

## Structures of Two Dimers formed from Oroselol with Acids

By Vinayak S. Kamat, Thakur D. Audichya (in part), Girish K. Trivedi, and Sasanka C. Bhattacharyya,\*  
Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India

The unidentified, high melting substance previously encountered during investigations of naturally occurring furocoumarins, is shown to be 4-methyl-2,4-bis-(2-oxofuro[2,3-*h*][1]benzopyran-8-yl)pent-1-ene (XI). It is accompanied by the isomeric substance, 4-methyl-2,4-bis-(2-oxofuro[2,3-*h*][1]benzopyran-8-yl)pent-2-ene (XII). The formation of (XI) and (XII) from oroselol {8-(1-hydroxy-1-methylethyl)furo[2,3-*h*][1]benzopyran-2-one} (VII) can be explained as occurring *via* the carbonium ion (XVI) and its subsequent condensation with oroselone (8-isopropenylfuro[2,3-*h*][1]benzopyran-2-one) (XIV). This postulated mechanism is supported by the formation in high yield of 8-( $\alpha$ -dimethylbenzyl)- (VIII), 8-(*p*-methoxy- $\alpha$ -dimethylbenzyl)- (IX), and 8-(*p*-ethoxy- $\alpha$ -dimethylbenzyl)furo[2,3-*h*][1]benzopyran-2-one (X) from (VII) in the presence of Lewis acids.

SEVERAL furocoumarin derivatives such as vaginol<sup>1</sup> (I), edultin<sup>2</sup> (II), peucenidin<sup>3</sup> (III), libanotin<sup>4</sup> (IV), archangelicin<sup>5</sup> (V), and athamantin<sup>6</sup> (VI), have been found in the plants of the *Umbelliferae* family in which

they generally co-occur with oroselol (VII). In the presence of acidic reagents, compounds (II)—(IV) yield oroselone (XIV) along with an unidentified product, m.p. 204°.

In connection with our work on the *Umbelliferae*

<sup>1</sup> K. Rajendran, C. K. Mesta, S. K. Paknikar, and S. C. Bhattacharyya, *Indian J. Chem.*, 1970, **8**, 200.

<sup>2</sup> H. Mitsuhashi and T. Itoh, *Chem. and Pharm. Bull. (Japan)*, (a) 1961, **9**, 170; (b) 1962, **10**, 514.

<sup>3</sup> (a) A. P. Prokopenko, *Zhur. obshchei Khim.*, 1964, **34**(12), 4111 (*Chem. Abs.*, 1965, **62**, 9117c); (b) E. Lemmich, J. Lemmich, and B. E. Nielsen, *Acta Chem. Scand.*, 1970, **24**, 2893.

<sup>4</sup> A. P. Prokopenko, *Khim. prirod. Soedinenii Akad. Nauk. Uz. S.S.R.*, 1965, **3**, 215 (*Chem. Abs.*, 1965, **63**, 14,638f).

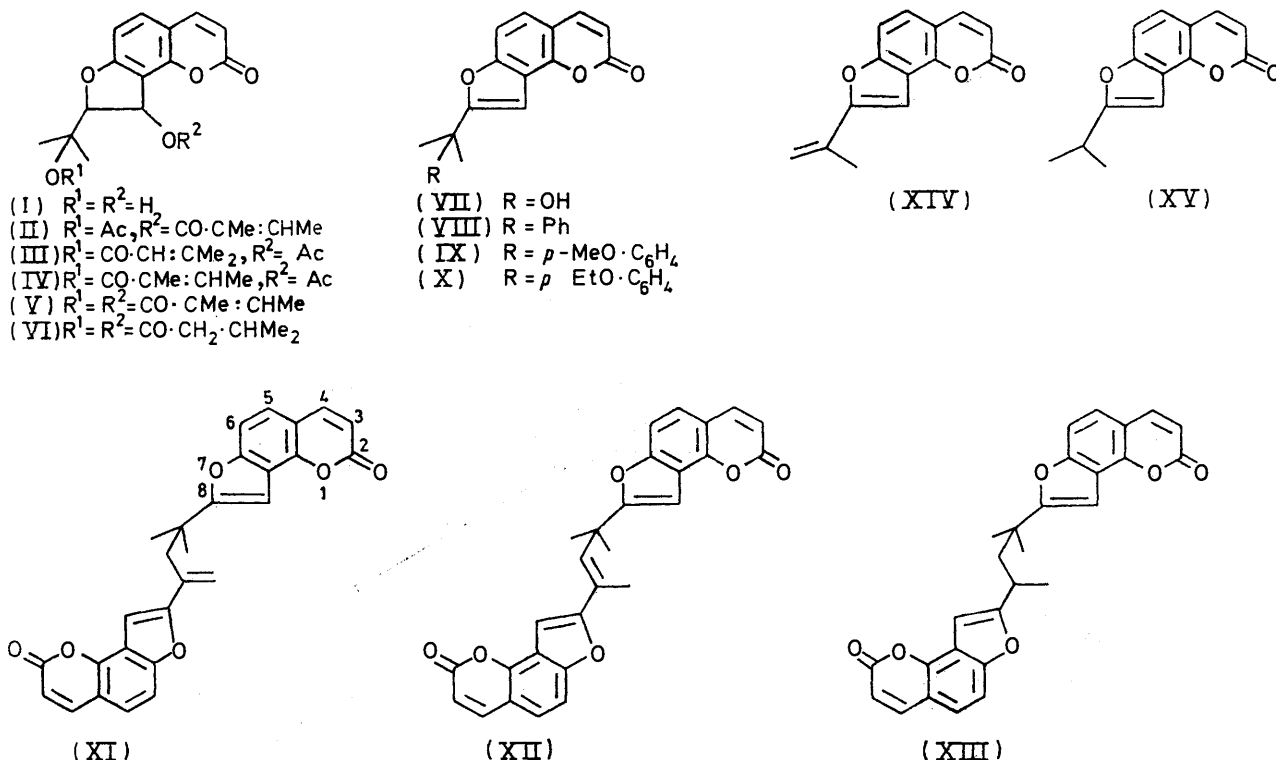
<sup>5</sup> B. E. Nielsen and J. Lemmich, *Acta Chem. Scand.*, 1964, **18**(4), 932.

<sup>6</sup> O. Halpern, P. Waser, and H. Schmid, *Helv. Chim. Acta*, 1957, **40**, 758.

plant, *Selinum vaginatum* C. B. Clarke,<sup>1,7</sup> we have isolated several furo- and pyrano-coumarins along with oroselol (VII). We now provide chemical and spectral evidence that the unknown substance encountered previously is the dimer (XI) of oroselone (XIV).

Oroselol (VII) in the presence of pyridine and phosphoryl chloride gave a nearly quantitative yield of oroselone (XIV), m.p. 179–180°. Hydrogenation of (XIV) in acetic acid in the presence of platinum oxide gave dihydro-oroselone (XV). The structures are supported by u.v., i.r., and n.m.r. spectra.

Similarly the magnetic equivalence of the geminal methyl protons was clear from the singlet at  $\tau$  8.53 (6H) and is in close agreement with the signal at  $\tau$  8.64 (6H) for (XV). Further, the two furanoid protons were seen at  $\tau$  3.47 (1H) and 3.38 (1H). The corresponding protons in (XIV) and (XV) absorbed at  $\tau$  3.08 (1H) and 3.29 (1H) respectively. In addition, the chemical shifts for 3- and 4-H of the two coumarin units were seen as two pairs of doublets ( $J$  9.5 Hz) at  $\tau$  3.81 (1H), 3.75 (1H) and 2.45 (1H), 2.41 (1H). The pairs of doublets ( $J$  8.5 Hz) at  $\tau$  2.67 (1H), 2.69 (1H) and 2.90 (1H),



Treatment of (VII) with methanolic hydrochloric acid (3:2) gave a mixture of (XIV) and the dimer (XI). On the other hand, treatment with boron trifluoride-ether complex in chloroform gave only traces of (XIV) and a much larger proportion of (XI), along with a small amount of its isomer (XII). Compounds (XI) and (XII) were also formed in variable yields when (VII) was treated with tin(IV) chloride or anhydrous aluminium chloride in chloroform.

The dimer (XI) ( $C_{28}H_{20}O_6$ ;  $M^+$  452) contains a *gem*-disubstituted alkene function, since the i.r. band at  $905\text{ cm}^{-1}$  (chloroform) disappears after hydrogenation of the substance in acetic acid in the presence of platinum oxide to give the dihydro-derivative (XIII) ( $M^+$  454). The major evidence for the structure of compound (XI) is a comparison of its n.m.r. spectrum with those of (XIV) and (XV). As in the spectrum of (XIV) [ $\tau$  4.74 (1H, q,  $J$  1 Hz) and 4.17 (1H, s) ( $>C=CH_2$ )], a pair of singlets was discernable in (XI) at  $\tau$  4.91 (1H) and 4.18 (1H) for the *gem*-disubstituted alkene protons.

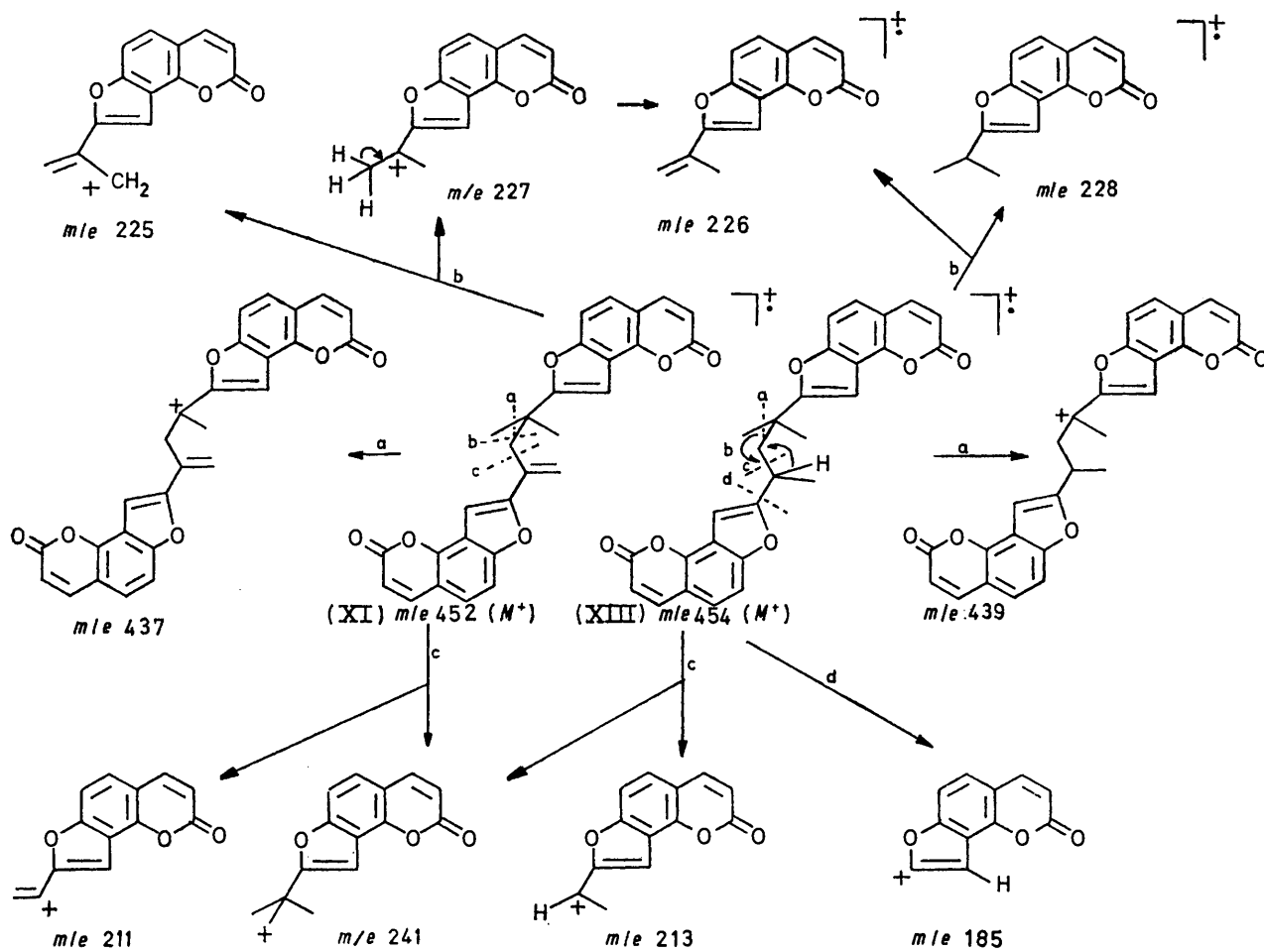
2.92 (1H) can be assigned to 5- and 6-H. The two methylenic protons were observed as a singlet at  $\tau$  7.14 (2H).

The presence of a *gem*-disubstituted alkene in (XI) was further supported by the absence of n.m.r. signals at  $\tau$  4.74 (1H) and 4.17 (1H) in (XIII) and the appearance of a doublet at  $\tau$  8.7 (3H,  $J$  7 Hz) due to a newly formed methyl group on a  $sp^3$  carbon atom. Besides this, the magnetic non-equivalence of the geminal methyl groups was clear from the singlets at  $\tau$  8.63 (3H) and 8.53 (3H). Also in agreement with the structure (XIII), the complex pattern at  $\tau$  8.3–6.8 (3H) corresponded to the two methylenic and a vicinal tertiary proton. The two furan protons exhibited two singlets at  $\tau$  3.76 (1H) and 3.72 (1H). The doublets at  $\tau$  3.76 (2H,  $J$  9.5 Hz), 2.46 (2H,  $J$  9.5 Hz), 2.82 (2H,  $J$  8.5 Hz), and 3.05 (2H,  $J$  8.5 Hz) corresponded to 3-, 4-, 5-, and

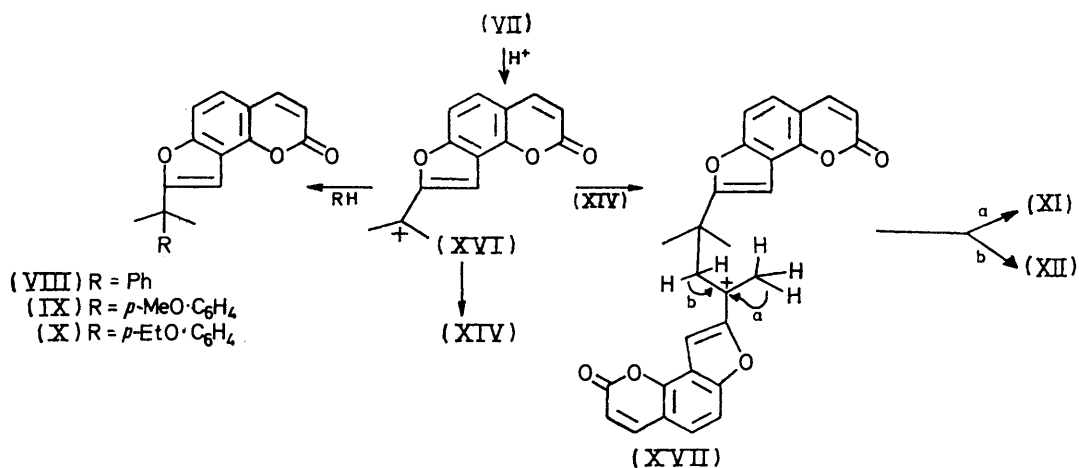
<sup>7</sup> (a) S. N. Shanbhag, C. K. Mesta, M. L. Maheshwari, S. K. Paknikar, and S. C. Bhattacharyya, *Tetrahedron*, 1964, 20, 2605; (b) C. K. Mesta, S. K. Paknikar, and S. C. Bhattacharyya, *Chem. Comm.*, 1968, 584.

6-H in the two coumarin units. The mass spectra of (XI) and (XIII) are in agreement with their structures. Compound (XII) ( $M^+ 452$ ) is isomeric with (XI) and can be obtained from the latter by acid equilibration. In the mass spectrum of (XI), the base peak is at  $m/e$  227, while in the mass spectrum of (XII), the ion at

$m/e$  437 ( $M^+ - \text{Me}$ ) is the base peak. Most of the major and significant ions in the mass spectra of (XI) and (XIII) are shown in Scheme 1. The mass spectrum of (XII) is similar to that of (XI) and (XIII). The fragmentation pattern is an added proof of the structure of (XII).



SCHEME 1



SCHEME 2

The mechanism in Scheme 2 can reasonably explain the formation of (XI) and (XII) from oroselol (VII) in the presence of Lewis acids. Oroselol in the presence of acidic reagents forms an intermediate ion (XVI), part of which is converted into (XIV) and the remainder reacting with the (XIV) formed to give another ion (XVII) which leads to the products (XI) and (XII). The formation of (XVI) is indicated by the ease of formation of the 8-(substituted benzyl) derivatives (VIII)—(X) in 60, 80, and 95% yields from oroselol on treatment with benzene, anisole, and ethyl phenyl ether respectively in the presence of anhydrous aluminium chloride, and of (IX) (90%) on treatment with anisole in the presence of boron trifluoride-ether complex. Only small amounts of (XI) and (XII) were obtained during the condensation with benzene and no detectable amount was obtained in the other three cases. However, (XI) and (XII) were formed in poor yield and (X) was not produced when (XIV) was treated with Lewis acids in chloroform and ethyl phenyl ether respectively.

#### EXPERIMENTAL

U.v. spectra were measured for solutions in ethanol on a Perkin-Elmer 402 u.v.-visible spectrophotometer. Unless otherwise stated i.r. spectra were measured for solutions in chloroform on a Perkin-Elmer 237B i.r. spectrophotometer. N.m.r. spectra were recorded for CDCl<sub>3</sub> solutions at 60 MHz using tetramethylsilane as internal standard. Neutral silica gel (Riedel) activated at 120° for 4 h was used for column chromatography. Solutions were dried by standard techniques. Chloroform was washed with aqueous (10%) H<sub>2</sub>SO<sub>4</sub>, water, dried (anhydrous K<sub>2</sub>CO<sub>3</sub>), and distilled.

**Isolation of Oroselol (VII).**—Oroselol was isolated from the petroleum extract of the roots of *Selinum vaginatum* C. B. Clarke, m.p. 149—150°,  $[\alpha]_D^{25}$  0° (Found: C, 68.95; H, 4.9. Calc. for C<sub>14</sub>H<sub>12</sub>O<sub>4</sub>: C, 68.85; H, 4.95%),  $\lambda_{\max}$  252 and 301 nm (log  $\epsilon$  4.40 and 4.02),  $\nu_{\max}$  (Nujol) 3460, 1725, 1700, 1620, 1580, 1383, 1374, 1309, 1279, 1160, 1135, 1100, 1075, 1025, 956, 930, 830, and 770 cm<sup>-1</sup>,  $\tau$  8.13 (6H, s), 3.68 (1H, d, *J* 9 Hz), 3.18 (1H, d, *J* 9 Hz), 3.1 (1H, s), 2.68 (1H, d, *J* 9 Hz), and 2.25 (1H, d, *J* 9 Hz).

**Oroselone (XIV).**—A mixture of oroselol (244 mg), dry pyridine (10 ml), and POCl<sub>3</sub> (0.6 ml) was heated in an oil-bath at 110° for 2 h. The mixture was cooled, poured into ice-water, and extracted with chloroform. The chloroform extract was successively washed with water, cold aqueous (10%) HCl, water, cold aqueous (5%) KOH, and water, dried, and concentrated to give a brownish residue. It was filtered through neutral alumina (grade III; 10 g) and washed with chloroform. The filtrate was concentrated and the residue recrystallised from alcohol to give *oroselone* (8-isopropenylfuro[2,3-h][1]benzopyran-2-one) (XIV) as needles (205 mg), m.p. 179—180° (Found: C, 74.0; H, 4.65. C<sub>14</sub>H<sub>10</sub>O<sub>3</sub> requires C, 74.35; H, 4.4%),  $\lambda_{\max}$  205, 284, 297, and 313sh nm (log  $\epsilon$  4.40, 4.58, 4.50, and 4.12);  $\nu_{\max}$  1727, 1623, 1554, 1450, 1406, 1375, 1300, 1275, 1154, 1125, 1110, 1073, 1024, 950, 905, and 840 cm<sup>-1</sup>,  $\tau$  7.86 (3H, d, *J* 1 Hz), 4.74 (1H, q, *J* 1 Hz), 4.17 (1H, s), 3.64 (1H, d, *J* 9.5 Hz), 3.08 (1H, s), 2.66 (2H, s), and 2.23 (1H, d, *J* 9.5 Hz).

**Dihydro-oroselone (XV).**—A mixture of oroselone (100 mg), acetic acid (5 ml), and platinum oxide (10 mg) was shaken in an atmosphere of hydrogen for 1 h. The catalyst

was filtered off, acetic acid was removed under vacuum, and the residue was extracted with chloroform, washed with water, dried, and concentrated. The residue was crystallised from alcohol to yield *dihydro-oroselone* (8-isopropylfuro[2,3-h][1]benzopyran-2-one) (XV) (98 mg), m.p. 142° (Found: C, 73.5; H, 5.05. C<sub>14</sub>H<sub>12</sub>O<sub>3</sub> requires C, 73.7; H, 5.25%),  $\lambda_{\max}$  205, 252, and 302 nm (log  $\epsilon$  4.44, 4.45, and 4.06),  $\nu_{\max}$  1725, 1620, 1588, 1448, 1400, 1384, 1372, 1328, 1298, 1272, 1148, 1112, 1075, 1016, 937, and 830 cm<sup>-1</sup>,  $\tau$  8.64 (6H, d, *J* 7 Hz), 6.88 (1H, m), 3.65 (1H, d, *J* 9.5 Hz), 3.29 (1H, s), 2.69 (2H, s), and 2.21 (1H, d, *J* 9.5 Hz).

**Treatment of Oroselol with Methanol-Hydrochloric Acid.**—Oroselol (138 mg) was dissolved in methanol (3 ml) and concentrated hydrochloric acid (2 ml) was added to it. The mixture was refluxed on a water-bath for 1 h, then cooled, poured into water, filtered, washed with water, and dried. The residue (120 mg) was chromatographed over silica gel (10 g). Chloroform-petroleum (3:7; 300 ml) eluted oroselone (XIV) (48 mg), m.p. 178—179° (from ethanol) (identical by mixed m.p. and t.l.c.). Elution with chloroform gave *4-methyl-2,4-bis-(2-oxofuro[2,3-h][1]benzopyran-8-yl)pent-1-ene* (XI) (60 mg). The product (XI) was dissolved in chloroform-ethanol and concentrated. The crystals which separated after cooling were recrystallised twice, m.p. 202—203° (Found: C, 74.4; H, 4.35. C<sub>28</sub>H<sub>20</sub>O<sub>6</sub> requires C, 74.35; H, 4.4%),  $\lambda_{\max}$  204, 257, 291, and 304 nm (log  $\epsilon$  4.70, 4.59, 4.54, and 4.51),  $\nu_{\max}$  1725, 1620, 1575, 1450, 1405, 1387, 1375, 1270, 1150, 1120, 1082, 1024, 905, and 835 cm<sup>-1</sup>,  $\tau$  8.53 (6H, s), 7.14 (2H, s), 4.91 (1H, s), 4.18 (1H, s), 3.81 (1H, d, *J* 9.5 Hz), 3.75 (1H, d, *J* 9.5 Hz), 3.47 (1H, s), 3.38 (1H, s), 2.96 (1H, d, *J* 8.5 Hz), 2.92 (1H, d, *J* 8.5 Hz), 2.69 (1H, d, *J* 8.5 Hz), 2.67 (1H, d, *J* 8.5 Hz), 2.45 (1H, d, *J* 9.5 Hz), and 2.41 (1H, d, *J* 9.5 Hz). The major peaks in the mass spectrum are shown in Scheme 1: the full spectrum is in Supplementary Publication No. SUP 21194 (4 pp.).\*

**Hydrogenation of (XI).**—Compound (XI) (100 mg) was shaken with acetic acid (5 ml) and PtO<sub>2</sub> (10 mg) in a hydrogen atmosphere. After completion of absorption the catalyst was filtered off and the filtrate was worked up as in the case of (XV) to give *2-methyl-2,4-bis-(2-oxofuro[2,3-h][1]benzopyran-8-yl)pentane* (XIII) (97 mg), m.p. 243° (from ethanol) (Found: C, 73.65; H, 5.4. C<sub>28</sub>H<sub>22</sub>O<sub>6</sub> requires C, 74.0; H, 4.9%),  $\lambda_{\max}$  205, 249, and 305 nm (log  $\epsilon$  4.66, 4.61, and 4.22),  $\nu_{\max}$  1724, 1612, 1575, 1440, 1400, 1372, 1265, 1147, 1112, and 825 cm<sup>-1</sup>,  $\tau$  8.7 (3H, d, *J* 7 Hz), 8.63 (3H, s), 8.53 (3H, s), 8.3—6.8 (3H, complex), 3.76 (2H, d, *J* 9.5 Hz), 3.76 (1H, s), 3.72 (1H, s), 3.05 (2H, d, *J* 8.5 Hz), 2.82 (2H, d, *J* 8.5 Hz), and 2.46 (2H, d, *J* 9.5 Hz). The main peaks of the mass spectrum are in Scheme 1, and the full spectrum in Supplementary Publication No. SUP 21194.

**Action of Boron Trifluoride-Ether Complex on Oroselol in Chloroform.**—Oroselol (976 mg) was dissolved in chloroform (60 ml), and boron trifluoride-ether complex (1 ml) was added. The solution changed from colourless to brownish and then to yellow giving finally a pale yellow, sticky mass. The mixture was stirred for 10 min at room temperature, water was added, and the mixture extracted with chloroform. The chloroform layer was washed with water until the aqueous layer was neutral to litmus, dried, and concentrated. The residue (800 mg) was chromatographed over silica gel (25 g). Elution with chloroform (100 ml)

\* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

gave (XIV) (20 mg), and further chloroform (500 ml) afforded (XI) (475 mg). Elution with chloroform-ethanol (9:1; 250 ml) gave 4-methyl-2,4-bis-(2-oxofuro[2,3-h][1]-benzopyran-8-yl)pent-2-ene (XII) (125 mg). Compound (XII) is soluble only in an excess of chloroform from which it precipitated on concentration and cooling as an amorphous powder, m.p.  $>330^\circ$  (Found: C, 73.65; H, 4.25.  $C_{28}H_{20}O_6$  requires C, 74.35; H, 4.4%),  $\lambda_{\max}$  205, 253, and 304 nm ( $\log \epsilon$  4.60, 4.45, and 4.21),  $\nu_{\max}$  (Nujol) 1724, 1608, 1570, 1450, 1400, 1372, 1275, 1145, 1105, 1050, 1008, 975, 938, 827, and 755  $\text{cm}^{-1}$ ,  $m/e$  452 (59), 437 (100), 227 (16), 226 (16), 198 (13), 141 (6), 128 (11), and 115 (14%); the full spectrum is in Supplementary Publication No. SUP 21194.

*Acid Equilibration of (XI).*—Compound (XI) (200 mg) was dissolved in chloroform (8 ml), boron trifluoride-ether complex (0.1 ml) was added, and the mixture stirred at room temperature for 1 h. The usual work-up and chromatography of the residue over silica gel (8 g) yielded (XI) (110 mg) and (XII) (40 mg).

*Reactions of Oroselol (VII) in the Presence of Lewis Acids.*—(a) *With tin(IV) chloride.* To oroselol (122 mg) in chloroform (8 ml) was added tin(IV) chloride (0.15 ml) and the mixture was stirred for 10 min at room temperature. Water was added and the mixture was extracted with chloroform and worked up in the usual way to give a residue (100 mg), which on chromatography over silica gel (8 g) yielded (XIV) (10 mg), (XI) (60 mg), and (XII) (12 mg).

(b) *With aluminium chloride.* A mixture of (VII) (122 mg) and aluminium chloride (130 mg) in chloroform (8 ml) was stirred at room temperature. After 4 h the mixture was worked up as usual. The residue (105 mg) on chromatography over silica gel (8 g) yielded (XIV) (65 mg), (XI) (25 mg), and (XII) (5 mg).

*Preparation of (VIII), (IX), and (X) from Oroselol (VII).*—(a) Aluminium chloride (220 mg) was added to a solution of (VII) (200 mg) in benzene (8 ml) and the mixture was stirred at room temperature. After 2 h, the usual work-up gave a residue which on chromatography over silica gel (10 g) and elution with petroleum-ethyl acetate (12:1; 500 ml) gave 8-( $\alpha$ -dimethylbenzyl)furo[2,3-h][1]benzopyran-2-one (VIII) (150 mg), m.p.  $167^\circ$  (from petroleum-ethyl acetate) (Found: C, 79.0; H, 5.75.  $C_{20}H_{16}O_3$  requires C, 78.95; H, 5.25%),  $\lambda_{\max}$  206, 253, and 303 nm ( $\log \epsilon$  4.50, 4.49, and 4.07),  $\nu_{\max}$  (Nujol) 1720, 1625, 1575, 1495, 1450, 1403, 1385, 1375, 1312, 1275, 1250, 1150, 1123, 1113, 1094, 1062, 1023, 940, 840, 805, 770, 755, and 700  $\text{cm}^{-1}$ ,  $\tau$  8.23 (6H, s), 3.67 (1H, d,  $J$  9.5 Hz), 3.15 (1H, s), 2.73 (7H, s), and 2.25 (1H, d,  $J$  9.5 Hz). Further elution with chloroform (200 ml) and chloroform-ethanol (10:1; 200 ml) yielded (XI) (40 mg) and (XII) (9 mg).

(b) As under (a), oroselol (VII) (244 mg) was dissolved in anisole (10 ml), and aluminium chloride (275 mg) was added. The mixture was stirred at room temperature for 5 h and

then the product was worked up in the usual way to give a residue which on chromatography over silica gel (15 g) and elution with petroleum-ethyl acetate (9:1; 500 ml) gave 8-(*p*-methoxy- $\alpha$ -dimethylbenzyl)furo[2,3-h][1]benzopyran-2-one (IX) (265 mg), m.p.  $118^\circ$  (from petroleum-ethyl acetate) (Found: C, 75.25; H, 5.3.  $C_{21}H_{18}O_4$  requires C, 75.45; H, 5.4%),  $\lambda_{\max}$  205, 253, and 303 nm ( $\log \epsilon$  4.54, 4.50, and 4.09),  $\nu_{\max}$  (Nujol) 1720, 1615, 1580, 1510, 1470, 1380, 1372, 1310, 1255, 1195, 1152, 1115, 1098, 1025, 937, 840, and 770  $\text{cm}^{-1}$ ,  $\tau$  8.25 (6H, s), 6.23 (3H, s), 3.67 (1H, d,  $J$  9.5 Hz), 3.18 (1H, s), 3.17 (2H, d,  $J$  8.5 Hz), 2.75 (2H, d,  $J$  8.5 Hz), 2.73 (2H, s), and 2.25 (1H, d,  $J$  9.5 Hz).

In a similar way substance (IX) (150 mg), m.p.  $118^\circ$ , was most conveniently obtained as the exclusive product by treating oroselol (122 mg) with anisole (8 ml) in the presence of boron trifluoride-ether (0.1 ml) for only 20 min and working up in the usual way.

(c) Oroselol (VII) (244 mg), on keeping with ethyl phenyl ether (10 ml) in the presence of aluminium chloride (275 mg) for 6 h at the room temperature, gave 8-(*p*-ethoxy- $\alpha$ -dimethylbenzyl)furo[2,3-h][1]benzopyran-2-one (X) (330 mg), m.p.  $104^\circ$  (from ethyl acetate-petroleum) (Found: C, 75.7; H, 5.6.  $C_{22}H_{20}O_4$  requires C, 75.85; H, 5.75%),  $\lambda_{\max}$  205, 253, and 305 nm ( $\log \epsilon$  4.62, 4.51, and 4.11),  $\nu_{\max}$  (Nujol) 1715, 1608, 1575, 1505, 1475, 1440, 1405, 1378, 1371, 1362, 1300, 1295, 1274, 1250, 1175, 1150, 1110, 1085, 1050, 1035, 1020, 925, 828, 760, and 725  $\text{cm}^{-1}$ ,  $\tau$  8.62 (3H, t,  $J$  7 Hz), 8.24 (6H, s), 5.98 (2H, q,  $J$  7 Hz), 3.65 (1H, d,  $J$  9.5 Hz), 3.15 (1H, s), 3.15 (2H, d,  $J$  8.5 Hz), 2.75 (2H, d,  $J$  8.5 Hz), 2.70 (2H, s), and 2.23 (1H, d,  $J$  9.5 Hz).

*Action of Boron Trifluoride-Ether Complex on Oroselone (XIV).*—(a) Oroselone (XIV) (113 mg) was dissolved in chloroform (8 ml), and boron trifluoride-ether complex (0.1 ml) was added. The mixture was stirred for 2 h at room temperature and worked up as usual. The residue (108 mg) on chromatography over silica gel (8 g) yielded (XIV) (55 mg), (XI) (35 mg), and (XII) (8 mg).

(b) Similarly when (XIV) (113 mg) was kept with ethyl phenyl ether (5 ml) and boron trifluoride-ether complex (0.1 ml) for 4 h at room temperature under stirring, compounds (XIV) (75 mg), (XI) (20 mg), and (XII) (5 mg) were obtained from the reaction product after chromatography over silica gel (8 g).

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