

✂ Solubilities of Six Cottonseed Oil Fatty Acid Methyl Esters in Methanol

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ABSTRACT

Solubilities of six cottonseed oil fatty acid methyl esters in methanol have been determined. The esters were: methyl oleate, methyl linoleate, methyl malvalate, methyl dihydromalvalate, methyl sterculate and methyl dihydrosterculate. The solubility/temperature data are presented in graphical and tabular form.

INTRODUCTION

Solubility data of fatty acid methyl esters in organic solvents are useful for fractional crystallizations. Linoleic and oleic acids are the two major unsaturated constituents of cottonseed oil triglycerides. Cottonseed oil triglycerides also contain the physiologically active cyclopropanoid fatty acids malvalic and sterculic (1-4). Dihydromalvalic and dihydrosterculic acids are their biological precursors (5), as well as their derivatives formed on partial hydrogenation (6). Analyses in our laboratory indicate that oils from domestic cottonseed usually contain less than 1% cyclopropanoids calculated as malvalic acid (7). The cyclopropanoid acids react readily with each other, making it preferable to work with them in the form of methyl esters.

These data were obtained in connection with a proposed method for the isolation and purification of the cyclopropanoid and cyclopropanoid fatty acids from cottonseed oil by low-temperature crystallization from methanol.

MATERIALS AND METHODS

Preparation and Purification of Methyl Esters

Pure methyl oleate was obtained from commercial grade methyl oleate by five successive low-temperature crystallizations from methanol. At this time, it still contained ca. 1% methyl palmitate which was removed by passing it through a silver nitrate-silicic acid column, on which the palmitate eluted before the methyl oleate. Gas liquid chromatography (GLC) did not detect any impurities in the purified methyl oleate. Pure methyl linoleate was prepared from analytical grade methyl linoleate by six successive fractional crystallizations in methanol; this methyl linoleate showed no detectable impurities when analyzed by GLC.

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Methyl sterculate was prepared by a method described previously (6). The purity of the methyl sterculate was 99.6%, determined by hydrogen bromide (HBr) titration in toluene (8).

Methyl malvalate, methyl dihydromalvalate and methyl dihydrosterculate were prepared by the methods described by White et al. (9). The final purity of the methyl malvalate was 99.4% as indicated by HBr titration in toluene. The methyl dihydromalvalate and methyl dihydrosterculate, when analyzed by GLC, were 98.9% and 100% pure, respectively.

Method for Solubility Determinations

The solubilities were determined by the thermostatic sealed tube method of Magne and Skau (10) in a constant-temperature/low-temperature alcohol bath. Duplicate samples of ca. 5 g of accurately weighed solution were sealed in vials. A freshly opened bottle of anhydrous reagent grade methanol was used each time. The solubility temperature was taken as the highest temperature at which the Tyndall effect could be observed for at least 2 hr. This temperature was recorded as the equilibrium point for the particular solute/solvent ratio used. Several such determinations with different solute/solvent ratios yielded the necessary equilibrium point temperatures to define the solubility curve in the desired concentration range for each of the six esters.

RESULTS AND DISCUSSION

Methanol (a polar solvent) dissolves strongly polar methyl esters more readily than the less polar ones. Melting points, heats of fusion and chain length also influence the solubilities of compounds. Skau et al. (11), demonstrated the difference in solubility characteristics between even and odd carbon atom members of a homologous series of fatty acids. Separate isotherms (due to difference of slopes) were obtained for odd- and even-numbered fatty acid methyl esters when logarithm of solubility was plotted against number of carbon atoms.

Figure 1 shows the solubility curves of the six methyl esters. The solubilities are expressed in terms of mole fractions and plotted on semilogarithmic coordinates against

TABLE I

Solubilities of Fatty Acid Methyl Esters in Methanol

Ester	g/100g Solvent	Temperature (C)	Ester	g/100g Solvent	Temperature (C)
Methyl oleate	4.90	-22.5	Methyl linoleate	6.73	-40.4
	2.84	-28.0		4.97	-41.6
	1.38	-33.5		3.78	-43.3
	0.92	-36.6		1.93	-48.0
	0.50	-39.9		1.01	-54.1
Methyl malvalate	5.63	-26.8	Methyl dihydromalvalate	5.54	- 7.7
	3.49	-29.6		4.21	-11.6
	1.62	-35.9		1.48	-20.4
	0.79	-41.7		0.78	-25.3
Methyl sterculate	4.84	-17.8	Methyl dihydrosterculate	4.50	- 8.7
	3.25	-19.7		2.89	-12.0
	1.51	-25.5		1.40	-17.6
	0.54	-34.7		0.50	-26.6

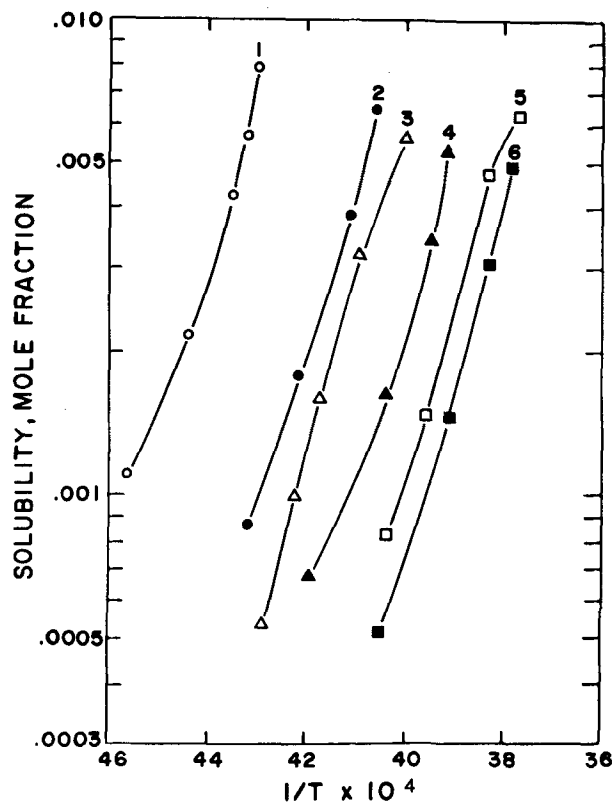


FIG. 1. Solubility curves for the methyl esters in methanol: (1) methyl linoleate; (2) methyl malvalate; (3) methyl oleate; (4) methyl sterculate; (5) methyl dihydromalvalate; (6) methyl dihydrosterculate.

the reciprocal of absolute temperature. The curves are approximately parallel, as might be expected from the related compounds. The solubility changed rapidly with temperature.

Table I lists the equilibrium point temperatures for each of the six esters at various solvent ratios. Within the concentration range covered, the escaping tendency of the solute is primarily influenced by the solvent molecules.

Table II lists the melting points, heats and entropies of fusion of five of the methyl esters. These data were selected from data reported by White et al. (9). There is good correlation between the melting points and solubilities. The

TABLE II

Melting Points, Heats and Entropies of Fusion

Ester	Melting point (C)	ΔH (cal/g)	ΔH (kcal/mole)	$\Delta H/T$
Methyl oleate	-19.8	35.4	10.5	0.039
Methyl malvalate	-22.4	33.0	9.7	0.039
Methyl dihydromalvalate	-3.4	28.4	8.4	0.031
Methyl sterculate	-14.3	36.1	11.2	0.043
Methyl dihydrosterculate	-3.6	32.4	10.1	0.037

effect of chain length is seen in the solubilities of methyl dihydromalvalate (melting point mp -3.4 C) and methyl dihydrosterculate (mp -3.6 C), with the former slightly more soluble than the latter. For all the others, solubilities are in order of decreasing melting points. No correlation exists between the heats of fusion and the solubilities. This could be due to the low solute/solvent ratios used in these experiments. Increasing the solute/solvent ratios much above the level used in these experiments would have caused the solute to separate out in a saturated liquid phase.

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