Alkyl Alpha-Acyloxyacetates and Propionates From Soaps and Alpha-Halogeno Esters[1]

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BUTYL and tetrahydrofurfuryl α-acyloxypropionates were prepared by Fein and Fisher (3) by the acylation of n-butyl and tetrahydrofurfuryl lactate with the acid chlorides of acetic, propionic, n-heptanoic, n-nonanoic, and lauric acids. The esters had plasticizing properties, and higher homologs have now been prepared for evaluation as plasticizers. Analogous compounds derived from glycolic rather than lactic acid are also included for comparison.

The present paper describes the synthesis and properties of 26 methyl, ethyl, and n-butyl α-acyloxyacetates and propionates, in which the acyl group is derived from a fat acid. The reactions are given by the equations:

a) Acid chloride method of synthesis

$$RCOCl + R'CHOHCO_2R'' \longrightarrow RCO_2CHR'CO_2R'' + HCl$$

b) Soap method of synthesis

$$RCO_2M + R'CHXCO_2R'' \longrightarrow RCO_2CHR'CO_2R'' + MX$$

in which R is derivable from a fat acid, R′ is H (glycolate series) or CH_3 (lactate series), R″ is CH_3,C_2H_5 or n-C_4H_9, M is Na or K, and X is Cl or Br.

The compounds may be named as derivatives of glycolic or lactic acid and the fat acid, for example, ethyl lactate palmitate, or more systematically, ethyl α-hexadecanoyloxypropionate.

High yields of the fat acid homologs were difficult to obtain by the use of acid chlorides (equation A). Acid chlorides of the fat acids are almost invariably contaminated with an appreciable quantity of the fat acid, which is carried over to the final ester and is difficult to remove without considerable sacrifice in yield.

Glycidyl and glycolate esters have been made from dry soaps and halogen compounds by Kester, Gaiser, and Lazar (5) and by Strain, Plati, and Warren (8), respectively. The synthesis of fat acid esters of alkyl glycolates and lactates (equation B) from soaps has been more satisfactory than that from the acid chlorides, particularly with regard to yield. For example, the yields of butyl lactate myristate, butyl lactate oleate, and butyl lactate stearate, were 60, 23, and 45%, respectively, by the acid chloride method (Table III) whereas yields of 82 and 79% were obtained for butyl lactate oleate and butyl lactate stearate by the soap method of synthesis.

Libermann (6) has reported yields of nearly 95% in making ethyl α-chloropropionate from ethyl lactate, with thionyl chloride and a small amount of pyridine as a catalyst. The two methods therefore may each have an alkyl lactate as the starting material.

Table I shows the methods of purifying the fat acids.

Acid chlorides were prepared by warming the fat acid with 10 equivalents of thionyl chloride at 60° for an hour and a half. The thionyl chloride had been freshly distilled from quinoline and then from linseed oil (4). Excess thionyl chloride was removed under reduced pressure, followed by the distillation of two portions of benzene from the residue under reduced pressure. The impure acid chloride contained 15-20% fat acid as determined by conversion to the anilide (1), and purity was not improved by vacuum distillation. The acid chloride was then caused to react with n-butyl lactate by the method of Fein and Fisher (3). The product was washed with water, hydrochloric acid, and sodium bicarbonate, and finally vacuum distilled.

Potassium soaps of the n-saturated acids were made by neutralization of the fat acids in hot alcoholic solution and crystallization. Since the sodium soaps were not crystallizable, the neutral aqueous or alcoholic solution was evaporated to dryness. Dryness of all reactants is essential to a high yield of pure product. Soaps containing moisture were dried in a vacuum oven immediately prior to use or dried azeotropically in xylene solution. In most cases the soaps of undecylenic, oleic, and phenylstearic acid were not isolated. The aqueous alcoholic solution was distilled to remove most of the alcohol and water, and the remainder was removed by adding xylene and distilling azeotropically.

α-Halogeno esters were either of a good technical grade or made by esterification of the corresponding acid (2, 7). Complete removal of all unesterified halogeno acid was essential.

The esters were prepared from the soaps by refluxing the dry soap and an excess of halogeno ester while stirring vigorously for 10 to 17 hours. Enough xylene was present to make the reaction mixture stirrable and keep the reflux temperature between 150 and 170°. The following example illustrates the preparation of an ester from a soap. A mixture containing 187.0 g. (0.635 mole) of potassium palmitate, 157.6 g. (0.870 mole) of ethyl α-bromopropionate, and 100 ml. of xylene was refluxed for 13 hours at 165 to 170°. The product was washed with water to remove inorganic compounds, the solvent was removed by distillation at reduced pressure, and the residual oil was vacuum distilled to give 214.6 g. (94% yield) of a colorless liquid, which distilled at 161-3° at .02 mm.

Tables II and III summarize the preparation, yield, and properties of fat acid esters from alkyl glycolates and alkyl lactates, respectively. The principal impurity in each product was a small amount of the corresponding free fat acid. An acid number of two represents about 1% of stearic acid. Acid numbers for the most part ranged from one to five.

Potassium rather than sodium soaps were preferred because the potassium soaps were more readily obtained in a dry crystalline state, gave less difficulty in gel formation during the reaction with the halogeno ester, and appeared to be generally more reactive than the sodium soap. Bromine in alkyl α-bromopropionates appears to be generally more reactive than chlorine in alkyl α-chloropropionates. The reac-

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[1] Presented at fall meeting, American Oil Chemists' Society, Oct. 31-Nov. 2, 1949, Chicago, Ill.

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TABLE I

Purification of Fat Acids

Fat Acid	Source	Purification	Neutral Equivalent		M.P. °C.
			Found	Theoretical	
Lauric	Armour Neofat	One crystallization from acetone at —40°C., 1 vacuum distillation	200.7	200.2	43.3-44.3
Myristic	Eastman Kodak	None	231.5	228.3	51.2-52.3
Palmitic	Armour Neofat	Two crystallizations from acetone at 0°C.	259.9	256.3	59.8-61.2
Oleic [a]	Olive oil	Two crystallizations from acetone at —60°C., one crystallization at —20°C., two vacuum distillations	282.0	282.3	....
Stearic	Armour Neofat	Two crystallizations from acetone at 0°C.	282.4	284.3	68.8-70.0

[a] I. V. of purified oleic acid 89.3 (theo. 89.9).

tion conditions of time and temperature were not identical however and do not permit a direct comparison of the relative reactivity of the soaps or of the halogen compounds.

The viscosity values in Tables II and III indicate that, in general, viscosity increases with increasing molecular weight, regardless of what portion of the molecule is increased, but there are several exceptions. The viscosity of the lactates is usually slightly less than that of the corresponding glycolates. In each table the viscosity of the methyl esters is usually greater than that of corresponding ethyl esters. The viscosity of the oleates is in some cases less than that of the palmitates. There are fewer exceptions to an increase in viscosity index with increasing molecular weight. Phenylstearic acid from the Friedel and Crafts' reaction is a mixture of isomeric acids, and esters derived from it show abnormal viscosity behavior.

Freezing points are also compared in Tables II and III. Freezing points increase with greater molecular weight when the number of carbon atoms of the n-saturated fat acid chain increase, but as additional hydrocarbon is added near the carboxyl end in going from glycolate to lactate or from methyl to ethyl to butyl, freezing points are lowered. This may be a result of less ease of crystal packing as greater amounts of hydrocarbon are placed around the polar end, but

TABLE II

FAT ACID ESTERS OF ALKYL GLYCOLATES

$RCO_2CH_2CO_2R''$

COMPOUND	MOLE RATIO $ClCH_2CO_2R''$ ÷ K SOAP	% YIELD	DISTN. RANGE, °C	f.p., °C	SAPON EQUIV.		ACID NO.	% C [a]		% H [a]		n^{20}_D	d^{20}_4	MOLECULAR REFRACTIVITY		VISCOSITY CST. 100° F	V.I.[b]
					FOUND	THEORY		FOUND	THEORY	FOUND	THEORY			FOUND	THEORY		
							METHYL GLYCOLATE SERIES										
PALMITATE	3.29	76	155-6$_{.03}$	32.5	165.5	164.2	5.9	69.75	69.47	11.24	11.05	--	--	--	--	10.842	96.5
OLEATE	2.19	83	164-8$_{.02}$	0	177.5	177.3	2.4	71.32	71.14	10.93	10.81	1.4553	.9392	102.49	102.02	10.469	115.1
STEARATE	1.97	81	162-9$_{.03}$	43	179.6	178.3	4.0	70.71	70.70	11.25	11.30	--	--	--	--	--	--
							ETHYL GLYCOLATE SERIES										
UNDECYLENATE	1.97[c]	68	111-8$_{.06}$	-22	136.3	135.2	13.9	66.55	66.63	9.81	9.69	1.4444	.9646	74.46	74.30	4.662	--
LAURATE	1.14	59	143-9$_{.03}$	11.2	143.3	143.2	5.1	67.19	67.09	10.64	10.56	1.4378	.9466	79.39	79.40	6.176	--
MYRISTATE	1.32	90	149-54$_{.4}$	22.6	158.1	157.2	2.4	68.77	68.75	11.12	10.90	1.4412	.9348	88.86	88.63	7.856	88.1
PALMITATE	1.39	84	153-4$_{.02}$	29.6	172.8	171.3	3.2	70.06	70.07	11.28	11.18	1.4444	.9294	97.97	97.87	10.045	111.9
OLEATE	1.54	75	182-92$_{.3}$	--	184.5	184.3	2.4	71.68	71.70	10.85	10.94	1.4541	.9322	107.08	106.64	11.104	126.0
STEARATE	1.59	78	169-73$_{.02}$	40.1	185.8	185.3	1.5	71.52	71.29	11.06	10.88	--	--	--	--	12.628	127.5
PHENYL-[d] STEARATE	2.71[c]	68	223-30$_{.1}$	--	220.2	223.3	0.9	75.46	75.29	10.44	10.38	1.4810	.9554	133.05	131.21	36.114	110.1
							BUTYL GLYCOLATE SERIES										
PALMITATE	1.45	85	176-8$_{.04}$	23	184.5	185.3	3.0	71.32	71.29	11.49	11.49	1.4436[e]	.9177[e]	107.18	107.41	11.856	132.8
OLEATE	1.54	77	184-7$_{.03}$	-23.4	197.7	198.3	1.0	72.33	72.68	11.37	11.18	1.4541	.9237	116.29	115.87	11.272	149.6
STEARATE	2.01	93	192-7$_{.03}$	38	200.1	199.3	3.7	72.38	72.31	11.65	11.63	--	--	--	--	14.105	141.5

a. Analyses by Jane Dixon and C. L. Ogg of this laboratory.

b. Viscosity index, Standard Oil Development Co., *CIRC. 30.50*, Oct. 24, 1938.

c. Na soap

d. Phenylstearic acid by the Friedel and Crafts reaction.

e. Values at 25° C.

TABLE III

FAT ACID ESTERS OF ALKYL LACTATES

$RCO_2CH(CH_3)CO_2R''$

COMPOUND	MOLE RATIO $CH_3CHBrCO_2R''$ ÷ K SOAP	% YIELD	DISTN. RANGE, °C	f.p., °C	SAPON EQUIV.		ACID NO.	% C [a]		% H [a]		n^{20}_D	d^{20}_4	MOLECULAR REFRACTIVITY		VISCOSITY CST. 100° F	V.I.[b]
					FOUND	THEORY		FOUND	THEORY	FOUND	THEORY			FOUND	THEORY		
							METHYL LACTATE SERIES										
MYRISTATE	1.06	89	135-42$_{.03}$	11.4	160.2	157.2	3.9	68.58	68.75	10.98	10.89	1.4407	.9317	89.09	88.64	7.850	85.6
PALMITATE	1.3	73	153-6$_{.03}$	22	172.0	171.3	2.8	70.17	70.13	11.34	11.18	1.4434	.9299	97.75	97.87	10.581	98.5
OLEATE	1.07	67	165-9$_{.04}$	--	184.0	184.4	2.2	71.97	71.69	11.01	10.94	1.4526	.9281	107.24	106.64	10.193	117.1
STEARATE	1.63	76	166-70$_{.03}$	31.5	185.8	185.3	4.0	71.24	71.30	11.40	11.42	--	--	--	--	13.324	111.4
							ETHYL LACTATE SERIES										
MYRISTATE	1.77	83	127-9$_{.06}$	22	163.0	164.2	1.6	69.76	69.47	11.30	11.05	1.4385	.9219	93.60	93.25	7.827	89.7
PALMITATE	1.37	95	158-63$_{.02}$	13	178.6	178.3	2.5	70.81	70.74	11.37	11.31	1.4432	.9274	102.70	102.49	9.858	107.4
OLEATE	1.95	79	174-6$_{.03}$	--	192.0	191.3	3.6	71.87	72.20	11.10	11.07	1.4510	.9207	111.88	111.25	10.532	129.2
STEARATE	1.96	82	177-82$_{.1}$	25.5	190.0	192.3	3.2	72.23	71.98	11.10	11.53	1.4424	.9227	110.36	111.72	12.353	128.7
PHENYL- [c] STEARATE	2.2	68	197-213$_{.05}$	--	231.1	230.3	3.0	75.50	75.60	10.56	10.50	1.4775	.9523	136.76	135.83	33.29	117.1
							BUTYL LACTATE SERIES										
MYRISTATE	ACID CHLORIDE METHOD	60	155-6$_{.06}$	--	177.7	178.3	1.1	70.96	70.73	11.27	11.31	1.4410	.9153	102.85	102.49	8.280	119.4
PALMITATE	1.4[d]	76	177-8$_{.10}$	5.0	192.6	192.3	2.0	71.58	71.82	11.38	11.51	1.4446	.9015	113.45	111.72	10.892	126.6
OLEATE	ACID CHLORIDE METHOD	23	170-2$_{.06}$	--	208.6	205.3	6.0	--	--	--	--	1.4512[e]	.9080[e]	121.90	120.49	--	--
OLEATE	1.29[d]	82	195-8$_{.4}$	--	203.7	205.3	5.0	73.01	73.12	11.33	11.29	1.4524	.9139	121.30	120.49	11.458	140.0
STEARATE	ACID CHLORIDE METHOD	45	174-86$_{.02}$	20-16.5	204.5	206.2	1.7	72.68	72.77	11.70	11.72	1.4456	.9113	120.92	120.96	13.334	140.7
STEARATE	1.64[d]	79	192-8$_{.12}$	16.1	204.4	206.2	2.5	72.96	72.77	11.71	11.72	1.4456	.9116	120.61	120.96	13.454	141.8

a. Analyses by Jane Dixon and C. L. Ogg of this laboratory.

b. Viscosity index, Standard Oil Development Co., *CIRC. 30.50*, Oct. 24, 1938.

c. Phenylstearic acid by the Friedel and Crafts reaction.

d. $CH_3CHClCO_2R''$

e. Values at 25° C.

these compounds are not sufficiently pure to serve as a basis for definite conclusions.

Preliminary tests showed that most of these compounds are compatible with ethyl cellulose and that some of the lower molecular weight members of the series are compatible with polyvinyl chloride. The alkyl α-acyloxyacetates and propionates derived from fat acids will be more completely evaluated as plasticizers.

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[Received November 11, 1949]