List of Research Papers

1. Studies in the synthesis of furocoumarins, Part XXI. Synthesis of furocoumestan derivatives by K.R.Shah and K.N.Trivedi., J. Ind. Chem. Soc., 52, 224 (1975).
2. Studies in the synthesis of furocoumarins : Part XXII. Synthesis of 7H-furo [3,2-f] [1] benzopyran-7-one by K.R. Shah and K.N.Trivedi., J. Ind. Chem. Soc., 52, 436 (1975).
3. Studies in the synthesis of furocoumarins : XXIII. Synthesis of substituted psoralenes from 2-bromo-resorcinol by K.R.Shah and K.N.Trivedi., Aust. J. Chem., 27, 1971-6 (1974); C.A., 81, No. 23, 152053 e (1974).

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Studies in the synthesis of Furocoumarins. Part XXI : Synthesis of Furocoumestan derivatives

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7-Allyloxy-4-hydroxycoumarin, on dehydrogenative coupling with catechol in the presence of potassium iodate gave 7-allyloxy-11, 12-dihydroxy coumestan ; which on methylation followed by Claisen migration, cyclisation with conc. sulphuric acid and dehydrogenation with palladised charcoal furnished 5′-methyl-11,12-dimethoxy furo (2,3-h) coumestan. 5′,8-Dimethyl-11,12-dimethoxy furo (3,2-g) coumestan was similarly synthesised from 7-allyloxy-8-methyl-4-hydroxy-coumarin.

COUMESTAN and Furocoumestan derivatives, such as coumestrol[1], Erosnin[2] etc. have assumed importance in recent years. They occur in nature and also possess estrogenic properties. It was, therefore, thought of interest to study some reaction of hydroxy coumestan derivatives and to build up furan ring on it and to study the structure activity relationship of the furocoumestan derivatives. We report here the synthesis of 5′-methyl-11, 12-dimethoxy furo (2,3-h) coumestan (IV) and 5′,8-dimethyl-11, 12-dimethoxy furo (3,2-g) coumestan (V).

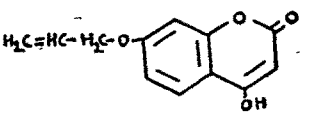
7-Allyloxy-4-hydroxycoumarin[3] (I) prepared by the condensation of 4-allyloxy-2-hydroxy acetophenone with diethyl carbonate in the presence of sodium metal according to Boyd and Robertson[4], on dehyrogenative coupling with catechol in the presence of potassium iodate[5], gave 7-allyloxy-11, 12-dihydroxy coumestan (IIa). This on methylation with dimethyl sulphate, gave 7-allyloxy- 11, 12-dimethoxy coumestan (IIb). (IIb), on Claisen migration in an atmosphere of nitrogen in refulxing dimethylaniline, afforded 7-hydroxy-8-allyl-11, 12-dimethoxy coumestan (IIc). This on trituration with conc. sulphuric acid, gave 5′-methyl-11,12-dimethoxy-4′, 5′-dihydrofuro (2,3-h) coumestan (III), which underwent dehydrogenation with palladised charcoal to give 5′-methyl-11, 12-dimethoxy-furo (2,3-h) coumestan (IV).

7-Allyloxy-8-methyl-4-hydroxycoumarin[3], on dehydrogenative coupling with catechol, gave 7-allyloxy-8-methyl-11, 12-dihydroxy coumestan (IId). This, on methylation and Claisen migration afforded 7-hydroxy-6-allyl-8-methyl-11,12-dimethoxy coumestan (IIe). (IIe) on cyclisation with con. sulphuric acid followed by dehydrogenation with palladised charcoal furnished 5′,8-dimethyl-II, 12-dimethoxy furo (3,2-g) coumestan (V).

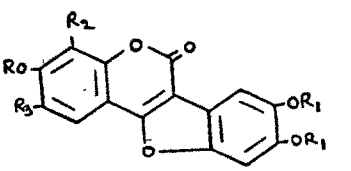
(a) $R = -CH_2-CH=CH_2$; $R_1 = R_2 = R_3 = H$

(b) $R = -CH_2-CH=CH_2$; $R_1 = CH_3$, $R_2 = R_3 = H$

(c) $R = R_3 = H$; $R_2 = -CH_2-CH=CH_2$; $R_1 = CH_3$



I



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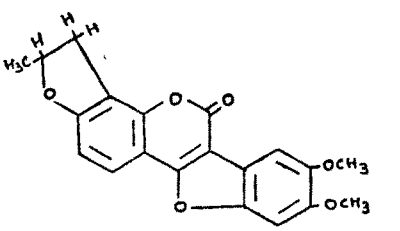
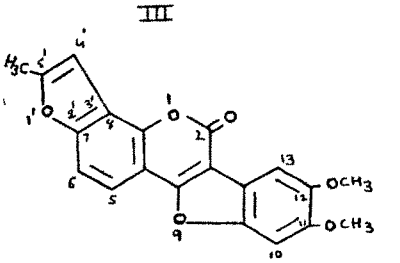
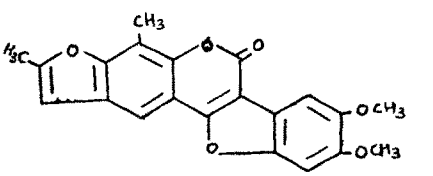


III



IV



V

(d) $R = -CH_2-CH=CH_2$; $R_1 = R_3 = H$; $R_2 = CH_3$

(e) $R = H$; $R_1 = R_2 = CH_3$; $R_3 = -CH_2-CH=CH_2$

(f) $R = -CH_2-CH=CH_2$; $R_1 = R_2 = CH_3$; $R_3 = H$

Experimental

U/V Spectra were recorded on Beckmann DU-2 model and i.r. spectra were recorded on Perkin-Elmer 457 model.

7-Allyloxy-11, 12- dimethoxy coumestan (IIb) : 4-Hydroxy-7-allyloxycoumarin[3] (1 g.), catachol (0.5 g), and sodium acetate (2 g.) was dissolved in acetone (25 ml.). The solution prepared by potassium iodate (0.5 g.) and sodium acetate (1 g.) in 10 ml. water was added to above solution dropwise with constant stirring allowed it to stand for 1 hr. The separated product was filtered, washed with sodium bicarbonate. Yield 0 8 g. m.p. >300° and it was insoluble in common organic solvents. It was insoluble in sodium bicarbonate and developed green colouration with ferric chloride solution. The product (2 g.), dimethyl sulphate (1.6 g.), anhydrous potassium carbonate (4 g.) in dry acetone (50 ml.) was refluxed on water bath for 8 hr. After the evaporation of acetone, the residue was decomposed with water. The product was filtered and washed with dil. sodium hydroxide. dried and crystallised from acetic acid m. p. 198°. Yield 1.8 g. (Found : C,68.47 ; H, 4.81%. $C_{20}H_{16}O_6$ requires C,68.19 ; H,4.54%.) IR Spectra (Nujol) : 1733 Cm^{-1} (lactonyl >C=O group), 1275 cm^{-1} (Aromatic ether linkage)

7-Hydroxy-8-allyl-11, 12-dimethoxy coumestan : (IIc) 7-Allyloxy-11, 12-dimethoxy coumestan (2 g.) was refluxed in dimethyl aniline (10 ml.) in the presence of nitrogen atmosphere for 6 hr. The reaction mixture was cooled and treated with ice and hydrochloric acid. The separated product was filtered and the residue was treated with dil. sodium hydroxide solution and filtered. The fiiltrate was acidified and the product crystallised from acetic acid, m. p. 258°. Yield 1.5 g. (Found : C,67.70 ; H,4.44%. $C_{20}H_{16}O_6$ requires C, 68.19 ; H,4.54%.) IR spectra : 1690 cm (lactonyl C=O group)

5'-Methyl-11,12-dimethoxy-4',5'-dihydro furo(2,3-h) coumestan : (III) 7-Hydroxy-8-allyl-11, 12-dimethoxy coumestan (0.7 g.) was triturated with con. sulphuric acid (4 ml.) for 10 min. The reaction mixture was decomposed with ice and water. The product was filtered, washed with dil. sodium hydroxide, dried and crystallised from the mixture of chloroform and petroleum ether, m. p. 203°. Yield 0.5 g. (Found: C,67. 72 ; H, 4.72%. $C_{20}H_{16}O_6$ requires C,68.19 ; H,4.54%.)

5'-Methyl-11,12-dimethoxy furo (2,3-h) coumestan : (IV) 5'-Methyl-11,12-dimethoxy-4', 5'-dihydro furo (2,3-h) coumestan (0.8 g.) was refluxed with palladised charcoal (0.6 g. ; 10%), in diphenyl ether (6 ml.) for 20 hr. The reaction mixture was filtered hot and after cooling light petroleum was added to the filtrate. The separated product was filtered and washed several times with light petroleum. It crystallised from benzene-petroleum ether, m. p. 253°. Yield 0.5 g. (Found: C,68.28 ; H,3.93%. $C_{20}H_{14}O_6$ requires C, 68.57 ; H,4.00%.) IR Spectra (Nujol) 1740 cm^{-1} (lactonyl) >C=O group) λ_{Max}^{MeoH}, 242 and 340 nm. (log ϵ 4.57 & 4.40)

5',8-Dimethyl-11,12-dimethoxy furo(3,2-g) coumestan : *7-Allyloxy-8-methyl-11,12-dimethoxy coumestan* : (IIf) 4-Hydroxy-7-allyloxy-8-methylcoumarin (1 g.)[3], catechol (0.5 g.) and sodium acetate (2 g.) was dissolved in acetone (25 ml). The solution prepared by potassium iodate (0.5 g.) and sodium acetate (1 g.) in 10 ml. water was added to above solution dropwise with constant stirring and allowed it to stand for 1 hour. The reaction mixture was worked up as before, m. p.> 300°. Yield 0.5 g. The product was insoluble in sodium bicarbonate and developed green colouration with ferric chloride solution. The product (2 g.), dimethyl sulphate (1.6 g.), potassium carbonate (4 g.), acetone (50 ml.) was refluxed on water bath for 8hr. The reaction mixture was worked up as before. The product crystallised from acetic acid, m. p. 212°, Yield 1.8 g. (Found : C, 68.42 ; H, 4.14%. $C_{21}H_{18}O_6$ requires C,68.85 ; H,4.91%)

7-Hydroxy-6-allyl-8-methyl-11, 12-dimethoxy coumestan : (IIe) 7-Allyloxy-8-methyl-11, 12-dimethoxy coumestan (2 g.) was refluxed in dimethyl aniline(10 ml.) in the presence of nitrogen atmosphere for 6 hr. The reaction mixture was worked up as before. The product crystallised from acetic acid, m. p. 247°. Yield 1.5 g. (Found : C,69.07 ; H,5.6%. $C_{21}H_{18}O_6$ requires C,68.85 ; H,4 92%)

5'-Methyl-11, 12-dimethoxy-8-methyl-4,' 5'-dihydro furo (3,2g) coumestan : 7 Hydroxy 6 allyl 8 methyl 11, 12 dimethoxy coumestan (0.8 g.) was triturated with con. sulphuric acid (4 ml.) for 10 min. The reaction mixture was decomposed with ice and water. The product was filtered, washed with dil. sodium hydroxide, dried and crystallised from acetic acid, m. p. 265°. Yield 0.5 g. (Found: C,68.55 ; H,4.60%. $C_{21}H_{18}O_6$ requires ,68.85 ; H,4.91%)

5'-Methyl-11,12-dimethoxy-8-methyl furo (3,2-g) *coumestan* : (V) 5'-Methyl-11, 12-dimethyoxy-8-methyl -4', 5'-dihydro furo (3,2 g) coumestan (0.8 g) was refluxed with palladised charcoal (0.6 g. ; 10%) in diphenyl ether (6 ml.) for 24 hr. The reaction mixture was worked up as before. The compound crystallised from glacial acetic acid, m. p. 288°. Yield 0.5 g. (Found: C,69.31 ; H,4.15%. $C_{21}H_{16}O_6$ requires C,69.23 ; H, 4.39%) IR Spectra (Nujol)1720 cm^{-1} (lactonyl > C=O group). λ_{Max}^{MeoH}, 286 and 350 nm (log ϵ 3.81 and 4.27).

Acknowledgement

Authors record their thanks to Prof. E. Gellert, Wollongong University College, Wollongong Australia, for IR Spectra, Professor S. M. Sethna for his keen interest in the work and to Dr. S. S. Lele for micro analysis of the samples.

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Studies in the Synthesis of Furocoumarins: Part XXII: Synthesis of 7H-Furo [3,2-f] [1] benzopyran-7-one

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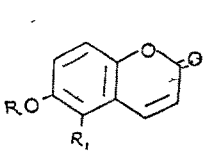
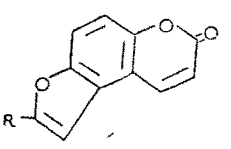
6-Hydroxycoumarin, on allylation followed by Claisen migration, gave 6-hydroxy-5-allylcoumarin (Ic), structure of which was confirmed by its N.M.R. spectrum. (Ic) was converted to (IIa) by treatment with osmium tetroxide followed by cyclisation with o-phosphoric acid. (IIb) was obtained by treating (Ic) with conc. sulphuric acid followed by dehydrogenation with palladised charcoal (10%).

SYNTHESIS of Furocoumarins from hydroquinone and its derivatives having alkyl substituents on furan and coumarin rings have been reported by Kaufman *et al.*[2,3]. We report here the synthesis of 7H-furo[2,3-f][1] benzopyran-7-one (IIa) and its 2-methyl derivative (IIb) for evaluating their psoralene like photosensitising activity.

6-Hydroxycoumarin[4] (Ia) was converted to its allyl ether (Ib), which underwent Claisen rearrangement in boiling dimethyl aniline to give 5-allyl-6-hydroxycoumarin (Ic). The structure of (Ic) was confirmed by NMR spectrum ($CDCl_3$) : δ 9.5, 1H singlet, hydroxylic proton, at 6-position : δ 7.17 and δ 7.0, 2H, doublets, (J = 8 Hz), H_7 and H_8 (aromatic), δ 6.35 and δ 7.95, 2H, doublets (J = 10 Hz), at H_3 and H_4, δ 6 1–5.7, 1H multiplet, = CH, δ 5.1 and δ 4.82, 2H, multiplet = CH_2, showing barely visible long range coupling (J = 1 Hz) : δ 3.62, 2H, doublet, $-CH_2$-CH =. The two proton doublets at δ 7.17 and δ 7.0 indicates the two aromatic proton at H_7 and H_8 are free to couple. If it were 7-allyl-6-hydroxycoumarin, NMR spectrum would have shown two singlet for proton at H_5 and H_8. (Ic), on treatment with osmium tetroxide[5] and potassium periodate gave 5-formyl methyl-6-hydroxycoumarin (Id), which was not isolated but cyclised directly with *o*-phosphoric acid to give the title compound (IIa)[5]. (Ic), when triturated with conc.sulphuric acid[6,7] gave 2-methyl-2,3-dihydro-7H-furo [3,2-f] [1] benzopyran-7-one (III), which on dehydrogenation with palladised charcoal in boiling diphenyl ether furnished 2-methyl-7H-furo [3,2-f] [1] benzopyran-7-one (IIb).





I a, R = R_1 = H
b, R = Allyl, R_1 = H
c, R = H, R_1 = Allyl
d, R = H, R_1 = $-CH_2CHO$

II a, R = H
b, R = CH_3

Experimental

Ultraviolet spectra were recorded on Beckmann DU-2 Model, IR spectra were recorded on Perkin Elmer 457 model and NMR spectra were recorded on Varian A-60 Model using TMS as an internal indicator.

6-*Allyloxycoumarin* (Ib) :

A mixture of 6-hydroxycoumarin (5 g.), allyl bromide (5 ml.) and anhydrous potassium carbonate (10 g) was refluxed in dry acetone (100 ml.) for 10 hr. After the evaporation of acetone, the residue was treated with water. The compound was filtered, washed with dilute sodium hydroxide, dried and crystallised from benzene-petroleum ether, m.p. 90°. Yield 3 g. (Found : C, 71.58; H, 4.83. $C_{12}H_{10}O_3$ requires C, 71.28; H, 4.95%). IR spectra (Nujol) : 1720 cm^{-1} (lactonyl > C = O group), 1265 cm^{-1} (aromatic ether linkage).

6-*Hydroxy-5-allylcoumarin* (Ic) :

6-Allyloxycoumarin (2 g.), and dimethylaniline (15–20 ml.) were refluxed for 6 hr in nitrogen atmosphere. The reaction mixture was poured into ice and hydrochloric acid. The product was treated with sodium hydroxide solution, filtered and acidified with dil. hydrochloric acid. The dried residue was purified by passing it over a short column of alumina using chloroform as eluent. It crystallised from chloroform, m.p. 172°. Yield 1.5 g. (Found : C, 71.19; H, 4.80. $C_{12}H_{10}O_3$ requires C, 71.28; H, 4.95%), IR spectra (Nujol) 1680 cm^{-1} (lactonyl > C = O group).

7-H-Furo[3,2-*f*][1]*benzopyran-7-one* (IIa) :

A solution of 6-hydroxy-5-allylcoumarin (0.5 g.) in ethyl acetate was vigorously shaken with 50 mg. osmium tetraoxide in water (100 ml.). Potassium periodate (2 g. in 100 ml. water) was added during the period of 2 hr. Ethyl acetate layer was separated, dried and evaporated. The residue was dissolved in benzene and passed over alumina. Evaporation of solvent left a residue. This was heated with *o*-phosphoric acid (5 ml.) on a water bath at 70°–80° for 1½ hr. The contents were poured into ice water. The product was extracted with ethyl acetate, washed with dilute sodium hydroxide and finally purified by chromatographing over alumina using benzene as eluent. It crystallised from benzene-petroleum ether mixture, m.p. 231°. Yield 0.2 g. (Found : C, 71.44; H, 3.67. $C_{11}H_6O_3$ requires C, 70.98; H, 3.22%). IR spectra (Nujol) 1740 cm^{-1} (lactonyl > C = O group) 890 cm^{-1} (furan). λ_{max}^{MeoH}, 252 and 300 nm (log ϵ, 3.96 and 3.64).

2-Methyl-2,3-dihydro-7H-furo[3,2-*f*][1] *benzopyran-7-one* (III) :

6-Hydroxy-5-allylcoumarin (1 g.) was triturated with concentrated sulphuric acid (6 ml.) for 1 hr at room temperature. The contents were poured into ice water. The separated product was filtered, washed with dilute sodium hydroxide solution to remove original compound and finally crystallised from benzene-petroleum ether mixture, m.p. 104°. Yield 0.7 g. (Found : C, 71.27; H, 4.84. $C_{12}H_{10}O_3$ requires C, 71.28; H, 4.95%).

2-Methyl-7H-furo [3,2-*f*] [1] *benzopyran-7-one* (IIb) :

A mixture of 2-methyl-2,3-dihydro-7H-furo(3,2-f) (1) benzopyran-7-one (0.5 g.), palladised charcoal (10%; 0.3 g.) and diphenyl ether (5 ml.) was refluxed for 20 hr. Reaction mixture was filtered hot and the product separated on cooling. It crystallised from diphenyl ether, m.p. 161°. Yield 0.3 g. (Found ; C, 71.58; H, 3.84. $C_{12}H_8O_3$ requires C, 72.00; H, 4.00%). $\lambda_{max.}^{MeoH}$, 318 nm (log ϵ 4.20).

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The authors thank Prof. E. Gellert, Wollongong University College, Wollongong, Australia for IR spectra, Shri S. G. Amin, Steven's Institute of Technology, U.S.A. for NMR spectra, Prof. S. Sethna for his keen interest in the work and Dr. S. S. Lele for microanalysis of the compounds.

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Studies in the Synthesis of Furocoumarins. XXIII* Synthesis of Substituted Psoralenes from 2-Bromoresorcinol

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Abstract

The synthesis of four different substituted psoralenes from 2-bromoresorcinol is described.

In continuation of our work on the synthesis of psoralene derivatives from 2-bromoresorcinol,[1] we report here the synthesis of 2-methyl-5-phenyl-7*H*-furo[3,2-*g*]-[1]benzopyran-7-one (5), 9-methyl-5*H*-benzofuro[6,5-*c*][2]benzopyran-5-one (8), 9-methyl-1,2,3,4-tetrahydro-5*H*-benzofuro[6,5,-*c*][2]benzopyran-5-one (7) and 8-methyl-1,2,3,4-tetrahydrocyclopenta[*c*]furo[3,2-*g*][1]benzopyran-4-one (10).

Pechmann condensation of 2-bromoresorcinol with ethyl benzoylacetate in the presence of concentrated sulphuric acid gave 8-bromo-7-hydroxy-4-phenylcoumarin (1a), which on allylation with allyl bromide afforded 7-allyloxy-8-bromo-4-phenylcoumarin (1b). This on Claisen rearrangement by refluxing it in dimethylaniline gave 6-allyl-7-hydroxy-4-phenylcoumarin (1c). The structure of (1c) was confirmed by its n.m.r. spectrum ($CDCl_3 + Me_2SO$); δ 10·15 (one-proton singlet, hydroxylic proton), 7·52 (five-proton singlet, phenyl group at position 4), 7·2 (one-proton singlet, H 5), 6·8 (one-proton singlet, H 8), 6·1 (one-proton singlet, H 4), 5·9–5·75 (one-proton multiplet, =CH), 5·1 and 4·8 (two-proton doublet, $=CH_2$, the latter showing a barely visible long-range coupling, J 1 Hz), 3·35 (two-proton doublet, $=CHCH_2$). The compound (1c) was triturated with concentrated sulphuric acid[2] to give 2-methyl-5-phenyl-2,3-dihydro-7*H*-furo[3,2-*g*][1]benzopyran-7-one (4), which when subjected to dehydrogenation with palladium–charcoal (10%) afforded (5).

2-Bromoresorcinol, on similar condensation with ethyl 2-oxocyclohexanecarboxylate, gave 4-bromo-3-hydroxy-7,8,9,10-tetrahydro-6*H*-dibenzo[*b,d*]pyran-6-one (2a). This on allylation and Claisen migration gave 2-allyl-3-hydroxy-7,8,9,10-tetrahydro-6*H*-dibenzo[*b,d*]pyran-6-one (2c), the structure of which was confirmed by its n.m.r. spectrum ($CDCl_3$): δ 7·2 (one-proton singlet, H 5) and 7·0 (one-proton singlet H 8). The compound (2c), on ring closure with concentrated sulphuric acid followed by dehydrogenation, gave (8). The compound (2c) was converted into (7) by Kaufman's method,[3] which comprised acetylation of (2c), addition of bromine to the allylic

* Part XXII, *J. Indian Chem. Soc.*, in press.

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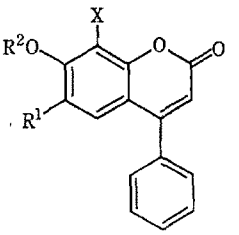
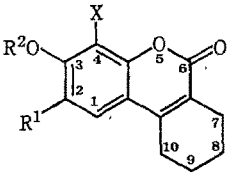
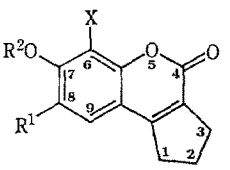
double bond, and subsequent ring closure of 2-(2′,3′-dibromopropyl)-6-oxo-7,8,9,10-tetrahydro-6*H*-dibenzo[*b*,*d*]pyran-3-yl acetate (2e) with ethanolic potassium hydroxide.



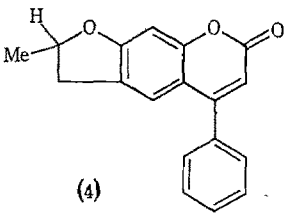
	R^1	R^2	X
(1a)	H	H	Br
(1b)	H	$CH_2CH{=}CH_2$	Br
(1c)	$CH_2CH{=}CH_2$	H	H



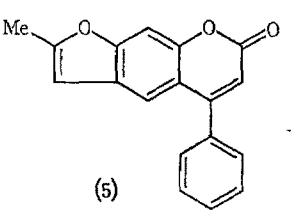
	R^1	R^2	X
(2a)	H	H	Br
(2b)	H	$CH_2CH{=}CH_2$	Br
(2c)	$CH_2CH{=}CH_2$	H	H
(2d)	$CH_2CH{=}CH_2$	$COCH_3$	H
(2e)	$CH_2CHBrCH_2Br$	$COCH_3$	H



	R^1	R^2	X
(3a)	H	H	Br
(3b)	H	$CH_2CH{=}CH_2$	Br
(3c)	$CH_2CH{=}CH_2$	H	H
(3d)	$CH_2CH{=}CH_2$	$COCH_3$	H
(3e)	$CH_2CHBrCH_2Br$	$COCH_3$	H



(4)



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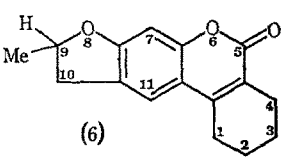

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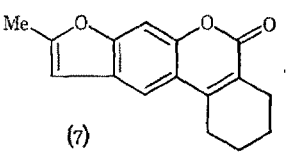

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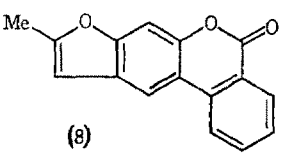

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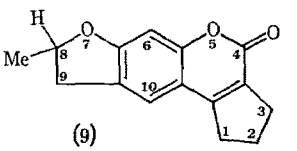

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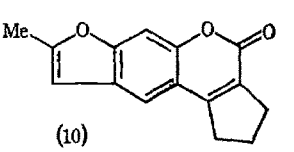

(10)

2-Bromoresorcinol, on similar condensation with ethyl 2-oxocyclopentanecarboxylate, gave 6-bromo-7-hydroxy-1,2,3,4-tetrahydrocyclopenta[*c*][1]benzopyran-4-one (3a), which on allylation and Claisen migration afforded 8-allyl-7-hydroxy-1,2,3,4-tetra-

hydrocyclopenta[*c*][1]benzopyran-4-one (3c). The structure of (3c) was confirmed by its n.m.r. spectrum ($CDCl_3$): δ 7·18 (one-proton singlet, H 5) and 6·82 (one-proton singlet, H 8). The compound (3c), after ring closure with concentrated sulphuric acid, failed to give (10) on dehydrogenation with palladium–charcoal (10%), and (10) was finally prepared from (3c) by acetylation and bromination, followed by ring closure with ethanolic potassium hydroxide.

Experimental

Melting points are uncorrected. Ultraviolet spectra were recorded on a Beckmann DU-2 spectrophotometer and infrared spectra (Nujol) were recorded on a Perkin–Elmer 457 instrument. The n.m.r. spectra were measured on a Varian A-60 spectrometer with tetramethylsilane as internal reference.

8-Bromo-7-hydroxy-4-phenylcoumarin (1a)

A mixture of 2-bromoresorcinol (5 g) and ethyl benzoylacetate (5 g) and concentrated sulphuric acid (80%, 45 ml) was kept at room temperature for 24 h. The reaction mixture was poured onto crushed ice. The separated product was collected and washed with water; it crystallized as colourless shining *flakes* with m.p. 267° from alcohol. Yield 4·5 g, 45% (Found: C, 56·5; H, 2·8; Br, 25·4. $C_{15}H_9BrO_3$ requires C, 56·7; H, 2·8; Br, 25·2%).

7-Allyloxy-8-bromo-4-phenylcoumarin (1b)

A mixture of 8-bromo-7-hydroxy-4-phenylcoumarin (5 g), allyl bromide (2 g) and anhydrous potassium carbonate (10 g) was boiled under reflux for 8 h in dry acetone (200 ml) on a water bath. After the evaporation of acetone, the residue was treated with water. The product was collected, washed with dilute sodium hydroxide solution and dried; it crystallized as colourless *cubes* with m.p. 138° from benzene. Yield 3·5 g, 62·2% (Found: C, 60·3; H, 3·6; Br, 22·1. $C_{18}H_{13}BrO_3$ requires C, 60·5; H, 3·6; Br, 22·4%). I.r. spectra (Nujol) 1720 (C=O group), 1270 cm^{-1} (aromatic ether linkage).

6-Allyl-7-hydroxy-4-phenylcoumarin (1c)

7-Allyloxy-8-bromo-4-phenylcoumarin (2 g) and dimethylaniline (15 ml) were refluxed for 6 h under nitrogen. The reaction mixture was cooled and poured into ice-cold hydrochloric acid. The separated product was treated with dilute sodium hydroxide solution and the solution was filtered. The filtrate was acidified with hydrochloric acid and the product crystallized as colourless *needles* with m.p. 222° from methanol. Yield 1·0 g, 62·5% (Found: C, 77·6; H, 4·6. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%). ν_{max} 1680 cm^{-1} (C=O group).

*2-Methyl-5-phenyl-2,3-dihydro-7*H*-furo[3,2-g]benzopyran-7-one (4)*

6-Allyl-7-hydroxy-4-phenylcoumarin (1 g) was triturated with concentrated sulphuric acid (6 ml) for 20 min. The contents were poured onto crushed ice. The separated product was collected, washed with dilute sodium hydroxide solution to remove the unchanged phenol, and dried. It crystallized as colourless *needles* with m.p. 172° from benzene. Yield 0·7 g, 70% (Found: C, 77·6; H, 4·6. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%). ν_{max} 1700 cm^{-1} (C=O group).

*2-Methyl-5-phenyl-7*H*-furo[3,2-g]benzopyran-7-one (5)*

A mixture of 2-methyl-5-phenyl-7*H*-2,3-dihydrofuro[3,2-*g*]benzopyran-7-one (0·5 g), palladium–charcoal (10%, 0·3 g) and diphenyl ether (6 ml) was refluxed for 24 h. The reaction mixture was filtered hot and diphenyl ether was removed by steam distillation. The separated product was filtered, dried and passed through alumina. It crystallized as yellow small *needles* with m.p. 179° from benzene–light petroleum. Yield 0·3 g, 61·2% (Found: C, 78·3; H, 4·3. $C_{18}H_{12}O_3$ requires C, 78·3; H, 4·3%). λ_{max} (chloroform) 254 (log ε 4·24) and 330 nm (3·99). ν_{max} 1710 (C=O), 870 cm^{-1} (furan).

*4-Bromo-3-hydroxy-7,8,9,10-tetrahydro-6*H*-dibenzo*[b,d]*pyran-6-one* (*2a*)

A mixture of 2-bromoresorcinol (5 g), ethyl 2-oxocyclohexanecarboxylate (4·5 g) and concentrated sulphuric acid (80%; 45 ml) was kept at room temperature for 24 h. The reaction mixture was worked up as described above. The separated product crystallized as colourless shining small *needles* with m.p. 260° (dec.) from alcohol. Yield 4·5 g, 47·9% (Found: C, 52·5; H, 4·0; Br, 27·3. $C_{13}H_{11}BrO_3$ requires C, 52·8; H, 3·7; Br, 27·1%).

*3-Allyloxy-4-bromo-7,8,9,10-tetrahydro-6*H*-dibenzo*[b,d]*pyran-6-one* (*2b*)

A mixture of 4-bromo-3-hydroxy-7,8,9,10-tetrahydro-6*H*-dibenzo[*b,d*]pyran-6-one (5 g), allyl bromide (2 g) and anhydrous potassium carbonate (10 g) was boiled under reflux for 10 h on a water bath in dry acetone (200 ml). The reaction mixture was worked up as before. The product crystallized as light yellow *flakes* with m.p. 183° from benzene. Yield 3·5 g, 61·6% (Found: C, 57·0; H, 4·4; Br, 23·5. $C_{16}H_{15}BrO_3$ requires C, 57·3; H, 4·4; Br, 23·8%). ν_{max} 1710 and 1280 cm^{-1}.

*2-Allyl-3-hydroxy-7,8,9,10-tetrahydro-6*H*-dibenzo*[b,d]*pyran-6-one* (*2c*)

3-Allyloxy-4-bromo-7,8,9,10-tetrahydro-6*H*-dibenzo[*b,d*]pyran-6-one (2 g) and dimethylaniline (15 ml) boiled for 6 h under nitrogen. The reaction mixture was worked up as before. The product crystallized as colourless silky *needles* with m.p. 166° from benzene. Yield 1·2 g, 78·5% (Found: C, 75·0; H, 6·0. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·2%). ν_{max} 1660 cm^{-1}.

*9-Methyl-1,2,3,4,9,10-hexahydro-5*H*-benzofuro*[6,5-c][2]*benzopyran-5-one* (*6*)

2-Allyl-3-hydroxy-1,2,3,4-tetrahydro-6*H*-dibenzo[*b,d*]pyran-6-one (1 g) was triturated with concentrated sulphuric acid (4 ml) for 20 min. The reaction mixture was poured onto crushed ice, filtered, washed with dilute sodium hydroxide solution and dried. It crystallized as cream-coloured small *needles* with m.p. 137° from benzene–light petroleum (40–60°) mixture. Yield 0·8 g, 80% (Found: C, 74·8; H, 5·9. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·2%). ν_{max} 1695 cm^{-1}.

*9-Methyl-5*H*-benzofuro*[6,5-c][2]*benzopyran-5-one* (8)

A mixture of 9-methyl-1,2,3,4,9,10-hexahydro-5*H*-benzofuro[6,5-*c*][2]benzopyran-5-one (0·5 g), palladium–charcoal (0·3 g; 10%) and diphenyl ether (6 ml) was boiled for 24 h. The reaction mixture was worked up as before. The product crystallized as brown small *needles* with m.p. 176° from benzene. Yield 0·35 g, 71·7% (Found: C, 77·2; H, 3·8. $C_{16}H_{10}O_3$ requires C, 76·8; H, 4·0%). λ_{max} (methanol) 276 (log ε 3·88) and 330 nm (4·00). ν_{max} 1705 and 880 cm^{-1}.

*2-Allyl-6-oxo-7,8,9,10-tetrahydro-6*H*-dibenzo*[b,d]*pyran-3-yl Acetate* (*2d*)

The acetoxy derivative of 2-allyl-3-hydroxy-7,8,9,10-tetrahydro-6*H*-dibenzo[*b,d*]pyran-6-one was prepared by boiling 2-allyl-3-hydroxy-7,8,9,10-tetrahydro-6*H*-dibenzo[*b,d*]pyran-6-one (1 g) with acetic anhydride (8 ml) and fused sodium acetate (1·5 g) for 5 h. It crystallized as colourless *needles* with m.p. 138° from alcohol. Yield 0·9 g, 77·3% (Found: C, 72·6; H, 6·0. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·0%). ν_{max} 1760 and 1710 cm^{-1}.

*2-(2′,3′-Dibromopropyl)-6-oxo-7,8,9,10-tetrahydro-6*H*-dibenzo*[b,d]*pyran-3-yl Acetate* (*2e*)

A solution of bromine (1·6 g; 0·01M) in acetic acid (25 ml) was added dropwise to a well stirred solution of 2-allyl-6-oxo-7,8,9,10-tetrahydro-6*H*-dibenzo[*b,d*]pyran-3-yl acetate (2·9 g; 0·01M) in acetic acid (25 ml) during 1 h. After being stirred for a further 1 h the solution was diluted with ice-cold water and allowed to stand. The separated product was collected, washed with a little alcohol, dried, dissolved in benzene and passed through alumina. The solution was evaporated and the residue crystallized as colourless *needles* with m.p. 220° from benzene. Yield 3·0 g, 66·7% (Found: C, 47·0; H, 3·6; Br, 35·1. $C_{18}H_{18}Br_2O_4$ requires C, 47·1; H, 3·9; Br, 34·9%).

*9-Methyl-1,2,3,4-tetrahydro-5*H*-benzofuro*[6,5-c][2]*benzopyran-5-one* (*7*)

A solution of 2-(2′,3′-dibromopropyl)-6-oxo-7,8,9,10-tetrahydro-6*H*-dibenzo[*b,d*]pyran-3-yl acetate (2 g) in ethanolic potassium hydroxide (2·5 g in 75 ml absolute alcohol) was heated under

reflux for 4 h and then concentrated to one-third of its volume. Water (50 ml) was added and the solution was immediately acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the ether gave a light red product which was washed with aqueous ammonia (10%) and then with water. It crystallized as colourless *needles*, m.p. 184° from alcohol. Yield 0·6 g, 54·1% (Found: C, 75·5; H, 5·5. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%). λ_{max} (methanol) 248 (log ε 4·45); 290 (3·98); 330 (3·98). ν_{max} 1700 and 860 cm^{-1}.

6-Bromo-7-hydroxy-1,2,3,4-tetrahydrocyclopenta[c][*1*]*benzopyran-4-one* (*3a*)

A mixture of 2-bromoresorcinol (5 g) and ethyl 2-oxocyclopentanecarboxylate (4·3 g) and concentrated sulphuric acid (80%; 45 ml) was kept at room temperature for 24 h and the reaction mixture was worked up as before. The product crystallized as colourless shining *needles* with m.p. 284° (dec.) from alcohol. Yield 5·5 g, 61·5% (Found: C, 51·3; H, 3·0; Br, 28·8. $C_{12}H_9BrO_3$ requires C, 51·2; H, 3·2; Br, 28·5%).

7-Allyloxy-6-bromo-1,2,3,4-tetrahydrocyclopenta[c][*1*]*benzopyran-4-one* (*3b*)

A mixture of 6-bromo-7-hydroxy-1,2,3,4-tetrahydrocyclopenta[*c*][1]benzopyran-4-one (5 g), allyl bromide (2 g) and anhydrous potassium carbonate (10 g) was boiled under reflux for 10 h in dry acetone (200 ml). The reaction mixture was worked up as before. It crystallized as colourless small needles with m.p. 159° from benzene. Yield 3·5 g, 61·3% (Found: C, 56·5; H, 4·1; Br, 24·5. $C_{15}H_{13}BrO_3$ requires C, 56·1; H, 4·0; Br, 24·9%). ν_{max} 1710 and 1290 cm^{-1}.

8-Allyl-7-hydroxy-1,2,3,5-tetrahydrocyclopenta[c][*1*]*benzopyran-4-one* (*3c*)

7-Allyloxy-6-bromo-1,2,3,4-tetrahydrocyclopenta[*c*][1]benzopyran-4-one (2 g) and dimethylaniline (15 ml) were boiled for 6 h under nitrogen. The reaction mixture was worked up as before. The product crystallized as colourless *needles* with m.p. 184° from alcohol. Yield 1·3 g, 86·2% (Found: C, 74·5; H, 5·7. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%). ν_{max} 1700 cm^{-1}.

8-Methyl-1,2,3,4,8,9-hexahydrocyclopenta[c]*furo*[*3,2*-g][*1*]*benzopyran-4-one* (*9*)

8-Allyl-7-hydroxy-1,2,3,4-tetrahydrocyclopenta[*c*]benzopyran-4-one (1 g) was triturated with concentrated sulphuric acid (6 ml) for 2 h and the reaction mixture was worked up as before. The product crystallized as colourless *needles* with m.p. 155° from benzene–light petroleum (40–60°) mixture. Yield 0·6 g, 60% (Found: C, 74·2; H, 5·9. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%).

8-Allyl-4-oxo-1,2,3,4-tetrahydrocyclopenta[c]*benzopyran-7-yl Acetate* (*3d*)

The acetyl derivative of 8-allyl-7-hydroxy-1,2,3,4-tetrahydrocyclopenta[*c*]benzopyran-4-one was prepared by boiling 8-allyl-7-hydroxy-1,2,3,4-tetrahydrocyclopenta[*c*]benzopyran-4-one (1 g) with acetic anhydride (8 ml) and fused sodium acetate (1·5 g) for 5 h. The product crystallized as brown *needles* with m.p. 158° from alcohol. Yield 0·9 g, 76·7% (Found: C, 71·8; H, 5·6. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%). ν_{max} 1760 and 1710 cm^{-1}.

8-(2′,3′-Dibromopropyl)-4-oxo-1,2,3,4-tetrahydrocyclopenta[c]*benzopyran-7-yl Acetate* (*3e*)

A solution of bromine (1·6 g, 0·01M) in acetic acid (25 ml) was added dropwise to a well stirred solution of 8-allyl-4-oxo-1,2,3,4-tetrahydrocyclopenta[*c*]benzopyran-7-yl acetate (2·8 g, 0·01M) in acetic acid (25 ml) during 1 h. The reaction mixture worked up as before. The product crystallized as colourless shining *needles* with m.p. 203° from benzene. Yield 3·0 g, 68·2% (Found: C, 45·7; H, 3·4; Br, 35·9. $C_{17}H_{16}Br_2O_4$ requires C, 45·9; H, 3·6; Br, 36·0%).

8-Methyl-1,2,3,4-tetrahydrocyclopenta[c]*furo*[*3,2*-g][*1*]*benzopyran-4-one* (*10*)

A solution of 8-(2′,3′-dibromopropyl)-4-oxo-1,2,3,4-tetrahydrocyclopenta[*c*]benzopyran-7-yl acetate (2 g) in ethanolic potassium hydroxide (2·5 g in 75 ml absolute alcohol) was heated under reflux for 4 h. The reaction mixture was worked up as before and the product crystallized as colourless *needles* with m.p. 202° from alcohol. Yield 0·5 g, 46·3% (Found: C, 75·3; H, 5·1. $C_{15}H_{12}O_3$

requires C, 75·0; H, 5·0%). λ_{max} (methanol) 248 (log ε 4·40); 296 (4·95); 334 nm (4·94). ν_{max} 1700 and 860 cm^{-1}.

Acknowledgments

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