A Revised Structure for Toxyloxanthone B

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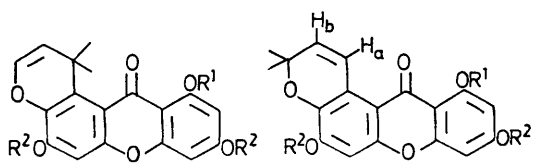
Summary A re-examination of the n.m.r. data for toxyloxanthone B trimethyl ether, and subsequent synthetic work, both show that toxyloxanthone B has the 2,2-dimethylpyranoxanthone structure (**2a**) and not the 4,4-dimethylpyranoxanthone system (**1a**) that was pre-previously assigned.

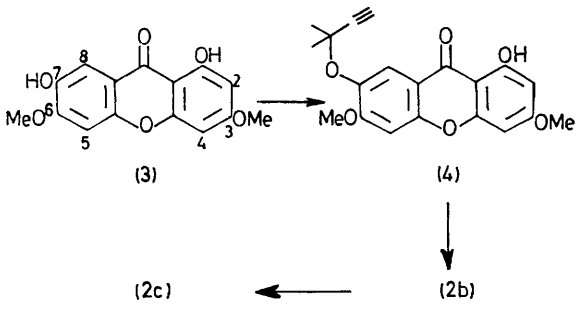
RECENTLY Deshpande *et al.*[1] isolated four new xanthones from the stem bark of *Toxylon pomiferum* Rafin (*Maclura pomifera* Schneid; *M. aurantiaca* Nutt; Osage orange) and



(1) (2)

(a) $R^1 = R^2 = H$
(b) $R^1 = H$, $R^2 = Me$
(c) $R^1 = R^2 = Me$

assigned the novel 4,4-dimethylchromene ring system (**1a**) to toxyloxanthone B. The biogenetically more likely 2,2-dimethylchromene structure (**2a**) was ruled out on the basis of the low chemical shift (τ 1·87) attributed to one of the vinyl protons in the chromene system of toxyloxanthone B trimethyl ether. The vinyl ether chromene system (**1c**) was therefore assigned on the basis of the n.m.r. data.



(3) (4) (2c) (2b)

SCHEME

In reconsidering this problem we now conclude that the structure of toxyloxanthone B should be revised to that of the 2,2-dimethylchromene isomer (**2a**). Thus examination of the chemical shifts of the olefinic protons in simple aryl vinyl ethers[2] show that they resonate at much higher field (τ 3·7—5·5).[2] The low chemical shift of the olefinic proton H_a at τ 1·87 is accounted for largely by the deshielding anisotropic influence of the xanthone carbonyl group which also deshields *e.g.* a proton[3] and a methylene group attached to position C-8 of the xanthone nucleus.[4] Furthermore, comparison with synthetic[5] and natural[6] pyrano[2′,3′:7,8]-

xanthones of the same oxygenation pattern, confirms that the low field olefinic proton (τ *ca.* 2·0) is deshielded by $>$ 1·0 p.p.m., compared to similar protons of pyranoxanthones with the pyran ring in other orientations.[7]†

The structure (**2a**) for toxyloxanthone B has now been confirmed by synthesis of its di- and tri-methyl ether derivatives (**2b** and **2c**) and by direct comparison with authentic specimens. 1,7-Dihydroxy-3,6-dimethoxyxanthone (**3**) slowly forms the prop-2-ynyl ether (**4**) at room temperature on stirring with 3-chloro-3-methylbut-1-yne in the presence of acetone and anhydrous potassium carbonate. The prop-2-ynyl ether undergoes a Claisen rearrangement and cyclisation in boiling methanol to give the 2,2-dimethylchromene (**2b**), m.p. 227—228 °C,‡ identical (mixed m.p., i.r. and n.m.r. spectra) with toxyloxanthone B dimethyl ether. Methylation of the product with dimethylsulphate gave toxyloxanthone B trimethyl ether (**2c**) m.p. 191—192 °C, lit.[1] 192—193 °C (Scheme) identical (mixed m.p., i.r. and n.m.r. spectra) with toxyloxanthone B trimethyl ether.

We thank the S.R.C. for a research studentship (to P.J.C.), and Professor K. Venkataraman for personal communications and authentic samples of toxyloxanthone B di- and trimethyl ethers.

(*Received*, 21*st April* 1975; *Com.* **454**.)

† By examination of this and other spectral data, earlier workers came to similar conclusions (J. K. Kirtany and S. K. Paknikar, *Indian J. Chem.* 1975, **13**, 104).

‡ In ref. 5 (**2b**) was reported to have m.p. 243° C. The n.m.r., u.v., and i.r. spectra of both samples are identical. Despande *et al.* (ref. 1) reported m.p. 210–212 °C but Professor K. Venkataraman has informed us that repeated recrystallisation raised the m.p to 228–229 °C.

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[7] *E.g.* A. J. Quillinan and F. Scheinmann, *J.C.S. Perkin I*, 1972, 1383; and previous papers in the series.