CHAPTER II

SYNTHESIS AND MESOMORPHIC PROPERTIES OF [S]-2-METHYLBUTYL

 $4-[4'-(\underline{trans}-4"-n-ALKOXY-\alpha-METHYLCINNAMOYLOXY)BENZOYLOXY]$

BENZOATES AND RELATED COMPOUNDS

II.1 BRIEF ACCOUNT OF MESOMORPHIC PROPERTIES OF DIESTERS CONTAINING TWO AND THREE PHENYL RINGS

Many organic compounds exhibiting liquid crystalline properties contain two phenyl rings with substituents in the para positions. On moving from two ring mesogens with one linking unit to three ring mesogens with two linking units, mesophase thermal stabilities are greatly enhanced. In a three ring system when two rings are linked by a unit which preserves conjugative interaction and molecular rigidity, e.g., -CH=N-, -CH=CH-, etc., the second linking unit can be more flexible, e.g., -CH₂-CH₂-, 0-CH₂-This implies that if a considerable portion of a lath-like etc. molecule is rigid and packs parallel to similar portions of neighbouring molecules, more flexible parts of the molecules may be constrained to lie in line with more rigid parts. However, a combination of a rigid and a flexible linking unit in three ring mesogens gives less thermally stable mesophases than those that occur with two rigid linking units.1 .

The changes in the mesomorphic properties on extension of the core in a molecule is illustrated by considering the two series of compounds II(i) and II(ii).² A comparison between the two series shows that because of the longer core of the molecules of series II(ii), both the melting points and the clearing temperatures are higher and the temperature ranges of mesophases are widened. All the homologues of series II(ii) (n=1 to n=10) show enantiotropic mesophases. The lower homologues (n=1 to n=3) exhibit only a chiral nematic phase. However, this phase exists over a wide range of temperature (about $125^{\circ}C$) for these homo-

$$H_{2n+1}C_n O - O - CH_2 - CH_2 - CH_3$$
 II (i)

 $n = 10, C 44.0 S_{C} * 51.5 S_{A} 63.5 I$



 $n = 10, C 92.0 S_{C} * 128.5 S_{A} 168.0 N^{*} 190.01$

logues. When $n \ge 4$ a smectic A phase is observed in addition to the chiral nematic phase. In series II(i) the chiral nematic phase is exhibited by only two homologues (n=6 and n=7). The smectic A phase is observed for compounds with n \ge 8. Although the S_C* phase exists for the homologues with n \ge 8 in both series, their temperature ranges are different.

The decyloxy compound of series II(i) has a thermal range for the S_{C^*} phase equal to 7.5 °C, whereas the corresponding homologue of series II(ii) has a range of 36.5 °C. Thus, temperature ranges of S_{C^*} phase have indeed been widened by increasing the length of the core of the molecule.

Similar conclusions can be drawn by considering series II(iii) and II(iv).³ There is no chiral nematic phase in both the series of compounds. It can be seen that the additional benzoyloxy group has increased the clearing temperature by about 110° C and the $S_{C^{\star}} - S_{A}$ transition temperature by about 90° C in the decyloxy homologue. In Series II(ii) the additional third ring induced a chiral nematic phase in the homologue n = 10. In the present case the more ordered smectic phases below the $S_{C^{\star}}$ phase observed in the higher homologues (n = 11,12) of Series II(ii) are eliminated in the corresponding homologues of Series II(iv).

Dewar and Goldberg⁴ synthesised two isomeric homologous series of esters, viz., the p-phenylene bis-p-alkoxybenzoates II(v) [X = OR] and the di-p-alkoxyphenyl terephthalates II(vi)[X = OR]. The observed higher N-I transition temperatures of the





 $n = 10, C 62.6 S_{C} \times 105.9 S_{A} 149.3 I$





quinol esters [II(v)] than those of the terephthalic esters [II(vi)] have been explained by associating the thermal stabilities with the mutual conjugation between the alkoxy group and the carbonyl of the ester linkage. This conjugation is present in the former compounds [II(v)] but absent in the latter [II(vi)]. The extent to which the N - I temperatures of the quinol esters exceed those of the corresponding terephthalic esters were greatest when the substituent X donated electrons readily by conjugation with the ring. For example, when $X = OCH_3$ conjugation can extend up to the -CO.O- function in quinol esters but not so in the terephthalic esters where the ester function is -0.0C-. Thus, the p-phenylene ring can promote the liquid crystal formation by permitting conjugative interactions between substituents. However, the difference in the N-I transition temperature was much more than expected when $X = NO_2$ (strongly electron withdrawing group), resulting in a monotropic phase in terephthalic esters.

Bristol and Schroeder⁵ synthesised p-phenylene bismethoxycinnamate and observed that the N-I transition temperature increased by more than 37° C when compared to the transition temperature of p-phenylene bis-methoxybenzoate The additional vinyl group increases molecular length and polarisability. An introduction of a methyl group at α -position of a cinnamate will be discussed later.

Byron et al.^{6,7,8} have demonstrated that a lateral dipolar substituent has different effects on the thermal stability of the nematic and the smectic phases. Several series of compounds containing halogen as a lateral substituent have been studied. In these series of compounds as the aromatic hydrogen is replaced by chlorine, bromine or iodine respectively, the N-I transition temperature decreases monotonically. This has been attributed to regular decrease in the intermolecular forces with increasing size of the substituent leading to a corresponding increase in the mean intermolecular separations. The effect of lateral substituents on $S_{C\star}$ phase has already been discussed in dipolar Arora et al.⁹ have introduced a methyl group in the I. Chapter central phenyl ring of p-phenylene bis-alkoxybenzoates [II(V)]. The diminished thermal stabilities of the mesophases as compared to the unsubstituted compound have been attributed to the in the anisotropy of polarisability. decrease This is a consequence of a decrease in the coplanarity of the conjugated groups in the molecule. An increase in the breadth of a molecule also reduces the thermal stability. Schroeder¹⁰ has reported a few homologous series with laterally substituted chloro and methyl groups in the central phenyl ring. In the dodecyloxy homologue of p-phenylene bis-alkoxybenzoate [II(v), $X = OC_{12}H_{25}$], the methyl group reduces the clearing temperature by $34^{\circ}C$ and the S - N transition temperature by $66^{\circ}C$. The melting point is also depressed by 28°C. The unsubstituted parent octyloxy homologue exhibits S phase which disappears in the corresponding methyl substituted compound. The change from a lateral methyl group to a lateral chloro group involves only a dipolar or a polarisability change, the size of chloro and methyl groups being more or less the same.¹¹ The mesophase transition temperatures are not much affected with this change.

II-2. RESULTS AND DISCUSSION

In an effort to obtain S_{C^*} phase at relatively low temperatures and study its properties upon changes in the molecular structure, a number of compounds were synthesised. These include [S]-2-methylbutyl 4- $[4'-(\underline{trans}-4''-n-alkoxycinnamoyloxy)$ benzoyloxy] benzoates and [S]-2-methylbutyl 4- $[4'-(\underline{trans}-4''-n-alkoxy-\alpha-methyl cinnamoyloxy)$ benzoyloxy]benzoates. In these compounds the central phenyl ring was also substituted with a methyl or a chloro group'. The transition temperatures of these compounds are given in table 1. An examination of this table indicates that three compounds exhibit the S_{C^*} phase. Out of these, two are enantiotropic while the other exhibits a monotropic S_{C^*} phase. Compound 2.d.6 exhibits the S_{C^*} phase at a relatively low temperature. Hence an investigation of the homologous series containing this compound was undertaken.

All the compounds were prepared according to the schemes shown in figures 1,2 and 3. The <u>trans</u>-p-n-alkoxycinnamic acids were prepared following a procedure described by Gray and Jones.¹² The <u>trans</u>-p-n-alkoxy-a-methylcinnamic acids were prepared according to the method described by Johnson.¹³ '4-Hydorxy-3- methylacetophenone was obtained by a Friedel-Craft's acylation reaction with acetyl chloride on O-cresol. However, 3-chloro-4-hydroxyacetophenone was obtained by a Fries rearrangement of 2-chlorophenyl acetate. The 'chloro and methyl substituted aryl methyl ketones were oxidised to their corresponding carboxylic acids using ice-cold sodium hypobromite solution in 1,4-dioxan⁵. The benzylation reactions were carried out using sodium ethoxide as a

Table 1

Transition temperatures (^oC) of



Compound number	х	Y	C	s _{C*}	SA	N*	I
2.a.6	н	Н	•	105.0 .	167.0 .	203.0 .	205.0 .
2.b.6	Н	CH3		132.0 -	•	148.5	153.0
2.c.6	Н	Cl		104.0 (.	93.0) .	148.0 .	157.0 .
2.d.6	CH ₃	H		64.5 .	68.5 .	- 151.5 -	
2.e.6	CH ₃	CH3		68.0 -		101.5	113.0 .
2.f.6	CH3	C1	•	56.5 -		96.0 .	113.5 .
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$$C_{6}H_{5}CH_{2}O \longrightarrow C-O-CH_{2}-CH-CH_{2}-CH_{3} \xrightarrow{H_{2}/5\%} Pd-C$$

 $I_{1,4-dioxan}$







FIGURE 1







FIGURE 2

(contd.)



$$\begin{array}{ccc} H_{2}/5\% & Pd-C \\ \hline H_{2}/5\% & Pd-C \\ \hline H_{0} & O \\ \hline CH_{3} \\ \hline CH_$$



(contd.)







base in ethanol solutions. Hydrogenolyses were performed in 1,4dioxan solutions using 5% palladium on carbon catalyst at room temperature. All the esterification reactions were carried out by condensing the appropriate carboxylic acid chlorides with substituted phenols in pyridine solution at room temperature.

As mentioned earlier, all the six compounds in table 1 exhibit chiral nematic and smectic A phases except the compound 2.d.6. However, only three compounds show a chiral smectic C phase. When X=H range of S_A phase is maximum for Y = H (compound 2.a.6). Similarly, when X = CH₃ the range of S_A phase is widest for Y = H (compound 2.d.6). The range of the N* phase follows an ascending order on going from compound 2.a.6 to 2.f.6. Amongst all the six compounds the melting point is highest Eor compound 2.b.6 and least for compound 2.f.6.

Leslie¹⁴ has synthesised a homologous series of compounds II(vii). The decyloxy homologue of this series can be compared with $[SI-2-methylbutyl 4-[4'-(\underline{trans}-4"-n-decyloxycinnamoyloxy)$ benzoyloxy]benzoate (2.a.6). The compound 2.a.6 has an additional benzoyloxy group compared to the decyloxy homologue of series II(vii). This results in an enhancement of the mesophase transition temperatures to a considerable extent. The thermal stabilities of S_A and S_{C*} phases increase by about 108°C and 96°C respectively. The range of S_{C*} phase has increased by about 50°C. A chiral nematic phase with a range of 2°C has also been induced in compound 2.a.6. [SI-2-Methylbutyl 4-[4'-($\underline{trans}-4$ "-n-decyloxycinnamoyloxy)-3'-methylbenzoyloxy]benzoate (2.b.6) has a lateral



 $n = 10, C 60.2 S_{C} * 71.1 S_{A} 95.2 I$



C 105.0 S_C* 167.0 S_A 203.0 N* 205.0 I

methyl group in the central phenyl ring. A comparison with the unsubstitued compound shows that in the methyl substituted compound the clearing temperature is reduced by $52^{\circ}C$ and the S_b -N* transition temperature by 54.5 $^{\circ}$ C. The melting point however, has increased by $27^{\circ}C$ and the $S_{C\star}$ phase has been eliminated. A Drieding model of this compound with a lateral substituent in the central ring shows an increase in its breadth. [S]-2-Methylbutyl 4-[3'-chloro-4'-(trans-4"-n-decyloxycinnamoyloxy)benzoate (2.c.6) has a chlorine in the central ring in place of methyl group of compound 2.b.6. Enhancement in the lateral dipole of the molecule can be expected without an increase in the breadth of the molecule when a chloro group replaces a lateral methyl group. The - N* and N* - I transition temperatures of compound 2.c.6 are S, only slightly affected compared to the corresponding transition temperatures of compound 2.b.6. However, the ${\rm S}^{}_{\rm C\star}$ phase present in the unsubstituted compound 2.a.6 persists as a monotropic phase in the chloro substituted compound 2.c.6. This phase, as was seen earlier, is absent in the methyl substituted compound 2.b.6.

A detailed comparison of transition temperatures of <u>trans</u>-pn-alkoxycinnamic acids and <u>trans</u>-p-n-alkoxy-a-methylcinnamic acids has been reported.¹⁵ The a-methyl group of the central linkage has a pronounced effect on the types as well as the transition temperatures of the mesophases when compared with those of the unsubstituted compounds. The melting points are reduced by about 40- 50° C and the smectic phases are eliminated in the a-methyl substituted compounds. The a-methyl group fills the space within the molecule without any substantial broadening. This thickening effect is considerably enhanced due to steric interaction between the methyl group and the ortho ring protons.¹⁶

A comparison of [S]-2-methylbutyl 4-[4'-(trans-4"-n-decyloxy- $<math>\alpha$ -methylcinnamoyloxy)benzoyloxy]benzoate (2.d.6) and the compound without the methyl group at the a-position (2.a.6) brings out the following features. The introduction of the methyl group results in a lowering of the melting points by about 40°C, and elimination of the chiral nematic phase. The S_{C*} - S_A transition temperature however is decreased by about 100°C, thus reducing the range of S_{C*} phase from 62°C in compound 2.a.6 to 4°C in compound 2.d.6.

[S]-2-Methylbutyl 4-[4'-(trans-4"-n-decyloxy- α -methylcinnamoyloxy) 3'- methylbenzoyloxy benzoate (2.e.6) and [SI-2-methyl 4-[3'-chloro-4'-(trans-4"-n-decyloxy-a-methylcinnamoyloxy) bu ty l benzoyloxylbenzoate (2.f.6) show a similar decrease in the transition temperatures compared to the corresponding cinnamates without the methyl group at the α position (2.b.6 and 2.c.6). Thus the melting point of compound 2.e.6 is lowered by 64°C when compared to that of compound 2.b.6 while the $S_A - N^*$ and the N^*-I transition show a decrease of 47°C and 40°C respectively. So temperatures also, the melting point of. compound 2.f.6 is less by 47.5°C while $S_{n}-N^{*}$ and $N^{*}-I$ transition temperatures are reduced by $52^{\circ}C$ and 43.5°C respectively than the corresponding transition temperatures of compound 2.c.6.

An introduction of a methyl (compound 2.e.6) or a chloro

(compound 2.f.6) group in the central phenyl ring of the <u>trans</u>-pn-alkoxy-a-methylcinnamates results in lowering the mesophase transition temperatures. The extent of decrease is about the same as observed upon introduction of the lateral groups in <u>trans</u>-p-nalkoxycinnamates (compounds 2.a.6, 2.b.6 and 2.c.6). However, the S_{C^*} phase present in the unsubstituted compound 2.d.6 is eliminated in the methyl as well as the chloro substituted compounds (2.e.6 and 2.f.6).

As was observed, the thermal stability of S_{C^*} phase of compound 2.a.6 is depressed by $74^{\circ}C$ in the corresponding chloro substituted compound 2.c.6. Considering this, an absence of S_{C^*} phase in compound 2.f.6 is not entirely unexpected. A very small deviation in the N*-I transition temperatures of compounds 2.e.6 and 2.f.6 compares well with the observations made by $Gray^{7,17}$ and Schroeder¹⁰ about the substituted 4.4'-di-(p-n-alkoxybenzylideneamino) biphenyls and the substituted p-phenylene bis-alkoxybenzoates respectively.

A combined effect of introduction of a methyl group on the double bond and a chloro group on the central phenyl ring is seen by comparison of compounds 2.a.6 and 2.f.6. The addition of these groups lower the S_A -N* and N*-I transition temperatures by 107°C and 91.5°C respectively. Also an S_{C*} phase having a range of 62°C in compound 2.a.6 is totally suppressed in compound 2.f.6.

The transition temperatures along with their enthalpies for the homologous series of [S]-2-methylbutyl 4-[4'-(trans-4"-nalkoxy- α -methylcinnamoyloxy)benzoyloxy]benzoates are given in table 2. All the eight compounds (n=5 to n=12) have a fairly large range of S_A phase (~75°C). Compounds 2.d.1, 2.d.2 and 2.d.3 exhibit S_A and N* phases only. The S_{C*} phase is injected into the series from the octyloxy homologue onwards. A monotropic S_{C*} phase is observed for compounds 2.d.4 and 2.d.5, while the remaining homologues (compounds 2.d.6, 2.d.7, 2.d.8) are enantiotropic. A plot of the number of carbon atoms in the alkoxy chain versus the transition temperatures is shown in figure 4. It is seen that N*-I transition temperatures decrease gradually on increasing the carbon chain length. A slow rise is seen for the S_A-N* transition temperatures. The S_{C*}-S_A transition temperatures also show a general increase with increasing carbon chain length.

The mesophase textures were observed using samples sandwiched between a glass slide and a cover slip, under a polarising microscope. A focal-conic fan texture of S_A phase and a banded focalconic fan texture of S_C^* phase of compound 2.d.8, obtained on slow cooling of isotropic liquid are shown in plates II.1 and II.2. respectively.

The temperature variations of the spontaneous polarisation (P_s) for compound 2.d.7 and 2.d.8 are shown in figure 5. The values of P_s at T-T_c =-5^OC are: 17 μ C/m² for compound 2.d.7 and 14 μ C/m² for compound 2.d.8.

In 1988, Nakauchi and Kageyama³ synthesised a homologous series of compounds II(viii). The molecular structure of these



Plate II.1: The focal-conic texture of S_A phase of the compound 2.d.8 at 145°C. (x 350)



Plate II.2: The banded focal-conic texture of S_C* phase of the compound 2.d.8 at 71°C. (x350).

Table 2

Transition temperatures ($^{\mathrm{O}}$ C) and heats of transition (Kcals/mole) of

	(CH ₃		ì		CH ₃
Compound number	n	С	s _{C*}	S _A	N*	I
2.d.1	5,	. •	71.5 - 6.36		147.5 . 0.27	167.5 . 0.13
2.d.2	6		76.0 - 5.0	•	152.0 . 0.33	165.0 . 0.11
2.d.3	7	•	81.5 – 6.39	•	151.5 . 0.42	159.5 . 0.13
2.d.4	8	•	77.0 (. 4.84	40.0) .	152.5 . 0.40	158.0 . 0.13
2.d.5	9	•	71.0 (. 5.16	67.5) .	153.0 . 0.38	155.0 . 0.10
2.d.6	10	•	64.5 . 5.05	68.5 .	151.5 - 0.98	
2.d.7	11	•	67.0 . 5.54	83.5 .	151.0 – 0.99	
2.d.8	12		65.0 . 6.20	81.0 .	150.5 - 1.07	



Figure 4: A plot of transition temperatures versus the number of carbon atoms in the alkoxy chain for the homologous series 2(d).



Figure 5: A plot of P as a function of relative temperature for compounds 2.d.7 (O) and 2.d.8 (Δ)



$$H_{2n+1}c_{n0} - \bigcirc CH = c - c - 0 - \bigcirc C - 0 - \bigcirc C - 0 - c + 2 - c + - c + 2 - c + 3$$

FIGURE 6

Table 3

n	с		s _{C*}		s _A		N*		I
9	•	78.5	•	93.1	•	178.9	•	189.4	•
10		77.5		117.1	•	178.2	•	185.0	•
11	•	76.7	•	128.0	•	177.1	•	181.7	
12	•	78.1	• .	139.0	•	176.7	•	179.4	
14	•	76.7		142.0	•	173.1	-		
16	•	72.6		141.0	•	170.3	-		

Transition temperatures (o C) for series II(viii)

compounds differ from that of compound in table 2 (shown in figure 6), with respect to the position of $-CH=C(CH_3)$ - group. In the homologous series discussed earlier this group lies in the central part of the core whereas in this series II(viii) it is at the end the core. The transition temperatures of the series of II(viii) shown in table 3. All the transition temperatures are higher are than the corresponding temperatures of the homologues of the former series. The $S_{C^{\star}}-S_{A}$ transition temperatures are higher by about $45-60^{\circ}$ C and the temperature range of S_{C*} is also larger by 35-45[°]C. Within the homologous series, range of S_{C*} phase increases with increasing carbon chain from about $15^{\circ}C$ for n = 9 to about $70^{\circ}C$ for n = 16.

EXPERIMENTAL

II.3 GENERAL METHODS OF INVESTIGATION

Anhydrous solvents used were prepared from commercial solvents following the standard procedures. All solid starting materials were crystallised before use. The melting and boiling points reported herein are all corrected and are in degree Celsius. Analytical tlc were carried out using silica gel supplied by BDH India Ltd. and the spots rendered visible by brief exposure to iodine vapour. Readymade tlc aluminium cards coated with silica gel with a fluorescent indicator manufactured by Fluka AG. were also used. Switzerland. The spots on these plates were rendered visible by exposing them to a DESAGA HP-UVIS lamps at 254 and 366 nm. Silica gel (60-120 mesh, ACME, India) was used for column chromatography.

Infrared absorption spectra were recorded on Shimadzu IR-435 The ultraviolet and visible absorption spectra spectrophotometer. were obtained on a Hitachi U-3200 spectrophotometer. The proton magnetic resonance spectra were taken on a Bruker WP80SY FΤ NMR spectrometer using tetramethylsilane as an internal reference The chemical shifts are quoted as δ (parts per million) standard. downfield from the reference. CDCl₃ was used as a solvent for all compounds unless otherwise stated. Elemental analyses were the carried out on a CARLO-ERBA 1106 elemental analyser. Specific rotations were measured either on a ROUSSEL JOUAN digital polarimeter TYPE 71 or on an optical activity AA-1000 polarimeter a t 5890[°]A sodium line.

The transition temperatures were measured under a Leitz Laborlux 12 POL polarising microscope equipped with a Mettler FP52 heating stage and a FP5 controller, by sandwiching samples between a glass slide and a cover slip. Simultaneously the mesophase textures were also observed. The enthalpies of transitions were determined from thermograms obtained on a Perkin-Elmer, Model DSC-2 or DSC-4 differential scanning calorimeter and are reported in kcals/mole. The heating and cooling rates were 5[°]/min. The calorimeters were calibrated using pure indium as a standard.

4-n-Decyloxybenzaldehyde

A solution of sodium ethoxide was prepared by dissolving sodium (2.3 g, 0.1 g atom) in absolute ethanol (100 ml). 4-Hydroxybenzaldehyde (12.2 g, 0.1 mol) was added to it. This mixture was stirred and refluxed for thirty minutes. 1-Bromodecane (24.3 g, 0.11 mol) was then added to it. The refluxing and stirring was continued for a further period of six hours. Ethanol was removed by distillation under reduced pressure, the residue was poured into ice cold water. This was extracted with ether (300 ml), washed with 10% aqueous sodium hydroxide (3x100 ml), water (3x100 ml) and dried (Na_2SO_4). Removal of the solvent afforded a liquid which was distilled under reduced pressure to give pure 4-ndecyloxybenzaldchyde (24.0 g, 70%). b.p.135-140°C/0.1 mm. (Reported¹² b.p. 185°C/4 mm).

The physical data of the cognate preparations of other 4-nalkoxybenzaldehydes are given in table 4.

trans-4-n-Decyloxycinnamic acid

This was prepared following the procedure of Gray and Jones. ¹² Thus, a mixture of 4-n-decyloxybenzaldehyde (15.7 g, 0.06 mol), malonic acid (12.5 g, 0.12 mol), pyridine (25 ml) and a few drops of piperidine was heated at 100° C in an oil bath for three hours. The mixture was then poured on to ice and concentrated hydrochloric acid. The precipitate so obtained was filtered, washed with water and dried. This was crystallised alternately from acetic acid and ethanol until the melting point was constant. (16.4g, 90%). m.p. 136.0°C (Reported¹² m.p. 136.0°C).

Table 4

Physical constants of 4-n-alkoxybenzaldehydes

			·
R n-alkyl	Observed b.p. ^O C/mm	Reported b.p. ^O C/mm	Reference
-C ₅ H ₁₁	130 -134/2	163 - 164/10	18
-C ₆ ^H 13	142 - 145/2	177 - 180/10	18
-C7 ^H 15	137 - 139/4	143 - 146/5	18
-C ₈ H ₁₇	155 - 157/2	141 - 144/0.1	18
- ^C 9 ^H 19	172 - 175/1	163 - 166/0.5	18
-C ₁₀ ^H 21	135 - 140/0.1	185/4	12
-C ₁₁ H ₂₃	180 - 183/1	185/1	16
-C ₁₂ ^H 25	160 - 163/1	194/8	12

$$RO - C_6H_4 - CHO$$

The physical data of the cognate preparations of other trans - 4 - n-alkoxycinnamic acids are given in table 5.

trans-4-n-Decyloxy-a-methylcinnamic acid

This was prepared following the procedure of Johnson. ¹³ Thus a mixture of 4-n-decyloxybenzaldehyde (15.7g, 0.06 mol), propionic anhydride (9.75g, 0.075 mol) and potassium propionate 6.729, 0.06 mol) was heated in an oil bath at 130° C for thirty hours. The warm reaction mixture was poured on to a stirred mixture of concentrated hydrochloric acid and ice cold water. The pale brown semi-solid hardened after about thirty minutes. It was filtered off, washed with water, dried and recrystallised from petroleum ether (b.p. $60-80^{\circ}$ C) (15.4g, 81%). m.p. 79.0°C (Reported¹⁵ m.p. 79.5°C).

The physical data of the cognate preparations of other <u>trans</u>-4-n-alkoxy-a-methylcinnamic acids are given in table 6.

Ethyl 4-benzyloxybenzoate

A solution of sodium ethoxide was prepared by dissolving sodium (4.6 g, 0.2 g atom) in absolute ethanol (150 ml). Ethyl 4hydroxybenzoate (33.2 g, 0.2 mol) was added to **it**. The resulting mixture was stirred and refluxed for thirty minutes. Benzyl chloride (27.8 g, 0.22 mol) was then added to **it**. The stirring and refluxing was continued for a further period of twelve hours. Excess ethanol was distilled off, the residue poured into cold water and extracted with ether (3x100 ml). The combined ethereal

Table 5

Physical constants of <u>trans</u>-4-n-alkoxycinnamic acids

R n-alkyl	Observed m.p. C	Reported m.p. C	Reference
- ^C 5 ^H 11	140.0	139.5	12
-C ₆ H ₁₃	152.0	153.0	12
-C7 ^H 15	148.0	148.0	12
-C ₈ H ₁₇	147.0	146.0	12
- ^C 9 ^H 19	138.0	138.5	12
-C ₁₀ ^H 21	136.0	136.0	12
-C ₁₁ H ₂₃	127.0	-	12
-C ₁₂ H ₂₅	132.0	132.0	. 12

 $RO - C_{6}H_{4} - CH = CH - COOH$

Table 6

Physical constants of <u>trans</u>-4-n-alkoxy-a-methylcinnamic acids

R n-alkyl	Observed m.p. C	Reported m.p. C	Reference
-C ₅ H ₁₁	95.0	97.0	15
-C ₆ H ₁₃	102.0	102.0	15
- ^C 7 ^H 15	93.5	93.0	15
-C ₈ ^H 17	82.0	83.0	15
-C ₉ ^H 19	84.5	82.5	15
-C ₁₀ H ₂₁	79.0	79.5	15
-C ₁₁ H ₂₃	88.0	88.2	15
-C ₁₂ H ₂₅	85.5	86.0	15

 $RO - C_6H_4 - CH = C(CH_3)COOH$

solution was washed with 10% aqueous sodium hydroxide (2x75 ml)and water (2x60 ml). The ethereal solution was dried (Na_2SO_4) and the solvent removed. The solid residue was crystallised from ethanol (40.0 g, 78%).m.p. 46.0°C (Reported¹⁹ m.p. 46.0°C).

4-Benzyloxybenzoic acid

A mixture of ethyl 4-benzyloxybenzoate (30.0 g, 0.12 mol), potassium hydroxide (8.6 g, 0.15 mol), water (10 ml) and ethanol (50 ml) was refluxed for six hours. Ethanol was removed by distillation and the residue poured into cold water. This was acidified by adding cold, concentrated hydrochloric acid. The white precipitate so obtained was filtered off, washed with water and dried. This was then crystallised from ethanol (25.0 g, 90%)m.p. 191.2°C (Reported ²⁰ m.p. 188.0°C).

[S]-2-Methylbutyl 4-benzyloxybenzoate

A mixture of 4-benzyloxybenzoic acid (15.0 g, 0.065 mol) and thionyl chloride (50 ml) was refluxed for six hours. Excess thionyl chloride was removed by distillation under reduced pressure. A solution of (S)-2-methylbutanol (6.3 g, 0.07 mol) in anhydrous pyridine (40 ml) was added to the crude acid chloride. This mixture was stirred at room temperature for sixteen hours and then poured on to a mixture of ice and concentrated hydrochloric acid. This was extracted with ether (2x100 ml). The combined ethereal solution was washed successively with water (2x50 ml), 10% aqueous sodium hydroxide (2x60 ml) and water (2x50 ml). It was then dried (Na_2SO_4) and the solvent removed. The crude product was chromatographed on silica gel and eluted with 50% chloroform-petroleum ether (b.p. $60-80^{\circ}C$) mixture. Removal of solvent from the eluate afforded a viscous liquid. (13.5 g, 69%). $[\alpha]_D^{25} = +3.3(c=2 \text{ in CHCl}_3)$. $v_{max}^{neat} 3000,1710,1610,1580, 1280,1250$ and 1150 cm^{-1} . $\delta:0.63-2.3(m,9H,2x-CH_3,CH_2)$ and $CH),4.15(dd,2H, COOCH_2),5.12(s,2H,PhCH_2OAr),6.91-8.15(m,9H,ArH)$.

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[Found: C,76.15;H,7.63% C<sub>19</sub>H<sub>22</sub>O<sub>3</sub> requires
C,76.50;H,7.38%].
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[S]-2-Methylbutyl 4-hydroxybenzoate

A mixture of [S]-2-methylbutyl 4-benzyloxybenzoate (12.0 g, mol) dissolved in 1,4-dioxan (100 ml) and 5% Pd/C catalyst 0.04 g) was stirred in an atmosphere of hydrogen till the cal-(6.0)culated quantity of hydrogen was absorbed. The reaction mixture filtered and dioxan removed by distillation under was reduced pressure. The residual product obtained was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the 'eluate afforded a viscous liquid (7.5g, 90%). $[\alpha]_{D}^{25} = +4.69(c=2)$ in CHCl₃). v_{max}^{neat} 3375,2940,1710,1605,1510 and 1290 cm⁻¹. δ :0.78-2.0(m,9H,2xC \underline{H}_3 ,C \underline{H}_2 and C \underline{H}),4.2(d,2H,COOC \underline{H}_2),6.9(d,2H,ArH),7.2(s, 1H,O<u>H</u>),7.9(d,2H,ArH).

[Found: C,69.54;H,7.50% C₁₂H₁₆O₃ requires C,69.23;H,7.69%].

[S]-2-Methylbutyl 4-(4'-benzyloxybenzoyloxy)benzoate

A mixture of 4-benzyloxybenzoic acid (6.85 g, 0.03 mol) and thionyl chloride (30 ml) was refluxed for six hours. Thionyl chloride was then removed by distillation under reduced pressure. A solution of [S]-2-methylbutyl 4-hydroxybenzoate (6.86 g, 0.033 mol) in anhydrous pryidine (25 ml) was added to the crude acid chloride. This mixture, protected from moisture through anhydrous calcium chloride guard tube, was stirred at room temperature for hours and then poured on to a mixture of ice and sixteen concentrated hydrochloric acid. This was extracted with ether ml) the combined ethereal solution was washed (2x100)and successively with water (2x40 ml), 10% aqueous sodium hydroxide (2x60 ml) and water (2x50 ml). It was then dried (Na_2SO_4) and the solvent removed. The crude product obtained was crystallised from acetonitrile (8.0 g, 64%). m.p. 99.0°C. $[\alpha]_{D}^{25} = +2.64$ (c=2 in $v_{\text{max}}^{\text{nujol}}$ 2940,1725,1700,1610,1520,1460 and 1275 cm⁻¹. 6: CHCl₂). $0.94-2.28(m,9H,2xCH_3,CH_2 \text{ and } CH), 4.35(dd,2H,COOCH_2), 5.18(s,2H,$ $PhCH_{2}OAr)$, 7.02-8.6(m,13H,ArH).

[Found: C,74.60;H,6.52% ^C26H26O5 requires C,74.64;H,6.22%]

[S]-2-Methylbutyl 4-(4'-hydroxybenzoyloxy)benzoate

A mixture of [S]-2-methylbutyl 4-(4'-benzyloxybenzoyloxy)benzoate (6.0 g, 0.014 mol) dissolved in 1,4-dioxan (100 ml) and 5% Pd/C catalyst (3.0 g) was stirred in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. The reaction mixture was then filtered and dioxan removed by distillation under reduced pressure. The residual liquid was chromatographed on silica gel and eluted with chloroform. Removal of the solvent from the eluate afforded a viscous liquid. (4.0 g, 87%). [α]²⁵_D = +2.86(c=2 in CHCl₃) v^{nujol} 3310,2950,1740,1690, 1600,1510,1450,1275 and 1070 cm⁻¹. δ :0.75-2.0(m,9H,2xCH₃,CH₂ and CH),4.1(d,2H,COOCH₂),6.5-8.1(m,8H,ArH)

[Found:C,69.1;H,6.3% C₁₉H₂₀O₅ requires C,69.5;H,6.1%]

[S]-2-Methylbutyl 4-[4'-(trans-4"-n-decyloxy-a-methyl cinnamoyloxy) benzoyloxy]benzoate (2.d.6)

A mixture of trans-4-n-decyloxy- α -methylcinnamic acid (0.32) mol) and thionyl chloride (10 ml) was refluxed for six g. 0.001 hours. Excess thionyl chloride was removed by distillation under reduced pressure. A solution of [S]-2-methylbutyl 4-(4'-hydroxy benzoyloxy)benzoate (0.36 g, 0.0011 mol) in pyridine (10 ml) was added to the crude acid chloride. This mixture, protected from moisture through anhydrous calcium chloride guard tube, was stirred at room temperature for sixteen hours and poured on to a mixture of ice and concentrated hydrochloric acid. This was extracted with ether (3x50 ml) and the combined ether extracts was washed successively with water (2x100 ml), 10% aqueous sodium hydroxide (3x100 ml) and water (3x100 ml). The ethereal solution then dried (Na_2SO_4) and the solvent removed. The crude was



'H NMR spectrum of the compound 2.d.6.

product thus obtained was chromatographed on silica gel and eluted with 60% chloroform-petroleum ether (b.p. $60-80^{\circ}C$). Removal of solvent from the eluate gave a solid residue which was crystallised repeatedly from ethanol (0.43 g, 68%). m.p. $64.5^{\circ}C$. $[\alpha]_{D}^{25} = +0.77(c=2 \text{ in CHCl}_{3})$. $\nu_{\text{max}}^{\text{nujol}}$ 2950,1740,1730,1720, 1605,1490,1270,1080 and 890 cm⁻¹. $\delta:0.75-1.95(m,28H,3xCH_{3},9xCH_{2})$ and CH_),2.27(d,3H,-C=C(CH_{3})-),4.0(t,2H,ArOCH_{2}),4.2(d,2H,-COOCH_{2}), 6.85-8.39(m,13H,ArH and vinyl H).

[Found: C,74.53;H,7.62% C,74.52;H,7.64%] C₃₉H₄₈O₇ requires

The physical data of the cognate preparations of other [S]-2-methylbutyl 4-[4'-(<u>trans</u>-4"-n-alkoxy-α-methylcinnamoyloxy) benzoyloxy]benzoates (table 2) are given below.

[S]-2-Methylbutyl 4-[4'-(trans-4"-n-pentyloxy-a-methylcinnamoyloxy)
benzoyloxy]benzoate (2.d.1)

Yield,70%; m.p. 71.5°C; $[\alpha]_{D}^{25} = +0.78(c=2 \text{ in } CHCl_{3}); \nu_{max}^{nujol}:$ 2950,1740,1730,1725,1605,1490 and 1280 cm⁻¹; $\delta:0.75-1.95(m,18H, 3xCH_{3},4xCH_{2})$ and $CH),2.28(d,3H,-C=C(CH_{3})-),4.0(t,2H,ArOCH_{2}),4.19(d,2H,-COOCH_{2}-),6.7-8.5(m,13H,ArH and vinyl H).$

[Found: C,72.85;H,6.90% C₃₄H₃₈O₇ requires C,73.12;H,6.81%] [S]-2-Methylbutyl 4-[4'-(trans-4"-n-hexyloxy-a-methylcinnamoyloxy)
benzoyloxy]benzoate (2.d.2)

Yield, 76%; m.p. 76.0°C; $[\alpha]_D^{25} = +0.8(c=2 \text{ in } CHCl_3); \nu_{max}^{nujol}$ 2950, 1720(br), 1605, 1490, 1280 and 1080 cm⁻¹; $\delta: 0.8-1.9(m, 20H, 3xCH_3, 5xCH_2)$ and CH_2 , 2.25(d, 3H, $-C=C(CH_3-), 4.0(t, 2H, ArOCH_2), 4.19(d, 2H, -COOCH_2-), 6.8-8.4(m, 13H, ArH and vinyl H).$

[Found: C,73.62;H,7.12% C₃₅H₄₀O₇ requires C,73.43;H,6.99%]

[S]-2-Methylbutyl 4-[4'-(trans-4"-n-heptyloxy-a-methylcinnamoyloxy) benzoyloxy]benzoate (2.d.3)

Yield,75%; m.p. 81.5°C; $[\alpha]_D^{25} = +0.77(c=2 \text{ in } CHCl_3)$; $\operatorname{max}^{\operatorname{nujol}}$ 2950,1720(br),1605,1490,1280 and 1080 cm⁻¹; $\delta:0.7-1.95(m,22H, 3xCH_3, 6xCH_2 \text{ and } CH_2), 2.22(d,3H, -C=C(CH_3)-), 3.97(t,2H, ArOCH_2), 4.17$ d,2H,-COOCH₂-),6.8-8.4(m,13H, ArH and vinyl H).

[Found: C,73.76;H,7.28% C₃₆H₄₂O₇ requires C,73.72;H,7.17%]

[S]-2-Methylbutyl 4-[4'-(trans-4"-n-octyloxy-a-methylcinnamoyloxy)
benzoyloxy]benzoate (2.d.4)

Yield,70%; m.p. 77.0°C; $[\alpha]_D^{25} = +0.74(c=2 \text{ in } CHCl_3); v_{max}^{nujol}$ 2950,1720(br),1605,1500,1280 and 1080 cm⁻¹; $\delta: 0.7-1.9(m, 24H, CHCl_3)$ $3xCH_3, 7xC\underline{H}_2$ and $C\underline{H}$, 2.25(d, 3H, $-C=C(C\underline{H}_3)-$), 4.0(t, 2H, $ArOC\underline{H}_2$), 4.19 (d, 2H, $-COOC\underline{H}_2-$), 6.75-8.4(m, 13H, $Ar\underline{H}$ and vinyl \underline{H}).

[Found: C,73.67;H,7.39% C₃₇H₄₄O₇ requires C,74.0;H,7.33%]

[S]-2-Methylbutyl 4-[4'-(<u>trans</u>-4"-n-nonyloxy-α-methylcinnamoyloxy)
benzoyloxy]benzoate (2.d.5)

Yield,68%; m.p. 71.0°C; $[a]_{D}^{25} = +0.72(c=2 \text{ in } CHCl_3); v \text{ nujol}_{max}^{2950,1720(br),1605,1490,1280,1080}$ and 890 cm⁻¹; $\delta:0.7-1.9(m,26H, 3xCH_3,8xCH_2)$ and $C\underline{H}$,2.25(d,3H,-C=C(CH_3)-),4.0(t,2H,ArOCH_2),4.17 (d,2H,-COOCH_2-),6.8-8.4(m,13H,ArH and vinyl H).

[Found: C,74.74;H,7.52% C₃₈H₄₆O₇ requires C,74.27;H,7.49%]

[S]-2-Methylbutyl 4-[4'-(trans-4"-n-undecyloxy-a-methylcinnamoyloxy)benzoyloxy]benzoate (2.d.7)

Yield, 70%; m.p. 67.0°C; $[\alpha]_{D}^{25} = +0.74(c=2 \text{ in } CHCl_{3});$ vnujol 2950, 1750, 1730, 1720, 1605, 1490, 1270, 1080 and 890 cm⁻¹; 6:0.8-2.0 (m, 30H, 3xCH₃, 10xCH₂ and CH), 2.25(d, 3H, -C=C(CH₃)-), 4.0(t, 2H, ArOCH₂), 4.18(d, 2H, -COOCH₂-), 6.8-8.4(m, 13H, ArH and vinyl H).

[Found: C,74.88;H,7.99% C₄₀H₅₀O₇ requires C,74.77;H,7.79%] [S]-2-Methylbutyl 4-[4'-(<u>trans</u>-4"-n-dodecyloxy-a-methylcinnamoyloxy)benzoyloxy]benzoate (2.d.8)

Yield,74%; m.p. 65.0°C; $[\alpha]_D^{25} = +0.71(c=2 \text{ in } CHCl_3); v_{max}^{10}$ 2950,1740,1725,1715,1605,1490,1260 and 1075 cm⁻¹; $\delta: 0.6-1.8(m, 32H, 3xCH_3, 11xCH_2^{-1} \text{ and } CH_2), 2.4(d, 3H, -C=C(CH_3)-), 3.92(t, 2H, ArOCH_2), 4.11$ $(d,2H, -COOCH_2-), 6.8-8.4(m, 13H, ArH and vinyl H).$

[Found: C,74.94;H,7.92% C₄₁H₅₂O₇ requires C,75.00;H,7.93%]

[S]-2-Methylbutyl 4-[4'-(trans-4"-n-decyloxycinnamoyloxy)benzoyloxy]benzoate (2.a.6)

A mixture of trans-4-n-decyloxycinnamic acid (0.30 g, 0.001 mol) and thionyl chloride (10 ml) was refluxed for six hours. Excess thionyl chloride was removed by distillation under reduced pressure. solution of [S]-2-methylbutyl 4-(4'-hydroxybenzoyloxy)benzoate А (0.36 g, 0.0011 mol) in pyridine (10 ml) was added to the crude acid chloride. This mixture, protected from moisture through anhydrous calcium chloride guard tube, was stirred at room ice temperature for sixteen hours and poured on to a mixture of and concentrated hydrochloric acid. This was extracted with ether (3x50 ml) and the combined ether extracts was washed successively with water (2x100 ml), 10% aqueous sodium hydroxide (3x100 ml) and water (3x100 ml). The ethereal solution was then dried (Na_2SO_4) and the solvent removed. The crude product thus obtained was chromatographed on silica gel and eluted with 40% chlroformpetroleum ether (b.p. 60-80[°]C) mixture. Removal of solvent from

the eluate gave a solid residue which was crystallised repeatedly from ethanol (0.45 g, 73%); m.p. 105.0° C; $[\alpha]_{D}^{25} = +1.55(c = 2 \text{ in } CHCl_3)$; v_{max}^{nujol} 2950,1720(br),1630,1600,1510,1460,1270 and 1160 cm⁻¹; $\delta:0.7-2.0(m,28H,3xCH_3,9xCH_2 \text{ and } CH)$, $4.0(t,2H,ArOCH_2)$,4.19 (d,2H,-COOCH₂-),6.26-8.46(m,14H,ArH and vinyl H).

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[Found: C,74.38;H,7.18% C<sub>38</sub>H<sub>46</sub>O<sub>7</sub> requires
C,74.27;H,7.49%]
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2-Chlorophenyl acetate

To an ice-cold solution of 2-chlorophenol (32.1 g, 0.25 mol) in pyridine (75 ml), acetyl chloride (19.6 g, 0.25 mol) was added dropwise over a period of one hour. This mixture was stirred at room temperature for four hours and then poured on to a mixture of ice and concentrated hydrochloric acid. This was extracted with chloroform (2x150 ml) and the combined chloroform extracts was washed with water (3x200 ml). The chloroform solution was dried (Na_2SO_4) and the solvent removed. The crude product so obtained was distilled under reduced pressure. (37.6 g, 88%). b.p. $65^{\circ}C/2-3$ mm. (Reported²¹ b.p. $103^{\circ}C/15$ mm).

3-Chloro-4-hydroxyacetophenone

A mixture of 2-chlorophenyl acetate (37.6 g, 0.2 mol) and anhydrous aluminium chloride (58.8 g, 0.4 mol) was heated for two hours at 120° C in an oil bath. It was then poured on to a mixture of ice and concentrated hydrochloric acid. The precipitate formed was filtered off, washed with water until the washings were neutral and then dried. The crude product thus obtained was crystallised from benzene. (24.0 g, 64%). m. p. 99.0°C. (Reported²¹ m.p. 100.0-100.5°C.)

4-Hydroxy-3-methylacetophenone

a one liter three-necked flask fitted with a mercury-Into sealed stirrer, a reflux condenser and a pressure equalising separatory funnel was introduced dry carbon disulphide (300 ml), anhydrous aluminium chloride (146.8 g, 1.1 mol) and O-cresol (54.0 g, 0.5 mol). To this stirred mixture was added freshly distilled acetyl chloride (39.25 g, 0.5 mol) dropwise over a period of forty minutes. The reaction mixture was refluxed for four hours and left overnight at room temperature. Carbon disulphide was then removed and the dark brown complex was decomposed by a careful addition ice and concentrated hydrochloric acid. The mixture was extracted with ether (2x200 ml) and the combined ether extracts was washed with water (3x250 ml) and dried (Na_2SO_4) . Removal of solvent gave a pale brown . material which was distilled under reduced pressure. The colourless product was crystallised from benzene (65.0 g, 87%). b.p. 175-180°C/1 mm; m.p. 110.0-112.0°C. (Reported²² m.p. 104.0°C).

4-Benzyloxy-3-chloroacetphenone

A solution of sodium ethoxide was prepared by dissolving sodium (4.6 g, 0.2 g atom) in absolute ethanol (100 ml). 3-

Chloro-4-hydroxyacetophenone (34.1 g, 0.2 mol) was added to it. This mixture was stirred and refluxed for thirty minutes. Benzyl. chloride (27.8 g, 0.22 mol) was then added and the stirring and refluxing were continued for a further eight hours. Ethanol was distilled off and the residue poured into cold water. This was extracted with ether (3x150 ml). The combined ethereal solution was washed with water (2x250 ml) and dried (Na_2SO_4) . Removal of solvent gave a residue which was chromatographed on silica gel and eluted with 30% chloroform-petroleum ether (b.p. 60-80°C) mixture. Removal of solvent from the eluate gave a colourless product which was crystallised from methanol (41.6 g, 80%). m.p. 111.5°C. v^{nujol} 2925,2875,1670,1595,1500,1480,1360,1275,1170,1060 and 820 cm⁻¹; δ :2.53(s,3H,COCH₃),5.2(s,2H,OCH₂Ph),6.88-8.13(m,8H, ArH).

[Found: C,69.26;H,4.50% $C_{15}H_{13}ClO_2$ requires C,69.10;H,4.99%]

4-Benzyloxy-3-methylacetophenone²³

Following a procedure similar to the one described above, 3-methyl-4-hydroxyacetophenone was benzylated using benzyl chloride in the presence of sodium ethoxide in ethanol. The crude product so obtained was crystallised from petroleum ether (b.p. $60-80^{\circ}C$).

Yield, 85%; m.p. 77.7°C.

4-Benzyloxy-3-chlorobenzoic acid

solution of sodium hypobromite was prepared by adding А bromine (64.0 g, 0.4 mol) to a solution of sodium hydroxide (32.0 0.8 mol) in water (400 ml) at 0[°]C. This was added to a vigoq. rously stirred solution of 4-benzyloxy-3-chloroacetophenone (26.05 g, 0.1 mol) in 1,4-dioxan (200 ml). The addition was carried out at 30-35°C during thirty minutes. Stirring was continued and the temperature was raised to 50°C and held there for one hour to ensure the completion of the reaction. Enough aqueous sodium metabisulphite was added to destroy the excess of hypobromite. Water (500 ml) was added and about 200 ml of the liquid was distilled. The residual clear solution was cooled and acidified with concentrated hydrochloric acid. The white precipitate obtained was filtered, washed thoroughly with water and dried. This was crystallised from ethanol (20.4 g, 78%). m.p. 209.0^OC. v nujol 2900(br),2700,1680,1600,1500,1460,1380,1270,1160 and 1060 cm⁻¹

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[Found:C,64.28;H,4.20% C<sub>14</sub>H<sub>11</sub>ClO<sub>3</sub> requires
•C,64.0; H,4.19%]
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4-Benzyloxy-3-methylbenzoic acid

Following a procedure similar to the one described above, 4benzyloxy-3-methylacetophenone was oxidised to the corresponding carboxylic acid. The crude product'so obtained was crystallised from ethanol. Yield,83%. m.p.183-5^oC.(Reported¹⁶ m.p.183-184^oC).

[S]-2-Methylbutyl 4-(4'-benzyloxy-3'-chloro)benzoyloxybenzoate

A mixture of 4-benzyloxy-3-chlorobenzoic acid (7.87 g, 0.03 mol) and thionyl chloride (30 ml) was refluxed for six hours. Excess thionyl chloride was removed by distillation under reduced pressure. A solution of [S]-2-methylbutyl 4-hydroxybenzoate (6.86 g,0.033 mol) in anhydrous pyridine (25 ml) was added to the crude mixture, acid chloride. This protected from moisture through anhydrous calcium chloride guard tube, was stirred at room temperature for sixteen hours and poured on to a mixture of ice and concentrated hydrochloric acid. This was extracted with ether (2x100 ml) and the combined ethereal solution was washed successively with water (2x50 ml), 10% aqueous sodium hydroxide (2x50 ml), water (3x50 ml) and dried (Na_2SO_4) . The solvent was removed and the crude product thus obtained was chromatographed on silica gel and eluted with 25% chloroform-petroleum ether (b.p. $60-80^{\circ}C$) Removal of solvent from the eluate gave a solid residue mixture. which was crystallised from ethanol. (9.5 g, 70%). m.p. 102.7°C. $[\alpha]_{D}^{25} = +2.06(c=2 \text{ in } CHCl_{3}); v_{max}^{nujol} 2950,1740,1720,1580,1460,1270$ and 1210 cm⁻¹. 6: 0.80-2.12(m,9H,2xCH₃,CH₂ and CH),4.49(d,2H, $-COOCH_2$),5.06(s,2H, PhCH₂O-),6.63-7.70(m,12H,ArH).

[Found: C,68.66;H,5.47% C₂₆H₂₅ClO₅ requires C,68.95;H,5.52%]

[S]-2-Methylbutyl 4-(4'-benzyloxy-3'-methyl)benzoyloxybenzoate

Following a procedure similar to the one described above, 4benzyloxy-3-methylbenzoic acid was esterified with [S]-2-methylbutyl 4-hydroxybenzoate. The chromatographed product was crystallised from ethanol. Yield, 81%; m.p.68.0 O C; $[\alpha]_{D}^{25} = +2.02$ (c=2 in CHCl₃); ν_{max}^{nujol} 2950,1720,1610,1510,1460,1280,1130 and 1110 cm⁻¹. δ :0.78-2.0(m,9H,2xCH₃,CH₂ and CH),2.34(s,3H,ArCH₃),4.18(d, 2H,-COOCH₂),5.18(s,2H,PhCH₂O),6.85-8.24(m,12H,ArH).

[Found: C,74.86;H,6.66% C₂₇H₂₈O₅ requires C,75.0;H,6.48%]

[S]-2-Methylbutyl 4-(3'-chloro-4'-hydroxy)benzoyloxybenzoate

A mixture of [S]-2-methylbutyl 4-(4'-benzyloxy-3'-chloro) benzoyloxybenzoate (4.53 g, 0.01 mol) dissolved in 1,4-dioxan (30 ml) and 5% Pd/C catalyst (2.3 g) was stirred in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. reaction mixture was filtered and dioxan removed The 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 gave a white solid which was crystallised from cyclohexane (3.3 g, 91%), m.p. 98.0°C; $[\alpha]_D^{25} = +2.6(c=2 \text{ in CHCl}_3); \nu_{max}^{nujol} 3350,2950,1720,1700,$ 1600,1580,1510,1460,1300,1270,1120,1110 and 760 cm⁻¹; δ :0.82-2.08 $(m,9H,2xCH_3,CH_2 \text{ and } CH),4.18(d,2H,-COOCH_2),6.31(s,1H,OH),7.0-8.33$ (m,7H,ArH).

[Found: C,63.03;H,5.11% C₁₉H₁₉ClO₅ requires C,62.89;H,5.24%]

[S]-2-Methylbutyl 4-(4'-hydroxy-3'-methyl)benzoyloxybenzoate

Following a procedure similar to the one described above, [S]-2-methylbutyl-4-(4'-benzyloxy-3'-methyl)benzoyloxybenzoate was subjected to hydrogenolysis in 1,4-dioxan using 5% Pd/C as a catalyst. The product was crystallised from n-heptane. Yield, 90%; m.p. 95.5°C; $[\alpha]_D^{25} = +2.32(c = 2 \text{ in CHCl}_3); v_{max}^{nujol}:$ 3440,2875,1710,1700,1605,1500,1460and 1290 cm⁻¹; 6:0.7-2.0(m,9H, 2xCH₃,CH₂ and CH),2.28(s,3H,ArCH₃),4.2(d,2H,-COOCH₂),6.31(s,1H, OH),6.69-8.26(m,7H,ArH).

[Found: C,70.23;H,6.02% C₂₀H₂₂O₅ requires C,70.17;H,6.43%]

[S]-2-Methylbutyl 4-[3'-chloro-4'-(trans-4"-n-decyloxy-a-methyl cinnamoyloxy)benzoyloxy]benzoate (2.f.6)

A mixture of <u>trans</u>-4-n-decyloxy-a-methylcinnamic acid (0.32 g, 0.001 mol) and thionyl chloride (10 ml) was refluxed for six hours. Excess thionyl chloride was removed by distillation under reduced pressure. A solution of [S]-2-methylbutyl 4-(3'-chloro-4'-hydroxy)benzoyloxybenzoate (0.40 g, 0.0011 mol) in pyridine (10 ml) was added to the crude acid chloride. This mixture, protected from moisture through anhydrous calcium chloride guard tube, was stirred at room temperature for sixteen hours and poured on to a mixture of ice and concentrated hydrochloric acid. This was extracted with ether (2x50 ml) and the combined ethereal solution was washed successively with water (2x75 ml), 10% aqueous sodium hydroxide (3x75 ml) water (3x75 ml) and dried (Na₂SO₄). The solvent was removed and the residue obtained was chromatographed on silica gel and eluted with 50% chloroform-petroleum ether (b.p. $60-80^{\circ}$ C) mixture. Removal of solvent from the eluate afforded a white material which was crystallised repeatedly from ethanol (0.48 g, 72.5%). m. p.56.5°C; [α]²⁵_D = +1.14(c = 2 in CHCl₃); v^{nujol}_{max} 2910,1740~1720,1600,1510,1460,1370 and 1080 cm⁻¹; δ :0.72-2.1(m,28H,3xCH₃,9xCH₂ and CH),2.22(d,3H, -C=C(CH₃)-),4.0(t,2H,ArOCH₂),4.19(d,2H,-COOCH₂),6.8-8.46(m,12H, ArH and vinyl H)

[S]-2-Methylbutyl 4-[3'-chloro-4'-(trans-4"-n-decyloxy cinnamoyloxy)benzoyloxy]benzoate (2.c.6)

Following a procedure similar to the one described above, <u>trans</u>-4-n-decyloxycinnamic acid was esterified with [S]-2-methyl butyl 4-(3'-chloro-4'-hydroxy)benzoyloxybenzoate. Yield, 74%; $[\alpha]_D^{25} = +1.14(c = 2 \text{ in CHCl}_3)$; $v_{\text{max}}^{\text{nujol}}$ 2950,1740, 1720(br),1630,1600,1510,1460,1270 and 1120 cm⁻¹; δ :0.7-2.0(m,28H, 3xCH₃,9xCH₂ and CH), 4.02(t,2H,ArOCH₂), 4.19(d,2H,-COOCH₂),6.39-8.52(m,13H,ArH and vinyl <u>H</u>)

[S]-2-Methylbutyl 4-(4'-(<u>trans</u>-4"-n-decyloxy-a-methyl cinnamoyloxy)-3'-methylbenzoyloxy]benzoate (2.e.6)

A mixture of trans-4-n-decyloxy- α -methylcinnamic acid (0.32) $0.0^{\circ}1$ mol) and thionyl chloride (15 ml) was refluxed for six q, hours. Excess thionyl chloride was removed by distillation under reduced pressure. A solution of [S]-2-methylbutyl 4-(4'-hydroxy-3'-methyl)benzoyloxybenzoate (0.38 g, 0.0011 mol) in anhydrous (10 ml) was added to the crude acid chloride. pyridine This mixture, protected from moisture through an anhydrous calcium chloride guard tube, was stirred at room temperature for sixteen hours and poured on to a mixture of ice and concentrated hydrochloric acid. This was extracted with ether (2x50 ml) and the combined ethereal solution was washed successively with water (2x60 ml), 108 aqueous sodium hydroxide (3x75 ml) and water (3x75 ml). The ether solution was then dried (Na_2SO_4) and the solvent removed. The residue obtained was chromatographed on silica gel and eluted with 50% chloroform-petroleum ether (b.p. $60-80^{\circ}C$). Removal of solvent from the eluate afforded a white material which was crystallised repeatedly from ethanol. (0.48 g, 75%). m.p. 68.0°C; $[\alpha]_{D}^{25} = +1.36(c=2 \text{ in } CHCl_{3}); \nu \frac{nujol}{max} 2900, 1730(br),$ 1710,1600,1490,1460 and 1260 cm⁻¹; δ :0.71-2.1(m,31H,4xCH₃,9xCH₂) and CH),4.0(t,2H,OCH2),4.17(d,2H,-COOC \underline{H}_2),6.83-8.33(m,12H,Ar \underline{H} and vinyl H)

[Found: C,74.56;H,7.88% C₄₀H₅₀O₇ requires C,74.76;H,7.79%] 70

[S]-2-Methylbutyl 4-[4'-(trans-4"-n-decyloxycinnamoyloxy)-3'methylbenzoyloxy]benzoate (2.b.6)

Following a procedure similar to the one described above, <u>trans-4-n-decyloxycinnamic</u> acid was esterified with [S]-2methylbutyl 4-(4'-hydroxy-3'-methyl)benzoyloxybenzoate. Yield, 72%. m. p. 132.0°C; $[\alpha]_D^{25} = +1.53(c = 2 \text{ in } CHCl_3); \prod_{max}^{nujol} 2950,$ 1740,1720(br),1630,1600,1510,1460 and 1260 cm⁻¹; $\delta:0.7-2.0(m,28H,$ $3xCH_3,9xCH_2$ and $CH),2.33(s,3H,ArCH_3),4.0(t,2H,ArOCH_2),4.19(d,2H,$ $-COOCH_2),6.35-8.26(m,13H,ArH and vinyl H)$

[Found: C,74.26;H,7.75% C₃₉H₄₈O₇ requires C,74.52;H,7.64%].

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