Esters of Lactyllactic Acid[1]

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The process of making esters of lactyllactic acid from lactide was discovered by Claborn,[2] who described the methyl, ethyl and butyl esters. Lactyllactates can also be made by the self-alcoholysis of esters of monomeric lactic acid.[3]

tate usually being 5 to 20%, depending on the ratio of alcohol to lactic acid used in the esterification.

Table I shows the esters studied and the physical properties determined

The boiling points shown were read from lines on a Cox chart. This chart was notable for the unusally low value of the Antoine constant C, its value being 183 instead of the usual 220–240. Paper

TABLE I

PHYSICAL PROPERTIES OF LACTYLLACTATES

Lactyllactate	$n^{20}D$	$n^{40}D$	d^{20}_4	d^{40}_4	Viscosity, cps. 20°	Viscosity, cps. 40°	Boiling points at various pressures[c] 0.1 mm.	1.0 mm.	10 mm.	Solubility in water, g./100 g. (25°)
Methyl[a]	1.4314	1.4240	1.1609	1.1396	28.14	9.36	44	73	111	∞
Ethyl[a]	1.4292	1.4212	1.1136	1.0929	17.09	6.77	48	77	116	∞
n-Propyl	1.4304	1.4222	1.0764	1.0567	14.20	6.09	54	85	124	2.2
n-Butyl[a]	1.4329	1.4247	1.0622	1.0425	17.06	7.04	63	94	134	0.92
n-Hexyl	1.4362	1.4282	1.0280	1.0094	21.64	8.55	79	111	153	.08
n-Octyl	1.4396	1.4317	1.0042	0.9866	26.57	10.45	97	131	176	< .01
s-Butyl	1.4295	1.4216	1.0528	1.0332	20.10	7.58	56	86	126	1.16
2-Octyl	1.4358	....	0.9894	....	...	...	89	122	164	< .01
Allyl[b]	1.4448	1.4366	1.1172	1.0971	18.60	7.45	58	88	128	4.2
2-Butoxyethyl	1.4390	1.4312	1.0760	1.0570	30.89	11.46	91	125	169	.38
2-(2-Butoxyethoxy)-ethyl	1.4433	1.4352	1.0726	1.0531	32.09	12.81	115	150	196	.31
Tetrahydrofurfuryl	1.4578	....	1.1691	....	...	...	120 (0.3 mm.)	...		....
2-Chloroethyl	1.4540	1.4458	1.2351	1.2152	60.20	18.31	94 (0.3 mm.)	...		....

[a] Previously reported by Claborn (ref. 2). The properties he reported are in substantial agreement with ours. [b] Previously reported [Rehberg, Dixon and Fisher, *J. Org. Chem.*, 15, 560 (1950)]. [c] Values read from a Cox chart.

TABLE II

ANALYSES OF LACTYLLACTATES[a]

Lactyllactate	Saponification equivalent Calcd.	Saponification equivalent Found	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Mol. refraction Calcd.	Mol. refraction Found 20°
n-Propyl	102.1	100.7	52.9	52.7	7.9	7.9	48.60	49.04
n-Hexyl	123.2	126.2	58.5	58.6	9.0	9.1	62.45	62.68
n-Octyl	137.2	138.4	61.3	61.2	9.6	9.7	71.69	71.94
s-Butyl	109.1	109.0	55.0	55.0	8.3	8.3	53.21	53.50
2-Octyl	137.2	142.4	61.3	61.9	9.6	9.8	71.69	72.47
2-Butoxyethyl	131.2	130.4	54.9	54.8	8.5	8.6	64.09	64.11
2-(2-Butoxyethoxy)-ethyl	153.2	159.5	54.9	54.7	8.6	8.5	74.97	75.77
Tetrahydrofurfuryl	123.1	125.3	53.6	53.8	7.4	7.5	57.27	57.45
2-Chloroethyl	15.8[b]	15.8[b]	42.8	42.9	5.8	5.9	48.84	29.25

[a] The authors are indebted to C. O. Willits, C. L. Ogg, and their associates, of this Laboratory, for the analyses shown [b] Chlorine, %.

Because the acylation of lactyllactates with monocarboxylic[3] and dicarboxylic[4–6] acids yields esters useful as plasticizers, it was of interest to characterize more fully those lactyllactates which were available to us. These esters were obtained as by-products in the preparation of simple lactates on a large laboratory scale, the conversion to lactyllac-

graduated for $C = 273$ was converted to $C = 183$ by adding 90° to each temperature on the scale.[7]

Most of the esters in Table I are new compounds, and analytical data on those not previously described are shown in Table II.

(7) C. E. Rehberg, *Ind. Eng. Chem.*, **42**, 829 (1950).

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(2) H. V. Claborn, U. S. Patent 2,371,281, March 13, 1945.

(3) E. M. Filachione, E. J. Costello, T. J. Dietz and C. H. Fisher, Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, AIC-295, Feb. 1951 (Processed).

(4) C. E. Rehberg, M. B. Dixon, T. J. Dietz and C. H. Fisher, *Ind. Eng. Chem.*, **42**, 1409 (1950).

(5) C. E. Rehberg and M. B. Dixon, THIS JOURNAL, **72**, 5757 (1950).

(6) C. E. Rehberg, T. J. Dietz, P. E. Meiss and M. B. Dixon, "Plasticizers from Lactic Acid. Lactate Esters Esterified with Dibasic Acids," submitted for publication in *Ind. Eng. Chem.*

Synthesis of Δ^1-Allopregnene-17α,21-diol-3,11,20-trione-21-acetate

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The recent publication by St. Kaufmann and Pataki[1] in which they describe the synthesis of Δ^1-allopregnene-17α,21-diol-3,11,20-trione-21-acetate ("Δ^1-allocortisone acetate") (II) has prompted us

(1) St. Kaufmann and J. Pataki, *Experientia*, **7**, 260 (1951).