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XANTHONES FROM *TOVOMITA PYRIFOLIUM**

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Key Word Index—*Tovomita pyrifolium*; Guttiferae; tovophyllin-*A*; tovophyllin-*B*; tovopyrifolin-*A*, tovopyrifolin-*B*; tovopyrifolin-*C*; 1,3,6-trihydroxy-2,5-diprenyl-6′,6′-dimethylpyrano(2′,3′:7,8)xanthone; 1,6-dihydroxy-5-prenyl-6′,6′-dimethylpyrano(2′,3′:3,2)-6″,6″-dimethylpyrano(2″,3″:7,8)xanthone; 1,6-dihydroxy-7-methoxy-5-prenyl-6′,6′-dimethylpyrano(2′,3′:3,2)xanthone; 1,5-dihydroxy-3,4-dimethoxyxanthone; 1,3,5-trihydroxy-2-methoxyxanthone.

Abstract—The wood of *Tovomita pyrifolium* (Guttiferae) contains the novel tovopyrifolins *A* [1,6-dihydroxy-7-methoxy-5-prenyl-6′,6′-dimethylpyrano(2′,3′:3,2)xanthone], *B* (1,5-dihydroxy-3,4-dimethoxyxanthone) and *C* (1,3,5-trihydroxy-2-methoxyxanthone) and also the known tovophyllins *A* and *B* [structure revised to 1,6-dihydroxy-5-prenyl-6′,6′-dimethylpyrano(2′,3′:3,2)-6″,6″-dimethylpyrano(2″,3″:7,8)xanthone].

The wood of *Tovomita macrophylla* (Pl. et Tr.) Walp. (Guttiferae) contains besides tovophyllin-*A* (**1a**) a small quantity of tovophyllin-*B* for which structure **2** was proposed [1]. Both compounds also occur in *T. pyrifolium* Pl. et Tr. besides three additional xanthones, tovopyrifolins *A*, *B* and *C*. Re-examination of the PMR spectrum of tovophyllin-*B* revealed the existence of a chelated hydroxyl (τ – 3·70). The structure had thus to be revised to **3a**, a proposal which is consistent with the formation of a monomethyl ether (**3b**) upon treatment with CH_2N_2 which continues to sustain the chelated OH (τ – 3·68). The *ortho*-position (C-2) relative to this OH must be substituted, since the UV spectrum of the compound is not affected upon addition of $AlCl_3$ [1]. The *para*-position, however, is indeed free of substitution, as shown by a positive Gibbs test [2] (λ_{max} 685 nm) and the fact that acetylation of both, tovophyllin-*B* (**3a** → **3c**) and its monomethyl ether (**3b** → **3d**), produced practically identical paramagnetic shifts (resp. 0·37 and 0·39 ppm) of the signals corresponding to the lone aromatic protons. If the prenyl group were sustained by C-4, a stronger shift would be expected for the diacetate than for the monoacetate. This question settled, no doubt exists with respect to the location of the ring-*B* substituents, due to the occurrence of a NaOAc UV-shift which requires a hydroxyl at C-6, and of the low field PMR AB doublets (τ 2·00 and 4·26, *J* 10 Hz), which distinguish dimethylpyrano(2′,3′:7,8) groups from identical substituents at other positions (τ 3·2 and 4·5, *J* 10 Hz) [1, 3].

An attempt to reconfirm the proposed positions for the aromatic H and the prenyl group by pyridine solvent shift was apparently successful. The observed shifts (Table 1) are in good agreement

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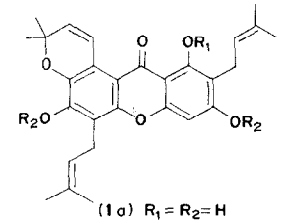
Table 1. Pyridine-induced solvent shifts for proton resonances of xanthones

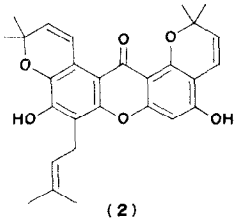
	H-4			CH_2-5			CH_2-2		
	τ $C_5D_5N_5$	τ $CDCl_3$	Δ (ppm)	τ $C_5D_5N_5$	τ $CDCl_3$	Δ (ppm)	τ $C_5D_5N_5$	τ $CDCl_3$	Δ (ppm)
1b	3·40	3·68	−0·28	6·41	6·40	+0·01	6·30	6·62	−0·32
3b	3·53	3·69	−0·16	6·39	6·43	−0·04	...	...	...
4b	3·48	3·63	−0·15	6·36	6·39	−0·03	...	...	...

with the values tabulated for unsubstituted and methyl-substituted phenols [4]. Shift values determined for simple phenols are, however, not fully applicable to the case of chelated representatives, Δ for *ortho*-protons being so abnormally low as to overlap the *para*-proton region (cf. **5**b, Experimental). The data of Table 1 are thus more significant if used comparatively as evidence that tovophyllin-*A* (**1**a), tovophyllin-*B* (**3**a) and tovopyrifolin-*A* (**4**a) have one prenyl group at equivalent positions. The sensitivity of the methylene resonance to the location of the prenyl group on the xanthone skeleton, again demonstrated in the case of tovophyllin-*A* (**1**a) (Table 1) is known [5]. Furthermore, still with reference to the data of Table 1, rings *A* of tovophyllin-*B* (**3**a) and tovopyrifolin-*A* (**4**a) should be identically substituted. Indeed, as expected consequently, also in the case of **4**a no UV $AlCl_3$-shift occurs, inspite of the existence of a 1-OH group indicated by the formation, by treatment with CH_2N_2, of a monomethyl ether which retains a chelated hydroxyl (τ − 3·33). The PMR shifts of the ring-*A* proton signals produced by acetylation of **3**a and **4**a are virtually identical (resp. 0·37 and 0·38 ppm). The structural analysis is concluded by placing the additional and acidic OH at C-6 (NaOAc UV-shift) and the additional aromatic proton at C-8. Its characteristic PMR singlet (τ 2·46) reveals *ortho*- and *meta*-dioxygenation [6], thus requiring the presence of the methoxyl at C-7.

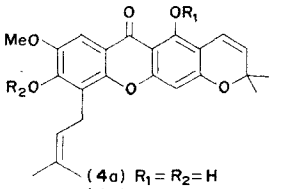
Treatment of the tovopyrifolins *B* (**5**a) and *C* (**6**a) with CH_2N_2 led to methyl ethers (resp. **5**b and **6**b) which preserved a chelated hydroxyl (τ − 2·7). Their PMR spectra defined the oxygenation patterns. These are identical for rings *B* (H-8: 2·15, *dd*, *J* 5·5, 4·0 Hz) but differ for rings *A*. The singlet at higher field (τ 3·57) represents H-2 (**5**b) and the singlet at lower field (τ 3·37) represents H-4 (**6**b) on trioxygenated xanthone rings [6]. The methyl ethers **5**b and **6**b as well as their fully etherified products **5**c and **6**c have already been described [7,8], and all their published data are identical with the corresponding data observed for the tovopyrifolin *B* and *C* derivatives. Thus only the relative location of one OH/two OMe in **5**a and two OH/one OMe in **6**a remain to be justified. This is achieved by measurement of the shifts produced by acetylation upon the H-2 (Δ − 0·24 ppm) and H-8 (Δ − 0·26 ppm) PMR signals of tovopyrifolin-*B* and the H-4 (Δ − 0·54 ppm) and H-8 (Δ − 0·25 ppm) PMR signals of tovopyrifolin-*C*. Clearly, while H-2 and 8 of **5**d as well as H-8 of **6**d are subject to the paramagnetic influence of only one acetoxyl at a conjugated position, H-4 of **6**d is under the influence of two such substituents. Indeed, C-4 of **5**a and C-2 of **6**a cannot be occupied by hydroxyls, since both compounds are stable in alkaline solution.



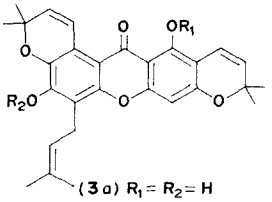
(1a) $R_1 = R_2 = H$
(1b) $R_1 = H$, $R_2 = Me$
(1c) $R_1 = R_2 = Ac$



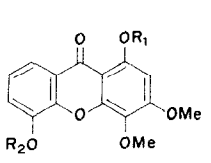
(2)



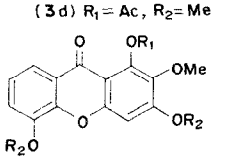
(4a) $R_1 = R_2 = H$
(4b) $R_1 = H$, $R_2 = Me$
(4c) $R_1 = R_2 = Ac$



(3a) $R_1 = R_2 = H$
(3b) $R_1 = H$, $R_2 = Me$
(3c) $R_1 = R_2 = Ac$
(3d) $R_1 = Ac$, $R_2 = Me$



(5a) $R_1 = R_2 = H$
(5b) $R_1 = H$, $R_2 = Me$
(5c) $R_1 = R_2 = Me$
(5d) $R_1 = R_2 = Ac$



(6a) $R_1 = R_2 = H$
(6b) $R_1 = H$, $R_2 = Me$
(6c) $R_1 = R_2 = Me$
(6d) $R_1 = R_2 = Ac$

EXPERIMENTAL

Isolation of the constituents. Trunk wood of a specimen, collected at Ducke Forest Reserve, Amazonas State, and identified by the botanist W. Rodrigues, INPA, Manaus, was reduced to saw dust (12 kg) and extracted with C_6H_6. The soln was evaporated and the residue (150 g) chromatographed on a Si column. The following fractions were eluted in order with the indicated solvents: A_1 and A_2 (C_6H_6), A_3 (C_6H_6–$CHCl_3$ 5:1), A_4 (C_6H_6–$CHCl_3$ 1:1), A_5 and A_6 ($CHCl_3$–MeOH 98:2). A_1 and A_2 were recrystallized from EtOH giving respectively **3**a (420 mg) and **1**a (1·5 g). A_3 was rechromatographed several times on SiO_2 to separate the less polar **4**a (30 mg) from aliphatic material (620 mg) and sitosterol (500 mg). A_4 was washed with Et_2O giving **5**a (135 mg). A_5 gave betulinic acid (12·8 g). A_6 was washed with Et_2O giving **6**a (41 mg).

Tovophyllin-A *derivatives.* 3,6-di-*O*-Methyl ether (**1**b) (**1**a, CH_2N_2, Et_2O), yellow crystals, mp 154–156° (EtOH). (Found: C, 73·51; H, 6·80. $C_{30}H_{34}O_6$ requires: C, 73·45; H, 6·99%.) λ_{max}^{EtOH} (nm): 248, 271, 330 (ε 43600, 53900, 35300); no $AlCl_3$ and NaOAc shifts; $\lambda_{max}^{EtOH+NaOAc}$ 253, 272, 325 (ε 40200, 43100, 24000). PMR ($CDCl_3$, τ): −3·33 (*s*, OH), 1·95 (*d*, *J* 10 Hz, H-4′), 3·68 (*s*, H-4), 4·25 (*d*, *J* 10 Hz, H-5′), 4·78 (*t*, *J ca* 7·5 Hz, 2 =CH), 6·02 (*s*, OMe), 6·05 (*s*, OMe), 6·40 (*d*, *J* 7·5 Hz, CH_2-5), 6·62 (*d*, *J* 7·5 Hz, CH_2-2), 8·10 (*s*, Me), 8·20 (*s*, Me), 8·30 (*s*, 2 Me), 8·50 (*s*, 2 Me-6′). PMR (C_5D_5N, τ): −3·30 (*s*, OH), 1·83 (*d*, *J* 10 Hz, H-4′), 3·40 (*s*, H-4), 4·20 (*d*, *J* 10 Hz, H-5′), 4·45 (*t*, *J ca* 7·5 Hz, 2 =CH), 6·00 (*s*, OMe), 6·18 (*s*, OMe), 6·30 (*d*, *J* 7·5 Hz, CH_2-2), 6·41 (*d*, *J* 7·5 Hz, CH_2-5), 8·14 (*s*, 2 CH_3), 8·32 (*s*, 2 Me), 8·55 (*s*, 2 Me-6′). A $CHCl_3$ soln was treated with a trace of $F_3C.CO_2H$, left overnight and evaporated. PMR of the residue ($CDCl_3$, τ): no low field signal, 1·95 (*d*, *J* 10 Hz, H-4′), 3·59 (*s*, H-4), 4·20 (*d*, *J* 10 Hz, H-5′), 4·73 (*t*, =CH), 6·00 (*s*, OMe), 6·06 (*s*, OMe), 6·40 (*d*, *J* 7·5 Hz, CH_2-5), 7·33 (*t*, *J* 7·5 Hz, $ArCH_2$), 8·10 (*s*, Me), *ca* 8·15 (overlapped $ArCH_2C\underline{H}_2$), 8·30 (*s*, Me), 8·53 (*s*, 2 Me), 8·56 (*s*, 2 Me). 1,3,6-tri-*O*-Acetyl ester (**1**c), slightly yellow crystals, mp 195–197° (EtOH). PMR ($CDCl_3$, τ): 2·11 (*d*, *J* 10 Hz, H-4′), 2·81 (*s*, H-4), 4·23 (*d*, *J* 10 Hz, H-5′), 4·93 (*t*, *J ca* 7·5 Hz, 2 =CH), 6·46 (*d*, *J* 7·5 Hz, CH_2-5), 6·73 (*d*, *J* 7·5 Hz, CH_2-2), 7·53 (*s*, COMe), 7·66 (*s*, 2 COMe), 8·17 (*s*, Me), 8·27 (*s*, Me), 8·33 (*s*, 2 Me), 8·60 (*s*, 2 Me-6′). Hexahydrotovophyllin-*A* (**1**a, H_2, Pd/C, EtOH), purified by column chromatography (Si gel, C_6H_6-petrol 3:7) and washing with petrol, pale yellow crystals, mp 190–193°. λ_{max}^{EtOH} (nm): 245, 263, 278 inf., 325, 370 infl. (ε 26800, 28600, 8700, 21700, 6900; no $AlCl_3$ and H_3BO_3 + NaOAc shifts; $\lambda_{max}^{EtOH+NaOAc}$ (nm): 245, 263, 278, 325, 370 (ε 25400, 28700, 8700, 20800, 6900). $\lambda_{max}^{EtOH+NaOH}$ (nm): 270, 308 (ε 19400, 8700). PMR ($CDCl_3$, τ): 3·57 (*s*, H-4), 6·56 (*t*, *J* 7 Hz, 2 H-4′), 7·0–7·6 (*m*, CH_2-2, CH_2-5), 8·13 (*t*, *J* 10 Hz, 2 H-5′), 8·4–8·7 (*m*, 2-CH), 8·64 (*s*, 2 Me-6′), 9·01 (*d J* 6 Hz, 4 Me).

Tovophyllin-B *derivatives.* 6-*O*-Methyl ether (**3**b) (**3**a, CH_2N_2, Et_2O), yellow crystals, mp 182–184° (EtOH). Found: C, 73·21; H, 6·41. $C_{29}H_{30}O_6$ requires: C, 73·40; H, 6·37%). λ_{max}^{EtOH} (nm): 250 inf., 292, 392 inf., 335 (ε 11900, 27000, 24600, 12800); no $AlCl_3$ and NaOAc shifts; $\lambda_{max}^{EtOH+NaOH}$ (nm): 235, 262 inf., 315 (ε 23700, 21800, 24700). PMR ($CDCl_3$, τ): −3·68 (*s*, OH), 1·97 (*d*, *J* 10 Hz, H-4′), 3·24 (*d*, *J* 10 Hz, H-4″), 3·69 (*s*, H-4), 4·24 (*d*, *J* 10 Hz, H-5′), 4·41 (*d*, *J* 10 Hz, H-5″), 4·78 (*t*, *J ca* 7·5, =CH), 6·10 (*s*, OMe), 6·43 (*d*, *J* 7·5 Hz, CH_2), 8·11 (*s*, Me), 8·31 (*s*, Me), 8·46 (*s*, 2 Me), 8·49 (*s*, 2 Me). PMR (C_5D_5N, τ): 1·87 (*d*, *J* 10 Hz, H-4′), 3·10 (*d*, *J* 10 Hz, H-4″), 3·53 (*s*, H-4), 4·19 (*d*, *J* 10 Hz, H-5′), 4·42 (*d*, *J* 10 Hz, H-5″), 4·70 (*t*, *J ca* 7·5 Hz, =CH), 6·02 (*s*, OMe), 6·39 (*d*, *J* 7·5 Hz, CH_2), 8·15 (*s*, Me), 8·35 (*s*, Me), 8·59 (*s*, 4 Me). 1,6-di-*O*-Acetyl ester (**3**c), slightly yellow crystals, mp 204–206° (EtOH). PMR ($CDCl_3$, τ): 2·04 (*d*, *J* 10 Hz, H-4′), 3·30 (*s*, H-4), 3·48 (*d*, *J* 10 Hz, H-4″), 4·25 (*d*, *J* 10 Hz, H-5′), 4·27 (*d*, *J* 10 Hz, H-5″), 4·82 (*t*, *J ca* 7·5 Hz, =CH), 6·50 (*d*, *J* 7·5 Hz, CH_2), 7·50 (*s*, COMe), 7·63 (*s*, COMe), 8·15 (*s*, Me), 8·37 (*s*, Me), 8·52 (*s*, 2 Me), 8·60 (*s*, 2 Me). 1-*O*-Acetyl-6-*O*-methyltovophyllin-*B* (**3**d) (**3**b, Ac_2O, C_6H_5N), slightly yellow crystals, mp 172–174° (MeOH). PMR ($CDCl_3$, τ): 2·09 (*d*, *J* 10 Hz, H-4′), 3·30 (*s*, H-4), 3·49 (*d*, *J* 10 Hz, H-4″), 4·24 (*d*, *J* 10 Hz, H-5′), 4·26 (*d*, *J* 10 Hz, H-5″), 4·76 (*t*, *J ca* 7·5 Hz, =CH), 6·07 (*s*, OMe), 6·45 (*d*, *J* 7·5 Hz, CH_2), 7·52 (*s*, COMe), 8·12 (*s*, Me), 8·32 (*s*, Me), 8·52 (*s*, 4 Me). Hexahydrotovophyllin-*B* (**3**a, H_2, Pd/C, EtOH), purified by column chromatography (Si gel, C_6H_6–petrol 1:9) and washing with C_6H_6, mp > 330°. λ_{max}^{EtOH} (nm): 245 inf., 263, 278 inf., 325, 370 inf. (ε 26800, 39500, 3200, 29800, 4100); no $AlCl_3$ and H_3BO_3 + NaOAc shifts; $\lambda_{max}^{EtOH+NaOAc}$ (nm): 245 inf., 263, 278 inf., 325, 370 inf. (ε 31200, 44100, 7800, 31800, 5300); $\lambda_{max}^{EtOH+NaOH}$ (nm): 266, 390 (ε 21200, 39500). PMR ($CDCl_3$, τ): −3·75 (*s*, OH), 3·68 (*s*, H-4), 6·63 (*t*, *J ca* 7·5 Hz, 2 H-4′), 7·13 (*t*, *J* 7·5 Hz, CH_2-5), 7·26 (*t*, 7·5 Hz, 2 H-4″), 8·13 (*t*, *J* 10 Hz, 2 H-5′), 8·16 (*t*, *J* 10 Hz, 2 H-5″), 8·4–8·75 (*m*, CH_2CH), 8·63 (*s*, 4 Me), 8·97 (*d*, *J* 6 Hz, 2 Me).

Tovopyrifolin-A (**4**a), yellow crystals, mp 248–251° (washings with MeOH). (Found: C, 70·90; H, 5·90. $C_{24}H_{24}O_6$ requires: C, 70·58; H, 5·92%.) λ_{max}^{EtOH} (nm): 279 inf., 292, 340 (ε 36700, 46900, 28200); no $AlCl_3$ and H_3BO_3 + NaOAc shifts; $\lambda_{max}^{EtOH+NaOAc}$ (nm): 280, 337 inf., 386 (ε 41200, 18400, 31400); $\lambda_{max}^{EtOH+NaOH}$ (nm): 324 (ε 29400). Gibbs test [2]. λ_{max} 700 nm. ν_{max}^{KBr} (cm^{-1}): 3250 (broad), 1653, 1603, 1595, 1575, 1470, 1440, 1410, 1170, 1150, 940, 838, 765, 700. MS (*m/e*): 410 (3) M^+ + 2, 409 (15) M^+ + 1, 408 (48) M^+, 407 (6), 395 (7), 394 (32), 393 (100), 392 (10), 338 (6), 337 (16), 335 (7), 294 (5), 205 (5), 195 (5), 188 (5), 169 (5). 6-*O*-Methyl ether (**4**b) (**4**a, CH_2N_2, Et_2O), yellowish crystals, mp 170–174°. PMR ($CDCl_3$, τ): −3·33 (*s*, OH), 2·46 (*s*, H-8), 3·24 (*d*, *J* 10 Hz, H-4′), 3·63 (*s*, H-4), 4·40 (*d*, *J* 10 Hz, H-5′), 4·80 (*t*, *J ca* 7·5 Hz, =CH), 6·01 (*s*, 2 OMe), 6·39 (*d*, *J* 7·5 Hz, CH_2-5), 8·11 (*s*, Me), 8·31 (*s*, Me), 8·51 (*s*, 2 Me). PMR (C_5D_5N, τ): 2·44 (*s*, H-8), 3·10 (*d*, *J* 10 Hz, H-4′), 3·48 (*s*, H-4), 4·39 (*d*, *J* 10 Hz, H-5′), 4·79 (*t*, *J ca* 7·5 Hz, =CH), 6·08 (*s*, 2 OMe), 6·36 (*d*, *J* 7·5 Hz, CH_2-5), 8·16 (*s*, Me), 8·36 (*s*, Me), 8·50 (*s*, 2 Me). 1,6-di-*O*-Acetyl ester (**4**c), colourless crystals, mp 195–197° (EtOH). PMR ($CDCl_3$, τ): 2·42 (*s*, H-8), 3·25 (*s*, H-4), 3·46 (*d*, *J* 10 Hz, H-4′), 4·24 (*d*, *J* 10 Hz, H-5′), 4·80 (*t*, *J ca* 7·5 Hz, =CH), 6·07 (*s*, OMe), 6·44 (*d*, *J* 7·5 Hz, CH_2-5), 7·44 (*s*, COMe), 7·60 (*s*, COMe), 8·09 (*s*, Me), 8·26 (*s*, Me), 8·54 (*s*, 2 Me). MS (*m/e*): 493 (5) M^+ + 1, 492 (15) M^+, 452 (7), 451 (24), 450 (75), 437 (8), 436 (30), 435 (100), 423 (8), 422 (7), 406 (5), 405 (20), 404 (17), 395 (5), 394 (20), 393 (75), 391 (9), 377 (7), 375 (7), 365 (7), 363 (7), 352 (5), 350 (10), 338 (5), 337 (23), 335 (10), 324 (10), 307 (5), 294 (6), 225 (5), 204 (5), 203 (8), 149 (10).

Tovopyrifolin-B (**5**a), yellow crystals, subl. 250–255°, mp 271–274° (closed capillary) (washings with Et_2O). (Found: C, 62·62; H, 4·32. $C_{15}H_{12}O_6$ requires: C, 62·50; H, 4·20%) λ_{max}^{EtOH} (nm): 247 inf., 257, 322, 372 (ε 20200, 23000, 18100, 9200); no H_3BO_3 + NaOAc shift $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 250 inf., 273, 330 (ε 15000, 19600, 15800); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 260, 286, 323 (ε 21000, 11800, 14100; $\lambda_{max}^{EtOH+NaOH}$ (nm); 350 (ε 9500). ν_{max}^{KBr} (cm^{-1}): 3200 (broad), 1650, 1610, 1592, 1550, 1490, 1455, 1125, 1025, 922, 750. MS (*m/e*): 289 (10) M^+ + 1, 288 (54) M^+, 274 (20), 273 (100), 245 (11), 243 (6), 137 (5), 136 (11), 121 (5), 120 (11). 5-*O*-Methyl ether (**5**b) (**5**a, CH_2N_2, Et_2O), mp, UV and PMR (in CH_2Cl_2) as required by Ref. 7 PMR ($CDCl_3$, τ): 2·16 (*dd*, *J* 6 and 4 Hz, H-8), 2·6–2·9 (*m*, H-6,7), 3·57 (*s*, H-2), 5·97 (*s*, OMe), 6·00 (*s*, OMe), 6·03 (*s*, OMe). PMR (C_5D_5N, τ): −2·93 (*s*, OH), 2·23 (*dd*, *J* 5 and 4 Hz, H-8), 2·8–3·0 (*m*, H-6, 7), 3·40 (*s*, H-2), 6·02 (*s*, OMe), 6·19 (*s*, OMe), 6·22 (*s*, OMe). MS (*m/e*): 303 (8) M^+ + 1, 302 (57) M^+, 288 (15), 287 (100), 272 (6), 259 (13), 244 (9), 216 (7), 160 (12), 151 (5), 107 (10). 1,5-di-*O*-Methyl ether (**5**c) (**5**a, Me_2SO_4, K_2CO_3, Me_2CO, reflux 12 hr), mp, UV and PMR (in

CH_2Cl_2) as required by Ref. [7] 1,5-di-*O*-Acetyl ester (**5d**), colourless crystals, mp 184–185° (EtOH). PMR ($CDCl_3$, τ): 1·90 (*dd*, *J* 7 and 3 Hz, H-8), 2·52 (*dd*, *J* 7 and 3 Hz, H-6), 2·70 (*t*, *J* 7 Hz, H-7), 3·33 (*s*, H-2), 6·00 (*s*, OMe), 6·03 (*s*, OMe), 7·50 (*s*, 2 COMe). MS (*m/e*): 373 (6) $M^+ + 1$, 372 (18) M^+, 333 (6), 331 (33), 330 (100), 329 (10), 316 (7), 315 (29), 299 (13), 298 (65), 297 (12), 284 (18), 283 (85), 282 (17), 245 (6), 244 (5).

Tovopyrifolin-C (**6a**), yellow crystals, mp 256–258° (washings with Et_2O). (Found: C, 61·19; H, 3·59. $C_{14}H_{10}O_6$ requires: C, 61·32; H, 3·68%.) λ_{max}^{EtOH} (nm): 206, 220, 243, 263 inf., 273 inf., 315, 360 (ϵ 27 200, 26 300, 40 300, 19 800, 16 500, 14 800, 13 500); no H_3BO_3 + NaOAc shift; $\lambda_{max}^{EtOH + NaOAc}$ (nm): 242, 264 inf., 275 inf., 360 (ϵ 39 500, 20 300, 16 200, 22 500); $\lambda_{max}^{EtOH + NaOH}$ (nm): 237, 257, 293, 353 (ϵ 32 900, 40 000, 21 100, 28 300); $\lambda_{max}^{EtOH + AlCl_3}$ (nm): 209 222, 244, 265, 280, 339, 425 (ϵ 26 600, 28 000, 27 400, 30 500, 24 200, 23 900, 3900). Gibb test [2] λ_{max} 730 nm. ν_{max}^{KBr} (cm^{-1}): 3450, 1655, 1615, 1585, 1505, 1470, 1485, 1395, 1300, 1270, 1220, 1160, 1100, 900, 780. MS (*m/e*): 275 (18) $M^+ + 1$, 274 (100) M^+, 273 (5), 260 (15), 259 (93), 258 (6), 257 (6), 256 (25), 255 (6), 245 (7), 232 (18), 231 (100), 230 (6), 228 (15), 203 (4), 202 (8), 147 (6), 139 (5), 137 (16), 136 (14), 122 (5), 108 (7), 107 (6), 101 (6). 3,5-di-*O*-Methyl ether (**6b**) (**6a**, CH_2N_2, Et_2O), mp, UV and PMR (in CH_2Cl_2) as required by Ref. 8 PMR ($CDCl_3$, τ): −2·73 (*s*, OH), 2·15 (*dd*, *J* 6 and 3 Hz, H-8), 2·71 (*m*, H-6, 7), 3·37 (*s*, H-4), 5·97 (*s*, OMe), 6·03 (*s*, OMe), 6·07 (*s*, OMe). 1,3,5-tri-*O*-Methyl ether (**6c**) (**6a**, Me_2SO_4, K_2CO_3, Me_2CO, reflux 12 hr), mp UV and PMR (in CH_2Cl_2) as required by Ref. [8] 3,5-di-*O*-Acetyl ester (**6d**), colourless crystals, mp 155–157°. PMR ($CDCl_3$, τ): 1·90 (*dd*, *J* 6·8 and 3 Hz, H-8), 2·53–2·90 (*m*, H-6, 7), 2·83 (*s*, H-4), 6·16 (*s*, OMe), 7·50 (*s*, COMe), 7·59 (*s*, COMe), 7·63 (*s*, COMe).

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