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## Liquid Crystals

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# Dimeric liquid crystals with two troponoid mesogenic moieties: effect of the direction of the carbonyl group on the mesomorphic properties

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Three twin types of troponoid liquid crystals, in which the directions of the troponone carbonyl groups are different from each other, were prepared to establish their thermal properties. Symmetrical type I dimers, in which the two troponone carbonyl groups are directed inwards, had monotropic smectic C phases, whereas two other symmetrical type IIa and IIb dimers, whose troponoid dipoles are directed outwards, were not mesomorphic except for one type IIa compound having two long terminal chains and a short alkylene spacer. Unsymmetrical type III dimers had smectic A phases. Among the dimers, unsymmetrical type III dimers had the highest clearing point when the number of atoms of the inner and outer spacers was fixed. X-ray diffraction studies of a type III dimer, in which the number of the atoms of the inner spacer was odd, showed that the molecules form an interdigitated layer structure. The binary system between type I and type IIb dimers showed an induced enantiotropic smectic A phase, in which the dipole moments of the troponone rings were cancelled.

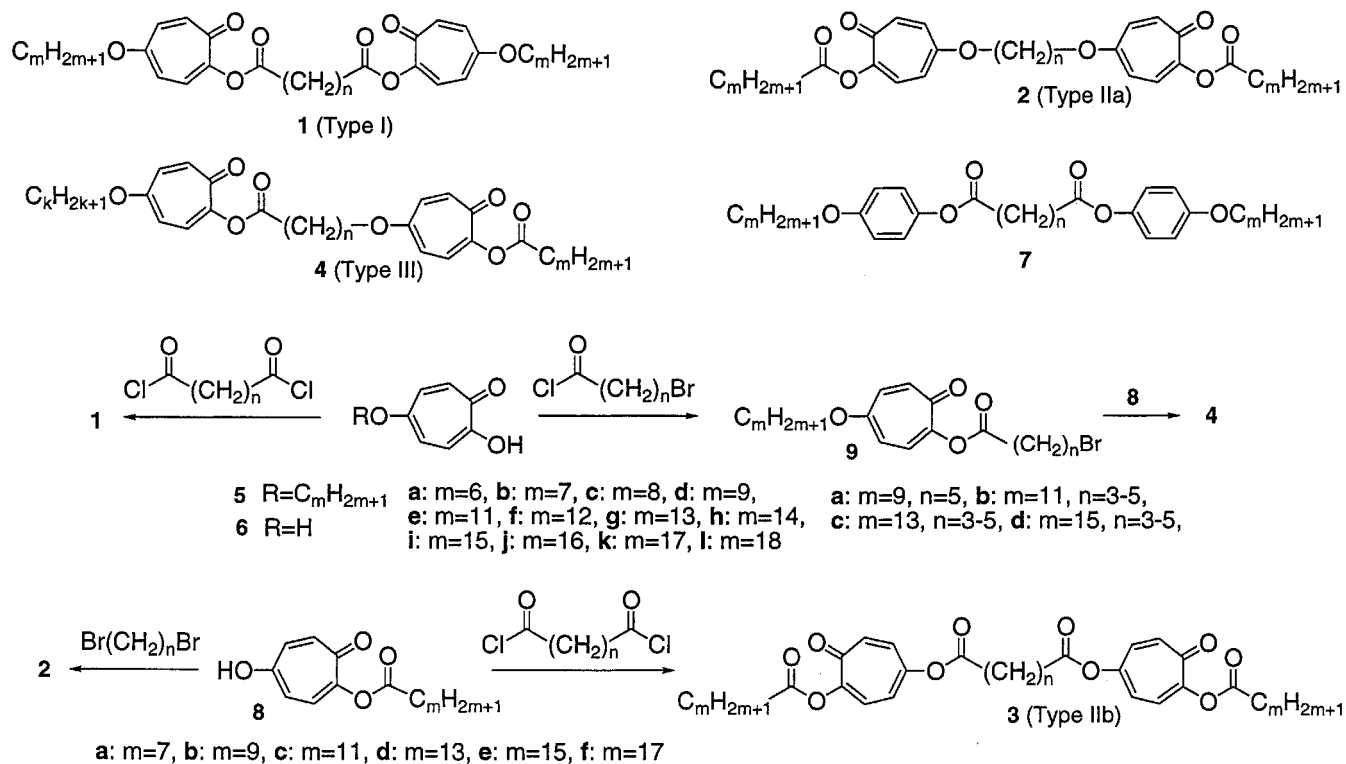
## 1. Introduction

Twin or dimeric liquid crystal materials, in which two mesogenic moieties are connected by a flexible spacer, have been synthesized intensively to study their thermal properties [1]. The phase behaviours of twin type liquid crystals are significantly influenced by the length of the spacer, as well as by the number of atoms in the spacer, the so-called odd–even nature. In the cases of dimers connected by an even spacer, the mesogenic units have more parallel orientations than in dimers with an odd spacer and exhibit more stable liquid crystalline states.

It is known that the direction of the dipole moments of the core parts of liquid crystal molecules is quite important in determining the molecular alignment in a mesophase. As observed in benzenoid systems such as three aromatic ring compounds linked by ester groups [2], the direction of the ester parts affects the thermal stability of the smectic A phases. The authors discussed their results from the standpoint not only of the electronic interactions, but also of the shapes of the molecules, which played important roles in regard to the appearance of the mesophases.

Recently, we synthesized troponoid liquid crystals in which the troponone carbonyl group played an important role in inducing mesomorphic properties [3]. For example,

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Scheme.

even compounds containing only one troponoid ring system with an aliphatic ester group at C-2 and with an alkoxy or an alkanoyloxy group at C-5 showed a monotropic smectic A phase, while the corresponding benzenoid systems are not mesomorphic [3, 4]. This was explained by the fact that troponoid mesogens have a large dipole moment (tropolone: 3.5 D [5]) and make antiparallel arrangements to form layer structures.

In this paper, we report the mesomorphic properties of dimer liquid crystals with two troponoid mesogenic units. There are three types of these troponoid dimers: type I (**1**) is a symmetrical dimer, in which the two troponoid carbonyl groups are directed inwards and an alkylene spacer links up the C-2 positions of the troponoids. Type IIa (**2**) and type IIb (**3**) are also symmetrical dimers, in which the two troponoid carbonyl groups are directed outwards and the two troponoids are connected through the C-5 positions. Type III (**4**) is an unsymmetrical case, in which the two carbonyl groups are oriented in the same direction. In the dimers, the direction of the dipole moment of the troponoids is more strongly fixed spatially by connecting with a spacer than it is in monomeric troponoids. Structures and synthesis routes are shown in the scheme.

## 2. Results and discussion

### 2.1. Symmetrical dimer type I

When a tetrahydrofuran solution of a 5-alkoxytroponone (**5**)†, which was prepared from 5-hydroxytroponone (**6**), and an alkandioyl dichloride were reacted in the presence of sodium hydride, type I dimer **1** was prepared in 22–97% yields [6]. The <sup>1</sup>H NMR spectrum of **1** showed a [1, 9] sigmatropic rearrangement. The activation free energy of **1a** was determined as 54.4 kJ mol<sup>-1</sup> at 298 K, which was identical with the value obtained for 2-acetoxy-5-methoxytroponone [7]. The transition temperatures and the thermal behaviour of the phases of the compounds **1** were determined using a polarizing optical microscope equipped with a hot stage and by DSC measurements. The results are summarized in table 1. The compounds **1** showed monotropic smectic C phases, while the corresponding benzenoid dimers **7** with a higher melting point [6] were not mesomorphic. From consideration of the structure of the compounds **1**, where both troponoid rings are directed inwards, a fully-overlapped alignment would not be reasonable because of dipole–dipole repulsion of the troponoid rings. Therefore,

†Compounds **5a** (*m*=6), **5c** (*m*=8), **5e** (*m*=11), **5f** (*m*=12), **5h** (*m*=14), and **5l** (*m*=18) are known; see [3*d*].

Table 1. Transition temperatures (°C) of compounds **1**.

	<i>m</i>	<i>n</i>	Cr	SmC	I
<b>a</b>	6	3	•	95.9	•
<b>b</b>	7	6	•	76.5	•
<b>c</b>	8	4	•	95.1	•
<b>d</b>	9	6	•	83.0	•
<b>e</b>	11	4	•	92.3	•
<b>f</b>	11	6	•	75.4	(• 49.3)
<b>g</b>	11	7	•	65.4	•
<b>h</b>	11	8	•	92.8	•
<b>i</b>	12	4	•	91.0	(• 71.2)
<b>j</b>	12	5	•	73.8	(• 30.1)
<b>k</b>	12	6	•	72.4	(• 54.8)
<b>l</b>	12	7	•	62.4	(• 22.5)
<b>m</b>	12	8	•	90.0	(• 32.5)
<b>n</b>	13	6	•	80.6	(• 60.8)
<b>o</b>	14	6	•	81.8	(• 65.0)
<b>p</b>	15	2	•	120.8	•
<b>q</b>	15	3	•	81.5	(• 51.0)
<b>r</b>	15	4	•	88.0	(• 78.7)
<b>s</b>	15	5	•	83.8	(• 45.2)
<b>t</b>	15	6	•	82.1	(• 64.6)
<b>u</b>	15	7	•	68.7	(• 39.2)
<b>v</b>	15	8	•	71.6	(• 47.3)
<b>w</b>	16	4	•	92.7	(• 82.0)
<b>x</b>	16	6	•	87.8	(• 71.1)
<b>y</b>	17	6	•	90.1	(• 73.2)
<b>z</b>	18	6	•	91.2	(• 74.4)

molecules **1** would tilt to relieve the dipole–dipole interaction and form a tilted smectic C phase.

There is observed an even–odd effect of the spacer for the compounds **1**. In general, the thermal and mesomorphic properties of twin compounds are dependent on the conformation of the central alkylene chain [8]. If the spacer has an all-*trans*-conformation, the mesogenic units with an even spacer are co-parallel, while they are not parallel with an odd spacer. The latter arrangement would reduce the clearing point.

Generally, the longer the alkoxy chain length is, the higher are the transition temperatures to the smectic C phases on cooling from the isotropic liquid. The effect of the alkoxy length on the melting points is less than that of the chain length of the alkylene spacer. Keeping *m* constant and comparing odd with odd spacers, or even with even spacers, compounds **1** with a shorter inner alkylene spacer generally have the higher mesophase thermal stability; here the two troponoid parts are closer together and form a large core part, whereas with a longer inner alkylene chain the units may behave independently.

### 2.2. Symmetrical dimer type II

Symmetrical type IIa dimers **2** were prepared by the reaction of 2-alkanoyloxy-5-hydroxytropone s (**8**) [6] and a 1,ω-dibromoalkane in the presence of sodium

hydride; their transition temperatures are summarized in table 2 and show that mesomorphic properties are less marked than for **1**. Generally, the melting points of **2** are higher and more supercooling is needed to form a phase. Twin dimer **2g** which has long alkyl chains and a short alkylene spacer, does however show a monotropic smectic C phase.

When a tetrahydrofuran solution of **8** and an alkanoyl dichloride was reacted in the presence of sodium hydride, symmetrical type IIb dimers **3** were prepared in 34–74% yields. The dimers **3** were not mesomorphic, as shown in table 3, and the melting points of **3** are higher than those of dimers **1**. This is consistent with the result that 2-alkanoyloxy-5-alkoxytropone s have lower melting points than 2,5-dialkanoyloxytropone s [9].

### 2.3. Unsymmetrical dimer type III

Unsymmetrical dimers **4** were prepared by the reaction of **8** with 5-alkoxy-2-ω-bromoalkanoyloxytropone s (**9**); the latter were prepared by the reaction of 5-alkoxytropone s (**5**) with ω-bromoalkanyl chlorides. Dimers

Table 2. Transition temperatures (°C) of compounds **2**.

	<i>m</i>	<i>n</i>	Cr	SmC	I
<b>a</b>	7	6	•	95.0	•
<b>b</b>	11	4	•	99.5	•
<b>c</b>	11	6	•	89.7	•
<b>d</b>	15	6	•	93.6	•
<b>e</b>	15	7	•	68.9	•
<b>f</b>	15	8	•	77.5	•
<b>g</b>	17	4	•	106.3	(• 97.1)
<b>h</b>	17	6	•	98.7	•
<b>i</b>	17	7	•	74.4	•
<b>j</b>	17	8	•	84.4	•

Table 3. Transition temperatures (°C) of compounds **3**.

	<i>m</i>	<i>n</i>	Cr	I
<b>a</b>	7	4	•	97.8
<b>b</b>	7	5	•	76.9
<b>c</b>	7	6	•	89.7
<b>d</b>	7	7	•	60.2
<b>e</b>	7	8	•	91.1
<b>f</b>	9	6	•	97.3
<b>g</b>	11	4	•	103.9
<b>h</b>	11	5	•	90.0
<b>i</b>	11	6	•	102.3
<b>j</b>	11	7	•	81.1
<b>k</b>	11	8	•	100.7
<b>l</b>	13	6	•	107.0
<b>m</b>	15	4	•	110.3
<b>n</b>	15	5	•	98.5
<b>o</b>	15	6	•	108.5
<b>p</b>	15	7	•	91.8
<b>q</b>	15	8	•	104.2

**4** showed mainly monotropic smectic A phases and the transition temperatures are summarized in table 4. The alkyl chain length slightly affected the melting points, while the clearing points increased when the alkyl chain lengths became longer. When the clearing points of **4** and **2** are compared, those of compounds **4** are higher.

Although we failed to make X-ray diffraction (XRD) studies on compounds **4** (**4d**, **4g**, and **4m**) with an odd  $n$  number due to the high melting points, XRD on **4f** indicated that the layer spacing is 41 Å. This is shorter than the molecular length (50 Å) calculated by the AM1 method. We therefore propose an interdigitated structure for the smectic A phase as shown in figure 1.

When the thermal stabilities are compared among **1r**, **2d**, and **4j**, in which the total number of atoms ( $n$ + carbon and oxygen atoms) of the inner spacer was fixed at 8, unsymmetrical twin dimer **4j** has the highest clearing point. In symmetrical troponoid twins **1** and **2**, the dipole moments of the two tropone carbonyl groups are directed oppositely, which means that molecules cannot form a fully overlapped parallel molecular arrangement. Twin dimers **4**, however, can form a fully overlapped head-to-tail layer structure to cancel the dipole moments of the tropone rings.

#### 2.4. Binary systems

In order to analyse the effect of the direction of the dipole moment of the troponoids, symmetrical type I dimers **1** were mixed with symmetrical type IIb dimers **3** [10]. The results for the binary system are summarized in table 5. Mixtures of **1w** and **3m** in ratios of 10:90 and 20:80 showed bâtonnets, which separated from the isotropic liquid, and focal-conic fan textures and homeotropic textures were formed, assigning the phases as smectic A phases. From the ratio 30:70 to 70:30, an enantiotropic smectic A phase appeared and had clearing

Table 4. Transition temperatures (°C) of compounds **4**.

	$k$	$m$	$n$	Cr	SmA	I
<b>a</b>	9	9	5	•	116.9	•
<b>b</b>	11	11	3	•	134.5	•
<b>c</b>	11	11	4	•	91.5	(• 84.9) •
<b>d</b>	11	11	5	•	117.7	(• 95.3) •
<b>e</b>	13	13	3	•	133.3	•
<b>f</b>	13	13	4	•	94.2	(• 92.0) •
<b>g</b>	13	13	5	•	118.7	(• 96.6) •
<b>h</b>	15	15	3	•	131.1	•
<b>i</b>	15	15	4	•	94.4	• 95.9 •
<b>j</b>	15	15	5	•	118.6	(• 100.7) •
<b>k</b>	11	15	3	•	130.7	•
<b>l</b>	11	15	4	•	91.6	• 92.7 •
<b>m</b>	11	15	5	•	115.5	(• 99.0) •
<b>n</b>	15	11	3	•	134.0	•
<b>o</b>	15	11	4	•	92.1	• 94.3 •

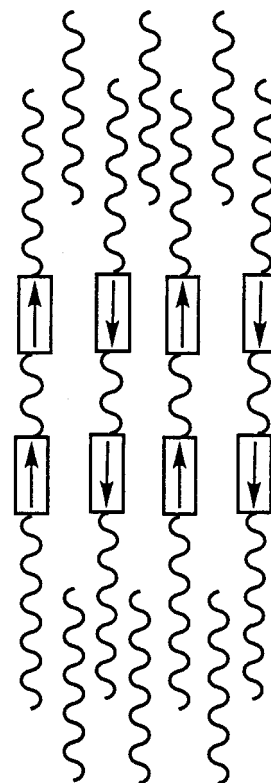


Figure 1. Schematic packing model for the smectic A phase of compound **4f**.

Table 5. Transition temperatures (°C) of binary systems of compounds **1w** and **3m**.

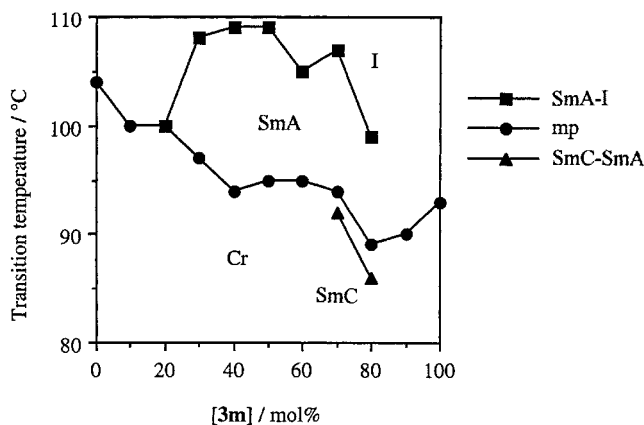
<b>1w</b> / mol %	<b>3m</b> / mol %	Cr	SmC	SmA	I
0	100	•	104		•
10	90	•	100 <sup>a</sup>		•
20	80	•	100	(• 100)	•
30	70	•	97	•	108 •
40	60	•	94	•	109 •
50	50	•	95	•	109 •
60	40	•	95	•	105 •
70	30	•	94	(• 92)	• 107 •
80	20	•	89	(• 86)	• 99 •
90	10	•	90 <sup>b</sup>		•
100	0	•	93 <sup>c</sup>		•

<sup>a</sup> A smectic A phase was observed at 98°C by microscopy.

<sup>b</sup> A smectic A phase was observed at 89°C by microscopy.

<sup>c</sup> Compound **1w** has the transition temperatures Cr 92.7 (SmC 82) I, as shown in table 1.

points that were approximately constant and higher than the melting points of pure **1w** and **3m** as shown in table 5 and in figure 2. Furthermore, for ratios with 70% and 80% of dimer **1w**, a monotropic smectic C phase also appeared. Since dimer **1w** showed a monotropic

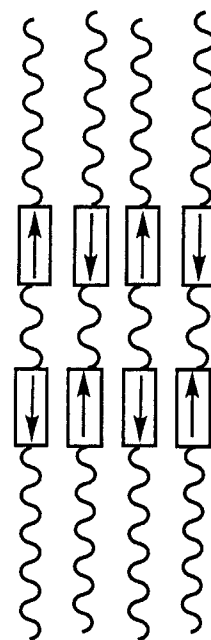
Figure 2. Phase diagram for mixtures of **1w** and **3m**.

smectic C phase and dimer **3m** was non-mesomorphic, the enantiotropic smectic A phase formed was actually induced by the mixing of these twins.

The layer spacing of the 50:50 mixed sample of twins **1w** and **3m** was found to be 51 Å at 80°C by XRD on the smectic A phase. On the other hand, the layer spacing of the 70:30 mixed sample of twins **1w** and **3m** was 46 Å at 90°C for the smectic C phase. The ratios of the layer spacing of the smectic A phase of the 50:50 mixed sample and of the smectic C phase of the 70:30 mixed sample to the extended molecular length are approximately 0.9 and 0.8, respectively, the extended molecular lengths of twins **1w** and **3m** being estimated as 56 and 58 Å, respectively, from AM1 calculations.

From these data, we propose the following molecular alignment for the induced smectic A phase of the mixture of **1w** and **3m**. Since we could observe that compound **1w** has a monotropic smectic C phase by optical microscopy as shown in table 5, compound **1w** can form a tilted layered structure to avoid dipole–dipole repulsion of tropon rings. When compound **3m** was mixed with compound **1w**, they should overlap to cancel their dipole moments. In the binary system of the 50:50 mixed system, it should therefore be possible to have a parallel arrangement of molecules perpendicular to the layer planes as shown in figure 3, in which the dipole moments of the tropon parts are cancelled. This molecular alignment is consistent with the appearance of a smectic A phase.

Next, the thermal behaviours of 50:50 mixed systems of systems **1** and **3** were investigated. Table 6 summarizes the transition temperatures of the 50:50 mixed system of compounds **1** and **3** when the alkylene chain length was changed. They have smectic A phases. For the results shown in table 7, the alkylene chain of **1** and **3** was fixed at 6 and the alkoxy chain lengths were changed. Again, the smectic A phase appeared.

Figure 3. Schematic packing model for the induced smectic A phases of mixtures of compounds **1w** and **3m**.Table 6. Transition temperatures (°C) of 1:1 mixtures of compounds **1** and **3** of fixed terminal chain length  $m = 11$  and 15.

	$m$	$n$	Cr	SmC	SmA	I
<b>1e 3g</b>	11	4	●	96	●	102
<b>1f 3i</b>	11	6	●	91	(● 83)	● 96
<b>1g 3j</b>	11	7	●	96		●
<b>1h 3k</b>	11	8	●	94	(● 69)	●
<b>1r 3m</b>	15	4	●	95	●	107
<b>1s 3n</b>	15	5	●	104	(● 94)	●
<b>1t 3o</b>	15	6	●	96	(● 94)	● 104
<b>1u 3p</b>	15	7	●	99		●
<b>1v 3q</b>	15	8	●	100		●

Table 7. Transition temperatures (°C) of 1:1 mixtures of compounds **1** and **3** with fixed alkylene chain length ( $n = 6$ ).

	$m$	$n$	Cr	SmC	SmA	I
<b>1f 3i</b>	11	11	●	91	(● 83)	● 96
<b>1n 3l</b>	13	13	●	94	(● 89)	● 101
<b>1t 3o</b>	15	15	●	96	(● 94)	● 104
<b>1f 3o</b>	11	15	●	97	(● 93)	●
<b>1n 3o</b>	13	15	●	93	(● 91)	● 101
<b>1t 3c</b>	15	7	●	80	(● 70)	● 91
<b>1t 3i</b>	15	11	●	93	(● 86)	● 99

### 3. Conclusion

Symmetrical twin troponoids **1** show monotropic smectic C phases and form layer structures in which the molecules tilt in order to relieve the dipole–dipole

repulsion. In contrast, unsymmetrical dimers **4** have smectic A phases because they can form a fully overlapped head-to-tail arrangement in order to cancel the dipole moments of the tropone carbonyl groups. By making the binary phases studied, a smectic A phase was induced. This result is explained in terms of the molecular arrangement of the binary system of twins **1w** and **3m**, in which the dipole moments of tropone parts are cancelled. Thus, the direction of the tropone carbonyl group is critical not only for the formation of mesophases, but also in controlling molecular organization.

Furthermore, contrast in the lengths of the terminal chains and the flexible spacer is quite important in inducing the mesomorphic state as observed in **2g**, which showed a monotropic smectic C phase, whereas other homologues were not mesomorphic.

#### 4. Experimental

The elemental analyses were made at the elemental analysis laboratory of Kyushu University. The melting points were obtained on a Yanagimoto micro melting point apparatus and are uncorrected. The NMR spectra were measured on a GSX 270H model spectrometer with CDCl<sub>3</sub> as solvent; the chemical shifts are expressed in  $\delta$  units. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were recorded on a JASCO IR-A102 spectrometer with KBr disks for crystalline compounds. The stationary phase for column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate, chloroform, and hexane. The transition temperatures were measured using a differential scanning calorimeter (Seiko DSC 200) and the mesomorphic phases observed by a polarizing microscope (Olympus BHSP BH-2) equipped with a hot stage (Linkam TH-600RMS). The XRD measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-K $\alpha$  radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

##### 4.1. Preparation of 5-alkoxytropolones (**5**)

To a solution of 5-hydroxytropolone (**6**, 500 mg, 3.6 mmol) in HMPA (hexamethylphosphoric triamide) (10 cm<sup>3</sup>), sodium hydride (60%, 150 mg, 3.8 mmol) was added at room temperature and the mixture stirred for 1 h. 1-Bromoheptane (0.57 cm<sup>3</sup>, 3.6 mmol) was added to the mixture. After stirring for 14 h at room temperature, the mixture was poured into 2M HCl and shaken with ethyl acetate. The organic layer was washed with NaCl solution and dried with Na<sub>2</sub>SO<sub>4</sub>. The organic layer was evaporated under reduced pressure to leave a residue which was chromatographed with hexane and ethyl acetate (2:1–1:1) on a silica gel column to give **5b**

(405 mg, 47%): m.p. 101.1°C, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.90 (3H, t,  $J$  = 6.8 Hz), 1.26–1.47 (8H, m), 1.80 (2H, m), 3.91 (2H, t,  $J$  = 6.2 Hz), 6.96 (2H, d,  $J$  = 12.3 Hz), and 7.29 (2H, d,  $J$  = 12.3 Hz); C<sub>14</sub>H<sub>20</sub>O<sub>3</sub>: C 71.26 (70.94), H 8.53 (8.45)% $\ddagger$ . **5d**: m.p. 103.9°C; C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>: C 72.69 (72.85), H 9.15 (9.17)%. **5g**: m.p. 96.8°C; C<sub>20</sub>H<sub>32</sub>O<sub>3</sub>: C 74.96 (74.98), H 10.07 (10.12)%. **5i**: m.p. 101.7°C; C<sub>22</sub>H<sub>36</sub>O<sub>3</sub>: C 75.82 (75.72), H 10.41 (10.43)%. **5j**: m.p. 103.9°C; C<sub>23</sub>H<sub>38</sub>O<sub>3</sub>: C 76.20 (75.96), H 10.57 (10.51)%. **5k**: m.p. 104.5°C; C<sub>24</sub>H<sub>40</sub>O<sub>3</sub>: C 76.55 (76.49), H 10.71 (10.70)%.

##### 4.2. Preparation of 2-alkanoyloxy-5-hydroxytropolones (**8**)

Octanoyl chloride was added to a solution of 5-hydroxytropolone (**6**, 500 mg, 3.6 mmol) in *N*-methyl-2-pyrrolidone (10 cm<sup>3</sup>) at room temperature and the reaction mixture was stirred for 3 h. The mixture was poured into 2M HCl and shaken with ethyl acetate. The organic layer was washed with NaCl solution and dried with Na<sub>2</sub>SO<sub>4</sub>. The organic layer was evaporated under reduced pressure to leave a residue which was recrystallized from ethyl acetate to give **8a** (445 mg, 47%): m.p. 166.8°C; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$ : 0.95 (3H, t,  $J$  = 6.6 Hz), 1.35–1.37 (8H, m), 1.68 (2H, m), 2.58 (2H, t,  $J$  = 6.8 Hz), 6.90 (2H, br s), 7.27 (2H, d,  $J$  = 11.7 Hz), and 11.16 (1H, s); C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>: C 68.16 (68.29), H 7.62 (7.58)%. **8b**: m.p. 163.9°C; C<sub>17</sub>H<sub>24</sub>O<sub>4</sub>: C 69.84 (69.78), H 8.27 (8.36)%. **8c**: m.p. 170.8°C; C<sub>19</sub>H<sub>28</sub>O<sub>4</sub>: C 71.22 (71.26), H 8.81 (8.87)%. **8d**: m.p. 170.3°C; C<sub>21</sub>H<sub>32</sub>O<sub>4</sub>: C 72.38 (72.33), H 9.26 (9.16)%. **8e**: m.p. 168.3°C; C<sub>23</sub>H<sub>36</sub>O<sub>4</sub>: C 73.41 (73.37), H 9.59 (9.64)%. **8f**: m.p. 166.7°C; C<sub>25</sub>H<sub>40</sub>O<sub>4</sub>: C 74.22 (74.22), H 9.96 (9.98)%.

##### 4.3. Preparation of compounds **1**

To a solution of 5-hexyloxytropolone (**5a**, 226 mg, 1.0 mmol) in tetrahydrofuran (5 cm<sup>3</sup>), 60% sodium hydride (53 mg, 1.3 mmol) was added at 0°C and the mixture stirred for 20 min. A solution of glutaroyl chloride (0.063 cm<sup>3</sup>, 0.49 mmol) in tetrahydrofuran (2 cm<sup>3</sup>) was added dropwise to the mixture and the temperature raised to room temperature. The reaction mixture was then stirred overnight, poured into NaCl solution and shaken with ethyl acetate. The organic layer was washed with NaCl solution and dried with Na<sub>2</sub>SO<sub>4</sub>. The organic layer was evaporated under reduced pressure to leave a residue which was chromatographed with hexane and ethyl acetate (2:1–1:1) on a silica gel column to give **1a** (259 mg, 98%): m.p. 95.9°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 0.91 (6H, t,  $J$  = 7.1 Hz), 1.34 (8H, m), 1.45 (4H, m), 1.80 (4H, m), 2.21 (2H, m), 2.81 (4H, t,  $J$  = 7.2 Hz), 3.92

$\ddagger$ The experimental data for all elemental analyses quoted are shown in parentheses.

(4H, t,  $J = 6.4$  Hz), 6.66 (4H, br s), and 7.17 (4H, d,  $J = 11.9$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 14.01, 20.04, 22.55, 25.60, 28.69, 31.42, 32.77, 68.81, 163.01, and 170.80.  $\text{C}_{31}\text{H}_{40}\text{O}_8$ : C 68.87 (68.80), H 7.46 (7.45)%. **1b**: m.p. 76.5°C;  $\text{C}_{36}\text{H}_{50}\text{O}_8$ : C 70.79 (70.53), H 8.25 (8.20)%. **1c**: m.p. 95.1°C;  $\text{C}_{36}\text{H}_{50}\text{O}_8$ : C 70.79 (71.05), H 8.25 (8.26)%. **1d**: m.p. 83.0°C;  $\text{C}_{40}\text{H}_{58}\text{O}_8$ : C 72.04 (71.97), H 8.77 (8.71)%. **1e**: m.p. 92.3°C;  $\text{C}_{42}\text{H}_{62}\text{O}_8$ : C 72.59 (72.57), H 8.99 (9.02)%. **1f**: m.p. 75.4°C;  $\text{C}_{44}\text{H}_{66}\text{O}_8$ : C 73.10 (73.11), H 9.20 (9.15)%. **1g**: m.p. 65.4°C;  $\text{C}_{45}\text{H}_{68}\text{O}_8$ : C 73.33 (73.39), H 9.30 (9.29)%. **1h**: m.p. 92.8°C;  $\text{C}_{46}\text{H}_{70}\text{O}_8$ : C 73.56 (73.46), H 9.39 (9.40)%. **1i**: m.p. 91.0°C;  $\text{C}_{44}\text{H}_{66}\text{O}_8$ : C 73.09 (72.95), H 9.20 (9.33)%. **1j**: m.p. 73.8°C;  $\text{C}_{45}\text{H}_{68}\text{O}_8$ : C 73.33 (73.22), H 9.30 (9.31)%. **1k**: m.p. 72.4°C;  $\text{C}_{46}\text{H}_{70}\text{O}_8$ : C 73.56 (73.40), H 9.39 (9.39)%. **1l**: m.p. 62.4°C;  $\text{C}_{47}\text{H}_{72}\text{O}_8$ : C 73.78 (73.67), H 9.49 (9.46)%. **1m**: m.p. 90.0°C;  $\text{C}_{48}\text{H}_{74}\text{O}_8$ : C 74.00 (73.89), H 9.57 (9.55)%. **1n**: m.p. 80.6°C;  $\text{C}_{48}\text{H}_{74}\text{O}_8$ : C 74.00 (73.97), H 9.57 (9.54)%. **1o**: m.p. 81.8°C;  $\text{C}_{50}\text{H}_{78}\text{O}_8$ : C 74.40 (74.16), H 9.74 (9.68)%. **1p**: m.p. 120.8°C;  $\text{C}_{48}\text{H}_{74}\text{O}_8$ : C 74.00 (73.95), H 9.57 (9.49)%. **1q**: m.p. 81.5°C;  $\text{C}_{49}\text{H}_{76}\text{O}_8$ : C 74.20 (74.07), H 9.66 (9.57)%. **1r**: m.p. 88.0°C;  $\text{C}_{50}\text{H}_{78}\text{O}_8$ : C 74.40 (74.67), H 9.74 (10.00)%. **1s**: m.p. 83.8°C;  $\text{C}_{51}\text{H}_{80}\text{O}_8$ : C 74.59 (74.52), H 9.82 (9.84)%. **1t**: m.p. 82.1°C;  $\text{C}_{52}\text{H}_{82}\text{O}_8$ : C 74.78 (74.96), H 9.90 (10.19)%. **1u**: m.p. 68.7°C;  $\text{C}_{53}\text{H}_{84}\text{O}_8$ : C 74.96 (75.13), H 9.97 (10.17)%. **1v**: m.p. 71.6°C;  $\text{C}_{54}\text{H}_{86}\text{O}_8$ : C 75.13 (75.04), H 10.04 (9.96)%. **1w**: m.p. 92.7°C;  $\text{C}_{52}\text{H}_{82}\text{O}_8$ : C 74.78 (74.73), H 9.90 (9.90)%. **1x**: m.p. 87.8°C;  $\text{C}_{54}\text{H}_{86}\text{O}_8$ : C 75.13 (74.90), H 10.04 (9.96)%. **1y**: m.p. 90.1°C;  $\text{C}_{56}\text{H}_{90}\text{O}_8$ : C 75.46 (75.38), H 10.18 (10.17)%. **1z**: m.p. 91.2°C;  $\text{C}_{58}\text{H}_{94}\text{O}_8$ : C 75.77 (75.53), H 10.31 (10.26)%.

#### 4.4. Preparation of compounds 2

To a solution of 5-hydroxy-2-octanoyloxytropon e (**8a**, 50 mg, 0.19 mmol) in HMPA (2 cm<sup>3</sup>), 60% sodium hydride (8 mg, 0.20 mmol) was added at room temperature and the mixture stirred for 1 h. To the mixture, 1,6-dibromohexane (0.015 cm<sup>3</sup>, 0.099 mmol) was added and the temperature raised to 70°C. The reaction mixture was then stirred for 4 h, poured into 2M HCl and shaken with ethyl acetate. The organic layer was washed with NaCl solution and dried with Na<sub>2</sub>SO<sub>4</sub>. The organic layer was evaporated under reduced pressure to leave a residue, which was chromatographed with hexane and ethyl acetate (2:1–1:1) on a silica gel column to give **2a** (18 mg, 31%): m.p. 95.0°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.81 (6H t,  $J = 6.6$  Hz), 1.18–1.47 (20H, m), 1.69 (4H, m), 1.78

(4H, m), 2.52 (4H t,  $J = 6.5$  Hz), 3.87 (4H t,  $J = 6.2$  Hz), 6.63 (4H br s), and 7.08 (4H d,  $J = 11.7$  Hz);  $\text{C}_{36}\text{H}_{50}\text{O}_8$ : C 70.79 (70.57), H 8.25 (8.25)%. **2b**: m.p. 99.5°C;  $\text{C}_{42}\text{H}_{62}\text{O}_8$ : C 72.59 (72.49), H 8.99 (8.97)%. **2c**: m.p. 89.7°C;  $\text{C}_{44}\text{H}_{66}\text{O}_8$ : C 73.10 (72.97), H 9.20 (9.12)%. **2d**: m.p. 93.6°C;  $\text{C}_{52}\text{H}_{82}\text{O}_8$ : C 74.78 (74.56), H 9.90 (9.84)%. **2e**: m.p. 68.9°C;  $\text{C}_{53}\text{H}_{84}\text{O}_8$ : C 74.96 (74.95), H 9.97 (10.01)%. **2f**: m.p. 77.5°C;  $\text{C}_{54}\text{H}_{86}\text{O}_8$ : C 75.13 (75.06), H 10.04 (10.01)%. **2g**: m.p. 106.3°C;  $\text{C}_{54}\text{H}_{86}\text{O}_8$ : C 75.13 (75.09), H 10.04 (10.05)%. **2h**: m.p. 98.7°C;  $\text{C}_{56}\text{H}_{90}\text{O}_8$ : C 75.46 (75.45), H 10.18 (10.19)%. **2i**: m.p. 74.4°C;  $\text{C}_{57}\text{H}_{92}\text{O}_8$ : C 75.62 (75.67), H 10.24 (10.26)%. **2j**: m.p. 84.4°C;  $\text{C}_{58}\text{H}_{94}\text{O}_8$ : C 75.77 (75.78), H 10.31 (10.37)%.

#### 4.5. Preparation of compounds 3

To a solution of 5-hydroxy-2-octanoyloxytropon e (**8a**, 50 mg, 0.19 mmol) in tetrahydrofuran (5 cm<sup>3</sup>), 60% sodium hydride (8 mg, 0.20 mmol) was added at room temperature and the mixture stirred for 1 h. Adipoyl chloride (0.014 cm<sup>3</sup>, 0.096 mmol) was added and the reaction mixture stirred for 5 h. The mixture was poured into NaCl solution and shaken with ethyl acetate. The organic layer was washed with NaCl solution and dried with Na<sub>2</sub>SO<sub>4</sub>. The organic layer was evaporated under reduced pressure and the residue was chromatographed with hexane and ethyl acetate (2:1–1:1) on a silica gel column to give **3a** (32 mg, 53%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.89 (6H, t,  $J = 6.6$  Hz), 1.30–1.46 (16H, m), 1.76 (4H, m), 1.85 (4H, m), 2.61 (8H, m), 6.68 (4H, d,  $J = 12.1$  Hz), and 7.16 (4H, d,  $J = 12.1$  Hz);  $\text{C}_{36}\text{H}_{46}\text{O}_{10}$ : C 67.69 (67.64), H 7.26 (7.25)%. **3b**:  $\text{C}_{37}\text{H}_{48}\text{O}_{10}$ : C 68.08 (68.04), H 7.41 (7.34)%. **3c**:  $\text{C}_{38}\text{H}_{50}\text{O}_{10}$ : C 68.45 (68.44), H 7.56 (7.49)%. **3d**:  $\text{C}_{39}\text{H}_{52}\text{O}_{10}$ : C 68.80 (68.77), H 7.70 (7.64)%. **3e**:  $\text{C}_{40}\text{H}_{54}\text{O}_{10}$ : C 69.14 (69.08), H 7.83 (7.85)%. **3f**:  $\text{C}_{42}\text{H}_{58}\text{O}_{10}$ : C 69.78 (69.80), H 8.09 (7.99)%. **3g**:  $\text{C}_{44}\text{H}_{62}\text{O}_{10}$ : C 70.37 (70.36), H 8.32 (8.30)%. **3h**:  $\text{C}_{45}\text{H}_{64}\text{O}_{10}$ : C 70.65 (70.53), H 8.43 (8.39)%. **3i**:  $\text{C}_{46}\text{H}_{66}\text{O}_{10}$ : C 70.92 (70.89), H 8.54 (8.51)%. **3j**:  $\text{C}_{47}\text{H}_{68}\text{O}_{10}$ : C 71.18 (71.12), H 8.64 (8.60)%. **3k**:  $\text{C}_{48}\text{H}_{70}\text{O}_{10}$ : C 71.43 (71.29), H 8.74 (8.76)%. **3l**:  $\text{C}_{50}\text{H}_{74}\text{O}_{10}$ : C 71.91 (71.91), H 8.93 (8.87)%. **3m**:  $\text{C}_{52}\text{H}_{78}\text{O}_{10}$ : C 72.36 (72.24), H 9.11 (9.13)%. **3n**:  $\text{C}_{53}\text{H}_{80}\text{O}_{10}$ : C 72.57 (72.60), H 9.19 (9.19)%. **3o**:  $\text{C}_{54}\text{H}_{82}\text{O}_{10}$ : C 72.77 (72.86), H 9.27 (9.31)%. **3p**:  $\text{C}_{55}\text{H}_{84}\text{O}_{10}$ : C 72.97 (72.89), H 9.35 (9.37)%. **3q**:  $\text{C}_{56}\text{H}_{86}\text{O}_{10}$ : C 73.17 (72.93), H 9.43 (9.40)%.

#### 4.6. Preparation of compounds 4

To a solution of 5-nonyloxytroponolone (**5d**, 70 mg, 0.27 mmol) in tetrahydrofuran (3 cm<sup>3</sup>), 60% sodium hydride (12 mg, 0.30 mmol) was added at room temperature and the mixture stirred for 1 h. 6-Bromohexanoyl chloride (0.041 cm<sup>3</sup>, 0.27 mmol) was added and the

§Three signals of the  $^{13}\text{C}$  NMR spectrum of compound **1a** were missing because the signals of the tropon e ring protons coalesced around room temperature: see [4].



reaction mixture was stirred for 3 h, poured into NaCl solution and shaken with ethyl acetate. The organic layer was washed with NaCl solution and dried with  $\text{Na}_2\text{SO}_4$ ; it was then evaporated under reduced pressure and the residue chromatographed with hexane and ethyl acetate (2:1–1:1) on a silica gel column to give **9a** (76 mg, 0.17 mmol). After measuring the  $^1\text{H}$  NMR spectra, compounds **9** were used for the following reactions.

To a solution of 2-decanoyloxy-5-hydroxytropon e (**8b**, 51 mg, 0.17 mmol) in HMPA (2  $\text{cm}^3$ ), 60% sodium hydride (8 mg, 0.20 mmol) was added at room temperature and the mixture stirred for 1 h. To the mixture, **9a** (76 mg, 0.17 mmol) was added and the temperature raised to 70°C. The reaction mixture was then stirred for 3 h, poured into 2M HCl and shaken with ethyl acetate. The organic layer was washed with NaCl solution and dried with  $\text{Na}_2\text{SO}_4$ . The organic layer was evaporated under reduced pressure and the residue chromatographed with hexane and ethyl acetate (2:1–1:1) on a silica gel column to give **4a** (17 mg, 10%): m.p. 116.9°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (6H, t,  $J = 5.7$  Hz), 1.28–1.89 (34H, m), 2.59 (2H, t,  $J = 7.4$  Hz), 2.64 (2H, t,  $J = 7.5$  Hz), 3.91 (2H, t,  $J = 6.4$  Hz), 3.95 (2H, t,  $J = 6.2$  Hz), 6.67 (4H, br s), and 7.15 (4H, d,  $J = 12.1$  Hz).  $\text{C}_{39}\text{H}_{56}\text{O}_8$ : C 71.75 (71.58), H 8.65 (8.64)%. **4b**: m.p. 134.5°C;  $\text{C}_{41}\text{H}_{60}\text{O}_8$ : C 72.32 (72.09), H 8.88 (8.87)%. **4c**: m.p. 91.5°C;  $\text{C}_{42}\text{H}_{62}\text{O}_8$ : C 72.59 (72.30), H 8.99 (8.94)%. **4d**: m.p. 117.7°C;  $\text{C}_{43}\text{H}_{64}\text{O}_8$ : C 72.85 (72.81), H 9.10 (9.13)%. **4e**: m.p. 133.3°C;  $\text{C}_{45}\text{H}_{68}\text{O}_8$ : C 73.33 (73.26), H 9.30 (9.28)%. **4f**: m.p. 94.2°C;  $\text{C}_{46}\text{H}_{70}\text{O}_8$ : C 73.56 (73.54), H 9.39 (9.38)%. **4g**: m.p. 118.7°C;  $\text{C}_{47}\text{H}_{72}\text{O}_8$ : C 73.79 (73.70), H 9.49 (9.38)%. **4h**: m.p. 131.1°C;  $\text{C}_{49}\text{H}_{76}\text{O}_8$ : C 74.20 (74.03), H 9.66 (9.59)%. **4i**: m.p. 94.4°C;  $\text{C}_{50}\text{H}_{78}\text{O}_8$ : C 74.40 (74.30), H 9.74 (9.64)%. **4j**: m.p. 118.6°C;  $\text{C}_{51}\text{H}_{80}\text{O}_8$ : C 74.59 (74.45), H 9.82 (9.73)%. **4k**: m.p. 130.7°C;  $\text{C}_{45}\text{H}_{68}\text{O}_8$ : C 73.33 (73.07), H 9.30 (9.20)%. **4l**: m.p. 91.6°C;  $\text{C}_{46}\text{H}_{70}\text{O}_8$ : C 73.56 (73.56), H 9.39 (9.34)%. **4m**: m.p. 115.5°C;  $\text{C}_{47}\text{H}_{72}\text{O}_8$ : C 73.79 (73.51), H 9.49 (9.37)%. **4n**: m.p. 134.0°C;  $\text{C}_{45}\text{H}_{68}\text{O}_8$ : C 73.33 (73.17), H 9.30 (9.22)%. **4o**: m.p. 92.1°C;  $\text{C}_{46}\text{H}_{70}\text{O}_8$ : C 73.56 (73.47), H 9.39 (9.34)%.

#### 4.7. Preparation of compounds 7

To a solution of 4-octyloxyphenol (50 mg, 0.23 mmol) in tetrahydrofuran (3  $\text{cm}^3$ ), 60% sodium hydride (10 mg, 0.25 mmol) was added at room temperature and the mixture stirred for 1 h. Adipoyl chloride (0.017  $\text{cm}^3$ , 0.12 mmol) was added and the reaction mixture stirred for 18 h, poured into NaCl solution and shaken with ethyl acetate. The organic layer was washed with sat.

NaCl solution and dried with  $\text{Na}_2\text{SO}_4$ . The organic layer was evaporated under reduced pressure and the residue chromatographed with chloroform on a silica gel column to give **7a** ( $m = 8$ ,  $n = 4$ , 57 mg, 59%): m.p. 87.3°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.89 (6H, t,  $J = 6.6$  Hz), 1.29–1.47 (20H, m), 1.76 (4H, m), 1.86 (4H, m), 2.60 (4H, m), 3.92 (4H, t,  $J = 6.6$  Hz), 6.86 (4H, d,  $J = 9.2$  Hz), and 6.98 (4H, d,  $J = 9.2$  Hz);  $\text{C}_{34}\text{H}_{50}\text{O}_6$ : C 73.61 (73.69), H 9.08 (9.11)%. **7b** ( $m = 8$ ,  $n = 5$ ): m.p. 86.1°C;  $\text{C}_{35}\text{H}_{52}\text{O}_6$ : C 73.91 (74.07), H 9.21 (9.22)%. **7c** ( $m = 8$ ,  $n = 6$ ): m.p. 77.5°C;  $\text{C}_{36}\text{H}_{54}\text{O}_6$ : C 74.19 (74.24), H 9.34 (9.31)%. **7d** ( $m = 8$ ,  $n = 7$ ): m.p. 87.2°C;  $\text{C}_{37}\text{H}_{56}\text{O}_6$ : C 74.46 (74.40), H 9.46 (9.43)%. **7e** ( $m = 8$ ,  $n = 8$ ): m.p. 78.8°C;  $\text{C}_{38}\text{H}_{58}\text{O}_6$ : C 74.72 (74.78), H 9.57 (9.55)%. **7f** ( $m = 15$ ,  $n = 3$ ): m.p. 105.6°C;  $\text{C}_{47}\text{H}_{76}\text{O}_6$ : C 76.58 (76.52), H 10.39 (10.39)%. **7g** ( $m = 15$ ,  $n = 4$ ): m.p. 99.0°C;  $\text{C}_{48}\text{H}_{78}\text{O}_6$ : C 76.75 (76.72), H 10.47 (10.49)%. **7h** ( $m = 15$ ,  $n = 5$ ): m.p. 97.6°C;  $\text{C}_{49}\text{H}_{80}\text{O}_6$ : C 76.92 (76.87), H 10.54 (10.54)%. **7i** ( $m = 15$ ,  $n = 6$ ): m.p. 92.3°C;  $\text{C}_{50}\text{H}_{82}\text{O}_6$ : C 77.07 (77.06), H 10.61 (10.62)%. **7j** ( $m = 15$ ,  $n = 7$ ): m.p. 97.3°C;  $\text{C}_{51}\text{H}_{84}\text{O}_6$ : C 77.22 (77.08), H 10.67 (10.63)%. **7k** ( $m = 15$ ,  $n = 8$ ): m.p. 92.5°C;  $\text{C}_{52}\text{H}_{86}\text{O}_6$ : C 77.37 (77.31), H 10.74 (10.75)%.

#### 4.8. Preparation of binary mixtures of **1w** and **3m**

Compounds **1w** (40 mg) and **3m** (40 mg) were placed separately in 25  $\text{cm}^3$  standard flasks and dissolved in chloroform. The appropriate volumes of the chloroform solutions were mixed and the resultant solution evaporated to obtain the homogeneous binary mixtures.

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