Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 22 Sep 2006.

To cite this article: Y. L. N. Murthy (1989): Study of 9, 19-Cyclopropane Triterpene Fatty Acid Esters as Cholesteric Liquid Crystals-Part I, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 173:1, 95-99

To link to this article: http://dx.doi.org/10.1080/00268948908033371

Mol. Cryst. Liq. Cryst., 1989, Vol. 173, pp. 95–99
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Printed in the United States of America

Study of 9,19-Cyclopropane Triterpene Fatty Acid Esters as Cholesteric Liquid Crystals—Part I

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(*Received July 22, 1988; in final form December 30, 1988*)

To investigate the effect of the methyl substituent at C-22 in the cyclopropane triterpenoid side chain, different alkyl esters of cycloswietenol and related compounds (isolated from the hexane extract of *Swietenia mahagoni Linn.*) were synthesized and found to exhibit cholesteric and smectic phases, with different textures.

Keywords: synthesis, cyclotriterpenes, cholesteric mesophase alkyl substituent effect

The concept of liquid-crystalline compounds has been reported in the literature since 1889.[1] At present the unique classification of these materials has aroused the interest of scientific and industrial community simultaneously. Friedel[2,3] concluded that there were three classes of such substances, one of which displayed some rather unique optical properties. In the mesophase region, these substances refracted light and a majority of compounds which exhibit such character are esters of cholesterol and hence they are termed as compounds exhibiting a cholesteric phase. Knapp[4] *et al.* observed that 24-methylene-cycloartanyl esters and related esters were the only cyclopropane triterpenoid esters having a methyl substitution at C-24 exhibiting cholesteric mesomorphism. During the course of our investigations[5] of the triterpenoid constituents of the bark of *Swietenia mahagoni Linn.*, we isolated cycloswietenol (I), 31-norcycloswietenol (II), cycloartenol, isocycloswietenol, and 31-norisocycloswietenol. These compounds do possess an unusual extra methyl group at the C-22 position and no substituent at C-24. Hence we prepared several fatty acid esters of some of the above triterpene compounds, with a view to understand the effect of the extra methyl group at C-22 in the side chain. Additionally, we prepared the respective alkanoates of the two 20,21-dihydroderivatives, cycloswietanol (Ia) and 31-norcycloswietanol (IIa).

In all the compounds, the esters were purified by preparative HPLC. In total four new smectic liquid crystals and ten cholesteric liquid crystals have been prepared and their phase transition data are formulated in Table I.

TABLE I

Phase Transition Temperatures (Mesophase Region) of Triterpenoid Esters

Ester	K (°C)	Mesophase	Isotropic liquid (°C)	Color under polarizing microscope
I Heptanoate	71°	Smectic	85°	Colorless
Ia (reduced)	72.5°	Smectic	88°	Colorless
I Octanoate	68.5°	Cholesteric	70.5°	Green
Ia (reduced)	69.5°	Cholesteric	72°	Green
I Nonanoate	62°	Cholesteric	65.5°	Violet
Ia (reduced)	64°	Cholesteric	68°	Violet
I Decanoate	58°	Cholesteric	62.5°	Violet/green
Ia (reduced)	59.5°	Cholesteric	65°	Violet/green
II Heptanoate	86°	Smectic	89.5°	Colorless
IIa (reduced)	87.5°	Smectic	90°	Colorless
II Octanoate	83°	Cholesteric	87°	Green
IIa (reduced)	84.5°	Cholesteric	90.5°	Green
II Nonanoate (could not be purified)				
II Decanoate	74°	Cholesteric	79°	Green
IIa (reduced)	76°	Cholesteric	81.5°	Green

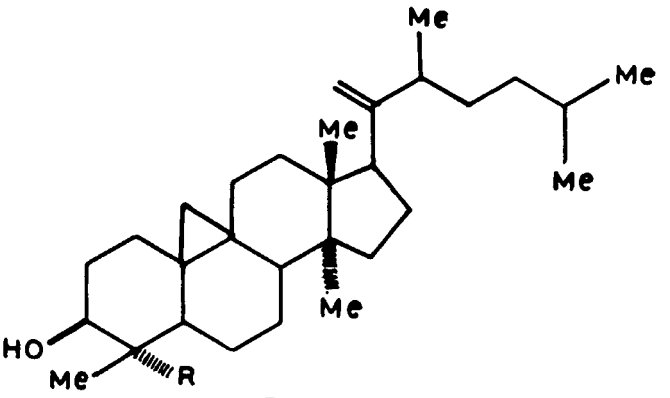
Reduced: Olefinic bond at C_{20-21} is reduced.

DISCUSSION

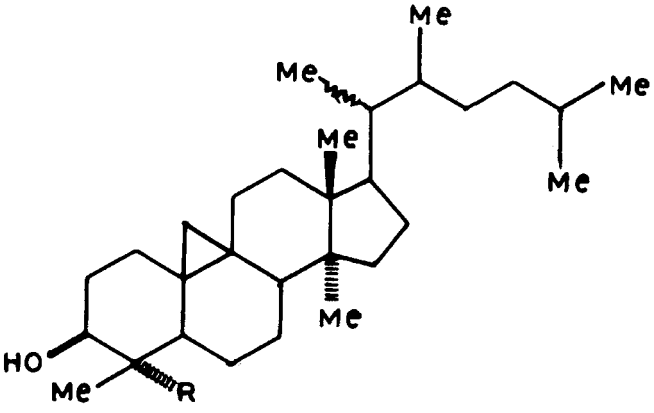
From the above data (Table I), it is interesting that the heptanoate esters of I and II (Ia and IIa also) showed smectic character. These substances when studied under a polarizing microscope exhibited a turbid, birefringent mesophase which is colorless. This smectic phase observed is highly viscous under crossed Nichols exhibiting mosaic textures.

All the other ten compounds (derivatives of I and II) exhibited a green color under crossed Nichols. The textures, when observed under a polarizing microscope, were identified as being cholesteric during heating. Similarly on cooling the isotropic liquid, the mesophase region was observed. Another important point to be noted is that Knapp *et al.* observed that C-24 methyl-substituted derivatives exhibit mesomorphism and also observed that it is mainly a steric effect. In this report we observe that similar properties were exhibited by these 22-methyl derivatives also. In this context, the role of the side-chain methyl-substituent is still to be understood. Alkanoates of steroids or triterpenes with bulky substituents (ethyl or ethylidene) at C-24 tend to be smectic only while the corresponding benzoates or cinnamates are cholesteric with the exception of 24-methylene in triterpenes.[4] A methylene group at C-20 also leads to a cholesteric phase. To summarize, it is obvious that the 9,19-cyclolanostane moiety does not inhibit the appearance of a mesomorphic phase but that size, polarity, and position of substituents along the 17β-side chain do influence the mesomorphic behavior.

These present data throw some more light on the structural effect upon the cholesteric mesophase.



I : R = Me
Ia : R = H



II : R = Me
IIa : R = H

STRUCTURE

Experimental section

Melting points were determined on a VEB, Analitica, Dreader HMK hotplate. IR spectra (KBr matrix) were recorded on a Shimodzu 408 spectrophotometer. PMR spectra were recorded on a Perkin Elmer R-32 instrument operating at 90 MHz (in $CDCl_3$); phase transitions were detected on a polarizing microscope equipped with a hot stage. All solvents were of analytical grade and were distilled before use. Transition temperatures were recorded on a Perkin Elmer DSC-2 differential scanning calorimeter.

Isolation of triterpenes

Compounds I and II were isolated from the hexane extract of the heartwood of *Swietenia mahagoni Linn.* They were crystallized from methanol-chloroform as

colorless, shining needles. The esters were purified by column chromatography using silica gel-G (100-mesh, Acme) and, wherever necessary, preparative TLC was used to obtain analytical purity. All the compounds were studied by HPLC (Shimodzu-LC-6A) for their purity; elemental analysis was carried out on a Perkin Elmer Automatic C, H & N Analyzer and Gallenkamp C, H & N Analyzer with Melter microbalance. They were dried for analysis at 60°/0.2 mm for 6 h and were found to give satisfactory elemental analysis.

Hydrogenation of the triterpenes I and II

Reduction of cycloswietenol. A solution of the triterpene (100 mg) in alcohol was shaken with freshly prepared platinum oxide (80 mg) in the presence of hydrogen at ambient temperature and pressure. After the absorption of hydrogen was complete (5 h), the catalyst was filtered off, the filtrate diluted with water and extracted with ether. The ether layer was dried over anhydrous $MgSO_4$ and evaporated. The product was crystallized from alcohol as colorless needles (60 mg) cycloswietanol, mp 115–7°, $[\alpha]_D$ 29.5° (C 1.0, $CHCl_3$).

Elemental analysis

Found: C, 87.23, H, 12.62; $C_{31}H_{54}O$ requires C, 87.25, H 12.75.

Synthesis of triterpene esters

The procedure adopted by Knapp *et al.*[6] was followed. The triterpene (50 mg) was refluxed with a 1.5 M excess of the acyl chloride in benzene containing a small amount of pyridine under anhydrous conditions. TLC monitoring was carried out after 1 h and 2 h to ensure complete esterification. The reaction mixture was diluted with water and extracted with ether. The ethereal layer was washed with 5% HCl and water successively, and the solvent was removed by distillation. The product obtained was chromatographed on silica gel (Acme) and eluted with benzene collecting 50-ml fractions. The ester thus isolated was recrystallized twice from methanol to a constant melting point. The purity of each ester, thus prepared, was carefully checked by both TLC and HPLC.

The following chemical abstracts registry number and the systematic names of the four compounds used are to be noted.

I. Cycloswietenol: [62875-16-5]; 22-methyl-9,19-Cyclolanost-20-en-3β-ol.

Ia. Cycloswietanol: [68798-97-0]; 22-methyl-9,19-cyclo-20ϵ-lanostan-3β-ol.

II. 31-Norcycloswietenol [75222-75-2]; 4α,14,22-trimethyl-9,19-cyclo-5α-cholest-20-en-3β-ol.

IIa. 31-Norcycloswietanol: [75222-80-9]; 4α,14,22-trimethyl-9,19-cyclo-5α,20ϵ,cholestan-3B-ol.

Acknowledgments

The author is grateful to Prof. C. P. Lillya, Chemistry Department, Univ. of Massachusetts, Amherst, MA, U.S.A., for his encouragement. He further thanks Dr. G. N. Babu, Scientist, 3M Co., St. Paul, MN, U.S.A., for his valuable suggestions.

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