Technical

Some Thermal Properties of Methyl Malvalate, Methyl Sterculate, and their Dihydro Derivatives

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ABSTRACT AND SUMMARY

Methyl esters of cyclopropene acids, malvalic and sterculic, and their dihydro derivatives, were highly purified and examined for melting points, polymorphic behavior, heats of fusion, and dilatometric behavior. Results revealed that the quickly chilled forms of the unsaturated methyl esters underwent a rapid monotropic transformation. The dihydro derivatives exhibited no detectable polymorphism. The melting dilation for methyl malvalate was significantly below the previously reported dilations of other fatty acid methyl esters.

INTRODUCTION

The leaves and seeds of many species of the order Malvales, which includes *Gossipium hirsutum* or upland cotton, contain the cyclopropene fatty acids malvalic and sterculic (1,2). Their cyclopropane derivatives, dihydromalvalic and dihydrosterculic acids, are the biological precursors of the corresponding cyclopropene fatty acids (3,4). Because both cyclopropene and cyclopropane fatty acids shown unusual physiological activity (1,5,6), it was of interest to obtain them in pure form to determine their thermal properties.

The cyclopropene fatty acids react readily with themselves, therefore it was preferable to work with them in the form of methyl esters. This paper reports on the following thermal properties of the methyl esters:

(a) Melting points at different rates of heating and after different thermal treatments.
(b) Heats of fusion.
(c) Temperatures of polymorphic transitions.
(d) Heats of polymorphic transitions.
(e) Expansion coefficients in solid and liquid state.
(f) Melting dilations.

MATERIALS AND METHODS

Preparation of Methyl Esters

Methyl malvalate was derived from *Hibiscus syriacus* oil, which contained about 16% malvalic acid as triglycerides. The oil was subjected to methanolysis catalyzed with sodium methoxide. The resulting methyl esters were subjected to a series of urea clathrations and fractional crystallizations from methanol. The methyl malvalate concentrate was further purified by counter double current distribution using a hexane-acetonitrile system similar to that described by Butterfield et al. (7), followed by reverse-phase column chromatography on diatomaceous earth impregnated with paraffin oil. The column was eluted with acetonitrile saturated with paraffin oil. Subsequently, the paraffin oil was removed from the concentrate by adsorption on a silicic acid column, elution of the paraffin oil with petroleum ether, and then elution of the methyl esters with methanol. The methyl malvalate was still not sufficiently pure, therefore it was subjected to additional urea clathrations, passed through a column of activated alumina, and eluted with hexane. The final purity of the methyl malvalate, as indicated by HBr titration (8) and gas liquid chromatography (GLC), was better than 99%.

Methyl dihydromalvalate was prepared from partially hydrogenated methyl esters of *Hibiscus syriacus* oil. The esters were hydrogenated at 45 C in heptane solution in the presence of a zirconium-promoted nickel catalyst. Under these conditions, 98% of the cyclopropenes were converted to cyclopropanes. The partially hydrogenated esters were fractionated on a silicic acid column impregnated with silver nitrate (9). The first fraction from the column contained the methyl dihydromalvalate and other saturated methyl esters. The methyl dihydromalvalate was purified by successive low temperature crystallizations from various solvents untile GLC indicated 98.8% purity.

Methyl sterculate was prepared from *Sterculia foetida* oil, which contained about 44% sterculic acid and 6% malvalic acid as triglycerides, according to the method of Nordby et al. (10).

Methyl dihydrosterculate was prepared by hydrogenating the methyl sterculate under the same conditions as used in the preparation of methyl dihydromalvalate. The hydrogenation product was dissolved in acetonitrile saturated with paraffin oil and was fractionated on a reverse-phase column packed with diatomaceous earth impregnated with paraffin oil. Dissolved paraffin oil was removed from the methyl dihydrosterculate by methods employed to purify methyl malvalate.

Physical Properties

Melting point determinations were made on small amounts of each compound sealed under dry nitrogen in capillary tubes, at different rates of heating, and after different thermal treatments. The "thrust in" technique was used extensively; that is, a carefully conditioned sample was thrust quickly into another bath set at a predetermined temperature.

Heats of fusion, heats of transition, and transition temperatures were measured in a Perkin Elmer model DSC-1 differential scanning calorimeter calibrated with indium. To ensure accuracy of the temperature readings, the instrument was calibrated by melting samples of palmitic acid, lauric acid, methyl palmitate, and ice, whose equilibrium melting-solidification temperatures had been previously determined with a calibrated thermometer. In each of the experiments, 5 to 10 mg of a carefully weighed sample was sealed in an aluminum sample pan. *2*-Octanol was sealed in the reference pan. The cryogenic cover of the sample holder was filled with liquid nitrogen, and the sample was solidified in about 40 sec. After cooling to the desired temperature, the sample was heated and cooled at 2.5 C/min. Areas under the recorded energy peaks were measured with a planimeter, and data obtained with standard samples indi-

TABLE I

Capillary Melting Points and DSC Data

Methyl ester	Melting point, C	Heat of fusion, cal/g	Transition temperature, C	Heat of transition, K cal/mole
Methyl malvalate	–22.5	33.0	–48	–1.49
Methyl dihydromalvalate	–3.5	28.4	–	–
Methyl sterculate	–14.3	36.2	–24	?
Methyl dihydrosterculate	–3.6	32.4	–	–
Methyl oleate	–19.8	35.4	–29	–1.69

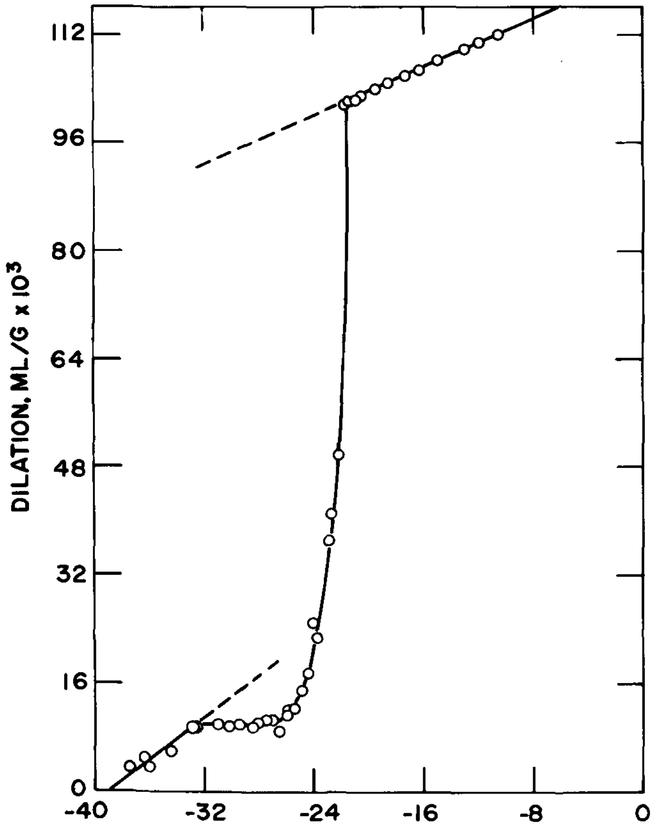

FIG. 1. Dilatometric curve for heating cycle of methyl malvalate.

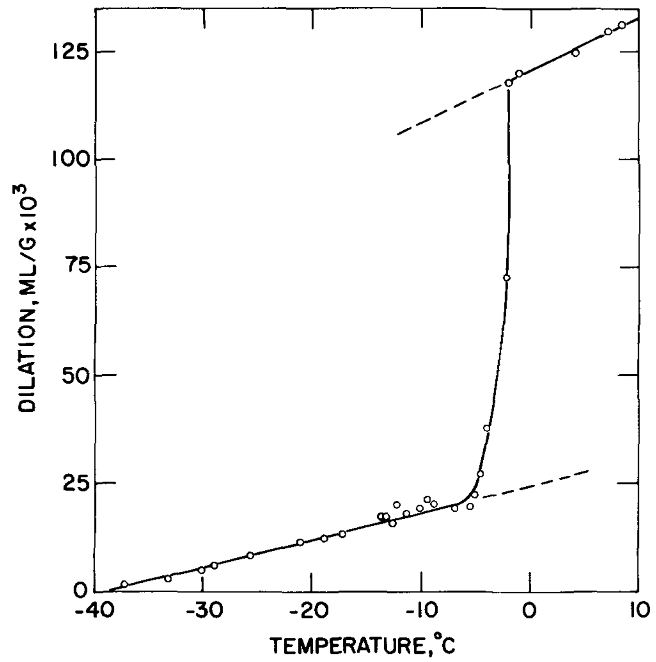

FIG. 2. Dilatometric curve for heating cycle of methyl dihydromalvalate.

cated about 99% accuracy for this procedure. The endothermic changes appear above the baseline, and the peak area is a direct caloric measure of the heat absorbed during the melting of a particular polymorph. Some of the lower melting polymorphs are insufficiently stable to completely melt before conversion to a higher polymorph. When a partial melting of a polymorph is accompanied by a conversion or transition to a higher polymorph, both endothermic and exothermic changes are represented in the endothermic peak. The peak area in such a case is a measure of the heat absorbed during melting, less the heat given off during the transition and crystallization to a higher polymorph. When a polymorph completely melts and then crystallizes to a higher polymorphic form, the endothermic peak area is the measure of the ΔH_f for that particular polymorph. The exothermic changes appear below the baseline, and the area of the exothermic peak that follows the melting of the polymorph is the measure of the ΔH_t for the transition and crystallization to a higher melting polymorph. In some instances, the transition from a lower to a higher melting polymorph takes place without melting. In this case, only an exothermic change takes place and the exothermic peak area below the baseline is the measure of ΔH_t.

Dilatometric examinations of tempered samples were conducted in gravimetric-type dilatometers, with mercury as the confining liquid. The construction of these dilatometers, their use, and methods employed in correcting dilatometric readings for the expansion of mercury and glass were in accordance with previously published descriptions (11,12).

RESULTS AND DISCUSSION

Much difficulty was encountered in determining capillary melting points, both after quick solidification and after tempering. The compounds could not be solidified in a reasonable length of time unless the temperature was reduced about 20 C below their melting points. Methyl malvalate and methyl dihydromalvalate, after having been seeded and stored at 5 C below their melting points for 10 days, did not solidify, nor was there a noticeable increase in the solid phase during the last 5 days of the storage period. Capillary melting points were determined for each compound. There was evidence of a polymorphic transformation of methyl sterculate, but the transformation was of such short duration that it was not possible to accurately determine the temperature at which it occurred. Capillary melting points and data obtained with the differential scanning calorimeter are listed in Table I. On DSC studies methyl malvalate and methyl sterculate showed polymorphic transformations; for methyl sterculate, the trans-

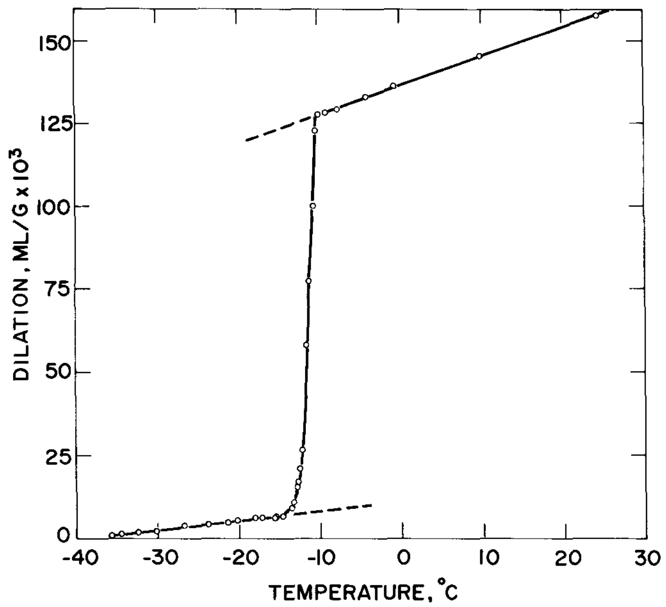

FIG. 3. Dilatometric curve for heating cycle of methyl sterculate.

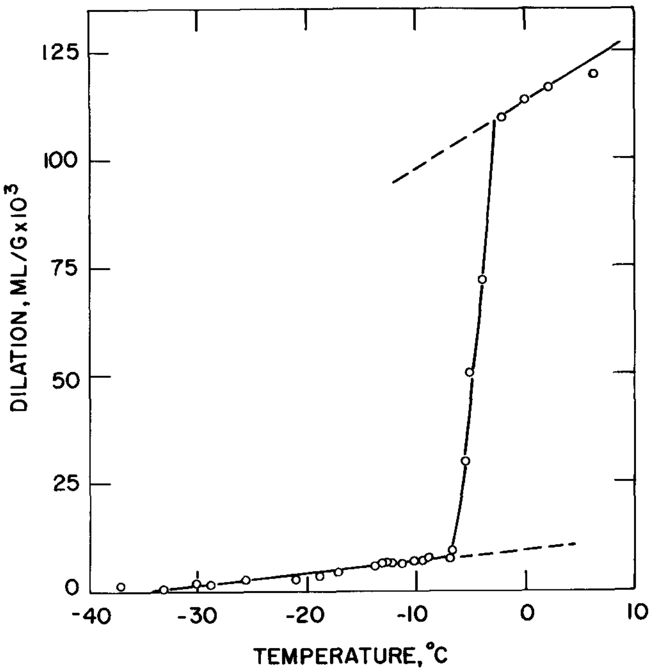

FIG. 4. Dilatometric curve for heating cycle of methyl dihydrosterculate.

formation occurred too close to the melting point to be measured accurately. Both transitions were monotropic and could be made to disappear by bringing the samples up to their melting points, then lowering the temperature and repeating the heating cycles. Neither methyl dihydromalvalate nor methyl dihydrosterculate showed any polymorphic transformations. Methyl oleate was also investigated; like methyl malvalate and methyl sterculate, it showed a monotropic polymorphic transformation.

Figure 1 shows the dilatometric heating curve for methyl malvalate. The lower, slanting line represents expansion of the solid as the temperature was increased. The methyl malvalate was in a lower melting polymorphic form and, at ca. -33 to -26 C converted to the higher melting polymorph, after which the methyl malvalate completely melted at ca. -21.8 C. A reliable coefficient of expansion could not be calculated for methyl malvalate. The vertical portion of the curve represents melting dilation. Although the melting point is not sharp, this does not indicate an impure compound. Previous investigators (13) have reported polymorphic transformations during melting of unsaturated compounds. The upper, slanting line represents dilation of the melt from which the coefficient of expansion of the liquid state was calculated.

Figures 2, 3, and 4 show the dilatometric heating curves for methyl dihydromalvalate, methyl sterculate, and methyl dihydrosterculate, respectively.

The expansivities, melting dilations, and dilatometric melting points of the four methyl esters and, for comparison, those of methyl palmitate, methyl stearate, and methyl oleate, as determined by Craig (14), are recorded in Table II.

The coefficient of expansion for the solid methyl sterculate and methyl dihydrosterculate are within the range of those for methyl palmitate and methyl stearate, but the coefficient of expansion for the methyl dihydromalvalates is about twice the amount. We know of no theoretical reason why the difference of one -CH_2- group in the hydrocarbon chains of dihydromalvalate and dihydrosterculate should result in such a large difference in the coefficients of expansion of their solid states. The coefficient of expansion for methyl malvalate and methyl sterculate compares closely to that for methyl oleate. However, the coefficient of expansion for methyl dihydromalvalate and methyl dihydrosterculate is considerably larger than that for methyl palmitate, stearate, or arachidate as well as that for triglycerides.

The melting dilations of methyl sterculate and methyl dihydrosterculate are comparable to that of methyl oleate (14). Melting dilations for methyl malvalate and methyl dihydromalvalate are significantly lower. Apparently the molecular arrangement for cyclopropenes and cyclopropanes in the solid state is not nearly so compact as that for methyl palmitate and methyl stearate.

The dilatometric melting points of methyl dihydro-

TABLE II

Dilatometric Properties of Methyl Esters

			Solid		Liquid	
Methyl ester	Dilatometric melting point, C	Melting dilation, ml/g	Temperature interval, C	Coefficient of expansion, μl/(g)(C)	Temperature interval, C	Coefficient of expansion, μl/(g)(C)
Methyl malvalate	−21.6	0.0922	–	–	−21.6 to −10.6	0.91
Methyl dihydromalvalate	−2.2	0.0948	−29.0 to −7.0	0.65	−2.2 to +8.0	1.18
Methyl sterculate	−10.5	0.1192	−36.8 to −14.6	0.27	−10.4 to +24.0	0.90
Methyl dihydrosterculate	−2.8	0.1007	−33.2 to −7.0	0.26	−2.8 to +2.0	1.42
Methyl palmitate[a]	30.1	0.1698	−38 to −20	0.25	–	0.99
Methyl stearate[a]	39.1	0.1726	−38 to −20	0.22	–	1.00
Methyl oleate[a]	−19.8	0.1187	−38 to −26	0.36	–	0.90

[a] See reference 14.

malvalate and methyl dihydrosterculate exhibited the typical relationship of saturated fatty acids and their derivatives. Melting points of the even-numbered carbon long-chain fatty acids differ by less than a degree from their next higher, odd-numbered homolog (16). We can assume, therefore, that the methyl dihydromalvalate behaves like a normal, even-numbered carbon fatty acid and the methyl dihydrosterculate as an odd-numbered carbon fatty acid. This is not true for methyl malvalate and methyl sterculate, since the 11 degree difference in their melting points is of the magnitude of the difference between two even-numbered unsaturated fatty acids in the homolog series. At present, we have no data on the melting points of unsaturated, odd-numbered carbon, long chain fatty acids.

REFERENCES

1. Phelps, R.A., F.S. Shenstone, A.R. Kemmerer, and R.J. Evans, Poultry Sci. 44:358 (1965).
2. Carter, F.L., and V.L. Frampton, Chem. Rev. 64:497 (1964).
3. Kircher, H.W., and B.W. Heywang, Poultry Sci. 45:1432 (1966).
4. Wilson, T.L., C.R. Smith, Jr., and K.L. Mikolajzcak, JAOCS 38:696 (1961).
5. Shone, G.G., Proc. Nutrition Society 25:37 (1966).
6. Wood, R., and R. Reiser, JAOCS 42:315 (1965).
7. Butterfield, R.O., H.J. Dutton, and C.R. Scholefield, Anal. Chem. 38:86 (1966).
8. Feuge, R.O., Z. Zarins, J.L. White, and R. Holmes, JAOCS 4:185 (1967).
9. De Vries, B., Ibid. 40:184 (1963).
10. Nordby, H.E., B.W. Heywang, H.W. Kircher, and A.R. Kemmerer, Ibid. 39:183 (1962).
11. Bailey, A.E., and E.A. Kraemer, Oil & Soap 21:251 (1944).
12. Bailey, A.E., and W.S. Singleton, Ibid. 22:265 (1945).
13. Singleton, W.S., and T.L. Ward, JAOCS 30:592 (1953).
14. Craig, B.M., Ibid. 32:459 (1955).
15. Bailey, A.E., "Melting and Solidification of Fats," Interscience Publishers, Inc., New York, NY 1950, pp. 000-000.

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