

A Convenient Synthesis of Dihydropyranoxanthenes

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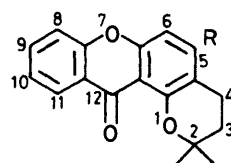
The condensation of hydroxyxanthenes, viz. 1-hydroxy-, 1,3-dihydroxy-, 1-hydroxy-3-methoxy-, 1,3-dihydroxy-5-methoxy-, and 1,3-dihydroxy-7-methoxy-xanthone, with isoprene in the presence of orthophosphoric acid, to give the corresponding dihydropyranoxanthenes, is described. The resulting dihydropyranoxanthenes or their methyl ethers have been dehydrogenated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. The synthesis of the methyl ethers of naturally occurring osajaxanthone, 6-desoxyjacareubin, and 6-desoxyisojacareubin has also been achieved

The 2,2-dimethylchromen moiety occurs frequently among isoprenoidxanthenes (*e.g.* osajaxanthone,¹ jacareubin,² 6-desoxyjacareubin,³ 6-desoxyisojacareubin⁴) and their number has been increasing.^{5,6} Dihydropyranoxanthenes act as a model and intermediate^{7,8} for such natural phenolic products, although tovophyllum A⁹ is the only example known so far in nature. In the past they have been obtained by Grover, Shah, and Shah condensation¹ of hydroxychroman with the appropriate *o*-hydroxybenzoic acid in the presence of zinc chloride and phosphorus oxychloride or by acid-catalyzed cyclisation of the corresponding *o*-hydroxyprenyl compounds,^{7,8} which themselves are difficult to prepare.^{8,10} Thus a convenient method for their synthesis was required.

In this paper, we describe a convenient one-step synthesis for dihydropyranoxanthenes involving condensation of hydroxyxanthenes with 2-methylbuta-1,3-diene^{11,12} (isoprene) in the presence of orthophosphoric acid. The reaction was carried out with 1-hydroxy-, 1,3-dihydroxy-, 1-hydroxy-3-methoxy-, 1,3-dihydroxy-5-methoxy-, and 1,3-dihydroxy-7-methoxy-xanthone.

Condensation of 1-hydroxyxanthone¹³ with isoprene in the presence of orthophosphoric acid gave only one product (yield 70%), which on elemental analysis showed the introduction of one isoprene unit. Its ¹H n.m.r. spectrum indicated the presence of a 2,2-dimethylchroman ring; the *gem*-dimethyl group appeared as a singlet at δ 1.45 and the methylene groups appeared as two distinct triplets (*J* 7 Hz) at δ 1.83 and 2.76. The condensation product was therefore assigned the structure 3,4-dihydro-2,2-dimethyl-2*H*,12*H*-pyrano[2,3-*a*]xanthen-12-one (1). Had it been the alternative 4,4-dimethylchroman structure, we should have observed a triplet at δ ca. 4 for methylene protons adjacent to O. Compound (1), on reaction with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in refluxing benzene, gave a product (80%), which was assigned the structure 2,2-dimethyl-2*H*,12*H*-pyrano[2,3-*a*]xanthen-12-one (2) on the basis of its ¹H n.m.r. spectral data, which showed a characteristic pair of doublets (*J* 10 Hz) at δ 5.65 and 6.35. The structure (2) was further confirmed by its u.v. spectrum [λ_{max} (MeOH) 206, 236, 272, 312, and 376 nm] which showed a bathochromic shift compared with that of compound (1) [λ_{max} (MeOH) 202, 232, 250, 292, and 354 nm] indicating extended conjugation in (2). The structure of the dehydrogenated product as (2) was also confirmed by its identity (m.p., m.m.p. and co-i.r.) with an authentic sample prepared by propynylation of 1-hydroxyxanthone with 3-chloro-3-methylbut-1-yne in dioxan, in the presence of anhydrous K₂CO₃ and KI.

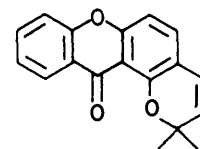
1,3-Dihydroxyxanthone,¹⁴ on similar condensation with isoprene, gave a mixture of three products A, B, and C in the ratio 5 : 3 : 2 (overall yield 70%), which were separated by column chromatography-silica gel. Compounds A and B gave a deep green colour with alcoholic FeCl₃ solution and



(1) R = H

(8) R = OMe

(9) R = OH

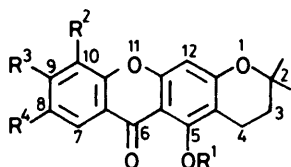


(2)

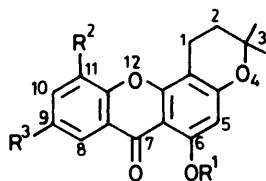
were shown to be isomeric by elemental analysis. The presence of the 2,2-dimethylchroman moiety was defined by the ¹H n.m.r. spectral data, which showed, besides other signals, a singlet of one aromatic proton (in compounds A and B) at δ 6.20. Further, a sharp low-field singlet at δ 13.40 (1 H, exchanged with D₂O) confirmed the presence of a chelated hydroxy group in both compounds A and B. So a clear distinction between A and B could not be made and either one could be assigned the structure 3,4-dihydro-5-hydroxy-2,2-dimethyl-2*H*,6*H*-pyrano[3,2-*b*]xanthen-6-one (3) or 1,2-dihydro-6-hydroxy-3,3-dimethyl-3*H*,7*H*-pyrano[2,3-*c*]xanthen-7-one (4). The slowest moving compound C gave a negative ferric reaction and its elemental analysis showed the introduction of two isoprene units. It was therefore assigned the structure 3,4,7,8-tetrahydro-2,2,6,6-tetramethyl-2*H*,6*H*,14*H*-dipyran[2,3-*a*:2',3'-*c*]xanthen-14-one (5) which was in agreement with its ¹H n.m.r. spectral data.

The structures of compounds A and B were established as (3) and (4), respectively, by their further reaction with isoprene. Unlike compound A, B underwent further reaction with isoprene to give C. Compound A was recovered unchanged from the reaction mixture. These assignments were further supported by comparing the chemical shift of the aromatic proton signal in the ¹H n.m.r. spectral data of the methyl ethers (6) and (7) of compounds A and B. A singlet due to one aromatic proton (δ 6.28) in compound B methyl ether (7) resonates 0.37 p.p.m. upfield to that of the methyl ether of compound A (6) (δ 6.65). Strong shielding of the aromatic proton in (7) can be explained as follows: in structure (6) the methoxy group is hindered because it is flanked by a carbonyl group on one side and a methylene on the other. Because of this it may be out of the plane of the benzene ring and its shielding of the *para* aromatic proton could therefore be reduced. In structure (7) the methoxy group is relatively unhindered and therefore contributes to the shielding of the *ortho* aromatic proton.

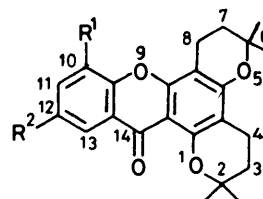
1-Hydroxy-3-methoxyxanthone,¹⁵ when treated similarly with isoprene, gave 3,4-dihydro-5-methoxy-2,2-dimethyl-



- (3) $R^1 = R^2 = R^3 = R^4 = H$
 (6) $R^1 = Me, R^2 = R^3 = R^4 = H$
 (10) $R^1 = R^3 = R^4 = H, R^2 = OMe$
 (13) $R^1 = Me, R^2 = OMe, R^3 = R^4 = H$
 (15) $R^1 = R^2 = R^3 = H, R^4 = OMe$
 (18) $R^1 = Me, R^2 = R^3 = H, R^4 = OMe$
 (26) $R^1 = R^2 = R^3 = H, R^4 = OH$
 (27) $R^1 = Ac, R^2 = R^3 = H, R^4 = OAc$
 (28) $R^1 = R^3 = R^4 = H, R^2 = OH$
 (29) $R^1 = Me, R^2 = R^3 = OMe, R^4 = H$



- (4) $R^1 = R^2 = R^3 = H$
 (7) $R^1 = Me, R^2 = R^3 = H$
 (11) $R^1 = R^3 = H, R^2 = OMe$
 (14) $R^1 = Me, R^2 = OMe, R^3 = H$
 (16) $R^1 = R^2 = H, R^3 = OMe$
 (19) $R^1 = Me, R^2 = H, R^3 = OMe$



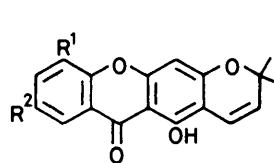
- (5) $R^1 = R^2 = H$
 (12) $R^1 = OMe, R^2 = H$
 (17) $R^1 = H, R^2 = OMe$

2*H*,12*H*-pyrano[2,3-*a*]xanthen-12-one (8), which was found to be different from either (6) or (7). Incidentally, this ruled out the alternative structure (9) for compound B, as this latter compound could also lead to compound C on further reaction with isoprene.

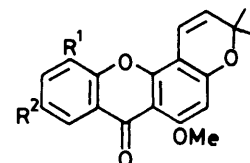
Similarly, condensation of 1,3-dihydroxy-5-methoxyxanthone¹⁶ with isoprene gave a mixture of three products D, E, and F in the ratio 4 : 3 : 3 (overall yield 60%), which were separated by column chromatography. Compounds D and E were found to be isomeric dihydropyrano-xanthenones from their elemental analyses and ¹H n.m.r. spectral data. Either of the compounds D and E could be assigned the structure 3,4-dihydro-5-hydroxy-10-methoxy-2,2-dimethyl-2*H*,6*H*-pyrano-[3,2-*b*]xanthen-6-one (10) or 1,2-dihydro-6-hydroxy-11-methoxy-3,3-dimethyl-3*H*,7*H*-pyrano[2,3-*c*]xanthen-7-one (11). Compound F was identified as 3,4,7,8-tetrahydro-10-methoxy-2,2,6,6-tetramethyl-2*H*,6*H*,14*H*-dipyran[2,3-*a*:2',3'-*c*]xanthen-14-one (12) on the basis of its ¹H n.m.r. spectral data and elemental analysis. Structures (10) and (11) were assigned to compound D and E, respectively, by further reaction of compound E with isoprene to give F. Further, the singlets due to one aromatic proton in the methyl ethers of compounds D and E (13) and (14) resonate at δ 6.66 and 6.20, respectively. Shielding of the aromatic proton by 0.46 p.p.m. in compound E methyl ether (14) led us to believe that the methoxy group and single aromatic proton are in close proximity within the molecule.

1,3-Dihydroxy-7-methoxyxanthone,¹⁴ when treated similarly, gave a mixture of three products, 3,4-dihydro-5-hydroxy-8-methoxy-2,2-dimethyl-2*H*,6*H*-pyrano[3,2-*b*]xanthen-6-one (15), 1,2-dihydro-6-hydroxy-9-methoxy-3,3-dimethyl-3*H*,7*H*-pyrano[2,3-*c*]xanthen-7-one (16), and 3,4,7,8-tetrahydro-12-methoxy-2,2,6,6-tetramethyl-2*H*,6*H*,14*H*-dipyran[2,3-*a*:2',3'-*c*]xanthen-14-one (17) in the ratio 4 : 4 : 2 (overall yield 65%), which were separated by column chromatography. These structures were assigned on the basis of elemental analysis and ¹H n.m.r. spectral data. Assignments were supported by further reaction of (16) with isoprene to give (17). In this case the singlets due to one aromatic proton in the methyl ethers of (15) and (16) [(18) and (19)] resonate at δ 6.61 and 6.24, respectively.

Dihydropyrano-xanthenones (1), (3), (10), and (15), on dehydrogenation with DDQ, gave the corresponding pyrano-xanthenones, 2,7-desoxyosajaxanthenone (20), 5-*O*-methyl-6-



- (20) $R^1 = R^2 = H$
 (21) $R^1 = OMe, R^2 = H$
 (22) $R^1 = H, R^2 = OMe$



- (23) $R^1 = R^2 = H$
 (24) $R^1 = OMe, R^2 = H$
 (25) $R^1 = H, R^2 = OMe$

desoxyjacareubin (21), and 7-*O*-methylsajaxanthenone (22), respectively. The dihydropyrano-xanthenones (4), (11), and (16) failed to dehydrogenate, but their methyl ethers (7), (14), and (19) underwent facile dehydrogenation with DDQ to give the corresponding pyrano-xanthenones (23), (24) (6-desoxyisajacareubin dimethyl ether), and (25), respectively. Earlier attempts to dehydrogenate dihydro-osajaxanthenone⁷ (26), its diacetate⁷ (27), dihydro-6-desoxyjacareubin⁸ (28), and the trimethyl ether of dihydrojacareubin⁸ (29) with DDQ were unsuccessful. A survey of the literature revealed that this is the first report of the dehydrogenation of dihydropyrano-xanthenones with DDQ.

Experimental

M.p.s were taken in a sulphuric acid bath and are uncorrected. ¹H N.m.r. spectra were recorded on a Perkin-Elmer R-32 (90 MHz) instrument for solutions in CDCl₃ with tetramethylsilane as the internal standard. Silica gel (60—120 mesh) was used for all chromatographic separations. Ether refers to diethyl ether.

Reaction of 1-Hydroxyxanthone with Isoprene. General Procedure.—A solution of isoprene (0.5 ml, 5.0 mmol) in xylene (2.0 ml) was added to a mixture of 1-hydroxyxanthone¹³ (0.5 g, 2.4 mmol), orthophosphoric acid (85%, 1.0 ml), and xylene (1.0 ml) with constant stirring at 30—35 °C during 2 h. Stirring was continued for further 6 h and then ether (50.0 ml) added. The ethereal layer was washed successively with sodium hydrogen carbonate solution (5%), water, dried

Table. Synthesis and physical data for compounds (1)–(8), (10)–(25)

Compd.	Yield ^a (%)	M.p. (°C)	Molecular formula	Found (Calc.) (%)		¹ H N.m.r. δ (<i>J</i> in Hz)
				C	H	
(1)	70 (1:2)	119–120	C ₁₈ H ₁₆ O ₃	76.9 (77.1)	5.9 (5.7)	1.45 (6 H, s, CMe ₂), 1.83 and 2.76 (each 2 H, each t, <i>J</i> 7 Hz, 3- and 4-H), 6.88 and 7.33 (each 1 H, each d, <i>J</i> 9 Hz, 5- and 6-H), 7.60 (3 H, m, 8-, 9-, and 10-H), and 8.18 (1 H, m, 11-H)
(2)	80 (1:2)	116–117	C ₁₈ H ₁₄ O ₃	77.5 (77.7)	5.2 (5.0)	1.56 (6 H, s, CMe ₂), 5.65 and 6.35 (each 1 H, each d, <i>J</i> 10 Hz, 3- and 4-H), 6.90 and 7.35 (each 1 H, each d, <i>J</i> 9 Hz, 5- and 6-H), 7.60 (3 H, m, 8-, 9-, and 10-H), and 8.30 (1 H, m, 11-H)
(3) ^b	35 ^e	145–146 (251–253) ¹⁷	C ₁₈ H ₁₆ O ₄	72.8 (73.0)	5.6 (5.4)	1.36 (6 H, s, CMe ₂), 1.84 and 2.74 (each 2 H, each t, <i>J</i> 7 Hz, 3- and 4-H), 6.20 (1 H, s, 12-H), 7.40 (3 H, m, 8-, 9-, and 10-H), 8.12 (1 H, m, 7-H), and 13.4 (1 H, s, exchanged with D ₂ O, 5-OH)
(4) ^b	21 ^f	185–186 (180–182) ¹⁷	C ₁₈ H ₁₆ O ₄	72.9 (73.0)	5.6 (5.4)	1.38 (6 H, s, CMe ₂), 1.86 and 2.78 (each 2 H, each t, <i>J</i> 7 Hz, 2- and 1-H), 6.20 (1 H, s, 5-H), 7.50 (3 H, m, 9-, 10-, and 11-H), 8.05 (1 H, m, 8-H), and 13.4 (1 H, s, exchanged with D ₂ O, 6-OH) ^h
(5) ^b	14 ^f	158–159 (152–153) ¹⁷	C ₂₃ H ₂₄ O ₄	75.6 (75.8)	6.7 (6.6)	1.33 and 1.41 (each 6 H, each s, 2 × CMe ₂), 1.80 (4 H, m, 3- and 7-H), 2.60 and 2.84 (each 2 H, each t, <i>J</i> 7 Hz, 4- and 8-H), 7.45 (3 H, m, 10-, 11-, and 12-H), and 8.32 (1 H, m, 13-H)
(6)	90 ^f	138–139	C ₁₉ H ₁₈ O ₄	73.3 (73.5)	6.0 (5.8)	1.37 (6 H, s, CMe ₂), 1.83 and 2.82 (each 2 H, each t, <i>J</i> 7 Hz, 3- and 4-H), 3.95 (3 H, s, 5-OMe), 6.65 (1 H, s, 12-H), 7.50 (3 H, m, 8-, 9-, and 10-H), and 8.27 (1 H, m, 7-H)
(7)	86 ^f	175–176	C ₁₉ H ₁₈ O ₄	73.3 (73.5)	6.0 (5.8)	1.37 (6 H, s, CMe ₂), 1.84 and 2.81 (each 2 H, each t, <i>J</i> 7 Hz, 2- and 1-H), 3.89 (3 H, s, 6-OMe), 6.28 (1 H, s, 5-H), 7.50 (3 H, m, 9-, 10-, and 11-H), and 8.28 (1 H, m, 8-H)
(8)	66 (3:1)	158–159	C ₁₉ H ₁₈ O ₄	73.3 (73.5)	5.9 (5.8)	1.42 (6 H, s, CMe ₂), 1.78 and 2.60 (each 2 H, each t, <i>J</i> 7 Hz, 3- and 4-H), 3.81 (3 H, s, 5-OMe), 6.43 (1 H, s, 6-H), 7.46 (3 H, m, 8- and 9-, and 10-H), and 8.26 (1 H, m, 11-H)
	24 ^f	160–161	C ₁₉ H ₁₈ O ₅	69.8 (70.0)	5.7 (5.5)	1.35 (6 H, s, CMe ₂), 1.82 and 2.70 (each 2 H, each t, <i>J</i> 7 Hz, 3- and 4-H), 3.94 (3 H, s, 10-OMe), 6.39 (1 H, s, 12-H), 7.20 (2 H, m, 8- and 9-H), 7.74 (1 H, q, 7-H), and 13.36 (1 H, s, exchanged with D ₂ O, 5-OH)
(11) ^c	18 ^g	214–215	C ₁₉ H ₁₈ O ₅	69.9 (70.0)	5.7 (5.5)	1.44 (6 H, s, CMe ₂), 1.94 and 2.97 (each 2 H, each t, <i>J</i> 7 Hz, 2- and 1-H), 4.06 (3 H, s, 11-OMe), 6.45 (1 H, s, 5-H), 7.42 (2 H, m, 9- and 10-H), 7.74 (1 H, q, 8-H), and 13.42 (1 H, s, exchanged with D ₂ O, 6-OH) ^h
(12) ^c	18 ^f	180–181	C ₂₄ H ₂₆ O ₅	72.9 (73.0)	6.8 (6.6)	1.32 and 1.35 (each 6 H, each s, 2 × CMe ₂), 1.80 (4 H, m, 3- and 7-H), 2.90 (4 H, m, 4- and 8-H), 3.94 (3 H, s, 10-OMe), 7.20 (2 H, m, 11- and 12-H), and 7.81 (1 H, q, 13-H)
(13)	86 ^f	195–196	C ₂₀ H ₂₀ O ₅	70.4 (70.6)	6.1 (5.9)	1.32 (6 H, s, CMe ₂), 1.79 and 2.80 (each 2 H, each t, <i>J</i> 7 Hz, 3- and 4-H), 3.90 and 3.92 (each 3 H, each s, 5- and 10-OMe), 6.66 (1 H, s, 12-H), 7.14 (2 H, m, 8- and 9-H), and 7.75 (1 H, q, 7-H)
(14)	91 ^f	215–216	C ₂₀ H ₂₀ O ₅	70.4 (70.6)	6.0 (5.9)	1.37 (6 H, s, CMe ₂), 1.85 and 2.87 (each 2 H, each t, <i>J</i> 7 Hz, 2- and 1-H), 3.87 and 3.89 (each 3 H, each s, 6- and 11-OMe), 6.20 (1 H, s, 5-H), 7.12 (2 H, m, 9- and 10-H), and 7.74 (1 H, q, 8-H)

Table. (continued)

Compd.	Yield ^a (%)	M.p. (°C)	Molecular formula	Found (Calc.) (%)		¹ H N.m.r. δ (<i>J</i> in Hz)
				C	H	
(15) ^d	26 ^f	173—174 (173—174) ⁷	C ₁₉ H ₁₈ O ₅	69.9 (70.0)	5.8 (5.5)	1.36 (6 H, s, CMe ₂), 1.80 and 2.67 (each 2 H, each t, <i>J</i> 7 Hz, 3- and 4-H), 3.82 (3 H, s, 8-OMe), 6.30 (1 H, s, 12-H), 7.28 (2 H, m, 9- and 10-H), 7.56 (1 H, m, 7-H), and 13.5 (1 H, s, exchanged with D ₂ O, 5-OH)
(16) ^d	26 ^g	194—195	C ₁₉ H ₁₈ O ₅	69.8 (70.0)	5.6 (5.5)	1.36 (6 H, s, CMe ₂), 1.83 and 2.80 (each 2 H, each t, <i>J</i> 7 Hz, 2- and 1-H), 3.85 (3 H, s, 9-OMe), 6.20 (1 H, s, 5-H), 7.28 (2 H, m, 10- and 11-H), 7.57 (1 H, m, 8-H), and 12.64 (1 H, s, exchanged with D ₂ O, 6-OH)
(17) ^d	13 ^f	228—229 (226—227) ⁷	C ₂₄ H ₂₆ O ₅	72.8 (73.0)	6.7 (6.6)	1.38 and 1.44 (each 6 H, each s, 2 × CMe ₂), 1.82 (4 H, m, 3- and 7-H), 2.60 and 2.85 (each 2 H, each t, <i>J</i> 7 Hz, 4- and 8-H), 3.82 (3 H, s, 12-OMe), 7.29 (2 H, m, 10- and 11-H), and 7.70 (1 H, m, 13-H)
(18)	77 ^f	170—171	C ₂₀ H ₂₀ O ₅	70.5 (70.6)	6.1 (5.9)	1.37 (6 H, s, CMe ₂), 1.81 and 2.81 (each 2 H, each t, <i>J</i> 7 Hz, 3- and 4-H), 3.85 and 3.92 (each 3 H, each s, 5- and 8-OMe), 6.61 (1 H, s, 12-H), 7.25 (2 H, m, 9- and 10-H), and 7.65 (1 H, m, 7-H)
(19)	86 ^f	155—156	C ₂₀ H ₂₀ O ₅	70.4 (70.6)	6.0 (5.9)	1.38 (6 H, s, CMe ₂), 1.87 and 2.84 (each 2 H, each t, <i>J</i> 7 Hz, 2- and 1-H), 3.86 and 3.91 (each 3 H, each s, 6- and 9-OMe), 6.24 (1 H, s, 5-H), 7.27 (2 H, m, 10- and 11-H), and 7.67 (1 H, m, 8-H)
(20)	90 (0 : 1)	169—170 (168) ¹⁷	C ₁₈ H ₁₄ O ₄	73.3 (73.5)	5.0 (4.8)	1.48 (6 H, s, CMe ₂), 5.56 (1 H, d, <i>J</i> 10 Hz, 3-H), 6.30 (1 H, s, 12-H), 6.70 (1 H, d, <i>J</i> 10 Hz, 4-H), 7.50 (3 H, m, 8-, 9-, and 10-H), 8.16 (1 H, m, 7-H), and 10.8 (1 H, s, exchanged with D ₂ O, 5-OH)
(21)	80 (1 : 4)	178—179 (178—180) ¹⁰	C ₁₉ H ₁₆ O ₅	70.2 (70.4)	5.0 (4.9)	1.50 (6 H, s, CMe ₂), 3.90 (3 H, s, 10-OMe), 5.56 (1 H, d, <i>J</i> 10 Hz, 3-H), 6.30 (1 H, s, 12-H), 6.67 (1 H, d, <i>J</i> 10 Hz, 4-H), 7.15 (2 H, m, 8- and 9-H), 7.72 (1 H, q, 7-H), and 13.32 (1 H, s, exchanged with D ₂ O, 5-OH)
(22)	90 (1 : 9)	184—185 (184) ¹⁸	C ₁₉ H ₁₆ O ₅	70.3 (70.4)	5.1 (4.9)	1.47 (6 H, s, CMe ₂), 3.86 (3 H, s, 8-OMe), 5.55 (1 H, d, <i>J</i> 10 Hz, 3-H), 6.25 (1 H, s, 12-H), 6.67 (1 H, d, <i>J</i> 10 Hz, 4-H), 7.25 (2 H, m, 9- and 10-H), 7.50 (1 H, m, 7-H), and 13.44 (1 H, s, exchanged with D ₂ O, 5-OH)
(23)	80 (3 : 1)	189—190	C ₁₉ H ₁₆ O ₄	73.8 (74.0)	5.3 (5.2)	1.56 (6 H, s, CMe ₂), 4.02 (3 H, s, 6-OMe), 5.68 (1 H, d, <i>J</i> 10 Hz, 2-H), 6.38 (1 H, s, 5-H), 6.95 (1 H, d, <i>J</i> 10 Hz, 1-H), 7.55 (3 H, m, 9-, 10-, and 11-H), and 8.35 (1 H, m, 8-H)
(24)	90 (4 : 1)	274—275 (273—275) ⁸	C ₂₀ H ₁₈ O ₅	70.8 (71.0)	5.4 (5.3)	1.53 (6 H, s, CMe ₂), 3.98 (6 H, s, 6- and 11-OMe), 5.55 (1 H, d, <i>J</i> 10 Hz, 2-H), 6.26 (1 H, s, 5-H), 6.96 (1 H, d, <i>J</i> 10 Hz, 1-H), 7.18 (2 H, m, 9- and 10-H), and 7.80 (1 H, q, 8-H)
(25)	80 (3 : 1)	164—165	C ₂₀ H ₁₈ O ₅	70.8 (71.0)	5.5 (5.3)	1.50 (6 H, s, CMe ₂), 3.89 and 3.98 (each 3 H, each s, 6- and 9-OMe), 5.56 (1 H, d, <i>J</i> 10 Hz, 2-H), 6.28 (1 H, s, 5-H), 6.84 (1 H, d, <i>J</i> 10 Hz, 1-H), 7.26 (2 H, m, 10- and 11-H), and 7.63 (1 H, m, 8-H)

^a Values in parentheses given after the yield are the ratio of benzene-light petroleum used as eluant. ^b Mixture of (3) + (4) + (5) separated by column chromatography on silica gel, eluting with light petroleum for (3), benzene-light petroleum (1 : 19) for (4) and benzene-light petroleum (3 : 7) for (5). ^c Mixture of (10) + (11) + (12) separated by column chromatography on silica gel, eluting with benzene-light petroleum (1 : 4) for (10), benzene-light petroleum (1 : 3) for (11) and benzene-light petroleum (1 : 1) for (12). ^d Mixture of (15) + (16) + (17) separated by column chromatography on silica gel, eluting with benzene-light petroleum (1 : 9) for (15), benzene-light petroleum (1 : 4) for (16) and benzene-light petroleum (2 : 3) for (17). Recrystallisation solvents ^e light petroleum; ^f benzene-light petroleum; ^g benzene; ^h CD₃COCD₃.

(Na_2SO_4) and distilled. The residue thus obtained was purified by column chromatography and the column eluted with benzene–light petroleum (1 : 2) to give compound (1) as colourless prisms (0.46 g), m.p. 119–120 °C. The compounds prepared in this way are given in the Table.

2,2-Dimethyl-2H,12H-pyrano[2,3-a]xanthen-12-one (2).—Compound (1) (0.1 g) was refluxed with 3-chloro-3-methylbut-1-yne (0.6 ml) in dioxan (15.0 ml) for 48 h in the presence of anhydrous K_2CO_3 (0.5 g) and anhydrous KI (0.08 g). The inorganic salts were filtered off, the dioxan distilled and the residue treated with crushed ice. It was then extracted with ether, the ether distilled off and the residue purified by column chromatography, eluting with benzene–light petroleum (1 : 2) to give compound (2) as colourless needles (0.04 g), m.p. 116–117 °C.

Dehydrogenation of 3,4-Dihydro-2,2-dimethyl-2H,12H-pyrano[2,3-a]xanthen-12-one (1) with DDQ. *General Procedure.*—Compound (1) (0.1 g, 0.36 mmol) in dry benzene (15.0 ml) was refluxed for 70 h with DDQ (0.09 g, 0.4 mmol). The solution was filtered, the filtrate distilled and the residue thus obtained was purified by column chromatography, eluting with benzene–light petroleum (1 : 2) to give (2) as colourless needles (0.08 g), m.p. 116–117 °C. The products obtained in this way are given in the Table.

3,4-Dihydro-5-methoxy-2,2-dimethyl-2H,6H-pyrano[3,2-b]xanthen-6-one (6). *General Procedure for Methylation.*—Compound (3) (0.1 g, 0.34 mmol) in dry acetone (20.0 ml) was refluxed with Me_2SO_4 (0.03 ml, 0.34 mmol) in the presence of anhydrous K_2CO_3 (0.4 g) for 8 h. The inorganic salts were filtered off and washed with more acetone. The combined filtrate was distilled and the residue treated with crushed ice. The separated solid was then crystallised from benzene–light petroleum to give compound (6) as colourless plates (0.094 g), m.p. 138–139 °C. The compounds obtained in this way are given in the Table.

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