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PHASE TRANSITIONS OF CHOLESTERYL CINNAMATES

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ABSTRACT

Phase transitions of two isomeric derivatives of cholesteryl cinnamate, cholesteryl ferulate(CF) and cholesteryl isoferulate(CI), were studied by means of DSC and TAM(Thermoanalytical Microscopy).

CF, cholesteryl 4-hydroxy-3-methoxycinnamate, showed two monotropic mesophases, smectic and cholesteric, and three solid polymorphs after having been melted, past the glass transition point.

CI, cholesteryl 3-hydroxy-4-methoxycinnamate, showed no glass transition but showed three solid polymorphs. It also showed a monotropic smectic phase and an enantiotropic cholesteric phase.

It was concluded from the thermal history of the samples that the solid polymorphs of CF are of metastable forms, whereas those of CI are of stable forms in their respective temperature ranges.

INTRODUCTION

As shown in a previous paper[1], cholesteryl acetylferulate(CAF), cholesteryl 4-acetyloxy-3-methoxycinnamate, displays complicated thermal behavior under DSC, namely, a glass transition and two types of cold crystallization (and two mesophase transitions), whereas cholesteryl cinnamate(CC) shows neither glass transition nor cold crystallization.

This paper reports a study similar to the previous one, but includes TAM, regarding two isomeric derivatives of CC, cholesteryl ferulate(CF) and cholesteryl isoferulate(CI) whose chemical names are given in the above abstract. However, the phase transition of CF was partially presented previously[2].

TAM is the abbreviation of "Thermoanalytical Microscopy", which means simultaneous measurement of thermal analysis and microscopy[3].

EXPERIMENTAL

Samples

Synthesis of CF was reported elsewhere[4], but that of CI has yet to be published. Disregarding the solvent's peak, both of the samples showed a single peak in high speed liquid chromatographs respectively.

Apparatus

Perkin-Elmer DSC-C2 and Mettler FP84 were employed. In order to carry out TAM, a specially designed cell adapted to fit the hot stage of FP84 was used. This cell is similar in design to previously reported ones[5, 6].

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Scannings were carried out at rates of 10, 5, 2.5, 1.25, and 0.625 K/min. Microscopy was carried out under 100x magnification with crossed polars.

RESULTS and DICUSSION

Phase Transition of CF

The sample showed complicated phase transitions. The characteristics of its thermal history are shown in Fig. 1. The crystals from the solution simply melt at 433 K and show no mesophases when first heated(run 1, photos. 1-3). However, upon cooling they show a cholesteric phase and a smectic one(type A) at 418 K and 384 K respectively(run 2, photos. 4 and 5). Crystallization depends on thermal history. CF aged at a temperature above the melting point usually does not crystallize on cooling but rather on reheating; so called cold crystallization takes place at around 368 K past the glass transition point, 313 K(run 3, photos. 6-8). The higher an ageing temperature, and the longer the ageing time and the more rapid the cooling is, the more effectively the cold crystallization takes place.

The cold crystallized CF transforms from the spherulitic form into another crystal form at 419 K. The new crystals melt at 429 K. At this point, new crystals appear which melt at 433 K(run 3, photos. 9-12)。 We denote these three solid polymorphs in order from highest to lowest melting point, as KI, KII , and KⅢ. The melting point of KI is the same as that of the original crystals from the solution. This suggests that KI is the original form of CF.

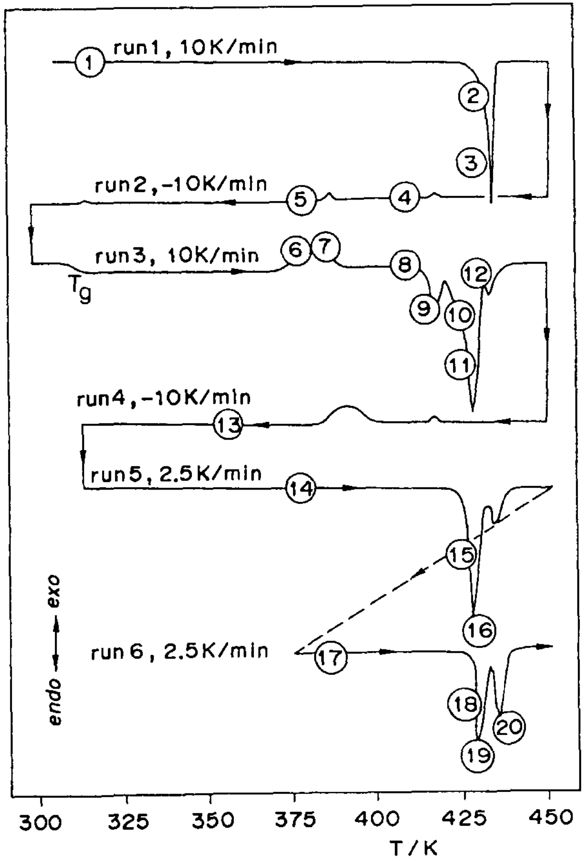
If the sample has not been aged above the melting point, CF crystallizes on cooling(run 4, photo. 13). The crystals formed during cooling show no exothermic peaks on reheating. However, they show two endothermic peaks, but lack the lowest peak in run 3(run 5, photos. 14-16). This suggests that the crystals produced by cold crystallization must be the same as the most unstable polymorph, KIII .

CF recrystallized from the smectic state by being held at 373 K (where cold crystallization would take place) gives a curve upon reheating whose peak area for fusion of KII decreases and whose peak area for fusion of KI increases(run 6, photos. 17-20). This suggests that KⅡ is also a metastable polymorph of CF.

Table 1, Transition temperatures and enthalpy changes of CF

Transition / course	Smectic - Chol.		Chol. - Iso.liq.		Cryst. - Iso.liq.	
	T	ΔH	T	ΔH	T	ΔH
	K	kJ.mol^{-1}	K	kJ.mol^{-1}	K	kJ.mol^{-1}
heating	-	-	-	-	431.5	38.8
cooling(a)*	384	-0.43	418	-0.57	-	-
cooling(n)*	-	-	420	-0.6	400	-18.4**

* (a); aged sample, (n); non-aged sample, ** Cryst.-Chol. transition



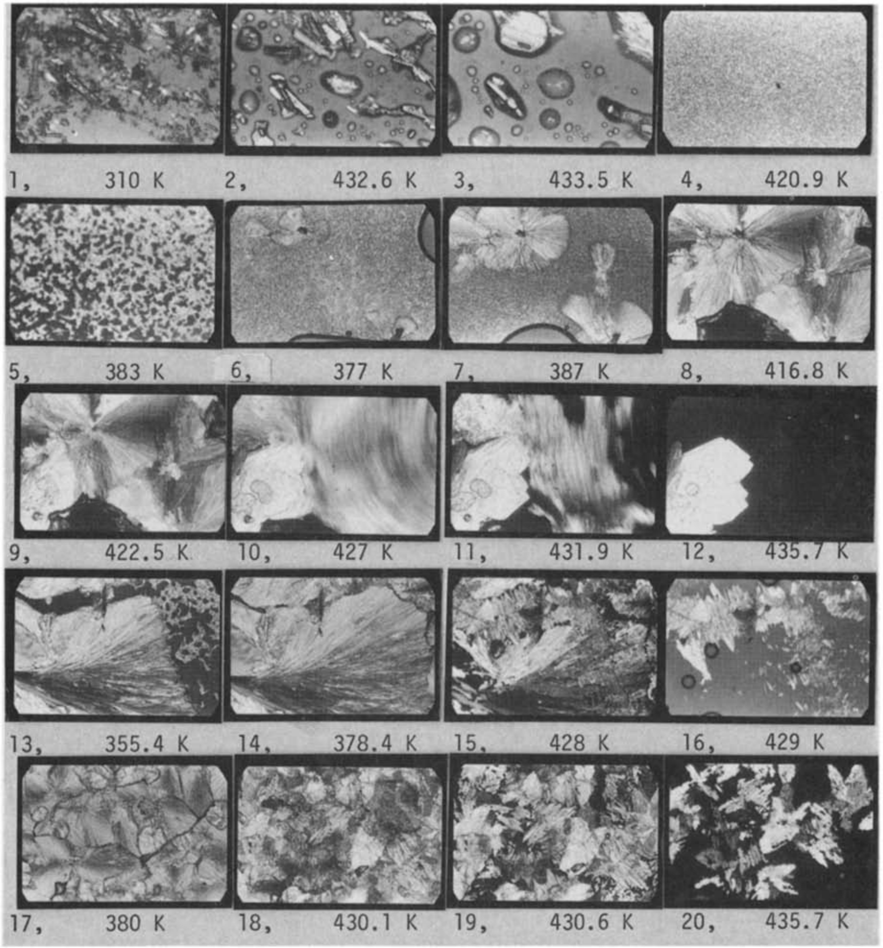
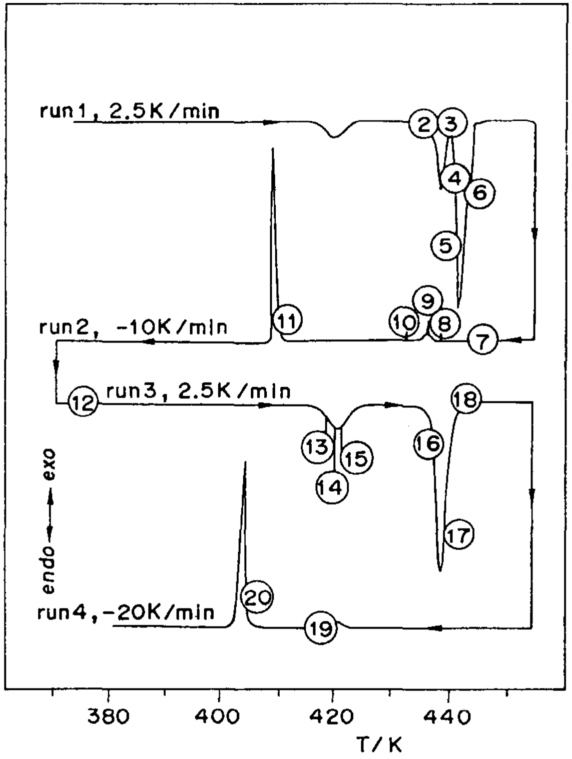


Fig. 1, Thermoanalytical microscopy of CF, 100x, crossed polars, Neopan ASA400



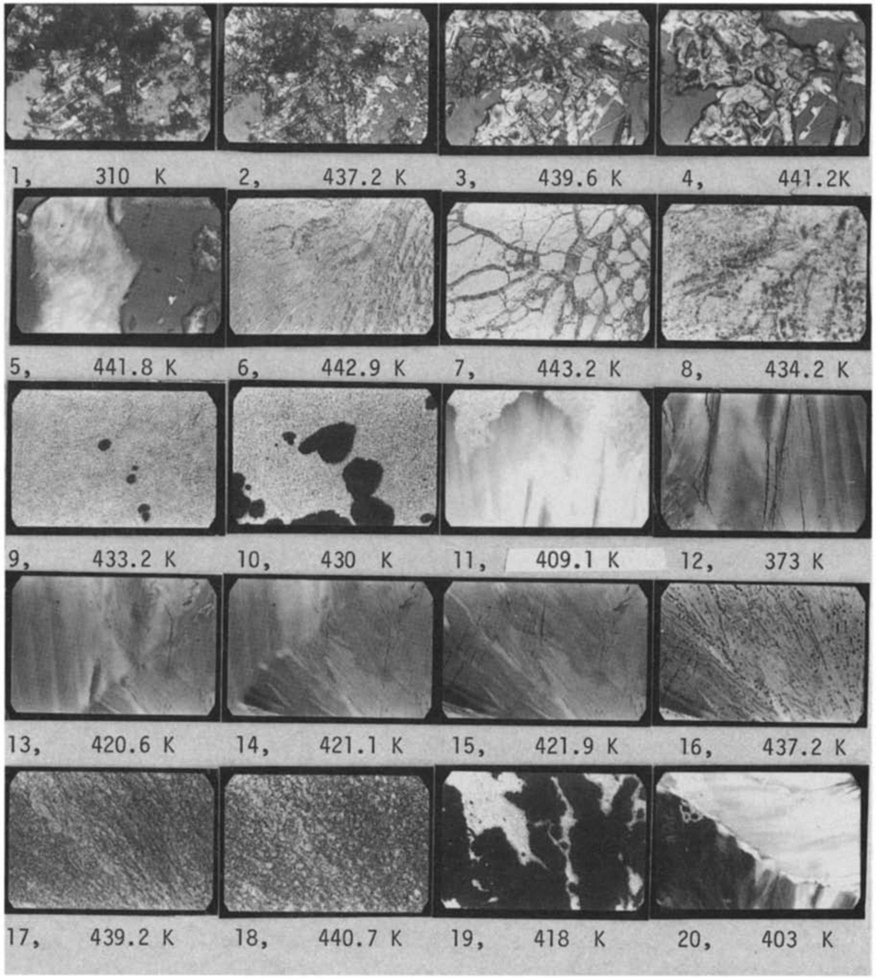


Fig. 2, Thermoanalytical microscopy of CI,
100x, crossed polars,
Neopan ASA 400

Table 1 gives the transition temperatures and enthalpy changes. Each value of the temperatures is the on set value for zero K/min extrapolated from those for the several scanning rates. The enthalpy changes were obtained by taking the average of the data.

Table 2 gives the transition values on reheating. In order to obtain T_g-point, the sample was quenched from 473 K to 223 K and then reheated with a rate of 10 K/min. The resulting reheating curve was used to determine the T_g-point. It was found by using TAM that the smectic-cholesteric transition takes place at 388.8 ±0.2 K on reheating even during cold crystallization. The enthalpy changes between the solid polymorphic transitions are not given, since they depend on thermal history.

Phase Transition of CI

CI shows three solid polymorphs and two mesophases, an enantiotropic cholesteric and a monotropic smectic-A. Table 3 gives the transition temperatures and the enthalpy changes were determined in a way similar to that used for CF. The bluish cholesteric texture persists up to 550 K, where CI seems to decompose gradually. Therefore cholesteric-isotropic liquid transition data have not been given.

Figure 2 shows the thermal characteristics of CI. First heating run shows a small peak at 416 K and two sharp peaks near the fusion range(run 1, photos. 1-6). These two peaks appear as a doubled peak on a more rapid heating. At 416 K, the colors of the crystals which appear due to the light retardations caused by the crossed polars begin changing into other colors within the crys-

Table 2, Transition data of CF on reheating

Transition / course	Sm(g) - Sm		Sm - KIⅡ		Sm-Ch	KⅢ -KⅡ	KⅡ -KI	KI -Iso.liq.
	T_g	ΔCp	T	ΔH	T	T	T	T
	K	J.mol^{-1}.k^{-1}	K	kJ.mol^{-1}	K	K	K	K
(a)*	313.0	125	368	-12	388.8	416	426	431.5
(n)*	-	-	-	-	-	-	423	431.5

* The sample notations are the same as in Table 1.

Table 3, Transition temperatures and enthalpy changes of CI

Transition / course	KA - KB		Sm - Ch		KB - KC		KC(KA) - Ch(Sm)	
	T	ΔH	T	ΔH	T	ΔH	T	ΔH
	K	kJ.mol^{-1}	K	kJ.mol^{-1}	K	kJ.mol^{-1}	K	kJ.mol^{-1}
heating	416	2.80	-	-	437.5	11.32	439.8	24.86
cooling	-	-	435.2	-0.24	-	-	(406)	(29.32)
reheating	414	2.98	-	-	434.8	9.43	438.3	18.17

tals, indicating a transformation into another crystal form. At 437.5 K, the crystals are entirely destroyed and new crystals differing in shape from the original appear. They melt soon at 439.8 K. The ratio of the area between the two peaks, separated by just 2.3 K from each other, is approximately 1:2. We denote the three crystal forms as KA, KB, and KC in order of their lowest stable temperatures. That is, 'KA' is stable from room temperature to 416 K, 'KB' stable from 416 K to 437.5 K and 'KC' exists between 437.5 K and 439. 8 K.

CI gives a small cholesteric-smectic transition peak and a sharp single peak of crystallization on cooling(run 2, photos. 7-11). On reheating, the transition from KA to KB again clearly takes place(run 3, photos. 13-15). This indicates that the transition is reversible and that crystallization from the smectic phase on cooling produces KA crystals. In most cases, the ratio between the peak areas of KB-KC and KC-Cholesteric transitions changes from 1:2 to 9:1. (Though run 3 only shows one peak,this indicates the direct transformation from KB to the cholesteric phase.) However, it can be restored to the original ratio, 1:2, if the sample is heated at a very low scanning rate, such as 0.625 K/min. Accordingly, it is considered that the three polymorphs of CI are not similar to the metastable polymorphs of CF, but are similar to the stable forms in their respective temperature ranges as mentioned above.

CONCLUSIONS

The above results lead to the following conclusions: (1) Both of the substances, CF and CI, have three solid polymorphs and two mesophases. (2) The three polymorphs of CF and CI, however,, are essentially different. Namely, CF has only one stable form and two other meastable forms, whereas CI has three stable forms which are thermodynamically stable in their respective temperature ranges. (3) The thermal features of CF are similar to those of CAF, both of which show cold crystallization. This contrasts with the fact that the behavior of CI is similar to that of CC, both of which show a sharp crystallization peak on cooling.

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