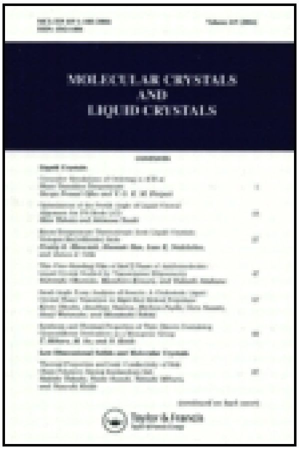


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Study of Orientation Effects on Mesophase Transitions of Axial and Equatorial Fatty Acid Esters of Friedelen (A Triterpene): Part II

Y. L. N. Murthy [a] & A. S. S. V. Srinivas [a]

[a] Department of Organic Chemistry, Andhra University, Visakhapatnam, 530 003, India

To cite this article: Y. L. N. Murthy & A. S. S. V. Srinivas (1992): Study of Orientation Effects on Mesophase Transitions of Axial and Equatorial Fatty Acid Esters of Friedelen (A Triterpene): Part II, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 220:1, 185-189

To link to this article: http://dx.doi.org/10.1080/10587259208033439

Mol. Cryst. Liq. Cryst., 1992, Vol. 220, pp. 185–189
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Study of Orientation Effects on Mesophase Transitions of Axial and Equatorial Fatty Acid Esters of Friedelen (A Triterpene): Part II

Y. L. N. MURTHY* and A. S. S. V. SRINIVAS
Department of Organic Chemistry, Andhra University, Visakhapatnam - 530 003, India

(Received November 20, 1991; in final form February 10, 1992)

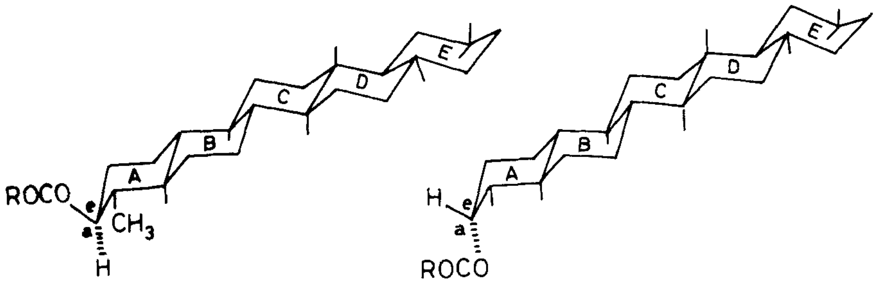
Earlier, phase transitions of triterpene fatty acid esters were studied for a few new triterpenes in this lab. In the present investigation, synthesis of axial and equatorial fatty acid esters of a triterpene were synthesised and their liquid crystal transition temperatures were determined using a polarising microscope. The effect of equatorial and axial orientation of the ester grouping on phase transitions was highlighted.

Keywords: synthesis, Friedelen, axial and equatorial esters, cholesteric mesophase

In a continuation of our study on the liquid crystalline properties of triterpene fatty acid esters,[1] we now investigate the mesophases of the esters of Friedelin-3 β_e-ol and Friedelin-3 α_a-ol. Liquid crystals[2] are characterised as substances exhibiting a high degree of anisotropy yet maintaining the properties of fluids. Approximately 5% of all known organic compounds[3] are transformed at their melting point into liquid crystals. These are thermodynamically stable, anisotropic liquids which in contrast to isotropic melts, appear turbid and are known as mesophases. Such melts are classified as smectic, nematic and cholesteric liquid crystalline phases depending upon the arrangement of the constituent molecules. In 1977 Chandrasekhar *et al.*[4,5] reported observation of a new type of thermotropic mesomorphism, i.e., liquid crystallinity in pure compounds, composed of disc-like molecules.

During the course of our investigations on the triterpenoid fatty acid esters, we isolated Friedelen (1) from the bark of swietenia Mahagoni linn[6] along with β-amirin, α-amirin and β-sitosterol, cycloswietenol, cycloartenol, lupeol benzoate and 31-Norcycloswietenol. In this present investigation, it is proposed to evaluate the orientation effects of the axial and equatorial ester chain on the mesophase transitions. Hence Friedelen was reduced with sodium borohydride[7] to give a mixture of the axial and equatorial alcohols (Friedelin-3 β_e-ol(II) and Friedelin-3 α_a-ol(III)) which was separated by column chromatography (See Scheme I). Compounds II and III each were esterified with the corresponding acid chlorides ($C_n H_{2n+1}$ COCl, n = 5,6,7) and the esters purified by preparative TLC, followed by HPLC. These were recrystallised from $CH_3OH-CHCl_3$ and their purity determined by HPLC to be 100%. Transition temperatures were determined using a polarising microscope and are formulated in Table I. The stereo chemical presentation of the axial (VII) and equatorial esters (VI) is as shown here:

STEREOCHEMICAL PRESENTATION



EQUATORIAL ESTER VI AXIAL ESTER VIII

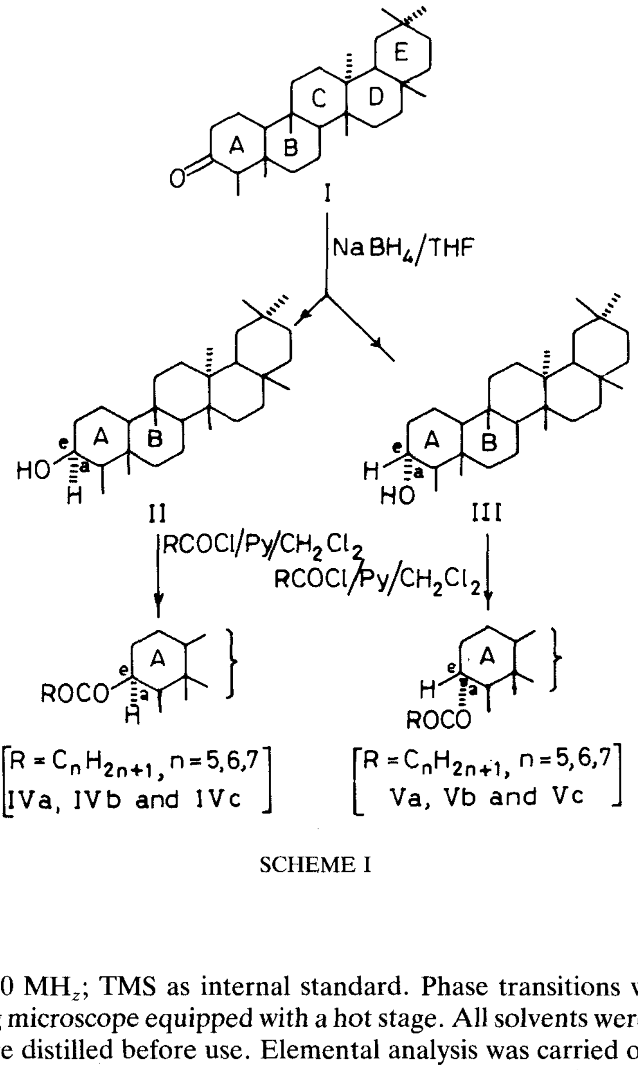
Stereochemical Presentation of Equatorial Ester (VI) and Axial Ester (VIII)

DISCUSSION

From Table I, it is evident that the axial esters of hexanoate, heptanoate and octanoate of III (Va, Vb and Vc) exhibit mesophases at a lower temperature than their corresponding equatorial esters of II (IVa, IVb and IVc) respectively. This is an interesting phenomena to be noteworthy. The equatorial esters are more linear with less steric hindrance. The axial esters provide an effect similar to branched chains or lateral substituents on typical liquid crystalline structures. All the esters exhibited green and blue coloured textures when studied using a polarising microscope under crossed nichols, which were identified as being cholesteric during heating. Similarly, the mesophase region was also observed on cooling the isotropic liquid. In this context, the mesophase transition temperature of axial esters, are taking less energy than the equatorial esters to exhibit a liquid crystal phase. The above data further highlights the structural effect on the mesophase.

EXPERIMENTAL SECTION

Melting points were determined on a VEB, Analitica, Dreader HMK hotplate. IR spectra ($CHCl_3$) were recorded on a Perkin Elmer R 841 infrared spectrophotometer and PMR spectra in $CDCl_3$ were recorded on a Perkin Elmer R-32 instrument



SCHEME I

operating at 90 MH$_z$; TMS as internal standard. Phase transitions were detected on a polarising microscope equipped with a hot stage. All solvents were of analytical grade and were distilled before use. Elemental analysis was carried out on CHNS-O EA 1108-Elemental analyser. Purity was checked by HPLC (Shimodzu-LC-6A) using Shim-pack CLC-ODS(0.15m × 6.0 ϕ) column.

Isolation of Friedelen

The chloroform extract of the bark of S. Mahagoni linn yielded a solid, which showed two spots on TLC and was chromatographed using silica gel. Elution with hexane-benzene (9:1) gave cycloswietenol and with hexane:benzene (1:1) gave Friedelen. This was recrystallised repeatedly from CH_3OH-$CHCl_3$ to a constant melting point. The purity was checked by HPLC (99.9%) mp:260–62° (Literature mp-262°) IR: 1710$^{cm^{-1}}$; NMR:δ 0.75, 0.84, 0.98, 1.02, 1.16 (all singlets, 24 H, 8 × Me), 2.16 (3 H, $C_2 - H_2$ and C_{4-H}), $[\alpha]_D^{30}$ − 20° (C, 1.0 in $CHCl_3$).

TABLE I

Phase transition temperature's (Mesophase Region) of Triterpene esters

Ester	K(^{0}C)	Mesophase	Isotropic Liquid	Colour under Polarising microscope
Fri-3 α_a-ol Octanoate (Vc)	87	Cholesteric	93	Blue
Fri-3 β_e-ol Octanoate (IVc)	91	Cholesteric	98	Blue
Fri-3 α_a-ol Heptanoate (Vb)	76	Cholesteric	84	Green
Fri-3 β_e-ol Heptanoate (IVb)	83	Cholesteric	88	Green
Fri-3 α_a-ol Hexanoate (Va)	74	Cholesteric	76	Green
Fri-3 β_e-ol Hexanoate (IVa)	81	Cholesteric	85	Green

Elemental Analysis

Calculated for $C_{30}H_{50}O$ C-84.45, H-11.85. Found C-84.2, H-11.6.

Reduction of Friedelen with $NaBH_4$

Friedelen (800 mg) was dissolved in THF (5 ml), treated with excess $NaBH_4$ needed and refluxed under anhydrous conditions for 5 hrs. Acetic acid (1 ml) was added to decompose any excess $NaBH_4$ and the mixture poured into water and extracted with $CHCl_3$. The $CHCl_3$ extract was dried over $MgSO_4$ and subjected to column chromatography on silica gel. Elution with hexane:benzene (1:1) yielded Friedelin-3 β-ol, mp 284–85°, $[\alpha]^{30}_{D}$ + 15° (C, 1.0 in $CHCl_3$) IR: 3400^{cm-1}, NMR ($CDCl_3$/TMS):δ 3.74 (1 H, m, 3 α − H), 1.54 (1 H, S, D_2O exchangeable), 1.17, 0.99, 0.96, 0.86 (all singlets, 24 H, 8 × Me) and with benzene yielded Friedelin-3 α −ol, mp. 305–06°, $[\alpha]^{30}_{D}$ + 20° (C, 1 in $CHCl_3$). IR: 3400^{cm-1}, NMR ($CDCl_3$/TMS):δ 3.2 (1 H, m, 3 β − H) 1.18, 0.97, 0.92, 0.78, 0.76 (24 H, 8 × Me). These were recrystallised from CH_3OH-$CHCl_3$ repeatedly to obtain a constant melting point which were confirmed by comparison with authentic samples. The NMR and IR spectral data were found in good agreement with the literature data.

Synthesis of Triterpene Ester

The procedure adopted by Knapp *et al.*[8] was followed. The triterpene (100 mg) was refluxed with 2 M excess of the acyl chloride and CH_2Cl_2, containing a small amount of pyridine under anhydrous conditions. TLC monitoring was carried out every ½ hour an it indicated 4 hrs were needed for complete esterification. The reaction mixture was diluted with water and extracted with $CHCl_3$. The organic layer was washed with 5% $NaHCO_3$, 5% HCl and water repeatedly; dried over anhydrous $MgSO_4$ filtered and the filtrate evaporated. The product obtained was chromatographed on preparative TLC silica gel (Acme) and eluted with 1:1, hexane:benzene collecting 250 ml fractions. The ester thus obtained was recrystallised twice from CH_3OH-$CHCl_3$. The purity of each ester was carefully checked by both TLC and HPLC (99.9%) and by elemental analysis.

Acknowledgment

We are grateful to Emeritus Prof. L. R. Row for his constant encouragement and one of us (ASSVS) is thankful to UGC and the financial support by CSIR, New Delhi is gratefully acknowledged.

References

1. Y. L. N. Murthy, *Mol. Cryst. Liq. Cryst.*, **173**, 95–99 (1989).
2. Blumstein, Alexandre *Low Molecular Weight Liquid Crystals*, Gordon and Breach Science Publishers, Inc. (1979).
3. R. Sleinstrasser and L. Pohl, *Angew Chem. Internal Edit* **12**, (8), 617 (1973).
4. S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, Pramana, **9**, 471 (1977).
5. S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, N. V. Madhusudana, S. Kumar, R. Sashidhar and G. Venkatesh, *J. Phys. Supp.*, **40**, C3-120 (1979).
6. Y. L. N. Murthy, M. A. Jairaj and A. S. S. V. Srinivas, *Ind. J. Chem.*, **30B**, 462–65 (1991).
7. V. Anjaneyulu, L. R. Row and D. N. Rao, *J. Indian Chem. Soc.*, **44**, 123 (1967).
8. F. F. Kanapp and H. J. Nicholas, *J. Org. Chem.* **33**, 3995 (1968).