The Structure of Mangostin

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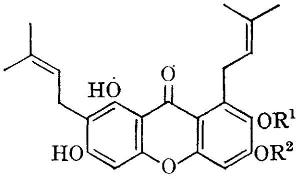
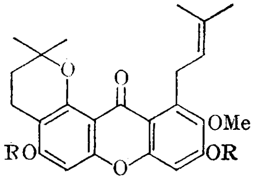
SCHEINMANN[1] has recently suggested on the basis of benzene-induced solvent shifts in n.m.r. spectra that mangostin[2] has the structure (II) rather than the previously suggested structure (I). We present evidence which entirely supports the original formulation.

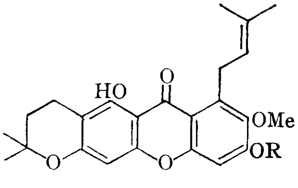
Mangostin on treatment with toluene-*p*-sulphonic acid in refluxing benzene or acetic acid at room temperature gives 1-isomangostin (III), $C_{24}H_{26}O_6$, m.p. 155—156°, identified by its conversion into dimethyl-1-isomangostin (IV), m.p. 129—130°,[3] on methylation with potassium carbonate and dimethyl sulphate in acetone. A non-crystalline product is also formed, which is converted by similar methylation to a compound, $C_{25}H_{26}O_6$, m.p. 139—140°; the infrared and n.m.r. spectra of these compounds establish that they are 3-isomangostin (V) and methyl-3-isomangostin (VI), respectively. No product is obtained in which the side-chain at C-8 has undergone cyclization. Such failure to cyclize is most improbable unless the oxygen atom at C-7 is blocked as the ether.



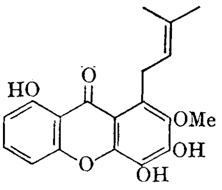
(I) R^1=Me, R^2=H
(II) R^1=H, R^2=Me



(III) R=H
(IV) R=Me



(V) R=H
(VI) R=Me



(VII)

Mass-spectral examination of a number of compounds of known structure containing prenyl and geranyl side-chains[4,5] has shown that if these are adjacent to hydroxy-groups fragmentation occurs with loss of C_4H_8 or C_9H_{16} (56 or 56 + 68 mass units). Adjacent methoxy-groups, however, lead to an additional rearrangement and the loss of C_3H_6 or C_8H_{15} (43 or 43 + 68 mass units). Mangostin shows clearly both modes of decomposition, indicating again that one of the side-chains is next to a methoxy-function.

Additional arguments may be made on the basis of the ultraviolet spectra of mangostin and its derivatives[2,5] which are consistent with a xanthone having a badly hindered 2-OMe group but not with one having a relatively unhindered 3-OMe group.

With regard to the benzene-induced n.m.r. shifts observed by Scheinmann, experiments in our laboratories under similar conditions (10% $CHCl_3$ in C_6H_6, 60 MHz.) have given $\Delta = 0{\cdot}48$ for mangostin, in reasonable agreement with his findings. At the same time, however, celebixanthrone[6] (VII), whose structure is defined unambiguously by *X*-ray crystallographic studies, shows $\Delta = 0{\cdot}43$. Thus it is clear that in this system solvent shifts in benzene do not necessarily serve to detect even very badly hindered methoxy-groups (in the solid, the celebixanthrone OMe is rotated 72° out of the adjacent aromatic plane).†

We thank Dr. Scheinmann for sending us a preprint of his paper.

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