Application of Aryllead(IV) Derivatives to the Preparation of 3-Aryl-4-hydroxy-1-benzopyran-2-ones

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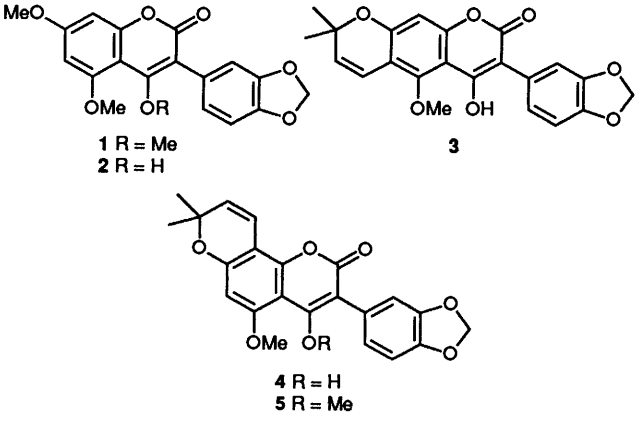
Aryllead triacetates are chemoselective and regioselective reagents for the preparation of 3-aryl-4-hydroxy-1-benzopyran-2-ones in good to excellent yields by C-3 arylation of the preformed 4-hydroxy-1-benzopyran-2-one ring. This approach was applied to the high-yielding synthesis of naturally occurring examples. A radical mechanism was discounted and the mechanism proposed involves the ligand coupling of an intermediate possessing an enolate-to-lead bond to afford arylated products.

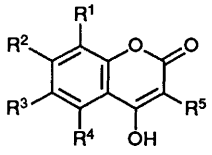
The 3-aryl-4-hydroxy-1-benzopyran-2-ones (common name 3-aryl-4-hydroxycoumarins) are a class of isoflavonoid [1] natural products which are found in the genus *Derris*, which belongs to the tribe Dalbergieae [2] or in the genus *Millettia*, which belongs to the tribe Millettieae,[3] of the Leguminosae, subfamily Papilionoideae. Species of these tribes are noted for the profuse production of flavonoids (including isoflavonoids) prenylated in ring A of the skeleton. All 13 naturally occurring examples,[4] with the exception of derrusnin **1**[5], conform to this pattern. In addition, each member is methoxylated at C-5, a feature which favours the coumarin structure, rather than the tautomeric 2-hydroxyisoflavone form.[6] A distinctive feature of the isoflavonoids is the biological activity exhibited by its members. The oestrogenic activities of isoflavones[7] and coumestans[8] and the insecticidal properties of rotenoids[9] are well-established. Phytoalexin properties are associated with, among others, the 3-aryl-4-hydroxy-1-benzopyran-2-ones. For example,[10] at concentrations of 5 ppm, synthetic examples significantly inhibit the growth of *Phytophthora parasitica*, a pathogenic fungus. In view of the structural similarity of 3-aryl-4-hydroxy-1-benzopyran-2-ones to warfarin and dicoumarol, their anticoagulant activity was investigated[11] and several examples exhibited even stronger anti-vitamin K properties than dicoumarol. The biological importance and considerable therapeutic potential of 3-aryl-4-hydroxy-1-benzopyran-2-ones, including their synthetic congeners the 3-arylcoumarins and the coumestans, have generated considerable interest in the design of efficient methodology for their synthesis.

The ring closure of acylated salicylates,[12–14] *via* an intramolecular Claisen condensation, and the reaction of substituted phenols with substituted malonic esters[15] were the earliest reported routes to these compounds. The addition of a single carbon atom in the form of either diethyl carbonate[16] or ethyl chloroformate[17] to a deoxybenzoin and subsequent ring closure is a further route which was applied to the synthesis of three naturally occurring 3-aryl-4-hydroxy-1-benzopyran-2-ones, namely derrusnin[17] **1**, robustin[18] **3** and isorobustin[18] **4**. No overall yield could be calculated for the preparation of **1** but **3** and **4** were prepared in an overall yield of 2 and 4%, respectively. The Lewis acid-mediated rearrangement of aurone epoxides and 2-(α-hydroxy)-2-methoxy-2-benzofuran-3(2*H*)-ones are two additional routes to 3-aryl-4-hydroxy-1-benzopyran-2-ones.[19,20] However, along with the specific requirements of these methods, their major limitation is the low-yielding preparation of the ring cyclisation reactants.



The nucleophilicity of the 3-position in 4-hydroxy-1-benzopyran-2-ones is well established.[21,22] As a result, the simplest synthetic route to these compounds is direct arylation at C-3. This approach was utilised in the direct coupling of 4-hydroxy-1-benzopyran-2-one with aryldiazonium salts in an acidic medium.[23,24] However, the reaction was totally unsuccessful when *ortho*-substituted arenediazonium salts were employed. The arylation of 4-hydroxy-1-benzopyran-2-one **6** and 4-hydroxy-7-methoxy-1-benzopyran-2-one **13** has recently been effected in good yield using pentavalent arylbismuth compounds.[25] The generality of this method is limited by the non-availability of suitably substituted (methoxy or methylenedioxy)triarylbismuth(V) reagents. Nevertheless, this C-3 arylation approach affords the highest reported yields of 3-aryl-4-hydroxy-1-benzopyran-2-ones and the possibility of using more suitable arylating agents was investigated.

In order to effect α-arylation, diverse routes and special reagents have been devised. Many methods involve metals such as palladium,[26,27,28] others use arylating agents such as diaryliodonium salts,[29] arylboranes[30] and diarylcuprates,[31,32] whilst some rely on the different reactivity afforded by using carbonyl synthetic equivalents, *e.g.* in the photostimulated arylation of ketone enolates.[33] These methods are of limited applicability to the preparation of 3-aryl-4-hydroxy-1-benzopyran-2-ones as the yield of α-arylation is low and/or the preparation of suitably substituted arylating agents is too difficult. Arylation using aryllead triacetates, a class of organometallics which readily arylate enolisable substrates



Compound	R^1	R^2	R^3	R^4	R^5
6	H	H	H	H	H
7	H	H	H	H	C_6H_5
8	H	H	H	H	4-$MeOC_6H_4$
9	H	H	H	H	4-MeC_6H_4
10	H	H	H	H	2,4-$(MeO)_2C_6H_3$
11	H	H	H	H	3,4-$(OCH_2O)C_6H_3$
12	H	H	H	H	2,4,6-$(MeO)_3C_6H_2$
13	H	MeO	H	H	H
14	H	MeO	H	H	C_6H_5
15	H	MeO	H	H	4-$MeOC_6H_4$
16	H	MeO	H	H	2,4-$(MeO)_2C_6H_3$
17	H	MeO	H	H	2,4,6-$(MeO)_3C_6H_2$
18	H	H	MeO	H	H
19	H	H	MeO	H	C_6H_5
20	H	H	MeO	H	4-MeC_6H_4
21	H	H	MeO	H	2,4-$(MeO)_2C_6H_3$
22	H	H	MeO	H	2,4,6-$(MeO)_3C_6H_2$
23	H	H	H	MeO	H
24	H	H	H	MeO	C_6H_5
25	H	H	H	MeO	2-$MeOC_6H_4$
26	H	H	H	MeO	3-$MeOC_6H_4$
27	H	H	H	MeO	4-$MeOC_6H_4$
28	H	H	H	MeO	4-MeC_6H_4
29	H	H	H	MeO	2,4-$Me_2C_6H_3$
30	H	H	H	MeO	3,4-$Me_2C_6H_3$
31	H	H	H	MeO	2,5-$Me_2C_6H_3$
32	H	H	H	MeO	3,4-$(OCH_2O)C_6H_3$
33	H	H	H	MeO	2,4,6-$Me_3C_6H_2$
34	MeO	MeO	H	H	H
35	MeO	MeO	H	H	C_6H_5
36	MeO	MeO	H	H	4-$MeOC_6H_4$
37	MeO	MeO	H	H	2,4-$(MeO)_2C_6H_3$
38	MeO	MeO	H	H	2,4,6-$(MeO)_3C_6H_2$
39	H	MeO	H	MeO	H
40	H	MeO	H	MeO	4-$MeOC_6H_4$
2	H	MeO	H	MeO	3,4-$(OCH_2O)C_6H_3$
41	H	MeO	H	MeO	2,4,6-$(MeO)_3C_6H_2$

such as β-diketones,[34] β-keto esters[35] and malonic ester derivatives,[36] was the only method that appeared to overcome both of these constraints. Indeed, we have recently employed these reagents for the synthesis of neoflavonoids,[37] 2-arylbenzofuran-2(3*H*)-ones[38] and in the copper catalysed *N*-arylation of amines.[39] In a previous communication[40] we outlined our preliminary results on the application of aryllead triacetates to the preparation of 3-aryl-4-hydroxy-1-benzopyran-2-ones and we now report herein a full account of our results in this area.

Many routes exist for the preparation of aryllead triacetates but only two of these are convenient for the preparation of alkoxyphenyllead triacetates with the oxygenation pattern required for the synthesis of B-ring substituted 3-aryl-4-hydroxy-1-benzopyran-2-ones. The direct plumbylation of aromatic compounds with lead(IV) acetate in the presence of halogen substituted acetic acids and subsequent metathesis with acetic acid is a route which affords a range of alkoxyphenyl- and alkylphenyl-lead triacetates.[41,42] As the nucleophilicity of the arene decreases, a more electron-withdrawing halogen acetic acid is required, *e.g.* 4-methoxyphenyllead triacetate **45** and 4-methylphenyllead triacetate **46** were prepared in the presence of dichloroacetic acid whilst 2,4-dimethoxyphenyllead triacetate **47** was prepared by the presence of chloroacetic acid and 2,4,6-trimethoxyphenyllead triacetate **51** could be prepared by the direct reaction of 1,3,5-trimethoxybenzene with lead(IV) acetate. Since plumbylation[42,43] like mercuriation[44] and thalliation[45] is

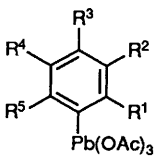


Table 1 Aryllead triacetates

Aryllead triacetate	R^1	R^2	R^3	R^4	R^5	Route[a]	Overall yield (%)
42	H	H	H	H	H	—	—
43	OMe	H	H	H	H	A	74
44	H	OMe	H	H	H	A	60
45	H	H	OMe	H	H	B	75
46	H	H	Me	H	H	B	57
47	OMe	H	OMe	H	H	B	74
48	H	OMe	OMe	H	H	A	47
49	OMe	H	H	OMe	H	A	55
50	H	H	$=OCH_2O-$		H	A	80
51	OMe	H	OMe	H	OMe	B	68

[a] Route A; tin-lead exchange: Route B; plumbylation. [b] Commercially available.

an electrophilic substitution reaction, the success of this modification is due to an increase in electrophilicity of lead when acetate is exchanged for a more electron-withdrawing ligand. One of the features of this route is the exclusive formation of one isomer where more isomers are possible. For example, in the case of mono-substituted benzenes, substitution occurs exclusively at the *para*-position although substitution at the *ortho*-position should also occur, in accordance with the rules of electrophilic aromatic substitution. The steric requirements of the lead(IV) electrophile may well contribute to this advantageous selectivity, although this is a limitation of the method as plumbylation cannot be used to prepare the *ortho*- and *meta*-isomers of mono-substituted phenyllead triacetates. Thus, although plumbylation of aromatics is a short and regioselective route to aryllead triacetates, it suffers from the limited range of aryl substitution patterns to which it is applicable. A more general route of preparing aryllead triacetates involves the reaction of an aryltributylstannane with lead(IV) acetate in the presence of a catalytic amount of mercuric acetate.[46] Aryltributylstannanes[47] are prepared in good yield from the reaction of chlorotributylstannane with either the arylmagnesium bromide or the aryllithium formed from the corresponding aryl halide. This route was used in the present study to prepare 2-methoxyphenyllead triacetate **43**, 3-methoxyphenyllead triacetate **44**, 3,4-dimethoxyphenyllead triacetate **48**, 2,5-dimethoxyphenyllead triacetate **49** and 3,4-methylenedioxyphenyllead triacetate **50**, in good yields (Table 1). The aryllead triacetate **44** was prepared in an overall yield of 60% from 3-bromoanisole which improved on its preparation in 10% yield from bis(3-methoxyphenyl)mercury and lead(IV) acetate.[48] The reagent **49** was prepared in better yield (55%) by this route compared to its low-yielding preparation *via* mercury–lead exchange.[49] Due to the widespread occurrence of the 3,4-methylenedioxyphenyl and 3,4-dimethoxyphenyl groups throughout many classes of naturally occurring compounds and, in particular, the isoflavonoids[1], the preparation of reagents **48** and **50** was highly desirable. Thus, 4-bromo-1,2-(methylenedioxy)benzene was converted (81%) into (3,4-methylenedioxyphenyl)tributylstannane which on reaction with lead(IV) acetate gave reagent **50** in 99% yield, thus giving an overall yield of 80% from the starting aryl halide. The reagent **48** was prepared in an analogous fashion from 4-bromoveratrole in a moderate overall yield of 47%.

The substrate initially investigated was the commercially available 1-benzopyran-2-one **6** and was arylated with variously

Table 2 Reaction of aryllead triacetates with 4-hydroxy-1-benzopyran-2-one **6**[a]

$ArPb(OAc)_3$	T/°C	Product (%)	Unchanged **6** (%)
42	40	**7** (40)	12
42	60	**7** (49)	14
45	40	**8** (44)	20
45	60	**8** (47)	18
46	40	**9** (59)	8
46	60	**9** (64)	10
47	40	**10** (77)	—
47	60	**10** (95)	—
50	40	**11** (49)	12
50	60	**11** (58)	trace
51	40	**12** (87)	—
51	60	**12** (87)	—

[a] Reactions were performed using a concentration (mol dm^{-3}) of substrate:aryllead triacetate:pyridine of 0.6:0.66:2.0. Reaction time was 16 h.

Table 3 Arylation of A-ring methoxylated 4-hydroxy-1-benzopyran-2-ones

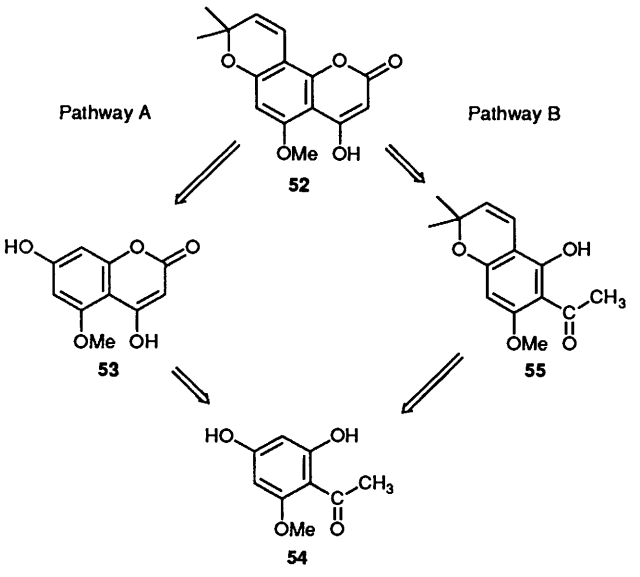
Entry	Substrate	$ArPb(OAc)_3$	t/h	Product (%)
1	**13**	**42**	16	**14** (48)
2	**13**	**45**	16	**15** (44)
3	**13**	**47**	8	**16** (85)
4	**13**	**51**	8	**17** (93)
5	**18**	**42**	16	**19** (53)
6	**18**	**46**	16	**20** (67)
7	**18**	**47**	16	**21** (94)
8	**18**	**51**	16	**22** (89)
9	**23**	**42**	16	**24** (71)
10	**23**	**43**	5	**25** (82)
11	**23**	**44**	6	**26** (70)
12	**23**	**45**	16	**27** (75)
13	**23**	**46**	16	**28** (72)
14	**23**	**47**	16	**29** (95)
15	**23**	**48**	16	**30** (68)
16	**23**	**49**	16	**31** (74)
17	**23**	**50**	16	**32** (60)
18	**23**	**51**	3	**33** (97)
19	**34**	**42**	16	**35** (67)
20	**34**	**45**	16	**36** (59)
21	**34**	**47**	6	**37** (92)
22	**34**	**51**	6	**38** (94)
23	**39**	**45**	12	**40** (81)
24	**39**	**50**	8	**2** (82)
25	**39**	**51**	4	**41** (96)
26	**52**	**45**	12	**57** (78)
27	**52**	**50**	12	**4** (84)
28	**52**	**51**	6	**58** (94)

substituted aryllead triacetates (Table 2). The concentrations (mol dm^{-3}) of substrate:aryllead triacetate:pyridine chosen were 0.6:0.66:2.0, a combination of those employed in the arylation of β-diketones[34] and β-keto esters[35]. A reaction temperature of 40 °C was initially selected as this was not thought to be sufficiently high to cause thermolysis of the aryllead compound. It can be seen from the results that substrate **6** reacted to give only the product of mono-arylation at C-3, the required position. At a reaction temperature of 40 °C, 3-aryl-4-hydroxy-1-benzopyran-2-ones were formed in modest to excellent yields (40–87%). An increase in temperature to 60 °C led in all cases to better yields of arylated product, *e.g.* 4-hydroxy-3-(2,4-dimethoxyphenyl)-1-benzopyran-2-one **10** was obtained in near quantitative yeild (95%) at 60 °C compared to the 77% yield obtained at 40 °C. The high-yielding introduction of the bulky, electron-rich 2,4,6-trimethoxyphenyl group is especially noteworthy. Also, the novel phenyllead triacetate **50** appeared to be a satisfactory arylating agent and this is important for the proposed syntheses of the naturally occurring derrusnin **1** and isorobustin **4**.

A range of 4-hydroxy-1-benzopyran-2-ones derivatives **13**, **18**, **23** and **34** were prepared in good yield by the condensation of the required *ortho*-hydroxyacetophenones with diethyl carbonate in the presence of sodium sand.[16] The attempted preparation of 4-hydroxy-5,7-dimethoxy-1-benzopyran-2-one **39** with sodium sand led to an intractible mixture of products but by using sodium hydride it was obtained in good yield (82%). The results of the reaction of a range of aryllead triacetates with these substrates are given in Table 3. The presence of a methoxy group at the 6- or 7-position (entries 1–8) had no adverse effect on the arylation reaction. The more electron-rich aryl groups were transferred in higher yields, *e.g.* the reaction of phenyllead triacetate **42** with the 4-hydroxy-1-benzopyran-2-one **13** (entry 1) gave 4-hydroxy-7-methoxy-3-phenyl-1-benzopyran-2-one **14** in modest yield (48%) whereas reagent **51** reacted with substrate **13** (entry 4) to give 4-hydroxy-7-methoxy-3-(2,4,6-trimethoxyphenyl)-1-benzopyran-2-one **17** in excellent yield (93%). Furthermore, the latter lead reagent **51** and the phenyllead triacetate **47** required shorter reaction times with **13** than **42** or **45**. As all of the naturally occuring 3-aryl-4-hydroxy-1-benzopyran-2-ones are methoxylated at carbon-5, the arylation of 4-hydroxy-5-methoxy-1-benzopyran-2-one **23** was investigated. In addition to a study of the substrate reactivity, the full range of aryllead triacetates employed in the present study were treated with substrate **39** to determine any differences in reagent reactivities. Arylated products were formed in good yields regardless of the substitution in the B-ring (entries 9–18), *e.g.* **42**, which had previously afforded only modest yields (40–55%), phenylated compound **23** in good yield (71%). The trend that the highest yields were obtained with the more electron-rich aryllead triacetates was again observed as, for example, (entries 14 and 18) both 3-(2,4-dimethoxyphenyl)-4-hydroxy-5-methoxy-1-benzopyran-2-one **29** and 4-hydroxy-5-methoxy-3-(2,4,6-trimethoxyphenyl)-1-benzopyran-2-one **33** were prepared in near quantitative yields (95 and 97%, respectively). The latter product was formed after a reaction time of 3 h compared to the 16 h normally required. This, along with the excellent yield, gives an indication as to the high reactivity of this aryllead triacetate. The position of the methoxy group in mono-methoxy substituted aryllead triacetates did not have a large effect on the yields of the corresponding arylated products (entries 10, 11 and 12). Importantly, reagent **50** again gave a satisfactory yield of arylated product (60%). These results suggest that 1-benzopyran-2-one **23** was a more reactive substrate than the isomeric 6- and 7-methoxy substituted 1-benzopyran-2-ones **13** and **18** and good yields of arylated products were obtained with each aryllead triacetate, regardless of its substitution pattern. In addition, the presence of the 5-methoxy group did not sterically hinder the introduction of bulky aryl groups to the 3-position. The arylation of 4-hydroxy-1-benzopyran-2-ones possessing two methoxy groups on the A-ring, namely 7,8-dimethoxy **34** and 5,7-dimethoxy **39** afforded results (entries 19–25) consistent with reagent reactivities previously observed with mono-methoxy substituted substrates. The reaction of the 1-benzopyran-2-one **39** with aryllead triacetate **50** afforded 4-hydroxy-3-5,7-dimethoxy-(3,4-methylenedioxyphenyl)-1-benzopyran-2-one **2** in 82% yield. Product **2** is the direct synthetic precursor of derrusnin **1**, and, as the methylation of **2** with diazomethane has previously been described,[50] this represents a formal total synthesis of derrusnin **1**, in an overall yield of 54% from readily available starting materials.

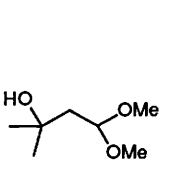
The preparation of isorobustin **4** was reported in a preliminary communication[51] with the key step involving arylation using aryllead triacetates and we now report on this

total synthesis in more detail. Retrosynthetic analysis of 8,8-dimethyl-4-hydroxy-5-methoxy-2*H*,8*H*-benzo [1,2-*b*:3,4-*b*']dipyran-2-one **52**, the proposed precursor of **4** leads to two possible pathways for its preparation, both having 2,4-dihydroxy-6-methoxyacetophenone **54** as the starting material (Scheme 1).



Scheme 1

Pathway A involves the formation of the 2,2-dimethylpyran ring after the formation of the 4-hydroxy-2*H*-1-benzopyran-2-one structure whilst pathway B involves formation of the 2,2-dimethylpyran ring prior to formation of the 4-hydroxy-1-benzopyran-2-one structure. The former pathway is disfavoured as it first requires the condensation of the acetophenone **54** with diethyl carbonate, a cyclisation which proceeds in poor yield when the substrate possesses two free hydroxy groups.[17] In addition, the formation of the 2,2-dimethylpyran ring requires selective methylation of the 4-hydroxy group of 4,7-dihydroxy-5-methoxy-1-benzopyran-2-one **53** prior to reaction with 3-chloro-3-methylbut-1-yne. On the other hand, in the latter pathway, the acetophenone **54** is the ideal substrate for reaction with 3,3-dimethoxy-1-methylbutan-1-ol **56**, a dimethylchromenylating agent under pyridine catalysis for *meta*-dihydric phenols having one hydroxy group engaged in chelation, as in **54**. This is known to afford isoevodionol[52] **55**, the required cyclisation substrate for condensation with diethyl carbonate as it possesses only the one required free hydroxy group. For these reasons pathway B was chosen. In the present investigation, the reaction of methylmagnesium bromide with acetoacetaldehyde dimethyl acetal afforded the reagent **56** in



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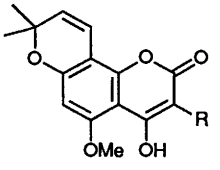


57 R = 4-MeOC$_6$H$_4$
58 R = 2,4,6-(MeO)$_3$C$_6$H$_2$

67% yield. The *o*-hydroxyacetophenone **54** was prepared in 73% yield from the Hoesch condensation of 5-methoxyresorcinol and acetonitrile. The heating together of **54** and **56** at 170 °C in pyridine for 10 h yielded the chromene **55** in 68% yield. As with the preparation of **39**, the use of sodium sand led to complex mixtures whereas condensation in the presence of sodium hydride afforded the required 4-hydroxy-1-benzopyran-2-one **52** in good yield (81%). The reaction of **52** with aryllead triacetate **45** afforded 8,8-dimethyl-4-hydroxy-5-methoxy-3-(4-methoxyphenyl)-2*H*,8*H*-benzo[1,2-*b*:3,4-*b*']dipyran-2-one **57** in good yield (78%). Again, reaction with **51** led to a near quantitative yield (94%) of the corresponding arylated product **58**. More importantly, reaction with reagent **50** afforded **4** in 84% yield. This represents an overall yield for isorobustin of 34% which is far superior to that obtained (2%) using the deoxybenzoin ring closure method.[18] As **4** is the synthetic precursor of the naturally occurring isorobustin methyl ether **5**, this represents also a formal total synthesis of this natural product.

The structure identification of each 3-aryl-4-hydroxy-1-benzopyran-2-one prepared was aided in particular by the information obtained from mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy. The mass spectral fragmentation patterns[53] characteristic of this class of compounds helped to determine the type and number of substituents on either ring. However, ^{1}H and ^{13}C NMR spectroscopic data not only confirmed the nature of the substituents, but, more importantly, also gave sufficient information so that the exact position of each substituent could be unambiguously determined. A selection of the ^{13}C NMR data obtained, namely that of 1-benzopyran-2-one **23** and its C-3 arylated products **24**–**33**, is compiled in Table 4.

In the spectrum of **23**, assignment of the signals at 92.83 and 166.06 ppm to C-3 and C-4 respectively, was consistent with the α,β-unsaturated lactone structure with hydroxylation at C-4. The lactone carbonyl gave rise to a signal at 162.83 ppm. The peak at 156.19 ppm was assigned to C-5 as it is deshielded by the methoxy group at this position. The resonances of C-6 and C-8 at 111.26 and 105.60 ppm, were shielded by the 5-methoxy and the pyran oxygen, respectively, with the latter signal being slightly more upfield due to the extra effect of the pyran oxygen. The signal at 132.57 ppm was assigned to the A-ring aromatic carbon, C-7, as substituents have little or no effect on *meta*-carbon atoms. The two remaining signals at 155.01 and 104.84 ppm were of low intensity, characteristic of quaternary carbons and were assigned to C-9 and C-10, respectively. The signal due to C-10 was shielded considerably by the effects of the two *ortho*-oxygens and the hydroxy function at C-4. The introduction of an aryl group at C-3 of **23** had little effect on the chemical shifts of the majority of the carbons of the 4-hydroxy-1-benzopyran-2-one nucleus. The only major difference was in the chemical shift of C-3, which becomes deshielded by ~20 ppm, and the magnitude of this shift is dependent on the nature of the aryl ring introduced, *e.g.* the C-3 resonance for 4-hydroxy-5-methoxy-3-phenyl-1-benzopyran-2-one **24** is at 124.05 ppm, whilst in 1-benzopyran-2-one **33**, it is considerably more upfield at 102.76 ppm. Small upfield shifts are observed for C-2 (~2 ppm) and C-4 (~5 ppm) and these shifts are essentially independent of the nature of the aryl ring introduced. The B-ring carbons gave rise to signal patterns which were consistent with both the nature and position of their substituents employing the additivity principles previously established for simple aromatic systems.[54] The data obtained may be of significant predictive value in the structure identification of new or unknown 3-aryl-4-hydroxy-1-benzopyran-2-ones.

In an attempt to elucidate the mechanism of this lead(IV)-mediated arylation, the possibility of a free-radical mechanism was first investigated in view of the well-documented radical chemistry of lead tetraacetate.[55] For this reason, the phenylation and arylation of **23** with reagents **42** and **51**, respectively, were studied in the presence of 1,1-diphenylethylene, a well-known trapping agent. (Table 5). The yields of phenylated/arylated products were not affected by the presence

Table 4 ^{13}C NMR data for 4-hydroxy-5-methoxy-1-benzopyran-2-one **31** and its C-3 arylated derivatives[a]

Carbon	23[b]	24	25	26	27[c]	28[c]	29	30	31[b]	32	33
C-2	162.83	106.93	160.88	161.82	160.98	160.66	160.96	160.69	160.71	160.80	162.20
C-3	92.83	124.05	121.10	104.57	112.17	104.54	113.13	104.49	122.51	104.32	102.76
C-4	166.06	161.25	161.56	161.98	161.48	161.25	161.20	161.31	162.16	161.22	162.47
C-5	156.19	156.50	156.46	156.58	156.61	156.39	156.30	156.39	156.60	156.39	156.37
C-6	111.26	109.71	109.67	110.08	110.20	109.65	109.60	109.60	109.56	109.62	110.73
C-7	132.57	132.90	132.60	132.46	132.32	132.73	132.57	132.65	132.46	132.73	133.63
C-8	105.60	106.63	106.42	106.18	106.31	106.55	106.47	106.63	106.44	106.57	107.61
C-9	155.01	153.20	153.46	153.50	153.67	153.04	153.29	153.02	153.58	153.01	154.58
C-10	104.84	104.39	103.87	101.98	104.97	104.38	104.43	105.02	105.09	104.41	105.65
C-1′	—	131.91	101.95	133.25	124.20	128.77	101.90	124.12	101.47	125.18	100.89
C-2′	—	127.54	157.37	116.45	131.95	130.50	160.30	114.66	151.69	107.55	159.95
C-3′	—	130.72	111.04	158.76	113.16	128.06	98.34	147.83	112.07	146.09	91.91
C-4′	—	127.11	131.98	112.54	158.94	136.24	158.32	147.96	113.33	146.47	157.36
C-5′	—	130.72	119.88	123.10	113.16	126.06	104.60	111.02	152.69	111.04	91.91
C-6′	—	127.54	128.99	128.47	131.95	130.50	132.35	123.32	117.92	124.26	159.95
5-OMe	55.07	57.10	56.93	57.10	57.09	57.06	56.93	57.04	56.87	57.04	58.04
Others	—	—	55.30	54.98	54.89	20.80	55.33	55.47	55.84	100.74	56.08
	—	—	—	—	—	—	55.14	55.44	55.33	—	56.38

[a] Spectra were recorded in [$^2H_6$]-DMSO at 67.80 MHz. [b] Recorded in $CDCl_3$. [c] Recorded in CD_3CN.

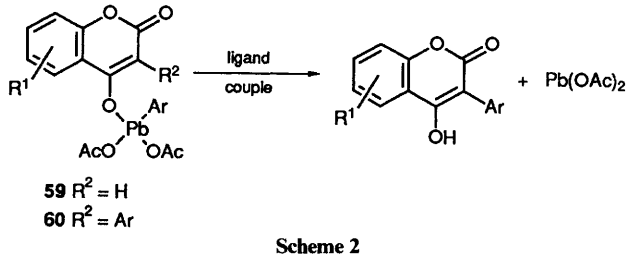
Table 5 Arylation of 4-hydroxy-5-methoxy-1-benzopyran-2-one **23** with aryllead triacetates in the presence of a spin trap[a]

$ArPb(OAc)_3$	DPE[b] (eq.)	*t*/h	Product (%)
42	0	16	**24** (71)
42	2	16	**24** (65)
42	10	16	**24** (66)
51	0	6	**33** (94)
51	2	6	**33** (90)
51	10	6	**33** (87)

[a] Reactions were carried out at 60 °C for the times indicated using a concentration (mol dm^{-3}) of substrate:aryllead triacetate:pyridine of 1.0:1.1:3.3. [b] DPE = 1,1-diphenylethylene.

of either a slight or large excess of radical trap and hence a free-radical mechanism was excluded.

In the bismuth(v)-mediated phenylation of enolisable substrates, an intermediate possessing a covalent Bi–O bond was detected by ^1H NMR spectroscopy and subsequently isolated.[56] Due to the similarity in chemistry between these two classes of organometallic reagents, an intermediate **59**, possessing a covalent Pb–O bond, was postulated in the case of the lead(IV)-mediated arylation of 4-hydroxy-1-benzopyran-2-ones (Scheme 2). This intermediate is proposed to ligand couple to afford the arylated product. This coupling involved the overlap of the π-systems of the aryl and enolate ligands with concomitant cleavage of the Pb–O and Pb–Ar bonds. The reaction may be viewed as a formal nucleophilic displacement of lead by the enolate anion with the driving force being provided by the change in oxidation state of lead. However, ^1H NMR



59 R^2 = H
60 R^2 = Ar

Scheme 2

monitoring of both the phenylation and arylation of the 4-hydroxy-5-methoxy-1-benzopyran-2-one **23** with reagents **42** and **51**, respectively, at 25 °C or at −31 °C did not furnish any evidence for the proposed intermediate. Instead, signals characteristic of product increased in intensity as the reactant peaks decreased in intensity. This did allow for the comparison of reaction rates between **42** and **51**. At room temperature, phenylation was 20% completed after 1 h and 58% completed after 12 h. In contrast, the arylation of **23** by **51** was 80% completed even after 5 min, and a near quantitative conversion was observed after 50 min. It was important that the reaction stopped after the transfer of one aryl group as required. It is presumed that the enolic hydroxy group has become too hindered to react further. Alternatively, it may be that an intermediate of the type **60** was formed but ligand coupling would then represent a thermodynamically disfavoured process as the aromaticity of the C-ring could not be regained. The proposed attack of the electron rich π-system of the enolate anion requires aryl cation behaviour for the aryl group in aryllead triacetates. The low downfield shift of the *ipso*-carbon in the ^{13}C NMR spectra of aryllead triacetates is in agreement with such behaviour.[57] One of the striking aspects of ligand coupling is the ease of synthesis of very hindered compounds under mild conditions and we have found this to be the case in the present study and in the preparation of hindered phenols[58] and diarylamines[59] using aryllead triacetates. The inertness of the C(9)=C(10) double bond of the 4-hydroxy-1-benzopyran-2-one **52** during its arylation is further evidence to support the proposed intermediate as it suggests a directing effect for the 4-hydroxy group. This confers chemoselective as well as regioselective properties on aryllead triacetates. However, although we have searched diligently, we have not yet been able to detect a Pb^{IV} intermediate. Of course, this may mean that it couples very rapidly once formed.[60]

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra were determined on Varian Gemini-200* and Jeol JNM-PMX270† instruments. All *J* values are given in Hz. IR spectra were recorded on a Perkin-Elmer 1710 Infrared Fourier Transform spectrophotometer.† Mass spectra were recorded on a VG Analytical 770 mass spectrometer with attached INCOS 2400 data system in the EI mode.† UV spectra were recorded on a Phillips PV 8720 spectrophotometer.

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Separations by column and flash chromatography were performed using Merck Kieselgel 60 (70–230 mesh ASTM) and 60 (230–400 mesh ASTM), respectively. Merck precoated Kieselgel $60F_{254}$ was used for thin layer chromatography and Merck Kieselgel $PF_{254+336}$ for preparative layer chromatography. Lead tetraacetate was dried prior to use over potassium hydroxide pellets at 0.1 mmHg for 6 h. Ether refers to diethyl ether. All solvents were purified by standard techniques. Phenyllead triacetate **42** is commercially available (Alfa).

Preparation of Aryllead Triacetates

4-Methoxyphenyllead triacetate **45** [75%, m.p. 137–139 °C (lit.,[61] m.p. 139–141 °C)], 4-methylphenyllead triacetate **46** [57%, m.p. 82–85 °C (lit.,[62] m.p. 86–88 °C)], 2,4-dimethoxyphenyllead triacetate **47** [78%, m.p. 143–145 °C (lit.,[63] m.p. 146–149 °C)] and 2,4,6-trimethoxyphenyllead triacetate **51** [68%, m.p. 175–179 °C (lit.,[49] m.p. 174–176 °C)] were prepared by plumbylation.

2-Methoxyphenyllead triacetate **42** [74%, m.p. 149–151 °C (lit.,[46] m.p. 148–151 °C)], 3,4-dimethoxyphenyllead triacetate **48** [47%, m.p. 125–129 °C (lit.,[46] m.p. 124–128 °C)] and 3,4-methylenedioxyphenyllead triacetate **50** (80%, m.p. 126.5–130 °C[59]) were prepared by tin–lead exchange.

3-*Methoxyphenyllead Triacetate* **44**.—Butyllithium (1.6 mol dm^{-3} in hexane; 72 cm^3, 0.115 mol) was added to a well-stirred solution of 3-bromoanisole (20 g, 0.106 mol) in dry THF (100 cm^3) under nitrogen at −78 °C, and the mixture was stirred at this temperature for 30 min. Chlorotributylstannane (42.10 g, 0.129 mol) was then added with stirring over 15 min at −78 °C. After being stirred for a further 30 min at this temperature, the reaction mixture was added to saturated aqueous ammonium chloride (80 cm^3) and then to water (250 cm^3) and the mixture extracted with ether (3 × 200 cm^3). The ether extract was washed with brine (2 × 200 cm^3), dried ($MgSO_4$), and the solvent removed to yield a yellow oil which upon distillation gave (3-*methoxyphenyl*)*tributylstannane* (31.15 g, 74%), b.p. 174–178 °C 3 mmHg; $\nu_{max}(CHCl_3)/cm^{-1}$ 3034, 1208, 940 and 648; δ_H(60 MHz; $CDCl_3$) 7.50 (1 H, t, *J* 8, 5-H), 7.30–7.00 (3 H, m, 2-H, 4-H, 6-H), 3.79 (3 H, s, 3-OCH_3) and 1.80–0.80 (27 H, m, 3 × C_4H_9); *m/z* 395 (M^+, 3%), 341 ($ArSn^+Bu_2$, 38), 285 ($ArSn^+Bu$, 12), 227 ($ArSn^+$, 24), 197 ($C_6H_5Sn^+$, 14), 120 (Sn^+, 6), 57 (13), 41 (48) and 29 (100) (Found: C, 57.3; H, 8.5. $C_{19}H_{34}OSn$ requires C, 57.45; H, 8.60%).

Lead tetraacetate (13.77 g, 0.031 mol) was stirred with (3 methoxyphenyl)tributylstannane (10.65 g, 0.027 mol) and mercuric acetate (0.497 g, 1.56 mmol) at 40 °C for 6 h in dry chloroform (40 cm^3). After this time, the reaction mixture was filtered through Celite, the solvent removed, and the residual oil allowed to solidify. Light petroleum (b.p. 40–60 °C) (30 cm^3) was added and the precipitate collected, washed with light petroleum (3 × 20 cm^3) and dried to give the title triacetate **8** (10.67 g, 81%) as pale yellow plates, m.p. 99.5–102 °C (lit.,[41] m.p. 98–99 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 3018, 2400, 1552, 1425, 1219, 780 and 669; $\lambda_{max}(CHCl_3)/nm$ 269 (5550); δ_H(200 MHz; $CDCl_3$) 7.51 (1 H, t, *J* 8.20, 5-H), 7.25–7.17 (1 H, m, 4-H, 6-H), 7.06–7.01 (1 H, m, 2-H), 3.85 (3 H, s, 3-OCH_3) and 2.12 (9 H, s, 3 × OAc); δ_C(50 MHz; $CDCl_3$) 181.05 (C=O), 162.23 (C-1), 161.79 (C-3), 131.65 (C-5), 123.30 (C-6), 118.61 (C-2), 116.38 (C-4), 55.95 (3-OCH_3) and 20.67 (CH_3); *m/z* 529 (0.2%), 481 (0.3), 433 (2.2), 315 (0.8), 267 (100), 214 (5.7) and 108 (35.3).

2,5-*Dimethoxyphenyllead Triacetate* **49**.—Butyllithium (1.6 mol dm^{-3} in hexane; 72.0 cm^3, 0.115 mol) was added to a well-stirred solution of 1-bromo-2,5-dimethoxybenzene (19.32 g, 0.089 mol) in dry THF (100 cm^3) under nitrogen at −78 °C and the mixture was stirred at this temperature for 30 min. Chlorotributylstannine (42.10 g, 0.129 mol) was then added with stirring over 15 min at −78 °C. After being stirred for a further 45 min at this temperature, the reaction mixture was added to saturated aqueous ammonium chloride (60 cm^3) and then to water (250 cm^3) and the mixture extracted with ether (3 × 200 cm^3). The ether extract was washed with brine (2 × 200 cm^3), dried ($MgSO_4$) and the solvent removed to yield a yellow oil which upon distillation gave (2,5-*dimethoxyphenyl*)-*tributylstannane* (24.33 g, 64%), 162–166 °C 5 mmHg; $\nu_{max}(CHCl_3)/cm^{-1}$ 3041, 1208, 961 and 669; δ_H(60 MHz; $CDCl_3$) 7.10–6.90 (1 H, m, 4-H), 6.75–6.68 (2 H, m, 3-H, 6-H), 3.73 (3 H, s, 2-OCH_3) 3.69 (3 H, s, 5-OCH_3) and 1.95–0.80 (27 H, m, 3 × C_4H_9); *m/z* 428 (M^+, 2%), 371 ($ArSn^+Bu_2$, 32), 315 ($ArSn^+Bu$, 11), 257 ($ArSn^+$, 24), 242 (14), 227 (16), 121 (Sn^+, 5), 57 (28), 41 (50) and 29 (100) (Found: C, 56.3; H, 8.35. $C_{20}H_{36}O_2Sn$ requires C, 56.25; H, 8.50%).

Lead tetraacetate (10.72 g, 24.2 mmol) was stirred with (2,5-dimethoxyphenyl)tributylstannane (10.26 g, 0.024 mol) and mercuric acetate (0.382 g, 1.2 mmol) at 40 °C for 5 h in dry chloroform (40 cm^3). After this time, the reaction mixture was filtered through Celite, the solvent removed, and the residual oil allowed to solidify. Light petroleum (b.p. 40–60 °C) (30 cm^3) was added and the precipitate collected, washed with light petroleum (3 × 20 cm^3), and dried to give the title triacetate **13** (10.77 g, 86%) as yellow plates, m.p. 162–165 °C (lit.,[49] m.p. 165–167 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 3020, 2400, 1570, 1488, 1435, 1219, 753 and 667; δ_H(200 MHz; $CDCl_3$) 7.41–7.32 (1 H, m, 4-H), 7.15–6.95 (2 H, m, 3-H, 6-H), 3.87 (3 H, s, 2-OCH_3), 3.81 (3 H, s, 5-OCH_3) and 2.09 (9 H, s, 3 × OAc); δ_C(50 MHz; $CDCl_3$) 180.59 (C=O), 156.25 (C-2), 152.37 (C-5), 151.05 (C-1), 119.86 (C-6), 116.23 (C-3), 113.63 (C-4), 57.43 (5-OCH_3), 56.41 (2-OCH_3) and 20.56 (CH_3); *m/z* 619 (0.6%), 541 (0.2), 463 (1.3), 404 (3.1), 345 (1.9), 274 (3.2), 267 (100), 208 (45) and 138 (66).

Preparation of 4-Hydroxy-1-benzopyran-2-ones

4-Hydroxy-7-methoxy-1-benzopyran-2-one **13** [63%, m.p. 255 °C, (lit.,[16] m.p. 256 °C)], 4-hydroxy-6-methoxy-1-benzopyran-2-one **18** [83%, m.p. 267–268 °C (lit.,[64] m.p. 270 °C (decomp.)], 4-hydroxy-5-methoxy-1-benzopyran-2-one **23** [83%, m.p. 151–152 °C (lit.,[65] m.p. 155 °C)] and 4-hydroxy-7,8-dimethoxy-1-benzopyran-2-one **34** [65%, m.p. 236–237 °C (lit.,[16] m.p. 238 °C)] were prepared by literature methods.[16] 4-Hydroxy-5,7-dimethoxy-1-benzopyran-2-one **39** [82%, m.p. 179–181 °C (lit.,[16] m.p. 183 °C)] was prepared using sodium hydride instead of sodium sand as in **52**.

4-*Hydroxy*-5-*methoxy*-8,8-*dimethyl*-2H,8H-*benzo*[1,2-b:3,4-b′]*dipyran*-2-*one* **52**.—Sodium hydride (80% dispersion in oil; 1.12 g, 26.35 mmol) was added slowly to a solution of 5-hydroxy-7-methoxy-2,2-dimethyl-1(2*H*)-benzopyran-6-yl methyl-ketone **55**[22] (0.50 g, 2.02 mmol) in dry diethyl carbonate (50 cm^3) and was slowly heated to reflux and was stirred for 20 min. Methanol (100 cm^3) was then added. Ether (250 cm^3) was added and the solution was extracted with water (2 × 100 cm^3) The aqueous extracts were acidified with (hydrochloric acid 10%) and then exhaustively extracted with chloroform (2 × 100 cm^3). The combined organic extracts were dried ($MgSO_4$) and concentrated to yield an orange solid which was purified by column chromatography (chloroform–methanol–water, 10:1: 0.1) to give the title benzodipyranone (0.447 g, 81%) as a solid which crystallised as needles from ethanol, m.p. 189.5–191 °C; $\nu_{max}(KBr)/cm^{-1}$ 3376, 1717, 1630 and 1600; λ_{max}(MeOH)/nm 276.5 (ε 20 719), 285.5 (24 010) and 318 (18 347); δ_H(270 MHz; $CDCl_3$) 9.35 (1 H, s, 4-OH), 6.80 (1 H, d, *J* 10.07, 10-H), 6.30 (1 H, s, 6-H), 5.60 (1 H, d, *J* 10.08, 9-H), 5.52 (1 H, s, 3-H), 4.01 (3 H, s, 5-OCH_3) and 1.47 (6 H, s, 2 × CH_3); δ_C(67.80 MHz; $CDCl_3$) 166.63 (C-4), 162.92 (C-2), 157.25 (C-12), 156.49

(C-5), 150.97 (C-13), 128.27 (C-9), 115.19 (C-10), 104.13 (C-11), 98.39 (C-6), 95.79 (C-14), 89.97 (C-3), 78.38 (C-8), 56.93 (5-OCH_3) and 28.20 [8-$(CH_3)_2$]; *m/z* 274 (M^+, 42%), 259 (82), 217 (100), 202 (8), 116 (5), 69 (7) and 43 (3) (Found: C, 65.7; H. 5.1. $C_{15}H_{14}O_5$ requires C, 65.70; H, 5.15%).

Arylation of 4-*Hydroxy*-1-*benzopyran*-2-*ones*

General Procedure.—Dry pyridine (3.3 equiv.) was added to a mixture of the 4-hydroxy-1-benzopyran-2-one (1 equiv.) and aryllead triacetate (1.1 equiv.) in dry chloroform (1 cm^3 per 0.60 mmol of substrate) and the resulting mixture was stirred at the indicated temperature for the times specified. The reaction mixture was then diluted with chloroform (60 cm^3) and washed with sulfuric acid (3 mol dm^{-3}; 2 × 50 cm^3). The aqueous phase was washed with chloroform (4 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$), filtered through Celite and concentrated to yield a residue which was purified by preparative TLC using the eluent system specified.

4-*Hydroxy*-3-*phenyl*-1-*benzopyran*-2-*one* **7**.—(TLC; chloroform–methanol–water, 8:1:0.1), m.p. 237.5–239 °C (lit.,[66] m.p. 239 °C); ν_{max}(KBr)/cm^{-1} 1673, 1619 and 691; δ_H(60 MHz; DMSO) 8.04 (1 H, d, *J* 8.0, 5-H) and 7.70–7.30 (8 H, m, Ar-H); *m/z* 238 (M^+, 77%), 181 (9), 152 (12), 121 (100), 118 (98) and 65 (29).

4-*Hydroxy*-3-(4-*methoxyphenyl*)-1-*benzopyran*-2-*one* **8**.—(TLC; chloroform–methanol–water, 8:1:0.1), m.p. 238–240 °C (lit.,[24] m.p. 242–243 °C); ν_{max}(KBr)/cm^{-1} 3058 and 1672; λ_{max}(MeOH)/nm 316 (5878); δ_H(60 MHz; DMSO) 8.04 (1 H, d, *J* 8.0, 5-H), 7.60–7.10 (5 H, m, 6-H, 7-H, 8-H, 2′-H, 6′-H), 6.80 (2 H, d, *J* 8.0, 3′-H, 5′-H) and 4.00 (3 H, s, 4′-OCH_3); *m/z* 268 (M^+, 85%), 148 (100), 121 (79), 93 (18) and 65 (39).

4-*Hydroxy*-3-(p-*tolyl*)-1-*benzopyran*-2-*one* **9**.—(TLC; chloroform–methanol–water, 10:1:0.1), m.p. 226–227.5 °C (lit.,[67] m.p. 226 °C); ν_{max}(KBr)/cm^{-1} 1662 and 1614; δ_H(60 MHz; DMSO) 9.85 (1 H, s, 4-OH), 7.82 (1 H, dd, *J* 7.7 and 1.0, 5-H), 7.36–7.07 (7 H, m, 6-H, 7-H, 8-H, 2′-H, 3′-H, 5′-H, 6′-H) and 2.21 (3 H, s, 4′-CH_3); *m/z* 252 (M^+, 87%), 149 (20), 132 (100), 121 (72) and 43 (94).

3-(2,4-*Dimethoxyphenyl*)-4-*hydroxy*-1-*benzopyran*-2-*one* **10**.—(TLC; chloroform–methanol–water, 8:1:0.1), needles (ethanol), m.p. 188–189.5 °C; ν_{max}(KBr)/cm 1677, 1617 and 1210; λ_{max}(MeOH)/nm 280 (7044) and 310 (8450); δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.91 (1 H, dd, *J* 7.78 and 1.10, 5-H), 7.65–7.59 (1 H, m, 8-H), 7.38–7.31 (2 H, m, 6-H, 7-H), 7.09 (1 H, d, *J* 8.24, 6′-H), 6.62 (1 H, d, *J* 2.39, 3′-H), 6.57 (1 H, dd, *J* 8.83 and 2.38, 5′-H), 3.81 (3 H, s, 4′-OCH_3) and 3.71 (3 H, s, 2′-OCH_3); δ_C(67.80 MHz; DMSO) 161.72 (C-4), 160.84 (C-2), 160.54 (C-4′), 158.80 (C-2′), 152.33 (C-9), 132.93 (C-6′), 131.76 (C-7), 123.62 (C-6), 123.55 (C-5), 116.66 (C-10), 115.91 (C-8), 112.81 (C-3), 104.81 (C-3′), 101.95 (C-1′), 98.47 (C-5′), 55.27 (2′-OCH_3) and 55.14 (4′-OCH_3); *m/z* 298 (M^+, 100%), 204 (39), 178 (76), 149 (22), 121 (50), 93 (8) and 65 (7) (Found: C, 68.5; H, 4.6. $C_{17}H_{14}O_5$ requires C, 68.45; H, 4.75%).

4-*Hydroxy*-3-(3,4-*methylenedioxyphenyl*)-1-*benzopyran*-2-*one* **11**.—(TLC; chloroform–methanol–water, 10:1:0.1), needles from ethanol, m.p. 219–221 °C, ν_{max}(KBr)/cm^{-1} 1665, 1600 and 1384; λ_{max}(MeOH)/nm 268 (6017) and 316 (7409); δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.95 (1 H, d, *J* 8.06, 5-H), 7.63–7.30 (3 H, m, 6-H, 7-H, 8-H), 6.96–6.88 (3 H, m, 2′-H, 5′-H, 6′-H) and 6.03 (2 H, s, OCH_2O); δ_C(67.80 MHz; DMSO) 162.13 (C-4), 162.01 (C-2), 152.26 (C-9), 146.60 (C-3′), 145.97 (C-4′), 131.67 (C-7), 126.29 (C-3), 124.91 (C-6′), 123.82 (C-6), 123.44 (C-5), 116.34 (C-10), 115.88 (C-8), 111.29 (C-5′), 107.75 (C-2′), 104.49 (C-1′) and 100.65 (OCH_2O); *m/z* 282 (M^+, 86%), 162 (100), 134 (24), 121 (76), 93 (12) and 65 (14) (Found: C, 67.8; H, 3.45. $C_{16}H_{10}O_5$ requires C, 68.10; H, 3.55%).

4-*Hydroxy*-3-(2,4,6-*trimethoxyphenyl*)-1-*benzopyran*-2-*one* **12**.—(TLC; chloroform–methanol–water, 8:1:0.1), needles from ethanol, m.p. 226–228 °C; ν_{max}(KBr)/cm^{-1} 1672, 1615 and 1205; λ_{max}(MeOH)/nm 269 (8338) and 308.5 (10 074); δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.88–7.85 (1 H, m, 5-H), 7.65–7.59 (1 H, m, 8-H), 7.38–7.32 (2 H, m, 6-H, 7-H), 6.29 (2 H, s, 3′-H, 5′-H), 3.83 (3 H, s, 4′-OCH_3) and 3.68 (6 H, s, 2′-OCH_3, 6′-OCH_3); δ_C(67.80 MHz; DMSO) 161.45 (C-4), 161.14 (C-2), 160.54 (C-4′), 159.40 (C-2′, C-6′), 153.31 (C-9), 131.78 (C-7), 123.68 (C-6), 123.32 (C-5), 116.29 (C-10), 115.90 (C-8), 100.73 (C-3), 98.67 (C-1′), 90.89 (C-3′, C-5′), 55.49 (2′-OCH_3, 6′-OCH_3) and 55.22 (4′-OCH_3); *m/z* 328 (M^+, 100%), 297 (29), 234 (23), 208 (69), 154 (42), 121 (34), 93 (6) and 65 (5) (Found: C, 65.6; H, 4.7. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.90%).

4-*Hydroxy*-7-*methoxy*-3-*phenyl*-1-*benzopyran*-2-*one* **14**.—(TLC; chloroform methanol–water, 10:1:0.1), m.p. 203–204.5 °C (lit.,[16] m.p. 204 °C); ν_{max}(KBr)/cm^{-1} 1679, 1615 and 691; δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.92 (1 H, d, *J* 9.34, 5-H), 7.41–7.27 (5 H, m, C_6H_5), 6.97–6.94 (2 H, m, 6-H, 8-H) and 3.87 (3 H, s, 7-OCH_3); *m/z* 268 (M^+, 54%), 150 (100), 118 (13) and 63 (10).

4-*Hydroxy*-7-*methoxy*-3-(4-*methoxyphenyl*)-1-*benzopyran*-2-*one* **15**.—(TLC; chloroform–methanol–water, 10:1:0.1), m.p. 218.5–220 °C (lit.,[16] m.p. 219–220 °C); ν_{max}(KBr)/cm^{-1} 1680 and 1615; δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.86 (1 H, d, *J* 9.16, 5-H), 7.37 (2 H, d, 8.80, 2′-H, 6′-H), 6.92-6.87 (4 H, m, 6-H, 8-H, 3′-H, 5′-H), 3.87 (3 H, s, 7-OCH_3) and 3.77 (3 H, s, 4′-OCH_3); δ_C(67.80 MHz; DMSO) 163.14 (C-4), 162.80 (C-2), 161.90 (C-7), 157.48 (C-4′), 154.04 (C-9), 131.94 (C-2′, C-6′), 125.93 (C-1′), 125.14 (C-5), 112.88 (C-3′, C-5′), 111.64 (C-10), 110.95 (C-6), 100.74 (C-3), 99.91 (C-8), 55.63 (7-OCH_3) and 54.90 (4′-OCH_3); *m/z* 298 (M^+, 80%), 151 (100), 147 (94), 120 (24), 95 (11) and 63 (7).

3-(2,4-*Dimethoxyphenyl*)-4-*hydroxy*-7-*methoxy*-1-*benzopyran*-2-*one* **16**.—(TLC; chloroform–methanol–water, 10:1:0.1), needles (ethanol), m.p. 204.5–206 °C (lit.,[16] m.p. 200 °C); ν_{max}(KBr)/cm^{-1} 1674, 1616 and 1207; λ_{max}(MeOH)/nm 285 (7012) and 315 (13 911); δ_H(270 MHz; DMSO) 8.30 (1 H, s, 4-OH), 7.81 (1 H, d, *J* 9.71, 5-H), 7.07 (1 H, d, *J* 8.24, 6′-H), 6.96–6.92 (2 H, m, 6-H, 8-H), 6.62 (1 H, d, *J* 2.20, 3′-H), 6.57 (1 H, dd, *J* 8.24 and 2.38, 5′-H), 3.87 (3 H, s, 7-OCH_3), 3.81 (3 H, s, 4′-OCH_3) and 3.70 (3 H, s, 2′-OCH_3); δ_C(67.80 MHz; DMSO) 162.32 (C-4), 162.01 (C-2), 160.85 (C-7), 160.52 (C-4′), 158.84 (C-2′), 154.07 (C-9), 133.04 (C-6′), 124.64 (C-5), 112.72 (C-3), 111.60 (C-6), 109.48 (C-10), 104.81 (C-3′), 100.18 (C-8), 99.73 (C-1′), 99.48 (C-5′), 55.77 (7-OCH_3), 55.27 (2′-OCH_3) and 55.16 (4′-OCH_3); *m/z* 328 (M^+, 79%), 204 (57), 178 (100), 151 (88), 57 (41) and 43 (53) (Found: C, 65.5; H, 5.05. Calc. for $C_{18}H_{16}O_6$; C, 65.85; H, 4.91%).

4-*Hydroxy*-7-*methoxy*-3-(2,4,6-*trimethoxyphenyl*)-1-*benzopyran*-2-*one* **17**.—(TLC; chloroform–methanol–water, 10:1:0.1), m.p. 230–231.5 °C; ν_{max}(KBr)/cm^{-1} 1682, 1615 and 1204; λ_{max}(MeOH)/nm 314 (17 758); δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.76 (1 H, d, *J* 9.35, 5-H), 6.95–6.90 (2 H, m, 6-H, 8-H), 6.28 (2 H, s, 3′-H, 5′-H), 3.87 (3 H, s, 7-OCH_3), 3.82 (3 H, s, 4′-OCH_3) and 3.67 (6 H, s, 2′-OCH_3, 6′-OCH_3); δ_C(67.80 MHz; DMSO) 162.18 (C-4), 161.47 (C-2), 161.29 (C-4′), 161.06 (C-7), 159.46 (C-2′, C-6′), 154.08 (C-9), 124.47 (C-5), 111.44 (C-6), 109.54 (C-10), 101.01 (C-3), 100.11 (C-8), 96.01 (C-1′),

90.86 (C-3′, C-5′), 55.73 (7-OCH_3), 55.46 (2′-OCH_3, 6′-OCH_3) and 55.19 (4′-OCH_3); *m/z* 358 (M^+, 67%), 234 (70), 208 (100), 151 (81), 95 (12) and 69 (16) (Found: C, 63.85; H, 5.2. $C_{18}H_{16}O_6$ requires C, 63.70; H, 5.05%).

4-*Hydroxy*-6-*methoxy*-3-*phenyl*-1-*benzopyran*-2-*one* **19**.—(TLC; chloroform–methanol–water, 10:1:0.1), m.p. 204–206 °C (decomp.) (lit.,[15] m.p. 205 °C); ν_{max}(KBr)/cm^{-1} 1665 and 1641; δ_H(270 MHz; DMSO) 7.51 (1 H, d, *J* 2.93, 5-H), 7.45–7.27 (6 H, m, 8-H, Ph), 7.21 (1 H, dd, *J* 8.79 and 2.93, 7-H) and 3.82 (3 H, s, 6-OCH_3); δ_C(67.80 MHz; DMSO) 162.16 (C-4), 161.39 (C-2), 155.11 (C-6), 146.66 (C-9), 132.90 (C-1′), 130.84 (C-2′, C-6′), 127.62 (C-3′, C-5′), 126.78 (C-4′), 119.49 (C-5), 117.61 (C-10), 117.21 (C-7), 105.96 (C-8), 105.14 (C-3) and 55.58 (6-OCH_3); *m/z* 268 (M^+, 49%), 150 (100), 118 (12) and 63 (9).

4-*Hydroxy*-6-*methoxy*-3-(p-*tolyl*)-1-*benzopyran*-2-*one* **20**.—(TLC; chloroform–methanol–water, 10:1:0.1), plates from ethanol, m.p. 212–214 °C; ν_{max}(KBr)/cm^{-1} 1668 and 1613; δ_H(270 MHz; CD_3CN) 7.47–7.40 (2 H, m, 5-H, 8-H), 7.30–7.16 (5 H, m, 7-H, 2′-H, 3′-H, 5′-H, 6′-H), 3.85 (3 H, s, 6-OCH_3) and 2.38 (3 H, s, 4′-CH_3); δ_C(67.80 MHz; CD_3CN) 162.84 (C-4), 160.08 (C-2), 155.62 (C-6), 146.99 (C-9), 137.20 (C-4′), 130.86 (C-2′, C-6′), 129.31 (C-1′), 128.74 (C-3′, C-5′), 119.54 (C-5), 117.35 (C-7), 116.48 (C-10), 106.12 (C-3), 105.71 (C-8), 55.50 (6-OCH_3) and 20.37 (4′-CH_3); *m/z* 282 (M^+, 100%), 254 (16), 211 (21), 150 (78) and 132 (83) (Found: C, 72.3; H, 4.95. $C_{17}H_{14}O_4$ requires C, 72.35; H, 5.00%).

3-(2,4-*Dimethoxyphenyl*)-4-*hydroxy*-6-*methoxy*-1-*benzopyran*-2-*one* **21**.—(TLC; chloroform–methanol–water, 10:1:0.1), needles from ethanol, m.p. 201–202 °C; ν_{max}(KBr)/cm^{-1} 1666, 1614 and 1209; λ_{max}(MeOH)/nm 278 (10 440) and 331 (10 546); δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.36–7.28 (2 H, m, 5-H, 8-H), 7.18–7.13 (1 H, m, 7-H), 7.04 (1 H, d, *J* 8.43, 6′-H), 6.59–6.52 (2 H, m, 3′-H, 5′-H), 3.81 (3 H, s, 6-OCH_3) 3.79 (3 H, s, 4′-OCH_3) and 3.67 (3 H, s, 2′-OCH_3); δ_C(67.80 MHz; DMSO) 161.38 (C-4), 161.21 (C-2), 160.26 (C-4′), 158.75 (C-2′), 155.38 (C-6), 147.12 (C-9), 132.39 (C-6′), 118.98 (C-5), 116.31 (C-10), 111.48 (C-3), 105.69 (C-8), 104.57 (C-3′), 102.30 (C-1′), 98.36 (C-5′), 55.46 (4′-OCH_3), 55.17 (2′-OCH_3) and 55.09 (6-OCH_3); *m/z* 328 (M^+, 4%), 248 (28), 189 (61), 95 (51), 55 (86) and 43 (100) (Found: C, 65.85; H, 4.85. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.90%).

4-*Hydroxy*-6-*methoxy*-3-(2,4,6-*trimethoxyphenyl*)-1-*benzopyran*-2-*one* **22**.—(TLC; chloroform–methanol–water, 10:1:0.1), needles from ethanol, m.p. 247–248.5 °C; ν_{max}(KBr)/cm^{-1} 1664, 1612 and 1204; λ_{max}(MeOH)/nm 325 (ε 11 742); δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.33–7.28 (2 H, m, 5-H, 8-H), 7.23–7.18 (1 H, m, 7-H), 6.29 (2 H, s, 3′-H, 5′-H), 3.83 (3 H, s, 6-OCH_3), 3.82 (3 H, s, 4′-OCH_3) and 3.67 (6 H, s, 2′-OCH_3, 6′-OCH_3); δ_C(67.80 MHz; DMSO) 161.41 (C-4), 161.29 (C-2), 160.36 (C-4′), 159.35 (C-2′, C-6′), 155.16 (C-6), 146.66 (C-9), 119.49 (C-5), 117.16 (C-7), 116.70 (C-10), 105.24 (C-8), 100.93 (C-3), 98.91 (C-1′), 90.87 (C-3′, C-5′) 55.57 (4′-OCH_3), 55.49 (2′-OCH_3, 6′-OCH_3) and 55.20 (6-OCH_3); *m/z* 358 (M^+, 90%), 327 (18), 271 (31), 234 (11), 208 (100), 179 (13) and 154 (28) (Found: C, 63.55; H, 5.0. $C_{19}H_{18}O_7$ requires C, 63.70; H, 5.05%).

4-*Hydroxy*-5-*methoxy*-3-*phenyl*-1-*benzopyran*-2-*one* **24**.—(TLC; chloroform–methanol–water, 10:1:0.1), needles from ethanol, m.p. 144.5–146 °C; ν_{max}(KBr)/cm^{-1} 1716 and 1610; δ_H(270 MHz; DMSO) 8.32 (1 H, s, OH), 7.62 (1 H, t, *J* 8.42, 7-H), 7.45–7.28 (5 H, m, Ph), 7.07 (1 H, s, 8-H), 7.04 (1 H, s, 6-H) and 4.03 (3 H, s, 5-OCH_3); δ_C(67.80 MHz; DMSO) 161.25 (C-4), 160.93 (C-2), 156.50 (C-5), 153.20 (C-9), 132.90 (C-7), 131.91 (C-1′), 130.72 (C-3′, C-5′), 127.54 (C-2′, C-6′), 127.11 (C-4′), 124.05 (C-3), 109.71 (C-6), 106.63 (C-8), 104.39 (C-10) and 57.10 (5-OCH_3); *m/z* 268 (M^+, 63%), 239 (5), 167 (6), 151 (100), 150 (53), 136 (14), 118 (14), 107 (12), 97 (20), 69 (56), 57 (47) and 43 (52) (Found: C, 71.5; H, 4.2. $C_{16}H_{12}O_4$ requires C, 71.65; H, 4.50%).

4-*Hydroxy*-5-*methoxy*-3-(2-*methoxyphenyl*)-1-*benzopyran*-2-*one* **25**.—(TLC; chloroform–methanol–water, 10:1:0.1), fine needles from ethanol, m.p. 199–201 °C; ν_{max}(KBr)/cm^{-1} 1714 and 1611; λ_{max}(MeOH)/nm 309 (14 005); δ_H(270 MHz; DMSO) 8.26 (1 H, s, 4-OH), 7.60 (1 H, t, *J* 8.42, 7-H), 7.34–7.30 (1 H, m, 4′-H), 7.18 (1 H, dd, *J* 7.30 and 1.84, 6′-H), 7.05 (1 H, s, 8-H), 7.01 (1 H, s, 6-H), 7.00–6.93 (2 H, m, 3′-H, 5′-H), 4.00 (3 H, s, 5-OCH_3) and 3.72 (3 H, s, 2′-OCH_3); δ_H(67.80 MHz; DMSO) 161.56 (C-4), 160.88 (C-2), 157.37 (C-2′), 156.46 (C-5), 153.46 (C-9), 132.60 (C-7), 131.98 (C-4′), 128.99 (C-6′), 121.10 (C-3), 119.88 (C-5′), 111.04 (C-3′), 109.67 (C-6), 106.42 (C-8), 103.87 (C-10), 101.95 (C-1′), 56.93 (5-OCH_3) and 55.30 (2′-OCH_3); *m/z* 298 (M^+, 62%), 283 (0.4), 267 (7), 174 (36), 151 (100), 149 (15), 148 (70) and 124 (44) (Found: C, 68.2; H, 4.75. $C_{17}H_{14}O_5$ requires C, 68.45; H, 4.75%).

4-*Hydroxy*-5-*methoxy*-3-(3-*methoxyphenyl*)-1-*benzopyran*-2-*one* **26**.—(TLC; chloroform–methanol–water, 10:1:0.1), needles from ethanol, m.p. 190–191 °C; ν_{max}(KBr)/cm^{-1} 1716 and 1609; λ_{max}(MeOH)/nm 313 (15 749); δ_H(270 MHz; DMSO) 7.94 (1 H, s, 4-OH), 7.56 (1 H, t, *J* 8.43, 7-H), 7.29 (1 H, t, *J* 8.06, 5′-H), 7.06–6.86 (4 H, m, 6-H, 8-H, 2′-H, 6′-H), 6.83 (1 H, dd, *J* 2.76 and 1.10, 4′-H), 4.07 (3 H, s, 5-OCH_3) and 3.79 (3 H, s, 3′-OCH_3); δ_C(67.80 MHz; DMSO) 161.98 (C-4), 161.82 (C-2), 158.76 (C-3′), 156.58 (C-5), 153.50 (C-9), 133.25 (C-1′), 132.46 (C-7), 128.47 (C-6′), 123.10 (C-5′), 116.45 (C-2′), 112.54 (C-4′), 110.08 (C-6), 106.18 (C-8), 104.98 (C-10), 104.57 (C-3), 57.10 (5-OCH_3) and 54.98 (3′-OCH_3); *m/z* 298 (M^+, 79%), 283 (0.8), 280 (9), 151 (100), 150 (20), 148 (47), 136 (8), 122 (3) and 108 (7) (Found: C, 68.35; H, 4.5. $C_{17}H_{14}O_5$ requires C, 68.45; H, 4.75%).

4-*Hydroxy*-5-*methoxy*-3-(4-*methoxyphenyl*)-1-*benzopyran*-2-*one* **27**.—(TLC; chloroform–methanol–water, 10:1:0.1), needles from ethanol, m.p. 172–173 °C; ν_{max}(KBr)/cm^{-1} 1718 and 1610; λ_{max}(MeOH)/nm 311 (14 811); δ_H(270 MHz; CD_3CN) 9.95 (1 H, s, 4-OH), 7.55 (1 H, t, *J* 8.43, 7-H), 7.39 (2 H, d, *J* 9.16, 2′-H, 6′-H), 7.03–6.94 (4 H, m, 6-H, 8-H, 3′-H, 5′-H), 4.05 (3 H, s, 5-OCH_3) and 3.82 (3 H, s, 4′-OCH_3); δ_C(67.80 MHz; CD_3CN) 161.48 (C-4), 160.98 (C-2), 158.94 (C-4′), 156.61 (C-5), 153.67 (C-9), 132.32 (C-7), 131.95 (C-2′, C-6′), 124.20 (C-1′), 113.16 (C-3′, C-5′), 112.17 (C-3), 110.20 (C-6), 106.31 (C-8), 104.97 (C-10), 57.09 (5-OCH_3) and 54.89 (4′-OCH_3); *m/z* 298 (M^+, 89%), 283 (4), 151 (92), 148 (100), 136 (12) 120 (22), 108 (14), 108 (12) and 77 (10) (Found: C, 68.25; H, 4.5. $C_{17}H_{14}O_5$ requires C, 68.45; H, 4.75%).

4-*Hydroxy*-5-*methoxy*-3-(p-*tolyl*)-1-*benzopyran*-2-*one* **28**.—(TLC; chloroform–methanol–water, 10:1:0.1), needles from ethanol, m.p. 132.5–133.5 °C; ν_{max}(KBr)/cm^{-1} 1718 and 1609; λ_{max}(MeOH)/nm 313 (7095); δ_H(270 MHz; CD_3CN) 9.94 (1 H, br s, 4-OH), 7.56 (1 H, t, *J* 8.43, 7-H), 7.33 (2 H, d, *J* 8.06, 2′-H, 6′-H), 7.22 (2 H, d, *J* 7.70, 3′-H, 5′-H), 7.02 (1 H, dd, *J* 8.43 and 0.74, 8-H), 6.97 (1 H, dd, *J* 8.79 and 0.73, 6-H), 4.05 (3 H, s, 5-OCH^{13}) and 2.37 (3 H, s, 4′-CH_3); δ_C(67.80 MHz; CD_3CN) 161.25 (C-4), 160.66 (C-2), 156.39 (C-5), 153.04 (C-9), 136.24 (C-4′), 132.73 (C-7), 130.50 (C-2′, C-6′), 128.77 (C-1′), 128.06 (C-3′, C-5′), 109.65 (C-6), 106.55 (C-8), 104.54 (C-3), 104.38 (C-10), 57.06 (5-OCH_3) and 20.80 (4′-CH_3); *m/z* 282 (M^+, 96%), 151 (100), 132 (76), 108, (13), 91 (10), 77 (11), 65 (8) and 39 (10) (Found: C, 72.3; H, 5.1. $C_{17}H_{14}O_4$ requires C, 72.35; H, 5.00%).

3-(2,4-*Dimethoxyphenyl*)-4-*hydroxy*-5-*methoxy*-1-*benzopyran*-2-*one* **29**.—(TLC; chloroform–methanol–water, 10:1:0.1), plates from ethanol, m.p. 210–211.5 °C; ν_{max}(KBr)/cm^{-1} 1710 and 1612; λ_{max}(MeOH)/nm 312 (11 646); δ_H(270 MHz; DMSO) 8.30 (1 H, s, 4-OH), 7.60 (1 H, t, *J* 8.43, 7-H), 7.08 (1 H, d, *J* 8.43, 6′-H), 7.06 (1 H, s, 8-H), 7.02 (1 H, s, 6-H), 6.61 (1 H, d, *J* 2.56, 3′-H), 6.56 (1 H, dd, *J* 8.42 and 2.20, 5′-H), 4.00 (3 H, s, 5-OCH$_3$) 3.80 (3 H, s, 4′-OCH$_3$) and 3.70 (3 H, s, 2′-OCH$_3$); δ_C(67.80 MHz; DMSO) 161.20 (C-4), 160.96 (C-2), 160.30 (C-2′), 158.32 (C-4′), 156.30 (C-5), 153.29 (C-9), 132.57 (C-7), 132.35 (C-6′), 113.13 (C-3), 109.60 (C-6), 106.47 (C-8), 104.60 (C-5′), 104.43 (C-10), 101.90 (C-1′), 98.34 (C-3′), 56.93 (5-OCH$_3$) 55.33 (2′-OCH$_3$) and 55.14 (4′-OCH$_3$); *m*/*z* 328 (M$^+$, 100%), 297 (6), 204 (59), 178 (96), 163 (23), 151 (83), 136 (16), 121 (18) and 107 (13) (Found: C, 65.75; H, 4.9. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.90%).

3-(3,4-*Dimethoxyphenyl*)-4-*hydroxy*-5-*methoxy*-1-*benzopyran*-2-*one* **30**.—(TLC; chloroform–methanol–water, 10:1:0.1), plates from ethanol, m.p. 214–215 °C; ν_{max}(KBr)/cm^{-1} 3269, 1718, 1637, 1606, 1517, 1241, 811 and 677; λ_{max}(MeOH)/nm 315 (12 984); δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.61 (1 H, t, *J* 8.43, 7-H), 7.07–6.97 (5 H, m, 6-H, 8-H, 2′-H, 5′-H, 6′-H), 4.03 (3 H, s, 5-OCH$_3$) 3.79 (3 H, s, 4′-OCH$_3$) and 3.74 (3 H, s, 3′-OCH$_3$); δ_C(67.80 MHz; DMSO) 161.31 (C-4), 160.69 (C-2), 156.39 (C-5), 153.02 (C-9), 147.96 (C-4′), 147.83 (C-3′), 132.65 (C-7), 124.12 (C-1′), 123.32 (C-6′), 114.66 (C-2′), 111.12 (C-5′), 109.60 (C-6), 106.63 (C-8), 105.02 (C-10), 104.49 (C-3), 57.04 (5-OCH$_3$) 55.47 (4′-OCH$_3$) and 55.44 (3′-OCH$_3$); *m*/*z* 328 (M$^+$, 100%), 313 (17), 178 (52), 163 (17), 151 (71), 136 (11) and 107 (10) (Found: C, 65.75; H, 4.85. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.90%).

3-(2,5-*Dimethoxyphenyl*)-4-*hydroxy*-5-*methoxy*-1-*benzopyran*-2-*one* **31**.—(TLC; chloroform–methanol–water, 10:1:0.1), plates from ethanol, m.p. 180–181.5 °C; ν_{max}(KBr)/cm^{-1} 1714 and 1609; λ_{max}(MeOH)/nm 303 (11 479); δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.59 (1 H, t, *J* 8.43, 7-H), 7.03 (1 H, s, 8-H), 7.00 (1 H, s, 6-H), 6.96 (1 H, d, *J* 8.80, 3′-H), 6.88 (1 H, dd, *J* 9.16 and 2.93, 4′-H), 6.76 (1 H, d, *J* 2.93, 6′-H), 3.98 (3 H, s, 5-OCH$_3$) 3.70 (3 H, s, 5′-OCH$_3$) and 3.65 (3 H, s, 2′-OCH$_3$); δ_C(67.80 MHz; DMSO) 162.16 (C-4), 160.71 (C-2), 156.60 (C-5), 153.58 (C-9), 152.69 (C-5′), 151.69 (C-2′), 132.46 (C-7), 122.51 (C-3), 117.92 (C-6′), 113.33 (C-4′), 112.07 (C-3′), 109.56 (C-6), 106.44 (C-8), 105.09 (C-10), 101.47 (C-1′), 56.87 (5-OCH$_3$) 55.84 (2′-OCH$_3$) and 55.33 (5′-OCH$_3$); *m*/*z* 328 (M$^+$, 89%), 313 (1), 297 (15), 204 (67), 178 (58), 164 (13), 163 (52), 151 (100), 136 (15), 108, (17) and 107 (16) (Found: C, 66.0; H, 4.9. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.90%).

4-*Hydroxy*-5-*methoxy*-3-(3,4-*methylenedioxyphenyl*)-1-*benzopyran*-2-*one* **32**.—(TLC; chloroform–methanol–water, 10:1:0.1), plates from ethanol, m.p. 188.5–190 °C; ν_{max}(KBr)/cm^{-1} 1719 and 1608; λ_{max}(MeOH)/nm 325 (12 577); δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.61 (1 H, t, *J* 8.43, 7-H), 7.06 (1 H, d, *J* 1.28, 8-H), 7.03 (1 H, d, *J* 0.92, 6-H), 6.96–6.88 (3 H, m, 2′-H, 5′-H, 6′-H), 6.03 (2 H, s, OCH$_2$O) and 4.02 (3 H, s, 5-OCH$_3$); δ_C(67.80 MHz; DMSO) 161.22 (C-4), 160.80 (C-2), 156.39 (C-5), 153.01 (C-9), 146.47 (C-4′), 146.09 (C-3′), 132.73 (C-7), 125.18 (C-1′), 124.26 (C-6′), 111.04 (C-5′), 109.62 (C-6), 107.55 (C-2′), 106.57 (C-8), 104.41 (C-10), 104.32 (C-3), 100.74 (OCH$_2$O) and 57.04 (5-OCH$_3$); *m*/*z* 312 (M$^+$, 73%), 162 (88), 151 (100), 141 (15), 134 (23), 127 (8), 108 (18), 75 (19) and 63 (10) (Found: C, 65.2; H, 3.8. $C_{17}H_{12}O_6$ requires C, 65.40; H, 3.85%).

4-*Hydroxy*-5-*methoxy*-3-(2,4,6-*trimethoxyphenyl*)-1-*benzopyran*-2-*one* **33**.—(TLC; chloroform–methanol–water, 10:1:0.1), needles from ethanol, m.p. 238–240 °C; ν_{max}(KBr)/cm^{-1} 1718 and 1615; λ_{max}(MeOH)/nm 309 (9775); δ_H(270 MHz; DMSO) 8.30 (1 H, s, 4-OH), 7.58 (1 H, d, *J* 8.43, 7-H), 7.03 (1 H, s, 8-H), 7.00 (1 H, s, 6-H), 6.26 (2 H, s, 3′-H, 5′-H), 3.98 (3 H, s, 5-OCH$_3$) 3.80 (3 H, s, 4′-OCH$_3$) and 3.66 (6 H, s, 2′-OCH$_3$, 6′-OCH$_3$); δ_C(67.80 MHz; DMSO) 162.47 (C-4), 162.20 (C-2), 159.95 (C-2′, C-6′), 157.36 (C-4′), 156.37 (C-5), 154.58 (C-9), 133.63 (C-7), 110.73 (C-6), 107.61 (C-8), 105.65 (C-10), 102.76 (C-3), 100.89 (C-1′), 91.91 (C-3′, C-5′), 58.04 (5-OCH$_3$), 56.68 (2′-OCH$_3$, 6′-OCH$_3$) and 56.38 (4′-OCH$_3$); *m*/*z* 358 (M$^+$, 88%), 341 (6), 327 (13), 234 (39), 208 (100), 193 (25), 179 (26), 165 (28), 154 (58), 151 (72), 136 (14), 121 (13) and 69 (12) (Found: C, 63.55; H, 5.1. $C_{19}H_{18}O_7$ requires C, 63.70; H, 5.05%).

4-*Hydroxy*-7,8-*dimethoxy*-3-*phenyl*-1-*benzopyran*-2-*one* **35**.—(TLC; chloroform–methanol–water, 8:1:0.1), fine needles from ethanol, m.p. 219–220 °C (lit.,[19] m.p. 218–220 °C); ν_{max}(KBr)/cm^{-1} 1671; δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.75 (1 H, d, *J*, 8.8, 5-H), 7.41–7.30 (5 H, m, Ph), 7.12 (1 H, d, *J* 9.1, 6-H), 3.92 (3 H, s, 8-OCH$_3$) and 3.84 (3 H, s, 7-OCH$_3$); *m*/*z* 298 (M$^+$, 73%), 181 (100), 152 (39), 120 (17) and 69 (20).

4-*Hydroxy*-7,8-*dimethoxy*-3-(4-*methoxyphenyl*)-1-*benzopyran*-2-*one* **36**.—(TLC; chloroform–methanol–water, 8:1:0.1), m.p. 221–222.5 °C; ν_{max}(KBr)/cm^{-1} 1673; λ_{max}(MeOH)/nm 312 (11 787); δ_H(270 MHz; DMSO) 8.30 (1 H, s, 4-OH), 7.69 (1 H, d, *J* 8.79, 5-H), 7.32 (2 H, dd, *J* 6.78 and 2.19, 2′-H, 6′-H), 7.11 (1 H, d, *J* 9.15, 6-H), 6.96 (2 H, dd, *J* 6.78 and 2.20, 3′-H, 5′-H), 3.92 (3 H, s, 8-COH$_3$) 3.83 (3 H, s, 7-OCH$_3$) and 3.79 (3 H, s, 4′-OCH$_3$); δ_C(67.80 MHz; DMSO) 161.38 (C-4), 161.06 (C-2), 158.20 (C-4′), 154.89 (C-7), 146.17 (C-9), 134.86 (C-8), 132.06 (C-2′, C-6′), 123.46 (C-1′), 118.71 (C-5), 114.18 (C-3), 113.29 (C-3′, C-5′), 111.14 (C-10), 108.35 (C-6), 60.63 (8-OCH$_3$), 56.19 (7-OCH$_3$) and 54.97 (4′-OCH$_3$); *m*/*z* 328 (M$^+$, 74%), 181 (68), 148 (100), 121 (18) and 69 (18) (Found: C, 66.05; H, 4.9. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.90%).

3-(2,4-*Dimethoxyphenyl*)-4-*hydroxy*-7,8-*dimethoxy*-1-*benzopyran*-2-*one* **37**.—(TLC; chloroform–methanol–water, 8:1:0.1), needles from ethanol, m.p. 198.5–200 °C; ν_{max}(KBr)/cm^{-1} 1693 and 1614; λ_{max}(MeOH)/nm 313 (12 882); δ_H(270 MHz; DMSO) 8.15 (1 H, s, 4-OH), 7.63 (1 H, d, *J* 8.97, 5-H), 7.10 (1 H, d, *J* 9.16, 6-H), 7.07 (1 H, d, *J* 8.24, 6′-H), 6.62–6.55 (2 H, m, 3′-H, 5′-H), 3.92 (3 H, s, 8-OCH$_3$), 3.84 (3 H, s, 7-OCH$_3$), 3.81 (3 H, s, 4′-OCH$_3$) and 3.71 (3 H, s, 2′-OCH$_3$); δ_C(67.80 MHz; DMSO) 161.61 (C-4), 160.69 (C-2), 160.58 (C-2′), 158.83 (C-4′), 154.94 (C-7), 146.28 (C-9), 134.96 (C-8), 133.00 (C-6′), 118.54 (C-5), 112.53 (C-3), 110.55 (C-10), 108.45 (C-6), 104.84 (C-5′), 99.95 (C-1′), 98.47 (C-3′), 60.63 (8-OCH$_3$) 56.20 (7-OCH$_3$), 55.27 (2′-OCH$_3$) and 55.16 (4′-OCH$_3$); *m*/*z* 358 (M$^+$, 88%), 204 (16), 181 (62), 178 (100), 149 (7) and 120 (5) (Found: C, 63.75; H, 4.8. $C_{19}H_{18}O_7$ requires C, 63.70; H, 5.05%).

4-*Hydroxy*-7,8-*dimethoxy*-3-(2,4,6-*trimethoxyphenyl*)-1-*benzopyran*-2-*one* **38**.—(TLC; chloroform–methanol–water, 8:1:0.1), needles from ethanol, m.p. 223–224.5 °C, ν_{max}(KBr)/cm^{-1} 1685, 1608 and 1204; λ_{max}/nm (MeOH) 313 (5745); δ_H(270 MHz; DMSO) 8.31 (1 H, s, 4-OH), 7.57 (1 H, d, *J* 8.97, 5-H), 7.08 (1 H, d, *J* 8.98, 6-H), 6.27 (2 H, s, 3′-H, 5′-H), 3.91 (3 H, s, 8-OCH$_3$) 3.83 (3 H, s, 4′-OCH$_3$) 3.82 (3 H, s, 7-OCH$_3$) and 3.66 (6 H, s, 2′-OCH$_3$, 6′OCH$_3$); δ_C(67.80 MHz; DMSO) 161.25 (C-4), 161.15 (C-2), 159.44 (C-2′, C-6′), 154.92 (C-7), 154.73 (C-4′), 146.39 (C-9), 135.41 (C-8), 118.41 (C-5), 112.34 (C-3), 110.34 (C-10), 108.26 (C-6), 101.34 (C-1′), 90.86 (C-3′, C-5′), 60.60 (8-OCH$_3$), 56.19 (7-OCH$_3$), 55.46 (2′-OCH$_3$, 6′-OCH$_3$) and 55.19 (4′-OCH$_3$); *m*/*z* 388 (M$^+$, 48%), 234 (36), 208 (100), 181 (55) and 121 (13) (Found: C, 61.55; H, 5.2. $C_{20}H_{20}O_8$ requires C, 61.85; H, 5.20%).

4-*Hydroxy*-5,7-*dimethoxy*-3-(4-*methoxyphenyl*)-1-*benzopyran*-2-*one* **40**.—(TLC; chloroform–methanol–water, 36:1.6:0.6), needles from ethanol, m.p. 236–237 °C (lit.,[16] m.p. 220 °C); ν_{max}(KBr)/cm^{-1} 1714, 1647, 1615, 1201, 1109, 822 and 669; λ_{max}(MeOH)/nm 326 (18 332); δ_H(270 MHz; $CDCl_3$) 9.62 (1 H, s, 4-OH), 7.46 (2 H, dd, *J* 6.78 and 2.20, 2′-H, 6′-H), 6.95 (2 H, dd, *J* 6.98 and 2.20, 3′-H, 5′-H), 6.53 (1 H, d, *J* 2.20, 8-H), 6.38 (1 H, d, *J* 2.38, 6-H), 4.03 (3 H, s, 5-OCH_3), 3.87 (3 H, s, 7-OCH_3) and 3.83 (3 H, s, 4′-OCH_3); δ_C(67.80 MHz; $CDCl_4$) 162.96 (C-4), 162.88 (C-2), 161.09 (C-7), 158.78 (C-5), 157.02 (C-4′), 155.44 (C-9), 131.78 (C-2′, C-6′), 123.54 (C-1′), 113.49 (C-3′, C-5′), 103.08 (C-3), 99.02 (C-10), 95.60 (C-8), 94.23 (C-6), 56.99 (5-OCH_3), 55.93 (7-OCH_3) and 55.25 (4′-OCH_3); *m*/*z* 328 (M^+, 74%), 313 (4), 285 (6), 181 (100), 164 (11), 148 (69), 135 (10), 120 (12), 83 (9) and 69 (7) (Found: C, 65.5; H, 4.9. Calc. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.90%).

4-*Hydroxy*-5,7-*dimethoxy*-3-(3,4-*methylenedioxyphenyl*)-1-*benzopyran*-2-*one* **2**.—(TLC; chloroform–methanol–water, 36:1.6:0.6), needles from ethanol, m.p. 232–233.5 °C, (lit.,[17] m.p. 234–235 °C); ν_{max}(KBr)/cm^{-1} 3246, 1691, 1402, 1158, 827 and 659; λ_{max}(MeOH)/nm 324 (16 432); δ_H(270 MHz; $CDCl_3$) 9.63 (1 H, s, 4-OH), 7.01-6.98 (2 H, m, 2′-H, 6′-H), 6.86 (1 H, d, *J* 8.42, 5′-H), 6.53 (1 H, d, *J* 2.19, 8-H), 6.38 (1 H, d, *J* 2.28, 6-H), 6.00 (2 H, s, OCH_2O), 4.03 (3 H, s, 5-OCH_3) and 3.87 (3 H, s, 7-OCH_3); δ_C(67.80 MHz; $CDCl_3$) 163.11 (C-4), 162.69 (C-2), 161.34 (C-7), 157.10 (C-5), 155.52 (C-9), 147.25 (C-4′), 146.87 (C-3′), 124.83 (C-1′), 124.36 (C-6′), 111.23 (C-5′), 108.08 (C-2′), 103.18 (C-3), 100.97 (OCH_2O), 98.96 (C-10), 95.67 (C-8), 94.31 (C-6), 57.02 (5-OCH_3) and 55.95 (7-OCH_3); *m*/*z* 342 (M^+, 78%), 313 (3), 299 (5), 181 (100), 180 (20), 162 (62), 156 (18), 149 (7), 134 (10), 69 (11) and 44 (40).

4-*Hydroxy*-5,7-*dimethoxy*-3-(2,4,6-*trimethoxyphenyl*)-1-*benzopyran*-2-*one* **41**.—(TLC; chloroform–methanol–water, 10:1:0.1), needles from ethanol, m.p. 242–243 °C; ν_{max}(KBr)/cm^{-1} 3338, 1693, 1605, 1508, 1208, 1113, 812 and 658; λ_{max}(MeOH)/nm 316 (28 432); δ_H(270 MHz; $CDCl_3$) 9.38 (1 H, s, 4-OH), 6.53 (1 H, d, *J* 2.19, 8-H), 6.35 (1 H, d, *J* 2.20, 6-H), 6.23 (2 H, s, 3′-H, 5′-H), 3.97 (3 H, s, 5-OCH_3), 3.86 (3 H, s, 7-OCH_3), 3.83 (3 H, s, 4′-OCH_3) and 3.77 (6 H, s, 2′-OCH_3, 6′-OCH_3); δ_C(67.80 MHz; $CDCl_3$) 162.75 (C-4), 162.29 (C-2), 162.04 (C-4′), 161.61 (C-7), 159.38 (C-2′, C-6′), 156.99 (C-5), 156.07 (C-9), 101.92 (C-3), 99.40 (C-10), 96.98 (C-1′), 95.25 (C-8), 94.31 (C-6), 91.36 (C-3′, C-5′), 56.79 (5-OCH_3), 56.12 (2′-OCH_3, 6′-OCH_3), 55.88 (7-OCH_3) and 55.36 (4′-OCH_3); *m*/*z* 388 (M^+, 52%), 357 (7), 234 (50), 208 (100), 193 (18), 181 (63), 154 (27), 137 (12), 91 (7) and 69 (5) (Found: C, 61.7; H, 5.3. $C_{20}H_{20}O_8$ requires C, 61.85; H, 5.20%).

4-*Hydroxy*-5-*methoxy*-3-(4-*methoxyphenyl*)-8,8-*dimethyl*-2H,8H-*benzo*[1,2-b:3,4-b′]*dipyran*-2-*one* **54**.—(TLC; chloroform–methanol–water, 36:1:0.1), needles from ethanol, m.p. 220–221.5 °C (lit.,[68] m.p. 220–221 °C); ν_{max}(KBr)/cm^{-1} 1715, 1642, 1594 and 720; λ_{max}(MeOH)/nm 278 (7432) and 326 (11 783); δ_H(270 MHz; $CDCl_3$) 7.43–7.39 (2 H, m, 2′-H, 6′-H), 6.85–6.81 (2 H, m, 3′-H, 5′-H), 6.63 (1 H, d, *J* 10.62, 10-H), 5.95 (1 H, s, 6-H), 5.49 (1 H, d, *J* 9.89, 9-H), 3.87 (3 H, s, 5-OCH_3), 3.77 (3 H, s, 4′-OCH_3) and 1.48 (6 H, s, 2 × 8-CH_3); δ_C(67.80 MHz; $CDCl_3$) 162.31 (C-4), 161.56 (C-2), 158.93 (C-4′), 156.71 (C-12), 156.39 (C-5), 149.98 (C-13), 131.87 (C-2′, C-6′), 128.08 (C-9), 124.21 (C-1′), 115.49 (C-10), 113.19 (C-3′, C-5′), 112.49 (C-3), 104.11 (C-14), 99.14 (C-11), 95.71 (C-6), 78.14 (C-8), 56.81 (5-OCH_3), 54.91 (4′-OCH_3) and 28.14 [8-$(CH_3)_2$]; *m*/*z* 380 (M^+, 76%), 365 (54), 233 (32), 232 (14), 217 (100), 148 (24) and 69 (6).

4-*Hydroxy*-5-*methoxy*-8,8-*dimethyl*-3-(3,4-*methylenedioxyphenyl*)-2H,8H-*benzo*[1,2-b:3,4-b′]*dipyran*-2-*one* **4**.—(TLC; chloroform–methanol, 36:1), fine needles from ethanol, m.p. 199–200 °C (lit.,[4] m.p. 202–204 °C); ν_{max}(KBr)/cm^{-1} 1712, 1600 and 1372; λ_{max}(MeOH)/nm 236 (34 466), 280 (14 749) and 335 (15 715); δ_H(270 MHz; $CDCl_3$) 9.74 (1 H, br s, 4-OH), 7.00–6.97 (2 H, m, 2′-H, 6′-H), 6.87 (1 H, d, *J* 8.43, 5′-H), 6.86 (1 H, d, *J* 10.08, 10-H), 6.33 (1 H, s, 6-H), 5.97 (2 H, s, OCH_2O), 5.65 (1 H, d, *J* 10.07, 9-H), 4.02 (3 H, s, 5-OCH_3) and 1.48 (6 H, s, 2 × 8-CH_3); δ_C(67.80 MHz; $CDCl_3$) 162.40 (C-4), 161.58 (C-2), 156.85 (C-12), 156.44 (C-5), 149.65 (C-13), 147.25 (C-4′), 146.85 (C-3′), 128.32 (C-9), 124.96 (C-1′), 124.36 (C-6′), 115.25 (C-10), 111.26 (C-5′), 108.10 (C-2′), 104.08 (C-14), 102.89 (C-3), 100.97 (OCH_2O), 98.67 (C-11), 96.00 (C-6), 78.36 (C-8), 57.04 (5-OCH_3) and 28.19 [8-$(CH_3)_2$]; *m*/*z* 394 (M^+, 81%), 379 (48), 233 (27), 232 (12), 217 (100), 189 (22), 162 (8), 91 (4) and 69 (3).

4-*Hydroxy*-5-*methoxy*-8,8-*dimethyl*-3-(2,4,6-*trimethoxyphenyl*)-2H,8H-*benzo*[1,2-b:3,4-b′]*dipyran*-2-*one* **58**.—(TLC; chloroform–methanol, 10:1), needles from ethanol, m.p. 251–252 °C; ν_{max}(KBr)/cm^{-1} 3353, 1719, 1643, 1596, 1206, 1127, 830 and 699; λ_{max}(MeOH)/nm 267 (6083) and 312 (2457); δ_H(270 MHz; $CDCl_3$) 9.48 (1 H, br s, 4-OH), 6.87 (1 H, d, *J* 10.08, 10-H), 6.30 (1 H, s, 6-H), 6.23 (2 H, s, 3′-H, 5′-H), 5.59 (1 H, d, *J* 10.08, 9-H), 3.97 (3 H, s, 5-OCH_3), 3.83 (3 H, s, 4′-OCH_3), 3.76 (6 H, s, 2′-OCH_3, 6′-OCH_3) and 1.48 [6 H, s, 8-$(CH_3)_2$]; δ_C(67.80 MHz; $CDCl_3$) 162.29 (C-4), 161.96 (C-2), 161.58 (C-4′), 159.36 (C-2′, C-6′), 156.45 (C-12), 156.36 (C-5), 150.22 (C-13), 128.01 (C-9), 115.55 (C-10), 104.08 (C-14), 102.70 (C-3), 100.64 (C-1′), 99.10 (C-11), 95.65 (C-6), 91.38 (C-3′, C-5′), 78.12 (C-8), 56.80 (5-OCH_3), 56.12 (2′-OCH_3, 6′-OCH_3), 55.34 (4′-OCH_3) and 28.12 [8-$(CH_3)_2$]; *m*/*z* 440 (M^+, 78%), 425 (30), 287 (4), 233 (18), 217 (100), 208 (95), 191 (16), 179 (10), 109 (4) and 69 (5) (Found: C, 65.45; H, 5.3. $C_{24}H_{24}O_8$ requires C, 65.45; H, 5.50%).

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