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Synthesis of some 3-phenyl chromenone-crown ethers and equilibrium studies on complexation with ion-pair extraction of sodium and potassium dyes

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Abstract

6,7-Dihydroxy-3-phenyl-*2H*-chromenones and 7,8-dihydroxy-3-(methoxyphenyl)-*2H*-chromenones, *o*-dihydroxy-3-phenylcoumarins, were prepared from phenylacetic acid/2,4,5-trihydroxybenzaldehyde, methoxyphenylacetic acid/2,3,4-trihydroxybenzaldehyde in NaOAc/Ac_2O, respectively. 3-Aryl-6,7-dihydroxy-*2H*-chromenone and 3-aryl-7,8-dihydroxy-*2H*-chromenone reacted with the polyethylene glycol ditosylate in CH_3CN/Me_2CO_3 to afford 12-crown-4,15-crown-5, and 18-crown-6-chromenones. The purified products were identified with IR, ^{1}NMR, low and high resolution mass spectroscopy and elemental analysis. Liquid–liquid extractive-spectrophotometric studies of sodium and potassium ion complexes of **3a**–**c**, **4a**–**h** coumarin-crown ethers and anionic dyes [4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (SPAR), and sodium picrate (SP), and potassium picrate (PP)], as the counter ion are described. The overall extraction equilibrium constants for the 1:1 complexes of the above coumarin-crown ethers with sodium and potassium ions, between the organic solvent and water, have been determined at 25 °C. They were conducted in various solvent–water systems maintaining an identical initial cation concentration in water, $[M_0^+]_w$, and a macrocyclic ligand concentration in the organic phase, $[L_0]_{org}$, so that in all extractions $[M_0^+]_w$:$[L_0]_{org}$ ratios were 1:1. An ion association complex formed between the alkali-crown ether complex ion and a dye anion was extracted into the CH_2Cl_2 organic solvent, and then the dye concentration of the separated aqueous phase was measured with an ultraviolet–visible spectrophotometer. According to the study, SPAR is the best associated dye with all the coumarin-crown ethers and the extracted dye occurs as the ion-pair complex. The extraction selectivity was interpreted quantitatively by the constituent equilibrium constants, i.e. K_{ext}, the ion-pair extraction constant of ML^+ and A^- in CH_2Cl_2.

Keywords: 3-Phenyl-chromenone crown ethers; Coumarin-crown ethers; Na^+, K^+-complexation; Ion-pair solvent extraction; Sodium and potassium dyes

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1. Introduction

Crown ethers show a remarkable ability to extract alkali and alkaline earth metal ions selectively, as well as other ions such as organic cations and anions [1–4]. These macrocyclic ligands have been widely used and several reviews have been published [5–10]. The particular role of liquid–liquid alkali cation transfer in membranes has expanded the area of interest. The cation binding selectivity of such molecules, particularly the crown ethers, have been investigated with different types of macrocyclic structures by several authors and have been well documented for molecular recognition [11–14]. The determination of sodium by means of ion-selective electrodes involving the use of crown ethers has been reported, as has their use as potentiometric titrants [15–18]. Crown ethers have also been used for chromatographic separations [3,19]. Photometric or fluorimetric determinations, particularly of alkali and alkaline earth metal ions, can be carried out by solvent extraction of the ion-pair formed between the crown ether complex and a coloured or fluorescent counter ion [4,20–26]. However, the cation extraction properties of the macrocyclic ethers with different side groups of various types were examined for their extractive abilities [11,12,27,28]. The spectrophotometric methods for solvent extraction of an ion association complex and an anionic dye have been commonly used [22–24,29,30]. Since a large anion is easily extracted into low dielectric constant solvents, the picrate anion was widely used as the counter ion [2,27,31–33].

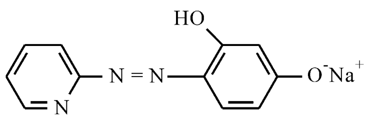
This paper also describes the extractive-spectrophotometric determination of sodium and potassium ions as ion-pairs using coumarin-crown ethers as complexing agents and anionic dyes as coloured counter ions. The effects of the cavity size and different functional groups and type of the crown compounds and also the size and two different functional groups of anionic dyes have been studied. For this purpose, the coumarin-crown ethers **3a–c**, **4a–h** have been synthesized, and the anionic dyes are 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (SPAR), sodium picrate (SP) and potassium picrat (PP) [22,27,32,33].

2. Results and discussion

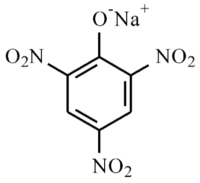
2.1. Synthesis

Starting products; the 6,7-dihydroxy-3-phenyl-*2H*-chromenones, 6,7-dihydroxy-3-phenylcoumarins **2a** have been prepared from 2,4,5-trihydroxybenzaldehyde **1a** with phenylacetic acid **1c**; and the 7,8-dihydroxy-3-phenyl-*2H*-chromenones, 7,8-dihydroxy-3-phenylcoumarins **2b**, **c** and **d** have been prepared from **1b** reacting with **1c**, **d** and **e** in $NaOAc/Ac_2O$ respectively. The chromenone-crown ethers have been obtained by the cyclic condensation of the *o*-dihydroxychromenones **2a–d** with bistosylate of polyglycols **1f–h**. Accordingly, **2a** has reacted with **1f**, **g** and **h** to afford the crown ethers **3a**, **b** and **c**. Compound **2b** has reacted with **1f** and **g** to afford the crown ethers **4a** and **b**. Compound **2c** has reacted with **1f**, **g** and **h** to provide the crown ethers **4c**, **d** and **e**. Compound **2d** has reacted with **1f**, **g** and **h** to provide **4f**, **g** and **h**, in the presence of alkali metal carbonate in acetonitrile (Scheme 1).

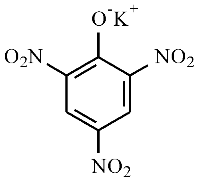
The characterization of novel coumarin-crown ethers (see Section 3) were made using ^{1}H NMR, IR, TLC, mass spectroscopy and elemental analysis.



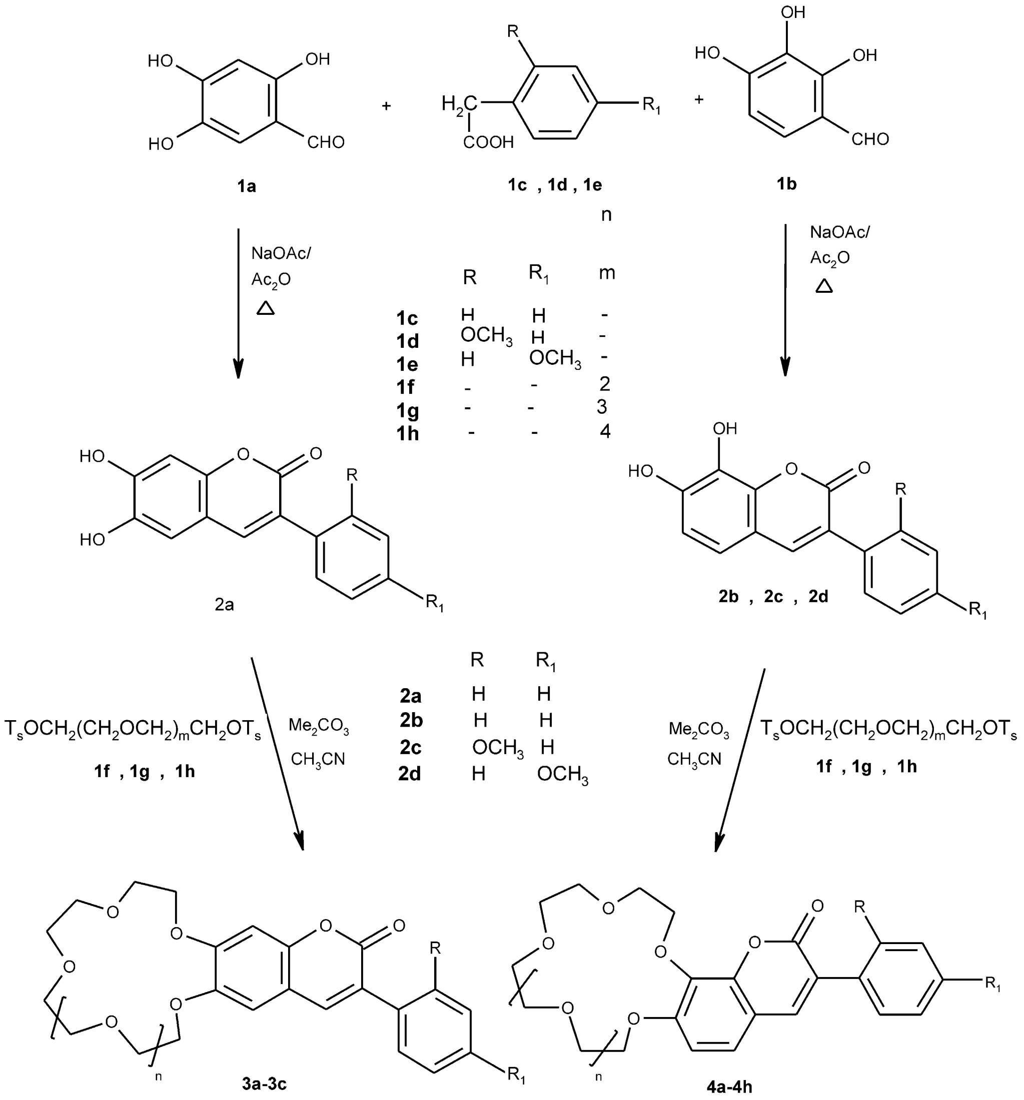
SPAR



SP



PP



	R	R_1	n m
1c	H	H	-
1d	OCH_3	H	-
1e	H	OCH_3	-
1f	-	-	2
1g	-	-	3
1h	-	-	4

	R	R_1
2a	H	H
2b	H	H
2c	OCH_3	H
2d	H	OCH_3

	R	R_1	n
3a	H	H	0
3b	H	H	1
3c	H	H	2

	R	R_1	n
4a	H	H	0
4b	H	H	1
4c	OCH_3	H	0
4d	OCH_3	H	1
4e	OCH_3	H	2
4f	H	OCH_3	0
4g	H	OCH_3	1
4h	H	OCH_3	2

Scheme 1.

The spectral data of the known compounds were in accordance with that of the literature [34].

2.2. Extraction equilibria

In the present work we made use of a common formalism of Eqs. (1–18) [35]. The equilibrium processes taking place during the extraction between an aqueous solution containing the alkali metal cation, $M^+_{(w)}$, and organic anion, $A^-_{(w)}$, and an organic solution containing crown ethers $L_{(org)}$, can be written as:

$$M^+_{(w)} + A^-_{(w)} + nL_{(w)} \rightleftharpoons ML_nA_{(Org)}$$

$$K_{ext} = \frac{[ML_nA]_{Org}}{[M^+]_w[A^-]_w\{[L]w\}^n}$$

$$\text{and} \quad K_D = [ML_nA]_{Org}/[M^+]_w \tag{1}$$

$$L_{(w)} \rightleftharpoons L_{(Org)}, \quad K_{D,L} = [L]_{Org}/[L]_w$$

$$M^+_{(w)} + A^-_{(w)} \rightleftharpoons MA_{(Org)} \tag{2}$$

$$K_{MA} = [MA]_{Org}/[M^+]_w[A^-]_w$$

$$\text{and} \quad K'_D = [MA]_{Org}/[M^+]_w \tag{3}$$

and

$$H^+_w + A^-_{(w)} \rightleftharpoons HA_{(Org)},$$

$$K_{HA} = [HA]_{Org}/[H^+]_w[A^-]_w \tag{4}$$

for the extraction process of an acid, HA, with the organic anion in the equations above, $[M^+]_w$, $[A^-]_w$ and $[ML_nA]_{Org}$ denote the concentrations of uncomplexed cation and anion in aqueous phase and the complex ion-pair extracted in the organic phase, respectively. Mass balances for these processes are expressed as:

$$[L_0] = [L]_w + [ML_nA]_{Org} + [L]_{Org} \tag{5}$$

$$[M^+_0] = [M^+]_w + [ML_nA]_{Org} + [MA]_{Org} \tag{6}$$

and

$$[A^-_0] = [M^+_0] = [ML_nA]_{Org} + [MA]_{Org} + [HA]_{Org} \tag{7}$$

where the subscript $(_0)$ designates the initial concentrations.

As can be seen from the results of blank experiments without the crown ethers in Table 1.

$$[ML_nA]_{Org} >> [MA]_{Org} + [HA]_{Org} \tag{8}$$

then,

$$[ML_nA]_{Org} \cong [A^-_0] - [A^-]_w \tag{9}$$

Therefore, for the overall extraction process, the following equation can be written by adding the Eq. (1) to the reverse of Eq. (2),

Table 1
Equilibrium constants for extractions of SPAR, SP and PP with coumarin derivatives of crown ethers in CH_2Cl_2 at 25 °C[a]

Dyes	K'_D	Value	Coumarin-crown ethers										
			3a	**4g**	**3b**	**4a**	**3c**	**4h**	**4f**	**4d**	**4b**	**4c**	**4e**
Spar	1.12[b]	Log K_{ext}	12.40 ±1.05	12.01 ±0.62	12.32 ±0.65	11.74 ±0.93	11.45 ±0.75	11.57 ±0.96	11.77 ±0.51	11.60 ±0.99	12.29 ±1.02	12.57 ±065	12.20 ±0.58
		$K_{D,L}$[c]	14.87	11.71	12.53	11.38	8.98	14.33	14.28	13.93	14.31	15.64	11.83
SP	0.02[b]	Log K_{ext}	9.18 ±0.96	9.30 ±1.02	9.63 ±0.96	9.41 ±1.02	9.12 ±0.78	9.28 ±0.95	9.47 ±0.99	9.27 ±0.97	9.36 ±1.25	9.60 ±0.68	9.42 ±1.05
		$K_{D,L}$[c]	1.09	1.23	1.73	1.46	1.10	0.86	1.41	1.32	1.37	1.61	1.43
PP	0.09[b]	Log K_{ext}	7.59 ±1.36	7.86 ±0.93	7.23 ±1.22	7.91 ±0.99	7.85 ±0.96	7.95 ±1.52	6.89 ±0.75	7.72 ±0.89	7.94 ±1.25	6.89 ±1.04	7.70 ±1.03
		$K_{D,L}$[c]	0.12	0.17	0.03	0.18	0.13	0.10	0.01	0.08	0.22	0.01	0.07

[a] Corr. coefficient 0.999.

[b] Without coumarin-crown ether.

[c] $K_{D,L} \approx K_D$.

$$M^+_{(w)} + A^-_{(w)} + nL_{(Org)} \rightleftharpoons ML_nA_{(Org)} \quad (10)$$

the equilibrium constant of the extraction process can be written as:

$$K_{ext} = \frac{[ML_nA]_{Org}}{[M^+]_w[A^-]_w\{[L]_{Org}\}^n} \quad (11)$$

and hence,

$$K_{ext} = \frac{[A_0^-] - [A^-]_w}{\{[A^-]_w\}^2[L]_{Org}} \quad (12)$$

at $n = 1$, which refers to a stoichiometric coefficient for the reaction. In this study, for hydrophobic coumarin-crown ethers $K_{D,L} >> 1$,

$$[L_0] = [MLA]_{Org} + [L]_{Org} \cong [L]_{Org}(\text{ if } [L]_{Org} >> [MLA]_{Org} \text{ holds}) \quad (13)$$

where $K_{D,L}$ denotes a distribution constant of a crown ether between water and organic solvent and is defined as,

$$K_{D,L} = [L]_{Org}/[L]_w \quad (14)$$

hence Eq. (12) at $n = 1$ is rewritten as,

$$K_{ext} = \frac{[A_0^-] - [A^-]_w}{\{[A^-]_w\}^2[L_0]}. \quad (15)$$

According to Eq. (15), K_{ext} values were obtained by determining $[A^-]_w$ spectrophotometrically. The results obtained for coumarin-crown ethers are shown in Table 1.

Anionic dyes have been examined with various coumarin-crown ethers. The selection of the optimum counter anion and coumarin-crown ether is made with regard to phase separation efficiency, determination sensitivity and accuracy of complexation constants (K_{ext}). The results of ion-pair extractions obtained in these experimental conditions of identical cation/ligand concentrations of monovalent Na-PAR (SPAR), Na-PICRAT (SP) and K-PICRAT (PP) salts are summarised in Table 1.

CH_2Cl_2 has been utilized as the organic solvent for the sodium and potassium ion extraction by coumarin-crown ether compounds which have different cavity sizes and functional groups.

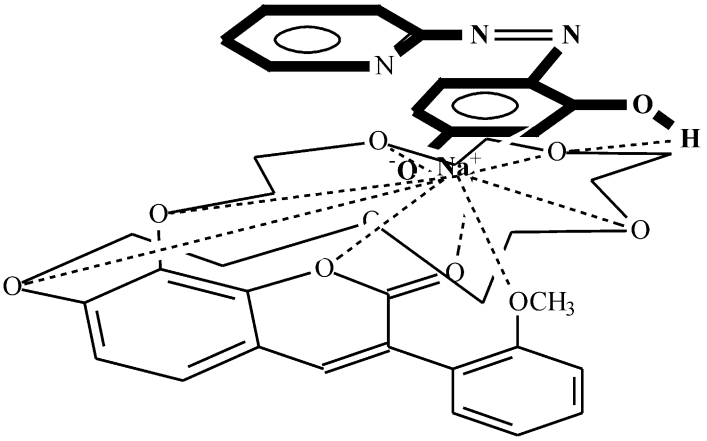
When the SPAR, SP and PP anionic dyes are extracted as 1:1 complexes with coumarin-crown ethers, the cation-complexing ability of the coumarin-crown ethers under experimental conditions show a selectivity order of {**4c** > **3a** > **3b** > **4b** > **4e** > **4g** > **4f** > **4a** > **4d** > **4h** > **3c**}; {**3b** > **4c** > **4f** > **4e** > **4a** > **4b** > **4g** > **4h** > **4d** > **3a** > **3c**} and {**4h** > **4b** > **4a** > **4g** > **3c** > **4d** > **4e** > **3a** > **3b** > **4f**, **4c**}.

The differences in complexing ability in CH_2Cl_2 between the coumarin-crown ethers which have different cavity size, and anionic dyes can be showed in the decreasing order of: (a) for coumarin derivatives of 18C6 with SPAR, SP and PP; {**4c** > **4b** > **4e**}, {**4c** > **4e** > **4b**} and {**4b** > **4e** > **4c**}; (b) coumarin derivatives of 15C5 with SPAR, SP and PP; {**4f** > **4d** > **4h** > **3c**}, {**4f** > **4h** > **4d** > **3c**} and {**4h** > **3c** > **4d** > **4f**}; and (c) coumarin derivatives of 12C4 with SPAR, SP and PP; {**3a** > **3b** > **4g** > **4a**}, {**3b** > **4a** > **4g** > **3a**} and {**4a** > **4g** > **3a** > **4c**} respectively.

In the PAR complexation state, when complexation involves a singly-charged cationic guest, there will be no need for a separate counter ion. A well-studied example of this type involves the dye anion-containing organic sodium salts [36,37]. The sodium ion of PAR is well surrounded by the electron pairs of the coumarin-crown oxygen atoms as illustrated [22].

Likewise the organic anion of PAR is well hydrogen bonded to the crown ether by the O-H hydrogen on the anionic dye counter ion. From the model of the [SPAR]–[**4c**] complex, it is apparent that **4c** with all oxygen electron pairs pointing inwards, also provides an ideal cavity for the guest molecule.

Thus, a solution of this coumarin-crown compound in a polar solvent, such as dichloromethane, has given much more sodium dye-extraction than other crown compounds [32,38,39]. The results demonstrate that the influence of solvent for picrat counter ion extraction by synthesized coumarin-crown complexing agents have been obtained, at a moderate level, by dichloromethane [27, 32,33,39]. However, the K_{ext} values are larger for SP than for PP. In general, the larger K_{ext} value of NaLA than KLA suggests that, even in the MLA form, Na^+ has a higher



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ability as an acceptor than K^+ in complexation with all synthesized coumarin-crown ethers. 12C4 is too small to accommodate Na^+ since its cavity is only about 1.5 Å at best and the ionic diameter of Na^+ is nearly 2 Å [1,39]. Another, and probably more serious difficulty is that 12C4 can provide only four donor groups and Na^+ prefers a solvation of a sandwich structure of stoichiometry $(crown)_2.Na^+A^-$ [40–42]. The difference between coumarin derivatives of 12C4 and other coumarin-crown ethers is especially obvious since the organic sodium dyes with coumarins armed 12C4 are shown to exist as crown separated ion-pairs (sandwich complexes). In this case, if we take into account only crown oxygen atoms, Na^+ is coordinated to eight oxygen atoms, but in the case of 15C5 and 18C6, Na^+ is coordinated to five and six oxygen atoms, respectively. As might be expected, the extraction complexation constant for coumarin derivatives of 12C4 were found to be many times higher than the coumarin analog derivatives of 18C6 and 15C5.

From the discussion above it was found that SPAR is more strongly associated with crown compounds and is the best extracted organic sodium dye as the ion pair complexes (90–93%) than other dyes (decreasing in order SPAR > SP > PP) [22–24,37].

In the previous study [37], it was found that stabilities of the 1:1 complexes of underivated 18C6, 15C5 and 12C4 compounds with SPAR and SP dye salts in CH_2Cl_2 are 12.61, 9.62, 9.94 and 6.58, 6.78, 6.46 respectively. In this study, new stability constants for 11 synthesized coumarin derivatived crown ethers, with SPAR and SP in CH_2Cl_2 at 25 °C are obtained and compared to previous results for underivated 18C6, 15C5 and 12C4 with the same organic sodium dyes in CH_2Cl_2. And we have previously obtained much smaller K_{ext} values for 18C6, 15C5 and 12C4 compounds with SPAR and SP in CH_2Cl_2 than in this study (Table 1).

Solvent media effects, and the anion in a salt–ligand system, play a fundamental role on both the stability of the ion-pair complexes, their solubilization and the resulting charge separation in solution [2,32,38,39].

Since in real extraction systems some amount of dye salts is soluble in organic solvent without crown compounds, the values of the solubility in organic solvents are also given in the first lines of Table 1.

3. Experimental

The starting chemicals **1a**–**h** were purchased from Aldrich or Merck unless other weise cited. Initial componds **2a**–**d**, **3a**–**c**, **4a**, **b**, **f** and **h** have been synthesized according our early study [34].

7,8-Dihydroxy-3-(2-methoxyphenyl)-*2H* chromenone **2c** and its macrocyclic polyethers **4c–e** have been newly prepared. IR spectra have taken as a KBr pellet with a JASCO FT-IR spectrometer, model 5300. High resolution EI mass spectra have been obtained with Fission Istruments, model VG-ZABSPEC.

1H NMR spectra have been obtained with a BRUKER spectrometer, model AVANCE-400 CPX and TMS was the initial standard. All melting points reported are uncorrected. Combustion analyses have been acquired with a LECO-932 CHN analyser.

Sodium dye, 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (SPAR) was commercial products from Aldrich dried over P_2O_5 for 48 h at 0.1 torr. Sodium and potassium picrates were prepared by adding an alkali metal hydroxyde solution to an aqueous solution of picric acid; the resulting precipitate of sodium picrate mono hydrate and potassium picrate were recrystallized from a water–ethanol (1:3) mixture and water, respectively. The picrate salts were dried at 100 °C for 24 h. The dichloromethane used was of analytical-reagent grade.

3.1. Extraction procedure

The extraction measurements were done in a 100 ml glass thermostated cell compartment with a mechanical stirrer where a 25-ml solution of an aqueous dye salt (4×10^{-5} M) and coumarin-crown ethers in CH_2Cl_2 organic solvent in appropriate concentration were placed and stirred for 30 min at 25 °C and subsequently allowed to stand for 30 min to complete the phase separation.

The optimum concentrations of the coumarin-crown ethers were determined by extracting the alkali salts with 10 ml of various concentrations of coumarin-crown ethers (4×10^{-5} M). All the extractions were carried out at the natural pH of the aqueous organic salt solution which were about 6.1–6.7.

3.2. Determination of the organic anions

The concentrations of SPAR, SP and PP in the aqueous phases have been determined spectrophotometrically (Varian Cary model 1E UV-visible spectrophotometer) at 407, 356.6 and 356 nm, respectively, with appropriate quartz cells 2–50 mm in length. Each absorbance value was the average of three subsequent measurements.

*3.3. 7,8-Dihydroxy-3-(2-methoxyphenyl)-2H-chromen-2-one (**2c**; $C_{16}H_{12}O_5$)*

In a two-necked round-bottomed flask charged with a mixture of 7.7 g **1b** (850 mmol), 8.3 g **1d** (50 mmol), 20 g (195 mmol) acetic anhydride, and 80 ml glacial acetic acid, 16 g (200 mmol) sodium acetate was heated to 160 °C under N_2 for 6 h. After the removal of acetic acid by distillation, the resulting mixture was triturated with water, and the precipitates were collected by filtration. The dried crude product was purified by recrystallisation from ethanol.

Yield: 8.8 g (62%); mp. 210 °C (ethanol); IR (KBr): $\nu=3490$ (OH), 2870 (C–H), 1700 (C=O), 1120 (C–O) cm^{-1}; ^1H NMR (acetone-d_6, 400 MHz): δ 3.5 (*s*, 3H, OCH_3), 6.84 (*d*, 2H, ArH), 6.96 (*d*, 2H, ArH), 7.12 (*d*, 2H, ArH), 7.90 (*s*, 2H, OH); MS: *m*/*z* 284 (M), 256 (M–28), 155. Anal. calcd. for $C_{16}H_{12}O_5$: C, 67.8; H, 4.3; found C, 67.92; H, 4.26.

*3.4. 14-(2-Methoxyphenyl)-2,3,5,6,8,9-hexahydro-13H-[1,4,7,10]tetraoxacyclododecino[3,3-h] chromen-13-one (**4c**; $C_{22}H_{22}O_7$)*

A mixture of 1 g **2c** (3.5 mmol), 1.49 g **1f** (3.5 mmol), 0.72 g anhyd. Na_2CO_3, and 100 ml CH_3CN was heated to reflux for 30 h under N_2. After the removal of solution by distillation, the precipitate was dissolved in $CHCI_3$, washed with water and dried on Al_2O_3. The residue was purified by column chromatography on silica gel ($CHCl_3$). The compound was then crystallised from ethanol.

Yield: 0.334 g (24% 9; mp. 126 °C; IR (KBr): $\nu=2830$ (CH_2), 1710 (C=O, lacton), 1295 (C–H), 1120 (C–O) cm^{-1}; ^1H NMR ($CDCI_3$, 400 MHz): δ 3.84 (*s*, 3H, OCH_3), 3.91 (*m*, 4H, OCH_2), 3.88 (*t*, 2H, OCH_2), 6.86 (*d*, 1H, Ar-H), 7.65 (*s*, 1H, Ar-H), 6.9–7.4 (*m*, 5H, Ar-H), 7.72 (*s*, 1H, cum-H); MS: *m*/*z* 398 (M), 399 (M + 1), 310 (M-$C_4H_8O_2$), 293, 255, 226, 195, 165, 155; for C_{22} H_{22} O_7 HRMAS calcd. 398.126986; found 398.127179.

*3.5. 17-(2-Methoxyphenyl)-2,3,5,6,8,9,11,12-octahydro-16H-[1,4,7,10,13]pentaoxacyclopentadecino[2,3-h]chromen-16-one (**4d**; $C_{24}H_{26}O_8$)*

A mixture of 0.850 g **2c** (3 mmol), 1.5 g **1g** (3 mmol), 0.740 g anhyd. Na_2CO_3, and 100 ml CH_3CN was heated at 85 °C for 28 h under N_2. After the removal of solution by distillation, the residue was extracted with $CHCl_3$, the organic layer washed with water and dried on $MgSO_4$. After the destillation of $CHCl_3$, the residue was purified by column chromatography on silica gel ($CHCl_3$).

Yield: 0.4 g (13.3%); mp. 160 °C; IR(KBr): $\nu = 2927$ (aliph.-H), 1727 (C=O, lacton), 1600 (C=C, lacton), 1293 (C–H), 1120 (C–O) cm^{-1}; ^{1}HNMR ($CDCl_3$, 400 MHz): δ 3.52 (*m*, 8H, 4 OCH_2), 3.84 (*s*, 3H, OCH_3), 3.87 (*t*, 2H, OCH_2), 4.10 (*t*, 2H, OCH_2), 4.29 (*t*, 2H, OCH_2), 6.86 (*d*, 1H, ArH), 6.99 (*d*, 2H, Arh), 7.20 (*d*, 1H, ArH), 7.49 (*d*, 2H, ArH), 7.74 (*s*, 1H, cumH); MS: $m/z = 442$ (M), 443 (M+1), 310 (M-$C_4H_8O_2$), 284, 226, 155; for $C_{24}H_{26}O_8$ HRMAS, calcd.: 442.162827; found 442.164020.

*3.6. 20-(2-Methoxyphenyl)-2,3,5,6,8,9,11,12,14,15-nonahydro-19H-[1,4,7,10,13,16]hexaoxacyclooctadecino[2,3-h]chromen-19-one (**4e**; $C_{26}H_{30}O_9$)*

A mixture of 0.71 g **2c** (2.5 mmol), 1.36 g **1h** (2.52 mmol), 0.830 g anhyd. K_2CO_3, and 150 ml CH_3CN was stirred and heated between 70–85 °C for 30 h under N_2. After the removal of CH_3CN by distillation, the residue was extracted with $CHCl_3$, the organic layer washed with water and dried on $MgSO_4$. The solvent was evaporated to dryness. The crude product was purified by column chromatography on silica gel ($CHCl_3$).

Yield: 0.218 g (18%); mp.: viscous; IR (KBr): $\nu = 2830$ (CH_2), 1716 (C=O, lacton), 1218 (C–H), 1160 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.72 (m, 4H, 2OCH_2), 3.80 (*m*, 8H, 4OCH_2), 3.86 (s, 3H, OCH_3), 3.95 (*t*, 2H, OCH_2), 4.12 (*t*, 2H, OCH_2), 4.27 (*t*, 2H, OCH_2), 4.40 (*t*, 2H, OCH_2), 6.88 (*d*, 2H, ArH), 6.70 (*d*, 2H, ArH), 7.21 (*d*, 1H, ArH), 7.67 (*d*, 2H, ArH), 7.70 (*s*, 1H, cumH); MS: *m*/*z* 486 (M), 487 (M+1) 310 (M-$C_8H_{16}O_4$), 284, 226, 115; for $C_{26}H_{30}O_9$ HRMAS calcd. 486.188883; found 486.187298.

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