CHAPTER III

SYNTHESIS AND MESOMORPHIC PROPERTIES OF

(i) [S]-4'-(2-chloro-4-methylpentyloxycarbonyl) phenyl trans-4"-n-alkoxycinnamates

(ii) [2S,3S]-4'-(2-chloro-3-methylpentyloxycarbonyl) phenyl trans-4"-n-alkoxycinnamates

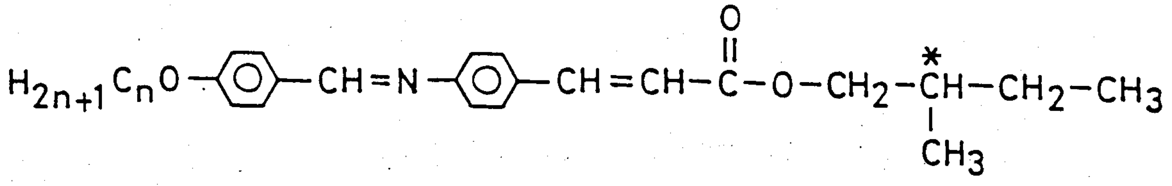
(iii) [S]-4'-(2-chloro-4-methylpentanoyloxy)phenyl trans-4"-n-alkoxycinnamates, and

(iv) [2S,3S]-4'-(2-chloro-3-methylpentanoyloxy)phenyl trans-4"-n-alkoxycinnamates

III.1 A BRIEF ACCOUNT OF MESOMORPHIC PROPERTIES OF COMPOUNDS CONTAINING OPTICALLY ACTIVE CHLOROALKYL CHAINS

The discovery of ferroelectricity in chiral smectic C (S_{C*}) phase' stimulated a search for new compounds exhibiting S_{C*} phase around room temperature with a wide range and also having a high value for spontaneous polarisation (Ps). As mentioned in chapter I, compounds exhibiting S_{C*} phase have to contain optically active groups. A variety of chiral moieties have been used for this purpose, e.g., [S]-2-methylbutanol,[2] [S]-4-methylhexanol,[3] [S]- -hydroxybutyrates,[4] [S]-ethylacetate,[5] [S]-2-chloro-4-methylpentanol,[6] [S]-2-chloro-3-methylbutanol[6] and [2S,3S]-2-chloro-3-methylpentanol.[6] The value for P_s in the S_{C*} phase is found to increase when there is a polar substituent on the chiral carbon atom.' Also a carbonyl group next to the chiral carbon atom seems to enhance the value for P_s.[8] Hence the optically active acids containing chloro substituents on the chiral carbon atom have been extensively used to obtain ferroelectric liquid crystals.

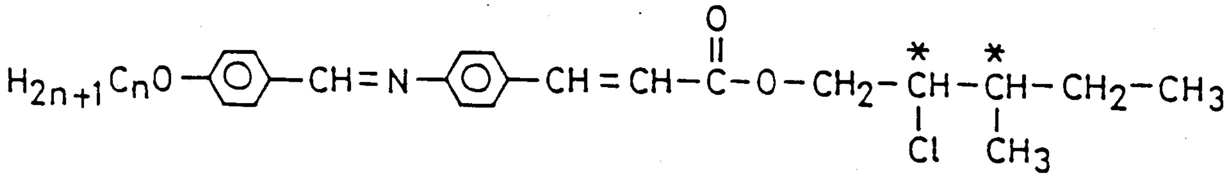
Sakurai et al.[9] have replaced [S]-2-methylbutyl group present in compound III(i)1,10 by [2S,3S]-2-chloro-3-methyl pentyl, [S]-2-chloro-4-methylpentyl, [S]-2-chloro-3-methylbutyl groups [Compounds III(ii), III(iii) and III(iv) respectively]. A comparison of these four series of compounds can be made by considering the decyloxy compound as a representative example. Compound III(ii) has the highest value for P_s. It is also seen that all the transition temperatures in the latter three



III (i)

n = 10, C 76.0 (S_B 63.0) S_C^* 95.0 S_A 117.0 I

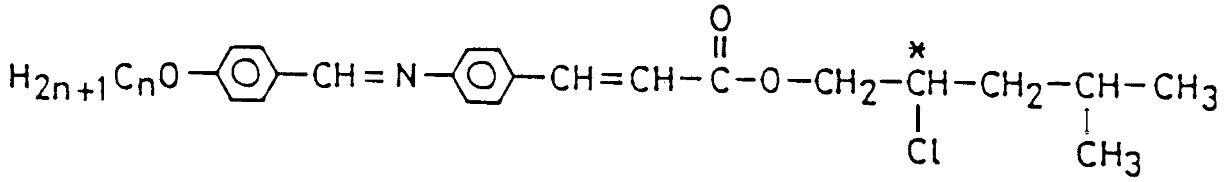
Ps = 60 $\mu C/m^2$



III (ii)

n = 10, C 43.0 S_C^* 80.0 S_A 104.0 I

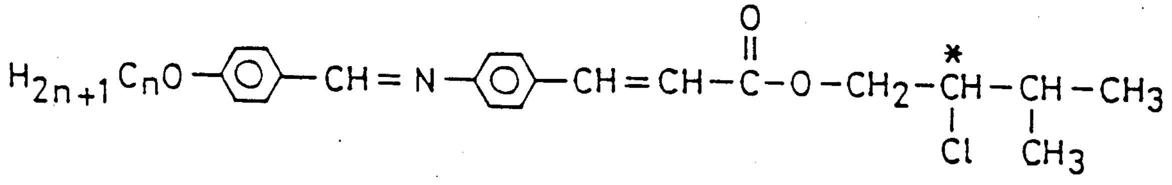
Ps = 500 $\mu C/m^2$



III (iii)

n = 10, C 49.0 S_C^* 80.0 S_A 94.0 I

Ps = 340 $\mu C/m^2$



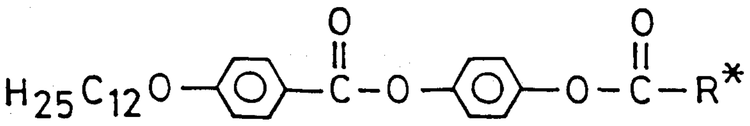
III (iv)

n = 10, C 59.0 S_C^* 78.0 S_A 105.0 I

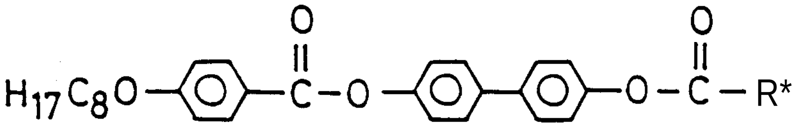
Ps = 170 $\mu C/m^2$

compounds III(ii), III(iii) and III(iv) get depressed compared to compound III(i). The S_{C*}-S_A transitions of these three compounds do not vary much. However, the melting point of compound III(ii) gets depressed considerably more than the other two compounds III(iii) and III(iv) thereby increasing its range of S_{C*} phase to 37°C. Thus, with respect to the spontaneous polarisation, the range of S_{C*} phase and the melting point, [2S,3S]-2-chloro-3-methylpentyl group seems to have the most desirable effect in these decyloxybenzylideneamino cinnamates.

In case of the phenyl benzoates[11] III(v), only a monotropic S_{C*} phase is observed. The thermal stability of the phase is highest for compound in which R* is [S]-1-chloro-2-methylpropyl group. The lower homologues (n=7 to n=10) of this series show an N* phase and also exhibit a blue phase. A change to biphenyl benzoates[12] III(vi), increases the mesophase transition temperatures more than the melting points, as a result of which even the octyloxy compounds exhibit enantiotropic S_{C*} phase. The compound III(vi) in which R* is [2S,3S]-2-chloro-3-methylbutyl group melts at 90°C and has an S_{C*} phase range of 87°C. Bahr and Heppke reported[6] compounds with only a biphenyl as the core which exhibited a high value for the spontaneous polarisation. This value, in case of compound III(vii) [n=7], rises up to 2900 $\mu C/m^2$ at the lowest temperature before crystallisation. It is also seen that Ps is considerably dependent on the length of alkyl chain. In the series III(vii), the heptyloxy homologue exhibits about twice the value obtained for the nonyloxy homologue at the same relative temperature, i.e., at a fixed value of (T_c-T). The

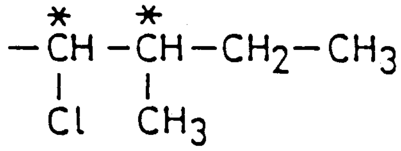


III (v)

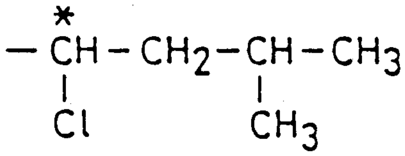


III (iv)

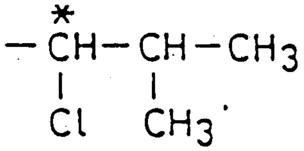
$R^* =$



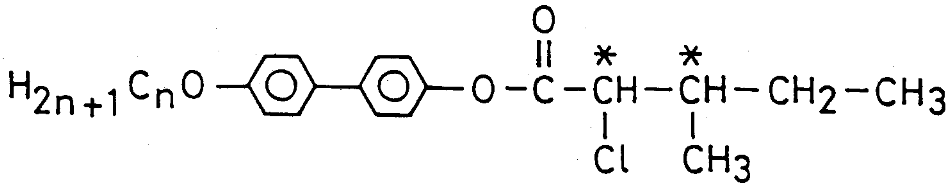
$-\underset{Cl}{\overset{*}{C}H}-\underset{CH_3}{\overset{*}{C}H}-CH_2-CH_3$



$-\underset{Cl}{\overset{*}{C}H}-CH_2-\underset{CH_3}{CH}-CH_3$



$-\underset{Cl}{\overset{*}{C}H}-\underset{CH_3}{CH}-CH_3$

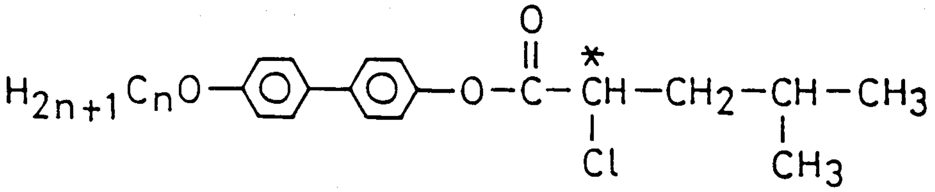


$$H_{2n+1}C_nO-C_6H_4-C_6H_4-O-\overset{O}{\overset{\|}{C}}-\underset{Cl}{\overset{*}{C}H}-\underset{CH_3}{\overset{*}{C}H}-CH_2-CH_3$$

III (vii)

n = 7, C 55.0 S_C^* 55.0 S_A 62.0 I

Ps = 2900 μC/m^2

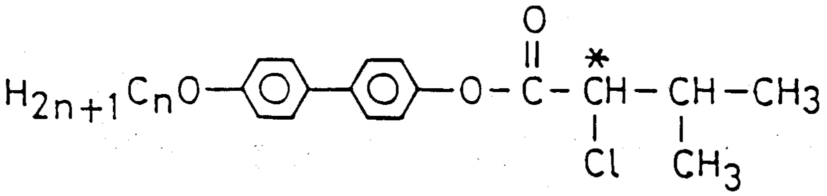


$$H_{2n+1}C_nO-C_6H_4-C_6H_4-O-\overset{O}{\overset{\|}{C}}-\underset{Cl}{\overset{*}{C}H}-CH_2-\underset{CH_3}{CH}-CH_3$$

III (viii)

n = 7, C 54.0 S_C^* 57.0 S_A 67.5 I

Ps = 800 μC/m^2

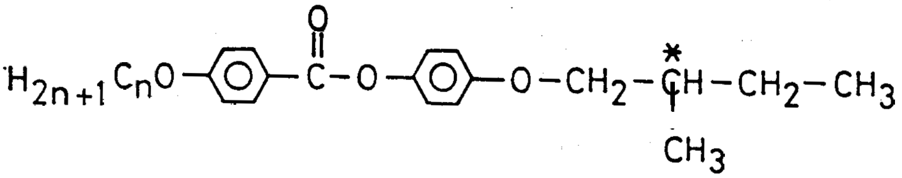


$$H_{2n+1}C_nO-C_6H_4-C_6H_4-O-\overset{O}{\overset{\|}{C}}-\underset{Cl}{\overset{*}{C}H}-\underset{CH_3}{CH}-CH_3$$

III (ix)

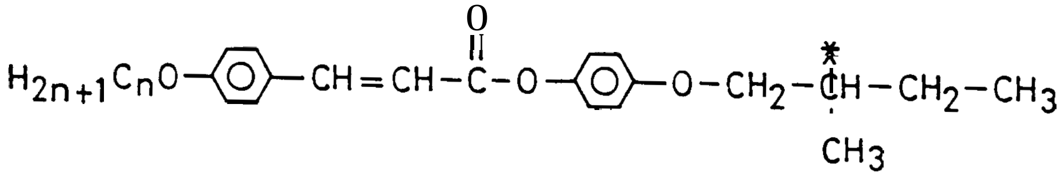
n = 7, C 72.0 ($S_?$ 71.0) S_C^* 73.5 S_A 81.5 I

Ps = 1400 μC/m^2



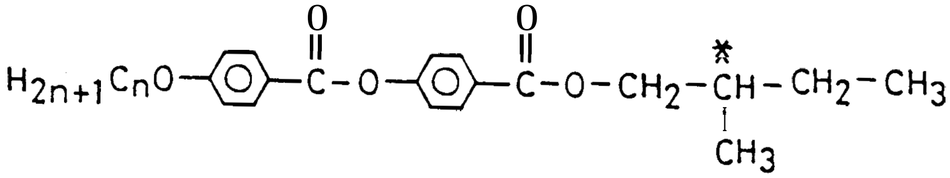
III (x)

n = 12, C 49.0 S_C* 52.0 S_A 65.0 I



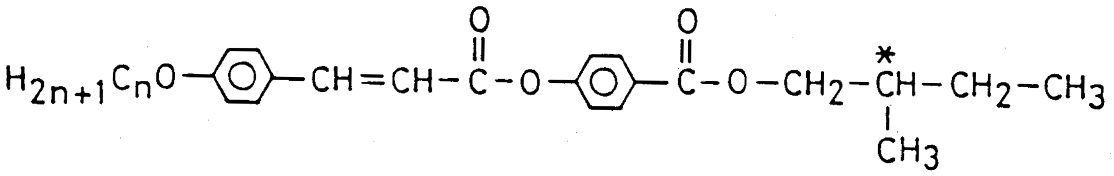
III (xi)

n = 12, C 79.3 (S_j* 50.7 S_I^*63.3) S_C* 94.9 S_A 103.8 I



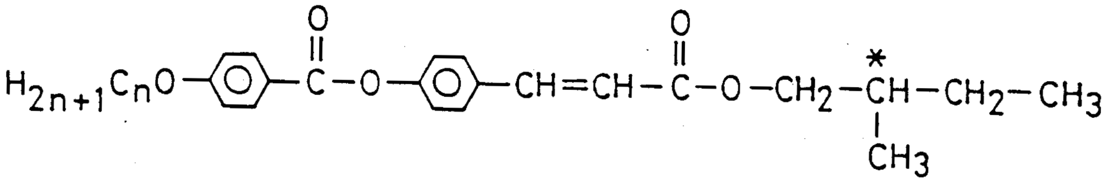
III (xii)

n = 10, C 52.0 (S_C* 35.0) S_A 95.2 I



III (xiii)

n = 10, C 60.2 S_C* 71.1 S_A 95.2 I



III (xiv)

n = 10, C 52.0 (S_C* 44.5) S_A 92.5 I enantiotropic S_{C^*} thermal ranges of these compounds are however very small. Many compounds involving cinnamic acid moiety have been reported in the literature.[13-17] Phenyl cinnamates have been effectively considered as 'two and a half ring systems'.[18] The double bond mimics half of a benzene ring and produces materials with properties similar to the two and three ring materials. A comparison of compounds III(x) and III(xi) shows that when -COO- is changed to -CH=CH-COO- linkage, higher order smectic phases are induced.[18,19] The thermal stability as well as the S_{C^*} mesophase range is found to increase. This is illustrated for the dodecyloxy homologue of series III(x) and III(xi).

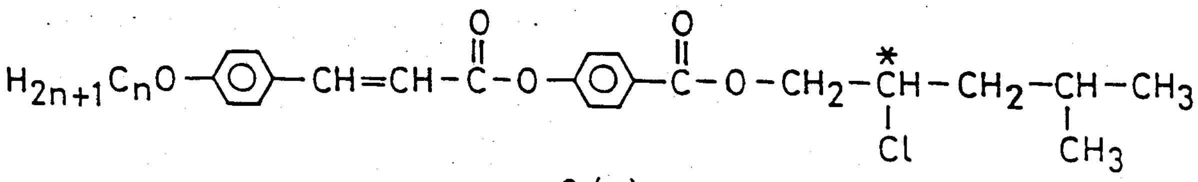
However, when a terminal [S]-2-methylbutyl chain is attached to an ester linkage, introduction of vinyl group seems to affect only the thermal stabilities of the existing phases. This is reflected in the transition temperatures of decyloxy homologues belonging to the series III(xii), III(xiii); and III(xiv).[20'21] It is also seen that when a double bond lies in between two phenyl rings [III(xiii)], the S_{C^*} phase is stabilised much more than when it is present at the end of the core [III(xiv)].

III-2. RESULTS AND DISCUSSION

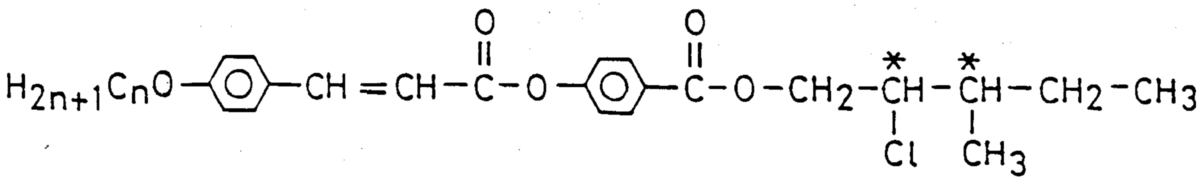
In an effort to obtain compounds exhibiting S_{C^*} phase with a high value for the spontaneous polarisation at relatively low temperatures a number of homologous series of compounds were synthesised. These include the esters of <u>trans</u>-p-n-alkoxycinnamic acids and trans-p-n-alkoxy-α-methylcinnamic acids shown in figure 1. The transition temperatures of the dodecyloxy homologues of these series of compounds are given in table 1. The compounds 3.e.7 and 3.f.7 exhibit a monotropic and an enantiotropic S_A phase respectively and neither of them shows any S_{C*} phase. Hence the synthesis of other homologues of these two series was not pursued any further. However, an S_{C*} phase was observed in the other four compounds (3.a.7 to 3.d.7) and the homologous series of these were investigated systematically.

It must be mentioned here that around the same time Tinh et al.[22] also investigated several homologues belonging to series 3(c) and 3(d). The transition temperatures reported by them for many of the homologues differ from what this author has observed. Tinh et al.[22] have not reported any thermodynamic data for their compounds.

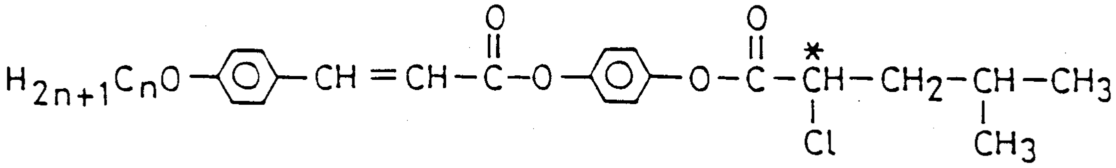
The synthesis of these compounds were carried out according to the scheme shown in figures 2 and 3 respectively. Compounds of series 3(a) and 3(c) were prepared in an analogous manner (see experimental section for detailed procedures). The optically active chloro acids, viz., [S]-2-chloro-4-methylpentanoic acid and [2S,3S]-2-chloro-3-methylpentanoic acid were obtained from l-leucine and l-isoleucine respectively, via their diazonium chloride solutions.[23] The chloro acids were converted to their respective methyl esters by refluxing them in methanol in presence of catalytic amount of sulphuric acid. The methyl esters were then reduced by lithium aluminium hydride to the



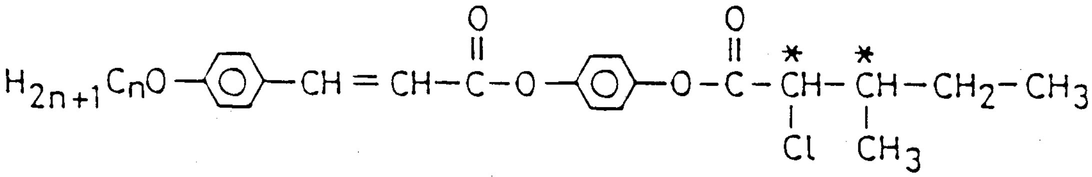
3 (a)



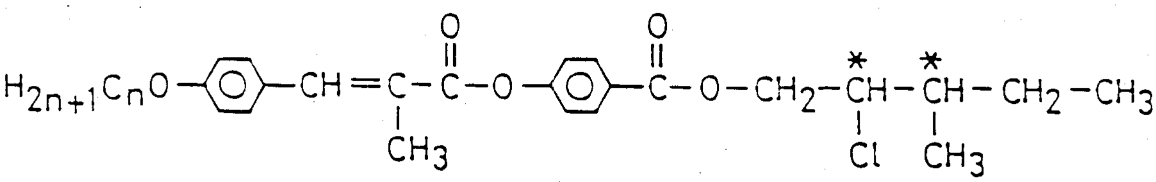
3(b)



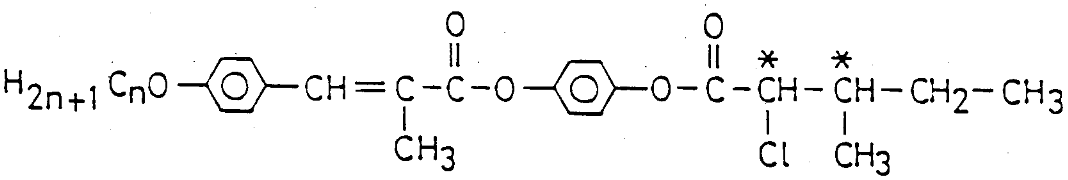
3(c)



3(d)



3(e)



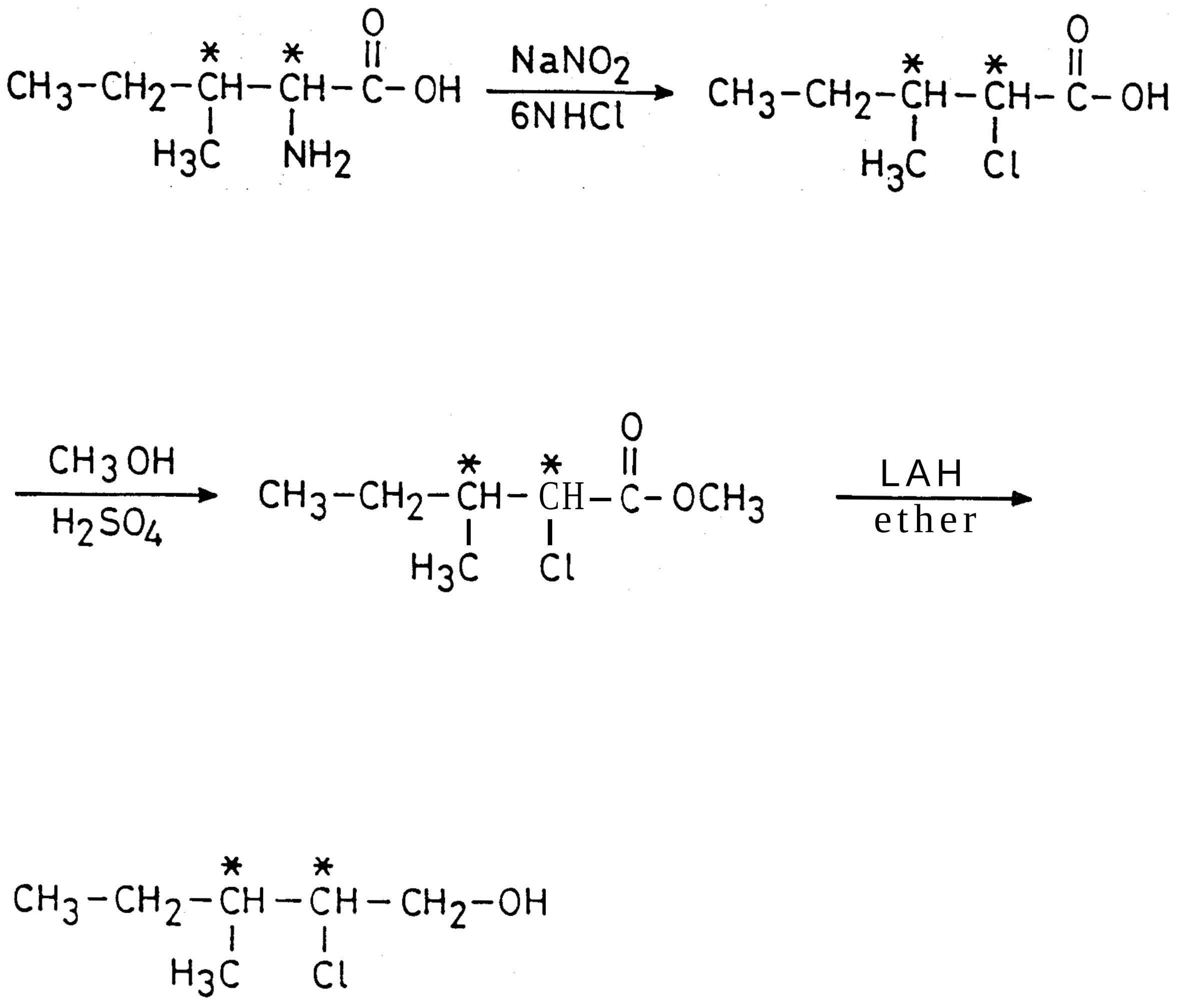
3(f)

FIGURE 1

Table 1

Transition temperatures (^{o}C) of compounds
3.a.7 to 3.f.7 ($n = 12$)

Compound number	C		S_{C*}		S_A		I
3.a.7	.	52.0	.	65.5	.	81.0	.
3.b.7	.	53.5	.	69.0	.	88.5	.
3.c.7	.	62.0	.	80.0	.	92.5	.
3.d.7	.	56.5	.	84.5	.	100.0	.
3.e.7	.	45.0	–		(.	38.0)	.
3.f.7	.	44.5	–		.	48.5	.



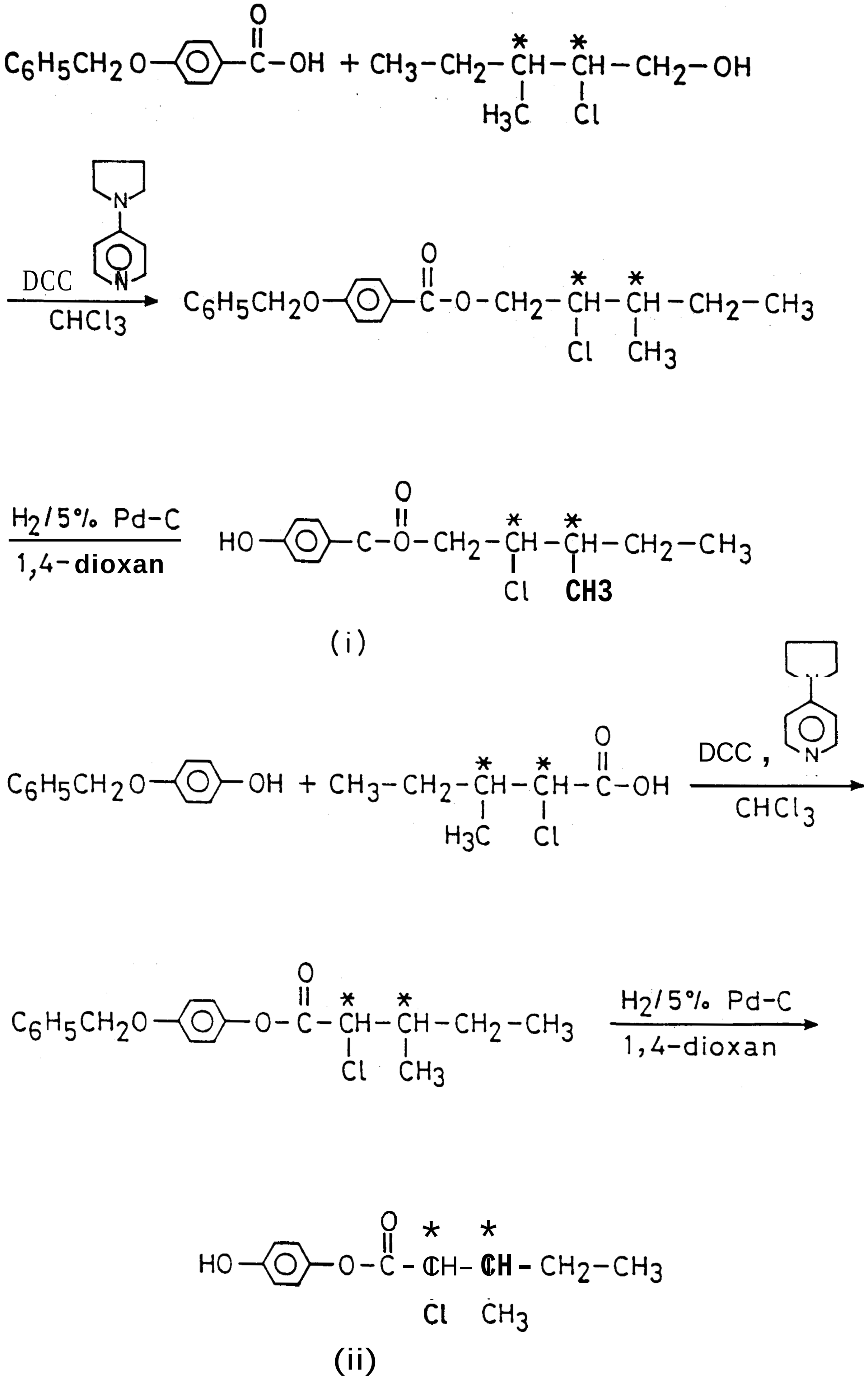
$$\mathrm{CH_3-CH_2-\underset{\underset{H_3C}{|}}{\overset{*}{C}}H-\underset{\underset{NH_2}{|}}{\overset{*}{C}}H-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[6N\,HCl]{NaNO_2} CH_3-CH_2-\underset{\underset{H_3C}{|}}{\overset{*}{C}}H-\underset{\underset{Cl}{|}}{\overset{*}{C}}H-\overset{\overset{O}{\|}}{C}-OH}$$

$$\mathrm{\xrightarrow[H_2SO_4]{CH_3OH} CH_3-CH_2-\underset{\underset{H_3C}{|}}{\overset{*}{C}}H-\underset{\underset{Cl}{|}}{\overset{*}{C}}H-\overset{\overset{O}{\|}}{C}-OCH_3 \xrightarrow[ether]{LAH}}$$

$$\mathrm{CH_3-CH_2-\underset{\underset{H_3C}{|}}{\overset{*}{C}}H-\underset{\underset{Cl}{|}}{\overset{*}{C}}H-CH_2-OH}$$

FIGURE 2

(contd.)



$C_6H_5CH_2O-C_6H_4-C(=O)-OH + CH_3-CH_2-\overset{*}{C}H(CH_3)-\overset{*}{C}H(Cl)-CH_2-OH$
DCC
CHCl$_3$
$C_6H_5CH_2O-C_6H_4-C(=O)-O-CH_2-\overset{*}{C}H(Cl)-\overset{*}{C}H(CH_3)-CH_2-CH_3$
H$_2$/5% Pd-C
1,4-dioxan
$HO-C_6H_4-C(=O)-O-CH_2-\overset{*}{C}H(Cl)-\overset{*}{C}H(CH_3)-CH_2-CH_3$
(i)
$C_6H_5CH_2O-C_6H_4-OH + CH_3-CH_2-\overset{*}{C}H(CH_3)-\overset{*}{C}H(Cl)-C(=O)-OH$
DCC ,
CHCl$_3$
$C_6H_5CH_2O-C_6H_4-O-C(=O)-\overset{*}{C}H(Cl)-\overset{*}{C}H(CH_3)-CH_2-CH_3$
H$_2$/5% Pd-C
1,4-dioxan
$HO-C_6H_4-O-C(=O)-\overset{*}{C}H(Cl)-\overset{*}{C}H(CH_3)-CH_2-CH_3$
(ii)

FIGURE 2

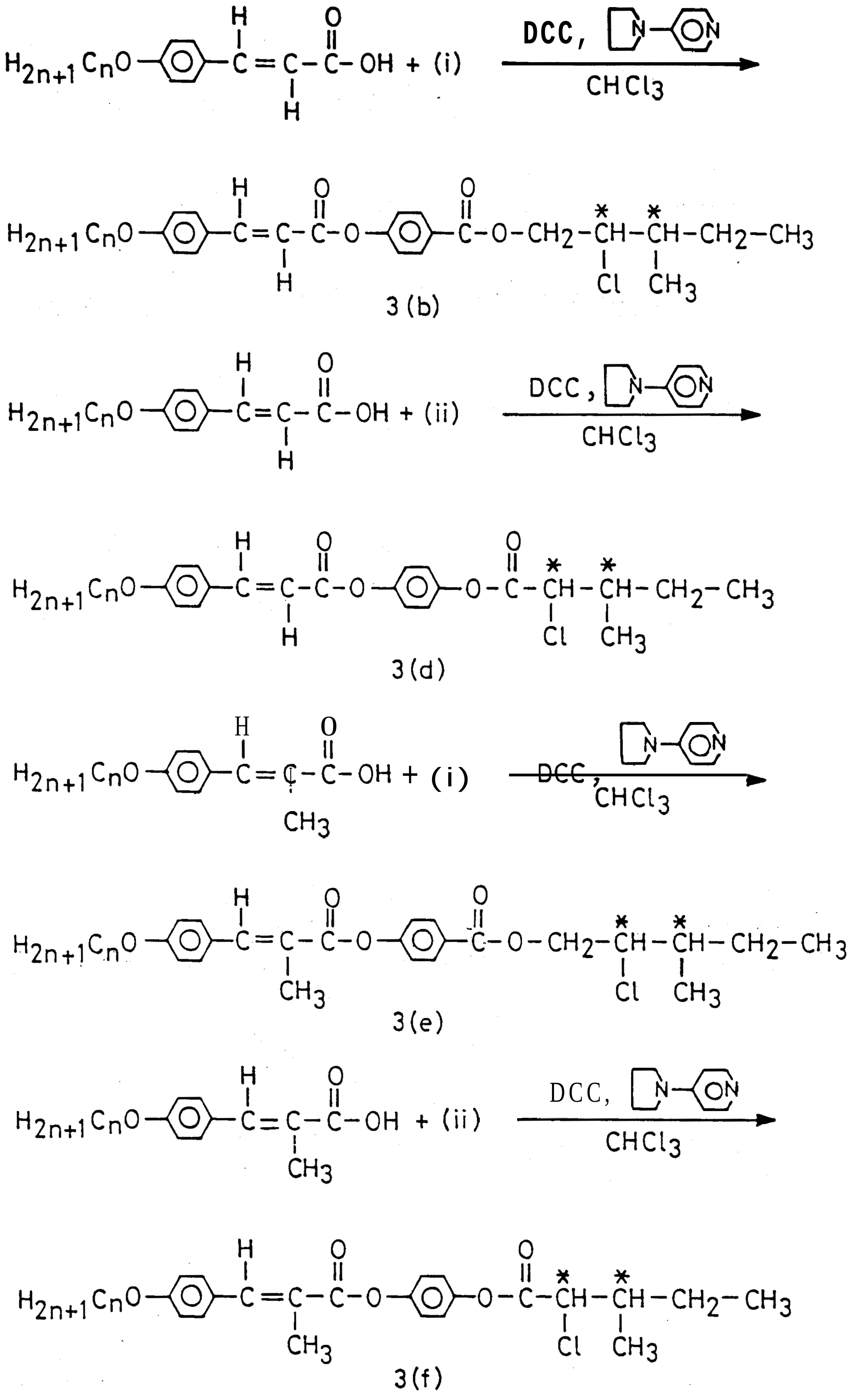


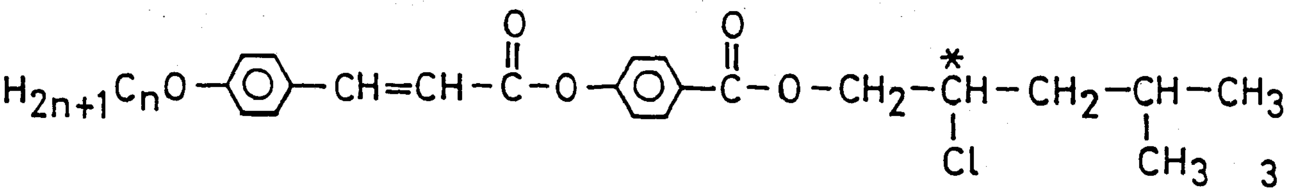
FIGURE 3

corresponding alcohols. None of the reactions involved affected the absolute configuration of the chiral centres. The optically active alcohols were condensed with 4-benzyloxybenzoic acid and the optically active acids with 4-benzyloxyphenol. The products of these reactions were subjected to hydrogenolysis with 5% palladium on charcoal as the catalyst. The phenols obtained upon debenzylation were reacted with trans-p-n-alkoxycinnamic acids in the presence of dicyclohexyl carbodiimide and 4-pyrrolidinopyridine.[24]

The measurements of the values for the spontaneous polarisations for these compounds were carried out by Prasad et al.[25] The transition temperatures of the compounds belonging to the homologous series [S]-4'-(2-chloro-4-methylpentyloxycarbonyl) phenyl trans-4"-n-alkoxycinnamate [3(a)] are given in table 2. Compounds 3.a.1 to 3.a.4 exhibit N* phase and have a narrow range of 1-2.5°C. All the compounds exhibit an enantiotropic S_A phase with a fan shaped texture. The range of S_A phase decreases on increasing the length of the carbon chain. Compounds 3.a.1, 3.a.2 and 3.a.4 show a monotropic S_C, phase and the remaining are enantiotropic. The range of S_{C*} phase does not show a regular increase or decrease with increasing carbon atoms in the alkoxy chain. This can be attributed to the irregularity in the melting points. Compound 3.a.4 with the highest melting point (62.0°C), exhibits a monotropic S_{C*} phase. Compound 3.a.5 with the lowest melting point (44.0°C) has the widest range of S_{C*} phase (19.5°C). A plot of the transition temperatures versus the number of carbon atoms in the terminal alkoxy chain is shown in figure

Table 2

Transition temperatures (°C) and heats of transition (Kcals/mole) of



$$H_{2n+1}C_nO-C_6H_4-CH{=}CH-\overset{O}{\overset{\|}{C}}-O-C_6H_4-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{Cl}{\underset{|}{\overset{*}{C}H}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

3(a)

Compound number	n	C		S_{C^*}		S_A		N^*		I
3.a.1	6	.	51.5	(.	41.5)	.	78.0	.	80.5	.
			9.1		0.05		0.35		0.2	
3.a.2	7	.	57.5	(.	50.0)	.	74.5	.	77.0	.
			7.9		0.1		0.25		0.22	
3.a.3	8	.	50.0	.	56.5	.	79.5	.	80.0	.
			5.8		0.08		0.21		0.16	
3.a.4	9	.	62.0	(.	60.5)	.	78.0	.	79.0	.
			10.0		0.1		0.2		0.2	
3.a.5	10	.	44.0	.	63.5	.	81.1	-		
			7.7		0.09		0.9			
3.a.6	11	.	55.5	.	64.5	.	80.5	-		
			9.1		0.06		0.9			
3.a.7	12	.	52.0	.	65.5	.	81.0	-		
			8.1		0.1		1.0			

4. The S_{C^*}-S_A transition temperatures which vary from 41.5°C to 65.5°C show a continuous increase with the increasing length of the alkoxy chain and form a smooth rising curve. The S_A-N*, the S_A-I and the N*-I transition temperatures show an alternation with successive homologues which diminishes with increase in chain length. The heats of transitions for these compounds are given in table 2 below their transition temperatures. The differential scanning calorimetric studies indicate that S_{C^*}-S_A transition is accompanied by a very small enthalpy.

Figure 5 shows the thermal variation of Ps for the compounds 3.a.2 to 3.a.7 in table 2. It can be seen that for all the compounds P_s increases with decreasing temperature. After an initial steep rise it attains a constant value. This pattern is observed for all the homologues. It can also be seen that with decreasing chain length P_s increases. Thus compound 3.a.2 (n=7) shows a Ps of about 500 $\mu c/m^2$ at the same value of $T-T_c$. This can be clearly seen in the inset of this figure 5, where the polarisation at $T-T_c = -10°C$ is plotted versus the number of carbon atoms in the chain.

The transition temperatures and the heats of transitions of the compounds belonging to homologous series [2S,3S]-4'-(2-chloro-3-methylpentyloxycarbonyl)phenyl trans-4"-n-alkoxycinnamates [3(b)] are given in table 3. All the compounds exhibit S_A phase. Compounds 3.b.1, 3.b.2 and 3.b.3 exhibit a narrow range of N* phase and also a blue phase. Except for compound 3.b.l all other compounds exhibit S_{C^*} phase. Compound 3.b.2 has the highest

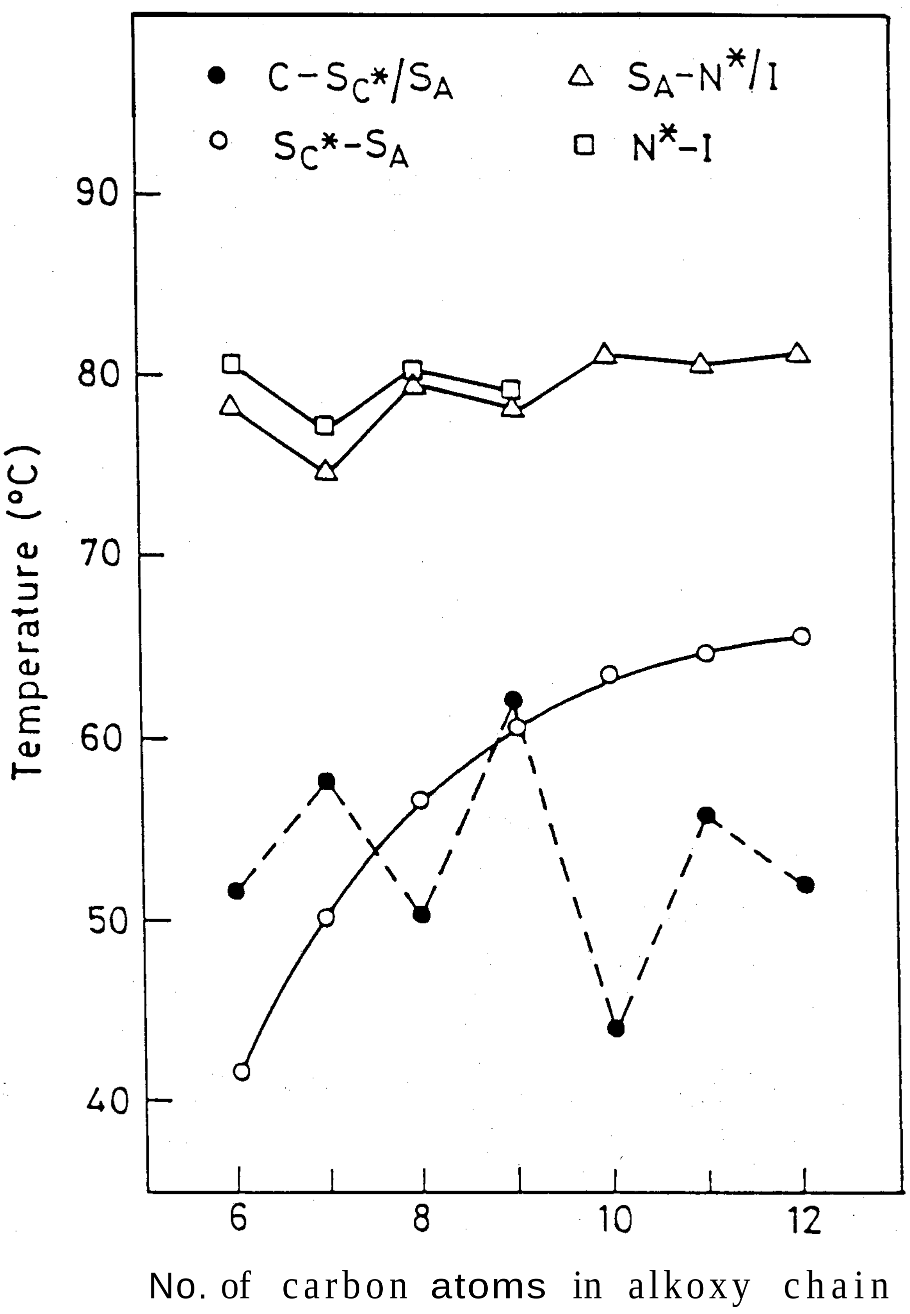


Figure 4: A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain 'for the homologous series 3(a).

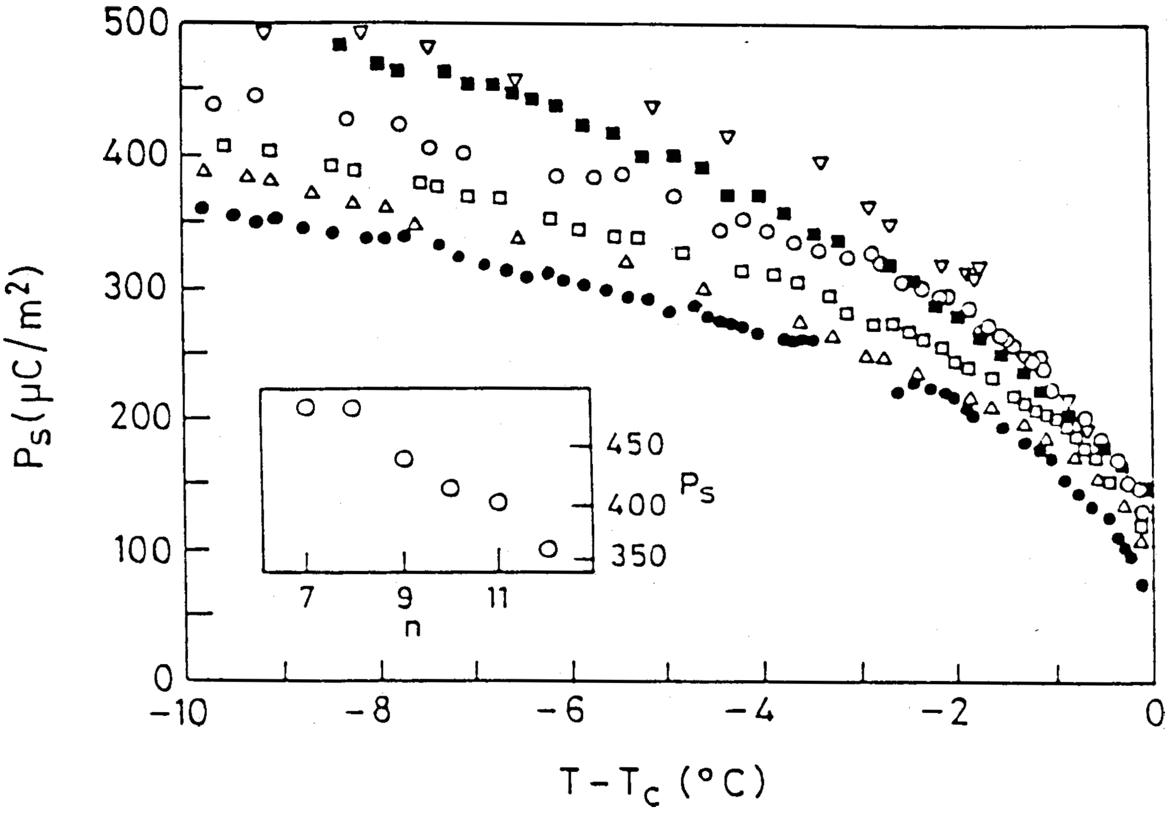
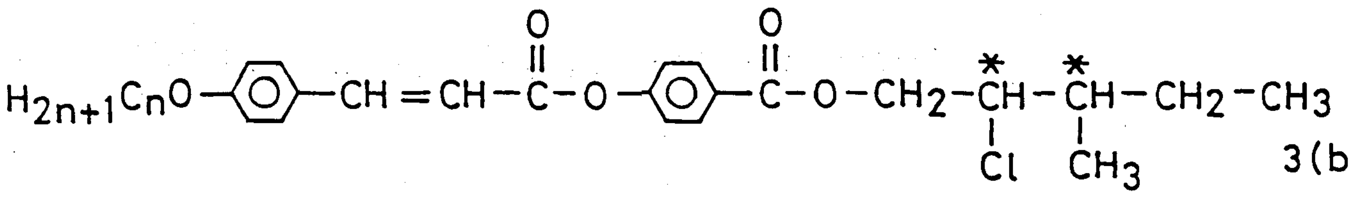


Figure 5: A plot of P_s as a function of relative temperature for compounds 3.a.2 (∇), 3.a.3 (■), 3.a.4 (O), 3.a.5 (□), 3.a.6 (A) and 3.a.7 (●).

Table 3

Transition temperatures (^{o}C) and heats of transition (Kcals/mole) of



3(b)

Compound number	n	C		S_{C^*}		S_A		N*		I
3.b.1	6	.	71.0 5.2	-		.	83.5 0.4	.	84.5 0.1	.
3.b.2	7	.	64.5 8.1	(.	52.5) 0.05	.	80.5 0.2	.	82.5 0.14	.
3.b.3	8	.	57.0 7.3	.	59.0 0.04	.	84.5 0.3	.	85.0 0.2	.
3.b.4	9	.	52.0 6.8	.	64.0 0.05	.	85.0 0.8	-		.
3.b.5	10	.	42.5 7.2	.	66.5 0.05	.	87.0 0.9	-		
3.b.6	11	.	62.5 9.2	.	68.5 0.04	.	88.0 0.97	-		
3.b.7	12	.	53.5 10.5	.	69.0 0.05	.	88.5 1.4	-		

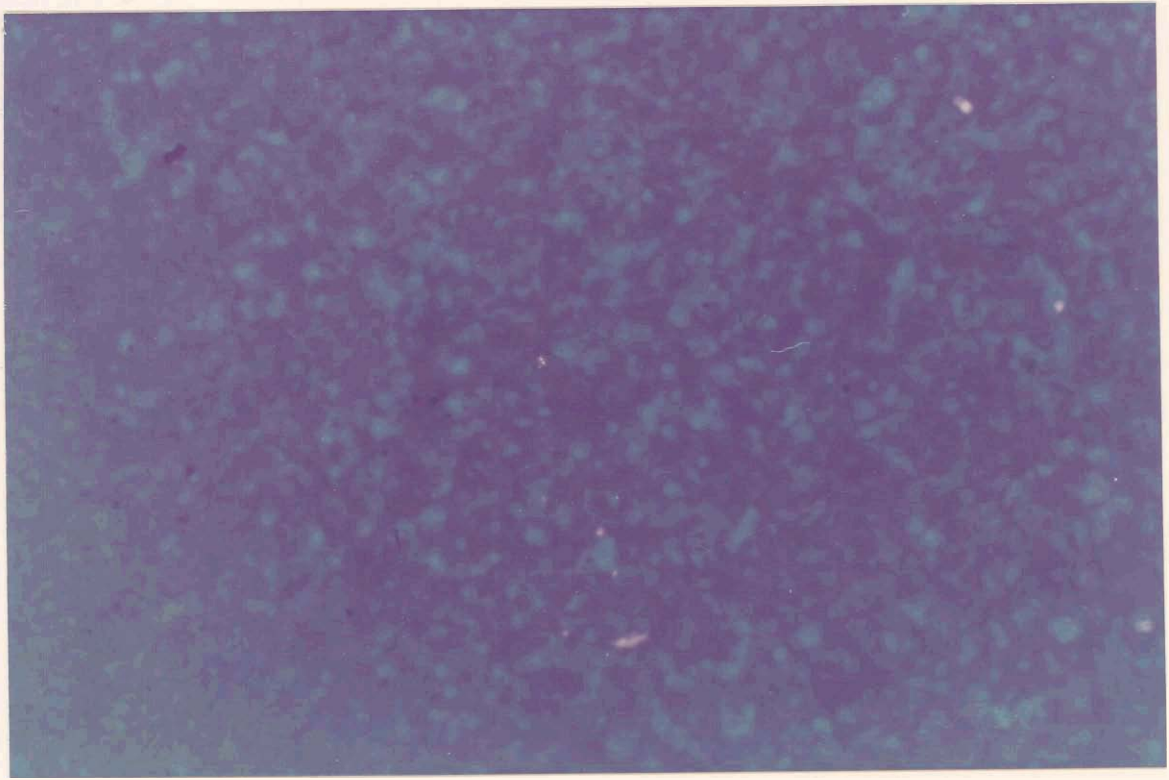


Plate III.1: The texture of blue phase of the compound 3.b.1 at 84.4°C. (x 300) melting point (64.5°C) and exhibits a monotropic S_{C*} phase 12°C below the melting point. Compound 3.b.5 has the widest range of S_{C*} phase. A plot of transition temperature versus the number of carbon atoms in the alkoxy chain is shown in figure 6. The S_{C*}-S_A transitions rise with an increasing length of the carbon chain.

Figure 7 shows the variation of Ps with temperature below S_A-S_{C*} transition. Ps increases with decreasing temperature. The decrease in Ps with increasing length of carbon chain is more explicit in the inset. The values at $T-T_c = -10°C$ for compound 3.b.2 and 3.b.7 are about 650 $\mu C/m^2$ and 350 $\mu C/m^2$ respectively. The rest of the compounds have intermediate values.

The transition temperatures and the heats of transitions of [S]-4'-(2-chloro-4-methylpentanoyloxy)phenyl <u>trans</u>-4"-n-alkoxycinnamates [3(c)] are given in table 4. All these compounds exhibit only S_A and S_{C*} phases. The range of S_A phase decreases continuously from 37.5°C for compound 3.c.1 to 12.5°C for compound 3.c.7. Compound 3.c.1 has the highest melting point (81.5°C) and a monotropic S_{C*} phase 25.5°C below the melting point. Compound 3.c.6 with lowest melting point (54.0°C) has the widest range of S_{C*} phase (25.0°C). A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain for this series is shown in figure 8. The S_{C*}-S_A transition temperatures increase continuously from 56.0°C to 80.0°C with increasing number of carbon atoms and fall on a smooth rising curve. The S_A-I transition temperatures show an alternation with successive homologues which diminish with increase in chain length.

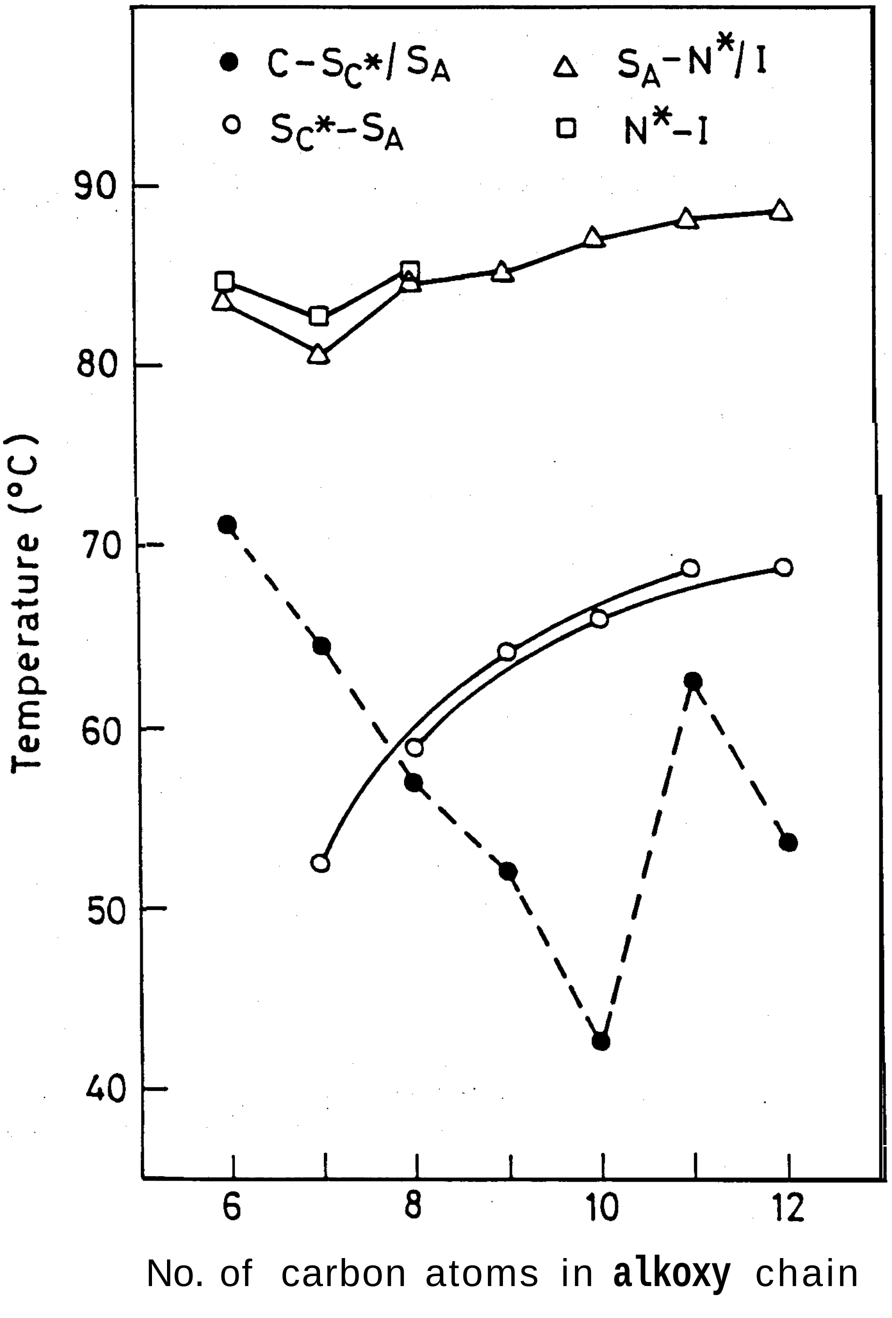


Figure *6:* A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain for the homologous series 3(b).

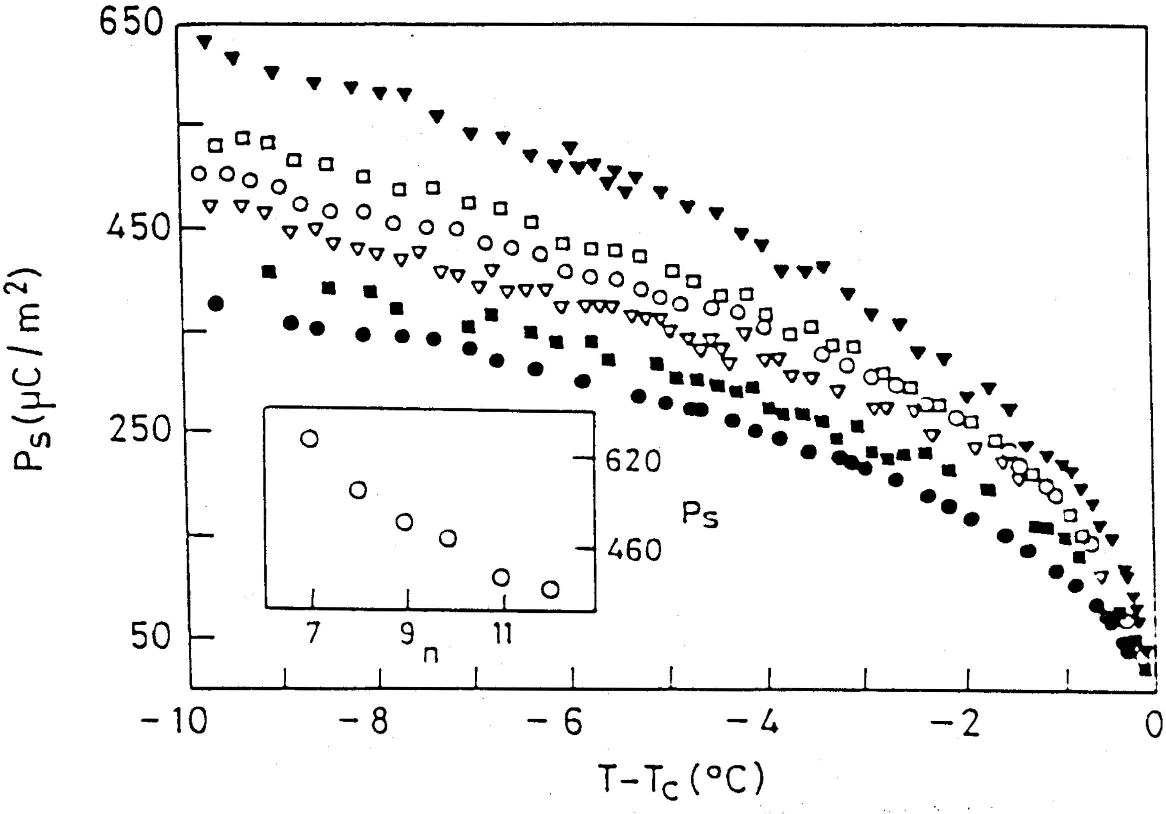
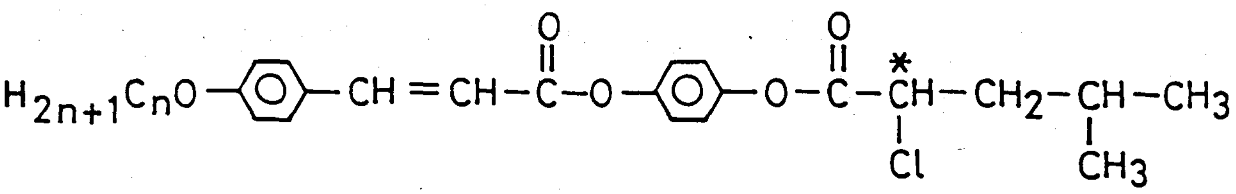


Figure 7: A plot of P_s as a function of relative temperature for compounds 3.b.2 (▼) 3.b.3 (□) 3.b.4 (O), 3.b.5(∇), 3.b.6 (■) and 3.b.7 (●).

Table 4

Transition temperatures ($^\circ C$) and heats of transition (Kcals/mole) of



$H_{2n+1}C_nO-C_6H_4-CH=CH-\overset{O}{\overset{\|}{C}}-O-C_6H_4-O-\overset{O}{\overset{\|}{C}}-\overset{*}{C}H(Cl)-CH_2-CH(CH_3)-CH_3$

3(c)

Compound number	n	C		S_{C^*}		S_A		I
3.c.1	6	.	81.5	(.	56.0)	.	93.5	.
			6.01		0.04		0.96	
3.c.2	7	.	55.0	.	67.0	.	90.5	.
			8.16		0.05		0.81	
3.c.3	8	.	62.0	.	73.0	.	92.5	.
			5.80		0.05		0.97	
3.c.4	9	.	73.0	.	75.5	.	90.5	.
			6.13		0.06		1.0	
3.c.5	10	.	69.0	.	78.0	.	92.5	.
			5.59		0.05		0.92	
3.c.6	11	.	54.0	.	79.0	.	92.0	.
			6.43		0.04		1.04	
3.c.7	12	.	62.0	.	80.0	.	92.5	.
			7.5		0.05		1.0	

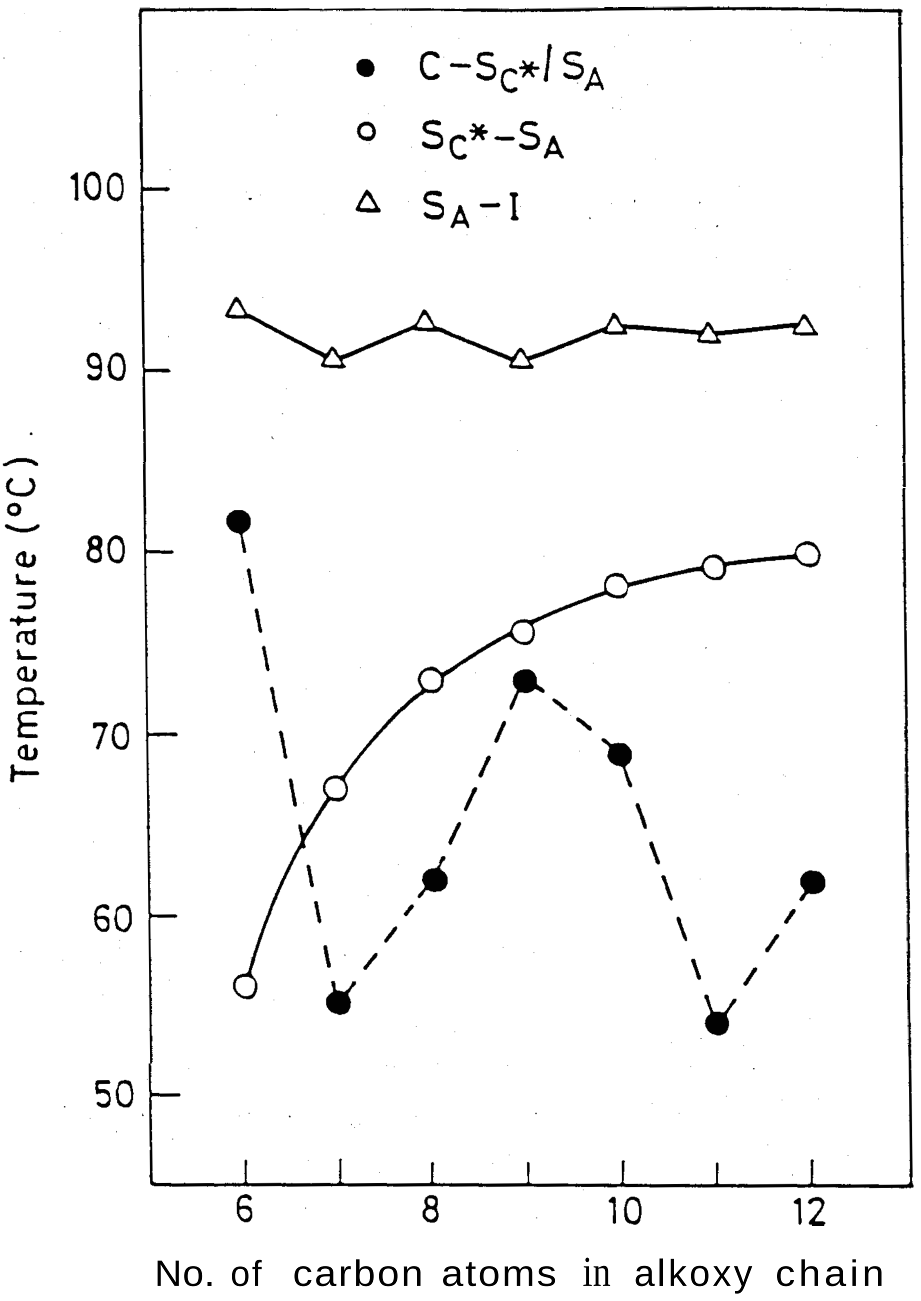


Figure 8: A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain for the homologous series 3(c).

Figure 9 shows a thermal variation of P_s for compounds 3.c.2 to 3.c.7. As is observed generally, P_s increases with lowering of temperature. In the inset of this figure it is seen that compound 3.c.2 has Ps of about 1000 $\mu C/m^2$ at $T-T_c = -10^oC$ and this value decreases on ascending the homologous series. Thus for compound 3.c.7 it is about 600 $\mu C/m^2$.

Table 5 shows the transition temperatures and the heats of transitions for [2S,3S]-4'-(2-chloro-3-methylpentanoyloxy)phenyl trans-4"-n-alkoxycinnamates [3(d)]. It is seen that compounds 3.d.1 to 3.d.5 show N* phase in addition to S_A and S_{C*} phases. The range of N* phase decreases continuously from 8^oC for compound 3.d.1 to 0.5^oC for compound 3.d.5. The range of S_A phase also decreases on increasing chain length. A monotropic S_{C*} phase is observed at 56.5^oC for compound 3.d.5 which melts at 81.0^oC. Compound 3.d.6 (n=11) which melts at 50.0^oC has an S_{C*} phase range of 33.5^oC. This is the widest range observed among the compounds of all the four homologous series synthesised.

Figure 10 shows a plot of transition temperatures versus the number of carbon atoms in the terminal alkoxy chain. The $S_{C*}-S_A$ transition temperatures form a smooth rising curve with increasing carbon atoms. The S_A-N*, the S_A-I and the N*-I transition points show a pattern very similar to the one observed for compounds 3(b).

The value of Ps for this series of compounds 3.d.2 to 3.d.7 are found to be more than 1000 $\mu C/m^2$. Ps for compound 3.d.2 (n=7)

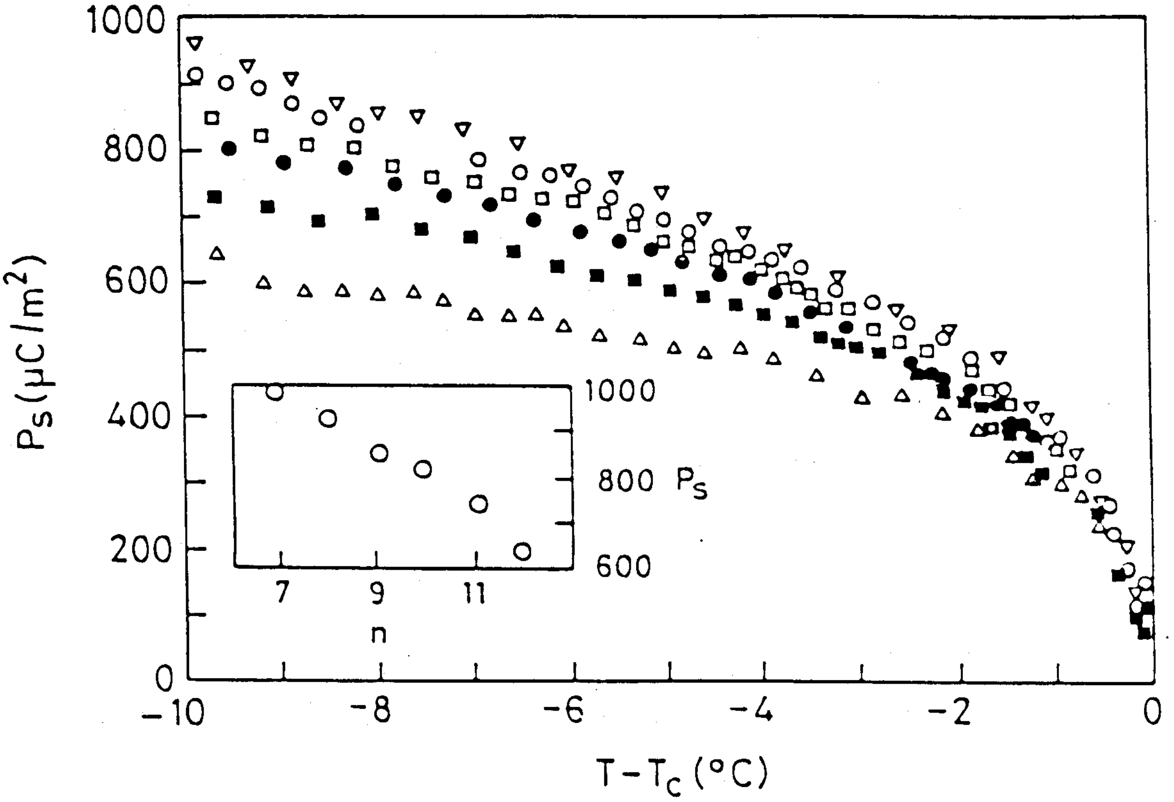
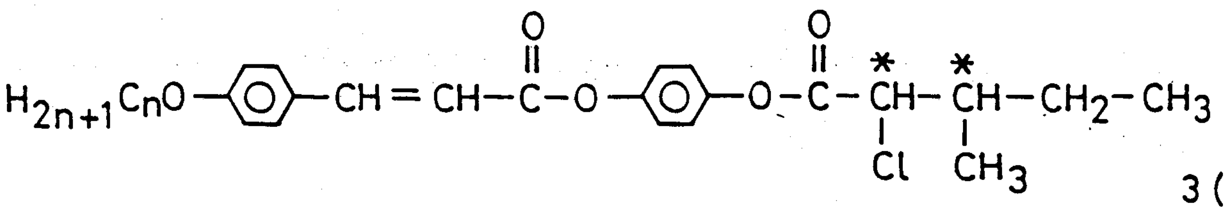


Figure 9: A plot of P_s as a function of relative temperature for compounds 3.c.2 (∇), 3.c.3 (O), 3.c.4 (□), 3.c.5 (●), 3.c.6 (■) and 3.c.7 (A).

Table 5

Transition temperatures (°C) and heats of transition (Kcals/mole) of



3(d)

Compound number	n	C		S_{C^*}		S_A		N*		I
3.d.1	6	.	81.0 6.0	(.	56.5) 0.03	.	90.5 0.13	.	98.5 0.14	.
3.d.2	7	.	61.5 8.7	.	68.5 0.06	.	88.0 0.12	.	95.0 0.21	.
3.d.3	8	.	61.0 4.5	.	73.0 0.05	.	93.0 0.10	.	96.5 0.18	.
3.d.4	9	.	69.0 7.3	.	78.0 0.06	.	95.0 0.05	.	97.0 0.23	.
3.d.5	10	.	56.0 8.0	.	80.0 0.04	.	98.5 0.07	.	99.0 0.21	.
3.d.6	11	.	50.0 5.43	.	83.5 0.06	.	99.5 0.89	-		
3.d.7	12	.	56.5 10.08	.	84.5 0.05	.	100.0 1.0	-		

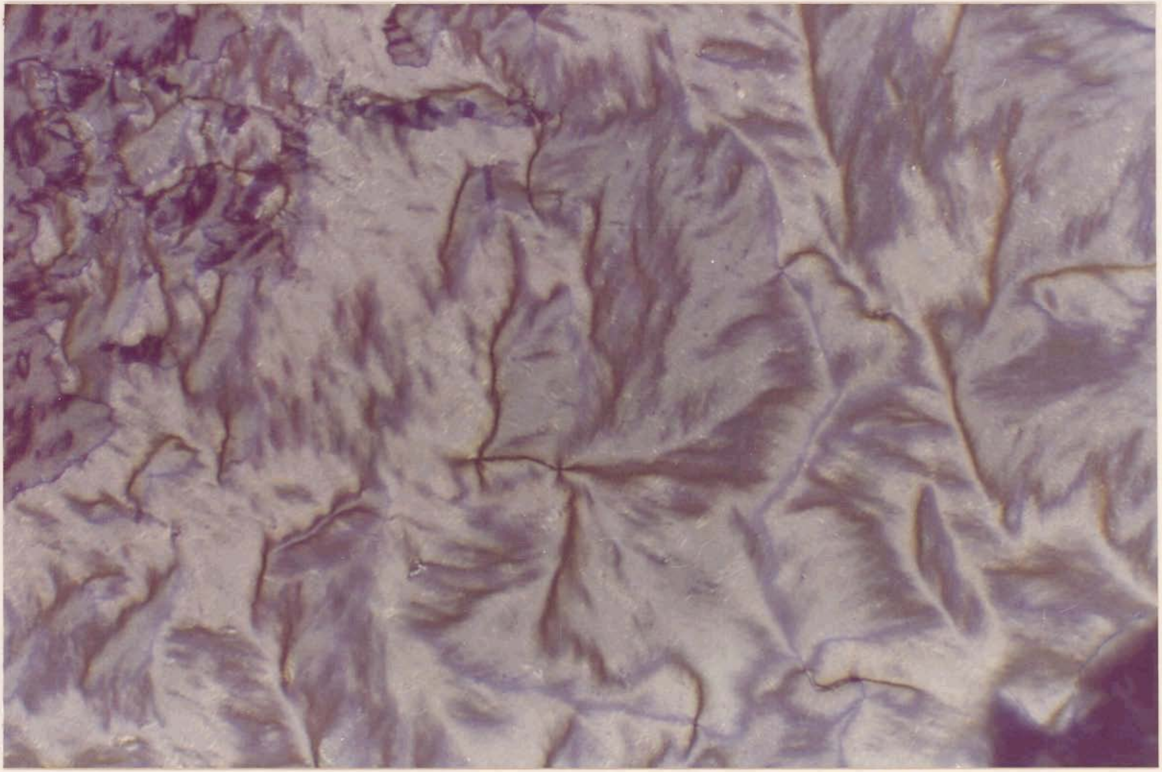


Plate III.2: The Schlieren texture of S_{C*} phase of the compound 3.d.7 at 80°C. (x300)

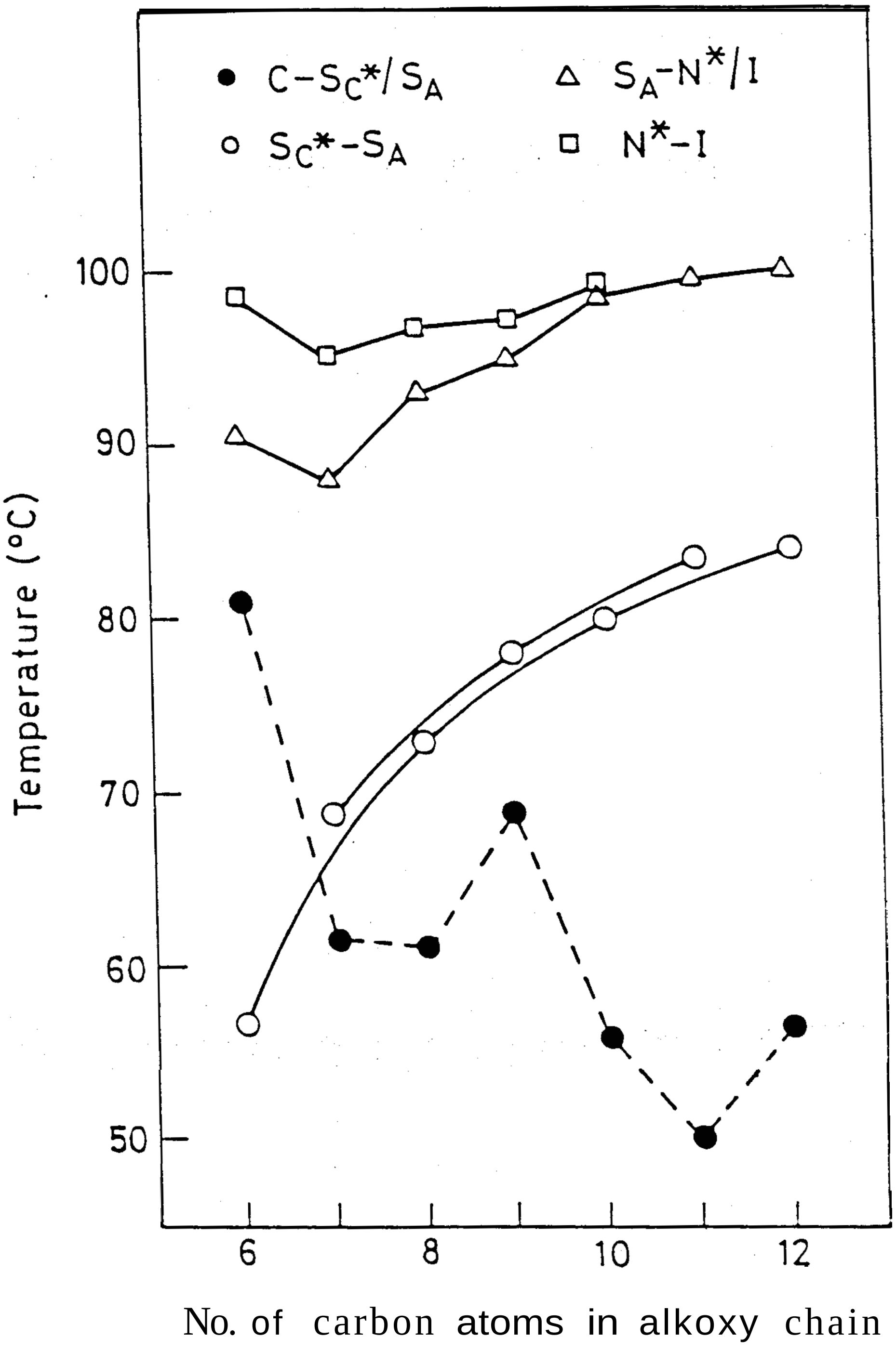


Figure 10: A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain for the homologous series 3(d).

is about 1500 $\mu C/m^2$. This is the highest value obtained among all the compounds of the four series. A plot of Ps versus $T-T_c$ is shown in figure 11. The inset shows the variation of Ps with length of the carbon chain. It can be seen that the value for compound 3.d.7 is about half the value for compound 3.d.2. Here too, the spontaneous polarisation has decreasing values as the number of methylenes increase.

Along with the spontaneous polarisation, rotational viscosity, tilt angle and response time have been measured for the decyloxy compounds of the four homologous series.[25]

The compounds [S]-4'-(2-chloro-4-methylpentyloxycarbonyl) phenyl trans-4"-n-alkoxycinnamates [3(a)] and [2S,3S]-4'-(2-chloro-3-methylpentyloxycarbonyl)phenyl trans-4"-n-alkoxycinnamates [3(b)] are isomeric. One methyl group of the pentyl chain from the 4-position in compound 3(a) has been shifted to position 3 in compound 3(b). This change also creates one more chiral centre. A comparison of these two series of compounds shows the following features. The N* phase exhibited in compound 3.a.4 (n=9) of 3(a) is absent in the corresponding homologue of 3(b). The N*-I transition temperatures in 3(b) are 4-5°C higher, though the range of N* phase is more or less the same. The S_A-N* and the S_A-I transition temperatures in 3(b) are higher by about 5-8°C and the range of S_A phase is more by only 2-4°C. The S_{C*}-S_A transitions are higher in 3(b) by about 2-4°C.

The compound 3(b) with the 2-chloro-3-methylpentyl group has two chiral carbon atoms adjacent to each other. Both the chloro

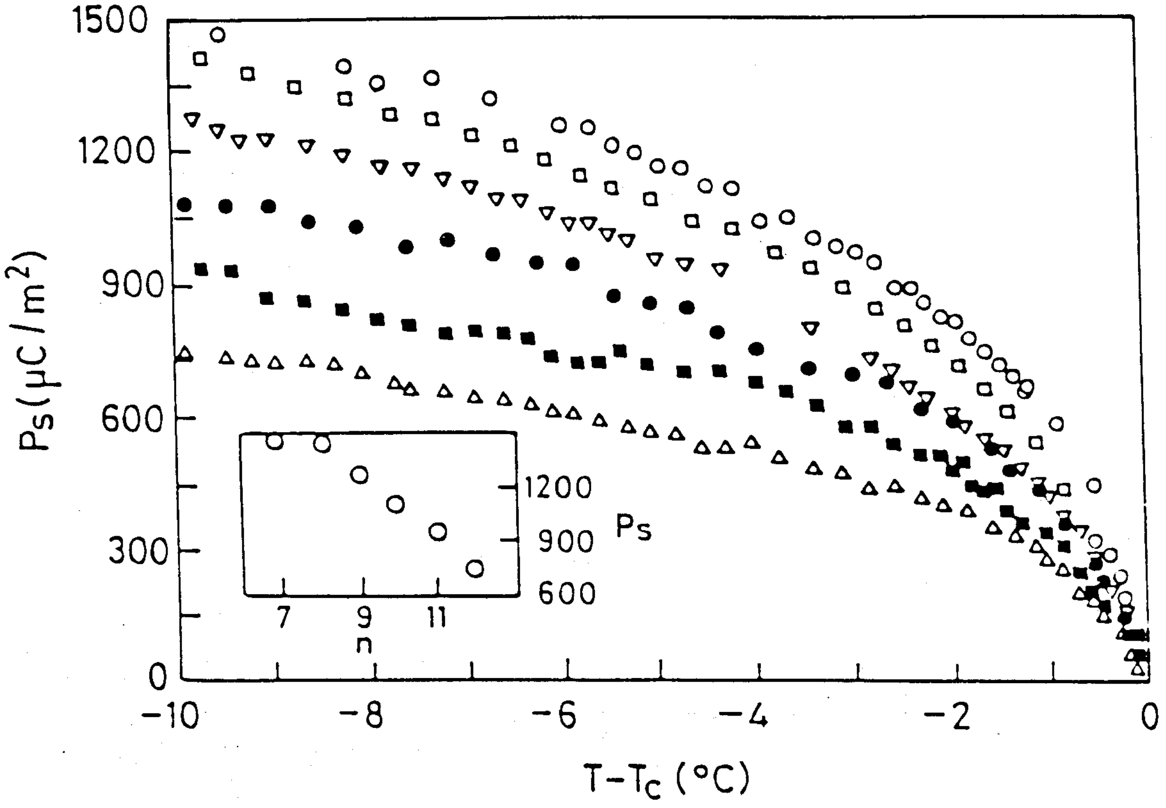
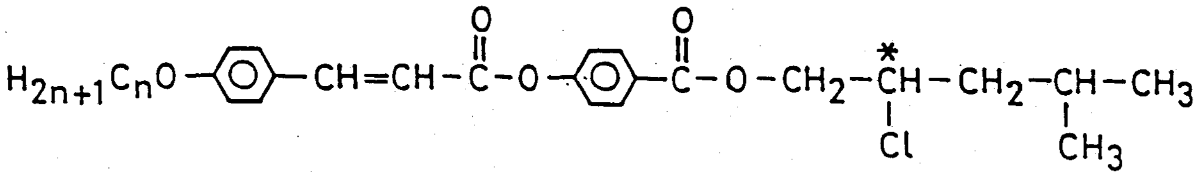
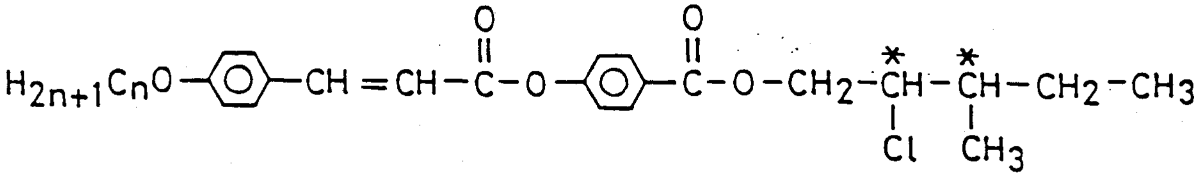


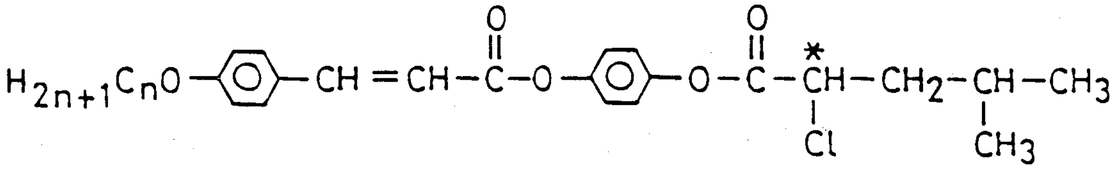
Figure 11: A plot of P_s as a function of relative temperature for compounds 3.d.2 (O), 3.d.3 , 3.d.4 (∇), 3.d.5 (●), 3.d.6 (■) and 3.d.7 (A).



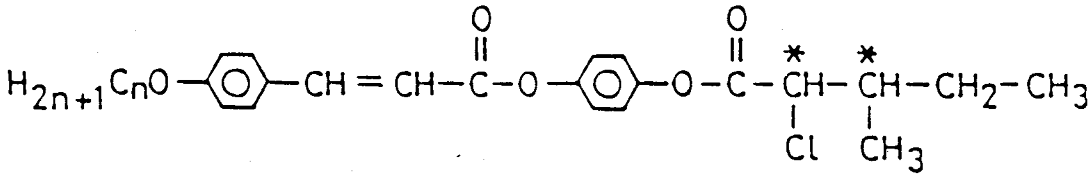
3 (a)



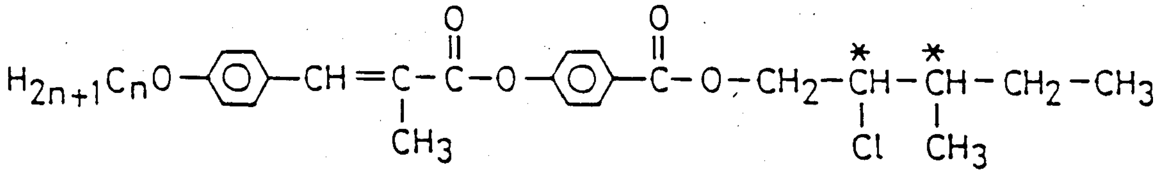
3 (b)



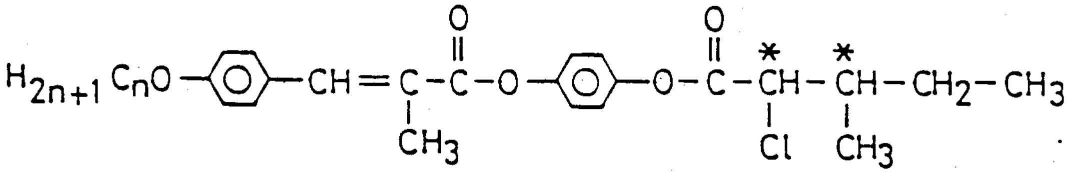
3 (c)



3 (d)



3 (e)



3 (f)

FIGURE 1

and the methyl groups on these carbon atoms will experience a hindrance to rotation around the main pentyl chain because of steric repulsion due to their proximity. And the conformation in which these are in 'anti' position is likely to be more favourable (figure 12). This semblence of locking the dipole on the chiral group should favour a dipolar ordering and enhance the values for the spontaneous polarisation. It is generally observed[26] that the configuration at the chiral carbon atom and the inductive effect of the group attached to it would contribute to the polarisation in an exactly reverse manner if this group were to be moved to the adjacent carbon atom. Considering this fact it could be said that the adjacent chiral carbons having configurations 'S' with the chloro and methyl groups having opposite inductive effects should add to the value of polarisation. However. Otterholm et al.[27] have reported an exception to this generalisation. Patel and Goodby[28] in their studies have indicated that the core of the molecule is usually tilted more than the overall structure. They also observe that for systems in which core is less tilted than the overall structure, there will be an inversion of polarisation producing anomalous results. Thus, the tilt of the core with respect to the overall molecular tilt is an important factor in determining the sign of polarisation.

The values for spontaneous polarisation of compounds 3(b) show a considerable increase in the lower homologues, viz., compounds 3.b.2 to 3.b.5. Compound 3.b.2 has a Ps 150 $\mu C/m^2$ more than the corresponding compound 3.a.2 of the series 3(a) at $T-T_c = -10^oC$.

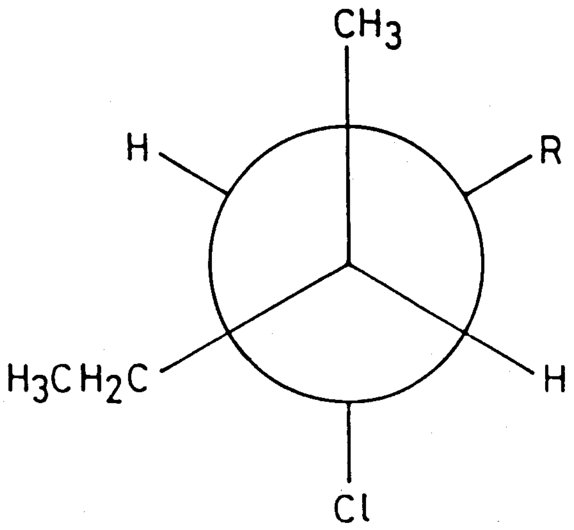


Figure 12: 'Anti' conformation of compounds containing [2S,3S I-2-chloro 3-methyl groups.

The compounds [S]-4'-(2-chloro-4-methylpentanoyloxy)phenyl trans-4"-n-alkoxycinnamates [3(c)] and [2S,3S]-4'-(2-chloro-3-methylpentanoyloxy)phenyl trans-4"-n-alkoxycinnamates [3(d)] are isomers which differ only in the position of the methyl group on the pentyl chain. As noticed earlier in series 3(a) and 3(b), the position of the methyl group has an effect on mesomorphic properties, which seems to be much more pronounced in series 3(c) and 3(d). An N* phase present in five compounds 3.d.1 to 3.d.5 of series 3(d) is totally absent in the compounds of series 3(c). The thermal stability as well as the range of S_A phase of compounds in series 3(d) is less in case of lower homologues [Compounds 3.d.1 (n=6) and 3.d.2 (n=7)] and more in case of the higher homologues [Compounds 3.d.3 to 3.d.7 (n=8...12)] than the corresponding compounds of series 3(c). The S_{C*}-S_A transition temperatures are more by about 2-5°C in the higher homologues of series 3(d). The melting points of the compounds in series 3(d) are generally less and the range of S_{C*} phase is more. For example, compound 3.d.6 (n=11) with the lowest melting point (50.0°C) in series 3(d) has S_{C*} phase range of 33.5°C. The corresponding compound 3.c.6 (n=11) of series 3(c) has a range of 25°C and it is also the compound with the lowest melting point (54.0°C) of that series.

The structural features of these compounds are as follows. The rotation of the chloro group in series 3(c) is already hindered due to the carbonyl adjacent to it.The two dipoles due to an electrostatic repulsion are likely to force themselves away from each other resulting in an 'anti' conformation (figure 12).

The additional methyl group on the adjacent carbon in series 3(d) should make it even more difficult for the chloro group to rotate about the parent pentyl chain.

The spontaneous polarisation of compounds in series 3(d) is considerably more than the corresponding homologues of series 3(c). The difference is found to increase continuously with decreasing length of the carbon chain. Thus, for compounds 3.c.7 and 3.d.7 (n=12) the difference is about 150 $\mu C/m^2$ and for compounds 3.c.2 and 3.d.2 (n=7) it is about 525 $\mu C/m^2$.

[S]-4'-(2-Chloro-4-methylpentyloxycarbonyl)phenyl trans-4"-n-alkoxycinnamates [3(a)] and [S]-4'-(2-chloro-4-methylpentanoyloxy)phenyl trans-4"-n-alkoxycinnamates [3(c)] have one chiral carbon atom each. The structural change involved in going from 3(c) to 3(a) is that of an inversion of the ester linkage and an addition of a methylene unit between the core and the chiral carbon atom. A comparison of these two series shows the following features. The compounds in series 3(c), as mentioned earlier do not exhibit an N* phase. It is seen that all the transition temperatures of compounds in series 3(c) are enhanced. However, there is little change in the mesophase ranges of S_A and S_{C*} phases. The chiral carbon in series 3(a) can be said to be a methylene unit away from the core. Hence the coupling between the rotational bias about the chiral carbon and the rotation of the core could be weaker than that in series 3(c). The Ps values for the compounds of series 3(c) are a little less than twice the values of the corresponding compounds of series 3(a).

The structural change involved in [2S,3S]-4'-(2-chloro-3-methylpentyloxycarbonyl)phenyl trans-4"-n-alkoxycinnamates [3(b)] and [2S,3S]-4'-(2-chloro-3-methylpentanoyloxy)phenyl trans-4"-n-alkoxycinnamates [3(d)] is the same as that involved in series 3(a) and 3(c). However, in this case with two chiral carbon atoms, the change seems to have some different implications. In case of series 3(a) and 3(c) the reversal of ester linkage and elimination of the methylene unit resulted in a total suppression of the N* phase. But in case of series 3(b) and 3(d) this change results in not only enhancing the thermal stability but also in the induction of this phase in compounds 3.d.4 and 3.d.5 of series 3(d). All the mesophases of the compounds in series 3(d) have higher thermal stabilities. Also the temperatures of N*-I, S_A-I, S_A-N* and S_{C*}-S_A transitions are higher by about 11-14°C, 10-13°C, 7-9°C and 14-16°C respectively. The range of S_A phase is wider in compounds of series 3(b) but the S_{C*} phase has a wider range in compounds of series 3(d).

The value for the spontaneous polarisation of compounds in series 3(d) is almost two to two and a half times more than that of the corresponding compounds of series 3(b). This difference is more in the lower and less in the higher homologues. For example, for compounds 3.b.2 and 3.d.2 (n=7) the difference is about 850 $\mu C/m^2$ and for compounds 3.b.7 and 3.d.7 (n=12) it is about 375 $\mu C/m^2$ at $T-T_c = -10°C$.

In conclusion, the following points can be highlighted on a comparison of mesomorphic properties of all the compounds synthesised. In the compounds with these structures no higher order smectic phases are observed. S_A and S_{C*} phases are predominant. The mesomorphism gets immensely diminished in case of esters of <u>trans</u>-p-n-alkoxy-a-methylcinnamic acids. The clearing temperature of all the compounds is less than 100°C. Compounds with a relatively rigid chiral chain where rotation of various groups is hindered due to the 'syn barriers' have a wide range of S_{C*} phase in spite of having relatively high melting points. In comparison a flexible chain with groups having more rotational freedom lowers the melting points. The value for spontaneous polarisation is increased when the chiral centre is moved closer to the core and a carbonyl group is present adjacent to the chiral carbon atom. Also two chiral carbon atoms adjacent to each other with groups having opposite inductive effects enhance the value for spontaneous polarisation.

III.3 EXPERIMENTAL

[S]-2-Chloro-4-methylpentanoic acid

This was prepared following the procedure of Fu et al.[22] Thus a mixture of l-leucine (52.4 g, 0.4 mol) and 6N hydrochloric acid (500 ml) contained in a one litre three-necked flask fitted with a mechanical stirrer and cooled in an ice-salt bath, was stirred vigorously. Sodium nitrite (44.0 g, 0.64 mol) was added to this mixture in small portions. The temperature of the reaction mixture was not allowed to exceed 0°C during the addition. The stirring was continued for a further period of five hours at 0°C after completion of the addition. The reaction mixture was then extracted with ether (3x150 ml) and the combined ether solution dried (Na_2SO_4). The residue obtained on removal of the solvent was distilled under reduced pressure to yield the pure product (30.0 g, 50%).b.p. 90°C/2.5 mm;$[\alpha]_D^{25}$ = -25.0(c=5 in C_2H_5OH).
[Reported[29] b.p. 112.4°C/20 mm; $[\alpha]_D^{16}$ = -24.6 (c=5 in C_2H_5OH)].

[2S,3S]-2-Chloro-3-methylpentanoic acid

This was prepared from l-isoleucine following a procedure similar to the one described above.
Yield, 49%; b.p. 84.0°C/3 mm; $[\alpha]_D^{25}$ = -2.62(c = 5 in CH_3OH).
[Reported[29] b.p. 88-90°C/1-2 mm; $[\alpha]_D^{27}$ = -2.9 (c=5 in CH_3OH)].

[S]-Methyl 2-chloro-4-methylpentanoate

A mixture of [S]-2-chloro-4-methylpentanoic acid (15.1 g, 0.1 mol), methanol (100 ml) and a few drops of concentrated sulphuric acid was refluxed for eight hours. The excess alcohol was removed by distillation and the residue was poured into water. This was extracted with ether (3x60 ml) and the combined ethereal solution was washed with 10% aqueous sodium bicarbonate (2x75 ml), water (2x100 ml) and dried (Na_2SO_4). Removal of the solvent afforded the required ester which was purified by distillation under reduced pressure. (16.1 g, 98%); b.p. 105°C/20 mm. [Reported[29] b.p. 72°C/11 mm].

[2S,3S]-Methyl 2-chloro-3-methylpentanoate

Following a procedure similar to the one described above, [2S,3S]-2-chloro-3-methylpentanoic acid was esterified with methanol in the presence of catalytic amount of concentrated sulphuric acid.

Yield, 98%; b.p. 94-98°C/20-25 mm. [Reported[29] b.p. 71-72°C/10 mm].

[S]-2-Chloro-4-methylpentanol

Lithium aluminium hydride (2.28 g, 0.06 mol) was added to sodium dried ether (200 ml) contained in a three-necked flask fitted with a condenser and a dropping funnel. This was cooled in an ice-bath and magnetically stirred. To this cold mixture was added dropwise a solution of [S]-methyl-2-chloro-4-methylpentanoate (16.45 g, 0.1 mol) in dry ether. After completion of addition, the mixture was stirred at room temperature for a period of two hours. The reaction mixture was again cooled thoroughly in an ice-bath and the excess lithium aluminium hydride was decomposed by a careful addition of damp ether (100 ml) followed by ice-cold water (4 ml). The stirring was continued till the decomposition was complete. The gelatinous white precipitate was filtered and washed thoroughly with warm ethyl acetate. The filtrate was dried (Na_2SO_4) and the solvent removed. The crude product so obtained was purified by distillation under reduced pressure (12.2 g, 90%). b.p. 80°C/3mm; $[\alpha]_D^{25}$ = -30.0 (c=2 in $CHCl_3$); ν_{max}^{neat} 3370, 2950,2850,1480,1360 and 1070 cm^{-1}; δ:0.9(dd,6H,$(C\underline{H}_3)_2$-CH-),1.2-1.9(m,3H,-C$\underline{H}$-C$\underline{H}_2$),2.7(s,1H,-O$\underline{H}$),3.5-4.25(m,3H,-C$\underline{H}$-C$\underline{H}_2$OH).

[2S,3S]-2-Chloro-3-methylpentanol

Following a procedure similar to the one described above, [2S,3S]-methyl- 2-chloro-3-methylpentanoate was reduced to the corresponding alcohol by lithium aluminiun hydride.
Yield 90%; b.p. 60°C/7 mm; $[\alpha]_D^{25}$ = -5.0(c=2 in $CHCl_3$); ν_{max}^{neat}: 3370,2960,2880,1480,1465,1380 and 1075 cm^{-1}; δ:0.7-1.1(m,6H, C$\underline{H}_3$CH_2-CH(C$\underline{H}_3$)-),1.1-2.0(m,3H,-C$\underline{H}_2$-C$\underline{H}$),2.6(s,1H,-O$\underline{H}$),3.55-4.1(m, 3H,-C$\underline{H}$(Cl)-C$\underline{H}_2$-OH).

[S]-2-Chloro-4-methylpentyl 4'-benzyloxybenzoate

This was prepared following the esterification procedure of Hassner and Alexanian.[24] Thus, a mixture of 4-benzyloxybenzoic acid (11.4 g, 0.05 mol), N,N-dicyclohexylcarbodiimide (11.3 g, 0.055 mol), [S]-2-chloro-4-methylpentanol (7.5 g, 0.055 mol), 4-pyrrolidinopyridine (0.74 g, 0.005 mol) and dry chloroform (100 ml), protected from moisture through anhydrous calcium chloride guard tube was stirred for six hours at room temperature. N,N-Dicyclohexyl urea formed was filtered and the filtrate was washed successively with water (2x50 ml), 5% acetic acid (2x70 ml), water (3x50 ml) and dried (Na_2SO_4). The residue obtained on removing the solvent was chromatographed on silica gel and eluted with 30% chloroform-petroleum ether (b.p. 60-80°C) mixture. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol (11.0 g, 64%). m.p. 51-52°C; $[a]^{25}_{D}$ = +3.92(c=2 in $CHCl_3$); ν^{nujol}_{max}:2950,1700,1605,1585,1510,1280,1240, 1175 and 1010 cm^{-1}; δ:0.75(dd,6H,HC($C\underline{H}_3$)$_2$CH-), 1.23-1.7(m,3H, -$C\underline{H}_2C\underline{H}(CH_3)_2$),3.3-3.7(m,3H,-COO$C\underline{H}_2C\underline{H}$Cl),4.1(s,2H,-O$C\underline{H}_2$),5.6(d,2H, Ar$\underline{H}$),5.9(s,5H,Ar$\underline{H}$),6.4(d,2H,Ar$\underline{H}$).

[Found: C,69.05;H,6.54% $C_{20}H_{23}ClO_3$ requires
C,69.26;H,6.64%].

[2S,3S]-2-Chloro-3-methylpentyl 4'-benzyloxybenzoate

Following a procedure similar to the one described above, 4-benzyloxybenzoic acid was esterified with [2S,3S]-2-chloro-3-methylpentanol in presence of N,N-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine using dry chloroform as solvent.
Yield, 62%; m.p. 48-50°C; $[\alpha]^{25}_{D}$ = +3.13(c = 2 in $CHCl_3$); ν^{nujol}_{max}: 2950,1715,1605,1510,1460,1260,1170 and 1100 cm^{-1}; 6:0.85-2.0(m,

9H,2x$C\underline{H}_3$,$C\underline{H}_2$ and $C\underline{H}$),4.06-4.68(m,3H,$COOC\underline{H}_2C\underline{H}Cl$),5.09(s,2H,$PhC\underline{H}_2OAr$), 6.82-8.18(m,9H,$Ar\underline{H}$).

[Found: C,69.68;H,6.18% $C_{20}H_{23}ClO_3$ requires C,69.26;H,6.64%].

[S]-4'-Benzyloxyphenyl 2-chloro-4-methylpentanoate

This was prepared following the esterification procedure of Hassner and Alexanian.[24] Thus, a mixture of [S]-2-chloro-4-methyl pentanoic acid (7.5 g, 0.05 mol), N,N-dicyclohexylcarbodiimide (11.3 g, 0.055 mol), 4-benzyloxyphenol (11.0 g, 0.055 mol), 4-pyrrolidinopyridine (0.74 g, 0.005 mol) and dry chloroform (100 ml), protected from moisture through anhydrous calcium chloride guard tube, was stirred for six hours at room temperature. N,N-Dicyclohexyl urea formed was filtered and the filtrate was washed successively with water (2x50 ml), 5% acetic acid (2x60 ml), water (3x50 ml) and dried (Na_2SO_4). The residue obtained on removal of the solvent was chromatographed on silica gel and eluted with 35% chloroform-petroleum ether (b.p. 60-80°C) mixture. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol (10.0 g, 60%). m.p. 67.5°C; $[\alpha]_D^{25}$ = -4.57(c=2 in $CHCl_3$); ν_{max}^{nujol} 2900,1760, 1595,1510,1460,1380,1300,1200,1150 and 1010 cm^{-1}; δ:0.78-2.09(m, 9H,2x$C\underline{H}_3$,$C\underline{H}_2$ and $C\underline{H}$),4.17(t,1H,$C\underline{H}Cl$),5.28(s,2H,$PhC\underline{H}_2O$), 6.95-8.39(m,9H,$Ar\underline{H}$).

[Found: C,68.09;H,6.53% $C_{19}H_{21}ClO_3$ requires C,68.57;H,6.31%].

[2S,3S]-4'-Benzyloxyphenyl 2-chloro-3-methylpentanoate

Following a procedure similar to the one described above [2S,3S]-2-chloro-3-methylpentanoic acid was esterified with 4-benzyloxyphenol in the presence of N,N-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine using dry chloroform as solvent. Yield, 64%; m.p. 60.5°C; $[\alpha]_D^{25}$ = +2.19(c=2 in $CHCl_3$); ν_{max}^{nujol}: 2900,1760,1595,1505,1460,1380,1300,1190 and 1020 cm^{-1}; δ:0.62-1.92(m,9H,2x$C\underline{H}_3$,$C\underline{H}_2$ and $C\underline{H}$),3.48(d,1H,$C\underline{H}Cl$),4.05(s,2H,$OC\underline{H}_2$),5.4-6.05(m,8H,Ar$\underline{H}$).

[Found: C,68.94;H,6.69% $C_{19}H_{21}ClO_3$ requires
C,68.57;H,6.31%].

[S]-2-Chloro-4-methylpentyl 4'-hydroxybenzoate

A mixture of [S]-2-chloro-4-methylpentyl 4'-benzyloxy benzoate (10.4 g, 0.03 mol) dissolved in 1,4-dioxan (100 ml) and 5% Pd/C catalyst (5.2 g) was stirred in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. The reaction mixture was filtered and dioxan removed by distillation under reduced pressure. The residual product so obtained was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol (7.0 g, 91%). m.p. 60.0°C; $[\alpha]_D^{25}$ = -6.2(c=2 in C_2H_5OH); ν_{max}^{nujol} : 3420,2950,1690, 1590,1460,1285 and 1165 cm^{-1}; δ:0.65-2.22(m,9H,2x$C\underline{H}_3$,$C\underline{H}_2$ and $C\underline{H}$), 3.57-4.60(m,3H,$COOC\underline{H}_2C\underline{H}Cl$),6.57(s,1H,O$\underline{H}$),6.92(d,2H,Ar$\underline{H}$),8.0(d,2H, ArH).

[Found: C,60.94;H,6.83% $C_{13}H_{17}ClO_3$ requires C,60.82;H,6.63%].

[2S,3S]-2-Chloro-3-methylpentyl 4'-hydroxybenzoate

Following a procedure similar to the one described above [2S,3S]-2-chloro-3-methylpentyl 4'-benzyloxybenzoate was subjected to hydrogenolysis in 1,4-dioxan using 5% Pd/C as a catalyst.

Yield, 90%; m.p. 59.0°C; $[\alpha]_D^{25}$ = -6.5(c=2 in C_2H_5OH); ν_{max}^{nujol} 3360,2980,1690,1615,1590,1515,1450,1270and 1165 cm^{-1}; δ :0.72-2.12(m,9H,2xC$\underline{H}_3$,C$\underline{H}_2$ and C$\underline{H}$),4.04-4.76(m,3H,COOC$\underline{H}_2$C$\underline{H}$Cl),6.80(s,1H, O$\underline{H}$), 6.88-8.48(m,4H,Ar$\underline{H}$)

[Found: C,61.03;H,6.90% $C_{13}H_{17}ClO_3$ requires C,60.82;H,6.63%].

[S]-4'-Hydroxyphenyl 2-chloro-4-methylpentanoate

A mixture of [S]-4'-benzyloxyphenyl 2-chloro-4-methyl pentanoate (10.0 g, 0.03 mol) dissolved in 1,4-dioxan (100 ml) and 5% Pd/C catalyst (5.0 g) was stirred in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. The reaction mixture was filtered and dioxan removed by distillation under reduced pressure. The residual product so obtained was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol (6.8 g, 94%). m.p. 77.5°C; $[\alpha]_D^{25}$ = +6.83(c=2 in C_2H_5OH); ν_{max}^{nujol} 3360,2940,1750, 1600,1510,1180,864 and 824 cm^{-1}; δ:0.73-2.0(m,9H,2xC$\underline{H}_3$,C$\underline{H}_2$ and C$\underline{H}$),4.35(t,1H,C$\underline{H}$Cl),5.92(s,1H,O$\underline{H}$),6.27-7.07(m,4H,Ar$\underline{H}$).

[Found: C,58.91;H,6.54% $C_{12}H_{15}ClO_3$ requires C,59.38;H,6.18%].

[2S,3S]-4-Hydroxyphenyl 2-chloro-3-methylpentanoate

Following a procedure similar to the one described above [2S,3S]-4'-benzyloxyphenyl 2-chloro-3-methylpentanoate was subjected to hydrogenolysis in 1,4-dioxan using 5% Pd/C as a catalyst.

Yield, 95%; m.p. 80.8°C; $[\alpha]_D^{25}$ = +3.4(c=2 in $CHCl_3$); ν_{max}^{nujol} 3400,2940,1740,1600,1510,1390,1180,940,715 and 700 cm_{-1}; δ:0.8-2.4(m,9H,2xC$\underline{H}_3$,C$\underline{H}_2$ and C$\underline{H}$),4.35(d,1H,C$\underline{H}$Cl),6.26(s,1H,O$\underline{H}$),6.82 (dd,4H,Ar$\underline{H}$).

[Found: C,59.86;H,6.25% $C_{12}H_{15}ClO_3$ requires C,59.38;H,6.18%].

[S]-4'-(2-Chloro-4-methylpentyloxycarbonyl)phenyl trans-4"-n-dodecyloxycinnamate (3.a.7)

This was prepared following the esterification procedure of Hassner and Alexanian.[24] Thus a mixture of trans-4-n-dodecyloxycinnamic acid (0.33 g, 0.001 mol), N,N-dicyclohexyl carbodiimide

(0.23 g, 0.0011 mol), [S]-2-chloro-4-methylpentyl 4'-hydroxybenzoate (0.28 g, 0.0011 mol), 4-pyrrolidinopyridine (0.015 g, 0.0001 mol) and dry dichloromethane (50 ml), protected from moisture through anhydrous calcium chloride guard tube, was stirred for one hour at room temperature. N,N-Dicyclohexyl urea formed was filtered and the filtrate was washed successively with water (2x25 ml), 5% acetic acid (3x30 ml), water (3x30 ml) and dried (Na_2SO_4). The residue obtained on removal of solvent was chromatographed on silica gel and eluted with 40% chloroform-petroleum ether (b.p. 60-80^{o}C) mixture. Removal of solvent from the eluate afforded a white solid which was crystallised several times from ethanol (0.4 g, 70%). m.p. 52.0^{o}C; $[\alpha]_D^{25}$ = -8.86(c=2 in $CHCl_3$); ν_{max}^{nujol}:2950,2850,1720,1620,1600,1480,1280 and 1120 cm^{-1}; δ:0.7-2.2(m,32H,3xC$\underline{H}_3$,11xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.15-4.56(m,3H,COOC$\underline{H}_2$C$\underline{H}$Cl),6.27-8.17(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,71.93;H,8.45% $C_{34}H_{47}ClO_5$ requires C,71.52;H,8.24%].

The physical data of the cognate preparations of other [S]-4'-(2-chloro-4-methylpentyloxycarbonyl)phenyl <u>trans</u>-4"-n-alkoxycinnamates [3(a)] are given below.

[S]-4'-(2-Chloro-4-methylpentyloxycarbonyl)phenyl <u>trans</u>-4"-n-hexyloxycinnamate **(3.a.1)**

Yield, 62%; m.p.51.5 ^{o}C; $[\alpha]_D^{25}$ = -9.43(c=2 in $CHCl_3$);ν_{max}^{nujol} 2950,2850,1720,1630,1600,1520,1460,1280,1140 and 1100 cm^{-1}; δ:0.75-2.25(m,20H,3xC$\underline{H}_3$,5xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.2-5.0

(m,3H,$COOC\underline{H}_2C\underline{H}Cl$),6.3-8.62(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,70.42;H,7.52% $C_{28}H_{35}ClO_5$ requires C,69.96;H,7.19%].

[S]-4'-(2-Chloro-4-methylpentyloxycarbonyl)phenyl <u>trans</u>-4"-n-heptyloxycinnarnate (3.a.2)

Yield, 70%; m.p. 57.5°C; $[\alpha]_D^{25}$ = -9.31(c=2 in $CHCl_3$);ν_{max}^{nujol}. 2950,2850,1720,1630,1600,1580,1520,1380,1140 and 1120 cm^{-1}; δ:0.6-2.0(m,22H,3x$C\underline{H}_3$,6x$C\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.22-4.62 (m,3H,$COOC\underline{H}_2C\underline{H}Cl$),6.4-8.4(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,69.60;H,7.55% $C_{29}H_{37}ClO_5$ requires C,69.53;H,7.31%].

[S]-4'-(2-Chloro-4-methylpentyloxycarbonyl)phenyl <u>trans</u>-4"-n-octyloxycinnamate (3.a.3)

Yield, 65%; m.p. 50.0°C; $[\alpha]_D^{25}$ = -9.29(c=2 in $CHCl_3$);ν_{max}^{nujol}. 2950,2875,1720,1630,1605,1520,1280,1140 and 1120 cm^{-1}; δ:0.5-2.2(m,24H,3x$C\underline{H}_3$,7x$C\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.2-4.7(m,3H, $COOC\underline{H}_2C\underline{H}Cl$),6.25-8.3(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,69.86;H,7.70% $C_{30}H_{39}ClO_5$ requires C,69.97;H,7.58%].

[S]-4'-(2-Chloro-4-methylpentyloxycarbonyl)phenyl trans-4"-n-**nonyloxycinnamate (3.a.4)**

Yield, 65%; m.p. 62.0^{o}C; $[\alpha]_D^{25}$ = -9.26(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2950,2850,1720,1630,1600,1580,1520,1460,1280 and 1140 cm^{-1}; 6: 0.65-2.2(m,26H,3xC$\underline{H}_3$,8xC$\underline{H}_2$ and C$\underline{H}$),3.9(t,2H,ArOC$\underline{H}_2$),4.05-4.47(m, 3H,COOC$\underline{H}_2$C$\underline{H}$Cl),6.16-8.2(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,70.79;H,8.03% $C_{31}H_{41}ClO_5$ requires C,70.39;H,7.76%].

[S]-4'-(2-Chloro-4-methylpentyloxycarbonyl)phenyl trans-4"-n-decyloxycinnamate **(3.a.5)**

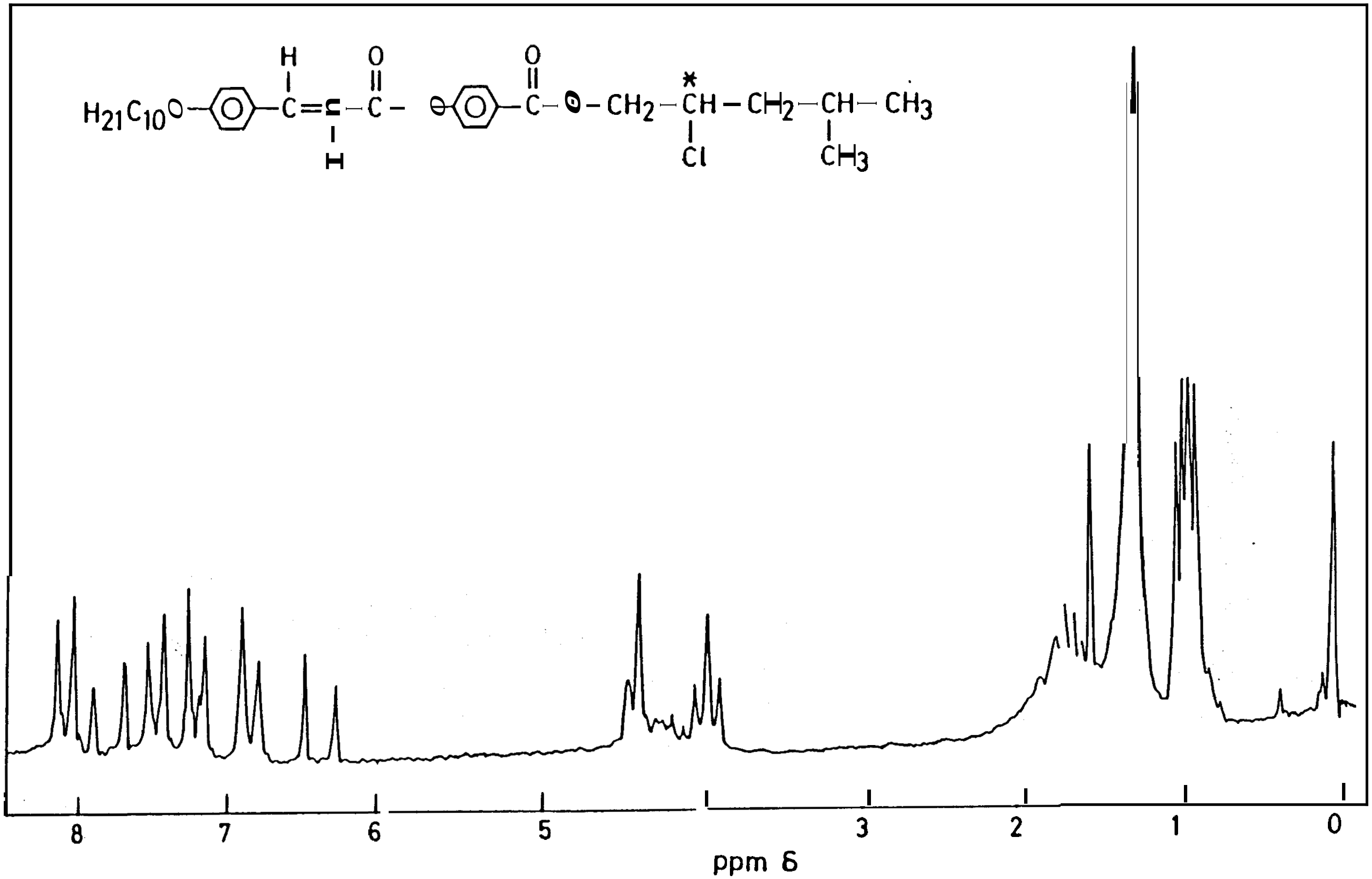
Yield. 68%; m.p. 44.0^{o}C; $[\alpha]_D^{25}$ = -9.06(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2950,2850,1720,1630,1600,1580,1520,1270 and 1120 cm^{-1}; δ:0.62-2.2 (m,28H,3xC$\underline{H}_3$,9xC$\underline{H}_2$ and C$\underline{H}$), 4.0(t,2H,ArOC$\underline{H}_2$), 4.1-4.57(m,3H, COOC$\underline{H}_2$C$\underline{H}$Cl),6.3-8.25(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,70.70;H,8.17% $C_{32}H_{43}ClO_5$ requires C,70.78;H,7.93%].

[S]-4'-(2-Chloro-4-methylpentyloxycarbonyl)phenyl trans-4"-n-undecyloxycinnamate **(3.a.6)**

Yield. 68%; m.p. 55.5^{o}C; $[\alpha]_D^{25}$ = -8.93(c=2 in $CHCl_3$);ν_{max}^{nujol} 2950,2850,1720,1600,1520,1480 and 1260 cm^{-1}; δ:0.7-2.0(m,30H,3xC$\underline{H}_3$, 10xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.1-4.57(m,3H,COOC$\underline{H}_2$C$\underline{H}$Cl),6.31-8.4 (m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,71.40;H,8.27% $C_{33}H_{45}ClO_5$ requires C,71.16;H,8.09%].



^{1}H NMR trum of the compound 3.a.5.

[2S,3S]-4'-(2-Chloro-3-methylpentyloxycarbonyl)phenyl trans-4"-n-dodecyloxycinnamate (3.b.7)

Esterification of trans-4-n-dodecyloxycinnamic acid with [2S,3S]-2-chloro-3-methylpentyl 4'-hydroxybenzoate, following a procedure similar to the one described for compound 3.a.7, afforded the desired ester 3.b.7.

Yield, 64%; m.p. 53.5°C; $[\alpha]_D^{25}$ = +9.23(c=2 in $CHCl_3$);ν_{max}^{nujol} 2900,1720,1605,1510,1480,1260 and 1160 cm^{-1}; δ:0.78-2.2(m,32H,3xC$\underline{H}_3$, 11xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.12-4.78(m,3H,COOC$\underline{H}_2$C$\underline{H}$Cl),6.3-8.6(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,71.88;H,8.48% $C_{34}H_{47}ClO_5$ requires C,71.52;H,8.24%].

The physical data of the cognate preparations of other [2S,3S]-4'-(2-chloro-3-methylpentyloxycarbonyl)phenyl trans-4"-n-alkoxycinnamate [3(b)] are given below.

[2S,3S]-4'-(2-Chloro-3-methylpentyloxycarbonyl)phenyl trans-4"-n-hexyloxycinnamate (3.b.1)

Yield, 70%; m.p. 71.0°C; $[\alpha]_D^{25}$ = +9.29(c=2 in $CHCl_3$);ν_{max}^{nujol} 2900,1720,1630,1600,1520,1480,1310,1270 and 1140 cm^{-1}; δ:0.06-2.18(m,20H,3xC$\underline{H}_3$,5xC$\underline{H}$2 and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.1-4.65(m,3H, COOC$\underline{H}_2$C$\underline{H}$Cl),6.2-8.3(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,69.59;H,7.35% $C_{28}H_{35}ClO_5$ requires C,69.06;H,7.19%].

[2S,3S]-4'-(2-Chloro-3-methylpentyloxycarbonyl)phenyl trans-4"-n-heptyloxycinnamate (3.b.2)

Yield, 68%; m.p. 64.5°C; $[\alpha]_D^{25}$ = +9.17(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2900,1720,1630,1600,1460,1290,1270,1160 and 1120 cm^{-1}; δ:0.62-2.28(m,22H,$3xC\underline{H}_3$,$6xC\underline{H}_2$ and $C\underline{H}$),4.0(t,2H,$ArOC\underline{H}_2$),4.12-4.68(m,3H, $COOC\underline{H}_2C\underline{H}Cl$),6.25-8.37(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,69.66;H,7.50% $C_{29}H_{37}ClO_5$ requires C,69.53;H,7.39%].

[2S,3S]-4'-(2-Chloro-3-methylpentyloxycarbonyl)phenyl trans-4"-n-octyloxycinnamate (3.b.3)

Yield. 60%; m.p. 57.0°C; $[\alpha]_D^{25}$ = +9.01(c=2 in $CHCl_3$);ν_{max}^{nujol}. 2900,1720,1630,1600,1500,1290,1270,1140 and 1120 cm^{-1}; δ:0.72-2.12(m,24H,$3xC\underline{H}_3$,$7xC\underline{H}_2$ and $C\underline{H}$),4.0(t,2H,$ArOC\underline{H}_2$),4.1-4.7(m,3H, $COOC\underline{H}_2C\underline{H}Cl$),6.3-8.27(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,70.07;H,7.72% $C_{30}H_{39}ClO_5$ requires C,69.97;H,7.58%].

[2S,3S]-4'-(2-Chloro-3-methylpentyloxycarbonyl)phenyl trans-4"-n-nonyloxycinnamate (3.b.4)

Yield, 65%; m.p. 52.0°C; $[\alpha]_D^{25}$ = +9.08(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2900,1720,1630,1600,1290,1270,1140 and 1120 cm^{-1}; δ:0.62-2.22(m, 26H,3x$C\underline{H}_3$,8x$C\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArO$C\underline{H}_2$),4.1-4.65(m,3H,COO$C\underline{H}_2$C$\underline{H}$Cl), 6.25-8.27(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,70.44;H,7.98% $C_{31}H_{41}ClO_5$ requires C,70.39;H,7.76%].

[2S,3S]-4'-(2-Chloro-3-methylpentyloxycarbonyl)phenyl <u>trans</u>-4"-n-decyloxycinnamate (3.b.5)

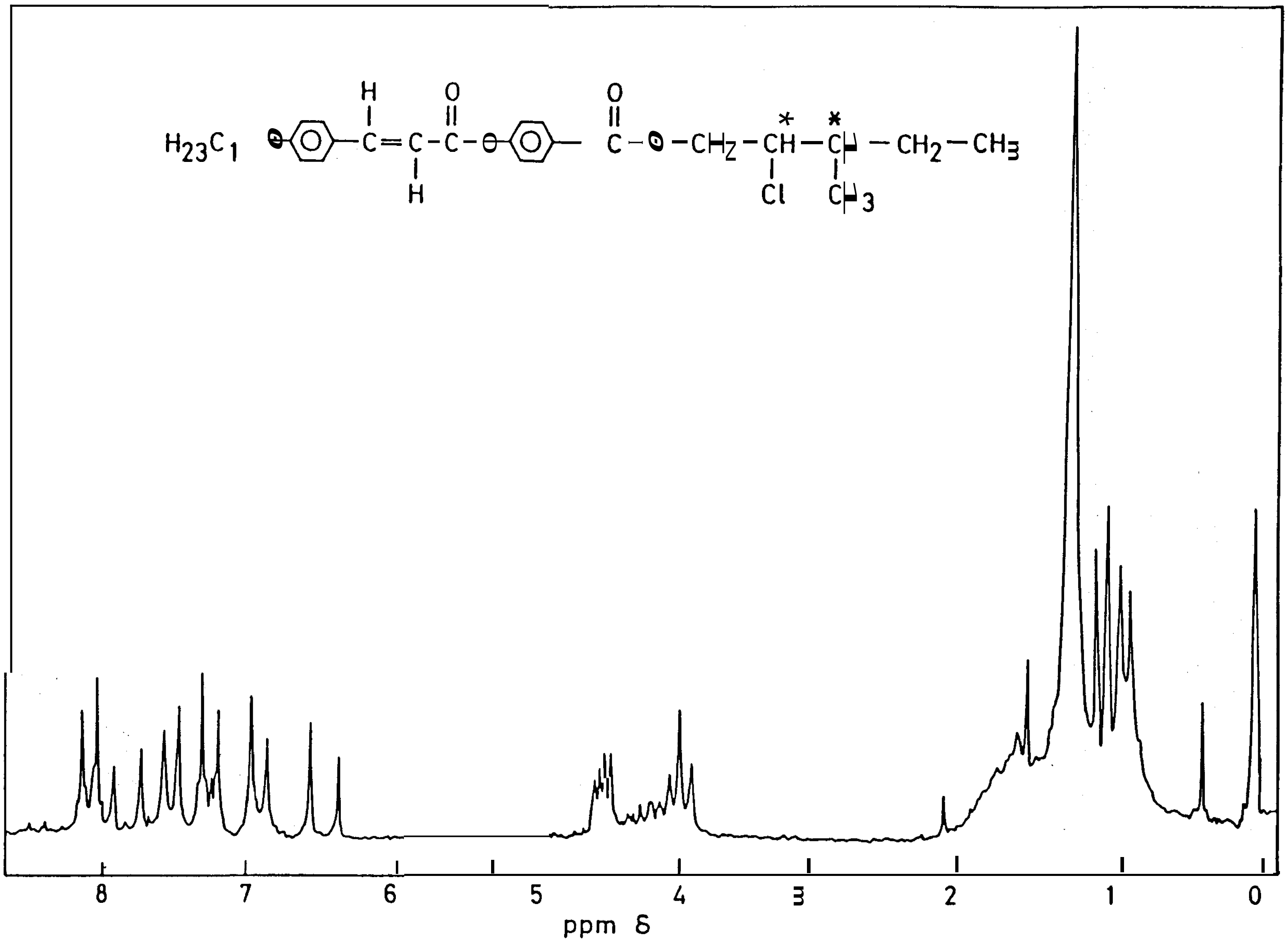
Yield, 65%; m.p. 42.5°C; $[\alpha]_D^{25}$ = +9.12(c=2 in $CHCl_3$);ν_{max}^{nujol} 2900,1720,1630,1610,1520,1460,1280,1260 and 1120 cm^{-1};δ:0.64-2.22 (m,28H,3x$C\underline{H}_3$,9x$C\underline{H}_2$ and C$\underline{H}$), 4.0(t,2H,ArO$C\underline{H}_2$), 4.13-4.66(m,3H, COO$C\underline{H}_2$C$\underline{H}$Cl),6.26-8.26(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,71.20;H,8.13% $C_{32}H_{43}ClO_5$ requires C,70.78;H,7.93%].

[2S,3S]-4'-(2-Chloro-3-methylpentyloxycarbonyl)phenyl <u>trans</u>-4"-n-undecyloxycinnamate (3.b.6)

Yield, 65%; m.p. 62.5°C; $[\alpha]_D^{25}$ = +9.18(c=2 in $CHCl_3$);ν_{max}^{nujol} 2900,1720,1630,1600,1510,1470,1280,1260 and 1120 cm^{-1}; δ:0.62-2.2 (m,30H,3x$C\underline{H}_3$,10x$C\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArO$C\underline{H}_2$),4.12-4.69(m,3H, COO$C\underline{H}_2$C$\underline{H}$Cl),6.3-8.3(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,71.00;H,8.31% $C_{33}H_{45}ClO_5$ requires C,71.16;H,8.09%].



^{1}H NMR spectrum of the compound 3.b.6.

[S]-4'-(2-Chloro-4-methylpentanoyloxy)phenyl trans-4"-n-dodecyloxycinnamate (3.c.7)

Following a procedure similar to the one described for compound 3.a.7, esterification of trans-4-n-dodecyloxycinnamic acid with [S]-4'-Hydroxyphenyl 2-chloro-4-methylpentanoate afforded the desired ester 3.c.7.
Yield, 64%; m.p. 62.0°C; $[\alpha]_D^{25}$ = -10.01(c=2 in $CHCl_3$); ν_{max}^{nujol}: 2950,1770,1720,1630,1600,1580,1510,1500,1480 and 1140 cm^{-1}; δ:0.78- 2.16(m,32H,3xC$\underline{H}_3$,11xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.5(t,1H, C$\underline{H}$Cl),6.3-8.0(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,70.83;H,8.26% $C_{33}H_{45}ClO_5$ requires
C,71.16;H,8.09%].

The physical data of the cognate preparations of other [S]-4'-(2-chloro-4-methylpentanoyloxy)phenyl trans-4"-n-alkoxycinnamates [3(c)] are given below.

[S]-4'-(2-Chloro-4-methylpentanoyloxy)phenyl **trans-4"-n-**hexyloxycinnamate (3.c.1)

Yield, 65%; m.p. 81.5°C; $[\alpha]_D^{25}$ = -10.41(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2950,1770,1720,1630,1600,1510,1500,1460,1260,1180 and 1140 cm^{-1}; δ:0.74-2.16(m,20H,3xC$\underline{H}_3$,5xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.48(t, 1H,C$\underline{H}$Cl),6.32-8.06(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,68.12;H,7.06% $C_{27}H_{33}ClO_5$ requires
C,68.57;H,6.98%].

[S]-4'-(2-Chloro-4-methylpentanoyloxy)phenyl *trans*-4"-n-heptyloxycinnamate **(3.c.2)**

Yield, 65%; m.p. 55.0°C; $[\alpha]_D^{25}$ = -10.42(c=2 in $CHCl_3$);ν_{max}^{nujol} 2950,1760,1740,1630,1620,1580,1510,1500,1470,1280,1250,1180 and 1120 cm^{-1}; δ:0.81-2.15(m,22H,3x$C\underline{H}_3$,6x$C\underline{H}_2$ and $C\underline{H}$),4.0(t,2H,$ArOC\underline{H}_2$), 4.53(t,1H,$C\underline{H}Cl$),6.31-8.0(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,69.29;H,7.34% $C_{28}H_{36}ClO_5$ requires
C,69.06;H,7.11%].

[S]-4'-(2-Chloro-4-methylpentanoyloxy)phenyl *trans*-4"-n-octyloxycinnamate **(3.c.3)**

Yield, 68%; m.p. 62.0°C; $[\alpha]_D^{25}$ = -10.81(c=2 in $CHCl_3$);ν_{max}^{nujol} 2950,1760,1720,1630,1600,1580,1500,1470,1280,1260,1180 and 1130 cm^{-1}; δ:0.72-2.22(m,24H,3x$C\underline{H}_3$,7x$C\underline{H}_2$ and $C\underline{H}$),4.0(t,2H,$ArOC\underline{H}_2$), 4.51(t,1H,$C\underline{H}Cl$),6.31-8.0(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,69.68;H,7.55 $C_{29}H_{37}ClO_5$ requires
C,69.53;H,7.39%].

[S]-4'-(2-Chloro-4-methylpentanoyloxy)phenyl *trans*-4"-n-nonyloxycinnamate **(3.c.4)**

Yield, 70%; m.p. 73.0°C; $[\alpha]_D^{25}$ = -10.28(c=2 in $CHCl_3$);ν_{max}^{nujol} 2950,1760,1720,1630,1600,1580,1520,1500,1470,1290,1260,1180 and 1160 cm^{-1}; δ:0.71-2.22(m,26H,3x$C\underline{H}_3$,8x$C\underline{H}_2$ and $C\underline{H}$),4.0(t,2H,$ArOC\underline{H}_2$), 4.51(t,1H,CHCl),6.3-8.0(m,10H,ArH and vinyl H).

[Found: C,69.55;H,7.68% $C_{30}H_{39}ClO_5$ requires C,69.97;H,7.58%].

[S]-4'-(2-Chloro-4-methylpentanoyloxy)phenyl trans-4"-n-decyloxycinnamate (3.c.5)

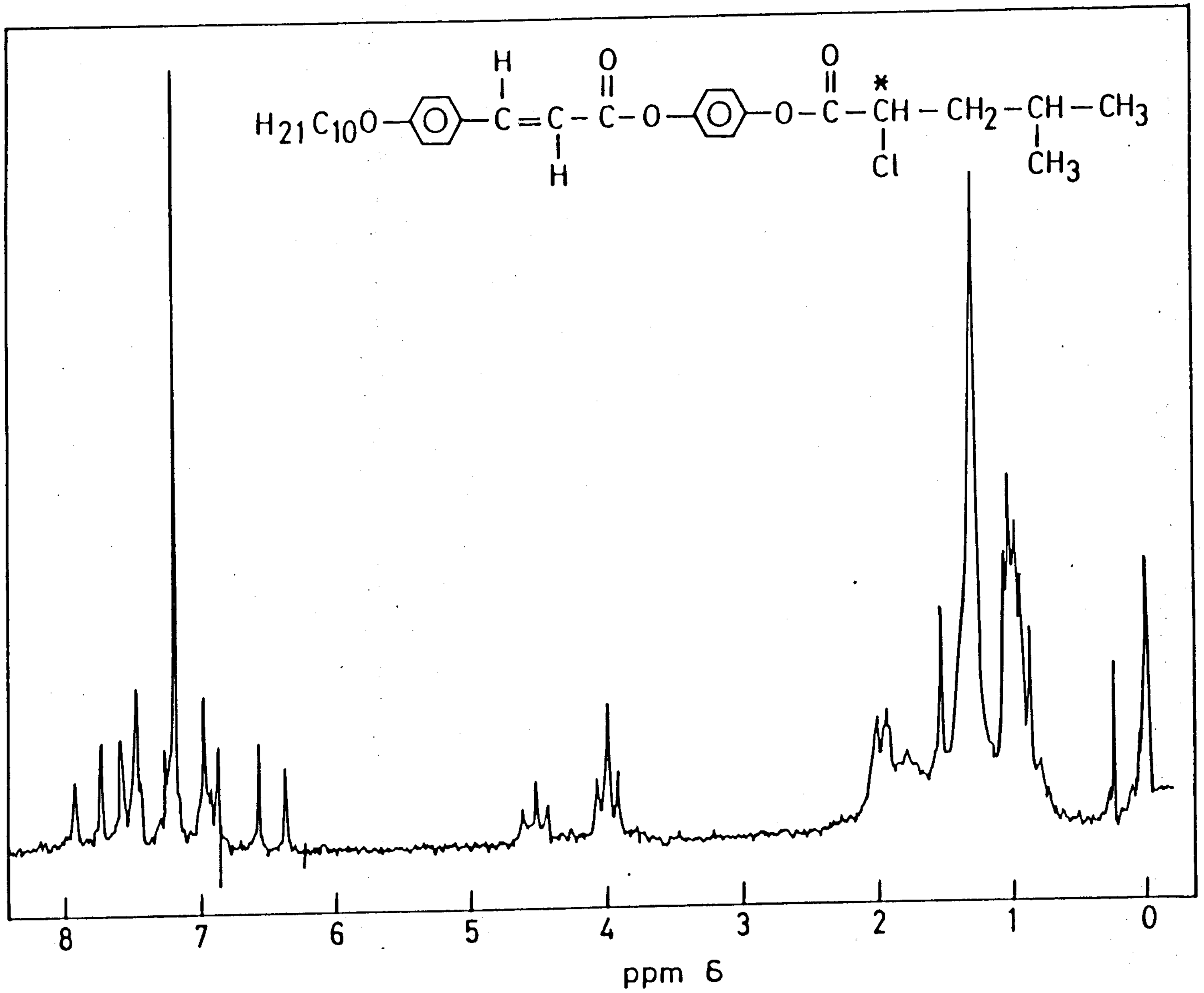
Yield, 68%; m.p. 69.0°C; $[\alpha]_D^{25}$ = -10.77(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2950,1760,1720,1630,1600,1520,1500,1460 and 1130 cm^{-1};δ:0.69-2.22 xm,28H,3xCH_3,9xCH_2 and CH),4.0(t,2H,ArOCH_2), 4.53(t,1H,CHCl),6.3-8.0(m,10H,ArH and vinyl H).

[Found: C,70.39;H,7.91% $C_{31}H_{41}ClO_5$ requires C,70.39;H,7.76%].

[S]-4'-(2-Chloro-4-methylpentanoyloxy)phenyl trans-4"-n-undecyloxycinnamate (3.c.6)

Yield, 62%; m.p. 54.0°C; $[\alpha]_D^{25}$ = -10.4(c=2 in $CHCl_3$); ν_{max}^{nujol}: 2950,1760,1720,1630,1600,1580,1510,1500,1460 and 1140 cm^{-1}; 6 : 0.71-2.29(m,30H,3xCH_3,10xCH_2 and CH),4.0(t,2H,ArOCH_2),4.53(t,1H,CHCl),6.3-8.07(m,10H,ArH and vinyl H).

[Found: C,70.47;H,8.02% $C_{32}H_{43}ClO_5$ requires C,70.78;H,7.98%].



^{1}H NMR spectrum of the compound 3.c.5.

[2S,3S]-4'-(2-Chloro-3-methylpentanoyloxy)phenyl <u>trans</u>-4"-n-dodecyloxycinnamate (3.d.7)

Following a procedure similar to the one described for the compound 3.a.7, esterification of <u>trans</u>-4-n-dodecyloxycinnamic acid with [2S,3S]-4'-hydroxyphenyl 2-chloro-3-methylpentanoate afforded the desired ester 3.d.7.

Yield, 65%; m.p. 56.5°C; $[\alpha]_D^{25}$ = +1.12(c=2 in CHCl$_3$);ν_{max}^{nujol} 2950,1720,1630,1605,1510,1500,1470 and 1130 cm^{-1}; δ:0.69-2.39(m, 32H,3xC$\underline{H}_3$,11xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.37(d,1H,C$\underline{H}$Cl), 6.3-8.0(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,71.41;H,8.24% $C_{33}H_{45}ClO_5$ requires
C,71.16;H,8.05%].

The physical data of the cognate preparations of other [2S,3S]-4'-(2-chloro-3-methylpentanoyloxy)phenyl <u>trans</u>-4"-n-alkoxycinnamates [3(d)] are given below.

[2S,3S]-4'-(2-Chloro-3-methylpentanoyloxy)phenyl <u>trans</u>-4"-n-hexyloxycinnamate (3.d.1)

Yield, 65%; m.p. 81.0°C; $[\alpha]_D^{25}$ = +1.06(c=2 in CHCl$_3$);ν_{max}^{nujol} 2950,1770,1720,1630,1600,1500,1470,1260,1180 and 1140 cm^{-1}; 6 : 0.7-2.35(m,20H,3xC$\underline{H}_3$,5xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.41(d,1H, C$\underline{H}$Cl),6.32-8.0(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,68.51;H,7.09% $C_{27}H_{33}ClO_5$ requires
C,68.57;H,6.98%].

[2S,3S]-4'-(2-Chloro-3-methylpentanoyloxy)phenyl <u>trans</u>-4"-n-heptyloxycinnamate (3.d.2)

Yield, 67%; m.p. 61.5°C; $[\alpha]_D^{25}$ = +1.08(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2950,1770,1750,1640,1610,1580,1510,1470,1140 and 875 cm^{-1}; 6: 0.7-2.38(m,22H,3xC$\underline{H}_3$,6xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.38(d,1H, C$\underline{H}$Cl),6.32-8.0(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,68.83;H,7.27% $C_{28}H_{35}ClO_5$ requires
C,69.06;H,7.19%].

[2S,3S]-4'-(2-Chloro-3-methylpentanoyloxy)phenyl <u>trans</u>-4"-n-octyloxycinnamate (3.d.3)

Yield, 648; m.p. 61.0°C; $[\alpha]_D^{25}$ = +1.18(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2950,1765,1740,1640,1605,1580,1510,1470,1140 and 875 cm^{-1}; 6 : 0.68-2.36(m,24H,3xC$\underline{H}_3$,7xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.38(d,1H, C$\underline{H}$Cl),6.3-8.0(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,69.84;H,7.55% $C_{29}H_{37}ClO_5$ requires
C,69.53;H,7.39%].

[2S,3S]-4'-(2-Chloro-3-methylpentanoyloxy)phenyl <u>trans</u>-4"-n-nonyloxycinnamate (3.d.4)

Yield, 75%; m.p. 69.0°C; $[\alpha]_D^{25}$ = +1.17(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2950,1770,1730,1630,1600,1580,1510,1500,1460 and 1140 cm$_{-1}$; δ : 0.68-2.43(m,26H,3xC$\underline{H}_3$,8xC$\underline{H}_2$ and C$\underline{H}$),4.0(t,2H,ArOC$\underline{H}_2$),4.39(d,1H, C$\underline{H}$Cl),6.21-8.03(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,69.85;H,7.68% $C_{30}H_{39}ClO_5$ requires
C,69.97;H,7.58%].

[2S,3S]-4'-(2-Chloro-3-methylpentanoyloxy)phenyl trans-4"-n-decyloxycinnamate (3.d.5)

Yield, 70%; m.p. 56.0°C; $[\alpha]_D^{25}$ = +1.06(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2950,1770,1730,1630,1600,1470 and 1130 cm^{-1}; δ:0.7-2.41(m,28H, $3xC\underline{H}_3$,$9xC\underline{H}_2$ and $C\underline{H}$),4.0(t,2H,$ArOC\underline{H}_2$),4.38(d,1H,$C\underline{H}Cl$),6.3-8.0(m, 10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,70.50;H,7.86% $C_{31}H_{41}ClO_5$ requires
C,70.39;H,7.76%].

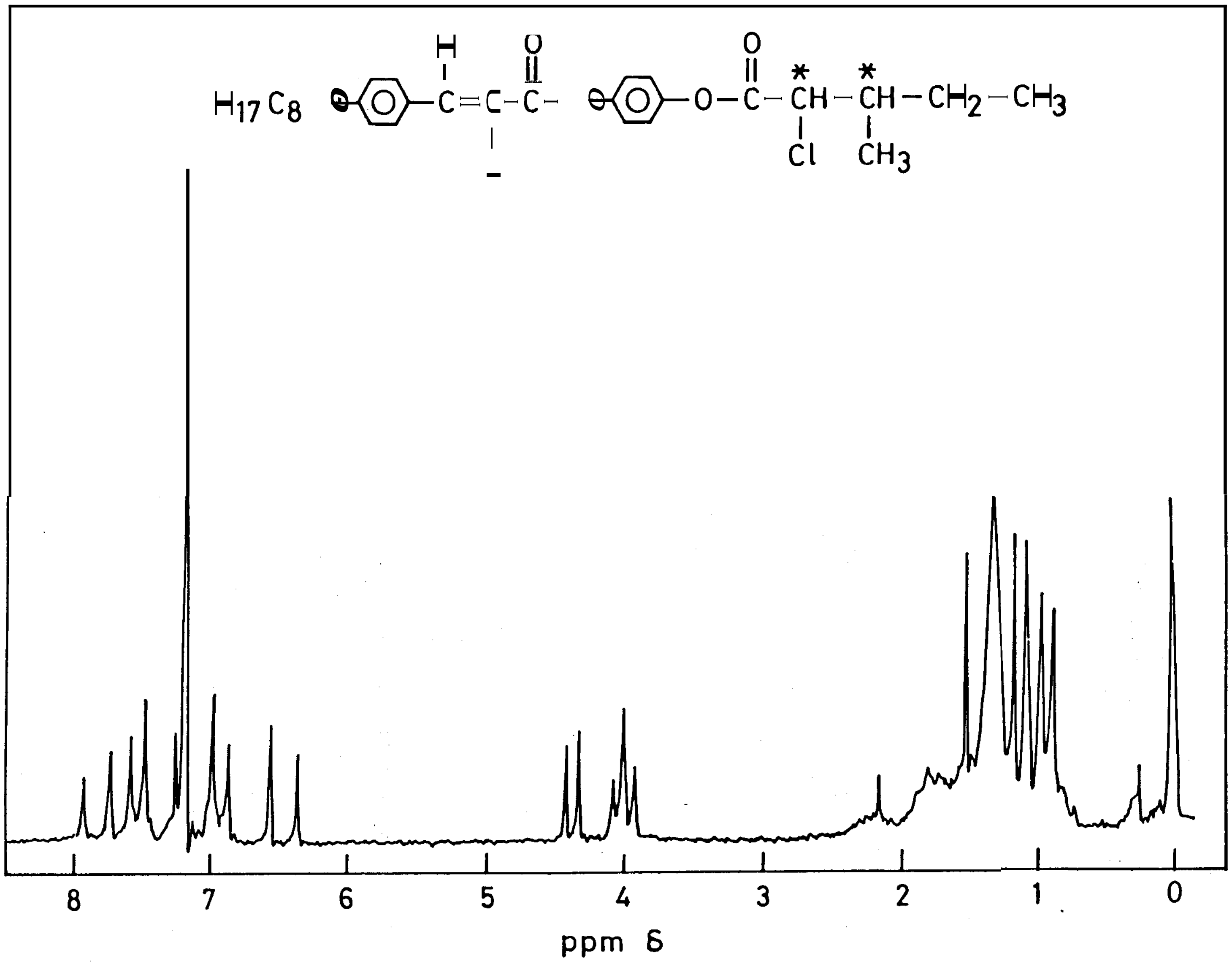
[2S,3S]-4'-(2-Chloro-3-methylpentanoyloxy)phenyl trans-4"-n-undecyloxycinnamate (3.d.6)

Yield, 70%; m.p. 50.0°C; $[\alpha]_D^{25}$ = +1.20(c=2 in $CHCl_3$);ν_{max}^{nujol}: 2950,1765,1730,1630,1600,1580,1470 and 1130 cm^{-1}; δ:0.73-2.39 (m,30H, $3xC\underline{H}_3$,$10xC\underline{H}_2$ and $C\underline{H}$),4.0(t,2H,$ArOC\underline{H}_2$),4.36(d,1H,$C\underline{H}Cl$), 6.3-8.0(m,10H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,70.42;H,8.04% $C_{32}H_{43}ClO_5$ requires
C,70.78;H,7.93%].

[2S,3S]-4'-(2-Chloro-3-methylpentyloxycarbonyl)phenyl trans-4"-n-dodecyloxy-α-methylcinnamate (3.e.7)

Following a procedure similar to the one described for the compound 3.a.7, esterification of trans-4-n-dodecyloxy-methyl-cinnamic acid with [2S,3S]-2-chloro-3-methylpentyl 4'-hydroxy-benzoate afforded the desired ester 3.e.7.



^{1}H NMR spectrum of the compound 3.d.3.

Yield, 65%; m.p. 44.8^{o}C; $[\alpha]_D^{25}$ = +8.8(c=2 in $CHCl_3$);ν_{max}^{nujol} 2950, 1730,1605,1510,1460,1260 and 1080 cm^{-1}; δ:0.71-2.12(m,32H, 3x$C\underline{H}_3$,11x$C\underline{H}_2$ and C$\underline{H}$),2.25(s,3H,C=C($C\underline{H}_3$)-),4.0(t,2H,ArO$C\underline{H}_2$),4.12-4.7(m,3H,COO$C\underline{H}_2$C$\underline{H}$Cl),6.8-8.3(m,9H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,72.08;H,8.62% $C_{35}H_{49}ClO_5$ requires
C,71.85;H,8.38%].

[2S,3S]-4'-(2-Chloro-3-methylpentanoyloxy)phenyl trans-4"-n-dodecyloxy-a-methylcinnamate (3.f.7)

Following a procedure similar to the one described for the compound 3.a.7, esterification of trans-4"-n-dodecyloxy-α-methylcinnamic acid with [2S,3S]-4'-hydroxyphenyl 2-chloro-3-methylpentanoate afforded the desired ester 3.f.7.

Yield, 64%; m.p. 44.4^{o}C; $[\alpha]_D^{25}$ = -1.82(c = 2 in $CHCl_3$);ν_{max}^{nujol} 2950,1755,1720,1600,1510,1500,1250,1165 and 1085 cm^{-1}; δ:0.5-2.0 (m,32H,3x$C\underline{H}_3$,11x$C\underline{H}_2$ and C$\underline{H}$),2.24(s,3H,C=C(CH_3)-),4.0(t,2H,ArO$C\underline{H}_2$), 4.4(d,1H,C$\underline{H}$Cl),6.8-8.0(m,9H,Ar$\underline{H}$ and vinyl $\underline{H}$).

[Found: C,71.89;H,8.45% $C_{34}H_{47}ClO_5$ requires
C,71.52;H,8.23%].

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