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XANTHONES FROM *TOVOMITA MACROPHYLLA**

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Key Word Index—*Tovomita macrophylla*; Guttiferae; tovophyllin-*A*; tovophyllin-*B*; 1,3,6-trihydroxy-2,5-diprenyl-6′,6′-dimethylpyrano (2′,3′:7,8)xanthone; 3,6-dihydroxy-5-prenyl-6′,6′-dimethylpyrano(2′,3′:1,2)-6″,6″-dimethylpyrano(2″,3″:7,8)xanthone.

Abstract—The wood of *Tovomita macrophylla* (Pl. et Tr.) Walp. (Guttiferae) contains β-amyrin, sitosterol, betulinic acid and two novel compounds for which the structures of 1,3,6-trihydroxy-2,5-diprenyl-6′,6′-dimethylpyrano(2′,3′:7,8)xanthone (tovophyllin-*A*) and 3,6-dihydroxy-5-prenyl-6′,6′-dimethylpyrano(2′,3′:1,2)-6″,6″-dimethylpyrano(2″,3″:7,8)xanthone (tovophyllin-*B*) are proposed.

TOVOXANTHONE (I), the only natural 6′,6′-dimethylpyrano (2′,3′:7,8)xanthone so far described, occurs in *Tovomita choisyana* Pl. et Tr. (Guttiferae). The presence of its olefinic double bond in the deshielding region of the carbonyl makes the allocation of the pyrano moiety by PMR spectrometry an easy task. While normally the H-4′ and H-5′ doublets occur at τ3·3 and 4·4 (*J* 10 Hz), in the spectrum of tovoxanthone these signals appear at τ 2·05 and 4·22 (*J* 10·0 Hz).[1]

The wood of another Amazonian species of the same genus, *T. macrophylla* (Pl. et Tr.) Walp., contains, besides β-amyrin, sitosterol and betulinic acid, two further xanthones, tovophyllin-*A*, $C_{28}H_{30}O_6$, and tovophyllin-*B*, $C_{28}H_{28}O_6$. Both are again 6′,6′-dimethylpyrano(2′,3′:7,8)xanthones, since their PMR spectra show the characteristic *AB* doublets at τ 2·0 and 4·2 (*J* 10·0 Hz), accompanied by the 6 proton methyl singlets at τ 8·6. Another common feature to both compounds is oxygenation at the 3 and 6 positions, as evidenced by the intense K bands of the UV spectra (tovophyllins-*A* λ_{max} 337 nm, ε 27 700, and *B* λ_{max} 338 nm, ε 16 100) and, indeed, the full oxygenation pattern. This is not immediately evident upon comparison of the UV spectra of both tovophyllins which are strikingly different with respect to their principal maxima. A more extended chromophore must exist in tovophyllin-*B* (λ_{max} 290 and 303 nm) than in tovophyllin-*A* (λ_{max} 246 and 265 nm). Upon catalytic hydrogenation (Pd–C, EtOH), however, both xanthones lead to derivatives with nearly superimposable UV spectra (λ_{max} 245, 263, 280 inf, 325, 370 inf nm, ε 29 800, 34 200, 3700, 20 000, 3100) which are closely comparable with the spectrum of the 1,3,6,7-tetraoxygenated xanthone II (λ_{max} 242·5, 261·5, 317, 366 nm, ε 26 300, 38 900, 22 900, 9750).[2] The same phenomenon occurs if the xanthones are left for a few minutes in contact with trifluoroacetic acid. The derivatives, obtained after evaporation of the acid, have UV spectra (λ_{max} 248, 272, 340 and 395 nm) which are very close to the spectrum of the less conjugated tovophyllin-*A*. This suggests that the additional conjugation of tovophyllin-*B* forms part of a unit involving an ether function at C-1 which is most easily transformed into a quelated fenol upon treatment with acid.

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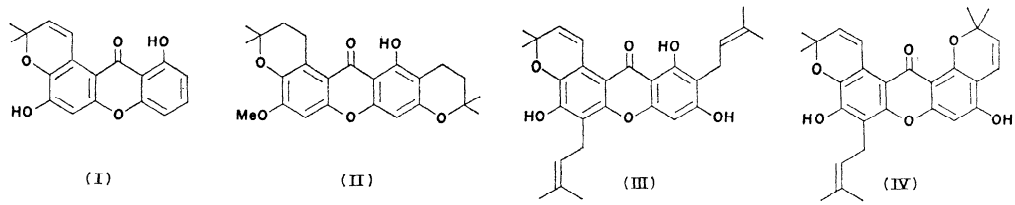
[1] S. J. GABRIEL and O. R. GOTTLIEB, *Phytochem.* **11**, 3034 (1972).
[2] P. YATES and G. H. STOUT, *J. Am. Chem. Soc.* **80**, 1691 (1958).

In tovophyllin-*A* this quelated fenol pre-exists, as shown by a low field one-proton singlet (τ — 3·67) and a positive Gibbs test indicative of a 1-hydroxyxanthone with a free 4-position. The PMR singlet due to this lone aromatic proton appears at τ 3·57, precisely the chemical shift value to be expected for a H-4 on a 1,3-di-oxygenated xanthone ring.[3] The two C-prenyl groups whose signals are unmistakable additional features of the PMR spectrum can, thus, only be located at C-2 and C-5, a final consideration which defines structure III for tovophyllin-*A*.

Tovophyllin-*B* also sustains a sole aromatic proton. This gives a signal at even higher field (τ 3·74, *s*) and can thus only be placed at the 2 or the 4 position of a 1,3-di-oxygenated xanthone ring.[3] The PMR spectrum is void of signals below τ 2·5, a fact which confirms the involvement of the oxygen at C-1 in an additional 6,6-dimethylpyrano group (*AB* system τ 3·37 and 4·37, *J* 10·0 Hz; 6 proton singlet τ 8·57). This leaves only position 4 for the lone aromatic hydrogen and position 5 for the C-prenyl group whose signals are discerned additionally in the PMR spectrum. The structural proposal IV thus emerges for tovophyllin-*B*.



(I) (II) (III) (IV)

EXPERIMENTAL

For experimental techniques see Ref. 4.

Isolation of the constituents of Tovomita macrophylla. Trunk wood, collected at Paraná Xiborena, Amazonas State, was reduced to saw dust (1·6 kg) and extracted with benzene. The extract (15 g) was chromatographed on silica, giving the following fractions with the indicated eluants: A_1 and A_2 (benzene), A_3 (benzene–$CHCl_3$, 10:1), A_4 (benzene–$CHCl_3$, 1:2–1:10), A_5 ($CHCl_3$ and $CHCl_3$–MeOH, 9:1). A_1–A_4 were recrystallized from EtOH giving respectively tovophyllin-*B* (27 mg), tovophyllin-*A* (12 mg), β-amyrin (65 mg) and sitosterol (50 mg). A_5 was washed with MeOH giving betulinic acid (1·5 g).

Tovophyllin-A (II). Yellow needles, m.p. 218–220° (EtOH). (Found: C, 72·82; H, 6·59, $C_{28}H_{30}O_6$ requires: C, 72·71; H, 6·54%.) λ_{max}^{EtOH} (nm): 246, 265, 337, 395 (ϵ 34 400, 33 200, 27 700, 10 200); no shift upon addition of H_3BO_3 + NaOAc or $AlCl_3$; $\lambda_{max}^{EtOH+NaOH}$ (nm): 248, 272 inf, 403 (ϵ 35 100, 23 100, 29 100); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 246, 265, 337, 395 (ϵ 29 100, 32 300, 18 900, 22 000). Gibbs test:[5] λ_{max} 450, 600 (*A* 0·33, 0·43). ν_{max}^{KBr} (cm^{-1}): 3300, 3425 (broad), 1653, 1615, 1595, 1500, 1440, 1410, 1330, 850, 810. PMR [$(CD_3)_2CO$,τ]: −3·67 (*s*, OH..O=C), 2·00 (*d*, *J* 10·0 Hz, H-4′), 3·57 (*s*, H-4), 4·20 (*d*, *J* 10·0 Hz, H-5′), 4·76 (secondarily split *t*, *J* 7·5 Hz, two prenyl =CH); 6·70 (*d*, *J* 7·5 Hz, two prenyl CH_2), 8·23 (*s*, two prenyl CH_3), 8·38 (*s*, two prenyl CH_3), 8·57 (*s*, two pyrano CH_3). MS: M + 2 464 (5%), M + 1 463 (26%), M 462 (63%), *m/e* (%) 448 (37), 447 (100), 445 (27), 419 (22), 408 (4), 407 (55), 391 (27), 335 (18), 281 (18), 207 (30), 188 (15), 187 (15), 186 (15), 168 (37), 167 (11), 165 (14), 149 (18), 147 (18), 141 (16), 135 (18), 129 (18), 128 (28), 127 (18), 123 (18), 121 (17), 119 (13), 115 (21), 111 (25), 109 (22), 107 (17), 100 (50).

Tovophyllin-B (III). Yellow needles, m.p. 190–191° (EtOH). (Found: C, 73·10, H, 6·15. $C_{28}H_{28}O_6$ requires: C, 73·02; H, 6·13%.) λ_{max}^{EtOH} (nm): 253, 290, 303, 338, 395 (ϵ 19 800, 33 100, 30 400, 19 800, 13 800); no shift upon addition of H_3BO_3 + NaOAc or $AlCl_3$; $\lambda_{max}^{EtOH+NaOH}$ (nm): 283, 306 inf, 335, 400 (ϵ 31 300, 16 600, 16 100, 23 000); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 283, 298, 335, 395 (ϵ 33 100, 30 400, 17 000, 18 400). Gibbs

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[5] A. A. LINS MESQUITA, D. DE BARROS CORRÊA, O. R. GOTTLIEB and M. TAVEIRA MAGALHÃES, *Anal. Chim. Acta* **42**, 311 (1968).

test: negative. ν_{max}^{KBr} (cm^{-1}): 3380, 1653, 1610, 1590, 1500, 1410, 1470, 1440, 1310, 1200, 880. PMR [$(CD_3)_2CO$,τ]: 2·07 (*d*, *J* 10 Hz, H-4′), 3·37 (*d*, *J* 10 Hz, H-4″), 3·74 (*s*, H-4), 4·18 (*d*, *J* 10 Hz, H-5′), 4·37 (*d*, *J* 10 Hz, H-5″), 4·73 (broad *t*, *J* ~ 7 Hz, prenyl =CH), 6·43 (*d*, *J* 7·5 Hz, prenyl CH_2), 8·14 (*s*, prenyl CH_3), 8·33 (*s*, prenyl CH_3), 8·57 (*s*, four pyrano CH_3). MS: M + 2 462 (4%), M+1 461 (7%), M 460 (43%), *m/e* (%) 447 (7), 446 (32), 445 (100), 443 (8), 404 (5), 390 (5), 389 (18), 387 (5), 375 (5), 373 (5), 371 (6), 347 (5), 215 (14), 214 (5), 203 (5), 193 (5), 188 (10), 187 (36).

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