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The synthesis of cholest-5-ene-3β-carboxylates and a comparison of their mesomorphic behaviour with isomeric cholesterol esters with a reversed ester linkage

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The syntheses of seven esters of cholest-5-ene-3β-carboxylic acid are reported and the melting points, transition temperatures and mesophase morphologies of the esters are compared with those of the isomeric 3β-cholesterol compounds which have the ester link reversed. For the examples reported, the cholest-5-ene-3β-carboxlates always have significantly lower melting points, but the differences in clearing temperatures for the two series of esters are usually much less. Several of the new compounds give an increased chiral nematic phase range and an intense selective reflection of light. They therefore represent a novel type of chiral nematic material for use in thermochromic applications.

1. Introduction

The first reported example of a thermotropic liquid crystal, cholesteryl benzoate (3β-benzoyloxycholest-5-ene) occupies a unique place in the history of liquid crystals [1, 2] and since its discovery over a 100 years ago, more than 3000 cholesterol derivatives have been reported [3, 4]. Derivatives of steroids were used extensively as thermochromic materials until the introduction of biphenyl-based thermochromics with (*S*)-2-methylbutylphenyl or (*S*)-2-methylbutylbiphenyl components [5–9] which offered advantages of greater chemical and photochemical stability and high purity. The reasons for cholesterol-based systems being less attractive for use in thermochromic applications lie in their photochemical instability, the variable purity of the cholesterol used (which is source-dependent), the possibility of molecular rearrangements in synthesis giving rise to impurities which are difficult to remove, the inability to produce both enantiomeric forms, a limited colour-play range, the discovery that microencapsulation can change colour play behaviour and the fact that more material is required to give a similar intensity of colour with respect to the intensity obtained for non-steroid-based systems. Some of these disadvantages are inherent for the steroid structure and are impossible to overcome, but cholesterol- and cholestanol-derived thermochromic materials still have the advantage of being cheaper to prepare than other chiral nematics, and provided that the problems of purity and photochemical stability can be overcome, they are valuable materials.

Vast numbers of esters of cholesterol have been prepared but it is surprising that very few esters based on cholest-5-ene-3β-carboxylic acid have been reported. Part of the reason for this may be attributed to the uncertainty and errors which arose in assigning the configuration of the cholest-5-ene-3-carboxylic acids. Corey and Sneen [10] discussed the carboxylation of cholesterylmagnesium chloride (**1a**) (and cholestanylmagnesium chloride) and concluded that the major product obtained, an acid of m.p. 226–227°C (melt opaque), was the 3β-acid (structure **Ib**; compound **2** in the scheme), contrary to an earlier report [11]. Marker *et al.* [12] had previously reported an acid of melting point 226–227°C (but were unable to assign its structure) which was subsequently shown to be the 3β-acid [10, 13]. Cataline *et al.* [14] (in a paper received for publication on 21 August 1953, before the publication of Corey and Sneen's work [10]) noted that an acid which they had prepared melted at 224°C and gave a cloudy melt which cleared sharply at 262–264°C, but they incorrectly believed that this acid was cholest-5-ene-3α-carboxylic

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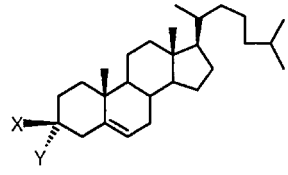
acid (structure **Ia**). They prepared fifteen alkyl esters (from methyl to dodecyl, tetradecyl, hexadecyl and octadecyl; in reality equatorial esters) and noted that 'on solidification from the melted state, these esters exhibit an iridescence similar to that shown by many of the cholesteryl esters'. However, transition temperatures and mesomorphic characteristics were not reported. Toliver *et al.* [15] attempted the preparation of nine cholest-5-ene-3β-carboxylates, but four of the preparations were unsuccessful or gave impure material; only one product (the phenyl ester) was positively claimed to be mesogenic, but only the melting point was recorded.

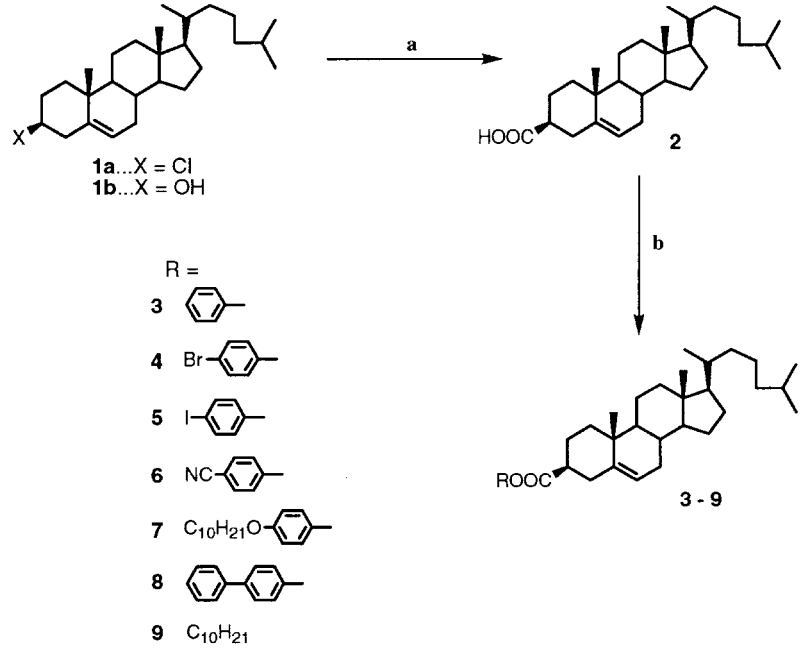


Ia; X=H, Y=CO_2H; Cholest-5-ene-3α-carboxylic acid, **axial** carboxyl group
Ib (≡**2**); X=CO_2H, Y=H; Cholest-5-ene-3β-carboxylic acid, **equatorial** carboxyl group

Nearly all the reports pertinent to the mesogenicity of cholest-5-ene-3β-carboxylic acid and its esters are either incomplete or have inaccuracies of structural assignments. We therefore decided to prepare a selection of cholest-5-ene-3β-carboxylates (including some of those referred to in [14] and [15]) and to compare and contrast their mesomorphic properties with those of the isomeric 3β-esters of cholesterol. Cholest-5-ene-3β-carboxylic acid (**2**, see the scheme) was prepared easily and efficiently following the method described by Corey and Sneen [10] and the esters were obtained by esterification of the acid with the appropriate phenol or alcohol using DCC (*N*,*N*′-dicyclohexylcarbodiimide).

2. Results and discussion

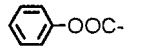
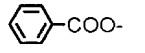
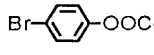
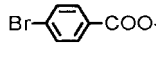
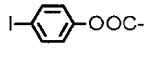
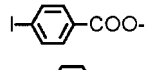
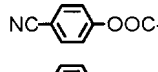
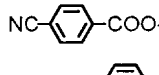
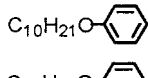
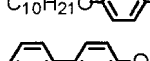
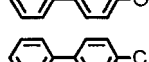
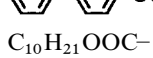
The transition temperatures and phase behaviours of the esters prepared (compounds **3–9**) are given in table 1, along with values for the analogues esters of cholesterol (compounds **3a–9a**). All the cholesteryl esters **3a–9a** show a chiral nematic phase; compound **9a** also exhibits a monotropic smectic A* phase, and **7a** shows an enantiotropic smectic A* and a monotropic smectic C* phase. For the reversed esters of cholest-5-ene-3β-carboxylic acid (**2**), only chiral nematic and related Blue Phases are given by compounds **3–5**, but the other compounds give a more varied sequence of mesophases. The esters **6**, **8** and **9** show a smectic A* phase, in addition to a chiral nematic phase, and for compound **6** a TGBA* phase is also present. Compound **7** is unusual in that on heating it clears directly from the smectic A* phase to the isotropic liquid but, on cooling, a Blue Phase appears which is distinguished by its blue platelet texture. On further cooling the Blue Phase transforms directly to a smectic A* phase without passing through a chiral nematic phase. The explanation for this behaviour is that on heating the smectic A* phase, for a transition to the Blue Phase to occur, the layers must be disrupted



Scheme. Synthetic route to the cholest-5-ene-3β-carboxylates.

a... **1a**, Mg, ether, bromoethane; CO_2; H_2SO_4 / H_2O
b... Phenol or alcohol, DCC, DMAP, DCM, DMF

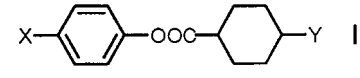
Table 1. Transition temperatures (°C) for 3β-derivatives of cholest-5-ene. The values given for compounds **3a–9a** are from the prime references in [3]. Our values are **3a** Cr 150.5 N* 182.6 BP 182.9 I; **4a** Cr 178.1 N* 254.9 I; **5a** Cr 187.3 N* 252.6 I; **6a** Cr 174.2 N* 282.4 I (°C).

Compound	*R*	Cr		SmC*		SmA*		TGBA*		N*		BP		I
3		•	106.7[a]	—	—	—	—	—	—	•	175.2	•	176.3	•
3a[16]		•	150.5	—	—	—	—	—	—	•	182.6	—	—	•
4		•	109.2	—	—	—	—	—	—	•	244.4	•	245.1	•
4a[17]		•	178.3	—	—	—	—	—	—	•	254.1	—	—	•
5		•	127.8	—	—	—	—	—	—	•	253.1	•	253.6	•
5a[18]		•	187	—	—	—	—	—	—	•	252	—	—	•
6		•	162.5	—	—	•	189.0	•	189.2	•	284	—	—	•
6a[19]		•	174	—	—	—	—	—	—	•	282	—	—	•
7		•	64.2	—	—	•	218.7	—	—	—	—	(•	217.6)	•
7a[20]		•	110.7	(•	97.7)	•	178.2	—	—	•	208.4	—	—	•
8		•	145.2	—	—	•	231.5	—	—	•	> 300 dec	—	—	•
8a[21]		•	178	—	—	—	—	—	—	•	290	—	—	•
9	$C_{10}H_{21}OOC–$	•	49.7[b]	—	—	(•	13.2	—	—	•	29.4)	—	—	•
9a[22]	$C_{10}H_{21}COO–$	•	85	—	—	(•	80.1)	—	—	•	90.4	—	—	•

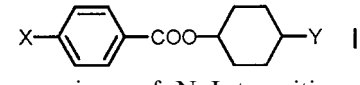
[a] M.p. 106–107°C reported in [15].
[b] M.p. 49–50°C reported in [14].

and defects allowed to form. On cooling from the isotropic liquid, no layer ordering exists, and so formation of a Blue Phase is relatively easy. This causes a hysteresis in the phase formation which permits the Blue Phase to be seen on cooling, but not necessarily on heating.

In order to assess whether the effect on melting points and transition temperatures of reversing the ester linkage is typical of the behaviour seen for non-steroid mesogenic systems, we have compared our results with those for compounds of similar structure. The essential structural difference between the substituted-phenyl cholesteryl-3β-carboxylates (**3–8**) and the cholesteryl substituted-benzoates (**3a–8a**) is that the former compounds are aryl esters of an alicyclic acid (**II**), whereas the latter are cycloalkyl esters of benzoic acids (**III**). Rather than select isolated examples of class **II** and **III** compounds for comparison, we have used the data in reference [3] to summarize the differences in melting points and N–I transition temperatures for all reported pairs of compounds of class **II** and **III**. For the melting point comparisons, 75 pairs of compounds are known but there is no obvious indication that the class **II** or **III** compounds generally have the higher melting point; in fact the data set is almost equally split as to which class of compounds has the higher melting point. For the compounds reported here (see table 1), the melting points of the cholesteryl-3β-carboxylates (**3–9**) are consistently *lower* (by 11.5 to 69.1°C) than the isomeric analogues **3a–9a** respectively.



II



III

For a comparison of N–I transition temperatures, values for 64 pairs are available and in nearly all cases (56) the type **II** compounds have higher clearing points (typically by 10–30°C). The clearing points of the cholesteryl-3β-carboxylates (**3–7**) are not greatly different

from those of their isomers; in some cases they are slightly lower (**3** and **4**) and in other cases slightly higher (**5–7**), but the changes are no more than 10°C. Only compound **9** (an aliphatic ester) gives a clear difference (61°C) in N–I transition temperature from its isomer **9a**, with the former compound having the lower value. Further aliphatic esters of this kind will be prepared in the future to establish whether the larger difference in clearing temperature found for **9** and **9a** is general for such materials.

The lower melting points of the cholesteryl-3β-carboxylates is a major general advantage in extending the chiral nematic phase ranges and although the colour-play behaviour of compounds **3**, **7** and **9** is not impressive, compounds **4–6** and **8** give very intense selective reflections. On cooling from the isotropic liquid, compounds **4** and **5** show a brilliant blue iridescence throughout the chiral nematic range, until the other colours of longer wavelength are produced over a few °C before recrystallization. Compounds **6** and **8** also give a deep blue reflected colour throughout the chiral nematic range, and the other spectral colours appear just before the transition to the smectic A* phase. In the course of examining the contact preparations (see below) for **3**/**3a**, **4**/**4a**, and **5**/**5a** (or indeed on comparing separate slide preparations for each pair of compounds), it was most noticeable that the 3β-carboxylates give much more vivid selective reflections than the cholesteryl esters. A more detailed evaluation of the optical properties of some of these compounds is currently being made.

All the 3β-carboxylates **3–9** were examined microscopically by the contact method [23] to determine their helical sense. None of the materials showed any discontinuity in texture associated with infinite pitch regions when in contact with cholesteryl benzoate (**3a**), which is a compound with a left-handed helix [24]. Contact preparations of the following pairs of compounds were also examined, **3**/**3a**, **4**/**4a**, **5**/**5a**, **6**/**6a** with the same result. These observations conform with the conclusion from Leder's study [25] that the rotatory sense and pitch of cholesteric liquid crystals is determined by the extent to which the 3β-substituent projects from the core; if the substituent projects by more than 2.08 Å from the core, then the helical sense is left-handed. For the compounds reported here, the reversal of the ester group will have no significant effect on the size of the 3β-substituent and both the cholesteryl and the reversed esters were expected to possess the same helical sense.

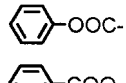
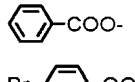
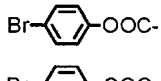
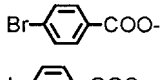
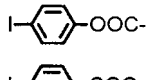
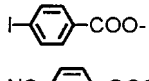
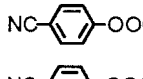
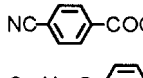
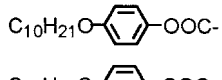
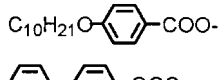
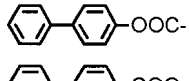
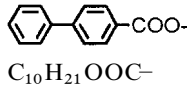
Several reports on the enthalpies and entropies of transition of cholesteryl esters have considered how the thermodynamic values are affected by the size of the ester unit at the 3-position [26–30]. The surprising conclusion reached was that the chain length of the side group determines the magnitude of the entropy of transition. This claim was tested [26] in one case by comparing the transition entropies for cholesteryl-3β-carboxylic acid (−COOH substituent) and cholester-3β-yl formate (−OOCH substituent), because the substituents in these two compounds project almost the same distance from the ring, since the groups only differ by the interchange of the carbonyl carbon and oxygen atoms. The entropy change for the solid → liquid transition was 14.9 and 14.2 cal mol^{-1} K^{-1} for the acid and formate, respectively, and this was taken to confirm the view that the magnitude of the entropy change is determined predominantly by the length of the side chain, even when there are large chemical differences in the nature of the substituents; for example, hydrogen bonding by the acid group leads to molecular association to give a dimer, whereas cholesteryl formate exists as a monomer. In a similar way, the esters we report here are structurally related to cholesteryl carboxylates by interchange of the carbonyl and oxygen units and the groups at the 3-position of cholesterol should project by similar distances for compounds **3–9** and the isomers **3a–9a**, respectively.

Compounds **3–9** were studied by DSC and the entropies of transition (obtained from the first heating scans at 10°C min^{-1}; the first and subsequent scans gave similar values) are shown in table 2 in comparison with values for the isomeric esters **3a–9a**, where available. The ΔS values for the overall changes from crystal to isotropic liquid are broadly in agreement for each of the isomeric pairs, but the correlation between the magnitude of the ΔS value and the distance to which the 3β-substituent extends from the cholesterol core is not convincing, although other contributing factors can be recognized. Although the ΔS values tend to increase as the substituents become longer, the cyano and iodo substituents are higher and lower, respectively, than the general trend. For the cyano substituent any antiparallel association of dipoles would result in a greater than expected entropy change (as observed) as the molecular ordering is disrupted. Conversely, for the iodo compound, the large spherical halogen unit may not allow efficient packing of molecules in the crystal and this would lead to a smaller entropy change.

3. Conclusions

A novel series of esters derived from cholesteryl-3β-carboxylic acid has been prepared; in comparison with the isomeric cholesteryl esters, the cholesteryl-3β-carboxylates have significantly lower melting points and similar clearing points. Several of the new compounds are potentially useful thermochromic materials and show intense selective reflections over the full chiral nematic range.

Table 2. Entropy changes (ΔS, cal mol^{-1} K^{-1}) for 3β-derivatives of cholest-5-ene.

Compound	*R*	ΔS for Cr to N*	ΔS for N* to I	ΔS for Cr to I
3		10.30	0.27	10.57
3a[a]		12.63	0.35	12.98
4		14.57	0.36	14.93
4a[b]		14.36	0.44	14.80
5		5.97	0.42	6.39
5a		[f]	[f]	[f]
6		17.64	0.88	18.52
6a		[f]	[f]	[f]
7[c]		[g]	[g]	21.20
7a[c,d]		21.08	0.55	21.63
8		16.76	[h]	[h]
8a		[f]	[f]	[f]
9	$C_{10}H_{21}OOC–$	20.67[i]	0.28	20.95
9a[e]	$C_{10}H_{21}COO–$	28.01	0.49	28.50

[a] Average of the values from [31–34].
[b] [31].
[c] For **7** and **7a**, the ΔS values for Cr–SmA are 18.79 and 20.75 and for SmA–I are 2.41 and 0.89 cal mol^{-1} K^{-1}, respectively.
[d] [35].
[e] [36, 37].
[f] Values not reported.
[g] Nematic phase not pesent.
[h] Decomposition occurs on clearing.
[i] Obtained by subtracting the N*–I value for the Cr–I value.

4. Experimental

Confirmation of the structures of intermediates and products was obtained by ^{1}H NMR spectroscopy (JEOL JNM LA400 FT NMR system), infrared spectroscopy (Perkin-Elmer 983G grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer); elemental analyses (Fisons EA1108 CHN) were obtained for all final products. Melting points and transition temperatures were measured using a Mettler FP5 hot stage and control unit in conjunction with an Olympus BH2 polarizing microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 and IBM data station), which was also used to obtain the enthalpies of melting points and mesophase transitions (indium was used as a reference material for the calibration of temperature and enthalpy). The purities of all final products were checked by HPLC analysis (Merck-Hitachi with Merck RP 18 column, Cat. No. 16 051) and were found to be $>99.9\%$ in each case.

4.1. *Cholest-5-ene-3β-carboxylic acid (**2**)*

3β-Cholesteryl chloride (**1a**) (50.0 g, 0.124 mol) in dry ether (50 ml) was added dropwise over the course of 3 h to a heated mixture of magnesium turnings (6.0 g, 0.248 mol) and dry bromoethane (13.5 g, 0.124 mol), as an initiator, in dry ether (120 ml). The addition was started at the onset of the vigorous reaction between the bromoethane and the magnesium. During the addition, and for 46 h thereafter, the reaction mixture was heated under gentle reflux. At the end of this period, the reaction mixture contained a grey-white precipitate and some unreacted magnesium. The reaction mixture was poured

onto solid carbon dioxide and further portions of solid carbon dioxide were added during an 8 h period. The mixture was then acidified with 10% sulphuric acid (300 ml) and the solid product was extracted into diethyl ether (2 × 100 ml); the combined organic extracts were washed successively with brine (2 × 100 ml) and water (2 × 100 ml) then dried (Na_2SO_4). The solvent was removed *in vacuo* and the product was recrystallized (chloroform) to give white crystals.

Yield 46.0 g, 90%; transition temperatures (°C) Cr 226.7 N* 253.0 BP 256.1 I; lit. [38] m.p. 226–227°C. ^{1}H NMR ($CDCl_3$) δ 0.69 (3H, s), 0.85–2.48 (42H, m), 5.37 (1H, d). IR (KBr) ν_{max} 3200–2600, 1709, 1468, 1381, 1283, 937, 804, 677, 528 cm^{-1}. MS *m/z*: (M^+) 414, 370, 301, 275, 215, 189, 161, 107, 91, 78 (100%), 67. $[\alpha]_D^{24} = -16.36°$ ($CHCl_3$, $c = 0.0731$ g ml^{-1}). ^{13}C NMR ($CDCl_3$ + DMSO) significant peaks for alkene and carboxylic acid carbons; 120.41, 140.87, 177.38.

4.2. *Phenyl cholest-5-ene-3β-carboxylate (**3**)*

N,*N*′-Dicyclohexylcarbodiimide (DCC) (0.50 g, 2.42 mmol) was added to a stirred solution of phenol (0.23 g, 2.42 mmol), compound **2** (1.00 g, 2.42 mmol), 4-*N*,*N*-dimethylaminopyridine (DMAP) (0.03 g, 0.24 mmol) in dichloromethane (DCM) (75 ml) and *N*,*N*-dimethylformamide (DMF) (3 ml), at room temperature and under an atmosphere of nitrogen. The reaction mixture was stirred overnight at room temperature (TLC analysis revealed complete reaction), filtered, and the solvent removed from the filtrate *in vacuo* to give a white solid. The crude product was purified by column chromatography (silica gel/HPLC grade hexane : ethyl acetate, 9 : 1), followed by recrystallization (ethanol) to give white crystals that were dried *in vacuo* ($CaCl_2$).

Yield 0.72 g, 60%; transition temperatures (°C) Cr 106.7 N* 175.2 BP 176.3 I; lit. [15] m.p. 106–107°C. ^{1}H NMR ($CDCl_3$) δ 0.69 (3H, s), 0.85–2.55 (41H, m), 5.41 (1H, d), 7.06 (2H, d), 7.22 (1H, t), 7.37 (2H, t). IR (KBr) ν_{max} 2953, 2123, 1753, 1597, 1494, 1380, 1200, 968, 845, 741, 690, 503 cm^{-1}. MS *m/z*: (M^+) 490, 476, 396, 370, 175, 135, 105, 94 (100%), 81, 69.

4.3. *4-Bromophenyl cholest-5-ene-3β-carboxylate (**4**)*

Compound **4** was prepared by a similar procedure to that described for the preparation of compound **3**, using 1.21 mmol of DCC, 4-bromophenol, compound **2** and 0.12 mmol of DMAP; recrystallization from ethanol.

Yield 55%; transition temperatures (°C) Cr 109.2 N* 244.4 BP 245.1 I. ^{1}H NMR ($CDCl_3$) δ 0.69 (3H, s), 0.85–2.55 (41H, m), 5.41 (1H, d), 6.96 (2H, d), 7.47 (2H, d). IR (KBr) ν_{max} 2940, 1752, 1562, 1483, 1378, 1282, 1199, 1124, 1067, 1009, 861, 804, 502 cm^{-1}. MS *m/z*: (M^+) 570, 568, 396, 369, 313, 287, 257, 229, 201, 147, 91 (100%), 81.

4.4. *4-Iodophenyl cholest-5-ene-3β-carboxylate (**5**)*

Compound **5** was prepared by a similar procedure to that described for the preparation of compound **3**, using 2.42 mmol of DCC, 4-iodophenol, compound **2** and 0.24 mmol of DMAP; recrystallization from ethanol. Yield 60%; transition temperatures (°C) Cr 127.8 N* 253.1 BP 253.6 I. ^{1}H NMR ($CDCl_3$) δ 0.69 (3H, s), 0.85–2.55 (41H, m), 5.41 (1H, d), 6.84 (2H, d), 7.67 (2H, d). IR (KBr) ν_{max} 2948, 1758, 1582, 1482, 1380, 1282, 1201, 1168, 1054, 1008, 967, 802, 501 cm^{-1}. MS *m/z*: (M^+) 616, 601, 531, 490, 461, 370, 353, 275, 243, 203, 175, 147, 121, 95 (100%), 81.

4.5. *4-Cyanophenyl cholest-5-ene-3β-carboxylate (**6**)*

Compound **6** was prepared by a similar procedure to that described for the preparation of compound **3**, using 2.41 mmol of DCC, 4-cyanophenol, compound **2** and 0.24 mmol of DMAP; recrystallization from ethanol.

Yield 70%; transition temperatures (°C) Cr 162.5 SmA* 189.0 TGBA* 189.2 N* > 275 I. ^{1}H NMR ($CDCl_3$) δ 0.69 (3H, s), 0.85–2.55 (41H, m), 5.41 (1H, d), 7.22 (2H, d), 7.68 (2H, d). IR (KBr) ν_{max} 2956, 2345, 2237, 1753, 1601, 1380, 1212, 1170, 864, 549 cm^{-1}. MS *m/z*: (M^+) 515, 402, 369, 325, 226, 161, 105, 95, 81, 43 (100%).

4.6. *4-Decyloxyphenyl cholest-5-ene-3β-carboxylate (**7**)*

Compound **7** was prepared by a similar procedure to that described for the preparation of compound **3**, using 1.21 mmol of DCC, 4-decyloxyphenol, compound **2** and 0.12 mmol of DMAP; recrystallization from ethanol.

Yield 50%; transition temperatures (°C) Cr 64.2 SmA* 218.7 (BP 217.6) I. ^{1}H NMR ($CDCl_3$) δ 0.69 (3H, s), 0.85–2.55 (60H, m), 3.92 (2H, t), 5.40 (1H, d), 6.86 (2H, d), 6.96 (2H, d). IR (KBr) ν_{max} 2935, 2858, 1755, 1597, 1382, 1246, 1131, 919, 860, 523 cm^{-1}. MS *m/z*: (M^+) 646, 632, 353, 301, 250 (100%), 201, 121, 95, 57.

4.7. *Biphenyl-4-yl cholest-5-ene-3β-carboxylate (**8**)*

Compound **8** was prepared by a similar procedure to that described for the preparation of compound **3**, using 2.42 mmol of DCC, 4-hydroxybiphenyl, compound **2** and 0.24 mmol of DMAP; recrystallization from ethanol.

Yield 60%; transition temperatures (°C) Cr 145.2 SmA* 231.5 N* > 300 I. ^{1}H NMR ($CDCl_3$) δ 0.69 (3H, s), 0.85–2.55 (41H, m), 5.42 (1H, d), 7.14 (2H, d), 7.34 (1H, t), 7.43 (2H, t), 7.58 (4H, m). IR (KBr) ν_{max} 3041, 2942, 1757, 1684, 1602, 1519, 1468, 1192, 756, 689, 487 cm^{-1}. MS *m/z*: (M^+) 566, 540, 397, 370, 228, 170 (100%), 131, 81, 57.

4.8. *Decyl cholest-5-ene-3β-carboxylate (**9**)*

Compound **9** was prepared by a similar procedure to that described for the preparation of compound **3**, using

4.83 mmol of DCC, decanol, compound **2** and 0.48 mmol of DMAP; recrystallization from ethyl acetate.

Yield 50%; transition temperatures (°C) Cr 49.7 (SmA* 13.2 N* 29.4) I; lit. [14], but mis-reported as the 3α-isomer, m.p. 49–50°C. ^{1}H NMR ($CDCl_3$) δ 0.69 (3H, s), 0.85–2.55 (60H, m), 4.05 (2H, t), 5.35 (1H, d). IR (KBr) ν_{max} 2931, 2862, 2124, 1731, 1469, 1379, 1299, 1167, 1030, 801, 722 cm^{-1}. MS *m/z*: (M^+) 554, 539, 428, 399, 368, 353, 301, 255, 222, 154, 43 (100%).

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