

LAURATES OF LACTIC ACID ESTERS

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Because of their potential importance as plasticizers (1) and synthetic lubricants, the laurates of several lactic esters were prepared and studied. The preparation and physical properties of these lactate laurates $[H(CH_2)_{11}COOCH(CH_3)COOR]$ are described in this paper.

The lactate laurates (Table I) were made conveniently in two steps: (a) the appropriate lactic ester was prepared by esterification of lactic acid or by the alcoholysis of methyl lactate (2-4), and (b) the lactic ester was then acylated with lauroyl chloride (5).

At room temperature, the lactate laurates were liquids having little or no color. Their boiling points at different pressures are given in Figures 1 and 2. For purposes of comparison, the boiling points of *n*-butyl, tetrahydrofurfuryl, and benzyl laurate were determined (Fig. 2). Comparison of the boiling points of the *n*-butyl, tetrahydrofurfuryl, and benzyl laurates at 1 and 4 mm. with the boiling points of the corresponding lactate laurates shows that the effect of the lactate segment in these compounds is to raise the boiling point approximately 30°.

The boiling points of the lactate laurates $[H(CH_2)_{11}COOCH(CH_3)COOR]$ at 1 and 4 mm. are roughly proportional to the normal boiling points of ROH (Fig. 3). These relationships, which are useful for predicting the boiling points of other lactate laurates, are expressed by the following equations:

$$y(1 \text{ mm.}) = 0.408 X + 108$$

$$y(4 \text{ mm.}) = 0.408 X + 135$$

where y = b. p. of lactate laurate at 1 or 4 mm., and X = b. p. of ROH at 760 mm. Boiling points calculated by these equations agree moderately well (3° or better) with the experimental boiling points in Figures 1 and 2.

The lactate laurates have boiling points between those of *n*-butyl phthalate and *n*-octyl phthalate, two widely used commercial plasticizers (Figs. 1 and 2). Results obtained in an evaluation of the lactate laurates as plasticizers for vinyl chloride resins will be published elsewhere.

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TABLE I
 PROPERTIES OF LACTATE LAURATES $[\text{H}(\text{CH}_2)_n\text{COOCH}(\text{CH}_3)\text{COOR}]$

R	BOILING POINT		n_D^{20}	d_4^{20}	MOLECULAR REFRACTION		ESTER EQUIVALENT		C		H		VISCOSITY, 20°	
	°C.	mm.			Calc'd	Found	Calc'd	Found	Calc'd	Found	Calc'd	Found	Centi-stokes	Centi-poise
<i>sec</i> -Butyl.....	155	1.3	1.4360	0.9181	93.25	93.56	164.2	164.3	69.47	69.55	11.05	11.11	11.88	10.90
Isobutyl.....	153	1.0	1.4372	.9199	93.25	93.58	164.2	165.0	69.47	69.30	11.05	11.14	12.22	11.24
2-Ethylhexyl.....	193	2.0	1.4441	.9122	111.72	112.00	192.3	189.0	71.83	71.86	11.53	11.61	17.85	16.27
2-Ethoxyethyl.....	170	1.3	1.4399	.9510	94.89	95.45	172.2	170.2	66.24	66.89	10.53	10.63	14.01	13.32
2-Butoxyethyl.....	204	3.2	1.4412	.9411	104.13	104.57	186.3	185.0	67.70	68.00	10.82	10.78	15.28	14.38
2-(2-Ethoxyethoxy)ethyl.....	180	0.7	1.4450	.9716	105.77	106.43	194.3	194.0	64.91	64.81	10.38	10.67	25.66	24.93
2-(2-Butoxyethoxy)ethyl.....	205	1.2	1.4441	.9570	115.01	115.60	208.3	207.5	66.31	66.23	10.65	10.60	20.40	19.52
Benzyl.....	206	2.3	1.4774	.9865	103.50	103.90	181.3	181.2	72.89	72.90	9.45	9.56	22.16	21.86
Cyclohexyl.....	184	1.5	1.4530	.9514	100.29	100.71	177.3	177.0	71.14	71.40	10.80	11.00	26.56	25.27
Methyl isobutyl carbonyl.....	168	1.5	1.4373	.9093	102.49	102.79	178.3	178.1	70.74	70.70 ^a	—	—	14.69	13.35
<i>n</i> -Butyl laurate ^b	145	3.0	1.4351	.8693	77.74	77.88	256.4	254.7	74.94	75.14	12.58	12.64	5.27	4.53
Benzyl laurate ^b	174	2.0	1.4820	.9375	88.00	88.31	230.4	232.1	78.57	78.55	10.41	10.37	8.90	8.34
Tetrahydrofurfuryl laurate ^b	154	1.2	1.4519	.9361	81.80	81.94	284.4	284.9	71.78	71.95	11.34	11.30	11.19	10.48

^a Carbon determined by wet oxidation. ^b Properties of the simple laurates are given for comparison.

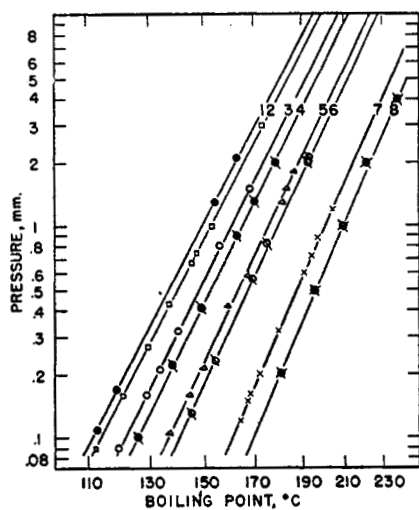


FIG. 1

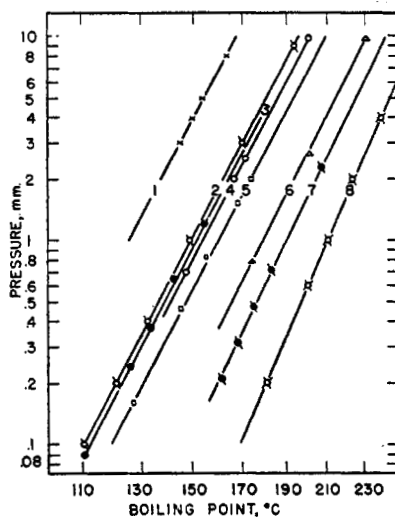


FIG. 2

FIG. 1. BOILING POINTS OF LACTATE LAURATES

1. *sec*-Butyl lactate laurate. 2. Isobutyl lactate laurate. 3. Methyl isobutyl carbinyl lactate laurate. 4. 2-Ethoxyethyl lactate laurate. 5. Cyclohexyl lactate laurate. 6. Ethylhexyl lactate laurate. 7. 2-(2-Butoxyethoxy)ethyl lactate laurate. 8. *n*-Octyl phthalate.

FIG. 2. BOILING POINTS OF LAURATES AND LACTATE LAURATES

1. *n*-Butyl laurate. 2. *n*-Butyl phthalate. 3. Tetrahydrofurfuryl laurate. 4. *n*-Butyl lactate laurate. 5. Benzyl laurate. 6. Tetrahydrofurfuryl lactate laurate. 7. Benzyl lactate laurate. 8. *n*-Octyl phthalate.

BOILING POINT OF ROH AT 760MM., °C.

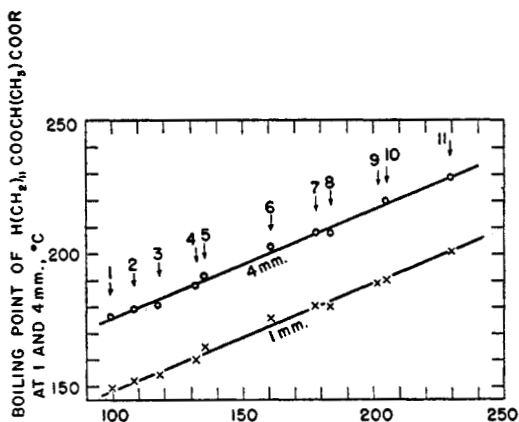


FIG. 3. RELATION BETWEEN BOILING POINTS OF ROH AND THOSE OF THE CORRESPONDING $\text{H}(\text{CH}_2)_{11}\text{COOCH}(\text{CH}_3)\text{COOR}$

R = 1, *sec*-Butyl; 2, Isobutyl; 3, *n*-Butyl; 4, Methyl isobutyl carbinyl; 5, 2-Ethoxyethyl; 6, Cyclohexyl; 7, Tetrahydrofurfuryl; 8, 2-Ethylhexyl; 9, 2-(2-Ethoxyethoxy)ethyl; 10, Benzyl; 11, 2-(2-Butoxyethoxy)ethyl.

Welsh, of the Analytical and Physical Chemistry Division of this Laboratory, for analytical data.

EXPERIMENTAL

Lactic esters. The 2-ethoxyethyl, 2-butoxyethyl, and 2-(2-butoxyethoxy)ethyl lactates were prepared by previously described methods (2, 3). Benzyl lactate was prepared by alcoholysis of methyl lactate: A mixture of 7 moles of benzyl alcohol, 3 moles of methyl lactate, and 6 g. of aluminum isopropoxide was refluxed under a 2-foot Vigreux column, through which methanol was removed as it was formed. When the reaction was complete, the excess benzyl alcohol and then the benzyl lactate were distilled. A center cut of benzyl lactate distilled at $114^{\circ}/3$ mm., and the index of refraction at 20° was 1.5142. This compound has been reported to boil at $134^{\circ}/4$ mm. (6) and $103\text{--}104^{\circ}/1.3$ mm. (7). *sec*-Butyl lactate, 2-ethylhexyl lactate, and methyl isobutyl carbonyl lactate were prepared by alcoholysis of methyl lactate. In each case, one mole of methyl lactate was reacted with 4 moles of the alcohol, 2 to 5 g. of *p*-toluenesulfonic acid being used as the catalyst. The procedure was that described above, except that the catalyst was neutralized before distillation. The physical constants observed for these three lactates were: *sec*-Butyl (8), b.p. $60.5^{\circ}/8$ mm., n_D^{20} 1.4160, d_4^{20} 0.9729; 2-ethylhexyl (8), b.p. $97\text{--}98^{\circ}/3.0$ mm., n_D^{20} 1.4357, d_4^{20} 0.9399; methyl isobutyl carbonyl, b.p. $52^{\circ}/1$ mm., $59.5^{\circ}/1.8$ mm., n_D^{20} 1.4220. 2-(2-Ethoxyethoxy)ethyl lactate could not be prepared readily as a pure derivative² because of the presence of glycol in the alcohol (9). The crude ethoxyethoxyethyl lactate contained a considerable amount of glycol monolactate, which was separated later as the dilaurate (see below).

Lactate laurates. These were prepared, as described previously (5), by treating the lactic esters with lauroyl chloride in the presence of dry pyridine. Commercial lauroyl chloride was redistilled through a 2-foot Vigreux column; the fraction boiling over the range $137\text{--}139^{\circ}/11$ mm., n_D^{20} 1.4452, was used in most acylations. Reagent grade (Eastman White Label) lauroyl chloride was used in several preparations. Ether, 200 ml. per mole of lactic ester, was used as a diluent. The yields ranged from 64–92% of the theoretical. These yields were influenced by losses due to emulsions, sometimes persistent, that formed during washing prior to distillation.

In the case of 2-(2-ethoxyethoxy)ethyl lactate laurate, a high-boiling fraction was isolated, which solidified when cooled. This material, recrystallized three times from ethanol, melted at $44.5\text{--}45^{\circ}$. From the analysis, this solid appears to be *glycol monolactate dilaurate*.

Anal. Calc'd: C, 69.84; H, 10.91; Ester equivalent, 166.24.

Found: C, 70.51; H, 10.43; Ester equivalent, 166.0.

These analytical values are quite different from those of glycol dilaurate, 2-(2-ethoxyethoxy)ethyl laurate, or glycol dilactate dilaurate, which might have been formed.

Benzyl and tetrahydrofurfuryl laurates. These esters were made in 95% yield by the reaction of 2 moles of the alcohol with one mole of lauric acid,³ with 200 ml. of toluene as entrainer, and 2 g. of *p*-toluenesulfonic acid (monohydrate) as catalyst. This mixture was heated in a flask fitted with a 2-foot Vigreux type column topped by a water-cooled Barrett moisture (modified Dean and Stark) trap. In each case, 2 hours were required to complete the esterification (18 ml. of water collected in trap). After the flask had cooled, 1 g. of sodium acetate (anhydrous) was added to neutralize the catalyst. The entrainer was distilled under a water-pump vacuum, and then the excess alcohol and the desired product were distilled under higher vacuum (oil pump). A commercial sample of *n*-butyl laurate was redistilled prior to determination of its physical constants.

Data for the boiling-point curves were obtained by distillation through a modified alembic still [an improved tensimeter-still (10)]. Other physical data were determined with carefully distilled, narrow-boiling fractions, as described previously (5). The boiling points

² Since this work was completed, a pure sample of 2-(2-ethoxyethoxy)ethanol was obtained, and the pure lactate was prepared by reaction with methyl lactate. Physical constants and analytical data for this lactate are: B.p. $117^{\circ}/3.0$ mm.; n_D^{20} 1.4390; d_4^{20} 1.0786; *Anal.* Calc'd: C, 52.41; H, 8.80. Found: C, 52.28; H, 8.87.

³ A commercial grade was used; average analysis given by the manufacturer: mean molecular weight, 203; lauric acid, 90%; myristic acid, 9%; and oleic acid, 1%.

of various alcohols at atmospheric pressure (Fig. 3) were taken from the literature (11-13). Boiling points of butyl and octyl phthalates (Fig. 2) were taken from reference (14).

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REFERENCES

- (1) FISHER AND FILACHIONE, Lactic Acid—Versatile Intermediate for the Chemical Industry: U. S. Dept. Agr., Bur. Agr. and Indus. Chem., AIC-178, Eastern Regional Research Laboratory, May 1948, (Processed).
- (2) FEIN, RATCHFORD, AND FISHER, *J. Am. Chem. Soc.*, **66**, 1201 (1944).
- (3) FEIN AND FISHER, *J. Am. Chem. Soc.*, **68**, 2631 (1946).
- (4) REHBERG, DIXON, AND FISHER, *J. Org. Chem.*, **13**, 254 (1948).
- (5) FEIN AND FISHER, *J. Am. Chem. Soc.*, **70**, 52 (1948).
- (6) BURNS, JONES, AND RITCHIE, *J. Chem. Soc.*, 400 (1935).
- (7) FILACHIONE, FEIN, LENGEL, AND FISHER, *J. Am. Chem. Soc.*, **70**, 526 (1948).
- (8) SMITH AND CLABORN, *Ind. Eng. Chem.*, **32**, 692 (1940).
- (9) SEIKEL, *Ind. Eng. Chem., Anal. Ed.*, **13**, 388 (1941).
- (10) RATCHFORD AND REHBERG, An Improved Tensimeter-Still, Preprint Booklet, A.C.S. Division of Paint, Varnish and Plastics Chemistry (April 1948).
- (11) *Synthetic Organic Chemicals*, 12th Ed., Carbide and Carbon Chemicals Corporation, New York, N. Y. (1945).
- (12) *Technical Bulletin No. 87A*, The Quaker Oats Company, Chicago, Illinois (1947).
- (13) STULL, *Ind. Eng. Chem.*, **39**, 517 (1947).
- (14) HICKMAN, *J. Franklin Inst.*, **221**, 383 (1936).