appearance of the C=C stretching vibrations at 1,650 and 1,600 cm^{-1} are indicative of a α-pyrone structure[5,5]. Another ketonic carbonyl is present as evidenced by the absorption at 1,620 cm^{-1}. The appearence of this band at such a low frequency indicates the presence of a strong intra molecular hydrogen bond with an –OH group. This would also explain the absence of v-OH bands in the 3,600–3,200 cm^{-1} region.

The nAr spectrum showed a three proton singlet at 1·75 which could be assigned to the—$COCH_3$ protons. Methyl protons associated with the carbonyl group (CH_3–CO–R) generally resonate at 2·2. The upfield shift of the methyl proton resonance is in consonant with the strongly intramolecular hydrogen bonded structure **9**, in which the methyl protons are associated with a C–O bond which is intermcdiate between a double and a single bond. In fact, the value of the methyl resonance $\delta = 1{\cdot}75$ is exactly midway between the chemical shifts of $CH_3{\cdot}CO{\cdot}R$ ($\delta = 2{\cdot}2$) and CH_3–C–O ($\delta = 1{\cdot}3$). The 15·8 signal is obviously then due to the strongly hydrogen bond –OH proton. The single proton resonance at 5·78 would correspond to the olefinic proton and the three proton singlet at 3·85 is due to the methoxyl protons. The aromatic protons appear at 6·98 and 7·25 as two sets of ortho coupled doublets (J = 8 Hz).

Experimental :

Melting points are uncorrected, ir spectra were recorded on a Perkin-Elmer ir spectrophotometer using KBr pellets, nmr were obtained from solutions in $CDCl_3$ on a Varian A–60 spectrometer with TMS as internal standard. Chemical shifts are in δ values.

4-Acetyl-3-(4'-methoxy phenyl) pent-2-ene-1, 5-dioic anhydride:

Compound 9 *a*, m.p. 132–133° C lit.[1] m.p. 132° C was prepared as previously described[1] and repeated crystallizations from alcohol yielded a sample for spectral analyses.

4-Acetyl-3-(2'-methyl-4'-methoxy)-5'-isopropyl phenylpent-2-ene-1,5-dioicanhydride. 6 *b*. 7·2 *g* (0·03 ml) of 1 *b*, fused sodium acetate (0·03 mol) and 5·1 ml of AC_2O gave 60% yields of a pale yellow crystalline solid 9 *b*. Recrystalized from alcohol to obtain a TLC pure product. A.p. 152–153° C. Anal. Calcd. for $C_{18}H_{20}O_6$: C, 68·36; H, 6·33

Found : C, 68·14; H, 6·42

ir (KBr) 1,750 and 1,640 cm^{-1} (two νC=O bands; one strongly chelated), 1,600 cm^{-1} (νC=C. nmr ($CDCl_3$).

1·18 (d, 6H, H_3C / H_3C >CH); 2·2 (S, 3H, Ar·CH_3),

3·86 (S, 3H, –OCH_3); 5·75(S, 1 H, –C CH)

3·30 (M, 1H, >CH); 6·78 and 6·9 (S, 1H each; Ar–H).

1·67 (S, 3H, –Co·CH_3), 15·75, (S, 1H, –OH)

Collapses on D_2O exchange.

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VALIDITY OF FRUMKIN DOUBLE-LAYER CORRECTION IN THE CASE OF SODIUM SULPHATE SUPPORTING ELECTROLYTE

ARAMATA AND DELAHAY[1] investigated the validity of Frumkin correction[2] for the reduction of zinc ion on zinc amalgam in various supporting electolytes, namely, $NaClO_4$, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$ and $Al(ClO_4)_3$ using galvanostatic method. They plotted logarithm of the apparent exchange current, ln i° (which is equivalent to the rate constant) against diffuse double layer potential, φ_2. The plot was linear with slope equal to $(\alpha n - Z_0)f$, where 'α' is the cathodic transfer coefficient, 'n', the number of electrons transferred, Z_0 is the valence of the oxidant and $f = F/RT$ (F is the faraday and other terms have their usual significance), A constant value of true exchange current i_0^0 was obtained for various supporting electrolytes used. In the case of sodium perchlorate supporting electrolyte, they got a negative value (– 0·38) for 'α'. This negative value was interpreted by Aramata and Delahay on the basis of monovalency of the cation Na^+ (which reflected on the differences in the ionic radii of Zn^{2+} and Na^+ in mixed electrolytes) whereas in barium and magnesium perchlorates, the cations were divalent.

Judging from the explanation of Aramata and Delahay[1], it is probable that Frumkin correction may not be valid for sodium sulphate supporting electrolyte. In order to check this, the discharge of Zn^{2+} ion at the dropping mercury electrode was investigated in 0·5 M, 0·25 M and 0·125 M concentration of sodium sulphate solution. The apparent rate constants ($k_{f,a}$) for the discharge of Zn^{2+} ion in various concentrations of sodium sulphate were calculated from current-potential data[3] using Koutecky's equations[4]. Values of φ_2 at each potential

and concentration of sodium sulphate supporting electrolyte were obtained from surface charge density-potential data[3] through Gouy-Chapman theory[5]. Employing these, a plot of $(\ln k_{f,a} + Z_0\varphi_2 f)$ *versus* $(\eta - \varphi_2)$ (the difference between the overpotenial 'η' and the Gouy drop, φ_2) was made for each of the sodium sulphate supporting electrolyte concentrations. The straight line plot obtained is shown in Fig. 1. From the slope of the plot, the value of

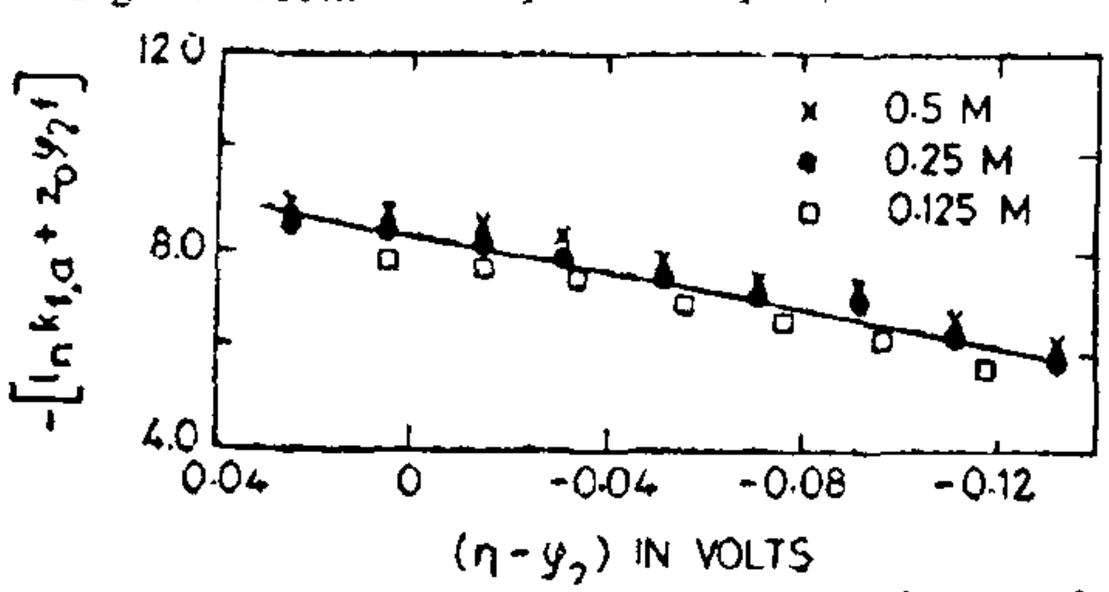

FIG. 1. Plot of $(\ln k_{f,a} + z_0 \varphi_2 f)$ *vs* $(\eta - \varphi_2)$ for Zn^{2+} ion reduction at the D.M.E. different conceetrations of sodium sulphate supposting electrolyte.

true cathodic transfer coefficient, *at* was calculated to be 0·24. Since the value of *at* obtained was not unreasonable[6] and $(\ln k_{f,a} + Z_0 \varphi_2 f)$ *versus* $(\eta - \varphi_2)$ plot was a straight line for different concentrations of sodium sulphate supporting electrolyte, it is concluded that Frumkin correction is valid for sodium sulphate. It may be mentioned that the explanation for the observation that Frumkin correction was not valid in sodium perchlorate medium might not be due to the monovalent nature of the cation.

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SYNTHESIS OF UNSYMMETRIC BIS-COUMARINOXY PHENOXY ALKANES

SEVERAL unsymmetric bis-coumarinoxy phenoxy alkanes have been synthesised by the condensation of *a*-coumarinoxy-*ω*-bromoalkanes with variously substituted phenols in presence of potassium carbonate and acetone.

1,3-BIS (2-carboxychroman-5-yloxy)-2-hydroxypropane disodium salt (DSCG) prepared by H. Cairns *et al.*[1] is a powerful antiallergic reagent and is known to possess antiasthamatic properties. Coumarin derivatives[2–6] and their DSCG analogues are reported to possess significant pharmacological properties[7]. The synthesis of a number of unsymmetric analogues of DSCG and its anti-allergic activity has been reported by this laboratory[8]. It was, therefore, thought worthwhile to synthesise some analogues of DSCG with substituted coumarinoxy and phenoxy groups.

We report the synthesis of several unsymmetric bis coumarinoxy phenoxy alkanes taking into consideration the parameters like (i) substituent in the phenoxy part, (ii) the length of alkane chain and (iii) the position of the attachment of the ether linkage to the benzene ring.

Hydroxy coumarins, the starting materials for the preparation of unsymmetric bis-coumarinoxy phenoxy alkanes were prepared by the known methods[9]. When one mole of hydroxy coumarin was refluxed with one mole of dihalo-alkane in the presence of potassium carbonate and acetone, a mixture of symmetric bis coumarinoxy alkane and *a*-coumarinoxy-*ω*-haloalkane was obtained. These two compounds were separated by ether extraction since *a*-coumarinoxy *ω*-haloalkane was ether soluble and the other compound ether insoluble (Fig. *a*). The physical data are presented in Table I.

TABLE I

Physical data of a-coumarinoxy ω-bromo alkanes
(Ref. Fig. *a*)

Sl. No.	R	Link	*n*	M.P.° C
1	CH_3	7′	2	112–13[b]
2	..	..	3	83[b]
3	..	..	4	66[a]
4	..	..	5	60[c]
5	..	6′	2	109[a]
6	..	..	3	85–86[b]
7	CH_2COOH_3	7′	2	118–20[a]

All compounds gave satisfactory C and H analyses.
a = Crystallised from mehanol.
b = Crystallised from ethanol.
c = Crystallised from petroleum ether.