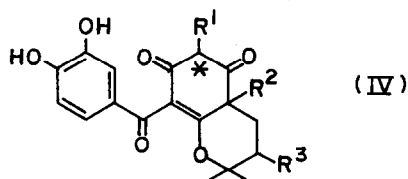
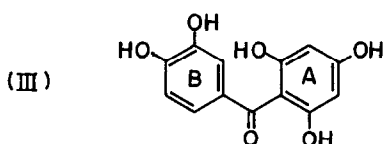
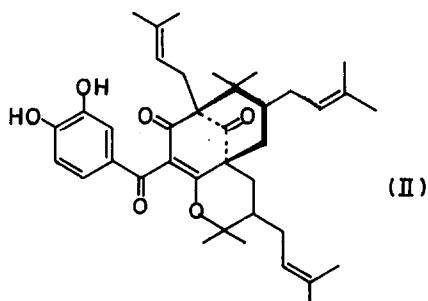
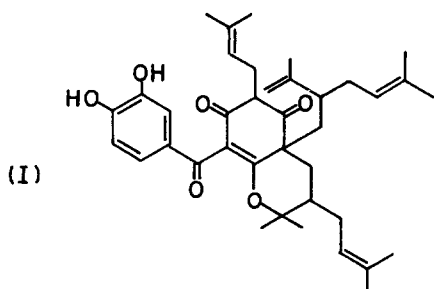


THE CONSTITUTION OF XANTHOCHYMOL AND ISOXANTHOCHYMOL*

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Garcinia species (Guttiferae) have yielded numerous xanthenes,¹ complex xanthone derivatives such as morellin,² and 3,8-linked biflavonoids such as morelloflavone (fukugetin).^{3,4} Our continued interest in the Indian species led us to examine G. pedunculata and G. xanthochymus. The unusually substituted 2,4,6,3',5'-pentahydroxybenzophenone and 1,3,5,7-tetrahydroxy-xanthone were encountered in the heartwood of the former.⁵ From G. xanthochymus fruits we have isolated xanthochymol (I) and isoxanthochymol (II) (very pale yellow needles, m.p. 135° and 222°, both optically active), which are derivatives of maclurin (III) modified in the A ring by the intervention of five prenyl groups.



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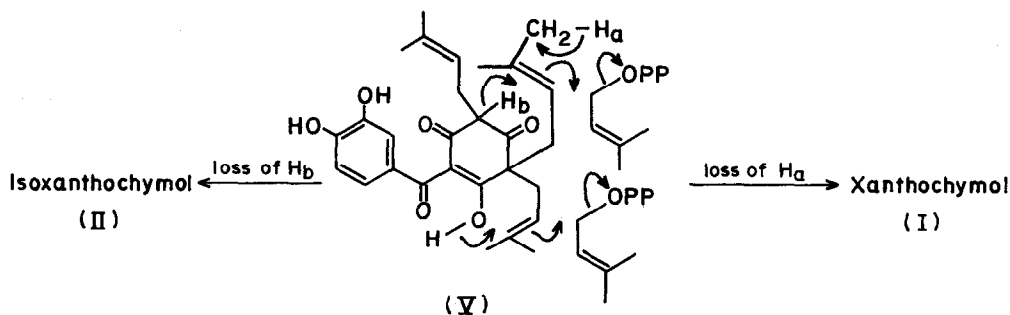
The major pigment, xanthochymol, $C_{38}H_{50}O_6$ (M^+ 602), λ_{\max} (nujol) 1715 cm^{-1} and 1660 cm^{-1} (unconjugated and conjugated carbonyl), λ_{\max} 264 and 364 nm (ϵ 12270; 9810) in cyclohexane, exhibits catechol colour reactions, confirmed by the formation of a methylene ether. Preliminary evidence of a catechol group with extended conjugation was thus obtained. The NMR spectrum ($CDCl_3$; chemical shifts on the τ scale) shows 3 aromatic H (2.95, q; 3.05, d, $J=2Hz$; 3.42, d, $J=9Hz$) characteristic of a 3,4-dihydroxybenzoyl group; 3 vinyl H (5.1, broad t); a terminal CH_2 showing geminal coupling (5.34, 5.55); 7 vinylic Me (8-8.4); Me_2 on C attached to O as in a 2,2-dimethylchroman (8.8, 8.95, s); and the remaining 13 H as a complex absorption (7.2 to 8.5) representing methylene (including allylic) and methine protons. Catalytic hydrogenation gave octahydro-xanthochymol in which the chromophore remained intact. Methylation (CH_2N_2 or $Me_2SO_4-K_2CO_3$ in acetone) gave two isomeric trimethyl ethers (amorphous, but chromatographically homogeneous) with nearly identical spectral properties. In their NMR spectra they were similar to xanthochymol except for OMe signals (6.05, 6H; 6.35, 3H). Alkaline hydrolysis of the two trimethyl ethers gave a single dimethyl ether, in the NMR spectrum of which the OMe signal at 6.35 disappeared. A carboxyl group in xanthochymol was excluded by its insolubility in aqueous sodium bicarbonate, colour reactions and the absence of any shift in $\nu_{C=O}$ after methylation. A β -diketone group capable of enolization in alternative directions was therefore indicated.

Isoxanthochymol closely resembles xanthochymol in its colour reactions, UV and IR spectra, but methylation of the former resulted in a single alkali-stable dimethyl ether, showing that the β -diketone group postulated in xanthochymol cannot enolise in isoxanthochymol. Ozonolysis of the dimethyl ether, followed by oxidation with the Jones reagent⁶ and treatment with diazomethane, gave a product $C_{34}H_{42}O_{12}$ (M^+ 642) containing three CH_2COOMe groups, as shown by the NMR spectrum. Isoxanthochymol thus suffered a loss of 9 C atoms. Reduction of the ozonide yielded acetone as the volatile product. Two important differences in the NMR spectra of xanthochymol and isoxanthochymol are the

absence of a terminal methylene group and the appearance of two Me groups on a saturated carbon (9.12 and 9.17) in the isoxanthochymol spectrum.

The mass spectra of xanthochymol and its ethers clearly demonstrate the presence of a dihydroxybenzoyl group, two C_6H_9 groups and one $C_{10}H_{17}$ group. The prominent loss of $C_{10}H_{20}$ in the mass spectrum of octahydroxanthochymol provided proof of a $C_{10}H_{17}$ chain adjacent to a CO group in xanthochymol. In conjunction with the UV and NMR data, and on the assumption of maclurin (III) as the biogenetic precursor in which the catechol group is unchanged and the phloroglucinol unit becomes the target of attack by five "active isoprene" groups, the part structure (IV) was revealed. In isoxanthochymol the indicated labile H is absent, apparently by cyclisation of R^2 at this point.

An X-ray crystallographic analysis of the di-*p*-bromobenzenesulphonate of isoxanthochymol enabled us to locate R^1 , R^2 and R^3 in xanthochymol(I), because isoxanthochymol has the structure (II).



Scheinmann *et al.*⁷ have demonstrated the significance of maclurin (III) in xanthone biosynthesis by a statistical analysis of xanthones in higher plants. Prenylation of both the A and B rings of (III) is involved in the biosynthesis of morellin; but prenyl groups attack the A ring only in the biosynthesis of (I) and (II). The intermediate (V) can react with two more prenyl groups as indicated. Loss of the proton H_a from a methyl group or the proton H_b can lead to xanthochymol or isoxanthochymol respectively.

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