# Synthesis and Aromatisation of the Linear Hepta-β-carbonyl System

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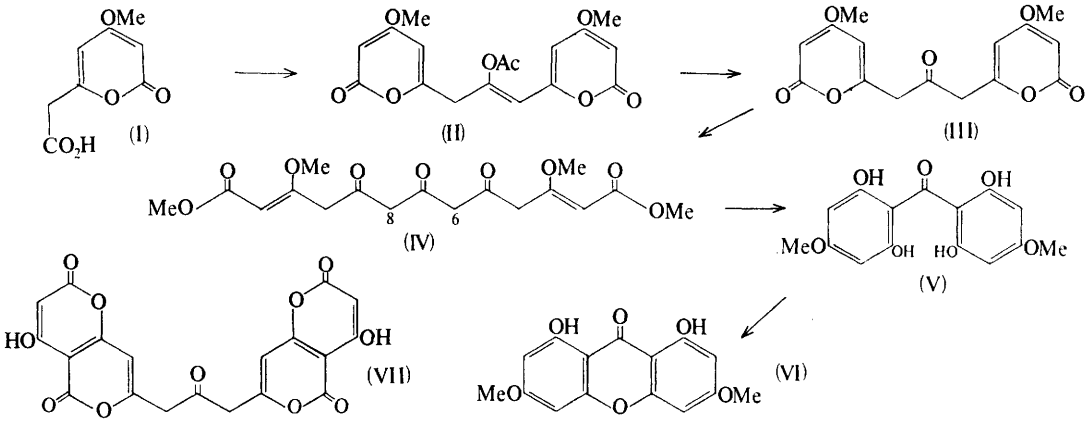
THE methods[1-5] so far developed for the preparation of linear poly-β-carbonyl compounds as models for polyketide biosynthesis[6] have culminated at the penta-β-carbonyl system.[3] Since further progression to higher members of this series either by the condensed polypyrone[1-3] or anion-acylation[5] routes presents certain practical problems, a new approach capable of extension to the synthesis of long chains of alternating carbonyl function has been developed. The extent to which the requirements of control of the subsequent cyclisation of such extended polyketones to phenolic compounds have been met are now illustrated for the linear hepta-β-carbonyl array.

Decarboxylative self-condensation[7] of 6-carboxymethyl-4-methoxy-2-pyrone† (I) in acetic anhydride–triethylamine–tetrahydrofuran solution (20°, 30 min.) afforded the enol acetate (II),[9] τ 4·05, 4·52 (pyrone-H), 4·20 (vinyl-H), 6·19 ($OCH_3$), 6·52 ($CH_2$), and 7·68 ($OCOCH_3$), in 42% yield. Quantitative conversion of (II) to the symmetrical ketone‡ (III) (τ 4·02d, 4·53d, 6·20s, 6·35s) was achieved in methanolic sodium hydroxide solution 2 min.). Ketone (III) contains a further six latent carbonyl functions which, by subsequent ring-opening, should give a linear hepta-β-carbonyl compound (IV) whose penultimate functions are protected as enol ethers. In this way cyclisation of (IV) should be directed to Claisen condensation at the preferred sites of anion formation, *i.e.* C-6 and C-8.

When a solution of (III) in methanolic potassium hydroxide was acidified after 17 hours at 20° the only detectable aromatic compound obtained in 15% yield was 1,8-dihydroxy-3,6-dimethoxyxanthone (VI), $\lambda_{max}$ 234, 247, 271, 325 mμ; τ — 2·0

† This compound was prepared from triacetic lactone by a procedure developed by Drs. T. Money, A. Neilson, and Mr. J. L. Douglas (University of British Columbia, Vancouver) *cf.* J. L. Douglas and T. Money *Canad. J. Chem.*, 1968, **46**, 695.

‡ Satisfactory analytical, spectroscopic, and mass spectral data were obtained for new compounds.




(2H), 3·65 (4H) and 6·13 (6H). 2,6,2′6′-Tetrahydroxy-4,4′-dimethoxybenzophenone (V), the expected precursor[8] of the xanthone (VI), could not be detected. The structure of (VI) was confirmed by methylation ($Me_2SO_4$–$K_2CO_3$–$Me_2CO$) to 1,3,6,-8-tetramethoxyxanthone, identical with a synthetic sample.[9] The several possible reactions of the extended hepta-carbonyl functionality of (IV) have presumably been controlled by a process which may be an analogy for the natural folding of acetate–malonate derived chains *via* enolised enzyme-bound intermediates.

Further studies of control of cyclisation chemistry of more extended poly-β-carbonyls (*e.g.* VII) which may be obtained from accessible α-pyrones[1–3] by application of the above procedure are in progress.

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