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Synthesis of new fluorescent ionophores: First examples of calix–coumarin analogs

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Abstract

Synthesis of three new calix–coumarin analogs **6a–c** is described. Preliminary fluorescence spectroscopic analysis in the presence and absence of Na^+, K^+, Cs^+ revealed that **6a** can be used for the development of new detection systems for sodium/potassium.

Key words : Fluorescent ionophores, calix–coumarin analogs.

1. Introduction

Recent reports[1–9] on the synthesis of fluorescent calixarene derivatives based upon spectrofluorometric properties of pyrene, anthracene and benzothiazole units for detecting alkali metal cations prompt us to report herein the synthesis of three calix-coumarin esters, 25, 26, 27-tris (ethoxycarbonylmethoxy)-28-(4-methyl-7-coumarinyloxycarbonylmethoxy) calix-4-arene; 25, 26, 27-tris (ethoxycarbonylmethoxy)-28-(4-methyl-6-nitro-7-coumariny-loxycarbonylmethoxy)calix-4-arene; 25, 26, 27-tris (ethoxycarbonylmethoxy)-28-(4-methyl-8-nitro-7-coumarinyloxycarbonylmethoxy)calix-4-arenes, **6a–c** for similar purpose through the reaction sequence depicted in Scheme 1.

2. Typical procedure for the synthesis of calix–coumarins

To a mixture of 7-hydroxycoumarins (*e.g.*, 7-hydroxy-4-methylcoumarin[10], 6-nitro-7-hydroxy-4-methylcoumarin, 8-nitro-7-hydroxy-4-methylcoumarin[11]) (1.5 mmol) and sodium hydride (0.126 g, 1mmol) taken in dry THF (20 ml), 5 (0.81 g, 1.13 mmol) was added and the resultant mixture stirred for 24 h. Removal of solvent under reduced pressure gave a residue which was dissolved in chloroform and washed with ice-cold water. The organic extract was dried (Na_2SO_4) and evaporated to yield **6a–c** which were purified by column chromatography over silica gel using chloroform–ethylacetate (1:1) as the eluant.

These new compounds were identified on the basis of spectral analysis, molecular weight determination by vapour pressure osmometry and elemental analysis (Table I).

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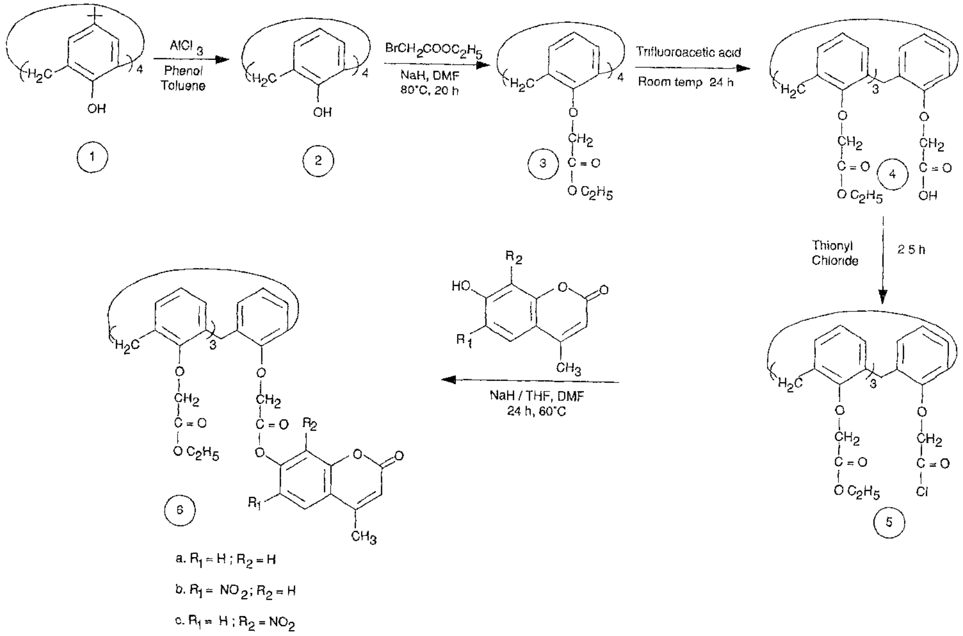

SCHEME 1. Schematic diagram for the synthesis of new calix–coumarins.

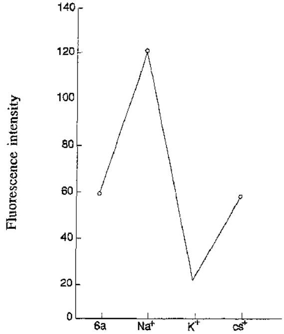

FIG.1. Plot for change in intensity of fluorescence emission by 6a (0.01M) at λ^{em}_{max}: 385 (λ^{ex}_{max}: 325) in the presence of alkali metal cations (Na^+, K^+, Cs^+) (1M).

It is worth recording that compound **6a** on excitation at 325 nm exhibited two peaks at 385 and 410 nm in their fluorescence emission spectrum in $CHCl_3$. Upon addition of NaSCN

Table I
Physical and spectroscopic data of calix–coumarins (6a–c)

Compound	*mp (°C)*	*Yield (%)*	*Molecular formula[#] (mol.wt*)*	*IR (cm^{-1})*	*^1H NMR (δ)*
6a	218	42	$C_{52}H_{50}O_{14}$ (898)	1720, 1750 (C=O)	7.5–6.8(m,15H, ArH), 6.07 (s,1H,C=CH), 4.90–3.52 (m, 16H, $ArCH_2Ar$, OCH_2CO), 3.25 (s, 3H, $C{=}CCH_3$), 3.10–2.90 (m, 6H, OCH_2Me), 1.25 (t,H, CH_3)
6b	243	30	$C_{52}H_{49}O_{16}N$ (943)	1720 1750 (C=O) 1530 (NO_2)	7.84 (s,1H,ArH), 7.58 (s, 1H, ArH), 6.85–6.70 (m, 12H, ArH) 5.82(s,1H,C=CH), 4.84–3.45 (m, 16H, $ArCH_2Ar$, OCH_2CO), 3.32(s,3H, $C{=}CCH_3$), 3.15–2.82 (m, 6H, OCH_2Me), 1.25 (t, 9H, CH_3).
6c	265	32	$C_{52}H_{49}O_{16}N$ (943)	1720, 1750(C=O) 1530 (NO_2)	7.55–6.82(m,14H,ArH), 5.98 (s,1H, C=CH), 4.70–3.55 (m, 16H, $ArCH_2Ar$, OCH_2CO), 3.40(s,3H, $C{=}CCH_3$), 3.25–2.82 (m, 6H, OCH_2Me), 1.32 (t, 9H, CH_3)

All the compounds gave satisfactory elemental analysis.

* As measured by vapour pressure osmometry.

(2.25×10^{-3}M in methanol), the fluorescence intensity of both the peaks was found to increase by over two times whereas the addition of KSCN under the same reaction conditions (Fig. 1) decreases the intensity of fluorescence emission revealing thereby that **6a** can be used for selective detection of sodium/potassium. Detailed work on this Na^+/K^+ selective fluorescence increase/decrease and its utilization for the development of new metal cation detection systems is in continuation and will be reported in due course.

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