Claisen Rearrangement of 1-Hydroxy-3-(3-methylbut-2-enyloxy)xanthones [1]

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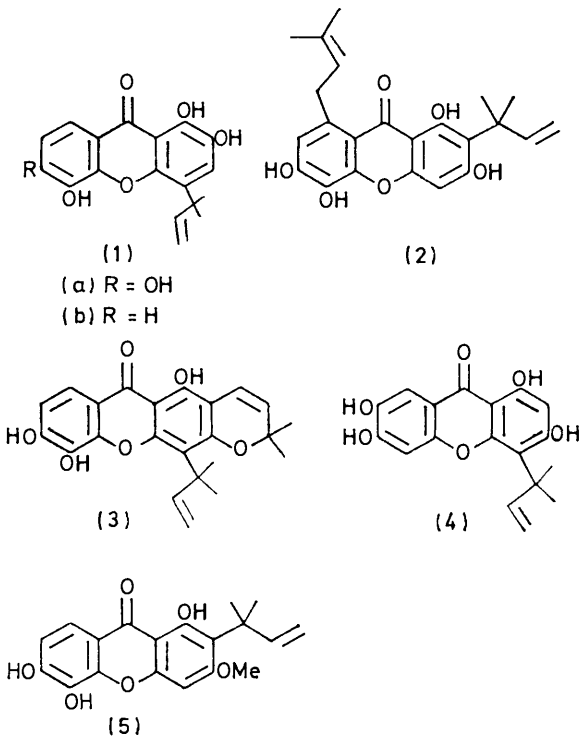
Claisen rearrangements of 1-hydroxy-3-(3-methylbut-2-enyloxy)xanthone (6a) and its 7-methoxy- (6b) and 6-methoxy- (6c) derivatives at 200—210° *in vacuo* yield mixtures of the corresponding dealkenylated xanthones (7a—c), angularly condensed 4,4,5-trimethyl-4,5-dihydrofuro-derivatives (8a—c), and their linear isomers (9a—c). These results show that normal Claisen rearrangement occurs in both the available *ortho*-positions, *viz.* 2 and 4, and is followed by spontaneous cyclisation to give linearly and angularly condensed dihydrofuro-derivatives. However, 1-hydroxy-5-methoxy-(3-methylbut-2-enyloxy)xanthone (6d) affords, besides the dealkenylated xanthone (7d), only linearly condensed dihydrofuroxanthones (9d) and (14).

AMONG naturally occurring isopentenylated xanthones, the C_5 unit is generally present as either 3-methylbut-2-enyl or condensed 2,2-dimethylpyran,[2] and such units have been introduced synthetically into hydroxyxanthones in a variety of ways.[3-11] The C_5 unit can also be present as 1,1-dimethylallyl; this unit has been formed by the Claisen rearrangement [12,13] of (3-methylbut-2-enyloxy)xanthones in a few cases. Thus 3,5,6-trimethoxy-1-(3-methylbut-2-enyloxy)xanthone yielded 2-(1,1-dimethylallyl) and 4-(3-methylbut-2-enyl) derivatives; the latter is the trimethyl ether of ugaxanthone, obtained from the heartwood of *Symphonia globulifera*.[14] The inversion of the alkenyl unit in the *ortho*-position and its retention in the *para*-position follow from the normal single and double intramolecular rearrangements.

In nature, the two xanthones symphoxanthone (1a) and globuxanthone (1b) contain a 1,1-dimethylallyl unit at C-4 and are hydroxylated at C-1 and C-2.[15] Their synthesis is difficult to achieve from the Claisen rearrangement of the corresponding 1-(3-methylbut-2-enyloxy)-xanthones, because this should yield the 4-(3-methylbut-2-enyl) derivative. However, four more 1,1-dimethylallylated xanthones, *viz.* alvaxanthone (2),[16] maclura-xanthone (3),[17] 1,3,6,7-tetrahydroxy-4-(1,1-dimethylallyl)xanthone (4),[18a] and cudraniaxanthone (5) [18b] are 1,3-dioxygenated compounds and have a 1,1-dimethylallyl unit at C-2 or C-4 and their synthesis may be accomplished by the Claisen rearrangement of the corresponding 1-hydroxy-3-(3-methyl-2-butenyloxy)-xanthone. Hence with a view to synthesising some of these natural compounds, the Claisen rearrangement of some model 1-hydroxy-3-(3-methylbut-2-enyloxy)xanthones has been studied.

1-Hydroxy-3-(3-methylbut-2-enyloxy)xanthone (6a), prepared by treating 1,3-dihydroxyxanthone (7a) with 1 mol. equiv. of 3-methylbut-2-enyl bromide and



characterised by the n.m.r. doublet of the methyleneoxy group at δ 4·72 (*J* 7 Hz), was subjected to the Claisen rearrangement by heating either alone *in vacuo* at 200—210° or with quinoline at 230—240°. In the first

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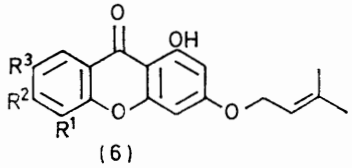
reaction a mixture of three products formed which was initially separated by alkali. The alkali-soluble part gave 1,3-dihydroxyxanthone (7a) and the insoluble part, after chromatographic separation, gave two isomeric products which were also isomeric with the starting material. Both gave a positive reaction with iron(III) and had only one free hydroxy-group [indicated by the formation of monoacetates and monomethyl ether having no iron(III) reaction]. Both have a condensed 4,4,5-trimethyl-4,5-dihydrofuro-unit as indicated by two singlets for two tertiary methyl groups, one doublet for a secondary methyl group and a fine quartet for one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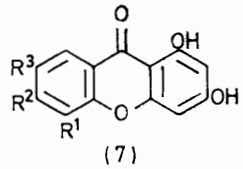
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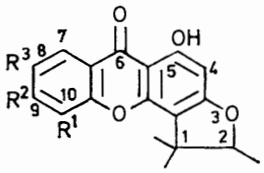
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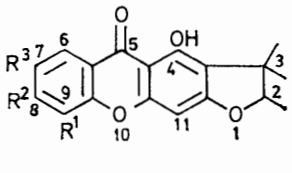
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a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^2 = H$, $R^3 = OMe$
c; $R^1 = R^3 = H$, $R^2 = OMe$
d; $R^1 = OMe$, $R^2 = R^3 = H$

proton in their n.m.r. spectra. The n.m.r. spectra further revealed that ring A has only one aromatic proton and that the ring B protons are intact. Hence the products must have a 4,4,5-trimethyl-4,5-dihydrofuro-ring condensed in either a linear or an angular way. The less polar compound proved to be the angular isomer (8a) because the ring A proton showed a marked downfield shift in its acetate (see the Table). Similarly

Comparison of n.m.r. chemical shifts (δ values) of ring A protons in hydroxy- and corresponding acetoxy-xanthones

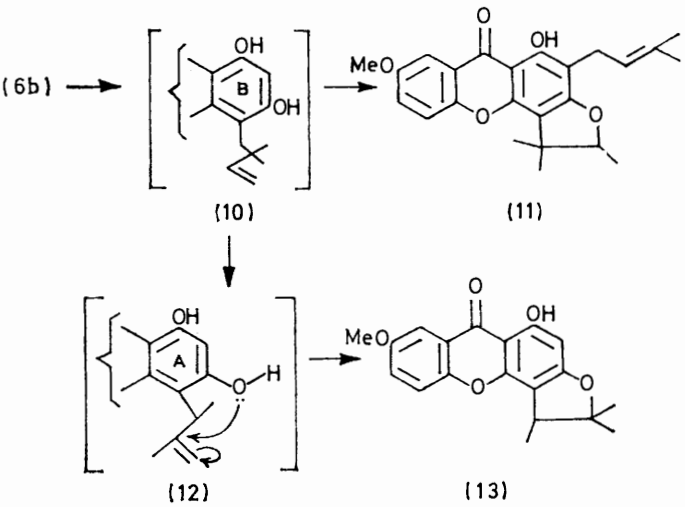
Compound	δ (H-2)	δ (H-4)	Δδ
Angular dihydrofuroxanthone (8a)	6·22		0·68
Acetate	6·90		
Linear dihydrofuroxanthone (9a)		6·20	0·32
Acetate		6·52	
Angular dihydrofuroxanthone (8b)	6·26		0·42
Acetate	6·68		
Linear dihydrofuroxanthone (9b)		6·18	0·28
Acetate		6·46	
Angular dihydrofuroxanthone (8c)	6·23		0·35
Acetate	6·58		
Linear dihydrofuroxanthone (9c)		6·30	0·10
Acetate		6·40	
Linear dihydrofuroxanthone (9d)		6·43	0·15
Acetate		6·58	

the more polar product was identified as the linear derivative (9a) because the ring A proton did not show any significant shift in its acetate.

When the foregoing Claisen rearrangement was carried out in quinoline, the reaction mixture decomposed extensively, but the same mixture [(8a) and (9a)] was obtained, albeit in considerably reduced yields. The formation of these dihydrofuro-derivatives can be explained by the occurrence of a normal Claisen rearrangement in both the available *ortho* positions to give (1,1-dimethylallyl)xanthones followed by spontaneous cyclisation involving the 3-hydroxy-group. This result is the same as observed in the Claisen rearrangement of 7-*O*-(3-methylbut-2-enyl)chrysin,[19] but different from that of 2-hydroxy-4-(3-methylbut-2-enyloxy)deoxybenzoin [20] where cyclised products resulted from normal and abnormal Claisen rearrangements. In order to check if the normal behaviour is general and that no demethylation occurs as in 3-*O*-methyl-7-*O*-(3-methylbut-2-enyl)galangin,[19] the Claisen rearrangement of three methoxylated 1-hydroxy-3-(3-methylbut-2-enyloxy)xanthones was studied.

1-Hydroxy-7-methoxy-3-(3-methylbut-2-enyloxy)xanthone [5] (6b) when heated *in vacuo* at 200—210° gave 1,3-dihydroxy-7-methoxyxanthone (7b) and the angular and linear furoxanthones (8b) and (9b), respectively identified as above. No demethylation occurred in any product.

After the completion of the above work, a paper by Scheinmann *et al.*[7] appeared in which the same Claisen rearrangement was carried out in *NN*-dimethylaniline medium. They also obtained three products of which only the first (7b) was the same; the other two were the angularly condensed furoxanthones (11) and (13). The formation of (11) may be explained by normal Claisen rearrangement to (10) followed by spontaneous cyclisation to the angular dihydrofuroxanthone which undergoes further (3-methylbut-2-enyl)ation by an intermolecular process. On the other hand, the formation of (13) involves further rearrangement of (10) to (12) and subsequent cyclisation. The difference from our results could be due to experimental conditions.


(6b) → (10) (11) (12) (13)

1-Hydroxy-6-methoxy-3-(3-methylbut-2-enyloxy)xanthone (6c) was prepared from 1,3-dihydroxy-6-methoxy-

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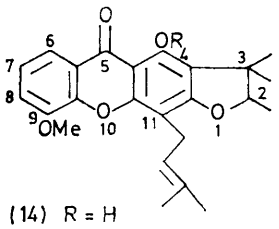
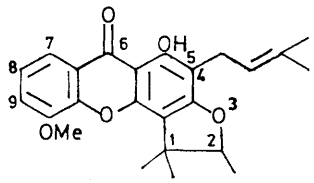
[20] A. C. Jain and S. M. Jain, *Indian J. Chem.*, 1972, **10**, 971.

xanthone [21] (7c) by the reaction with 1 mol. equiv. of 3-methylbut-2-enyl bromide and was characterised by a doublet for a methyleneoxy proton at δ 4·58 (*J* 7 Hz) in its n.m.r. spectrum. The products of the Claisen rearrangement were (7c), (8c), and (9c) which were similar to those described above. However 1-hydroxy-5-methoxy-3-(3-methylbut-2-enyloxy)xanthone [22] (6d) yielded a different mixture. Besides the dealkenylated xanthone (7d),[23] two other products were obtained. The less polar product, obtained in minor amount, analysed for a di-isopentenylated derivative of (7d). These two isopentenyl units were identified as 3-methylbut-2-enyl and condensed 4,4,5-trimethyl-4,5-dihydrofuro in ring A, on the basis of its n.m.r. spectrum. Thus there was no free aromatic proton in ring A but two singlets of two tertiary methyl groups at δ 1·30 and 1·53, a doublet of one secondary methyl group centred at 1·43 (*J* 7 Hz), a doublet of two unsaturated methyls at 1·80 (*J* 10 Hz), a doublet of two benzylic protons at 3·46 (*J* 7 Hz), a quartet of one proton centred at 4·53 (*J* 7 Hz), and a triplet of one methine proton at 5·33, besides signals for the other expected protons. Hence this product could be either the linear furoxanthone (14) or



(14) R = H
(16) R = Me



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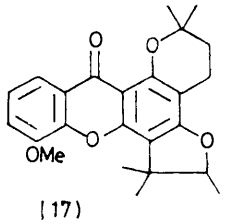

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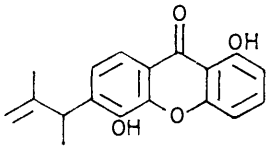

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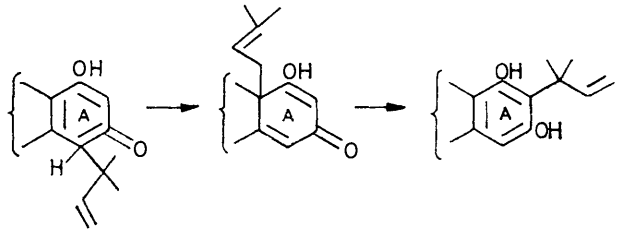
its angular isomer (15). The former structure was proved by its reaction with formic acid when the starting material was recovered even after prolonged heating. Had it been the angular isomer (15), it would have formed the corresponding dihydropyrano-dihydrofuro-derivative (17). The structure (14) having a *p*-(3-methylbut-2-enyl)phenol system was further confirmed by its mass spectrum which showed no $(M - 56)^+$ fragment [24] but characteristic fragment ions at *m/e* 379, 351, and 339. The more polar major product was identified as the linear furoxanthone (9d). Thus only linear dihydrofuro-derivatives could be isolated. These results are also different from those of Scheinmann *et al.*[7] who did not get any linear dihydrofuro-derivative but isolated only the angular dihydrofuro-derivative (8d); this result could again be due to different experimental conditions.

Two points warrant comment. First, no acyclic *O*-(1,1-dimethylallyl)phenolic products could be isolated. This might be due to the presence of an acidic 3-hydroxy-group which enhances cyclisation, because the Claisen rearrangement of 1-hydroxy-5-(3-methylbut-2-enyloxy)xanthone earlier [8] did yield the cyclic rearrangement product (18) having a less acidic 5-hydroxy-group. Secondly, with regard to the reason for allyl migration



(19) (20) (21)

to both position C-2 and C-4 in the present experiments while previous work [7,25] has shown exclusive migration to C-4: the reason may be that rearrangement does take place first at C-4 position (19) even in our experiments but since enolisation is not helped by solvent, further migration occurs first to the position *para* to 3-hydroxy (20) at the ring junction and finally to C-2 (21).

EXPERIMENTAL

U.v. data are recorded in MeOH and the figures in parentheses after $\lambda_{max.}$ are log ε values. I.r. spectra were measured on a Perkin-Elmer infrared spectrophotometer and n.m.r. spectra were recorded on a 60 MHz machine in $CDCl_3$. Light petroleum used had b.p. 60—80°; silica gel was used for column chromatography and t.l.c. was carried out on silica gel G Chromoplates using one of the following solvents systems; (A) benzene, (B) benzene–ethyl acetate (95 : 5), (C) benzene–ethyl acetate (90 : 10). The plates were sprayed with either 10% H_2SO_4 or 1% alcoholic $FeCl_3$.

1-*Hydroxy*-3-(3-*methylbut*-2-*enyloxy*)*xanthen*-9-*one* (6a).—To an acetone solution of 1,3-dihydroxyxanthone (7a) (250 mg) was added 3-methylbut-2-enyl bromide (0·12 ml) and potassium carbonate (1 g). The mixture was refluxed for 4 h. Acetone was removed and water added, and the solid thus obtained crystallised from benzene–light petroleum yielding the *xanthone* (6a) as light yellow needles (200 mg), m.p. 147—149°; reddish brown Fe(III) reaction; R_F 0·6 (solvent B); δ 1·85 (6H, d, *J* 2 Hz, Me_2C=), 4·72 (2H, d, *J* 7 Hz, $-OCH_2$), 5·66 (1H, m, $-CH$=), 6·50 and 6·54 (2H, 2d, *J* 2 Hz, H-2 and H-4), 7·55 (3H, m, H-5, -6, and -7), and 7·84 (1H, m, H-8) (Found: C, 72·9; H, 5·3. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%).

Claisen Rearrangement of the Xanthone (6a).—*Method* (*a*). The xanthone (6a) (4 g) was heated in vacuum at 200—210° for 2 h. The product was taken up in ether and extracted

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[25] G. S. Puranik and S. Rajagopal, *Rec. Trav. chim.*, 1965, **84**, 1014.

with aqueous 10% Na_2CO_3. The alkaline solution on acidification gave 1,3-dihydroxyxanthone (7a) (1 g). The ether-soluble fraction showed two spots on t.l.c. (solvent B). It was subjected to column chromatography and eluted with light petroleum–benzene (90 : 10 followed by 70 : 30) to give two fractions, A and B.

Fraction A crystallised from benzene–light petroleum to give 1,2-*dihydro*-5-*hydroxy*-1,1,2-*trimethylfuro*[2,3-c]*xanthen*-6-*one* (8a) as yellow needles (0·35 g), m.p. 153—155°; green Fe(III) reaction; R_F 0·9 (solvent B); δ 1·27 and 1·49 (6H, 2s, two tertiary Me), 1·37 (3H, d, *J* 7 Hz, secondary Me), 4·50 (1H, q, *J* 7 Hz, H-2), 6·22 (1H, d, H-4), 7·52 (3H, m, H-8, -9, and -10), and 8·17 (1H, m, H-7) (Found: C, 73·0; H, 5·4. $C_{18}H_{16}O_4$ requires C, 72·9; H, 5·4%). The *acetate* (prepared using acetic anhydride–pyridine) crystallised from EtOAc–light petroleum as white flakes, m.p. 145—147°; R_F 0·5 (solvent B); δ 1·25 and 1·50 (6H, 2s, two tertiary Me), 1·42 (3H, d, *J* 6 Hz, secondary Me), 2·58 (3H, s, OAc), 4·67 (1H, q, *J* 6 Hz, 2-H), 6·90 (1H, s, 4-H), 7·54 (3H, m, H-8, -9, and -10), and 7·81 (1H, m, H-7) (Found: C, 71·3; H, 5·7. $C_{20}H_{18}O_5$ requires C, 71·0; H, 5·3%).

Fraction B gave 2,3-*dihydro*-4-*hydroxy*-2,3,3-*trimethylfuro*[3,2-b]*xanthen*-5-*one* (9a) which crystallised from benzene as yellow needles (0·7 g), m.p. 179—181°; green Fe(III) reaction; R_F 0·65 (solvent B); δ 1·25 and 1·50 (6H, 2s, two tertiary Me), 1·42 (3H, d, *J* 7 Hz, secondary Me), 4·63 (1H, q, *J* 7 Hz, H-2), 6·20 (1H, s, H-11), 7·35 (3H, m, H-7, -8, and -9), and 8·18 (1H, m, H-6) (Found: C, 72·8; H, 5·4. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%). The *acetate* (Ac_2O–py) crystallised from EtOAc–light petroleum mixture as white needles, m.p. 134—136°; R_F 0·7 (solvent C); δ 1·42 and 1·61 (6H, s, two tertiary Me), 1·46 (3H, d, *J* 7 Hz, secondary Me), 2·48 (3H, s, OAc), 4·65 (1H, q, *J* 7 Hz, 2-H), 6·52 (1H, s, H-11), 7·41 (3H, m, H-7, -8, and -9), and 8·20 (1H, m, H-6) (Found: C, 70·9; H, 5·6. $C_{20}H_{18}O_5$ requires C, 71·0; H, 5·3%).

The 4-O-*methyl ether* was prepared by refluxing the xanthone (9a) (250 mg) with dimethyl sulphate (0·1 ml) and K_2CO_3 (2 g) in acetone until the Fe(III) reaction was negative, and crystallisation from methanol afforded light yellow plates (200 mg), m.p. 200—202°; R_F 0·35 (solvent C); δ 1·36 and 1·62 (6H, 2s, two tertiary Me), 1·46 (3H, d, *J* 7 Hz, secondary Me), 4·06 (3H, s, OCH_3), 4·69 (1H, q, *J* 7 Hz, H-2), 6·45 (1H, s, H-11), 7·61 (3H, m, H-7, -8, and -9), and 7·75 (1H, m, H-6) (Found: C, 73·6; H, 5·9. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·8%).

Method (*b*). A solution of the xanthone (6a) (3·5 g) in quinoline (40 ml) was refluxed over a sand-bath for 10 h. The mixture was then cooled and acidified with HCl and extracted with ether. The residue from evaporation yielded on column chromatography (8a) (150 mg) and (9a) (300 mg) identical (m.p. and t.l.c.) with the samples described above.

Claisen Rearrangement of 1-*Hydroxy*-7-*methoxy*-3-(3-*methylbut*-2-*enyloxy*)*xanthen*-9-*one* (6b).—The xanthone (6b) [5] (4 g) was heated in vacuum at 200—210° for 2 h. The product was taken up in ether and the ether solution extracted with aqueous 10% Na_2CO_3. The carbonate extract on acidification gave 1,3-dihydroxy-7-methoxyxanthone (7b) (1·2 g). The residue from evaporation of the ethereal extracts on column chromatography [elution with light petroleum followed by light petroleum–EtOAc (95 : 5)] gave two fractions, A and B.

Fraction A crystallised from methanol to give 1,2-*dihydro*-5-*hydroxy*-8-*methoxy*-1,1,2-*trimethylfuro*[2,3-c]*xanthen*-6-*one* (8b) as light yellow needles (0·3 g), m.p. 210—212°; green Fe(III) reaction; R_F 0·48 (solvent A); $\lambda_{max.}$ 269, 301, and 386 nm (4·58, 4·02, and 3·68); δ 1·27 and 1·52 (6H, 2s, two tertiary Me), 1·41 (3H, d, *J* 6·5 Hz, secondary Me), 3·89 (3H, s, OCH_3), 4·50 (1H, q, *J* 6·5 Hz, H-2), 6·26 (1H, s, H-4), 7·25 (2H, m, H-9 and -10), and 7·54 (1H, m, H-7) (Found: C, 69·9; H, 5·7. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·6%). The *acetate* (Ac_2O–py) crystallised from EtOAc–light petroleum as white flakes, m.p. 172—173°; R_F 0·57 (solvent B); $\lambda_{max.}$ 264, 308, and 362 nm (4·44, 4·53, and 3·83); δ 1·25 and 1·48 (6H, 2s, two tertiary Me), 1·41 (3H, d, *J* 8 Hz, secondary Me), 2·63 (3H, s, OAc), 3·90 (3H, s, OCH_3), 4·49 (1H, q, H-2), 6·68 (1H, s, H-4), 7·24 (2H, m, H-9 and -10), and 7·59 (1H, m, H-7) (Found: C, 68·7; H, 5·6. $C_{21}H_{20}O_6$ requires C, 68·5; H, 5·5%). The *methyl ether* (Me_2SO_4–K_2CO_3) crystallised from $CHCl_3$–light petroleum as a white solid (200 mg), m.p. 176—177°; R_F 0·5 (solvent B); $\lambda_{max.}$ 264, 308, and 362 nm (4·52, 4·34, and 3·74) (Found: C, 70·9; H, 6·4. $C_{20}H_{20}O_5$ requires C, 70·6; H, 6·0%).

Fraction B crystallised from methanol to yield 2,3-*dihydro*-4-*hydroxy*-7-*methoxy*-2,3,3-*trimethylfuro*[3,2-b]*xanthen*-5-*one* (9b) as yellow needles (0·5 g), m.p. 146—147°; green Fe(III) reaction; R_F 0·38 (solvent A); $\lambda_{max.}$ 262, 302, and 368 nm (4·49, 3·24, and 3·62); δ 1·27 and 1·54 (6H, 2s, two tertiary Me), 1·39 (3H, d, *J* 7 Hz, secondary Me), 3·86 (3H, s, OCH_3), 4·50 (1H, q, *J* 7 Hz, H-2), 6·18 (1H, s, H-11), 7·24 (2H, m, H-8 and -9), and 7·3 (1H, m, H-6) (Found: C, 69·8; H, 5·7. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·6%). The *acetate* (Ac_2O–py) crystallised from EtOAc–light petroleum as white flakes, m.p. 150—151°; R_F 0·5 (solvent B); δ 1·37 and 1·62 (6H, 2s, two tertiary Me), 1·47 (3H, d, *J* 7 Hz, secondary Me), 2·49 (3H, s, OAc), 3·90 (3H, s, OCH_3), 4·60 (1H, q, *J* 7 Hz, 2-H), 6·46 (1H, s, H-11), 7·28 (2H, m, H-8 and -9), and 7·61 (1H, m, H-6) (Found: C, 68·7; H, 5·6. $C_{21}H_{20}O_6$ requires C, 68·5; H, 5·5%). The 4-O-*methyl ether* (Me_2SO_4–K_2CO_3) crystallised from $CHCl_3$–light petroleum as cream needles (175 mg), m.p. 162—163°; R_F 0·4 (solvent B); $\lambda_{max.}$ 264, 301, and 372 nm (4·52, 4·32, and 3·60) (Found: C, 70·4; H, 6·3. $C_{20}H_{20}O_5$ requires C, 70·6; H, 6·0%).

1-*Hydroxy*-6-*methoxy*-3-(3-*methylbut*-2-*enyloxy*)*xanthen*-9-*one* (6c).—To an acetone solution of 1,3-dihydroxy-6-methoxyxanthone (7c) [21] (4 g) was added 3-methylbut-2-enyl bromide (2 ml) and dry K_2CO_3 (20 g) and the mixture was refluxed for 4 h. Acetone was removed and water added, and the resulting solid crystallised from $CHCl_3$–light petroleum as pale yellow *flakes* (6c) (2 g); m.p. 110—112°; R_F 0·52 (solvent B); reddish green Fe(III) reaction; δ 1·79 (6H, d, Me_2C=), 3·83 (3H, s, OCH_3), 4·58 (2H, d, *J* 7 Hz, $-OCH_2$), 5·0 (1H, t, *J* 6 Hz, $-CH$=), 6·34 (2H, d, *J* 2 Hz, H-2 and -4), 6·86 (2H, m, H-5 and -6), and 8·13 (1H, d, *J* 9 Hz, H-8) (Found: C, 69·9; H, 5·3. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·6%).

Claisen Rearrangement of the Xanthone (6c).—The xanthone (6c) (5 g) was heated at 200—210° for 3 h *in vacuo*. The product was extracted with aqueous 10% Na_2CO_3 which on acidification gave 1,3-dihydroxy-6-methoxyxanthone (7c) (1·5 g). The remaining product on chromatography [elution with benzene–light petroleum (1 : 1) and (3 : 1)] yielded two fractions, A and B.

Fraction A crystallised from benzene–light petroleum to afford 1,2-*dihydro*-5-*hydroxy*-9-*methoxy*-1,1,2-*trimethylfuro*-[2,3-c]*xanthen*-6-*one* (8c) as yellow needles (250 mg), m.p. 152—154°; green Fe(III) reaction, R_F 0·6 (solvent B); δ 1·30 and 1·56 (6H, 2s, two tertiary Me), 1·41 (3H, d,

J 7 Hz, secondary Me), 3·93 (3H, s, OCH_3), 4·53 (1H, q, *J* 7 Hz, H-2), 6·23 (1H, s, H-4), 6·80 and 7·0 (2H, 2d, *J* 3 Hz, H-8 and -10), and 8·16br (1H, d, *J* 10 Hz, H-7) (Found: C, 69·8; H, 6·1. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·6%). The *acetate* (Ac_2O–NaOAc) crystallised from EtOAc–light petroleum as white needles, m.p. 140—141°; R_F 0·7 (solvent B); δ 1·33 and 1·59 (6H, 2s, two tertiary Me), 1·43 (3H, d, *J* 7 Hz, secondary Me), 2·45 (3H, s, OAc), 3·91 (3H, s, OCH_3), 4·61 (1H, q, *J* 7 Hz, H-2), 6·58 (1H, s, H-2), 6·80 and 6·98 (2H, 2m, *J* 2·5 Hz, H-8 and -10), and 8·20 (1H, d, *J* 9 Hz, H-7) (Found: C, 68·1; H, 6·0. $C_{21}H_{20}O_6$ requires C, 68·5; H, 5·5%).

The 5-O-*methyl ether* (Me_2SO_4–K_2CO_3) crystallised from methanol as a cream powder (175 mg), m.p. 196—198°; R_F 0·6 (solvent C); δ 1·23 and 1·48 (6H, 2s, two tertiary Me), 1·38 (3H, d, *J* 7 Hz, secondary Me), 3·90 and 4·03 (6H, 2s, $2OCH_3$), 4·50 (1H, q, *J* 7 Hz, H-2), 6·57 (1H, s, H-4), 6·93 (2H, m, H-8 and -10), and 8·23 (1H, d, *J* 10 Hz, H-7) (Found: C, 70·8; H, 6·2. $C_{20}H_{20}O_5$ requires C, 70·6; H, 6·0%).

Fraction B crystallised from benzene to yield 2,3-*dihydro*-4-*hydroxy*-8-*methoxy*-2,3,3-*trimethylfuro*[3,2-b]*xanthen*-5-*one* (9c) as yellow flakes (0·6 g), m.p. 179—180°; green Fe(III) reaction; R_F 0·4 (solvent B); δ 1·26 and 1·54 (6H, 2s, two tertiary Me), 1·43 (3H, d, *J* 6·5 Hz, secondary Me), 3·89 (3H, s, OCH_3), 4·50 (1H, q, *J* 6 Hz, H-2), 6·31 (1H, s, H-11), 6·85 and 6·92 (2H, 2m, *J* 3·6 Hz, H-7 and -9), and 7·99 (1H, d, *J* 9 Hz, H-6) (Found: C, 70·3; H, 6·0. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·6%). The *acetate* (Ac_2O–NaOAc) crystallised from methanol as white flakes, m.p. 158—160°; R_F 0·54 (solvent B); δ 1·31 and 1·54 (6H, 2s, two tertiary Me), 1·45 (3H, d, *J* 6 Hz, secondary Me), 2·42 (3H, s, OAc), 3·94 (3H, s, OCH_3), 4·64 (1H, q, *J* 6 Hz, H-2), 6·40 (1H, s, H-11), 6·78 and 6·94 (2H, 2d, *J* 3 Hz, H-7 and -9), and 8·23 (1H, d, *J* 9 Hz, H-6) (Found: C, 68·0; H, 5·7. $C_{20}H_{20}O_6$ requires C, 68·5; H, 5·5%).

Claisen Rearrangement of the Xanthone (6d).—The xanthone (6d) (5 g) was heated *in vacuo* at 200—210° for 2 h. The product yielded 1,3-dihydroxy-5-methoxyxanthone as a sodium carbonate-soluble fraction. The remaining product on column chromatography and elution with light petroleum–benzene (9 : 1) gave two fractions, A and B.

Fraction A crystallised from methanol to give 2,3-*dihydro*-4-*hydroxy*-9-*methoxy*-2,3,3-*trimethyl*-11-(3-*methylbut*-2-*enyl*)-*furo*[3,2-b]*xanthen*-5-*one* (14) as yellow needles (250 mg), m.p. 128—129°; R_F 0·7 (solvent A); δ 1·30 and 1·53 (6H, 2s, two tertiary Me), 1·43 (3H, d, *J* 7 Hz, secondary Me). 1·80 (6H, d, *J* 10 Hz, Me_2C=), 4·53 (2H, q, *J* 7 Hz, CH_2), 3·99 (3H, s, OCH_3), 4·53 (1H, q, *J* 7 Hz, H-2), 5·33 (1H, t, –CH=), 7·20 (2H, m, H-7 and -8), and 7·80 (1H, q, H-6); *m/e* 394 (M^+), 379, 376, 351, and 339 (Found: C, 72·9; H, 6·7. $C_{24}H_{26}O_5$ requires C, 73·1; H, 6·6%). The *acetate* (Ac_2O–py) crystallised from methanol as white flakes, m.p. 168—169°; R_F 0·5 (solvent A); $\lambda_{max.}$ 268, 282, 319, and 380 nm (4·51, 4·49, 4·13, and 3·66); δ 1·16 and 1·37 (6H, 2s, two tertiary Me), 1·28 (3H, d, *J* 5 Hz, secondary Me), 1·72 (6H, d, *J* 8 Hz, Me_2C=), 2·42 (3H, s, OAc), 3·50 (2H, d, *J* 4 Hz, $-CH_2-$), 3·85 (3H, s, OCH_3), 4·40 (1H, q, *J* 4 Hz, H-2), 5·30 (1H, t, –CH=), 7·06 (2H, m, H-7 and -8), and 7·69 (1H, q, H-6) (Found: C, 72·0; H, 6·6. $C_{26}H_{28}O_6$ requires C, 71·5; H, 6·5%). The 4-O-*methyl ether* (Me_2SO_4–K_2CO_3) crystallised from $CHCl_3$ to give white flakes, m.p. 150°; R_F 0·6 (solvent D); $\lambda_{max.}$ 271, 286, 310, and 380 nm (4·58, 4·49, 4·43, and 3·52) (Found: C, 73·0; H, 7·0. $C_{25}H_{28}O_5$ requires C, 73·3; H, 6·8%).

Fraction B crystallised from benzene–light petroleum to give 2,3-*dihydro*-4-*hydroxy*-9-*methoxy*-2,3,3-*trimethylfuro*-[3,2-b]*xanthen*-5-*one* (9d) as yellow flakes (0·6 g), m.p. 158—159°; R_F 0·5 (solvent A); $\lambda_{max.}$ 264, 282, 312, and 369 nm (4·52, 4·38, 4·10, and 3·64); δ 1·28 and 1·50 (6H, 2s, two tertiary Me), 1·41 (3H, d, *J* 7 Hz, secondary Me), 3·99 (3H, s, OCH_3), 4·53 (1H, q, *J* 7 Hz, H-2), 6·43 (1H, s, H-11), 7·23 (2H, m, H-7 and -8), and 7·32 (1H, q, H-6) (Found: C, 69·7; H, 6·0. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·6%). The *acetate* (Ac_2O–py) crystallised from EtOAc–light petroleum as white flakes, m.p. 227—228°; R_F 0·5 (solvent B); δ 1·39 and 1·65 (6H, 2s, two tertiary Me), 1·57 (3H, d, *J* 7 Hz, secondary Me), 2·46 (3H, s, OAc), 3·99 (3H, s, OCH_3), 4·63 (1H, q, *J* 7 Hz, H-2), 6·58 (1H, s, H-11), 7·20 (2H, m, H-7 and -8), and 7·82 (1H, q, H-6) (Found: C, 68·6; H, 5·2. $C_{21}H_{20}O_6$ requires C, 68·5; H, 5·5%). The 4-O-*methyl ether* (Me_2SO_4–K_2CO_3) crystallised from benzene–light petroleum as cream needles, m.p. 243—244°; R_F 0·6 (solvent C) (Found: C, 70·3; H, 6·1. $C_{20}H_{20}O_5$ requires C, 70·5; H, 6·0%).

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