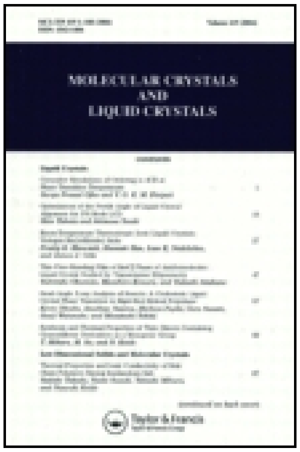

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Characterisation of Lupeol (A Tri Terpene) Esters As Liquid Crystals

Y. L. N. Murthy [a] & P. Aruna Sree [a]

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

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Characterisation of Lupeol (A Tri Terpene) Esters As Liquid Crystals

Y. L. N. MURTHY* and P. ARUNA SREE

Department of Organic Chemistry, Andhra University, Visakhapatnam – 530 003, India

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Earlier, phase transition temperatures of triterpene fatty acid esters were studied for a few new triperpenes in this laboratory. In this present investigation, fatty acid esters of lupeol were synthesised and their liquid crystal transition temperatures were determined using a polarising microscope and were further confirmed by differential scanning calorimetry (Perkin-Elmer DSC-4) and the mesophases & the colors of the textures were recorded.

Keywords: Synthesis; lupeol esters; textures; transition temperatures

In continuation of our studies on the liquid crystalline properties of triterpene fatty acid esters [1–4] we now investigate the liquid crystal properties of lupeol esters.

During the course of our investigations, lupeol was isolated from Albizzia Lebbeck as white crystalline solid, m.p: 212°C; $[\alpha]_D^{30} + 23°$ (C 1.0, $CHCl_3$). Its ^1H NMR spectrum showed the following signals. $\delta 0.9-1.1$ (18H, six methyls); $\delta 1.69$ (s, 3H, methyls on an olefinic system); $\delta 4.85$ (2H, vinyl, methylene protons). Lupeol afforded a mono acetate, shining needles from methanol. m.p. 221°C; $[\alpha]_D^{30} + 41°$ (C 1.0, $CHCl_3$). The above data was compared with an authentic sample [5], (CoTLC, mmp and CoNMR) and is in full agreement with the structure of the Lupeol. This was crystallised twice from methanol for constant melting point and the purity was checked by TLC & HPLC (99.9%).

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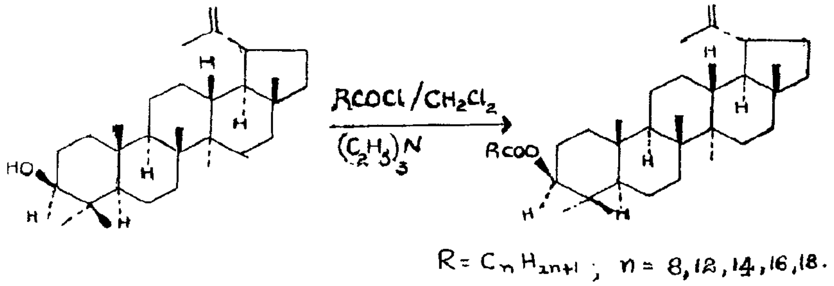
*Corresponding Author.

Lupeol was treated with the corresponding [6] acid chloride ($C_nH_{2n+1}COCl$; $n = 8, 12, 14, 16, 18$) in presence of $(C_2H_5)_3N$ (Scheme-I) and the corresponding esters, octanoate, laurate, myristate, palmitate and Stearate were prepared and purified by column chromotography; solvent system: 1% ethyl acetate-hexane. These were repeatedly crystallised from methanol (spec. grade) and purity was checked by TLC & HPLC (99%).



SCHEME 1

The ^{1}H NMR spectrum of lupeol esters were recorded and is in accordance with structures. In total, five esters were prepared, and these esters were carefully purified to get 99.9% pure on HPLC. The above synthesised esters were studied for their mesophase using a polarising miscroscope equipped with hot stage (Auto Melpo, MRK, Inc, Japan) at a scanning rate of 5°/min and the textures were recorded in the mesophase region. Lupeol palmitate exhibited a 'leaf-like' texture around 80°C and lupeol octanoate exhibited a 'broken fan' texture during the mesophase. Lupeol stearate exhibited a combination of pale pink and dark green colors.

The liquid crystal phase was further confirmed by differential scanning calorimetry and the transition temperatures were recorded on Perkin-Elmer DSC-4 at a scanning rate of 5°/min. The mesophase region of lupeol laurate was recorded to be between 59°–71°C, $\Delta H = 51$ cal/gm during heating. The transition temperatures observed for the above five esters, the mesophase colors, and the type of textures are presented in Table I.

DISCUSSION

Generally cholesteryl alkonoates [7] show decrease in transition temperatures haphazardly as the chain length increases. But lupeol esters showed reverse trend. This may be attributed to skeletal changes of Lupeol to that of Cholesterol. All the Lupeol esters showed only green & pink colors [8],

TABLE I Phase transition temperatures (mesophase region) and heat of transitions of lupeol esters (on Perkin-Elmer DSC-4)

Ester	*Temperature in °C crystal-mesophase*	*Mesophase & color & type of the texture*	*Mesophase-Isotropic °C*	*ΔH(Cal/gm) during-Mesophase-Isotropic*
Lupeol octanoate	38.5	Cholesteric, green color broken fan texture	45.3	49.36
Lupeol laurate	59.0	Cholesteric pale green & pink	71.5	51.10
Lupeol myristate	69.5	Cholesteric scale-like texture, Dark green	78.4	51.89
Lupeol Palimitate	80.0	Cholesteric leaf-like texture	80.8	
Lupeol stearate	49°	Cholesteric pale pink & dark green	50.0	

infers their absorption region does not very with the chain length. For all these molecules only cholesteric mesophase is observed. There is an increase in ΔH values with increase of chain length as reported earlier [8].

Observation of the transition temperatures reveal that these lupeol esters viz., lupeol octanoate, lupeol laurate, lupeol myristate exhibited a mesophase over a range of 7–11°C and the textures exhibited a green, pale green and pink and dark green colors during the mesophase region. Further there is a small increase of heat of transition (ΔH) in the above three compounds, viz., from lupeol octanoate to lupeol myristate i.e, 49.36 cal/gm to 51.80 cal/gm.

In the case of lupeol palmitate the mesophase is observed from 80° to 80.8°C with a leaf-like texture, over a small range. Only in the case of lupeol stearate the mesophase region is observed at a very low temperature, between 49° to 50°C (over a small range) and the texture was observed with pale pink and dark green color. It is interesting to note that all the five esters have showed normal liquid crystal properties (transition temperature and textures) ranging from 38.5°C to 80.8°C.

EXPERIMENTAL

Melting points were determined on a VEB Analitica, Dreader HMK hot plate, IR spectra were recorded on Perkin-Elmer R-84 Infrared spectrophotometer, and PMR spectra in $CDCl_3$ were recorded on Jeol JNM EX-90 FT-NMR, TMS as an internal standard. Phase transitions were observed under a polarising microscope equipped with a hot stage (Auto Melpo, MRK Inc, Japan). Transition temperatures were recorded on a Perkin-Elmer DSC-4. All solvents were of analytical grade and were distilled before use. Purity was checked by HPLC (Shimodzu-LC-6A) using a shimpack CLC-ODS (0.15 m × 6.ϕ) column.

SYNTHESIS OF LUPEOL ESTERS

The procedure adopted by Ekachai and Neubert [6] was followed. Lupeol (100 mg) was refluxed with an excess of acyl chloride in CH_2Cl_2 containing a small amount of triethyl amine under anhydrous conditions. This mixture was refluxed for 4 hours with TLC monitoring every 30 minutes. After the completion of the reaction the reaction mixture was worked up and chromatographed on silica gel (Acme-100-200 mesh) column and eluted with 1% ethyl acetate-hexane collecting 100 ml fractions. The ester was recrystallised twice from methanol and the purity of each ester was carefully checked by both TLC & HPLC. The spectral data of lupeol laurate is given below and others are similar.

^{1}H NMR ($CDCl_3$/TMS)

δ0.7–0.95 (methyls), δ1.2–1.9, (methylenes) δ2.1 (t, 2H-$OCOCH_2$) δ4.3 (m, 1H, C_3-H) and δ4.6–4.88 (dd, 2H; olefinic protons).

IR_{max} ($CHCl_3$): 2910, 1720, 1460, 1380 and 890 cm^{-1}.

HPLC EXPERIMENTAL CONDITIONS

Mobile phase: $CHCl_3$, Column: Shim-pack CLC-ODS (0.15 m × 6.0 ϕ); Flow rate: 1 ml/min; Detector: UV (240 nm); Injected quantity: 10 µl; purity: 99.8%; Retention time: 3.28 minutes.

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