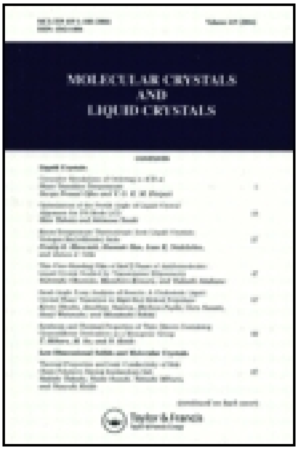

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Characterization of Diosgenin (A Steriod) Esters as Liquid Crystals

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Characterization of Diosgenin (A Steriod) Esters as Liquid Crystals

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Earlier,[1,2] phase transition temperatures of triterpene fatty acid esters were studied for a few new triterpenes in this lab. In the present investigation, synthesis of fatty acid esters in diosgenin were synthesized and their liquid crystal transition temperatures were determined using a polarizing microscope and were further confirmed by Perkin Elmer DSC-4 and these compounds were found to exhibit cholesteric phase during mesophase region. The above esters were also studied on a Dupont 9990 differential scanning calorimeter at low temperatures using liquid nitrogen and the mesophases were recorded.

Keywords: synthesis, diosgenin esters, cholesteric mesophase, textures, transition temperatures

In continuation of our study on the liquid crystalline properties of triterpene fatty acid esters,[1,2] we now investigate the liquid crystal properties of diosgenin esters (a highly oxygenated steriod). F. F. Knapp *et al.*[3] have synthesized thirteen fatty acid esters of ergosterol (24 α-methyl-5,7,22-cholestatrien-3β-ol) and studied their liquid crystalline properties. Many of these esters were polymorphic, forming both smectic and cholesteric mesophases.[4,5] Various β-sitosteryl fatty acid esters also form smectic mesophases.[6] In 1979, the mesomorphic properties of some esters of β-sitosterol; synthesized by treating aromatic acids with β-sitosterol, were reported.[7] The interdependence of the molecular structure and mesogenic properties of 3 β-sterol derivatives has been recently investigated.[8–10] Tanaka *et al.*[11] have identified β-sitosteryl-3-methoxy-4-acyloxy cinnamates as cholesteric liquid crystals. These substituents may induce mesophases or may destroy the mesomorphic properties of the steriod compounds. Studies by Pohlmann et al.[8] and Atallah *et al.*[12] on the influence of the position of a double bond in steriods and triterpenes on the formation and type of mesophases revealed that mesophase formation is not supported by a C-1, C-4 or C-8 double bond in the steriod molecule, where as a double bond between C-9 and C-11 permits a cholesteric phase. The nature and length of the 17 β-side chain also exert a considerable influence on the mesomorphic behavior of the molecule.[9] A homologous series of cholesteryl-*n*-alkyl

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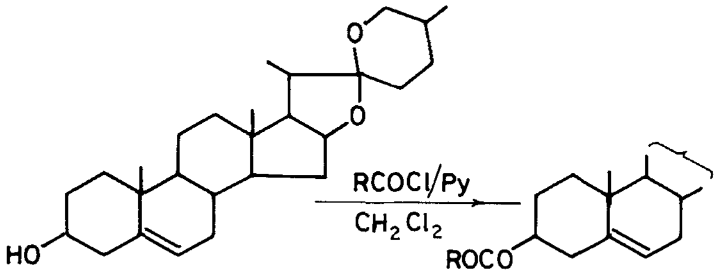

I

[R = C_nH_{2n+1} ,
n = 6, 7, 9, 13 & 17]

II : n = 6, HEPTANOATE
III : n = 7, OCTANOATE
IV : n = 9, DECANOATE
V : n = 13, MYRISTATE
VI : n = 17, STERATE

SCHEME 1

TABLE I

Retention times and percentage of purity of diosgenin esters

S.NO.	Compound	Retention time (in minutes)	Purity (%)
1.	Diosgenin heptanoate (II)	3.210	99.2
2.	Diosgenin octanoate (III)	3.225	99.1
3.	Diosgenin decanoate (IV)	3.240	100.0
4.	Diosgenin myristate (V)	3.092	97.4
5.	Diosgenin sterate (VI)	3.275	98.9

Experimental Conditions :

Mobile phase : Methanol
Column : Shim-pack CLC-ODS (0.15m x 6.00)
Flow rate : 1 ml/min
Detector : UV (240 nm)
Injected Quantity : 10 μl.

FIGURE 1 "Schlieren" texture.

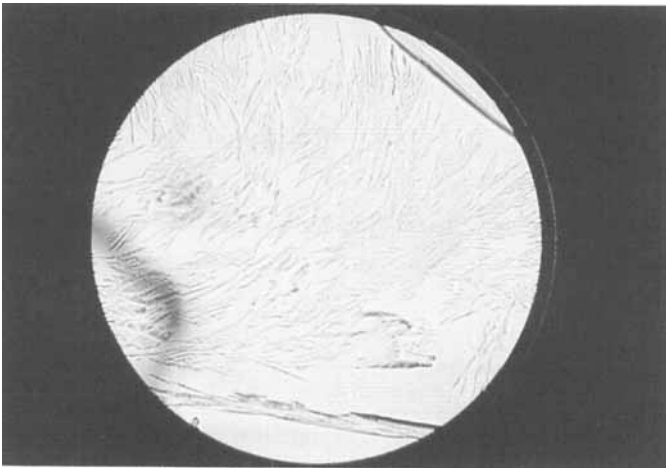

FIGURE 2 "Leaf like" texture.

carbonates has been prepared and their mesophases were investigated by Elser *et al.*[13]

For the present investigation, diosgenin, which was commercially available from Aldrich Chemical Co., U.S.A.; was kindly supplied by Dr. A. Sree.[14] This was recrystallized twice from benzene for constant melting point and the purity of the compound was checked by both TLC and HPLC (99.5%). It was confirmed by its physical and spectral data. Diosgenin was treated with the corresponding acid chloride (C_nH_{2n+1} COCl, n = 6, 7, 9, 13 and 17) in presence of pyridine (Scheme 1) and the corresponding esters of heptanoate, octanoate, decanoate, and myristate and sterate were prepared and purified by preparative TLC. These were repeatedly crystallized from benzene and the purity was checked by HPLC (99%). The proton

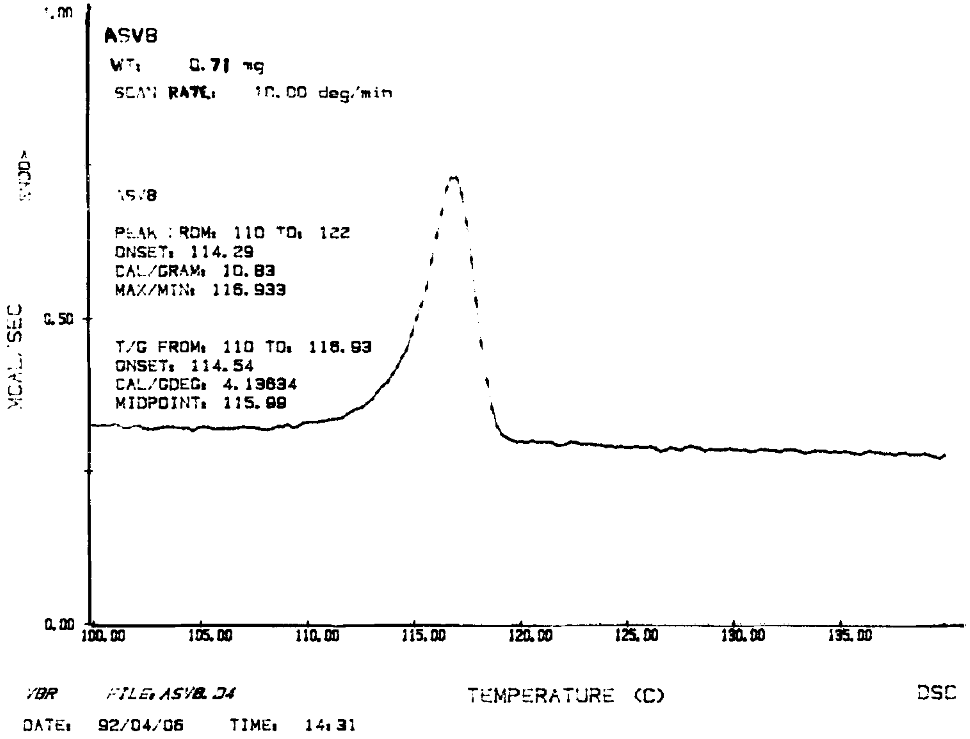

FIGURE 3 DSC Spectrum of diosgenin decanoate on Perkin Elmer DSC-4.

TABLE II

Phase transition temperatures (Mesophase region) and heat of transitions of diosgenin esters (on Perkin Elmer DSC-4)

Ester	K(°C)	Mesophase	Isotropic Liquid	ΔH(Cals/gm)
Diosgenin heptanoate (II)	121.28	Cholesteric	128.93	10.12
Diosgenin Octanoate (III)	114.0	Cholesteric	124.0	11.97
Diosgenin decanoate (IV)	110.0	Cholesteric	122.0	10.83
Diosgenin myristate (V)	135.6	Cholesteric	144.8	-
Diosgenin sterate (VI)	171.4	Cholesteric	182.1	-

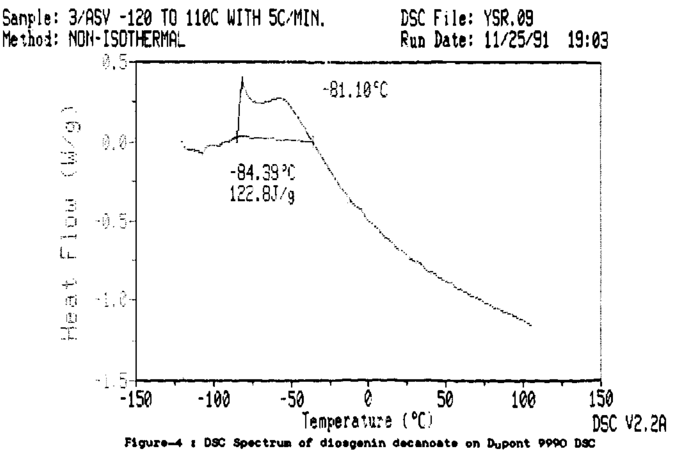

FIGURE 4 DSC Spectrum of diosgenin decanoate on Dupont 9990 DSC.

TABLE III

Phase transition temperature (Mesophase region) and heat of transitions of diosgenin esters (on Dupont 9990)

Ester	K(°C)	Mesophase	Isotropic Liquid	ΔH(Cals/gm)
Diosgenin heptanoate (II)		Data Awaited		
Diosgenin Octanoate (III)	-100.25	Cholesteric	-96.22	10.22
Diosgenin decanoate (IV)	-84.39	Cholesteric	-81.10	29.35
Diosgenin myristate (V)		Data Awaited		
Diosgenin sterate (VI)	-89.37	Cholesteric	-71.82	7.74

NMR spectrum of diosgenin esters were recorded and is in accordance with the structure. The retention times and percentage of purity for all the five esters were given in Table I. In total five esters were prepared and their textures were studied using a polarizing microscope equipped with hot stage (Auto Melpo, MRK, Inc., Japan) at a scanning rate of 1°/min and the textures were recorded at the mesophase region. Diosgenin decanoate exhibited a "Schlieren" texture at 122°C (Figure 1) and diosgenin sterate showed a "leaf like" texture at 179°C (Figure 2).

The liquid crystal phase was further confirmed by differential scanning calorimeter data and the transition temperatures were recorded on a Perkin Elmer DSC-4 at a scanning rate of 10°/min. The transition phase of diosgenin decanoate was recorded between 110–120°C; $\Delta H = 10.83$ Cals/gm. The DSC spectrum of diosgenin decanoate was shown in Figure 3. Similarly, during cooling also the transition phase of diosgenin decanoate was recorded between 84.83–71.25° at a scanning rate of −10°/min. The transition temperatures were presented in Table II.

Besides the above study, we have also studied the above five compounds (**II–VI**) on a Dupont 9990 differential scanning calorimeter at low temperatures using liquid nitrogen at a scanning rate of 5°/min. The DSC spectrum of diosgenin decanoate was shown in Figure 4 and the transition temperatures were presented in Table III.

DISCUSSION

From Table II, it is interesting to note that these compounds exhibit liquid crystal phase at low temperatures (−70 to −100°C approximately) and above the room temperature. We are unable to study these mesophases at very low temperature under the polarizing microscope in our labs. The DSC data (on Dupont 9990 and Perkin Elmer DSC-4) definitely infers that these steriod esters exhibit mesophases:

1. at very low temperatures and
2. above room temperatures also.

This is an interesting phenomena to be note worthy. All the esters exhibited blue colored textures when studied using a polarizing microscope under crossed nichols, which were identified as being cholesteric during heating. Similarly, the mesophase region was also observed on cooling the isotropic liquid.

EXPERIMENTAL

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 operating at 90 MH_z; TMS as internal standard. Phase transitions were detected on a polarizing microscope equipped with hot stage (Auto Melpo, MRK, Inc., Japan). Transition temperatures were recorded on Perkin Elmer DSC-4 and Dupont 9990 differential scanning calorimeter. All solvents were of analytical grade and were distilled before use. Elemental analysis was carried out on Carlo Erba CHNS-OEA 1108-Elemental analyzer. Purity was checked by HPLC (Shimodzu-LC-6A) using Shim-pack CLC-ODS (0.15 m × 6.0ϕ) column.

SYNTHESIS OF DIOSGENIN ESTER

The procedure adopted by Knapp *et al.*[15] was followed. Diosgenin (100 mg) was refluxed with 3M excess of the acyl chloride and CH_2Cl_2, containing a small amount of pyridine under anhydrous conditions. This was refluxed for 4 hrs following the TLC monitoring for every 1/2 hour. The reaction mixture was diluted with water and extracted with chloroform. The organic layer was washed with 5% $NaHCO_3$ (100 ml), 5% HCl (100 ml) and water thoroughly; dried over anhydrous $MgSO_4$ and the solvent was evaporated. The product was chromatographed on silicagel (Acme) column and eluted with 1:2, hexane:benzene collecting 250 ml fractions. The ester was recrystallized twice from benzene and the purity of each ester was carefully checked by both TLC and HPLC (99.5%). The spectral data of diosgenin decanoate was given below.

Elemental analysis: Found C-78.12, H-50.59
$C_{37}H_{60}O_4$ requires C-78.16, H-10.56

IR $\nu\frac{\mathrm{CHCl_3}}{\max}$: 3100, 2910, 1730, 1460, 1340 and 890 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): δ0.7–0.95 (methyls), 1.2–1.9 (methylenes), 2.1 (t, 2H, $-\mathrm{OCO}\underline{\mathrm{CH}}_2$), 3.25 (d, 2H, $-\mathrm{O}\underline{\mathrm{CH}}_2$), 4.3 (m, 1H, C_3—H) and 5.25 (t, 1H, olefinic proton).

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