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The Use of Simple Sugars for the Synthesis of Chiral Monophilic Liquid Crystals

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The Use of Simple Sugars for the Synthesis of Chiral Monophilic Liquid Crystals

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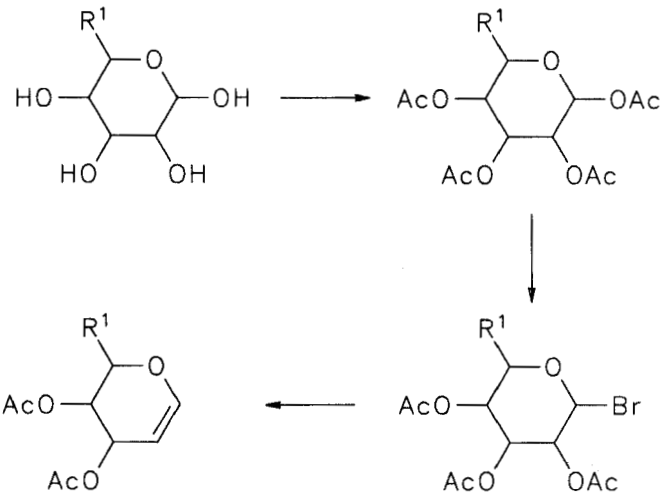
By Ferrier glycosylation of glycals and subsequent hydrogenation 2,3-dideoxyglycosides were obtained. Starting with glucose, xylose or rhamnose this reaction sequence led to thermotropic non-amphiphilic chiral liquid crystals. The synthesized compounds show cholesteric and smectic as well as blue and other cubic phases. The liquid crystalline properties were influenced by the anomeric effect.

Keywords: deoxy sugars, Ferrier reaction, chiral liquid crystals, cubic phase, oxygen heterocycles

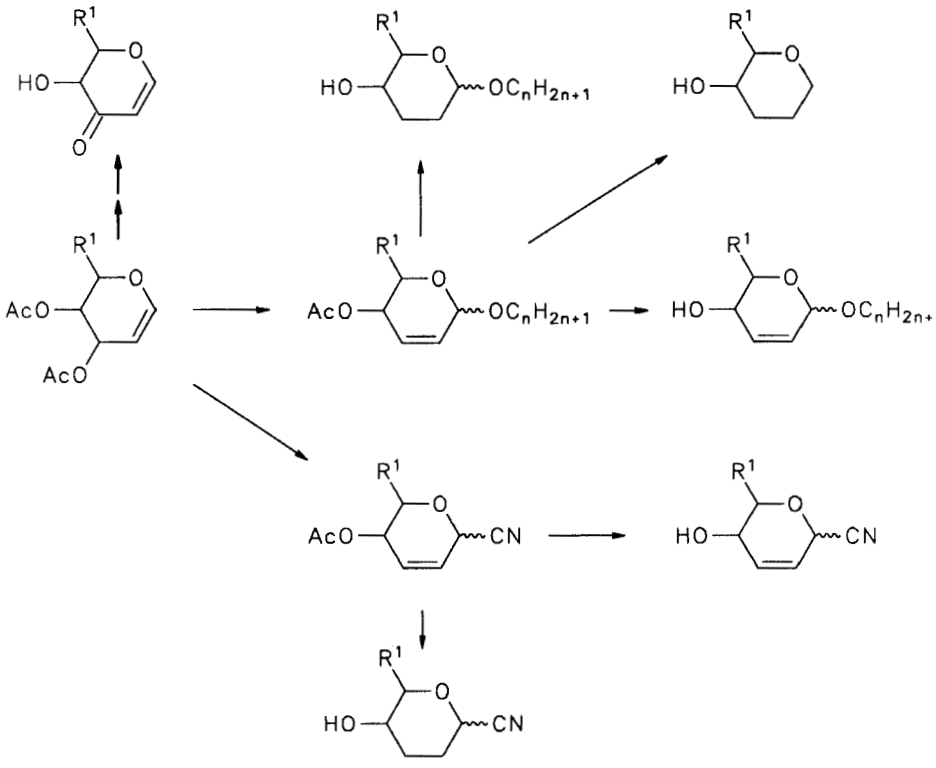
INTRODUCTION

Investigation of carbohydrate-derived amphiphilic[1–5] and discotic[6,7] liquid crystals were intensively studied since the beginning of the eighties. The use of such compounds for synthesis of monophilic (non-amphiphilic) calamitic liquid crystals was rarely considered previously.[8–10] To present conception high-substituted polar chain and annular saccharides are in contrast to the assumption which are believed to be essential for calamitic liquid crystals.



R^1 = H, CH_3, CH_2OAc

SCHEME 1



R^1 = H, CH_3, CH_2OAc

SCHEME 2

SYNTHESIS

The glycals were prepared according to the literature[11,12] via acetylated sugars and glycosyl bromides (Scheme 1). By Lewis-acid catalyzed rearrangement (Ferrier I reaction)[13] these glycals gave compounds of hex- or pent-2-enopyranoside structure. On further hydrogenation these could be transformed into 2,3-dideoxysugar derivatives (Scheme 2). When pentanol was used as nucleophile, the desired 1,4-*trans* configurated β-glycosides were obtained.[14] Reaction with trimethylsilylcyanide[9,15,16] afforded an anomeric mixture of hex-2-enopyranosyl cyanides which was separated by chromatography. Hydrogenation of double bonds was performed on palladium/charcoal (5%), for deacetylation methanolic sodium methoxide was used. Esterification with long-chain acids was performed classically using acid chloride in situ, prepared from the acid with thionyl chloride, in pyridine and subsequent addition of the corresponding sugar.

PROPERTIES

To show the potential of carbohydrates for the synthesis of liquid crystals, we studied quite different chemical structures (**1–27**, Table I). For the discussion, we will classify them into five groups.

Group 1: Compounds with Classical Calamitic Structure 1–5, 11–18, 23–24

These compounds show typical structures of calamitic liquid crystals. In fact, a number of phases such as blue (**12–14**), cholesteric (**1, 11–14, 16, 17**), cubic (**13–14**) and/or smectic (**1, 2, 4, 12, 24**) phases were observed. Clearing points are surprisingly low and mostly just monotrop. This can be explained by the configuration and conformation of these compounds. Liquid crystals with alicyclic rings show high clearing points when substituents are arranged 1,4-*trans* being predominantly in diequatorial position.[17,18] However, with increasing polarity substituents prefer the axial orientation.[19] This undesired effect is reinforced by the anomeric effect[20] as well as 1,4-dipolar interactions.[21] Owing to this, pentopyranosides **1–5** exhibit low clearing points. In hexopyranosides **11–18** and **24** conformation with diequatorial positioned substituents R^1 and R^2 is stabilized by the methyl group, which prefers an equatorial position for steric reasons, and therefore forces all other substituents into equatorial orientations. Whereas the methyl group as a lateral substituent has a favorable influence with respect to the conformation, it impairs the calamitic form of the molecule so that only moderately high clearing points are obtained.

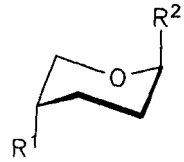
Compounds **4, 5, 15–18** and **24** are handicapped by the double bond in the ring which lead to a distortion as well as an increased rate of inversion.

In **23** the substituents R^1 and R^2 are orientated *trans*, but are forced into unfavorable diaxial positions by the methyl group. **23** represents the "conformation analogue" to **17**.

In particular both the glycosides **13** and **14** show a cubic mesophase. Cubic phases are observed in globular compounds,[22] but few examples are documented for cal-

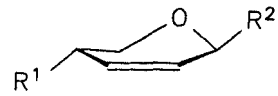
TABLE I

Liquid crystals derived from sugars



ß-D-*glycero*-Pentopyranosides

No	R^1	R^2	Phase Transition
1	C_7-Cy-Ph-COO-	H	Cr 50.3 (S 4.8 Ch 12.2) I
2	C_{10}-O-Ph-Ph-COO-	H	Cr 78.8 (S_A 61.4) I
3	C_{10}-O-Ph-Ph-COO-	O-C_5	Cr 49.1 I



ß-D-*glycero*-Pent-2-enopyranosides

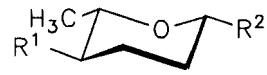
No	R^1	R^2	Phase Transition
4	C_7-Cy-Ph-COO-	O-C_5	Cr 26.1 (S 4.4) I
5	C_{10}-O-Ph-Ph-COO-	O-C_5	(110) Cr 125 I

ß-D-*erythro*-Hexopyranosides

No	R^1	R^2	R^3	Phase Transition
6	C_7-Cy-Ph-COO-	-OH	-OMe	Cr 116 (S 40) I
7	C_7-Cy-Ph-COO-	= R^1	-OMe	Cr 71 I
8	C_8O-Ph-COO-Ph-COO-	-OH	-CN	Cr 64 (S <?)[a] I
9	C_{10}-O-Ph-Ph-COO-	-OH	-CN	Cr 79.6 (S 63.5) I
10	C_{10}-O-Ph-Ph-COO-	= R^1	-CN	(124) Cr 132 I

a) monotropic transition, temperature not recorded.

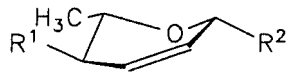
TABLE I (*Continued*)



6-Deoxy-ß-L-*erythro*-hexopyranosides

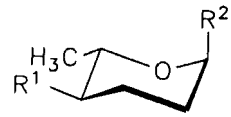
No	R^1	R^2	Phase Transition
11	C_7-Cy-Ph-COO-	-CN	Cr 86.4 (Ch 79.9) I
12	C_7-O-Ph-Ph-COO-	-CN	Cr 92.5 (S_A 47.4) Ch 95.2 BP 96.3 I
13	C_{10}-O-Ph-Ph-COO-	-CN	Cr 85.5 (Q 56.3) Ch 91.5 BP 92.0 I
14	C_8-Py-Ph-COO-	-CN	Cr 99.8 (Q 85)[a] (Ch 76.7 BP 76.6) I

a) see text



6-Deoxy-ß-L-*erythro*-hex-2-enopyranosides

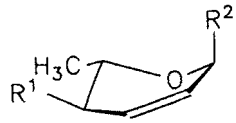
No	R^1	R^2	Phase Transition
15	C_7-Cy-Ph-COO-	-COOMe	Cr 63 I
16	C_7-Cy-Ph-COO-	-CN	Cr 82 (Ch 48) I
17	C_{10}-O-Ph-Ph-COO-	-CN	Cr 97.7 (Ch 63.9) I
18	C_8-Py-Ph-COO-	-CN	(47) Cr 100.3 I



6-Deoxy-α-L-*erythro*-hexopyranosides

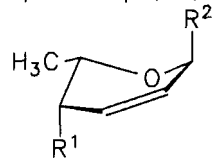
No	R^1	R^2	Phase Transition
19	C_7-O-Ph-Ph-COO-	-CN	(67) Cr 102.1 I
20	C_{10}-O-Ph-Ph-COO-	-CN	(59) Cr 91.2 I

TABLE I (*Continued*)



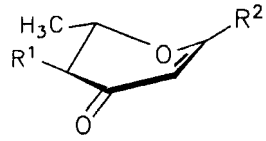
6-Deoxy-α-L-*erythro*-hex-2-enopyranosides

No	R^1	R^2	Phase Transition
21	C_7-Cy-Ph-COO-	-COOMe	Cr 31 I
22	C_7-O-Ph-Ph-COO-	-CN	(77) Cr 95.4 I



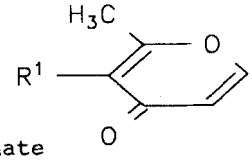
6-Deoxy-α-L-*threo*-hex-2-enopyranoside

No	R^1	R^2	Phase Transition
23	C_7-O-Ph-Ph-COO-	-CN	(100) Cr 111.8 I



1,5-Anhydro-2,6-dideoxy-3-keto-L-*erythro*-hex-1-enitols

No	R^1	R^2	Phase Transition
24	C_7-Cy-Ph-COO-	-COOMe	Cr 103.2 (S 34.3) I
25	Chol-OCOO-	-H	Cr 142.7 (S 97.7) I



Maltol Ester and Carbonate

No	R^1	R^2	Phase Transition
26	C_7-Cy-Ph-COO-	-H	(103) Cr 120.5 I
27	Chol-OCOO-	-H	(96) Cr 148 (S 105) I

Abbreviations : C_n = alkyl chain with n carbon atoms, Cy = *trans*-1,4 substituted cyclohexane, Ph = 1,4 substituted benzene, Py = 5-pyrimidinyl-2, Chol = 3ß-Cholest-5-ene, value in parentheses = solidification temperature, Q = cubic mesophase.

amitic derivatives[23,24,25] in which a considerable intramolecular contrast in polarity leads to a spherical aggregation of molecules. This may cause the mesophase in **13** and **14**. The cubic phases can be spread readily, but neither by laying nor by shearing or tempering an optic anisotropy can be proved. Further, it was possible to undercool the transition Ch → Q for some degrees, and the cholesteric phase of **14** is even metastable to the cubic phase.

These compounds show a favorable behavior in mixtures in which they transfer their chirality. In addition to non-chiral liquid crystals blue high twisted cholesteric and ferroelectric phases are obtained. The clearing points of these mixtures correspond to data obtained by extrapolation.

In contact with nematic liquid crystals, cyanide **13** shows an inversion of the helix of the cholesteric phase dependent on concentration.

Group 2: Compounds with Calamitic Structure but Wrong Configuration: 19–22

As expected, these compounds are not liquid crystalline. In **19–22** the substituents R^1 and R^2 are arranged *cis* to each other. These compounds can be used to prepare blue, cholesteric and ferroelectric mixtures, but with lower effect as with compounds of group 1. In addition to that, clearing points are considerably reduced.

Group 3: Compounds of Conditional Calamitic Structure: 25–27

In these compounds the carbohydrate part of the molecule represents merely a mesogenic structure. Nevertheless, compounds **25** and **27** are monotrop liquid crystalline which can be explained by mesogenic power of the cholesterol. Additionally, the intramolecular contrast between the non-polar cholesterin and the polar sugar part (including the carbonate group) supports the formation of a smectic phase.

Group 4: Calamitic Compounds with Distinct Amphiphilic Character: 6, 8, 9

These compounds are at the border between amphiphilic and monophilic liquid crystals. The alicyclic ring possesses a mesogenic group, however, the type of substitution is in contradiction to the demands of a monophilic liquid crystal, because the arrangement of substituents is not linear and the lateral hydroxyl groups cannot be included to a stabilizing intramolecular hydrogen bridge. The molecules show a distinct intramolecular contrast, but one hydroxyl group is not sufficient to enforce amphiphilic behavior. Only the sum of both properties yields to formation of a mesophase. The formation of a smectic phase may be understood as the result of the separation of molecular parts with different polarity.[26]

These smectic phases cannot be mixed with the S_A phases of the alkyl glycosides.[5] In contact with *p*-hexyloxyphenyl *p*-dodecyloxybenzoate (HOPDOP: Cr 62.5 S_E 38 S_B 44.5 S_C 77.5 S_A 83.3 N 88.9 I[27]) the following properties could be detected. N, S_B, S_C and S_E are sensitively distributed by the addition. The twisting power in N is low, in S_C nondetectable with optical means. The S_A phase is disturbed least, and in **6** both smectic phases are miscible.

Group 5: Wedge-Shaped Dimers: 7, 10

These compounds are not liquid crystalline. Because of the wedge-form of these compounds and their strong polarity gradient only a columnar-discotic phase with low clearing points could be expected. After HPLC the highly pure **10** forms an anisotropic, moderately viscous paste, which may represent a discotic liquid crystal. Typical textures could not be obtained, because viscous liquid crystals form characteristic textures only in cooling of the isotropic phase, respectively, metamorphic textures to preceding phases are formed. **10** crystallizes during heating and could not be undercooled out of the melt. The considerable difference in the rate of crystallization may be explained by the high molecular weight.

The behavior as mixing components is better than in group 4. Clearing points are higher and cholesteric phases can be generated.

EXPERIMENTAL

All reactions were followed by thin layer chromatography on silica gel foils 60 F_{254} (Merck). Detection was by UV and/or spraying with sulfuric acid/ethanol 1:5 and subsequently heating (200°C). Flash chromatography was performed with silica gel 60 (230–400 mesh). ^{1}H NMR (250 MHz) and ^{13}C NMR (62 MHz, broad band decoupling) were elaborated on Bruker spectrometer CA 250. HPLC was performed using the combined instruments: pump 64, differential refractometer type 98.00 (Knauer) with column Lichrosorb Si 100, 5 μ, solvent toluene/ethylacetate.

Transition temperatures were measured on an Olympus polarization-microscope BH, with a heating stage Mettler FP 82. Mesogenic phases are classed by characteristic textures. Mixing behavior is investigated in contact preparation with 4-methoxy-4′-butyl-azoxy-benzene ('Nematische Phase IV') and the *p*-hexyloxyphenyl-*p*-decyloxybenzoate (HOPDOB).

^{1}H- and ^{13}C-NMR data were routinely obtained and interpreted for structural assignment. As an example, NMR data of the *erythro* configurated compound **9** are given.

2,3-Dideoxy-6-*O*-*p*,*p*′-decyloxybiphenyl-β-*D*-*erythro*-hexanopyranosylcyanide (**9**). ^{1}H NMR ($CDCl_3$): δ = 4.25 (dd, H-2), 2.21 (dd, H-3_{ax}), 2.05 (dd, H-3_{eq}), 1.20–2.00 (m, 12 CH_2, H-4ax, H-4eq), 3.47 (ddd, H-5), 3.39 (ddd, H-6), 4.83 (dd, H-7a), 4.44 (dd, H-7b), 4.04 (t, Oc$\underline{H}_2$), 6.95, 7.30 and 8.10 (m, 8H, Aryl-H), 0.90 (m, 3H, C$\underline{H}_3$). $J_{2,3ax}$ = 11.4, $J_{2,3eq}$ = 2.8, $J_{4a,5}$ = 10.1, $J_{4e,5}$ = 5.0, $J_{5,6}$ = 10.0, $J_{6,7a}$ = 3.2, $J_{6,7b}$ = 1.6, $J_{7a,7b}$ = 12.4 Hz.

^{13}C NMR ($CDCl_3$): δ = 114.4 (C-1), 81.6 (C-2), 29.1 and 29.3 (C-3, C-4), 64.4, 65.6 (C-5, C-6), 63.8, 68.4 (C-7, O-CH_2), 14.1 ($\underline{C}H_3$), 22.6, 26.0, 30.8 and 31.8 ($\underline{C}H_2$), 117.5, 120.0, 126.7 and 155.3 (Aryl-C), 163.8, 164.3 and 167.0 (Ester-C=O).

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