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Liquid crystals and life

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Liquid crystals and life

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The molecules of living systems invariably exhibit both thermotropic and/or lyotropic liquid crystalline properties. In some cases the mesophases formed by bio-materials have lamellar structures, whereas in other situations they form columnar phases. Many liquid crystal bio-materials are found in cell membranes, indicating that such structures have properties that are dependent on liquid crystallinity for their function. In this article the mesomorphic behaviour of a variety of bio-materials is discussed.

1. Introduction

> Liquid crystals stand between the isotropic liquid and the strongly organized solid state, life stands between complete disorder, which is death and complete rigidity, which is death again [1].

The above quotation aptly describes the importance of liquid crystals in, and to, living organisms [2]. Although the history of liquid crystals began with scientific discourse between a botanist and a physicist concerning the melting behaviour of a biologically active material [3], it is only over the last 20–30 years that interest in the biological aspects of liquid crystals has resurfaced.

As with many topics of scientific fascination, the drive for a physical understanding of the phenomenon in question usually precedes and, to some degree, leads chemical and biological evaluation and development. Liquid crystals are not atypical in this respect; research from the 1920s to recent times was driven by the desire for a physical understanding of the phenomena of molecular self-assembly and self-organization. Our comprehensive understanding of these phenomena has led directly to practical applications in terms of display devices. Even for the modern era, the time elapsed between discovery, comprehension, invention and exploitation of liquid crystals has been incredibly short; for example, the first display devices, which were invented in the 1960s, formed the basis for the development of the multi-billion dollar industry of the 1990s. This rapid development and exploitation inevitably leads those involved in research to question the likelihood of the continuation of invention and subsequent exploitation [4].

In this set of publications, we celebrate George Gray's contributions to the field of liquid crystals, and in particular his development of stable room-temperature nematic liquid crystals which were suitable for display device applications [5]. At Hull, however, throughout the period of the development of the 4′-alkyl-4-cyanobiphenyls and their related clones, George, because of similar questions concerning the likelihood of the continuation of invention, maintained an 'eye' to the future. Thus, many aspects of liquid crystals, other than their use in display devices, were tested at Hull during this period. One of the topics originating from 1977 forms the basis for this article.

In this study, we investigated the possibility of columnar liquid crystal phases being formed by fully substituted carbohydrates (figure 1). Investigations of the liquid crystal properties of these compounds comprised the first study that we performed on derivatives of carbohydrates, but unfortunately, none of the materials we investigated was a liquid crystal [6]. Nevertheless, this work provided our first insights into possibilities of synthesizing or creating bio-related liquid crystals.

2. Liquid crystals in living cells

Most bio-liquid crystals are not synthetic, but are derived from natural sources, e.g. from cell walls or membranes; however, it should be remembered that even materials such as DNA can also exhibit mesomorphic behaviour.

There are two major classifications of cells [7]; the eukarotes, which have a membrane enclosed nucleus, and prokaryotes, which lack this form of organelle. The prokaryotes can be further subdivided into the archaebacteria and the eubacteria domains. For all of these groups, the structures of their cell walls can be described by the fluid mosaic model, where integral proteins float like icebergs in a two-dimensional lipid sea. The lipids

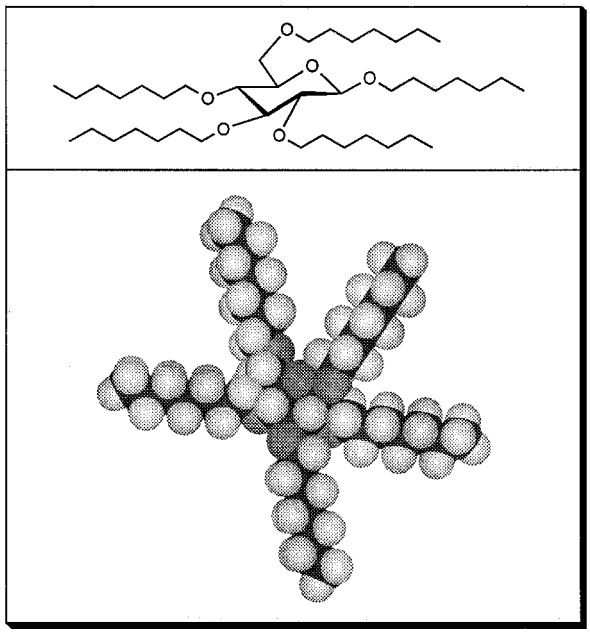


Figure 1. Structure of penta-heptyl gluco-β-D-pyranoside.

which make up membranes are varied in type, structure, and constitution depending on which cell group they are derived from. They can be ionic as in phospholipids, non-ionic as in cholesterol derivatives, and hydrogen bonding as in glycolipids. The proportions of the various lipid classes vary from cell type to cell type. Table 1 shows a typical distribution pattern for lipids found in human erythrocyte and human myelin [7]. The use of phospholipid hydrolysing enzymes, e.g. phospholipases, shows also that the distributions of lipids within membranes themselves are not uniform. Such studies can show, for example, that glycolipids are located exclusively on the external surfaces of plasma membranes, thereby making them important in cell recognition processes. Figure 2 shows a cartoon of a plasma cell membrane with integral proteins. Phospholipids and cholesterol, which is thought to modify the viscosity in membranes, are incorporated into the cell wall, whereas glycolipids and oligosaccharides can extend from the surface of the cell.

Each of the membrane lipid classes (and related derivatives) has been shown to possess mesomorphic

Table 1. Constituents (%) of human erythrocyte and myelin.

Constituent	Human erythrocyte	Human myelin
Phosphatic acid	1·5	0·5
Phosphatidylcholine	19	10
Phosphatidylethanolamine	18	20
Phosphatidylglycerol	0	0
Phosphatidylinositol	1	1
Phosphatidylserine	8·5	8·5
Cardiolipin	0	0
Sphingomyelin	17·5	8·5
Glycolipids	10	26
Cholesterol	25	26

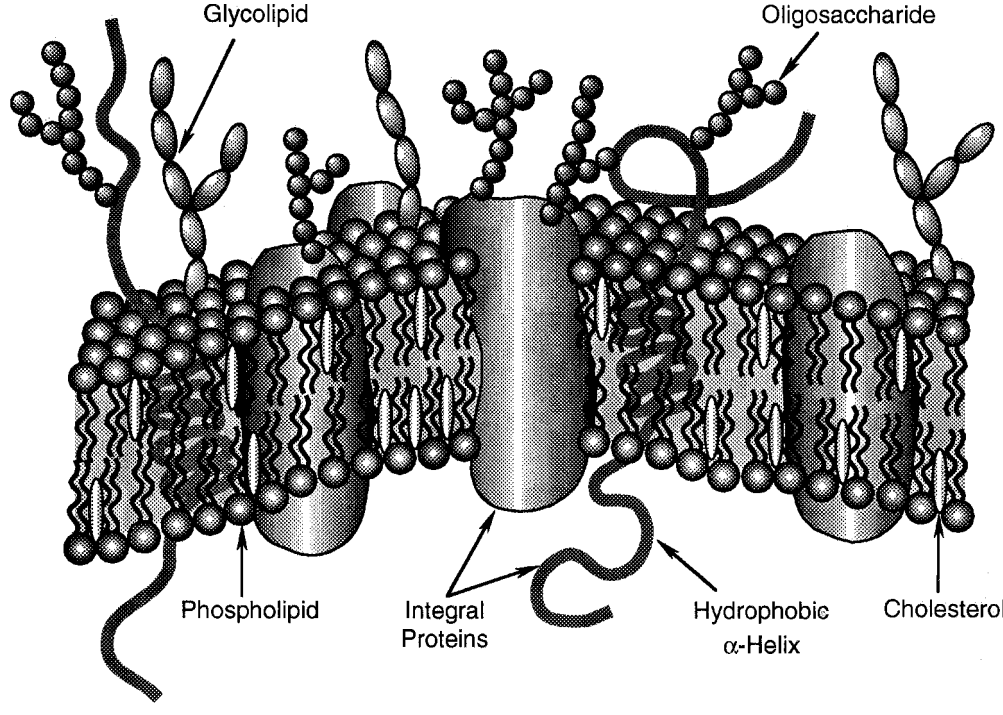


Figure 2. Schematic representation of a plasma membrane.

properties. In particular, aliphatic derivatives of cholesterol were among the first thermotropic liquid crystals to be discovered and investigated. Cholesterol in fact gave its name to one of the earliest classes of liquid crystal subgroup to be defined, i.e. the cholesteric or chiral nematic phase. The liquid crystal properties of phospholipids, like those of cholesterol derivatives, have been extensively examined both in their lyotropic, as well as their thermotropic states. Unlike cholesterol derivatives, phospholipids can form either lamellar, cubic or columnar phases in their liquid crystal (lyotropic or thermotropic) states. Figure 3 shows the structure and molecular shape of a phosphatidyl choline which exhibits a thermotropic columnar mesophase (see defect texture insert).

Many membrane components and lipids are also associated with various diseases [8]. For example, cholesterol build-up is associated with two very common diseases: gallstones and atherosclerosis. Both diseases can be life threatening if not treated; treatment, however, can involve extensive invasive surgery either resulting in the removal of the gall bladder in the case of gallstones or the grafting of new blood vessels to the heart as in atherosclerosis. Table 2 lists a number of lipid types in relation to their place in biological systems and the diseases with which they are associated.

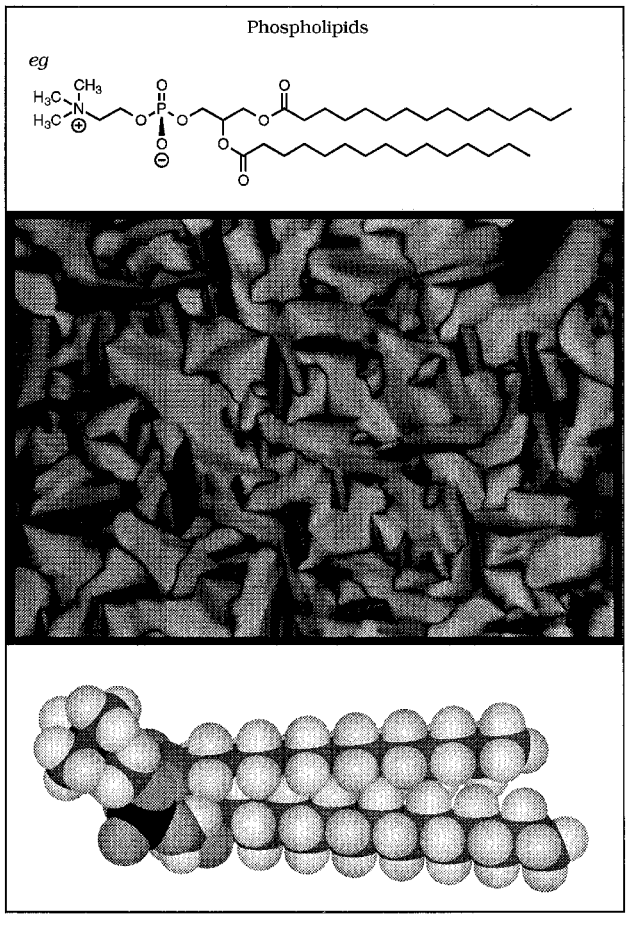


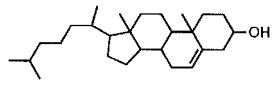
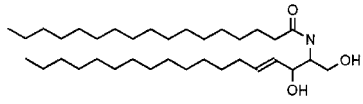
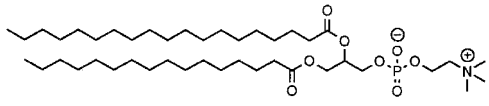
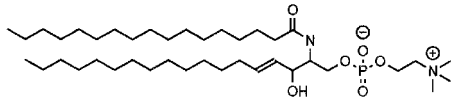
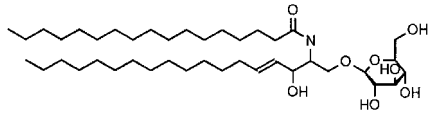
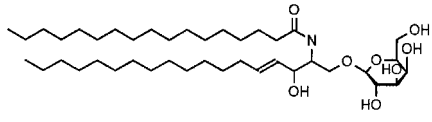
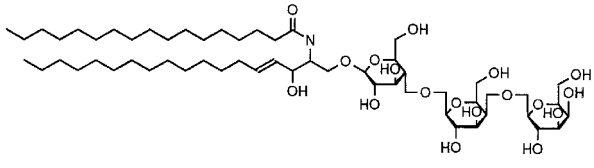
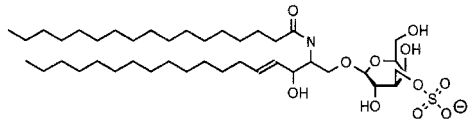
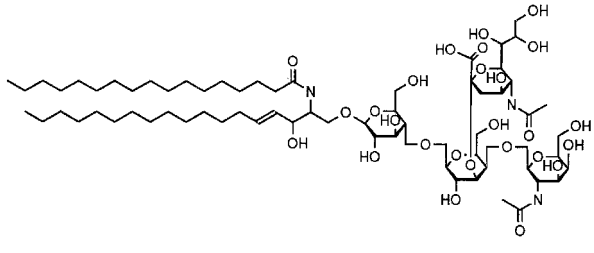
Figure 3. Texture of the thermotropic columnar phase exhibited by long chain phospholipids.

3. Glycolipids

Glycolipids are a particularly important class of membrane components. Principally they are only found in the exterior of the lipid layer of cell walls, where they are involved in intercellular recognition processes. Cerebrosides, globosides and gangliosides are three classes of glycolipids derived from sphingosine. Sphingosine provides each of these types of glycolipid with the possibility of having two aliphatic (saturated and unsaturated) aliphatic chains attached to a sugar head-group, thereby allowing for molecular structures to be formed that have similar shapes to those of phospholipids, i.e. the shapes of glycolipids and phospholipids are similar and consequently they are conducive to forming membranes. The number and variety of carbohydrate residues in the head group determine the type of glycolipid. Figure 4 shows the molecular structures of examples of cerebrosides and gangliosides. Cerebrosides, which have a single carbohydrate unit in the head-group, are often found in nerve tissue, and in cases where there is a ceramidase enzyme deficiency, there is a build up of cerebrosides in the system leading to diseases such as Gaucher's disease and Krabbe's disease. Gangliosides are a group of more complex glycolipids which act as specific receptors for certain pituitary glycoprotein hormones. In addition they act as receptors for bacterial proteins such as cholera toxin, and they behave as specific determinants for cell–cell recognition. They have an important role in the growth and differentiation of tissues, which can also lead on to problems of carcinogenesis. Disorders of gangliosides can produce hereditary diseases such as the fatal neurological Tay–Saches disease [9].

Cerebrosides, like phospholipids, are potentially thermotropic and lyotropic liquid crystals. Figure 5 shows the structures of two cerebrosides, taken from a much larger number, that have been investigated at Hull [10]. These compounds, which were extracted from bovine brain tissue, exhibit thermotropic columnar phases, just like phospholipids; in addition they also exhibit lyotropic hexagonal phases. The thermotropic and lyotropic phases do not appear to be continuously miscible with change in water concentration, leading us to the view that the structures of the two liquid crystal phases are inverted with respect to one another, i.e. they are essentially H_1 and H_2 phases. It is also interesting that some naturally occurring cerebrosides carry aliphatic chains that possess a degree of unsaturation. It can be seen

Table 2. Constituents of cell membranes and related diseases [8].

Compound structural class	Biological use	Disease
	Cholesterol Constituent of membranes	Gallstones Atherosclerosis
	Ceramide Involved in sphingolipid metabolism	Farber's disease
	Lectithin Major component of membranes	LCAT deficiency
	Sphingomeylin Major component of membranes	Niemann–Pick disease
	Glucose cerebroside Component of nervous tissue	Gaucher's disease
	Galactose cerebroside Component of nervous tissue	Krabbe's disease
	Globoside-3 Minor component of tissue	Fabry's disease
	Galactose cerebroside sulphate Minor component of tissue	Metachromatic leucodystrophy
	Gangliosides, e.g. GM2 Minor components of many tissues	Tay–Sachs disease

from figure 5 that unsaturation lowers melting points. In addition, unsaturation modifies the molecular structure, leading to wedge-shaped molecules that have a smaller arc size which in turn affects the degree of bend produced in bilayer structures. Interestingly, our studies show there is little variation of clearing point with change in aliphatic chain length or carbohydrate type.

These results show that cells can use liquid crystal

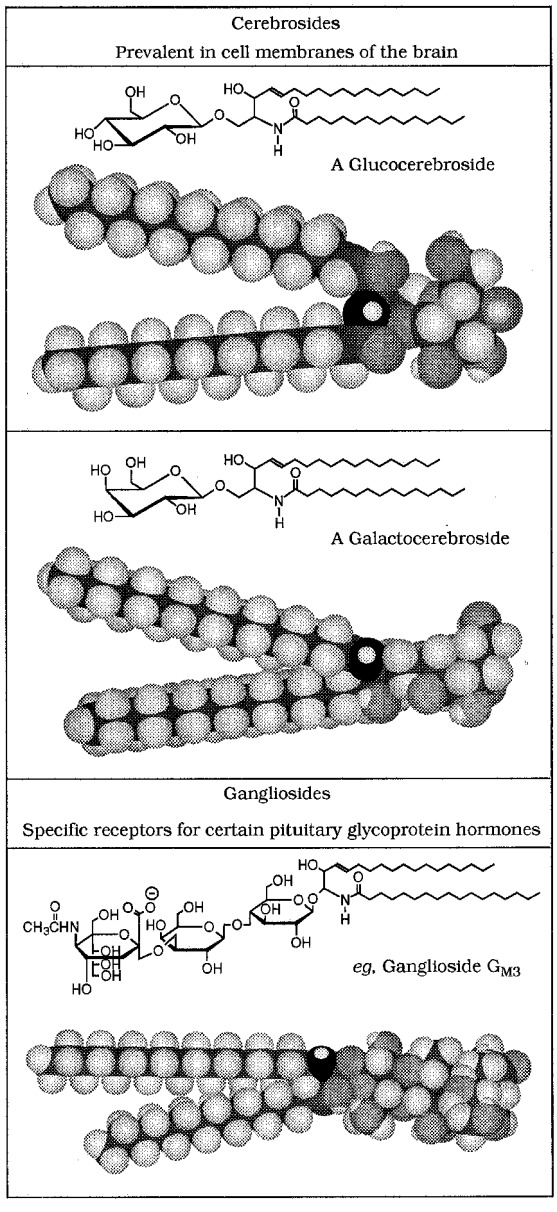


Figure 4. Molecular models of gluco- and galactocerebrosides and ganglioside G_{M3}.

technology, typical of materials for display device applications, for modifying their behaviour/properties. For example, cells use eutectic mixtures to maintain wide operating temperatures, they use molecular shape and polarity to vary elastic properties (as in bilayer bend) and viscosity, they use *cis*- and *trans*-double bonds to modify melting behaviour and to fine tune viscoelastic properties, and they use chirality in molecular recognition processes in a similar way to its use in thermochromics or ferroelectrics. We can take this analogy further if we examine the structures of membrane components found in the archaea domain.

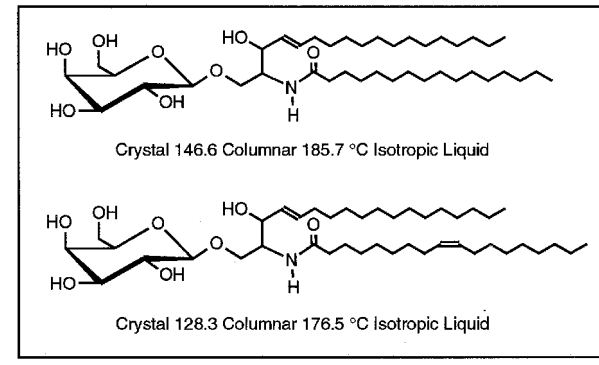


Figure 5. Liquid crystal properties of some galactocerebrosides.

The archaea domain can be subdivided into three different kinds of organism; the methanogens, halobacteria, and thermoacidophiles. All three types of archaebacteria are stable to extreme environmental stress such as high temperatures, lack of oxygen, etc. (conditions that might be found in volcanoes for example). In order to survive such extreme conditions, archaeabacteria possess membrane components that have a higher degree of chemical stability. Better chemical stability often leads to higher melting points, but with the use of isoprenic units, archaebacteria use chain branching to reduce the onset of crystallization (figure 6). Ether linkages, which are more difficult to synthesize, bolaphiles (i.e. dimers where two polar head groups are joined together by a bridging chain) and macrocyclic units are also used to stabilize the membrane structure with respect to extreme environmental conditions [11].

Bolaphiles and macrocyclic lipids are interesting because they effectively span the bilayer structure (see examples of membrane structures in figure 7). This adds strength to the overall bilayer structure, but at the same time it also reduces the abilities of both macrocyclic and non-macrocyclic lipids to move within the membrane. The structure of the bilayer will be stiffer, bend less easily, and the motions of the two halves of the bilayer structure relative to one another will be hindered; consequently, the viscoelastic liquid crystalline properties will be affected accordingly. Although these attributes

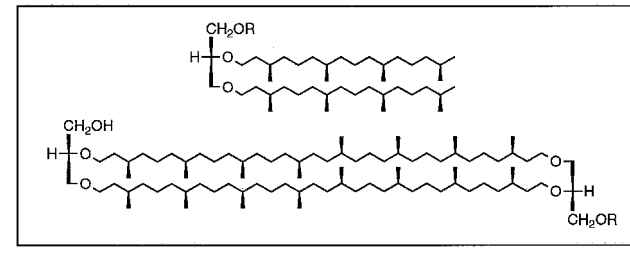


Figure 6. Structures of materials found in archaebacteria which contain isoprene units.

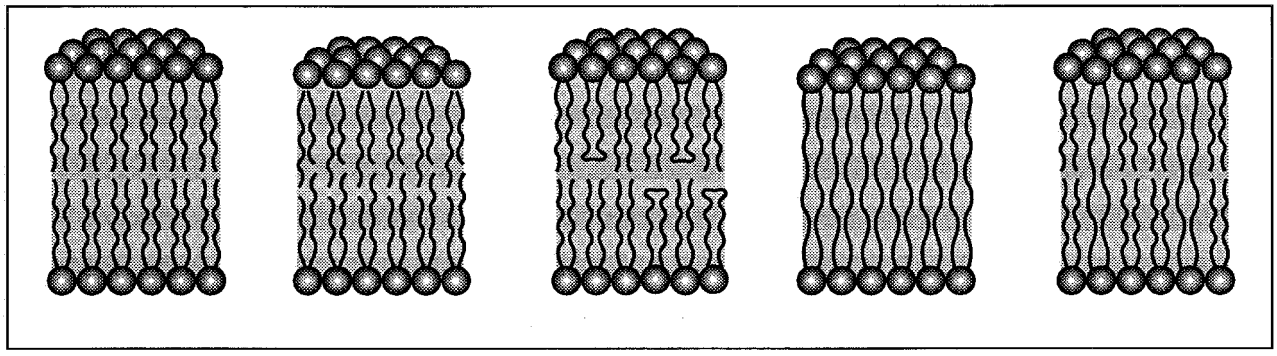


Figure 7. Models of membranes.

greatly stabilize membrane structures against external stress, they can be a hindrance in the development of more advanced life systems, where complex functionality is required.

The problems posed by incorporating bolaphiles (i.e. dimers where two polar head groups are joined together by a bridging chain) into membranes are exemplified for model materials. For instance many synthetic bolaphiles, although sometimes exhibiting lyotropic phases, only rarely show thermotropic mesomorphic behaviour. This behaviour suggests that these materials are not particularly good liquid crystal materials, which in turn implies that they would not be suitable in the formation of membranes.

Ether linked two chain glycolipids, with structures similar to those found in eubacteria and eukarotes, can be found in archaebacteria. Figure 8 shows a synthetic material which has a structural design based on typical glycolipids, except in this case the sugar residue is in its furanose form [12]. This material forms a columnar phase on heating and a hexagonal lyotropic phase on the addition of water. The clearing point, in comparison with cerebrosides, etc. is very low because of the extensive chain branching introduced by the isoprenic units. Thus, this material is in its liquid crystal phase at room temperature and can be cooled down to $-50°C$ without recrystallization occurring. The ether linkages make the material more chemically stable than do the corresponding ester and amide linkages found in the eubacteria and eukarote domains. The use of unsaturation to modify physical and biological properties is this time not suitable because of the potential reactivity of double bonds. Thus modification of melting and clearing points has to be achieved in another way, i.e. by chain branching. Dimers and macrocyclic systems related to the material shown in figure 8 show similar phase behaviour, as might be expected because the membrane components (monomers and dimers) are required to be compatible.

Archaebacteria, therefore, use chain branching to reduce melting point and to improve upon the temperature range, just as chemists use the same techniques to modify liquid crystal properties and mesophase temperature ranges for materials used in electro-optic devices. *Thus in an uncanny parallel, synthetic chemists involved in the creation of novel mesomorphic materials have been relearning the rules first employed by nature in the design of membrane components.*

By and large, nature tends to use two aliphatic chains in conjunction with a single polar head-group in the design of membrane components. Single chain/single polar head-group systems are not quite so common in nature, yet much recent research in the fields of liquid crystals and biotechnology concerns materials of this type. Many of these substances act as surfactants and can be used as detergents. For example, commercially available mono-alkyl glycolipids, such as *n*-octyl-1-*O*-*β*-D-glucopyranoside [13], are used as non-ionic detergents in the extraction of proteins from cell walls without denaturization occurring. In addition, they can be used as non-selective bactericides. Thus, in some senses two chain glycolipids can be seen to stabilize membrane structures, whereas mono-chain systems appear to perform the opposite task and destabilize them.

One of the first families of mono-alkyl substituted glycolipids to be examined for their liquid crystalline tendencies were the *n*-alkyl-1-*O*-*β*-D-glucopyranosides [14, 15]. As noted, some members of this family are commercially available, e.g. from the Sigma Chemical Co. Figure 9 shows a schematic representation of the liquid crystalline phases exhibited by the octyl homologue. Upon heating, it forms a smectic A_d^* phase, where the molecules are arranged in interdigitated bilayers. The material exhibits three crystal states before melting to the smectic phase at 67°C. The mesophase is then stable upon further heating to 106°C when it transforms to the liquid. Even though the compound contains many asymmetric centres, and is strongly optically active, there is no indication of the formation of a TGB phase at the clearing point. Cooling from the liquid results in the formation of the smectic A_d^* phase again, which this time

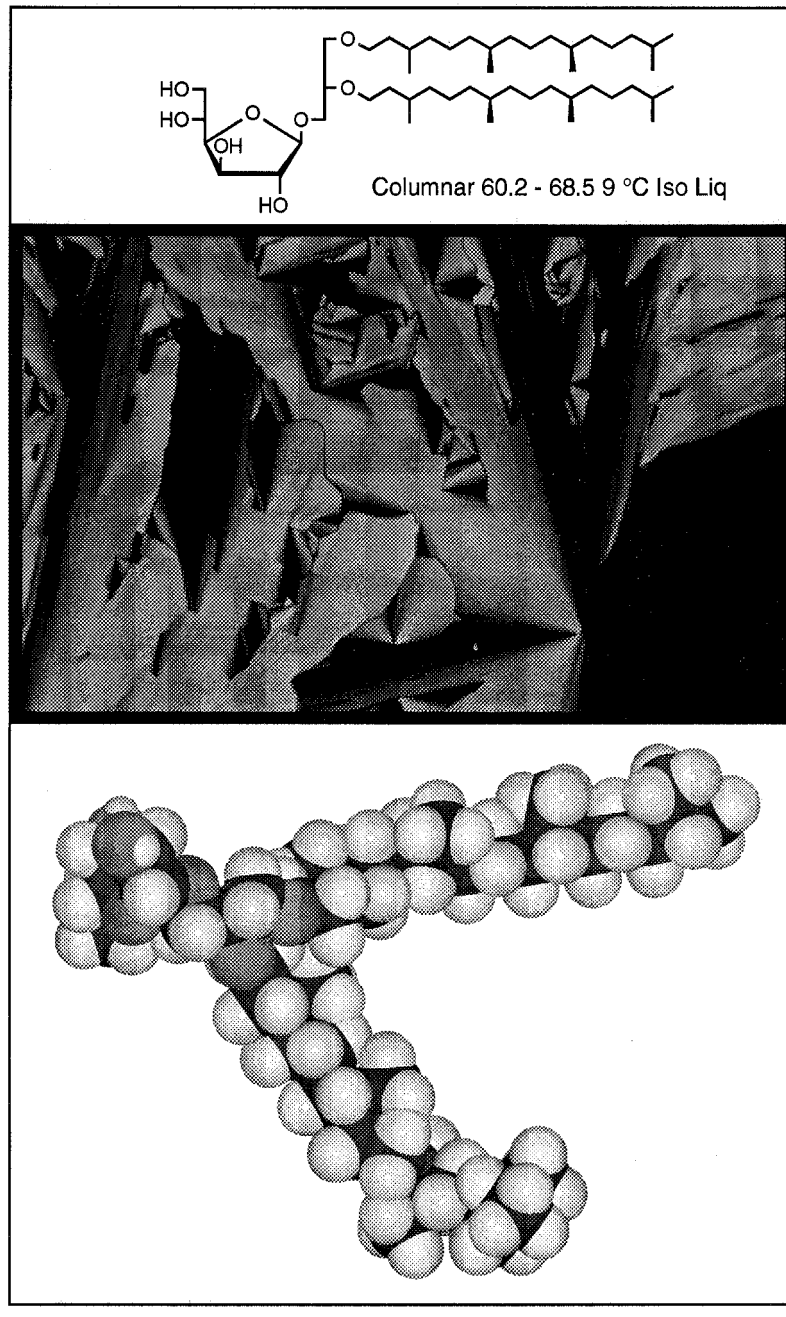


Figure 8. A synthetic mimic of an archaebacteria membrane component. This material exhibits a columnar mesophase [12] as shown by the texture in the inset (magnification $\times 100$).

can be supercooled to room temperature. Further cooling results in the formation of a glassy state. (It is interesting that some sugar systems, e.g. galactose, tend to form crystals on cooling whereas others, e.g. glucose, tend to form glasses.) Upon addition of water to the octyl homologue, lamellar, hexagonal and cubic lyotropic phases are formed. Thus the octyl homologue shows a varied and rich polymorphism, and can be accurately described as being amphitropic (i.e. thermotropic and lyotropic).

4. Carbohydrate structure and form

Unlike conventional thermotropic liquid crystals, carbohydrates can exist in a variety of structural forms which can affect transition temperatures, enthalpies of transition, and physical properties. Glucose, for example,

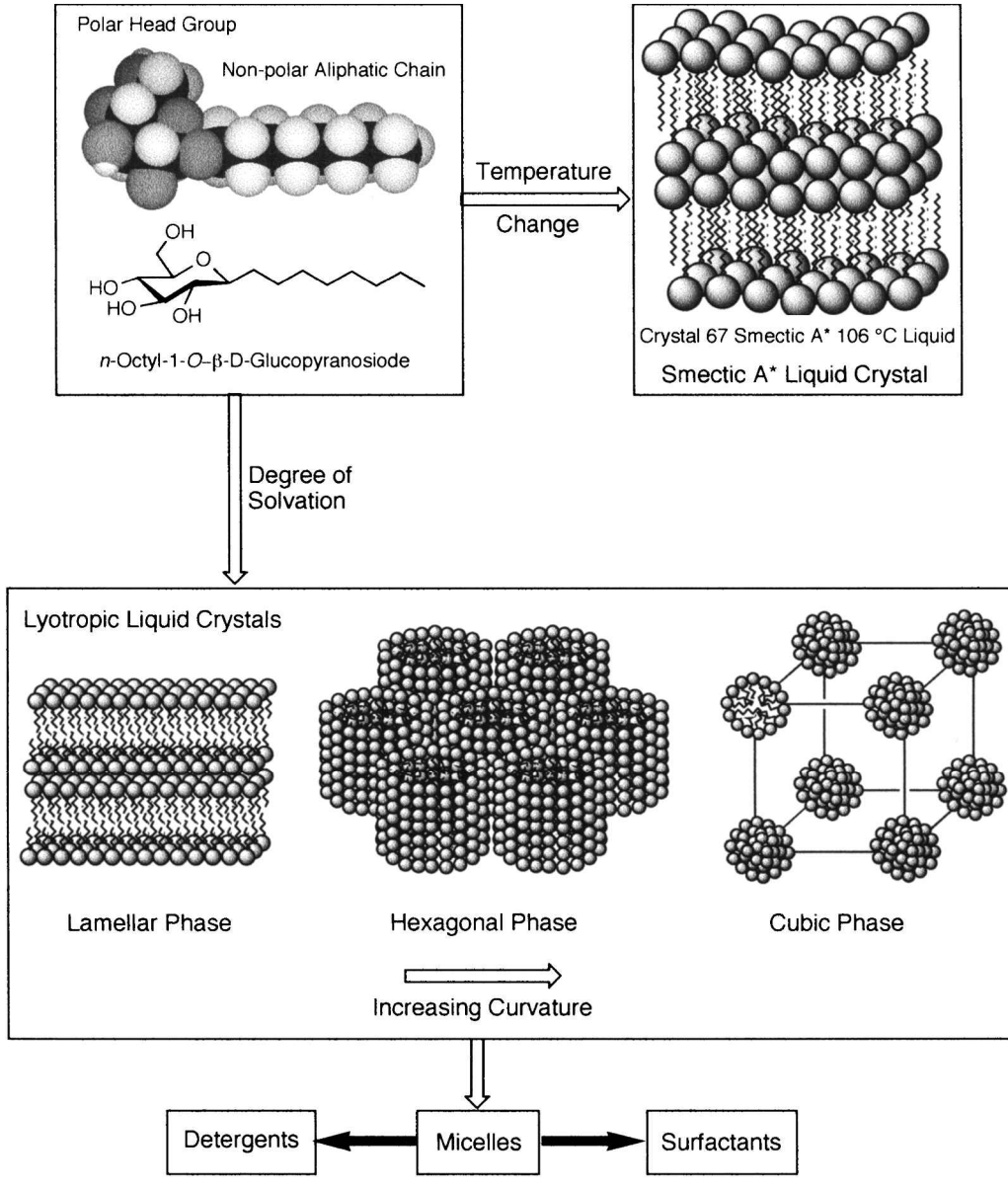


Figure 9. Schematic representation of the amphitropic properties of octyl 1-*O*-β-D-glucopyranoside.

can exist in an open chain (acyclic) form, in a six-membered ring (pyranose) form, or in a five-membered ring (furanose) form. In addition, it is difficult to specify the exact stereochemistry at the 1-position (the anomeric position), because in some cases sugars invert their structures easily at the anomeric position and at best only a ratio of the amount of α- (axial) substitution to β- (equatorial) substitution can be given. This is particularly true for situations where the 1-position is unsubstituted. Thus, it is possible to give a number of transition temperatures for a compound described, e.g. as simply octyl glucoside. In figure 10 the thermotropic transition temperatures are given for the α- and β-substituted pyranose and furanose forms of octyl glucoside [16]. It can be seen from this figure that the pyranose forms have higher clearing temperatures, with the α-form being higher than the β-form for the pyranoside, whereas the order is reversed for the furanoside. However, unlike conventional thermotropic systems, this observation does not herald the introduction of a property/structure activity correlation as the order of clearing temperatures:

$$\alpha\text{-pyranoside} > \beta\text{-pyranoside} > \beta\text{-furanoside} > \alpha\text{-furanoside},$$

does not necessarily translate to other sugar systems. Thus it is very difficult to develop property/structure

correlations for the thermotropic properties of substituted sugars.

The difficulty in developing property/structure correlations for clearing temperatures of substituted sugars can be comprehended through scrutiny of figure 11. In this figure the structures of the various forms of dodecyl glucopyranoside are shown. In the figure the dodecyl chain is moved from the 1- to the 6-position, but at the same time the ratio of α- to β-anomer varies from one compound to the next (except for the 1-position where we can be sure that we have 100% α or 100% β). The clearing points vary from 140 to 167·2°C, with the 6-substituted compound having the highest clearing temperature and the 4-substituted compound the lowest [17]. However, unless we know the proportions of α to β we cannot claim that we have a property/structure correlation, nor can we develop a testable theory as to why this is the order of the clearing points.

The situation improves a little for acyclic systems. For example, recent studies showed that when a dodecyl chain was moved sequentially from one position to the next in dodecyl D-xylitols the clearing temperatures increased and then decreased on passing from the 1- to the 5-position [18]. The 2- and 4-substituted compounds had the same transition temperatures (the 1- and 5-substituted systems are in fact the same compound). The 3-substituted material had the highest clearing point, which is to be expected as it has the most symmetrical structure, even though it has the lowest molecular anisotropy. It is also interesting that the effect of chirality (D and L isomers can be obtained for the 2- and 4-substituted systems) is minimal on clearing points. Figure 12 shows a plot of the transition temperatures for the dodecyl D-xylitols. It is remarkable however that such flexible acyclic systems should have such high clearing temperatures. For related hexoses, it is found that the clearing temperatures are on a par or often higher than those of the analogous cyclic systems. This seems at first glance to be contrary to convention, where stiffer ring systems have higher transition temperatures. However, unlike conventional systems, carbohydrate-containing liquid crystals have their mesophase structures stabilized by the number of hydroxyl groups that are available for the purposes of hydrogen bonding. In the case of acyclic systems, their inherent flexibility makes all of the hydroxyl groups available, whereas in cyclic systems often one of the hydroxyl moieties will be tucked away behind a ring or a substituent chain, thereby reducing the number of hydrogen bonding sites.

Thus, although we cannot make too many tentative property/structure correlations for carbohydrate liquid crystals, we can infer that clearing temperatures are affected by the number and availability of hydroxyl groups that are able to hydrogen bond. We also must consider, for the purposes of forming and stabilizing mesophase structure, that the hydrogen bonds are dynamic.

Apart from the position of substitution and stereochemical structure, carbohydrate containing liquid crystals can have more than one sugar unit [19], e.g. disaccharides or trisaccharides, etc. In such circumstances the sugar residues may be cyclic or acyclic, thereby providing for the formation of families of compounds where the sugar units appear in one form or another (e.g. acyclic, furanose, or pyranose forms). For instance, disaccharides can be obtained where both of the sugar moieties are cyclic, or where both are acyclic, or where one is cyclic and the other acyclic. For combinations of cyclic and acyclic sugar residues, the position of attachment of the cyclic moiety to the acyclic chain can give linear or branched systems, etc. Table 3 shows the structures and thermotropic liquid crystal phase transitions for three disaccharides [19, 20]. It is interesting to note from the table that the two-ring system, which has a structure that resembles a typical thermotropic liquid crystal, has a relatively high clearing point, whereas mixed systems tend to have lower clearing points. Interestingly, the second compound in table 3 has a lower clearing temperature than the third compound, this may be due to the fewer number of hydroxyl groups available for hydrogen bonding for the second compound in comparison with the third, which concurs with remarks made earlier.

Sugar residues can also be incorporated into more typical structures of liquid crystals, e.g. structures that might contain phenyl as well as alkyl units. Figure 13 shows some examples where a phenyl ring has either been directly attached to a sugar residue or else appended through the anomeric oxygen atom [21, 22].

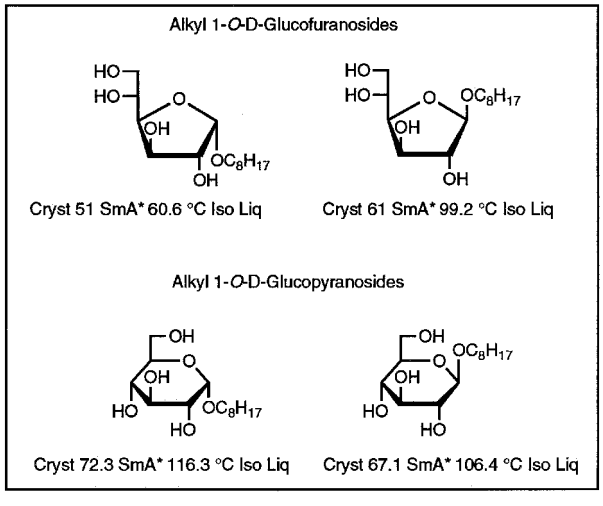


Figure 10. Comparison of the mesomorphic properties of octyl glucofuranosides with those of octyl glucopyranosides.

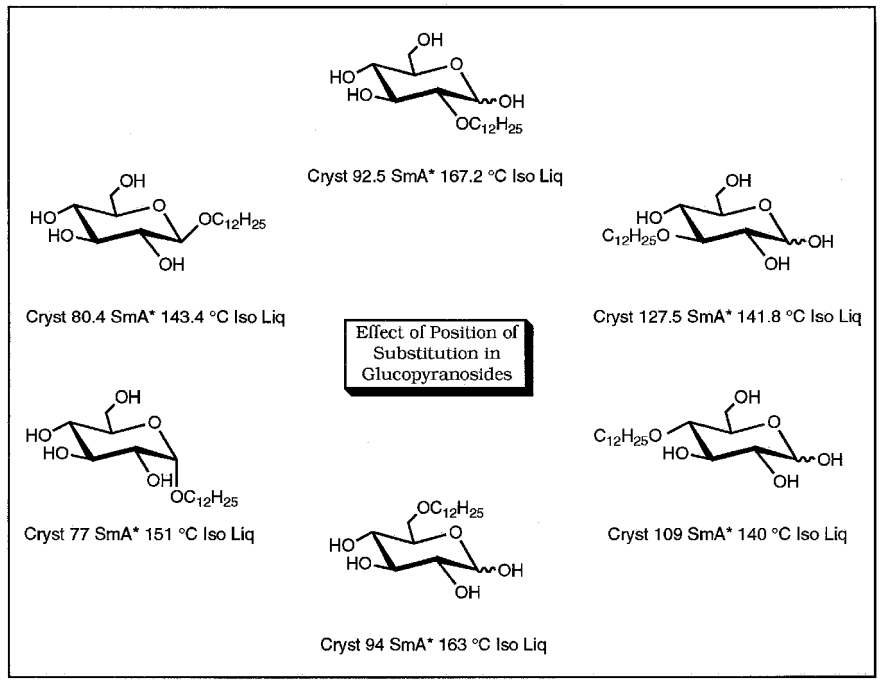


Figure 11. Effect of the position of aliphatic substitution on the mesomorphic properties in dodecyl glucopyranosides.

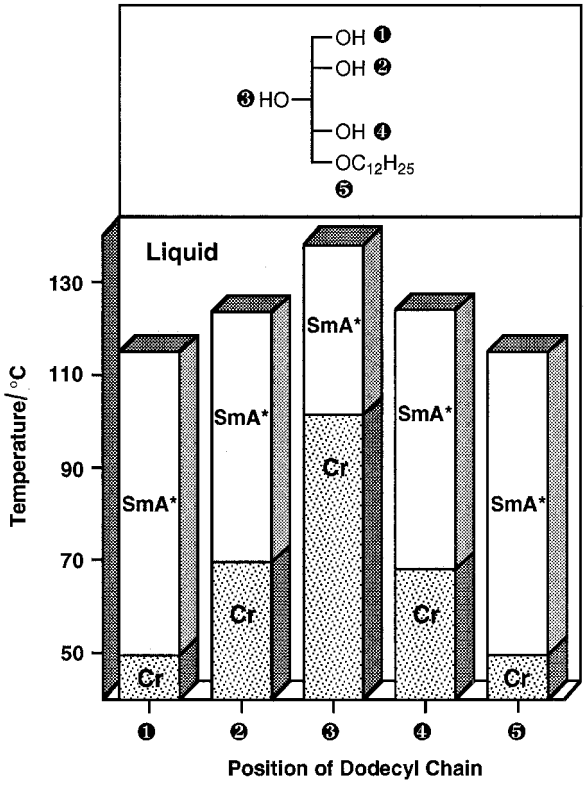
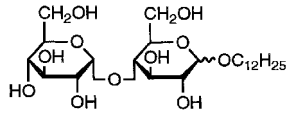
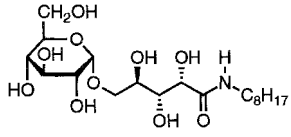
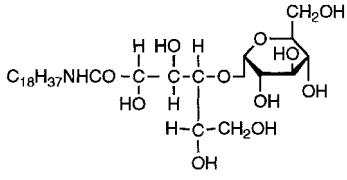


Figure 12. Effect of position of aliphatic substitution on the mesomorphic properties in dodecyl xylitols.

Phenyl substituted systems appear to produce more stable thermotropic phases in comparison to equivalent systems where the phenyl group is omitted. The ether linked systems shown in figure 13 have previously been tested for their antiviral properties. The directly linked mono-alkyl material exhibits a smectic A* phase as expected, but when the number of alkyl chains attached to the phenyl group is increased to three, columnar phases appear. This behaviour is similar to that found for thermotropic phasmidic crown ethers [23] and substituted inositols [24–26]. As with the case of the substituted inositols, the trisubstituted system is expected to form hydrogen bonded clusters which in turn stabilize the formation of columnar mesophases.

Synthetic materials have also been prepared where more than one aliphatic chain is attached to the carbohydrate residue. In these cases, however, the point of attachment is through a single bond, with a second aliphatic chain attached to the first through a branching point. This arrangement produces materials with similar molecular templates to the cerebrosides, where the number of hydroxyl groups available for hydrogen bonding is maximized. Again this is a structural feature used by nature to maintain liquid crystallinity in membranes. Attaching two chains directly to the polar head group severely reduces the chances of the material in question exhibiting a liquid crystal phase. Figure 14 shows some examples of synthetic materials where two aliphatic

Table 3. Comparison of the mesomorphic behaviour for related disaccharides.

Carbohydrate amphiphile	Transition temperatures
	*n*-Dodecyl maltoside Cryst 102 SmA*>245°C Iso Liq
	*N*-(1-octyl)-5-*O*-(α-D-glucosyl)-D-arabinonamide Cryst 63 SmA* 133°C Iso Liq
	*n*-Octadecyl maltobionamide Cryst 109·5 SmA*>207°C Iso Liq

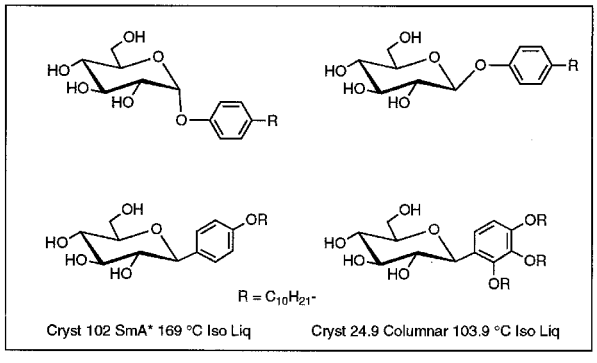


Figure 13. Structures and mesomorphic properties of phenyl substituted glycolipids.

chains have been joined to the polar head-group through a branching carbon or nitrogen atom [27–29]. Just like natural systems, the thermotropic behaviour of both cyclic and acyclic systems is the same: columnar phases are formed. With these systems bilayer columnar structures become feasible, particularly in cases where the materials also form vesicles. The lower part of figure 14 shows the cross-sectional area of a column of such a phase/vesicle. In the case of vesicles, water can permeate along the central axis of the column as well as between the columns.

5. Other bio-materials

So far the structures of the amphiphiles that have been discussed have been composed of a polar entity of a certain type coupled to one or more aliphatic chains. However, the variety of template structures which can

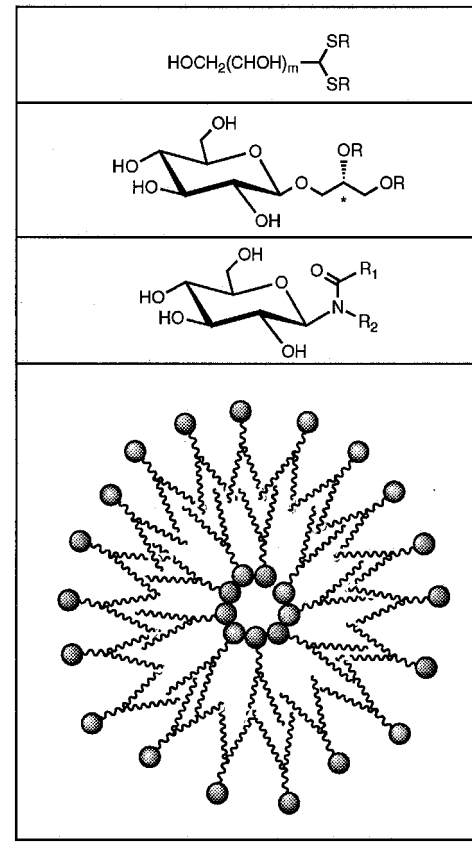


Figure 14. Structures of mesomorphic carbohydrate systems that carry two aliphatic groups attached to the sugar residue through a single linking unit.

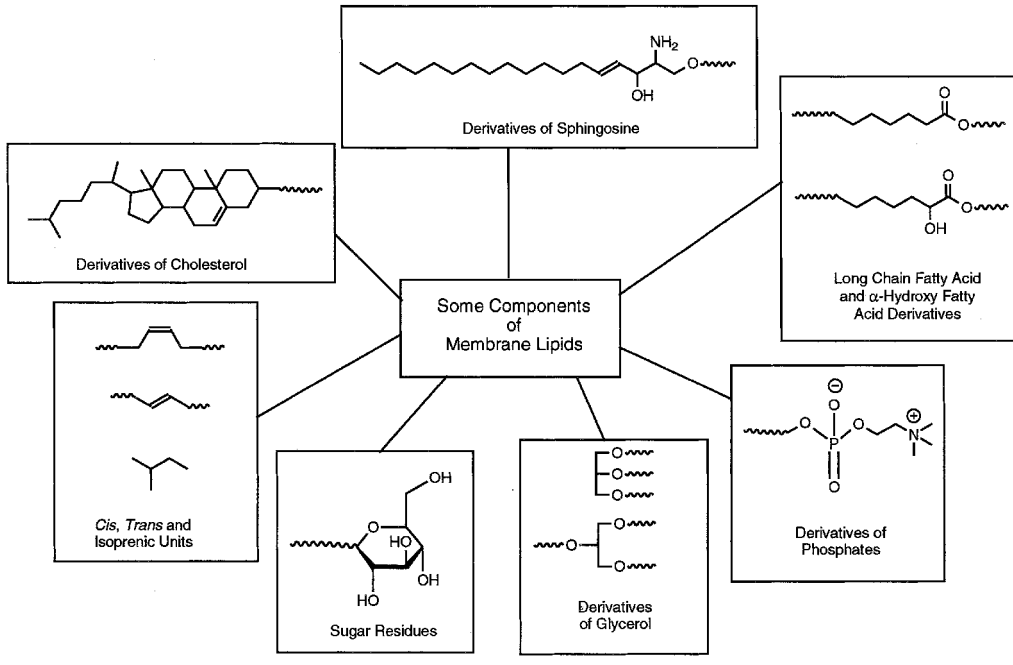


Figure 15. Structural components of membrane lipids.

be incorporated into amphiphilic/membrane systems is relatively broad. Figure 15 shows some of the structural elements that have been employed in the systems described so far, but examples of materials that have structures which are made up of combinations of the components shown have been limited. In addition, the materials described have all been related to membrane materials.

In this last section, the liquid crystal properties of other related bio-materials are discussed. Firstly, there are other carbohydrate related systems that exhibit liquid crystal properties; for example, certain aliphatic derivatives of vitamin C exhibit thermotropic smectic A* phases [30] (figure 16). It can be seen from the figure that aliphatic substituted ascorbic acid has only three hydroxyl groups available for hydrogen bonding, but unlike carbohydrate-related systems, the unsaturated ring system of ascorbic acid is relatively rigid; consequently such materials exhibit liquid crystal phases with good thermal stability ranges.

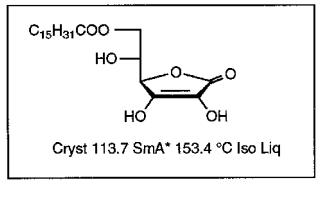


Figure 16. A liquid crystal with a structure based on vitamin C.

Secondly, materials with structural combinations other than an aliphatic chain linked to a polar group, can also exhibit mesomorphism. Figure 17 shows the structure of solanin [17] which has three polar sugar residues in the head group which is joined to a steroidal moiety. This material exhibits a thermotropic smectic A* phase at temperatures between 263 and 283°C, which is relatively high and may be due to the fact that solanin has nine hydroxyl groups available for hydrogen bonding, coupled to a stiff steroid unit. Overall, the molecular structure is relatively rigid and, as it can hydrogen bond, the material will have high melting and clearing points.

Obviously, there are many more types of bio-material that could sustain mesomorphic properties, and there are many that are involved in bio-processes (e.g. intercellular recognition) and bio-applications (e.g. surfactants

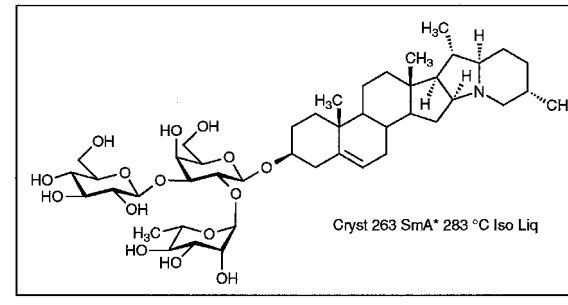


Figure 17. Structure and mesomorphic properties of solanin.

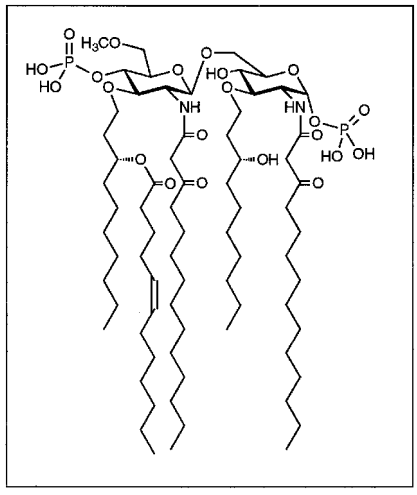


Figure 18. Structure of E5531.

and detergents). However, there are also bio-materials that are related to liquid crystals which could have interesting properties or uses, e.g. pharmaceuticals. For example E5531 (figure 18) is a candidate for use in the treatment of bacterial sepsis (systemic inflammatory response syndrome) [31]. Sepsis is known to kill approximately 250 000 people every year. The host cells over-respond to bacterial release of endotoxin (lipopolysaccharide LPS), and produce inflammatory agents such as cytokins. These agents induce fever, shock and organ failure. E5531 was designed to mimic the binding effects of the endotoxin without the harmful effects of subsequent cellular activation.

The structure of E5531 is similar to bio-liquid crystalline materials that have complex structures. E5531 combines sugar residues with phosphates and aliphatic chains with alkenic linkages, i.e. template components that can be found in figure 15. Thus, it would not be a

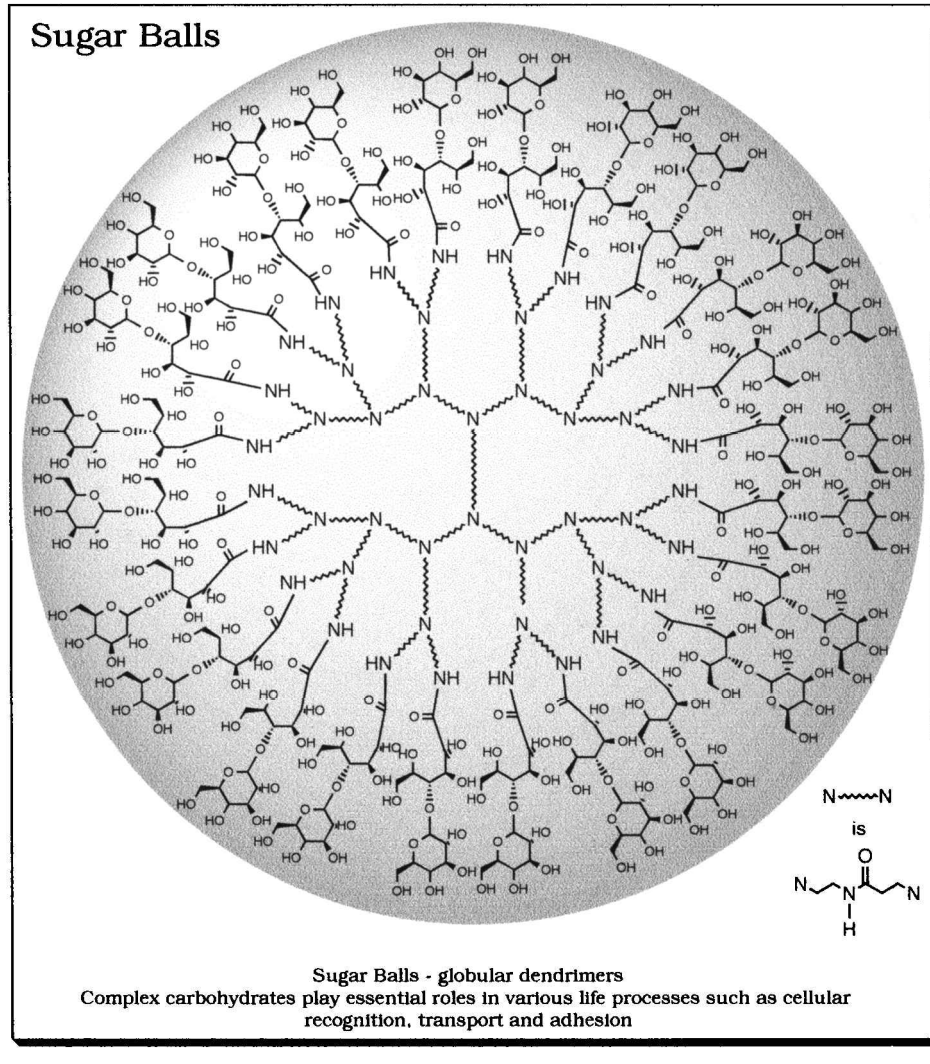


Figure 19. A sugar-based dendrimer.

surprise if E5531 was a liquid crystal, and it would then be interesting to ask what part liquid crystallinity plays in the use of E5531 as a treatment.

Bio-materials need not necessarily be of use solely in or to living systems. It is also possible that bio-related compounds could be of use in the conventional materials theatre. For example, there has been much attention paid to, and use made of, bio-polymers, and recently the first bio-dendrimers have been produced. Materials such as the one shown in figure 19 may not be liquid crystalline, but it is conceivable in the future that liquid crystalline bio-dendrimers will be prepared and will have interesting bio- and material-properties.

6. Conclusion

I have tried to demonstrate the diversity of bio-materials, that reside in living systems, which exhibit liquid crystal properties. The variety of materials selected for discussion only touches the tip of the iceberg of available compounds. These uniquely engineered substances could have wide uses to both living and conventional material systems, thereby demonstrating that research in this area of liquid crystals could have a bright future.

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Finally, happy birthday George.

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