

MARUPONE, A BENZOPHENONE FROM *MORONOBEA PULCHRA**

JOÃO P. DE P. DIAS, OTTO R. GOTTLIEB and ANTONIO A. LINS MESQUITA

Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Belo Horizonte, Brasil

(*Received* 5 *November* 1973)

Key Word Index—*Moronobea pulchra*; Guttiferae; marupone; 2-geranyl-1,3-dihydroxy-6-methoxybenzophenone.

Abstract—The trunk wood of *Moronobea pulchra* Ducke (Guttiferae) contains a yellow pigment designated marupone for which the structure of 2-geranyl-1,3-dihydroxy-6-methoxybenzophenone is proposed.

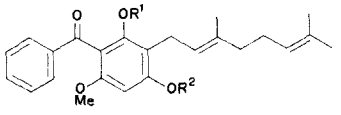
Moronobea pulchra Ducke is an arboreous Guttiferae species, known as "marupá" in the Amazon region. Its trunk wood contains a yellow pigment $C_{24}H_{28}O_4$, designated marupone. This was recognised as a benzophenone (UV: λ_{max} 255, 315 nm), substituted by a geranyl (MS: $[M\text{-}C_5H_9]^+$ 39%, $[M\text{-}C_9H_{15}]^+$ 81%; PMR 220 MHz: required signals; formation of tetrahydroderivative), a methoxy (PMR: *s*, τ 6·63) and two hydroxy (formation of diacetate and dimethyl ether) groups. One of the aromatic rings exists in form of a phenyl group (MS: $C_6H_5CO^+$ 100%, $C_6H_5{}^+$ 31%) and, consequently, all four substituents are located on the other. Indeed, this sustains a lone hydrogen on a phloroglucinol type ring (PMR: *s*, τ 4·10). While one of the hydroxyls must be placed at C-1, because there is chelation (PMR: *s*, τ −2·70), the other is situated at C-3, since there is high acidity (UV: NaOAc shift). This leaves only C-6 for the methoxyl. At this position it would, indeed, be expected to suffer anisotropic shielding (PMR: *s*, τ 6·63) by the neighbouring phenyl, as long as both aromatic rings are locked in one plane by the chelate bridge. If this is disrupted through replacement at C-1 of the hydroxyl by acetoxyl or methoxyl, the τ-value of the C-6 methoxyl falls to the normal 6·39.

The allocation of the geranyl group to C-2 (**1a**), and not to the alternative C-5 position, is based on two experimental facts: absence of UV $AlCl_3$ shift, which requires the presence of a bulky substituent *ortho* to the chelated hydroxyl, and formation of two cyclization products upon acid treatment, which requires its presence *ortho* to both hydroxyls. The less polar of these products (**2**) preserves the coplanarity determined by the C-1 hydroxyl (PMR: *s*, τ −2·8, OH; *s*, τ 6·56, OCH_3), but is exempt of the acidic C-3 hydroxyl (UV: no NaOAc shift). The more polar one (**3**) is exempt of the C-1 hydroxyl (PMR: no lowfield signal; *s*, τ 6·46, OMe). While it certainly preserves the C-3 hydroxyl (UV: NaOH shift), this is now of diminished acidity (UV: no NaOAc shift) due to lack of coplanarity of the system.

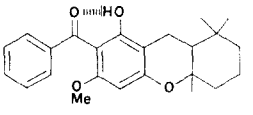
* Part XXXIII in the series "The Chemistry of Brazilian Guttiferae". For Part XXXII see Ref. 1. Taken from part of the M.S. thesis submitted by J.P. de P.D. to the Universidade Federal de Minas Gerais (1973). Sponsored by Instituto Nacional de Pesquisas da Amazônia, Conselho Nacional de Pesquisas, Manaus.

[1] BRAZ FILHO, R., COUTINHO LEMOS, M. DE J. and GOTTLIEB, O. R. (1973) *Phytochemistry* **12**, 947.

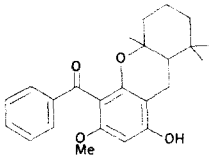
Absence of substitution on one of its benzene rings is, clearly, the reason why marupone accumulates in *Moronobea pulchra*. The presence of hydroxyl at a *meta*-position of the shikimate derived moiety is a prerequisite for oxidative cyclization of benzophenones to xanthones,[2] the characteristic metabolites of Guttiferae.[3]



(1a) R^1 = H; R^2 = H
(1b) R^1 = Me; R^2 = Me
(1c) R^1 = Ac; R^2 = Ac
(1d) R^1 = H; R^2 = Me
(1e) R^1 = Ac; R^2 = Me



(2)



(3)

EXPERIMENTAL

Isolation of marupone (1a). *Moronobea pulchra* Ducke, identified by the botanist W. Rodrigues (through comparison with herbarium specimen 5925, INPA), was collected in the vicinity of Manaus, Amazonas State. A sample of trunk wood was dried, reduced to powder (54 g) and extracted with EtOH. The extract (7·5 g) was chromatographed on silica. $CHCl_3$–MeOH (99:1) eluted, in order, marupone (62 mg) and sitosterol (5 mg).

Marupone (1a). Yellow crystals, m.p. 125–127° (petrol.). [Found: C, 75·59; H, 7·39. $C_{24}H_{28}O_4$ requires: C, 75·76; H, 7·42]. UV λ_{max}^{EtOH} (nm): 257, 315 (ε 7600, 15200); $\lambda_{max}^{EtOH+NaOH}$ (nm): 255, 355 (ε 9500, 21600); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 255, 345 (ε 7600, 15200); no shifts upon add. of $AlCl_3$ or H_3BO_3 + NaOAc. Gibbs test λ_{max}(nm): 615, 670. IR ν_{max}^{KBr} (cm^{-1}): 3193, 1643, 1610, 1553, 1468, 1443, 1258, 1183, 1093, 793, 693. PMR ($CDCl_3$, 220 MHz, τ): −2·70 (*s*, OH) 2·53 (*dd*, *J* 8·0, 1·3 Hz, H-2′, 6′), 2·6–2·7 (*m*, H-3′,4′,5′), 3·70 (*s*, OH), 4·10 (*s*, H-5), 4·70 (*t*, *J* 7 Hz, =CH), 4·94 (*t*, *J* 7 Hz, =CH), 6·57 (*d*, *J* indet., $ArCH_2$), 6·63 (*s*, OMe), 7·9 (*m*, 2 CH_2), 8·20, 8·34, 8·37 (singlets, 3 Me). MS (*m/e*): 381 (14%) M + H, 380 (52) M, 311 (39), 295 (12), 258 (16), 257 (81), 233 (16), 179 (26), 105 (100), 77 (31). Catalytic hydrogenation of **1a** (H_2, EtOH, Pd/C, room temp. and pressure) gave the *tetrahydro derivative*, purified by chromatography on silica, m.p. 140–143°. [Found: C, 75·11; H, 8·41. $C_{24}H_{32}O_4$ requires: C, 74·97; H, 8·39]. UV λ_{max}^{EtOH} (nm): 229 infl., 259 *sh*., 320 (ε 8350, 5700, 8750); IR ν_{max}^{KBr} (cm^{-1}): 3195, 1645, 1555, 1475, 1450, 1275, 1215, 1135, 1095, 805, 705. PMR ($CDCl_3$, τ): −2·4 (*s*, OH), 2·4–2·65 (*m*, H-2′-6′), 4·07 (*s*, H-5), 6·59 (*s*, OMe), 7·39 (*t*, *J* 7 Hz, $ArCH_2$), 8·2–8·8 (*m*, 2 CH, 8 CH_2), 9·0 (*d*, *J* 6 Hz, Me), 9·13 (*d*, *J* 6 Hz, 2 Me). MS (*m/e*): 384 (24%) M, 271 (5) M-C_8H_{17}, 258 (40), 257 (100) M-C_9H_{19}, 243 (5), 241 (5), 179 (40), 105 (25), 77 (14). Methylation of **1a** (Me_2SO_4, K_2CO_3, Me_2CO, reflux, 6 hr) gave the *dimethyl ether* (**1b**), oil. [Found: C, 76·40; H, 7·78. $C_{26}H_{32}O_4$ requires: C, 76·44; H, 7·90]. UV λ_{max}^{EtOH} (nm): 245, 280 infl. (ε 13050, 6700). Gibbs test: negative. IR ν_{max}^{film} (cm^{-1}): 1675, 1600, 1482, 1275, 1125, 762. PMR ($CDCl_3$, τ): 2·12 (*dd*, *J* 8, 2·5 Hz, H-2′,6′), 2·4–2·6 (*m*, H-3′,4′,5′), 3·64 (*s*, H-5), 4·65–5 (*m*, 2=CH), 6·10, 6·30, 6·39 (singlets, 3 OMe), 6·67 (*d*, *J* 7 Hz, $ArCH_2$), 8·00 (broad *s*, 2 CH_2), 8·27, 8·34, 8·40 (singlets, 3 Me). Acetylation of **1a** (Ac_2O, C_5H_5N, room temp., 24 hr) gave the *diacetate* (**1c**), oil; IR ν_{max}^{film} (cm^{-1}): 1778, 1673, 1618, 1373, 1323, 1273, 1193, 1118, 1083, 893, 763, 693. PMR ($CDCl_3$, τ): 2·23 (*dd*, *J* 7, 2 Hz, H-2′,6′), 2·5–2·7 (*m*, H-3′,4′,5′), 3·37 (*s*, H-5), 4·95 (2 superimp. *t*, *J ca* 7 Hz, 2 =CH), 6·39 (*s*, OMe), 6·93 (*d*, *J* 7 Hz, $ArCH_2$), 7·74 (*s*, COMe), 8·03 (*s* superimp. on *m*, COMe, 2 CH_2), 8·30, 8·33, 8·40 (singlets, 3 Me). Methylation of **1a** (CH_2N_2, Et_2O, room temp., 24 hr) gave the *monomethyl ether* (**1d**), purified by chromatography on alumina, as an oil. [Found: C, 75·90; H, 7·53. $C_{25}H_{30}O_4$ requires: C, 76·11; H, 7·66]. UV λ_{max}^{EtOH} (nm): 237 infl., 257 infl., 314 (ε 12200, 7900, 11400); $\lambda_{max}^{EtOH+NaOH}$ (nm): 240 (ε 21700); no $AlCl_3$ or NaOAc shifts; Gibbs test λ_{max} (nm): 665. IR ν_{max}^{film} (cm^{-1}): 3420, 1630, 1510, 1470, 1415, 1300, 1235, 1125, 800, 720. PMR (CCl_4, τ): 2·57 (*dd*, *J* 8, 2 Hz, H-2′,6′), 2·7–2·8 (*m*, H-3′,4′,5′), 4·20 (*s*, H-5), 4·93 (*m*, =CH), 5·08 (*m*, =CH), 6·17, 6·59 (singlets, 2 OMe), 6·81 (*d*, *J* 7 Hz, $ArCH_2$), 8–8·20 (*m*, 2 CH_2), 8·29, 8·41, 8·46 (singlets, 3 Me). Acetylation of **1d** (Ac_2O, C_5H_5N, room temp., 24 hr) gave the *1-O-acetyl-3-O- methyl derivative* (**1e**), oil; IR ν_{max}^{film} (cm^{-1}): 1765, 1665, 1610, 1205, 1090, 705. PMR ($ClCl_4$, τ): 2·27 (*dd*, *J* 8, 2 Hz, H-2′,6′), 2·45–2·85 (*m*, H-3′,4′,5′), 3·67 (*s*, H-5), 4·94 (2 superimp. *t*, *J ca* 7 Hz, 2=CH), 6·12, 6·41 (singlets, 2 OMe), 6·86 (*d*, *J* 7 Hz, $ArCH_2$), 8·03 (*s*, COMe, superimp. on *m*, 2 CH_2), 8·32, 8·35, 8·42 (singlets, 3 Me). Cyclization of **1a** (30 mg in 0·3 ml $CHCl_3$, 1 drop TFA, room temp., 12 hr, evap. of solvents under *vacuum*) gave a mixture which was separated by preparative TLC (SiO_2, $CHCl_3$–AcOEt 17:3) into the less polar **2** (7 mg) and the more polar **3** (14 mg). **2**, oil. [Found: C, 75·87; H, 7·47. $C_{24}H_{28}O_4$ requires: C, 75·76; H, 7·42]. UV λ_{max}^{EtOH} (nm): 256, 317 (ε 7700, 12800); $\lambda_{max}^{EtOH+NaOH}$ (nm): 246, 277 inf. (ε 18500, 5500); $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 256, 328 (ε 7700, 11850); no NaOAc shift. PMR ($CDCl_3$, τ): −2·80 (*s*, OH), 2·2–2·6 (*m*, H-2′,3′,4′,5′,6′), 4·13 (*s*, H-5), 6·56 (*s*, OMe), 7·29 (*m*), 8–8·7 (*m*), 8·67 (*s*, Me), 8·89 (*s*, Me), 8·99 (*s*, Me). **3**, oil. [Found:

[2] LOCKSLEY, H. D. and MURRAY, I. G. (1971) *J. Chem. Soc.* (C) 1332.
[3] ANDRADE DA MATA REZENDE, C. M. and GOTTLIEB, O. R. (1973) *Biochem. Syst.* **1**, 111.

C, 75·66; H, 7·50; $C_{24}H_{28}O_4$ requires: C, 75·76; H, 7·42]. UV λ_{max}^{EtOH} (nm): 250, 300 infl. (ϵ 13 550, 4950); $\lambda_{max}^{EtOH+NaOH}$ (nm): 254, 365 (ϵ 13 300, 5650); no $AlCl_3$ and NaOAc shifts. PMR ($CDCl_3$, τ): 2·18 (*dd*, *J* 8, 2 Hz, H-2′,6′), 2·4–2·65 (*m*, H-3′,4′,5′), 3·93 (*s*, H-5), 6·46 (*s*, OMe), 7·38 (*m*, ArCH), 8·15–9·10 (*m*), 8·59 (*s*, Me), 8·95 (*s*, 2 Me).

Acknowledgement—The 220 MHz PMR and MS were recorded by Dr. Afrânio Aragão Craveiro, by courtesy of Prof. Ernest Wenkert, Indiana University, U.S.A.