9-(2,3,5-Tri-*O*-acetyl-D-ribofuranosyl)-N^2-nonanoylguanine (18).—The 9 isomer **18** from the Florisil column was a solid foam: $[\alpha]^{22}\text{D}$ −43 (*c* 0.50, $CHCl_3$); nmr (DMSO-d_6) δ 8.10 (s, H-8 of β-**18**), 7.94 (s, H-8 of α-**18**), 5.95 (d, $J_{1',2'}$ = 5.5 Hz, H-1′ of β-**18**) with H-1′ of α-**18** not discernible above noise level, but perhaps at 6.3; the peak areas for H-8 of α:β are 1:6; uv max was like that of **6**; R_f 0.11 in TA.

Anal. Calcd for $C_{25}H_{35}N_5O_9$: C, 54.6; H, 6.42; N, 12.7. Found: C, 54.3; H, 6.38; N, 12.5.

Registry No.—**3** (α isomer), 27460-34-0; **3** (β isomer), 27460-35-1; **5**, 27460-36-2; **6** (α isomer), 27460-37-3; **6** (β isomer), 27460-38-4; **8** (α isomer), 27460-39-5; **8** (β isomer), 27460-40-8; **9** (α isomer), 27462-38-0; **9** (β isomer), 27462-39-1; **10**, 27462-40-4; **12** (α isomer), 27462-41-5; **12** (β isomer), 27462-42-6; **17** (α isomer), 27617-86-3; **17** (β isomer), 27462-43-7; **18** (α isomer), 27570-86-1; **18** (β isomer), 27462-43-7.

Furano Compounds. XII. Synthesis of Furano[2,3-*b*]xanthones

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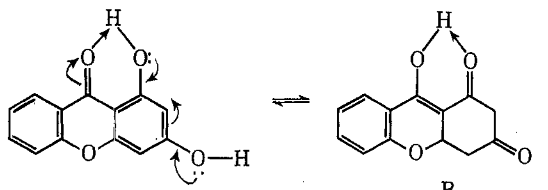
Syntheses of furano[2,3-*b*]xanthones from 3-hydroxyxanthone have been recorded earlier.[1b] Since many naturally occurring xanthones possess a phloroglucinol unit, attempts have now been made to add a furan ring to 1,3-dihydroxyxanthone.

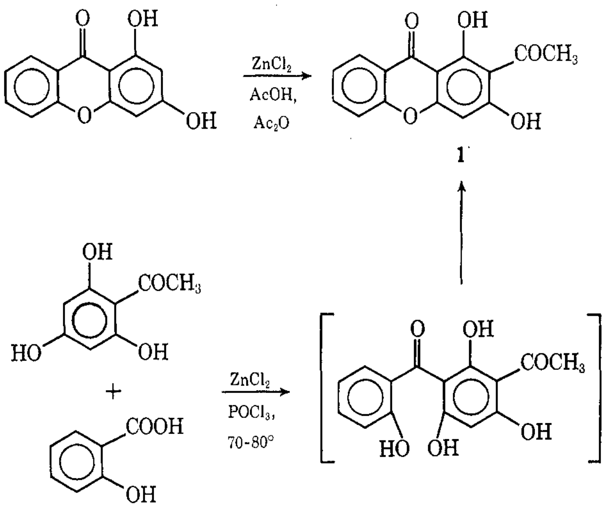
For the addition of a [2,3-*b*]-fused furan ring, the essential step is to introduce a 2-formyl or 2-acetyl group into the 1,3-dihydroxyxanthone molecule. 1,3-Dihydroxyxanthone undergoes formylation to yield 1,3-dihydroxy-4-formylxanthone.[2] However, acetylation of 1,3-dihydroxyxanthone under normal Friedel–Crafts or Fries conditions results in a mixture of products. Using freshly fused $ZnCl_2$, HOAc, and Ac_2O, Badawi, *et al.*,[3] acetylated 2-methyl-5,7-dihydroxychromone to get 2-methyl-5,7-dihydroxy-6-acetylchromone. When 1,3-dihydroxyxanthone was submitted to acetylation under these conditions, a single crystalline product could be obtained. This was identified as 1,3-dihydroxy-2-acetylxanthone (**1**).

The reactivity of the 2 position of 1,3-dihydroxyxanthone may be attributed to the presence of its 2,4-dihydroxybenzoyl moiety A which may undergo tautomeric change to a β-diketonic structure B containing a reactive methylene group in the 2 position.



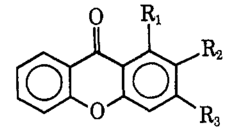
A B

The identity of **1** has been proved by another synthesis involving condensation of phloroacetophenone with salicylic acid in the presence of freshly fused $ZnCl_2$ and $POCl_3$. This reaction probably entails the nonchelated *p*-hydroxyl group in the formation of the γ-pyrone ring.

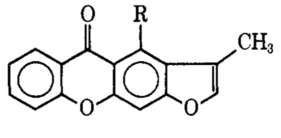


Location of the acetyl group at the 2 position is confirmed by the fact that **1** affords a new 1,2,3-trihydroxyxanthone upon Dakin oxidation. The trimethyl ether of this is different from 1,3,4-trimethoxyxanthone.[2] On acetylation using $B(OAc)_3$ and Ac_2O, 1,2,3-diacetoxyxanthone gave 1-hydroxy-2,3-diacetoxyxanthone, since the chelated hydroxyl forms a boracetate complex while the nonchelated hydroxyls undergo normal acetylation. Acetylation using Ac_2O and a drop of pyridine yielded 1,2,3-triacetoxyxanthone. Methylation of 1-hydroxy-2,3-diacetoxyxanthone using methyl iodide and silver oxide in acetone yielded 1-methoxy-2,3-diacetoxyxanthone which on hydrolysis with alkali gave 1-methoxy-2,3-dihydroxyxanthone.

Condensation of ethyl bromoacetate with **1** using acetone/K_2CO_3 yielded exclusively ethyl 1-hydroxy-2-acetyl-9-oxo-3-xanthyloxyacetate (**2g**) since the 1-hydroxyl group is strongly chelated by both the xanthone and acetyl carbonyls. Hydrolysis of **2g** with 5% Na_2CO_3 in acetone gave 1-hydroxy-2-acetyl-9-oxo-3-xanthyloxyacetic acid (**2h**). When heated with sodium acetate/acetic anhydride, **2h** underwent cyclization with decarboxylation and acetylation yielding 1-acetoxy-3-methylfurano[4,5-*b*]xanthone (**3a**). Hydrolysis with 5% alcoholic potash smoothly converted it into the required 1-hydroxy-3-methylfurano[2,3-*b*]xanthone **3b**.



2a, $R_1, R_2, R_3 = OH$
b, $R_1, R_2, R_3 = OCH_3$
c, $R_1 = OH$; $R_2, R_3 = OCOCH_3$
d, $R_1, R_2, R_3 = OCOCH_3$
e, $R_1 = OCH_3$; $R_2, R_3 = OCOCH_3$
f, $R_1 = OCH_3$; $R_2, R_3 = OH$
g, $R_1 = OH$; $R_2 = COCH_3$; $R_3 = \text{-}OCH_2COOEt$
h, $R_1 = OH$; $R_2 = COCH_3$; $R_3 = \text{-}OCH_2COOH$



3a, $R = OCOCH_3$
b, $R = OH$

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Experimental Section

1,3-Dihydroxy-2-acetylxanthone.[1]—Freshly fused $ZnCl_2$ (4 g) was dissolved in acetic acid (8 ml) by heating. Acetic anhydride (4 ml) and 1,3-dihydroxyxanthone (4 g) were added. The reaction mixture was heated at 145–150° for 1–5 hr, cooled, and poured into ice–water. Solid gradually separated out and was filtered and washed with water. The crude product was sublimed at 240–250° (8 mm). Crystallization from alcohol/acetic acid yielded **1** as pale yellow needles, mp 208–209° (1.4 g). It gave a blood red color with ethanolic ferric chloride.

Anal. Calcd for $C_{15}H_{10}O_5$: C, 66.67; H, 3.70. Found: C, 66.34; H, 3.98.

Its 2,4-dinitrophenylhydrazone formed tiny orange needles, mp 297° (acetic acid).

Anal. Calcd for $C_{21}H_{14}O_8N_4$: N, 12.45. Found: N, 12.24.

A mixture of salicylic acid (2 g), phloroacetophenone (3.5 g), freshly fused $ZnCl_2$ (6 g), and $POCl_3$ (20 ml) were heated at 70–80° for 2 hr. The reaction product was cooled and poured into ice–water. The yellow solid that separated was filtered and washed with 10% $NaHCO_3$ and water. The crude product was sublimed at 248–250° (8 mm). Crystallization from ethanol/acetic acid yielded **1** as pale yellow needles, mp and mmp (with the above sample) 208–209°, yield 0.8 g.

Anal. Calcd for $C_{15}H_{10}O_5$: C, 66.67; H, 3.70. Found: C, 66.43; H, 3.88.

1,2,3-Trihydroxyanthone (2a).—**1** (1.35 g) was dissolved in 10 ml of 4% NaOH, 10 ml of pyridine was added, and the mixture was cooled in an ice bath. Hydrogen peroxide (12 ml, 20 vol) was added dropwise with shaking during 5 min. The reaction mixture was left for 1 hr. Acidification yielded **2a** as a yellow solid. It crystallized from alcohol as yellow needles, mp 265°, yield 0.75 g. The ethanolic solution gave a dark green color with ferric chloride solution.

Anal. Calcd for $C_{13}H_8O_5$: C, 63.93; H, 3.28. Found: C, 64.17; H, 3.54.

1,2,3-Trimethoxyxanthone (2b).—**2a** (0.2 g) was refluxed with Me_2SO_4 (0.6 g) and anhydrous K_2CO_3 (2 g) for 10 hr. Potassium salts were filtered off and the filtrate after removal of solvent furnished **2b** as a colorless solid. It crystallized from alcohol as needles, mp 191°. It gave no color with $FeCl_3$ solution.

Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.89. Found: C, 66.97; H, 4.63.

1,3,4-Trimethoxyxanthone.—1,4-Dihydroxy-3-methoxyxanthone[4] (0.2 g) in anhydrous acetone (100 ml) was treated with anhydrous potassium carbonate (2.0 g) and dimethyl sulfate (2.5 ml), and the mixture was refluxed for 54 hr. The potassium salts were filtered and the solvent was removed. The residue on crystallization from alcohol gave 1,3,4-trimethoxyxanthone as needles, mp 164°, yield 0.12 g. It gave no color reaction with ethanolic ferric chloride.

Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.1; H, 4.9. Found: C, 67.4; H, 5.0.

1,2,3-Triacetoxyxanthone (2d).—**2a** (0.1 g) with acetic anhydride (5 ml) and pyridine (a drop) gave **2d** as colorless shining cubes, mp 213° (alcohol), $FeCl_3$ test negative.

Anal. Calcd for $C_{19}H_{14}O_8$: C, 61.62; H, 3.78. Found: C, 61.88; H, 3.95.

1-Hydroxy-2,3-diacetoxyxanthone (2c).—**2a** (1.0 g) was refluxed with boron triacetate (1.5 g) and acetic anhydride (8 ml) for 10 min. The yellow diacetoborate that separated on cooling was filtered and washed with anhydrous ether. Subsequently it was suspended in water (50 ml) and heated to boiling when it decomposed. **2c** thus obtained crystallized from alcohol as pale yellow needles, mp 203–204°, yield 0.8 g. It gave a dark brown ferric chloride test.

Anal. Calcd for $C_{17}H_{12}O_7$: C, 62.19; H, 3.66. Found: C, 62.55; H, 3.91.

1-Methoxy-2,3-diacetoxyanthone (2e).—**2c** (0.5 g) in acetone (100 ml) was refluxed with methyl iodide (2 ml) and active Ag_2O (1 g) for 20 hr. The reaction product was filtered and the filtrate on removal of solvent yielded **2e** which crystallized from alcohol as colorless needles, mp 111°, yield 0.45 g. It gave a negative ferric chloride test.

Anal. Calcd for $C_{18}H_{14}O_7$: C, 63.15; H, 4.09. Found: C, 63.37; H, 3.90.

1-Methoxy-2,3-dihydroxyanthone (2f).—**2e** (0.25 g) was refluxed with alcoholic potash (5%, 10 ml) for 1 hr. Subsequent acidification yielded **2f** which crystallized from alcohol as colorless pale yellow needles, mp 176°. With $FeCl_3$ it gave a green color immediately changing to reddish brown.

Anal. Calcd for $C_{14}H_{10}O_5$: C, 65.11; H, 3.88. Found: C, 65.58; H, 3.67.

Ethyl 1-Hydroxy-2-acetyl-9-oxo-3-xanthyloxyacetate (2g).—**1** (1.35 g) in acetone (300 ml) was refluxed with ethyl bromoacetate (0.85 g) and anhydrous K_2CO_3 (6 g) for 10 hr. The potassium salts were filtered off and the solvent was removed from the filtrate. As no residue was obtained, the potassium salts were suspended in water and decomposed with dilute HCl. The solid that separated was filtered and washed with water. **2g** thus obtained crystallized from alcohol/acetic acid as colorless plates, mp 210°. It gave a reddish brown color with $FeCl_3$, yield 0.9 g.

Anal. Calcd for $C_{19}H_{16}O_7$: C, 64.04; H, 4.49. Found: C, 64.22; H, 4.63.

1-Hydroxy-2-acetyl-9-oxo-3-xanthyloxyacetic Acid (2h).—**2g** (0.75 g) in acetone (300 ml) was refluxed with aqueous Na_2CO_3 (60 ml, 5%) for 3 hr. Removal of acetone and acidification yielded **2h** which crystallized from acetic acid as colorless plates, mp 253°. It gave a reddish brown color with $FeCl_3$, yield 0.6 g.

Anal. Calcd for $C_{17}H_{12}O_7$: C, 62.19; H, 3.66. Found: C, 62.51; H, 3.84.

1-Acetoxy-3-methylfurano[4,5-*b*]xanthone (3a).—**2h** (0.55 g) was refluxed with NaAc (0.6 g) and Ac_2O (6 ml) for 2 hr. Subsequent work-up gave **3a** which crystallized from aqueous alcohol as pale yellow needles, mp 173–174°, yield 0.45 g. It gave a negative $FeCl_3$ test.

Anal. Calcd for $C_{18}H_{12}O_5$: C, 70.13; H, 3.89. Found: C, 70.59; H, 4.01.

1-Hydroxy-3-methylfurano[2,3-*b*]xanthone (3b).—**3a** (0.4 g) was refluxed with alcoholic potash (5%, 15 ml) for 1 hr. Subsequent acidification gave **3b** which crystallized from alcohol as yellow needles, mp 232°, yield 0.3 g. It gave a green color with $FeCl_3$.

Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.18; H, 3.76. Found: C, 72.66; H, 3.81.

Registry No.—**1**, 27460-08-8; **1** 2,4-DNP, 27460-09-9; **2a**, 27519-51-3; **2b**, 27460-10-2; **2c**, 27460-11-3; **2d**, 27460-12-4; **2e**, 27460-13-5; **2f**, 20362-26-9; **2g**, 27460-14-6; **2h**, 27460-15-7; **3a**, 27460-16-8; **3b**, 27460-17-9; 1,3,4-trimethoxyxanthone, 27460-18-0.

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The Cyclization of *cis*- and *trans*-2-(2-Methoxycyclohexyl)ethanol to *cis*- and *trans*-Perhydrobenzofurans[1]

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We have reported[2] that compounds of type **1** undergo cyclization with tosyl chloride–pyridine to form perhydrobenzofurans **2**, with loss of a methoxyl group. This reaction, which we first observed in degradations of the antibiotic fumagillin,[3] involves a methoxonium ion intermediate.[4]

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[1] Aided by Grant 2252-C from the Petroleum Research Fund of the American Chemical Society, for which we express our appreciation.

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