

Reactions of Triacetic Acid Lactone with Carbonyl Compounds.
X-Ray Structure Determination of 3-Acetoacetyl-2-chromenone and
3,6,9,12-Tetramethyl-1*H*,6*H*,7*H*,12*H*-6,12-Methanodipyran[4,3-*b*:4,3-*f*]-
dioxocin-1,7-dione

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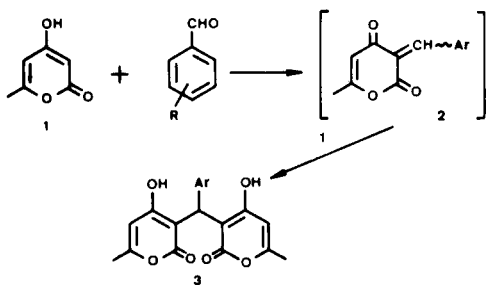
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The structure of 3-acetoacetyl-2-chromenone has been definitely assigned to the product resulting from the reaction of 4-hydroxy-6-methyl-2-pyrone, **1**, with 2-hydroxybenzaldehyde. Also, the reaction of the pyrone **1** with pentane-2,4-dione in a 2:1 molar ratio gives 3,6,9,12-tetramethyl-1*H*,6*H*,7*H*,12*H*-6,12-methanodipyran[4,3-*b*:4,3-*f*]dioxocin-1,7-dione. X-Ray analyses of both products are presented.

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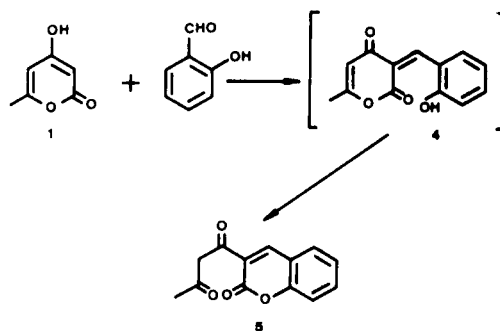
Some of us have been extensively studying the reactivity of 4-hydroxy-6-methyl-2-pyrone **1**. The pyrone **1**, reacts with aromatic aldehydes in a 2:1 ratio to afford products **3**, formed through the intermediacy of the strongly electrophilic species **2** [1] (Scheme 1).

Scheme 1



However, when **1** reacted with 2-hydroxybenzaldehyde, a product was isolated whose analytical data agreed with a structure arising from a 1:1 condensation reaction in which a molecule of water was lost [2]. We found the product was not 3-(2-hydroxybenzylidene)-6-methylpyran-2,4-dione, **4**, (Scheme 2), but 3-acetoacetyl-2-chromenone, **5**. This was substantiated on spectroscopic basis and by comparison with a sample of **5** independently prepared by Dean *et al.* by a different route and kindly supplied by him [3].

Scheme 2

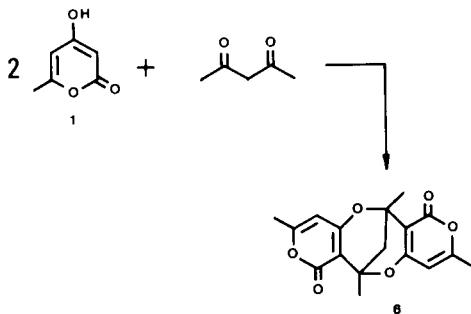


Moreover, very recently structure **5** has been assigned in the patent literature [4] to the product arising from reaction between **1** and 2-hydroxybenzaldehyde in the presence of triethylamine in boiling toluene.

Since the possibility of the opposite conversion, namely **5** into **4**, was still theoretically possible, we decided to perform an X-ray structural analysis on product **5** to fully confirm its structure beyond any reasonable doubt. Moreover, reactions of 2-hydroxybenzaldehydes with different 4-hydroxycoumarins have been reported [5-7] and, in all cases, the probably erroneous 3-(2-hydroxybenzylidene)-chroman-2,4-dione structures have been attributed to the reaction products. These are additional reasons to perform an X-ray analysis of our compound **5**, which has seen now its structure confirmed.

Also, when some of us studied the reactions of **1** with pentane-2,4-dione, a product was isolated to which the 3,6,9,12-tetramethyl-1*H*,6*H*,7*H*,12*H*-6,12-methanodipyrano[4,3-*b*:4,3-*f*]dioxocin-1,7-dione, **6**, structure was assigned on spectroscopic grounds [8] (Scheme 3). An X-ray analysis was considered of interest, not only to confirm the proposed structure but also to check if any distortion was introduced into the pyrone ring as a consequence of the framework rigidity.

Scheme 3



X-Ray Analysis of Compound 5.

Crystal data: C₁₃H₁₀O₄, M = 230.21; triclinic, space group P $\bar{1}$; a = 8.894(4), b = 9.981(4), c = 6.771(3) Å; α = 103.84(4), β = 108.83(4), γ = 82.40(3) $^\circ$; V = 551.4 Å³; Z = 2; D_c = 1.39 g cm⁻³; μ = 7.72 cm⁻¹; F(000) = 240.

Yellow prismatic crystals were obtained as described [2]. The monocrystal was mounted on a Siemens four-circle diffractometer. Graphite monochromatized Cu K α radiation (λ = 1.5418 Å) was used at room temperature. Of the 2020 reflections measured, 1791 were considered as observed I \geq 2.5 σ (I). Data were corrected for Lorentz, polarization and absorption.

The structure was solved by direct methods (MULTAN) [9] and refined by full matrix least-squares methods (SHELX) [10]. The H-atoms were positioned except H on O(15). The final R was 0.0738, wR = 0.0958, W = K/($\sigma^2(F)$ + 0.298 F²).

The X-ray analysis of compound **5** confirms its structure as a chromene derivative. The acetoacetyl moiety appears as an enol form with intramolecular hydrogen bonding (O(14)-O(15) 2.496 Å). The molecule is depicted in Figure 1

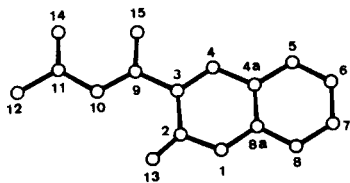
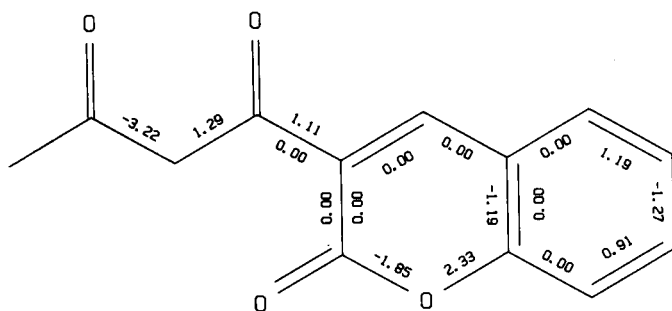
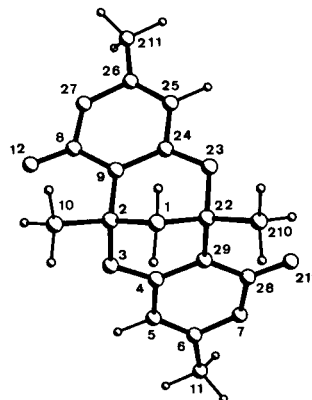
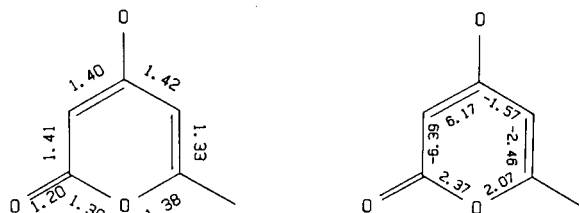
Figure 1. General view of the molecule **5** with atom numbering.Figure 2. Selected torsion angles of product **5**.Figure 3. General view of the molecule **6** with atom numbering. A binary axis bisects C(2)-C(1)-C(22) angle.Figure 4. Bond lengths and intra-annular torsion angles of the pyrone moiety of product **6**.

Table I

Bond Lengths (Å) for compound **5**

O(1)-C(2)	1.391(2)	C(5)-C(6)	1.384(3)
O(1)-C(8a)	1.365(2)	C(6)-C(7)	1.390(4)
C(2)-C(3)	1.469(3)	C(7)-C(8)	1.381(3)
C(2)-O(13)	1.191(2)	C(8)-C(8a)	1.399(3)
C(3)-C(4)	1.353(3)	C(9)-C(10)	1.368(3)
C(3)-C(9)	1.487(3)	C(9)-O(15)	1.315(3)
C(4)-C(4a)	1.441(3)	C(10)-C(11)	1.445(3)
C(4a)-C(5)	1.401(3)	C(11)-C(12)	1.492(3)
C(4a)-C(8a)	1.385(3)	C(11)-O(14)	1.257(3)

[11], and bond lengths and angles are collected in Tables I and II. The keto-enol and the lactone rings are practically coplanar. Torsion angles are in Figure 2 [11].

X-Ray Analysis of Compound 6.

Crystal data: $C_{17}H_{16}O_6$, $M = 316.30$; orthorhombic space group $P2_12_12_1$; $a = 7.091(7)$, $b = 7.965(6)$, $c = 10.725(9)$ Å; $V = 742.7$ Å³; $Z = 2$; $D_c = 1.42$ g cm⁻³; $\mu = 6.66$ cm⁻¹; $F(000) = 332$.

Table II

Bond angles (°) for compound 5

C(2)-O(1)-C(8a)	123.2(2)	C(6)-C(7)-C(8)	120.7(2)
O(1)-C(2)-C(3)	116.2(2)	C(7)-C(8)-C(8a)	118.5(2)
O(1)-C(2)-O(13)	115.3(2)	O(1)-C(8a)-C(4a)	121.3(2)
C(3)-C(2)-O(13)	128.4(2)	O(1)-C(8a)-C(8)	117.0(2)
C(2)-C(3)-C(4)	120.1(2)	C(4a)-C(8a)-C(8)	121.7(2)
C(2)-C(3)-C(9)	120.2(2)	C(3)-C(9)-C(10)	125.1(2)
C(4)-C(3)-C(9)	119.7(2)	C(3)-C(9)-O(15)	113.5(2)
C(3)-C(4)-C(4a)	121.7(2)	C(10)-C(9)-O(15)	121.3(2)
C(4)-C(4a)-C(5)	123.7(2)	C(9)-C(10)-C(11)	120.1(2)
C(4)-C(4a)-C(8a)	117.5(2)	C(10)-C(11)-C(12)	119.6(2)
C(5)-C(4a)-C(8a)	118.8(2)	C(10)-C(11)-O(14)	121.0(2)
C(4a)-C(5)-C(6)	119.9(2)	C(12)-C(11)-O(14)	119.4(2)
C(5)-C(6)-C(7)	120.4(2)		

Table III

Bond lengths (Å) for compound 6

C(1)-C(2)	1.49(1)
C(2)-O(3)	1.47(2)
C(2)-C(9)	1.57(2)
C(2)-C(10)	1.54(2)
O(3)-C(4)	1.32(1)
C(4)-C(5)	1.42(1)
C(4)-C(29)	1.40(2)
C(5)-C(6)	1.33(2)
C(6)-O(7)	1.38(1)
C(6)-C(11)	1.42(2)
O(7)-C(28)	1.39(1)
C(8)-C(9)	1.40(2)
C(8)-O(12)	1.20(1)

Crystals of poor quality were obtained as described [8]. The unit-cell parameters and intensities were measured on an Enraf-Nonius CAD-4 automatic four-circle diffractometer using graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) at room temperature. One standard reflection monitored every 50 measurements showed no significant variation. The intensity data were corrected for Lorentz and polarization effects but not for absorption.

442 Reflections (out of 668 measured) were considered reliable $I \geq 1.5 \sigma(I)$ and used in the crystal structure analysis. The structure was solved by direct methods (MULTAN) [9]. The atomic parameters were refined by full matrix least-squares methods (SHELX) [10]. The final

R value was 0.097, $wR = 0.093$, $w = K/(\sigma^2(F) + 0.0288 F^2)$. The hydrogen atoms were positioned geometrically.

The molecular structure of **6** is shown in Figure 3 [12]; and the Figure 4 [11] shows the bond lengths and intramolecular torsion angles of the pyrone ring. The bond lengths are collected in Table III.

The effect of the tension introduced by the rigid framework in product **6** is revealed by torsion angles around C(4), C(29), C(28) (and C(24), C(9), C(8)) and by the C(9)-C(24) distance of 1.402 Å, higher than the corresponding distance in similar compounds which are in the range 1.338-1.372 Å [13-17] (Figure 4).

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