# CHAPTER II

## Studies in the Synthesis of Benzofuro-coumarins

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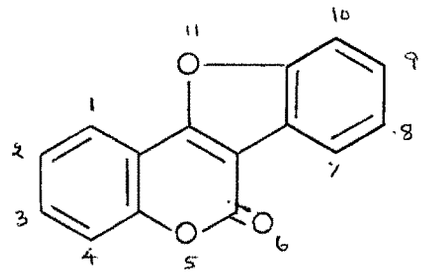
## T H E O R E T I C A L

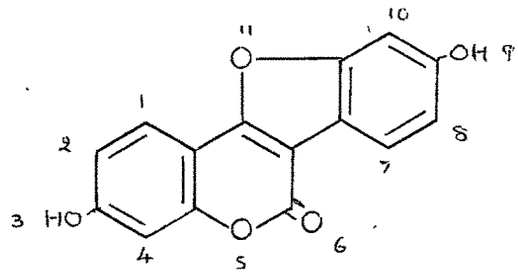
The group coumaronocoumarin or coumarino-benzofuran or benzofuro-a-benzopyrone is represented by naturally occurring coumestrol, wedelolactone, trifoliol, medicagol and psoralidin. The benzofuro(3,2-c)benzopyrans are of structural interest in that they are related to the coumarinochromans and the 3-arylcoumarins.

The trivial name, coumestan (1), has been proposed for the skeletal structure of the heterocyclic four ring system having the systematic name, 6-oxo-6H-benzofuro(3,2-c) benzopyran[1].




(1)

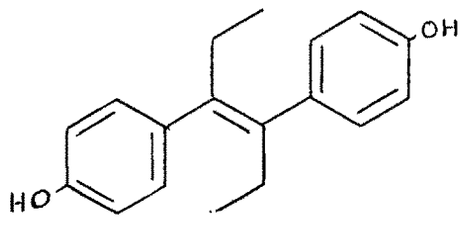
A discussion of oestrogenic activity in coumarin type compounds may include a brief consideration of the closely related isoflavones, which were the first of the plant phenolics to show such activity. The isoflavones may well be the source of coumarin oestrogens, e.g. coumestrol (2) in the plant.




(2)

Bickoff and coworkers[2,3] isolated coumestrol which was 30 times as potent as genistein. The relationship of coumestrol structure to its biological activity has been investigated[4,5], and a number of correlations of structure with activity was observed.

The oestrogenic activity is attributed to its stilbene-like structure analogous to that of diethylstilbestrol (3) and to the natural estradiol (4).

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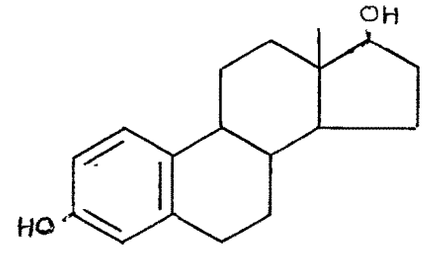


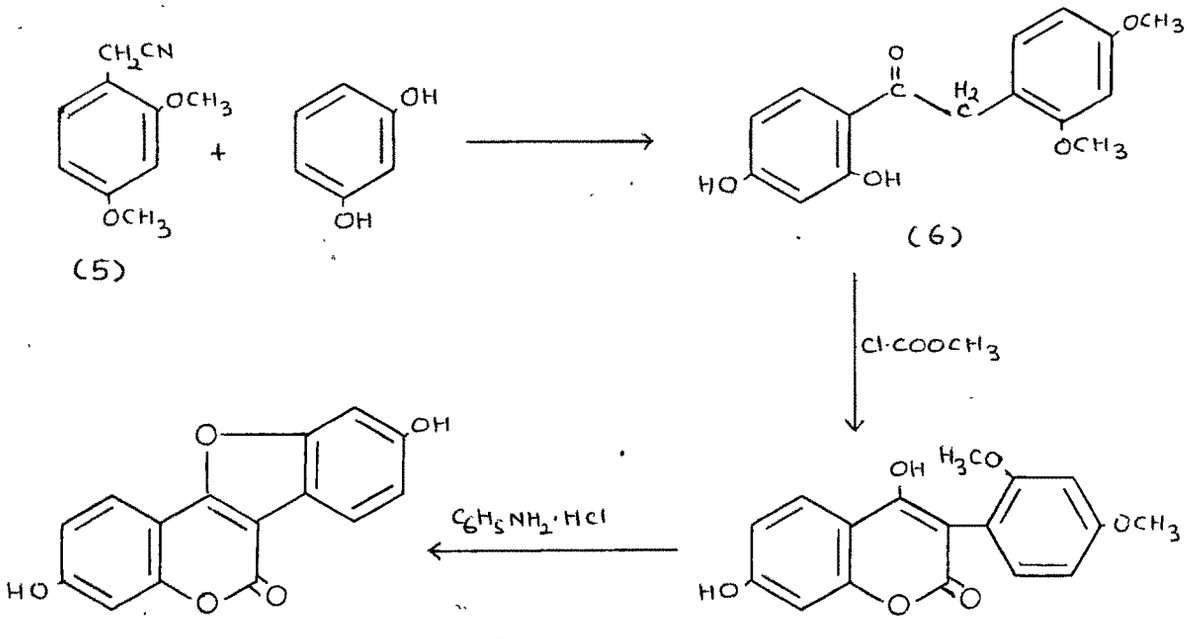

(4)

The ether bridge in coumestrol (2) stabilizes the double bond in 6a,11a positions to maintain the stilbene-like structure. When this ring is opened, this double bond is free to resonate and keto-enol tautomerism exists[6]. The α-pyrone ring structure is important as the furan structure for maintenance of the oestrogenic activity of coumestrol.

The methods of synthesis of some of the naturally occurring benzofuro(3,2-c)benzopyrans are reviewed here.

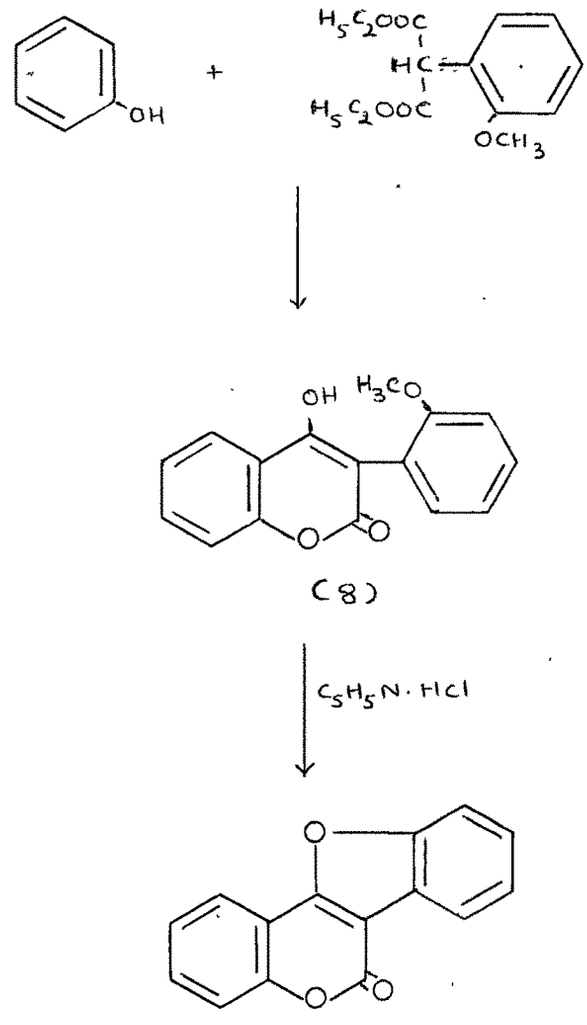
Coumestrol or 3,9-dihydroxy-6-oxo-6H-benzofuro (3,2-c)benzopyran is an oestrogenic substance found in ladino clover in alfalfa[2,7] and in other legumes[8].

Emerson and Bickoff[9] condensed 2,4-dimethoxy-phenylacetonitrile (5) with resorcinol and obtained α-(2,4-dimethoxyphenyl)-2,4-dihydroxyacetophenone (6),

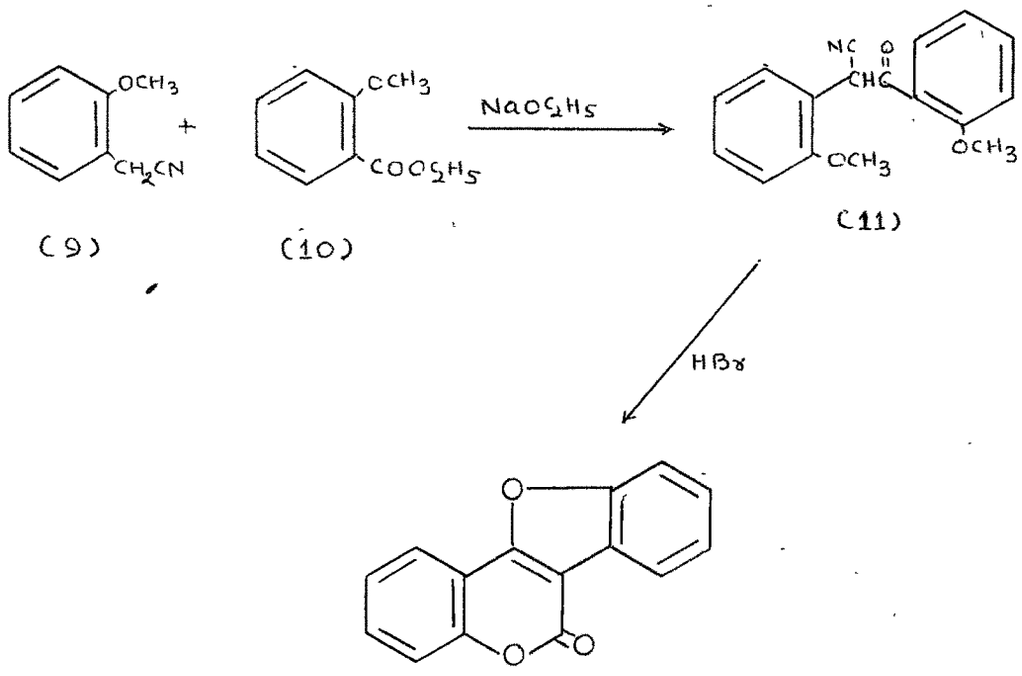


which on treatment with methyl chloroformate yielded 3-(2,4-dimethoxyphenyl)-4,7-dihydroxycoumarin (7). It was then cyclised by heating with aniline hydrochloride to coumestrol (2).

Coumestan or 6-oxo-6H-benzofuro(3,2-c)benzopyran (1) was synthesised by Mentzer et al.[10] phenol on thermal condensation with o-methoxyphenylmalonate gave 3-(2-methoxy phenyl)-4-hydroxycoumarin (8) which on treatment with pyridine hydrochloride produced coumestan (1).



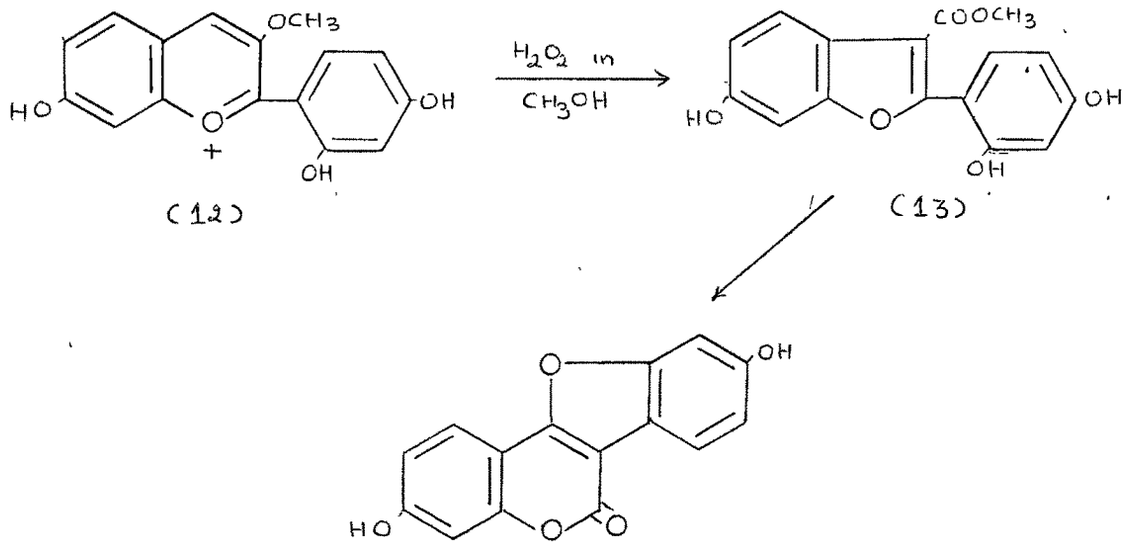
Coumestan was also synthesised by Chatterjea and Roy[11]. They condensed o-methoxyphenylacetonitrile (9) with ethyl-o-methoxybenzoate (10) in the presence of sodium ethoxide and obtained an intermediate ketonitrile (11) which on treatment with hydrobromic acid gave coumestan.




(9) (10) (11)

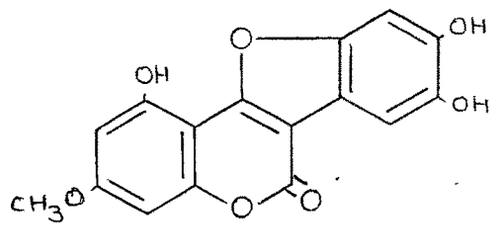
Jurd[12] synthesised coumestrol and related compounds by hydrogen peroxide oxidation of appropriately substituted 2'-hydroxy-3-methoxyflavylium salts. 2',4',7-Trihydroxy-3-methoxyflavylium chloride (12) when oxidised with hydrogen peroxide in aqueous methanol gave 3-carbomethoxybenzofuran (13)

which on acidification lactonizes rapidely to coumestrol.




(12) (13)

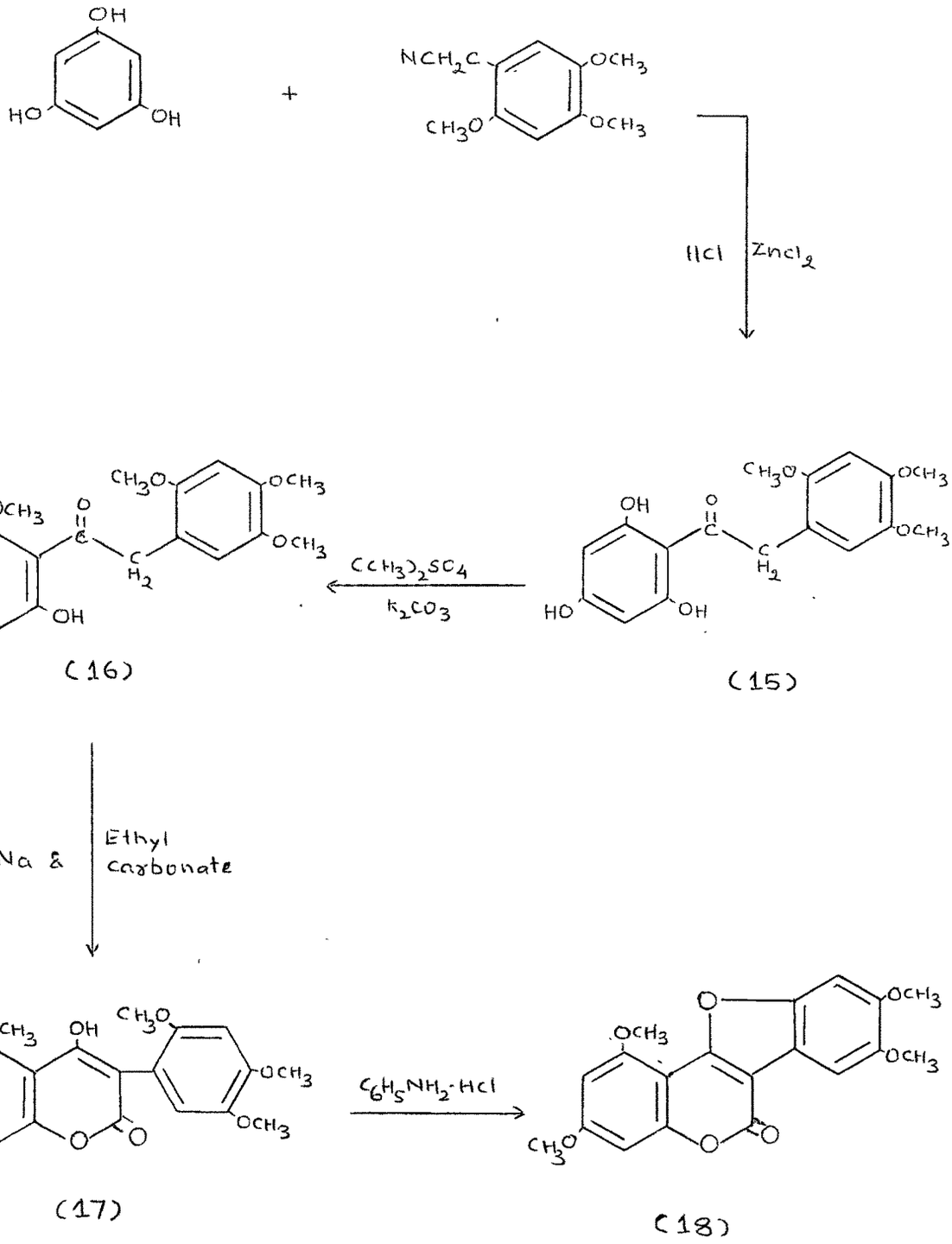
Govindachari and coworkers[13] have isolated wedelolactone (1,8,9-trihydroxy-3-methoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran) (14) from the leaves of Wedelia calendulacea (compositae).




(14)

Govindachari et al.[14] have synthesised tri-o-methylwedelolactone. Asarylaldehyde, obtained in nearly quantitative yield from 1,2,4-trimethoxybenzene by treatment with dimethylformamide was converted into 2,4,5-trimethoxybenzyl cyanide, through 2,4,5-trimethoxyphenyl pyruvic acid. The deoxybenzoin (15) obtained by Hoesch reaction of this cyanide with phloroglucinol was converted by selective methylation into the dimethyl ether (16) and then by ethyl carbonate and sodium into the 4-hydroxy-coumarin (17) which when heated with aniline hydrochloride was converted into the benzofurobenzopyran, tri-o-methyl-wedelolactone (18).

Chatterjee and Prasad[15] have recently synthesised tri-o-methylwedelolactone (18). The keto nitrile (19), obtained by the condensation of 2,4,5-trimethoxybenzyl cyanide and ethyl 2,4,6-trimethoxybenzoate in the presence of sodium hydride, was treated with pyridine hydrochloride to yield (20) which was readily methylated to tri-o-methylwedelolactone (18).


OH
HO
OH
+
NCH2C
OCH3
CH3O
OCH3
HCl
ZnCl2
CH3O
OCH3
OH
O
C
CH2
OCH3
HO
OH
(CH3)2SO4
K2CO3
CH3O
OCH3
O
C
CH2
OCH3
CH3O
OH
(15)
(16)
Na &
Ethyl
carbonate
OCH3
OH
CH3O
OCH3
CH3O
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(17)
C6H5NH2·HCl
O
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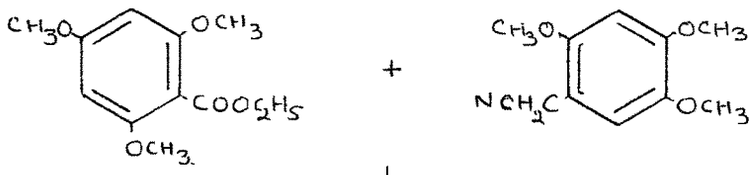
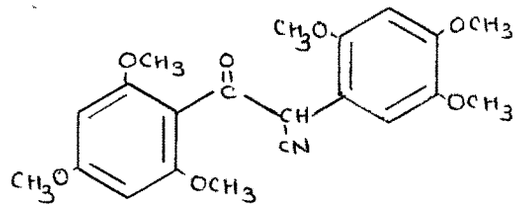
CH3O
O
O
(18)

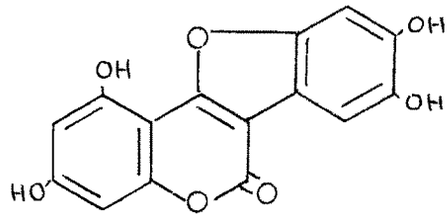


NaH



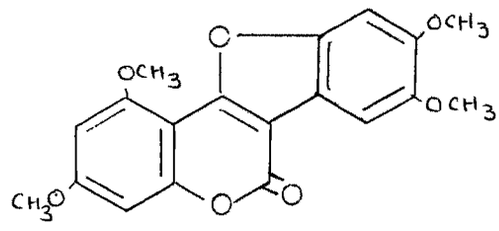
(19)

$C_5H_5N \cdot HCl$

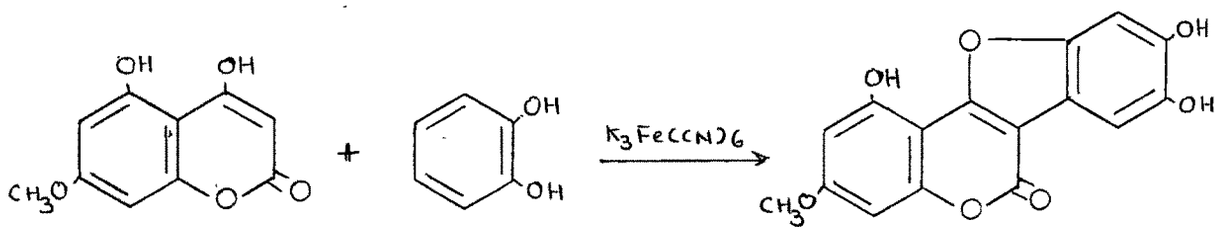


(20)

$(CH_3)_2SO_4$

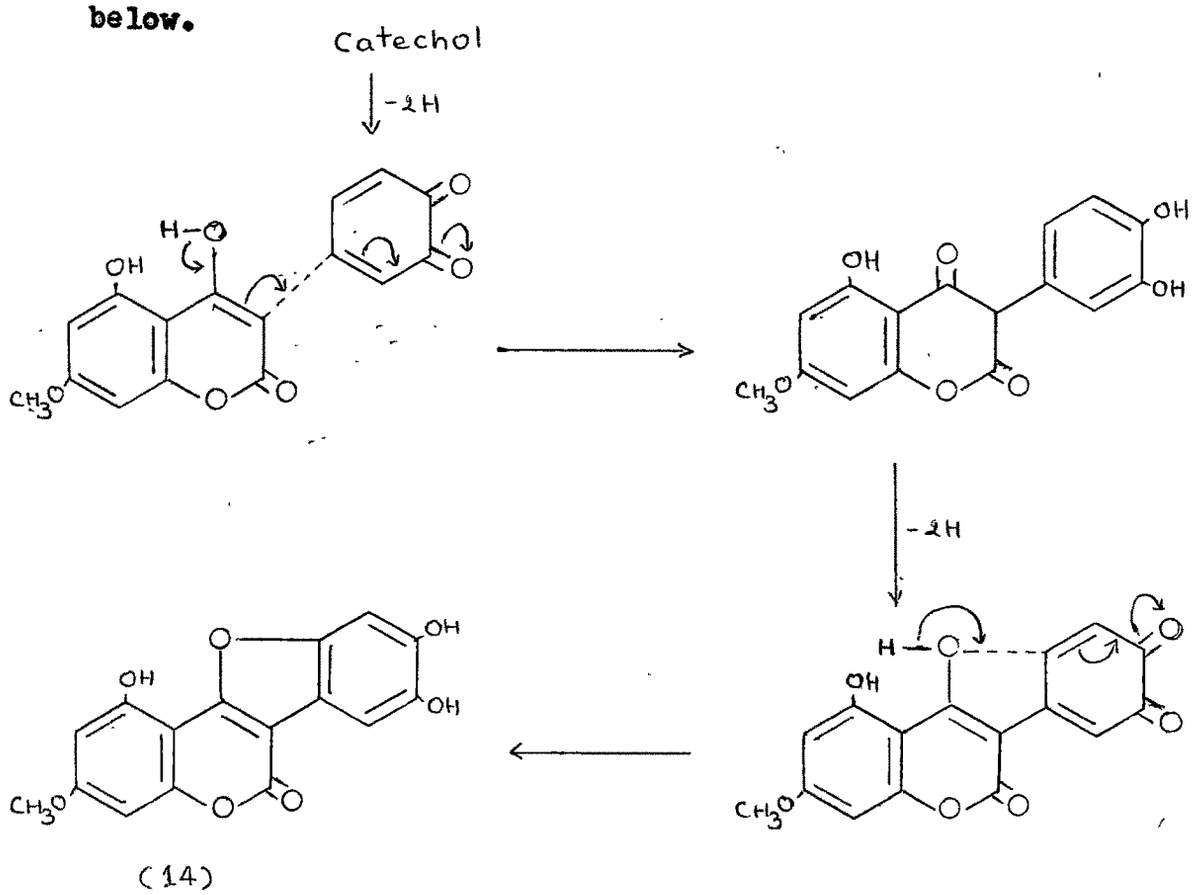


Wanzlick and coworkers[16] prepared wedelolactone (14) by dehydrogenative coupling of catechol with 4,5-dihydroxy-7-methoxycoumarin (21) and potassium ferricyanide. In place of potassium ferricyanide, potassium iodate is also used in the syntheses of benzofurobenzopyrans.



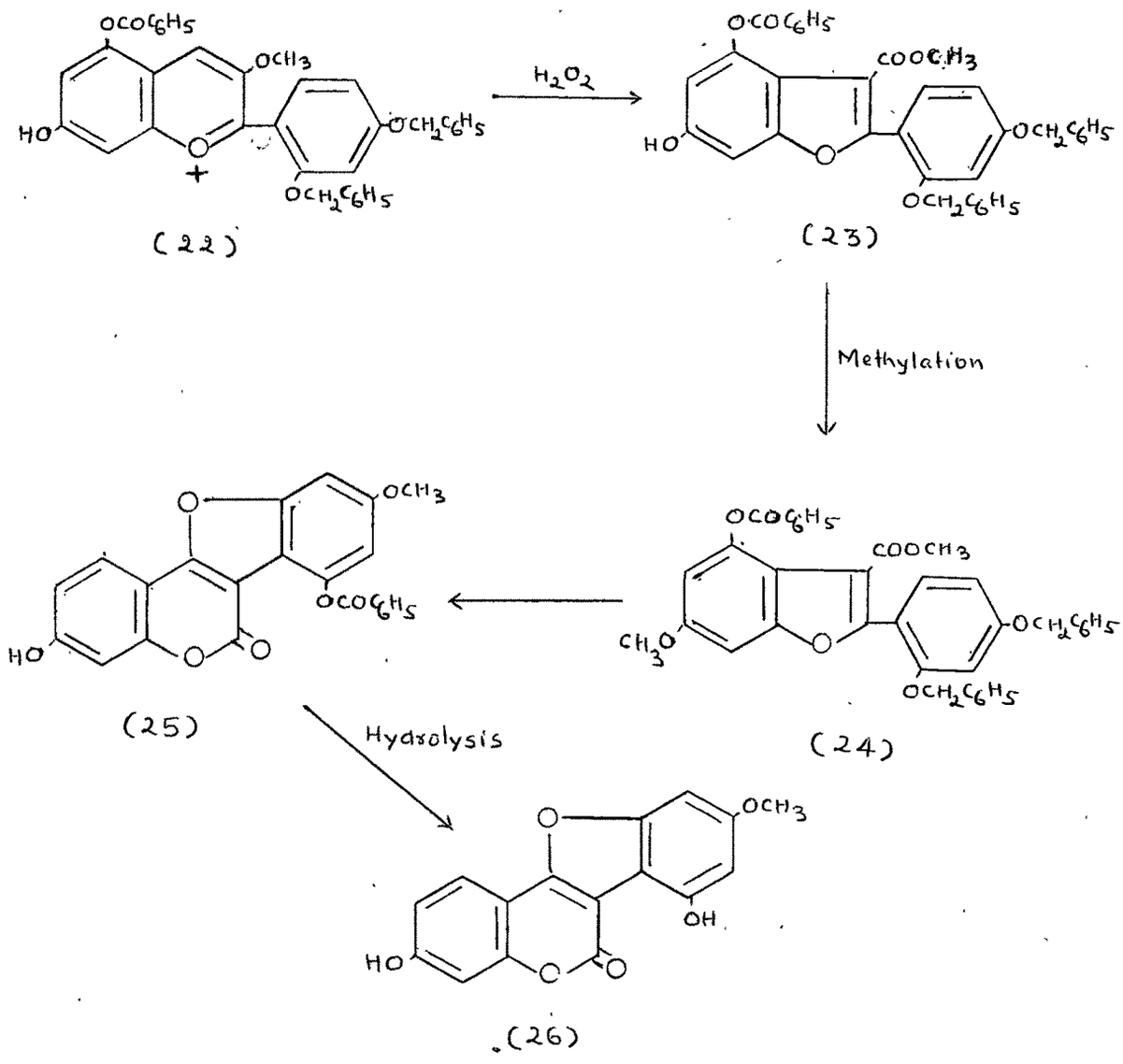

(21) (14)

The mechanism given by the authors is as shown below.




(14)

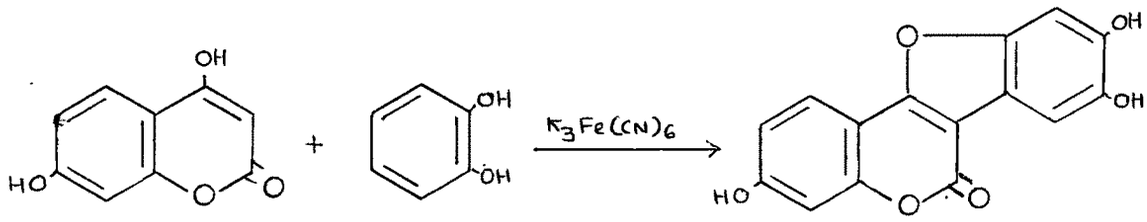
Trifoliol (3,7-dihydroxy-9-methoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran ) (26) was isolated from ladino clover by L.Jurd and coworkers[17]. The structure of trifoliol was proved on the basis of U.V. and NMR spectra and also by degradation method. The structure was confirmed by its synthesis, starting with 5-benzoyloxy-7-hydroxy-3-methoxy-2',4'-dibenzyloxyflavylium chloride (22)



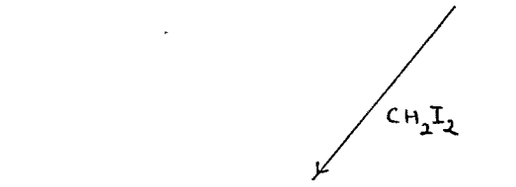

(22) (23) (24) (25) (26)

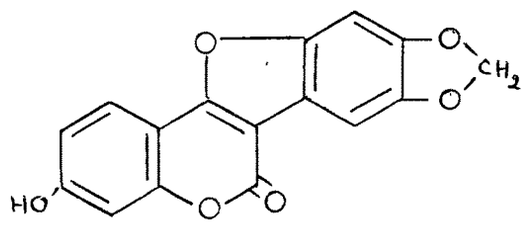
Peroxide oxidation of the flavylium salt gave the intermediate (23) which was methylated to (24) and then debenzylated to give 7-benzoyloxy-3-hydroxy-9-methoxy-coumestan (25). Alkaline hydrolysis of the latter compound furnished 3,7-dihydroxy-9-methoxycoumestan (trifoliol) (26).

Medicagol (3-hydroxy-8,9-dioxymethylene-6-oxo-6H-benzofuro(3,2-c)benzopyran (29) is isolated as a mixture with pisatin from alfalfa meal. It was synthesised by oxidative condensation of 4,7-dihydroxycoumarin (27) with catechol. Methylenation of (28) with methylenediiodide gave medicagol (29).




(27) (28)

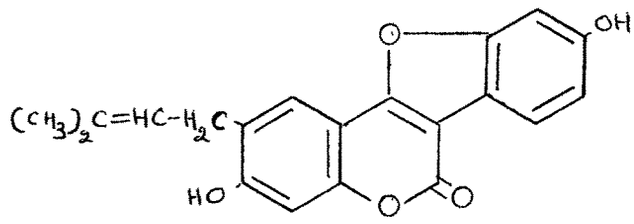



(29)

L.Jurd[18] has synthesised medicagol recently by carrying out hydrogen peroxide oxidation of 3-methoxy-6,7-methylenedioxy-2',4'-dihydroxyflavylium chloride.

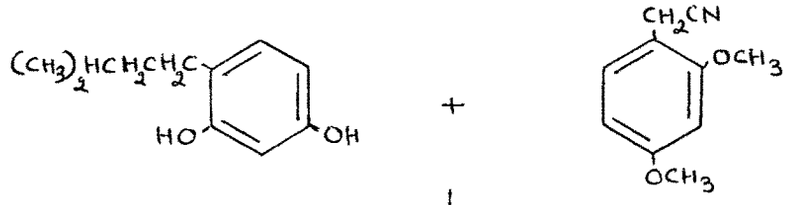
Psoralidin or 2-isopentenyl-3,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (30) was first isolated from the pericarp of the seeds of P.Corylifolia L. by Chakravarti and coworkers[19].

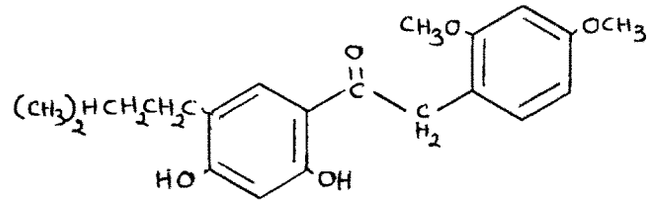



(30)

Later Sengupta and coworkers[20] isolated the same psoralidin from the alcoholic extract of the seed kernel of Psoralea Corylifolia Linn and proved that it is the isopentenyl derivative of coumestrol.

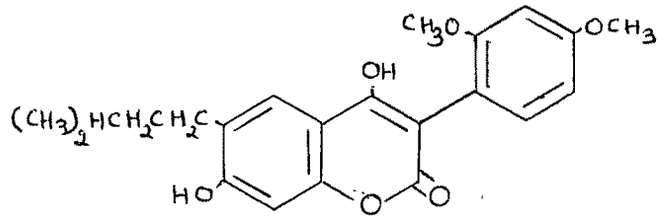
As psoralidin is labile to acids, it has not been synthesised but many workers have synthesised dihydro-psoralidin (33). Nasipuri and Pyne[21] and Bickoff et al.[22] have treated 2,4-dihydroxy-5-isopentyl-2,4-dimethoxy-benzyl ketone (31), which was obtained by Hoesch reaction of 2,4-dimethoxybenzyl cyanide and 4-isopentyl resorcinol with ethyl chloroformate, followed by treatment with alkali and then with acid to give 4,7-dihydroxy-6-isopentyl-3-(2',4'-dimethoxyphenyl)coumarin (32). When this coumarin (32)





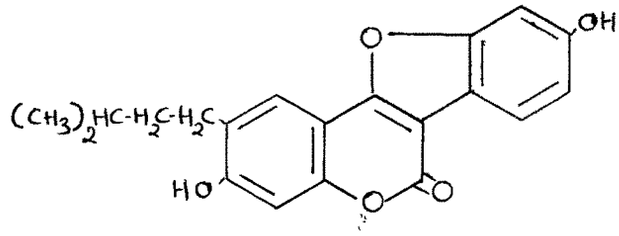
(31)

$Cl{\cdot}COOC_2H_5$



(32)

$C_6H_5NH_2{\cdot}HCl$



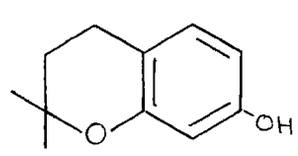
(33)

was treated with aniline hydrochloride, it gave dihydropsoralidin (33).

The authors have also synthesised isopsoralidin (37). Hoesch condensation of 2,4-dimethoxybenzyl cyanide with 7-hydroxy-2,2-dimethylchroman (34) furnished 2,4-dimethoxybenzyl-7-hydroxy-2,2-dimethylchroman-6-yl ketone (35) which was converted into the 4-hydroxycoumarin derivative (36) by sodium and ethyl carbonate and thence into isopsoralidin (37) by heating it with aniline hydrochloride.

Similarly they have condensed methyl-2,2-dimethyl-7-methoxychroman benzoate with 2,4-dimethoxybenzyl cyanide in the presence of sodium hydride followed by the treatment with pyridine hydrochloride to yield isopsoralidin.

Chatterjea, Banerjee and Prasad[23] have prepared dihydropsoralidin (33) and isopsoralidin (37). Methyl-2,4-dimethoxy-5-isopentenylbenzoate (38) was condensed with 2,4-dimethoxybenzyl cyanide in the presence of sodium hydride to yield a keto nitrile (39) which was then heated with pyridine hydrochloride to dihydropsoralidin (33).



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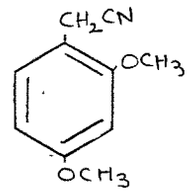
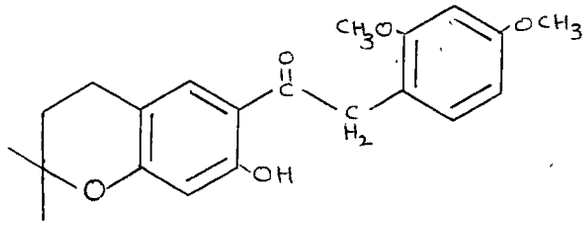
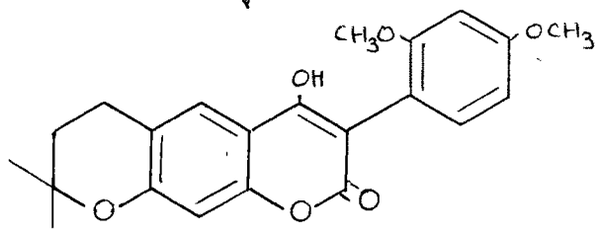




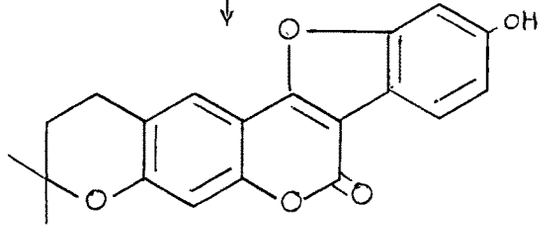
(35)

Na & Ethyl carbonate



(36)

$C_6H_5NH_2 \cdot HCl$



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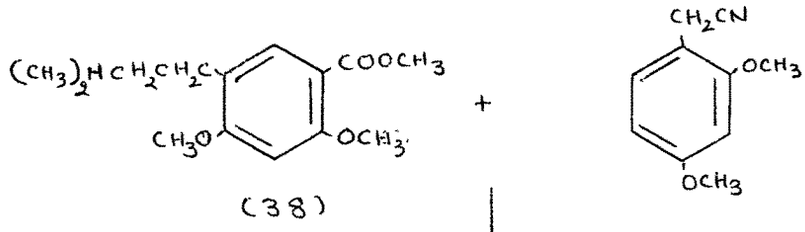

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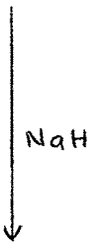


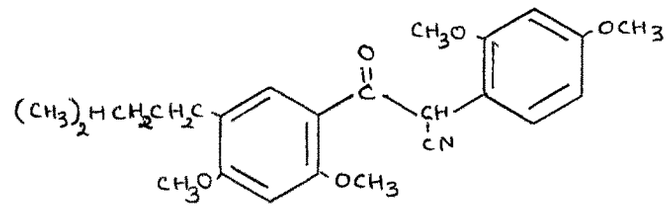

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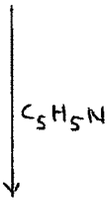
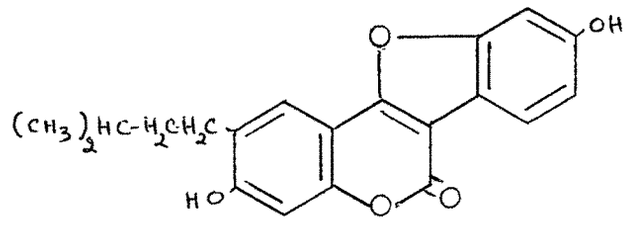


(33)

In view of the pharmacological activity of coumestrol derivatives, it was throught of interest to synthesise different benzofurobenzopyrone derivatives having substituents like OH, $-CH_3$, $-OCH_3$ groups in the benzanoid parts of the coumestrol molecule.

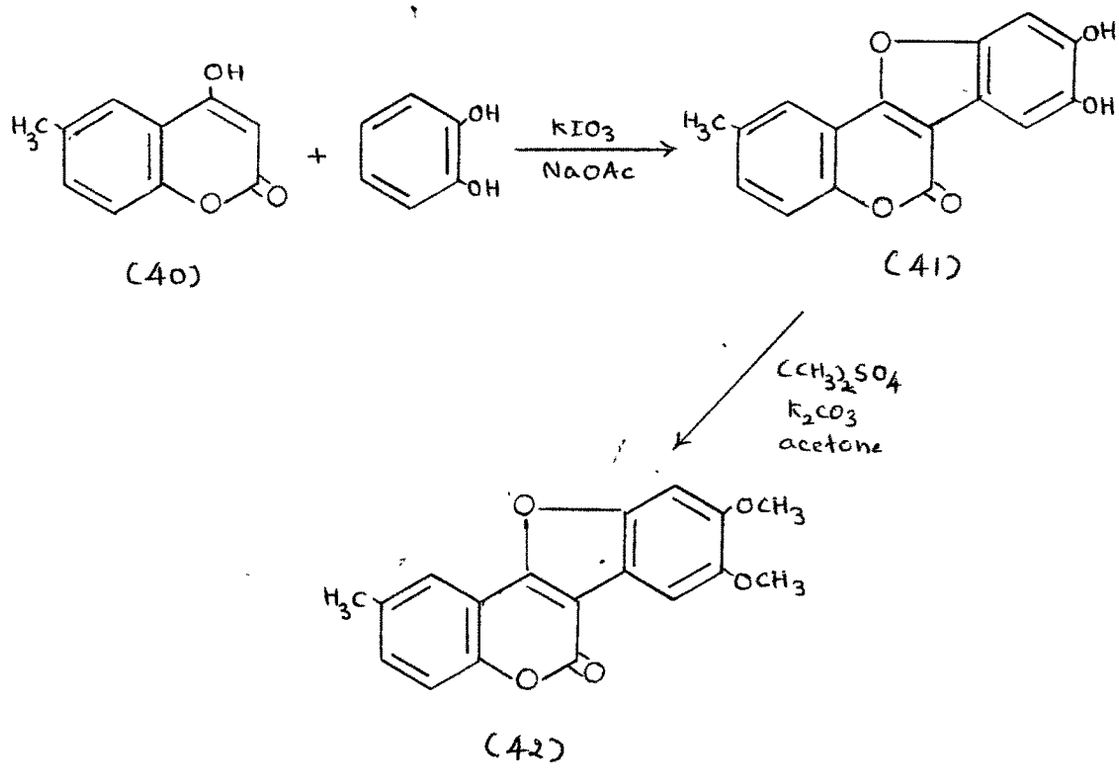
The following benzofurocoumarins are synthesised by the oxidative condensation of catechol with different 4-hydroxycoumarins.

1. 2-Methyl-8,9-dimethoxy-6-oxo-6H-benzofuro(3,2-c) benzopyran.
2. 2,8,9-Trimethoxy-6-oxo-6H-benzofuro(3,2-c) benzopyran.
3. 4-Methyl-3,8,9-trimethoxy-6-oxo-6H-benzofuro (3,2-c)benzopyran.
4. 1,8,9-Trimethoxy-6-oxo-6H-benzofuro(3,2-c) benzopyran.
5. 3,4,8,9-Tetramethoxy-6-oxo-6H-benzofuro(3,2-c) benzopyran.

Synthesis of 2-Methyl-8,9-dimethoxy-6-oxo-6H-benzofuro(3,2-c) benzopyran (42) :

On oxidative condensation of catechol with 4-hydroxy-6-methylcoumarin (40) in the presence of potassium iodate and sodium acetate yielded 2-methyl-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (41).

The above benzofurocoumarin (41) was then methylated with dimethyl sulphate and anhydrous potassium carbonate in acetone to give 2-methyl-8,9-dimethoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (42).

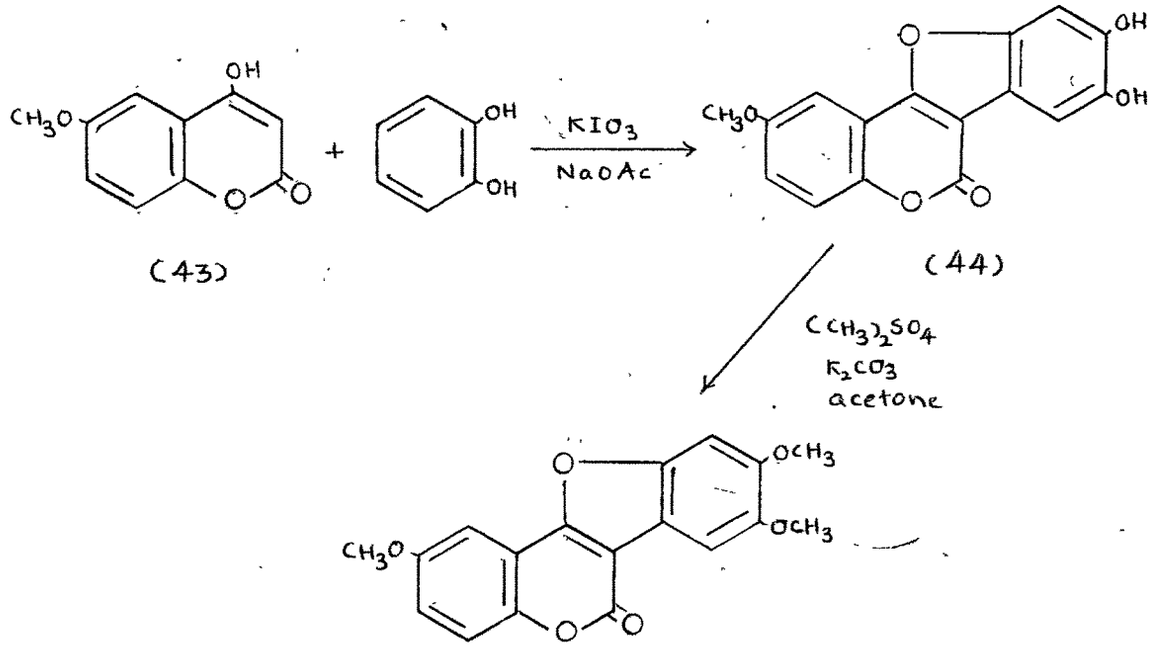



(40) (41) (42)

Synthesis of 2,8,9-Trimethoxy-6-oxo-6H-benzofuro(3,2-c) benzopyran (45) :

4-Hydroxy-6-methoxycoumarin (43) on oxidative condensation with catechol in the presence of potassium iodate and sodium acetate afforded 2-methoxy-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (44).

This 2-methoxy-8,9-dihydroxy-6-oxo-6H-benzofuro (3,2-c)benzopyran (44) was then methylated with dimethyl sulphate as usual and 2,8,9-trimethoxy-6-oxo-6H-benzofuro (3,2-c)benzopyran (45) was obtained.



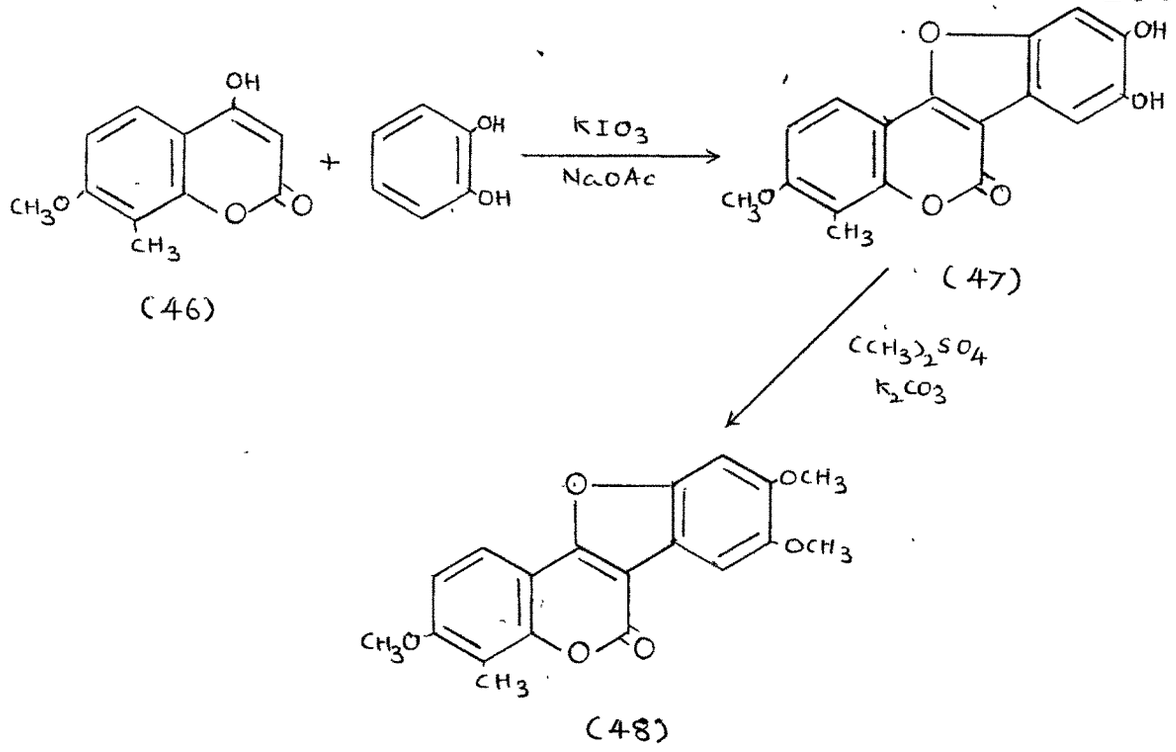

(43) (44) (45)

Synthesis of 4-Methyl-3,8,9-trimethoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (48) :

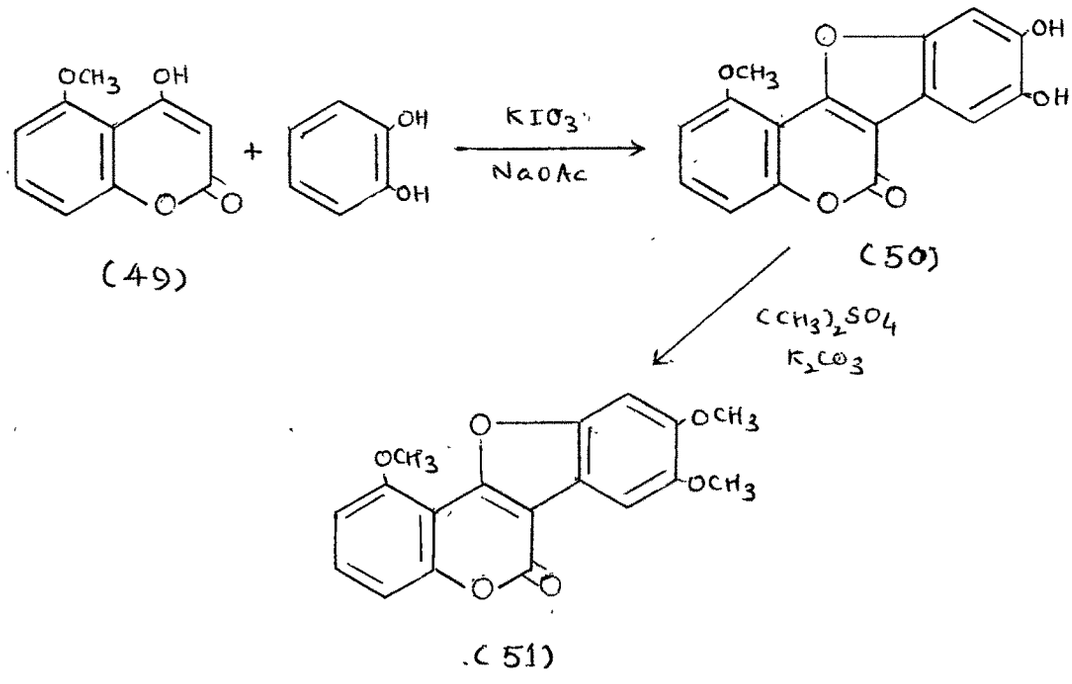
When 4-hydroxy-7-methoxy-8-methylcoumarin (46) was condensed with catechol in the presence of potassium iodate and sodium acetate it afforded 4-methyl-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (47). It was then methylated as usual to 4-methyl-3,8,9-trimethoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (48).

Synthesis of 1,8,9-Trimethoxy-6-oxo-6H-benzofuro(3,2-c) benzopyran (51) :

4-Hydroxy-5-methoxycoumarin (49) when condensed with catechol as described earlier yielded 1-methoxy-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (50).

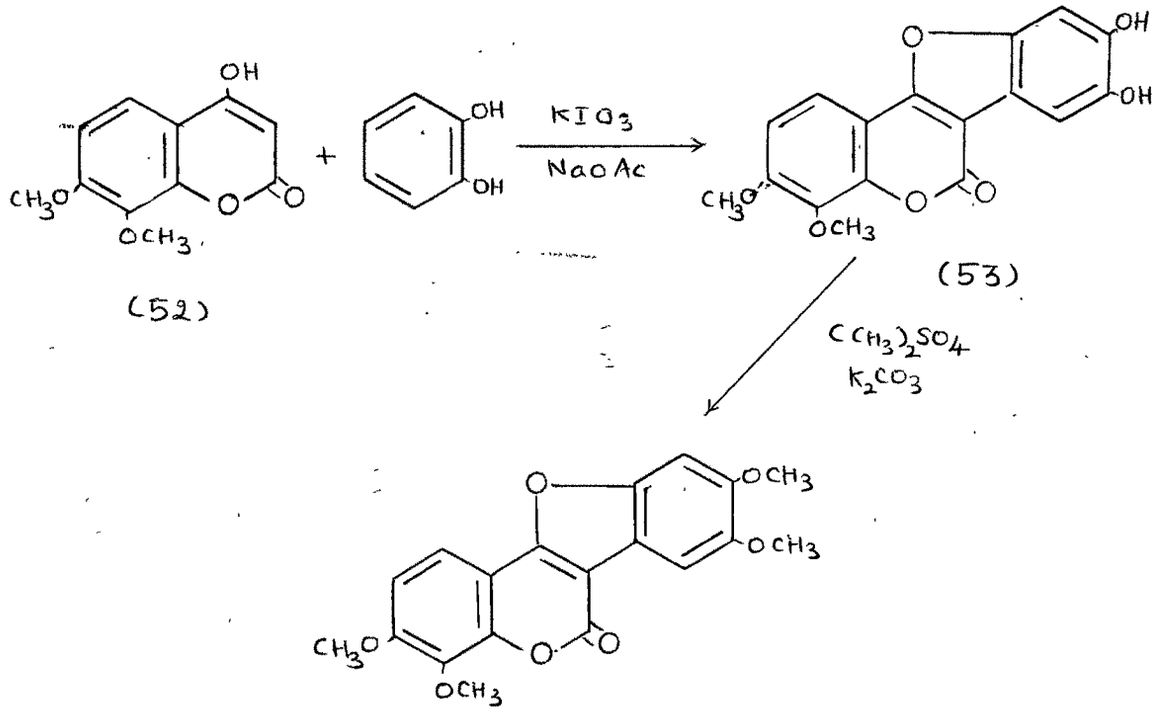



This 1-methoxy-8,9-dihydroxy-6-oxo-6H-benzofuro (3,2-c)benzopyran (50) was then methylated as usual to give 1,8,9-trimethoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (51).



Synthesis of 3,4,8,9-Tetramethoxy-6-oxo-6H-benzofuro (3,2-c)benzopyran (54) :

When 4-hydroxy-7,8-dimethoxycoumarin (52) was condensed with catechol as described earlier 3,4-dimethoxy-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (53) was obtained. It was then methylated to give 3,4,8,9-tetramethoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (54).




(52)

(53)

(54)

## EXPERIMENTAL

Synthesis of 2-Methyl-8,9-dimethoxy-6-oxo-6H-benzofuro (3,2-c)benzopyran :

Oxidative condensation of catechol with 4-hydroxy-6-methylcoumarin : 2-Methyl-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran :

To the solution of 4-hydroxy-6-methylcoumarin (0.8 g.), catechol (0.4 g.) and sodium acetate (2.0 g.) in acetone-water (20 ml. ; 1:1), a solution of potassium iodate (0.5 g.) and sodium acetate (1.0 g.) in water(10 ml.) was added slowly with constant stirring. After 5 minutes the separated product was filtered, washed with water and crystallised from acetic acid, m.p. 348°. Yield 0.5 g.

Analysis : Found : C,68.00 ; H,3.11 %.
$C_{16}H_{10}O_5$ requires : C,68.08 ; H,3.57 %.

2-Methyl-8,9-dimethoxy-6-oxo-6H-benzofuro(3,2-c) benzopyran :

A mixture of 2-methyl-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (0.4 g.), dimethyl sulphate (1 ml.) and anhydrous potassium carbonate (2.0 g.) in dry acetone (100 ml.) was refluxed on a steam bath for 8 hr. On evaporation of acetone, the separated product was filtered,washed with dilute sodium hydroxide solution and crystallised from dil.acetic acid,m.p.210°. Yield 0.3 g.

Analysis : Found : C,69.31 ; H,4.56 %.
$C_{18}H_{14}O_5$ requires : C,69.67 ; H,4.55 %.

Synthesis of 2,8,9-Trimethoxy-6-oxo-6H-benzofuro (3,2-c)benzopyran :

Oxidative condensation of catechol with 4-hydroxy-6-methoxycoumarin : 2-Methoxy-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran* :

To the solution of 4-hydroxy-6-methoxycoumarin (1 g.), catechol (0.5 g.) and sodium acetate (2.5 g.) in acetone-water (25 ml. ; 1:1), a solution of potassium iodate (0.6 g.) and sodium acetate (1.2 g.) in water (10 ml.) was added slowly with constant stirring. The product which separated immediately was filtered, washed with water and dried. As it could not be crystallised from any common organic solvents, it was methylated directly, m.p. above 320°.

2,8,9-Trimethoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran :

A mixture of 2-methoxy-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (0.4 g.), dimethyl sulphate (1 ml.) and anhydrous potassium carbonate (2.0 g.) in dry acetone (100 ml.) was refluxed on a steam bath for about 10 hr. The reaction mixture was worked up as usual and the product crystallised from benzene-petroleum ether, m.p. 240°. Yield (0.2 g.)

Analysis : Found : C,66.24 ; H,4.29 %.

$C_{18}H_{14}O_6$ requires : C,66.25 ; H,4.32 %.

Synthesis of 4-Methyl-3,8,9-trimethoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran :

Oxidative condensation of catechol with 4-hydroxy-7-methoxy-8-methylcoumarin : 4-Methyl-8,9-dihydroxy-3-methoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran* :

To the solution of 4-hydroxy-7-methoxy-8-methylcoumarin (0.5 g.),catechol (0.2 g.) and sodium acetate (1.2 g.) in water-acetone (10 ml. ; 1:1), a solution of potassium iodate (0.3 g.) and sodium acetate (0.6 g.) in water (5 ml.) was added slowly with constant stirring. The separated product was filtered,washed with water and dried. It could not be crystallised from any solvent and hence it was methylated directly.

4-Methyl-3,8,9-trimethoxy-6-oxo-6H-benzofuro(3,2-c) benzopyran :

A mixture of 4-methyl-8,9-dihydroxy-3-methoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (0.5 g.),dimethyl sulphate (1 g.) and anhydrous potassium carbonate (2 g.) in dry acetone (150 ml.) was refluxed on a steam bath for 10 hr. The reaction mixture was worked up as usual and the product crystallised from benzene-petroleum ether,m.p.238°. Yield 0.3 g.

Analysis : Found : C,66.79 ; H,4.68 %.

$C_{19}H_{16}O_6$ requires : C,67.05 ; H,4.75 %.

Synthesis of 1,8,9-Trimethoxy-6-oxo-6H-benzofuro (3,2-c)benzopyran :

Oxidative condensation of catechol with 4-hydroxy-5-methoxycoumarin : 1-Methoxy-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran* :

To the solution of 4-hydroxy-5-methoxycoumarin (0.6 g.), catechol (0.3 g.) and sodium acetate (1.5 g.) in acetone-water (10 ml. ; 1:1), a solution of potassium iodate (0.35 g.) and sodium acetate (0.75 g.) in water (6 ml.) was added slowly with constant stirring. After 5 minutes the separated product was filtered,washed with water,dried and methylated directly.m.p.above 320°.

1,8,9-Trimethoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran :

A mixture of 1-methoxy-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (0.3 g.),dimethyl sulphate (1 ml.) and anhydrous potassium carbonate (2 g.) in dry acetone (100 ml.) was refluxed on a water bath for 6 hr. The reaction mixture was worked up as usual and the product crystallised from benzene,m.p.263°. Yield 0.1 g.

Analysis : Found : C,65.97 ; H,4.11 %.

$C_{18}H_{14}O_6$ requires : C,66.25 ; H,4.32 %.

Synthesis of 3,4,8,9-Tetramethoxy-6-oxo-6H-benzofuro (3,2-c)benzopyran :

Oxidative condensation of catechol with 4-hydroxy-7,8-dimethoxycoumarin : 3,4-Dimethoxy-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran :

To a solution of 4-hydroxy-7,8-dimethoxycoumarin (0.8 g.),catechol (0.4 g.) and sodium acetate (2.0 g.) in acetone-water (20 ml. ; 1:1), a solution of potassium iodate (0.5 g.) and sodium acetate (1.0 g.) in water (10 ml.) was added slowly with constant stirring. After 10 minutes the separated product was filtered,washed with water,dried and methylated directly,m.p. above 320°.

3,4,8,9-Tetramethoxy-6-oxo-6H-benzofuro(3,2-c)benzopyran :

A mixture of 3,4-dimethoxy-8,9-dihydroxy-6-oxo-6H-benzofuro(3,2-c)benzopyran (0.5 g.),dimethyl sulphate (1 ml.) and anhydrous potassium carbonate (2.0 g.) in dry acetone (100 ml.) was refluxed on a steam bath for 8 hr. The reaction mixture was worked up as usual and the product crystallised from benzene-petroleum ether, m.p. 204°. Yield 0.3 g.

Analysis : Found : C,63.93 ; H,4.73 %.
$C_{19}H_{16}O_7$ requires : C,64.04 ; H,4.53 %.

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