

XANTHONES FROM *TOVOMITA EXCELSA**

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Abstract—The trunk wood of *Tovomita excelsa* (Guttiferae) from north-eastern Brazil contains, besides betulinic acid, 1,5-dihydroxy-6-methoxyxanthone, 1,6-dihydroxy-5-methoxyxanthone, 5,6-dihydroxy-1-methoxyxanthone and 1,7-dihydroxy-6-methoxyxanthone

The five Brazilian *Tovomita* species (Guttiferae), *T. brasiliensis* [2], *T. choisyana* [3], *T. macrophylla* [4], *T. mangle* [5] and *T. pyriformis* [6], were shown to contain sitosterol, stigmasterol, β -amyirin and betulinic acid, besides eight xanthones differing in oxygenation and prenylation patterns. The present report concerns a fifth species, *T. excelsa* Andrade-Lima et G Mariz [7]. Its wood yielded sitostenone, sitosterol, stigmasterol, heptacosanoic acid and betulinic acid, besides the four simple xanthones **1a**, **1b**, **1c** and **2**. 1,5-Dihydroxy-6-methoxyxanthone (**1a**) has been prepared synthetically and bichanaxanthone (**1b**) has been isolated from another Guttiferae species, *Garcinia bichanensis* [8], these were identified by spectral comparisons. The other two xanthones have not been described previously.

Mass spectra suggested both compounds to be dihydroxymonomethoxyxanthones. The $^1\text{H NMR}$ spectrum of compound **1c** in CDCl_3 revealed the presence of two groups of adjacent aromatic protons. One group with two *ortho* protons must be placed at the 7,8-positions. Indeed the low field signal (δ 7.97) of one of the two doublets ($J = 9$ Hz) is compatible only with the *peri*-position of the corresponding hydrogen. The other group

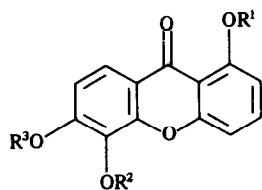
with two *ortho*, *meta* (broad doublets, $J = 8.5$ Hz) and one *ortho*, *ortho* (*t*, $J = 8.5$ Hz) coupled protons must be placed at the 2,3,4-positions. Indeed both broad doublets (δ 6.82 and 6.97) appear at a relatively high field incompatible with their location at C-1. This *peri*-position should be occupied by the methoxyl in view of the chemical shift of its signal (δ 4.14) which denotes strong deshielding. The two hydroxyls must consequently occupy the 5,6-positions, their vicinality being assured by the lability of the compound in alkali and the modification of its UV spectrum upon addition of H_3BO_3 and NaOAc .

The other novel xanthone (**2**) was soluble enough for $^1\text{H NMR}$ spectroscopy in CDCl_3 only after acetylation. The spectrum of the diacetate revealed the presence of two *para* related protons (two singlets, δ 6.93 and 7.88), which hence can only occupy the 5,8-positions, and three adjacent protons (2 *dd*, $J = 8.5$ and 1 Hz, 1 *t*, $J = 8.5$ Hz). The doublets appear at relatively high field (δ 7.00, 7.37) and C-1 must thus be substituted. Indeed the compound possesses a chelatable hydroxyl at this position, as indicated by an AlCl_3 UV shift. The second hydroxyl cannot be situated at C-6 where it would impart strong acidity, incompatible with the negligible NaOAc UV shift of **2**.

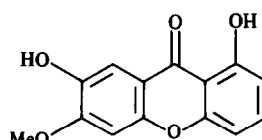
EXPERIMENTAL

Isolation of the constituents Trunk wood of *T. excelsa* was collected in a forest region near São Miguel dos Campos,

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- 1a** $\text{R}^1 = \text{R}^2 = \text{H}$, $\text{R}^3 = \text{Me}$
1b $\text{R}^1 = \text{R}^3 = \text{H}$, $\text{R}^2 = \text{Me}$
1c $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{R}^3 = \text{H}$



2

Alagoas, Brazil [7], reduced to powder (31 kg) and percolated with C_6H_6 . The extract (15 g) was chromatographed on a silica gel column (280 g). The following fractions of 100 ml were eluted in order with the indicated solvents: Frs 1–8 solid (19 mg, C_6H_6), 9–27 sitosterone + sitosterol (32 mg), $C_6H_6-CHCl_3$, 20 1), 28–79 sitosterol + stigmasterol (64 mg, $C_6H_6-CHCl_3$, 5 1), 80–120 **1a** (13 mg, $C_6H_6-CHCl_3$, 1 3), 121–137 **1c** (7 mg, $C_6H_6-CHCl_3$, 1 5), 138–150 **1b** (16 mg, $C_6H_6-CHCl_3$, 1 7), 151–160 **2** (30 mg, $CHCl_3$), 161–198 heptacosanoic acid (18 mg, $CHCl_3-MeOH$, 99 1), 199–219 betulinic acid (260 mg, $CHCl_3-MeOH$, 97 3).

5,6-Dihydroxy-1-methoxyxanthone (1c) Mp 218–223° (washed with MeOH) $[M]^+$ found 258 0538, $C_{14}H_{10}O_5$, requires 258 0528 MS m/z (rel int) 259 $[M+1]$ (9), 258 $[M]^+$ (100), 243 (51), 215 (34), 187 (27) IR ν_{max}^{KBr} cm^{-1} 3380, 1648, 1608, 1580, 1520, 1485, 1460, 1365, 1335, 1288, 1238, 1202, 1165, 1078, 1065, 1025, 805, 778, 748, 694 UV λ_{max}^{EtOH} nm 238, 243, 265 sh, 290 sh, 375 (ϵ 21800, 21900, 11900, 5800, 12600), $\lambda_{max}^{EtOH+NaOH}$ nm 238, 248, 265, 285 sh, 350 sh, 385 (ϵ 22300, 22700, 13900, 5800, 8800, 11600), $\lambda_{max}^{EtOH+NaOAc}$ nm 235, 243, 265, 285 sh, 373 (ϵ 21700, 21400, 13200, 5800, 15100), $\lambda_{max}^{EtOH+NaOAc+H_3BO_3}$ nm 235, 246, 290, 325, 368 (ϵ 21600, 22000, 5300, 6100, 9500) 1H NMR ($CDCl_3$, 270 MHz) δ 7.97 (d, J = 9 Hz, H-8), 7.03 (d, J = 9 Hz, H-7), 6.97 (br d, J = 8.5 Hz, H-4), 7.58 (t, J = 8.5 Hz, H-3), 6.82 (br d, J = 8.5 Hz, H-2), 4.14 (s, OMe).

1,7-Dihydroxy-6-methoxyxanthone (2) Mp 265–268° (washed with $CHCl_3$) $[M]^+$ found 258 0520, $C_{14}H_{10}O_5$, requires 258 0528 MS m/z (rel int) 259 $[M+1]$ (13), 258 (100), 243 (13), 215 (22), 187 (21) IR ν_{max}^{KBr} cm^{-1} 3450, 1647, 1628, 1600, 1578, 1493, 1465, 1436, 1400, 1368, 1342, 1298, 1275, 1234, 1205, 1160, 1050, 1010, 848, 815, UV λ_{max}^{MeOH} nm 253, 272 sh, 293, 375 (ϵ 24000, 12600, 10100, 8100), $\lambda_{max}^{MeOH+NaOH}$ nm 262, 280 sh (ϵ 22500, 11100), $\lambda_{max}^{MeOH+NaOAc}$ nm 252, 272 inf, 293, 377 (ϵ 22200, 14200, 10100, 5300), $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm 253, 272

sh, 293, 375 (ϵ 22800, 11400, 9000, 7900), $\lambda_{max}^{MeOH+AlCl_3}$ nm 231, 260, 282, 317 (ϵ 19100, 17400, 18100, 12100) 1H NMR ($CDCl_3$, 270 MHz) of 7-*O*-acetyl derivative δ 7.90 (s, H-8), 6.95 (s, H-5), 6.90 (dd, J = 8, 1 Hz, H-4), 7.57 (dd, J = 8.5, 8 Hz, H-3), 6.80 (dd, J = 8.5, 1 Hz, H-2), 3.97 (s, OMe), 2.36 (s, OAc) 1H NMR ($CDCl_3$, 270 MHz) of 1,7-di-*O*-acetyl derivative δ 7.88 (s, H-8), 6.93 (s, H-5), 7.37 (dd, J = 8, 1 Hz, H-4), 7.67 (dd, J = 8.5, 8 Hz, H-3), 7.00 (dd, J = 8.5, 1 Hz, H-2), 3.95 (s, OMe), 2.33 and 2.48 (2s, 2 OAc).

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REFERENCES

- 1 Miraglia, M da C M, Mesquita, A A L, Gottlieb, H E and Gottlieb, O R (1981) *Phytochemistry* **20**, 2041
- 2 Braz Fo, R, Miranda, C A S, Gottlieb, O R and Magalhães, M T (1983) *Acta Amazonica* **12**, 801
- 3 Gabriel, S J and Gottlieb, O R (1972) *Phytochemistry* **11**, 3035
- 4 Oliveira, W G de, Gottlieb, O R and Mesquita, A A L (1972) *Phytochemistry* **11**, 3323
- 5 Marta, M, Delle Monache, F, Marini-Bettolo, G B, Lyra, D A, Mello, J F de and Lima, O G de (1976) *Gazz Chim Ital* **106**, 651
- 6 Mesquita, A A L, Oliveira, W G de, Nerva, R M T and Gottlieb, O R (1975) *Phytochemistry* **14**, 803
- 7 Mariz, G (1974) *Bull Torrey Bot Club* **101**, 367
- 8 Jackson, B, Locksley, H D, Moore, I and Scheinmann, F (1968) *J Chem Soc C* 2579