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31-Norcycloartanol Fatty Acid Esters: Cholesteric Liquid Crystals from a Triterpene of Plant Origin†

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Abstract—The triterpene 31-norcycloartanol, previously reported present in pollen of *Taraxacum den leonis,* was isolated from the ester fraction but not the free sterol fraction, of lipid extracts of this pollen. Even chain esters of this triterpene from the acetate to the palmitate were found to be mesomorphic. The acetate, butyrate, hexanoate and octanoate formed only a cholesteric mesophase while the decanoate, laurate, myristate and palmitate formed both smectic and cholesteric mesophases. Only the palmitate ester could be specifically detected by gas–liquid chromatography in the naturally occurring fraction, but the probability of other liquid crystalline forms in the complex ester mixture seemed very likely.

1. Introduction

The liquid crystalline properties of some 9,19-cyclopropane tetracyclic triterpene esters have been described recently,(1–4) and the importance of side-chain constituents in the formation of the cholesteric mesophase has been indicated.(1–4) In order to extend these observations we have selected the pollen of *Taraxacum dens leonis* as a source of triterpenes and sterols for additional study, since this pollen has been reported to contain cycloartenol, I; cycloartanol, II; pollinastanol, III; 31-norcycloartanol, IV and several Δ^5 and Δ^7 sterols.(5–7) The mesomorphic behavior of compounds I and II have been previously reported by our laboratory.(3) We now wish to report the mesomorphic behavior of 31-norcycloartanol fatty

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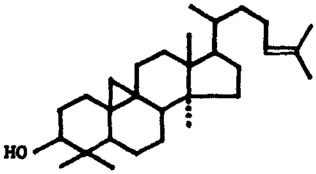
† Paper II of a series " Naturally Occurring Liquid Crystals ". The first paper of this series is reference.(4)



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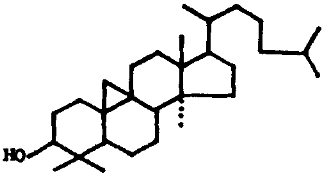

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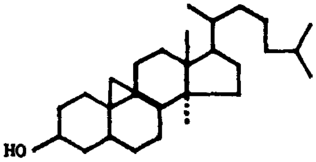

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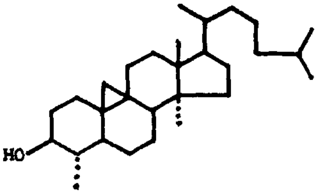

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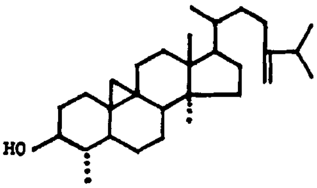

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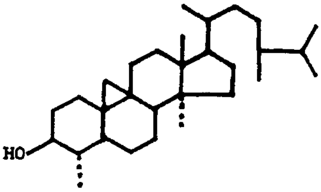

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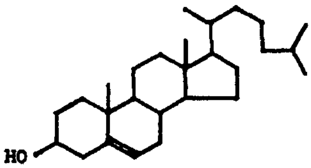

VII

Figure 1. Formulas for selected compounds.

acid esters and some tentative observations on the distribution of these compounds in pollen.

2. Experimental

Materials—All chemicals were analytical grade. Solvents were distilled before use, except the ethanol used for extraction of the pollen. The petroleum ether had b.p. 30–60 °C. Solvents were supplied by either the Mallinckrodt Chemical Company or Fisher Scientific Company. Acyl chlorides were obtained from Eastman Organic Chemical Company. Alumina was obtained from Merck A.G. period Silica Gel G was purchased from Brinkmann.

Melting points were determined on a Fisher–Johns hot stage apparatus and were found to be correct using benzoic acid standard for calorimetry supplied by Fisher Scientific Company. Phase-transition temperatures were determined on a Nalge–Axelrod hot-stage polarizing microscope. Samples for inspection were placed on a thoroughly cleaned glass cover slip. After fusion, the melt was covered with an additional cover slip so that the melt was uniformly distributed between both glass slips. Air bubbles and dust were scrupulously avoided during the microscopic examinations.

Pollen of *Taraxacum dens leonis* was supplied by Mr. Louis de Lescure, Apiculteur, Laverne, Severac-le-Chateau, France. Authentic 31-norcycloartanol as a reference sample was kindly supplied by Professor G. Berti.

Column Chromatography (CC) was performed using Merck neutral aluminum oxide. Pollen neutral lipids were chromatographed on a 7 cm diameter glass column and purification of individually synthesized esters was performed with small columns 1 cm in diameter.

Thin-Layer Chromatography (TLC) was performed on 250 μ thick silica gel G on glass plates 20 × 20 cm. For preparative purposes 500 μ thick silica gel G plates were used. The solvent system used for separation of 31-norcycloartanol from the accompanying 4,4-dimethyl sterols on a preparative scale was a 1 : 3 mixture of ethyl acetate-hexane (1 : 3), and anhydrous ethyl ether-benzene (12 : 88). Plates were developed 3 times to the height of 5 cm, 10 cm and 15 cm respectively. 31-norcycloartanol esters were tested for purity using

250 mm thick silica gel G glass plates using the solvent system: petroleum ether–anhydrous ethyl ether (95 : 5) at 0 °C. Plates were visualized by spraying with anisaldehyde reagent (anisaldehyde-sulfuric acid-ethanol 5 : 5 : 90) followed by heating at 120 °C for 5 minutes.

Gas–Liquid Chromatography (GLC) and GLC-Mass Spectrometry (GLC-MS)

Gas–liquid chromatography (GLC) was performed on a Varian Aerograph series 1740–10 gas chromatograph equipped with hydrogen flame ionization detector. The purity test for 31-norcycloartanol was carried out with a 180 cm long glass column (I.D. 4 mm) packed with 3% OV-17 on 100/120 gas chrom Q (Applied Science Lab., Inc.) at column temperature 285 °C. Nitrogen was used as a carrier gas at 60 ml/min. For the analysis of esters a 60 cm long glass column (I.D. 4 mm) was used, packed with 1% SE-30 on 100/120 gas chrom Q (Applied Science Lab., Inc.) and operated at 300 °C.

Gas–liquid chromatography-mass spectrometry (GLC-MS) was accomplished in a LKB Model 9000 single focusing gas chromatography-mass spectrometer. A 180 cm long glass column (I.D. 4 mm) packed with 3% OV-17 on 100/120 gas chrom Q was used at 285 °C. Other conditions were as follows: helium flow 30 ml/min, molecular separator 262 °C. Ion source 240 °C, ionizing energy 70 eV.

Phase Transitions are abbreviated as follows: isotropic, iso; smectic, sm; cholesteric, cho. Arrows show the direction of change for isotropic to smectic: iso → sm, etc. Color changes were observed by the naked eye at glancing angles while other transitions were examined under crossed polaroids. The light source used was a 75 watt white bulb.

Isolation of 31-*Norcycloartanol*—Ten kg of pollen was extracted exhaustively with hot absolute ethanol. The extract was distilled to low volume, with last traces of ethanol and H_2O removed under N_2 on the steam bath. The black gummy residue so-obtained (weight 1430 g) was extracted thoroughly with hot ethyl ether. The ether extract was reduced in volume to about 2 liters and then extracted successively with 5% aqueous KOH (to remove acids) and H_2O. Distillation of the ether, with residual solvent removed on the steam bath under N_2, gave 644 g of deep red oil which will be referred to in subsequent publications as the " neutral lipid fraction ".† 200 g of this fraction were placed on a 7 cm diameter column containing 2000 g of neutral aluminum oxide. The column was then washed with 2000 ml of petroleum ether (Fraction 1) to remove hydrocarbons (which were not examined). Subsequent elution of the column with 1000 ml fractions of benzene (each monitored by TLC) showed that the triterpene and sterol esters were present in fraction 2 to 4. These were combined and saponified as previously described.⁽⁸⁾ The nonsaponifiable fraction so-obtained weighed 23 g. This was chromatographed on a 5 cm diameter column containing 500 g of neutral aluminum oxide. Fractions containing 4,4-dimethyl and 4α-methyl sterols were eluted with petroleum ether-ethyl ether 6 : 4. The 4α-methyl compounds were separated by preparative TLC using the solvent system mentioned above. The purification of 31-norcycloartanol was performed by repeated preparative TLC and several crystallizations. The product thus obtained (450 mg) was of high purity (> 99%) as judged by GLC, GLC-MS, the melting point (130–131 °C) and identical in all tests to authentic 31-norcycloartanol.

Synthesis of 31-*Norcycloartanol Fatty Acid Esters*—Fatty acid esters of 31-norcycloartanol were prepared by refluxing for 3 hours 50 mg of the triterpene with 25 mg of acyl chloride, 2 ml of anhydrous pyridine and 20 cc anhydrous benzene to increase the yield of esters.⁽⁹⁾ The cooled mixtures were poured into water and extracted with ethyl ether. The ether was washed with dilute HCL and H_2O, respectively, then dried over anhydrous Na_2SO_4. Distillation of the ether left a crude ester fraction which was purified by passing through a thin column packed with 10 g of aluminum oxide. First the columns were eluted with petroleum ether then the esters were eluted from the column with benzene fractions, 20 ml each. The esters were usually eluted quantitatively in the first benzene fraction.

Each ester was repeatedly crystallized from acetone and dried in a Abderhalden drying apparatus at the boiling point of acetone for 5 hours under 15 mm Hg vaccum pressure. The esters so obtained were found to be of high purity by GLC (> 99%).

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† Pollinastanol, III and several other triterpenes and their esters are under investigation for mesomorphic behavior.

3. Results

A. *Crude Synthesized Esters*

The non-crystalline esters obtained by elution from an alumina column with benzene readily illustrated the effect of traces of solvent on phase transition temperatures.⁽¹⁰⁾ When fused and subsequently cooled to room temperature all esters except the acetate exhibited a cholesteric color to the naked eye, persisting for 10 minutes to 2 hours. The butyrate produced a brick red to orange color which persisted for ten minutes, subsequently changing to green and blue color before disappearing. The hexanoate and octanoate behaved as the butyrate, but the color persisted for 15 minutes at room temperature. The decanoate gave a green color on cooling, changing to red, then purple, green and yellow respectively, finally acquiring a blood-red coloration persisting for 40 minutes. The laurate acquired a bright red color changing to a pink which persisted for 2 hours. The myristate gave a green color changing to blue, which persisted for 40 minutes. The palmitate also gave a bright green color persisting for 30 minutes.

B. *Highly Purified and Dried Esters*

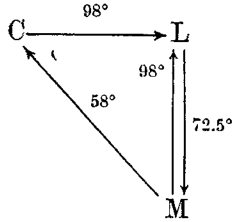
Table 1 shows the phase transition temperatures for the recrystallized and thoroughly dried 31-norcycloartanol esters both on heating and cooling. The appearance of the colored cholesteric mesophases was observed by the naked eye on the microscope stage at different glancing angles. It is here emphasized that the onset of color only is not the phase transition indicated as cholesteric, but rather the appearance of the cholesteric Grandjean planes under crossed polaroids.⁽¹¹⁾ Melting points are the stage at which the melt is free of solid crystalline structure. Phase transition temperatures were recorded on cooling the melt from the isotropic liquid and again heating the melt before crystallization.

31-*Norcycloartanyl Acetate:* m.p. 98–99°. The melt passed directly to the isotropic liquid. Heating was continued to 120 °C. On cooling the isotropic melt under crossed polaroids, the birefringent mosaic type of the cholesteric mesophase appeared at 72.5°. This changed at 61.5° to an aggregate of coil and fingerprint structure. A transient red-green color appeared at 67.5° when the preparation was observed

TABLE 1 Phase Transition Temperatures of 31-Norcycloartanol Esters

Ester	M.W.	M.F.	M.P. °C	T_1 °C solid→sm			T_2 °C sm→cho			T_3 °C solid→cho			T_4 °C cho→iso			T_5 °C solid→iso		
				a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
Acetate	456	$C_{31}H_{52}O_2$	98–99							98	58		98	72.5	98	98		
Butyrate	484	$C_{33}H_{56}O_2$	80–82							80	31		103	103.5				
Hexanoate	512	$C_{35}H_{60}O_2$	68–69							68	34		98	97				
Octanoate	540	$C_{37}H_{64}O_2$	73–74							73	32		88	87.5	84			
Decanoate	568	$C_{39}H_{68}O_2$	78–80		30			57	59	78			88	87	84			
Laurate	596	$C_{41}H_{72}O_2$	73–75		31			65	63.5	73			83	83.5	80.5			
Myristate	624	$C_{43}H_{76}O_2$	67–68		30			68	64	67			78	80.5	77			
Palmitate	652	$C_{45}H_{80}O_2$	62		27			68	65	62			75	78				

a; first heating, b; cooling, c; second heating at glancing angles on the microscopic stage. At this stage when the cover slip was mechanically disturbed by applying light pressure with a needle, a brilliant play of violet, red, orange, green, blue and yellow colors appeared. This rainbow disappeared instantly on raising the needle. Reheating the melt at this stage gave the isotropic liquid at 98 °C. On cooling, the same sequence occurred and crystallization took place at 58 °C. Phase transitions may be represented as follows:



31-*Norcycloartanyl Butyrate:* m.p. 80–82 °C. The melt passed to a very strong birefringent flowing liquid with parallel flowing lines as seen under crossed polaroids. This changed quickly to a network of fine filaments. The cholesteric plane texture appeared at 101 °C and the isotropic liquid was formed at 103 °C. Heating was continued at 120 °C. On cooling the isotropic liquid the Grandjean planes appeared at 103.5 °C as seen under crossed polaroids. This changed to the mosaic type then to a coil and fingerprint-like texture and again to the mosaic at 92 °C. A faint red-green color appeared at 85 °C as seen with the naked eye at a glancing angle but the mosaic texture persisted to 60 °C. On applying mechanical pressure to the cover slip at this stage the mosaic texture was completely disrupted and a network texture was formed (oily streaks). The same structure is also exhibited by cholesteryl butyrate(12) and other cholesteryl esters.(13) This texture persisted down to 37 °C at which point a very bright-red orange color was observed with the naked eye at a glancing angle on the microscopic stage. However, no microscopic changes took place under crossed polaroids. The color observed then changed to a bright green mixed with blue, red, orange and yellow colors at 31 °C Crystallization occurred directly from the colored mesophase at the same temperature. Although the brilliant colors did not appear on gradual heating, the quick heating of the slide with a weak flame gave a very strong transient brick-red color mixed with a bright yellow. Also the quick cooling of the heated slide resulted in a reversible play of colors which persisted for about 2 min. at room temperature. The phase transitions can be summarized as follows:

$$\begin{tikzcd}
C \arrow[r, shift left, "80^\circ"] & M \arrow[l, shift left, "31^\circ"] \arrow[d, shift right, "103^\circ"'] \\
 & L \arrow[u, shift right, "103.5^\circ"']
\end{tikzcd}$$

31-*Norcycloartanyl Hexanoate:* m.p. 68–69 °C to a strongly birefringent mesophase under crossed polaroids, which with the naked eye appeared brick red in color. The isotropic liquid occurred at 98 °C. Heating was continued to 120 °C. On cooling, the cholesteric Grandjean planes appeared at 97 °C and became more distinct on further cooling. The same phase when examined by the naked eye at a glancing angle was seen to acquire a strong green color at 65 °C changing to blue at 55 °C. Disturbing the preparation at this stage by applying mechanical pressure to the cover slip resulted in the destruction of the cholesteric Grandjean planes with subsequent appearance of the network texture (oily streaks). The color at this point became much more intense but changed to a mixture of green, blue, red and yellow and disappeared at 40 °C. Crystallization occurred at 34 °C. The phase transition sequence can be summarized as follows:

$$\begin{tikzcd}
C \arrow[r, shift left, "68^\circ"] & M \arrow[l, shift left, "34^\circ"] \arrow[d, shift left, "98^\circ"] \\
 & L \arrow[u, shift left, "97^\circ"]
\end{tikzcd}$$

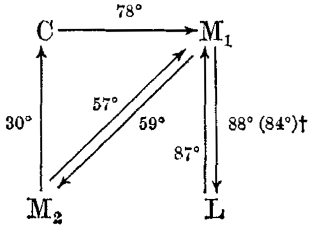
31-*Norcycloartanyl Octanoate:* m.p. 73–74 °C. The melt appeared strongly birefringent with many flowing parallel lines replaced quickly by a network of birefringent filaments. The isotropic liquid formed at 88 °C. Heating was continued to 120 °C. On cooling the isotropic melt the cholesteric Grandjean planes appeared at 87.5 °C as seen under crossed polaroids. A faint green color appeared to the naked eye at 66 °C while the cholesteric planes were still persisting. The color gradually changed to bluish green then to blue at 55 °C. A rainbow of beautiful bright mixed red, yellow, violet, green and blue developed at 40 °C. This play of colors became more intense on application of mechanical pressure to the preparation but the Grandjean planes changed to a network of fine filaments (oily streaks) as seen under crossed nicols. The color disappeared at 30 °C. Reheating the mechanically disturbed preparation at this stage resulted in the reappearance of the same play of colors at 40 °C persisting but increasing in intensity until it disappeared at 74 °C. The oily streaks persisted under crossed polaroids up to 86 °C at which point the Grandjean planes were reformed. The preparation became isotropic at 87 °C. On cooling the preparation the mesophase transitions were followed by crystallization at 32 °C. The phase transitions can be summarized as follows:

$$\begin{tikzcd}
C \arrow[r, shift left, "73^\circ"] & M \arrow[l, shift left, "32^\circ"] \arrow[d, shift left, "88^\circ(84^\circ)\dagger"] \\
& L \arrow[u, shift left, "87.5^\circ"]
\end{tikzcd}$$

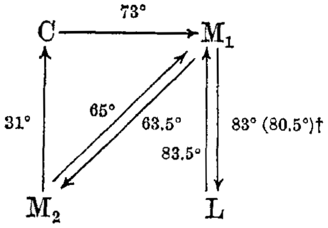
31-*Norcycloartanyl Decanoate:* m.p. 78–80 °C. The melt was viscous and birefringent, then formed a mobile structure of long parallel filaments as seen under crossed polaroids. The isotropic liquid was reached at 88 °C. Heating was continued to 120 °C and on cooling, the Grandjean planes appeared at 87 °C. A red color appeared, to the naked eye at 70 °C changing to green at 68 °C then the preparation acquired a red color again at 59 °C. At 57 °C the fan shaped smectic texture appeared and persisted till 30 °C at which temperature crystallization occurred. In another experiment reheating the smectic mesophase at 35 °C resulted in the cholesteric

† M→L in the second reading

mosaic texture and the partial appearance of a network of bright filaments at 59 °C as observed under crossed polaroids. At this temperature the red color appeared changing to green at 67 °C and lasting till 77 °C. The isotropic liquid was formed at 84 °C. Phase transitions are summarized as follows:

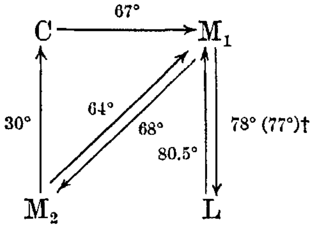


31-*Norcycloartanyl Laurate:* m.p. 73–75 °C. The melt was first viscous and birefringent, then gave a flowing liquid intercepted by many long parallel filaments as observed under crossed polaroids. The isotropic liquid was formed at 83 °C and heating was continued to 120 °C. On cooling the isotropic melt the Grandjean planes appeared at 83.5 °C. A strong green color developed at 79 °C changing to pink on further cooling. The typical smectic mesophase appeared at 65 °C and persisted to 34 °C. Again on raising the temperature of the preparation at this point the smectic mesophase disappeared at 63.5 °C giving rise to a network of filaments which was seen under crossed polaroids. This change was associated with a strong green color which changed to red at 68 °C and disappeared at 74 °C. These color changes were observed by the naked eye on the microscopic stage. The isotropic liquid was formed at 80.5 °C. On cooling the preparation the same sequence of changes occurred as for the first cooling process and crystallization occurred at 31 °C. The phase-transitions can be demonstrated as follows:



† $M_1 \rightarrow L$ in the second reading

31-*Norcycloartanyl Myristate:* m.p. 67–68 °C. A viscous birefringent liquid first appeared changing to a fast moving fluid intercepted with numerous long, parallel, thick, strongly birefringent filaments seen under crossed nicols. The melt was associated with an intense green color at 72.5 °C with the naked eye. Both color and birefringence disappeared at 78 °C giving rise to the isotropic liquid. On cooling, the cholesteric Grandjean planes were formed from the isotropic liquid at 80.5 °C. The green-red color appeared to the naked eye at 70 °C and changed to red. At 68 °C the typical smectic structure was formed. Cooling was further continued to 35 °C with no changes in the microscopic features. Reheating the smectic structure from 35 °C caused it to disappear at 64 °C giving rise to the plane cholesteric structure. The field then acquired a faint network appearance and a green color appeared at 70 °C changing to red which disappeared at 73 °C. The melt became less dense and the network faded out but there were still traces of fine lines. Further heating to 77 °C caused the formation of the isotropic liquid. On cooling the melt again the same series of transitions were repeated and crystallization occurred at 30 °C.



31-*Norcycloartanyl Palmitate:* m.p. 62 °C. The melt formed a viscous, strongly birefringent liquid, then it began to flow acquiring an intense green color and birefringent parallel filaments flowed in the melt. The color which was observed with the naked eye turned red at 74 °C and disappeared at 75 °C. The isotropic liquid was also formed at 75 °C as observed under crossed polaroids. Heating was continued up to 120 °C with no changes. On gradually cooling the isotropic liquid, the Grandjean planes appeared at 78 °C and were observed under crossed polaroids. The intense green color appeared at 75 °C and changed to red at 74 °C. This was seen with the naked

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† $M_1 \rightarrow L$ in the second reading

eye. The Grandjean planes disappeared at 68 °C and were instantly replaced by the smectic structure which became very distinct at 65 °C. Cooling was continued to 60 °C and when this smectic mesophase was reheated at this stage it very sharply disappeared at 65 °C giving rise to the plane cholesteric structure which was ill-defined under crossed polaroids. This was accompanied by the green color seen by the naked eye. The color changed to red-green at 72 °C, red at 73 °C and the melt became colorless and isotropic at 75 °C.

Cooling the isotropic liquid led to the same sequence of transitions and finally to crystallization from the smectic phase at 24 °C. The phase transition can be illustrated as follows:

$$\begin{tikzcd}
C \arrow[r, "62^\circ"] & M_1 \arrow[d, shift left, "75^\circ"] \arrow[dl, shift left, "68^\circ"] \\
M_2 \arrow[u, "27^\circ"] \arrow[ur, shift left, "65^\circ"] & L \arrow[u, shift left, "78^\circ"]
\end{tikzcd}$$

However, during cooling of the isotropic liquid, the Grandjean planes which appeared at 78 °C were mechanically disturbed by applying pressure to the cover slip at 77 °C. This caused the planes to vanish instantly, being replaced by a typical cholesteric network of bright filaments (oily streaks) and the instant appearance of a red color at 77 °C instead of appearing at 75 °C. This, however, changed to green at 75 °C, the same temperature at which it appeared in the undisturbed preparation. The smectic mesophase was formed at 68 °C, which is the same temperature at which it appeared in the undisturbed preparation. It appears that the mechanical disturbance of the preparation in this case brings about a certain change in the onset of the color but does not change the phase-transition temperatures.

Naturally Occurring Esters

Examination by GLC of the original oily crude ester fraction obtained by column chromatography from the neutral lipid fraction

† $M_1 \rightarrow L$ in the second heating

indicated great complexity. Resolution was not attempted but a peak corresponding to the palmitate of 31-norcycloartanol was obtained, indicating the natural occurrence of this ester in pollen. However, the fatty acids found in this fraction were lauric 55%, palmitic 21%, stearic 21% and arachidic 3% by GLC of the methyl esters of the fatty acids obtained by saponification of the ester fraction.

4. Discussion

While none of the earlier synthesized 9,19-cyclopropane tetracyclic triterpene acetates(1–4) exhibited any kind of mesophase, 31-norcycloartanyl acetate was found to be cholesteric. The butyrate of this compound formed also a beautiful play of cholesteric colors whereas that of cycloeucalanol (VI) with a C_{24} methyl group did not.(3) Cycloeucalenyl butyrate (V) was reported to be cholesteric but no phase transition temperature was recorded.(3)

Table 2 shows that the cholesteric mesophase appears uniformly throughout the series of acyl esters of 31-norcycloartanol, a behavior that is not exhibited by either cycloeucalenol (V) or cycloeucalanol (VI).(3) This again emphasizes previous observations indicating that the presence of a substituent at C_{24} affects (in one way or another) the formation of a mesophase.

On the other hand data published for cholesteryl esters(12,14) show their close resemblance to 31-norcycloartanol esters in regard to the uniformity of appearance of the cholesteric phases along the series. Another resemblance is also manifested in the occurrence of only the cholesteric mesophase in the lower homologues and both cholesteric and smectic mesophases in the higher homologues. This is probably related to the fact that the configuration of the rings in 31-norcycloartanol is the same as for cholesterol. The cyclopropane ring at C9,19 and the substituents at C_4 and C_{14} do not therefore seem to affect the formation of a mesophase to a great extent, as already observed in other compounds such as I, V, VI and their reduced forms.(3)

Pollinastanyl (III) palmitate was found to be cholesteric.† However-

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† Unpublished observations. A report on the mesomorphic behaviour of acyl esters of this 9,19-cyclopropane sterol are being completed and will form the subject of a future publication.

TABLE 2 Mesophases exhibited by Cholesterol, 31-Norcycloartanol, Cycloeucalenol and Cycloeucalanol Fatty Acid Esters

	Cholesterol VII	31-Norcycloartanol IV	Cycloeucalenol V	Cycloeucalanol VI
Acetate	cholesteric	cholesteric		
Butyrate	cholesteric	cholesteric	cholesteric	
Hexanoate	cholesteric	cholesteric	cholesteric	cholesteric
Octanoate	cholesteric-smectic	cholesteric	cholesteric	cholesteric
Decanoate	cholesteric-smectic	cholesteric-smectic	cholesteric	cholesteric
Laurate	cholesteric-smectic	cholesteric-smectic	smectic	cholesteric
Myristate	cholesteric-smectic	cholestetic-smectic	smectic	cholesteric
Palmitate	cholesteric-smectic	cholesteric-smectic		

ever, cholesteric colors were not as intense or stable as those of 31-norcycloartanyl palmitate. The only difference between the two compounds is the absence in pollinastanol of a 4α-methyl group.

The possible role of liquid crystalline substances in biological systems has been discussed in several publications.(15–18) It is important from the biological point to note that the pollen ester fraction of *Taraxacum dens leonis* is composed of many triterpenoids and sterols. As noted, cycloartenol, cycloartanol, 31-norcycloartanol, pollinastanol(5–7) and 31-nordihydrolanosterol(8) are the main isoprenoid components of this fraction. Cholesterol was also found in this pollen.(5–7) All these compounds except 31-nordihydrolanosterol, which was not studied for mesomorphic behavior, are able to form cholesteric mesophases when esterified with fatty acids. Since pollen is part of the male reproductive system in plants it seems therefore that the presence of liquid crystalline substances might play an important role in the vital process of reproduction of plants. It would be of interest to study the composition of the flower ovaries to determine the triterpenoid and steroidal content and whether they contain substances capable of forming liquid crystalline mesophases.

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REFERENCES

1. Knapp, F. F. and Nicholas, H. J., *J. Org. Chem.* **33**, 3995 (1968).
2. Knapp, F. F., Nicholas, H. J. and Schroeder, J. P., *J. Org. Chem.* **34**, 3328 (1969).
3. Knapp, F. F. and Nicholas, H. J., " Liquid Crystals and Ordered Fluids " (Plenum Press, 1970).
4. Knapp, F. F. and Nicholas, H. J., *Mol. Cryst. and Liq. Cryst.* **6**, 319 (1970).
5. Hügel, M-F., *Ann. Abeille*, **8**, 309 (1965).
6. Devys, M. and Barbier, M., *Bull Soc. Chim. Biol. t* **49**, 865 (1967).
7. Devys, M., Audier, D. and Barbier, M., *C. R. Acad. Sc. Paris, Series D*, *t* **269**, 798 (1969).
8. Atallah, A. and Nicholas, H. J., *Steroids*, **17**, 611–618 (1971).
9. Kuksis, A. and Beveridge, J. M. R., *J. Org. Chem.* **25**, 1209 (1960).

10. Vogel, M. J., Barrall II, E. M. and Mignosa, C. P., " Liquid Crystals and Ordered Fluids " (Plenum Press, 1970).
11. Grandjean, F. C. R., *Acad. Sci.* **172**, 71 (1921).
12. Irvin, B. W., *J. Colloid and Superface Sci.* **23**, 221 (1967).
13. Chistyakov, I. G. and Usol Tseva, V. A., *Izv. Vysshykh Uchebn. Zavedenii, Khim. i Khim. Teknol.* **5**, 585 (1962).
14. Kast, W., Londolt-Bornstein 6th edition, vol. II, part 2a p. 266, (1959).
15. Gray, G. W. " Molecular Structure and the Properties of Liquid Crystals ", (Academic Press, New York, 1962).
16. Fergason, J. L. and Brown, G. H., *J. Am. Oil Chem. Soc.* **45**, 122 (1968).
17. Stewart, T., *Mol. Cryst.* **1**, 563 (1966).
18. Athenstaedt, H., *Naturwissenschaften* **48**, 465 (1961); **49**, 433 (1962).