Preparation of Some Polymerizable Esters of Long-Chain Saturated Aliphatic Acids with Unsaturated Alcohols

BY DANIEL SWERN AND E. F. JORDAN, JR.

If long-chain aliphatic compounds could be co-polymerized with olefinic monomers of low molecular weight, the long chain would be chemically bound in the polymer molecule and the problems of exudation, evaporation and leaching of the modifying agent would be eliminated. The intramolecularly modified polymer would retain its original properties for a long time and perhaps for its entire period of use. By the proper selection of monomers and the relative proportions of low molecular weight olefinic monomer to fatty compound, a wide range of modified polymers could be obtained. The major obstacle, perhaps, to the preparation of such intramolecularly modified copolymers in the past has been the unavailability of pure long-chain compounds containing the necessary functional groups.

In a previous publication we described a series of polymerizable esters of oleic acid, and discussed briefly polymers obtained from some of them, as well as their copolymers with vinyl acetate.[2] The copolymers or intramolecularly modified polymers displayed a wide range of properties (hard, glass-like products to tough or soft rubber-like materials or viscous liquids), depending on the content of oleate ester. When only 1% of the more reactive and also the more promising oleate esters (vinyl, 2-chloroallyl, methallyl and allyl) were employed, insoluble hard, glass-like copolymers, which differed only slightly from unmodified polyvinyl acetate, were obtained. Since soluble, thermoplastic copolymers with a wide range of physical properties are of great industrial importance and their production is steadily increasing, we undertook the preparation of reactive monofunctional esters from long-chain, saturated aliphatic acids for use as intramolecular modifiers for low molecular weight olefinic monomers.

The purpose of the present paper is to describe the preparation and some of the physical properties of the vinyl, 2-chloroallyl, methallyl, allyl, 3-buten-2-yl, crotyl and furfuryl esters of caproic, caprylic, pelargonic, capric, lauric, myristic, palmitic and stearic acids, as well as to report briefly on the polymerization and copolymerization of some of the more reactive esters.

Examination of the literature revealed that some of the esters we wished to prepare had been described by earlier workers, primarily in patents and usually with little or no experimental details, and, in general, the products were incompletely

characterized. Furthermore, in these publications no information regarding the purity of the starting materials or final products was given. Inasmuch as commercially available long-chain saturated fatty acids, which the earlier workers apparently employed, are not pure compounds and are almost invariably contaminated with unsaturated acids, it is highly probable that the products reported in the literature were impure and, more important, were not monofunctional. In preparing soluble, thermoplastic, intramolecularly modified copolymers of the type described earlier in this paper, the purity of the monomers, especially with respect to their functionality, is of the utmost importance. In fact, the difficulty experienced by earlier investigators in preparing soluble copolymers of high molecular weight in which one of the monomers is a long-chain compound, was undoubtedly due to the presence of polyfunctional impurities in the long-chain compound.

Vinyl esters of long-chain saturated aliphatic acids have been described in patents[3,4] and in a recent publication.[5] 2-Chloroallyl laurate[6] and stearate,[6] and the methallyl esters of long-chain acids from caprylic to stearic have also been reported in recent patents.[7] Allyl caproate,[8,9] pelargonate,[10] laurate,[11] palmitate[8,12] and stearate[12] have been described in several papers and patents. Furfuryl palmitate has been described in two publications.[13,14] No reference to the preparation or properties of crotyl and 3-buten-2-yl esters of long-chain fatty acids could be found.

The vinyl esters were prepared by the procedure of Toussaint and MacDowell.[4] The results are summarized in Table I. The vinyl esters were colorless, mobile liquids, with the exception of the palmitate and stearate, which were crystalline solids melting at 27 and 35°, respectively. They were insoluble in water and soluble in organic solvents. The short-chain esters had fruit-like odors and the long-chain esters were odorless.

When the purified vinyl esters were analyzed, low iodine and high saponification numbers were

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted. This paper was presented at the meeting of the American Chemical Society held in Chicago, Ill., April 19–23, 1948.

(2) Swern, Billen and Knight, THIS JOURNAL, 69, 2439 (1947).

(3) Reppe, German Patent 588,352 (1933); U. S. Patent 2,066,075 (1936).

(4) Toussaint and MacDowell, Jr., U. S. Patent 2,299,862 (1942).

(5) Powers, Ind. Eng. Chem., 38, 837 (1946).

(6) Coleman and Hadler, U. S. Patent 2,208,960 (1940).

(7) Price and Kapp, U. S. Patent 2,341,060 (1944); Brit. Patent 545,415 (1942).

(8) Golendeev, J. Gen. Chem. (U. S. S. R.), 10, 1408 (1940).

(9) Moffett and Smith, U. S. Patent 2,390,164 (1945).

(10) Alekseeva and Isaev, Masloboino-Zhurovaya Prom., 16, No. 5/6. 54 (1940).

(11) Dean, U. S. Patent 2,374,081 (1945).

(12) Golendeev, J. Gen. Chem. (U. S. S. R.), 6, 1841 (1936).

(13) Tatiiri, J. Chem. Soc. Japan, 60, 442 (1939).

(14) Norris and Terry, Oil and Soap, 21, 193 (1944).

TABLE I

VINYL ESTERS OF SATURATED ALIPHATIC ACIDS

Ester	Yield,[a] %	Boiling point °C.	Mm.	Iodine no.[b] Calcd.	Found	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	d^{20}_4	n^{20}D(Abbe)[c]	Molecular refraction Calcd.	Found
Caproate	40	98–99	100	178.5	173.1	67.57	67.53	9.92	9.87	0.8837	1.4159	40.33	40.38
Caprylate	55	134–135	100	149.1	144.3	70.56	70.21	10.66	10.60	.8719	1.4256	49.57	49.95
Pelargonate	55	133–133.5	50	137.8	136.0	71.69	71.94	10.94	11.19	.8689	1.4291	54.19	54.70
Caprate	45	148	50	128.0	125.6	72.68	72.60	11.18	11.38	.8670	1.4320	58.81	59.33
Laurate	55	142	10	112.2	110.5	74.30	74.36	11.58	11.84	.8639	1.4368	68.04	68.65
Myristate	60	147–148	4.8	99.8	97.9	75.53	75.22	11.88	11.93	.8617	1.4407	77.28	77.92
Palmitate[d]	35	168–169	4.5	89.8	87.7	76.53	76.74	12.13	12.21	.8602[e]	1.4438	86.51	87.18
Stearate[f]	30	187–188	4.3	81.7	79.4	77.36	77.58	12.34	12.46	.8517[g]	1.4423[g]	95.75	96.46

[a] Pure products after two to three distillations, with the exception of the stearate, which was purified by recrystallization of the once-distilled product from acetone.   [b] One-hour Wijs method and a 200% excess of iodine chloride solution.   [c] Δn per degree = −0.0004.   [d] M. p. 26.7–27.1°.   [e] d^{35}_4 0.8571.   [f] M. p. 35–36°.   [g] At 40°.

obtained.[2] The failure to obtain correct iodine numbers was attributed to the reduction in the rate of addition of iodine chloride to the double bond because of the effect of the electron-attracting acyloxy group in reducing the nucleophilic properties of the double bond.[15] Reasonably

$$R—CO_2 \leftarrow CH{=}CH_2$$
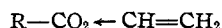
satisfactory iodine numbers (97 to 99%) (Table I) were obtained by allowing the iodine number determination to proceed for twenty-four hours or, preferably, by employing a 200% excess of Wijs solution and a one-hour reaction period. Since it was noticed that the saponification number increased as the reflux time was lengthened, the anomalous saponification number was attributed to the consumption of alkali by acetaldehyde, the tautomer of vinyl alcohol. The procedure finally employed consisted in a five-minute reflux period followed by rapid chilling of the sample in ice water and immediate titration. Fairly satisfactory results were obtained in this way (saponification numbers ranging from 95 to 105% of theoretical values), but difficulty was experienced in duplicating the analyses. For this reason saponification numbers are not listed in Table I.

Polymerization of the vinyl esters in the presence of 0.5% benzoyl peroxide as catalyst[16] yielded soft, elastic polymers, with the exception of polymerized vinyl palmitate and stearate, which were white wax-like solids.[3,17] The iodine numbers of the polymers were usually less than five, thus indicating fairly complete polymerization, although occasionally somewhat higher iodine numbers were obtained. The polymerized vinyl esters were thermoplastic. They were readily soluble in benzene and hot amyl acetate and, with the exception of polymerized vinyl caproate, insoluble or slightly soluble in acetone and glacial acetic acid, and insoluble in water.

Copolymerization of the vinyl esters with vinyl acetate or styrene[16] yielded products which ranged

in physical appearance from hard and glass-like (low content of long-chain ester) to very soft and elastic (high content of long-chain ester), with the exception of the copolymers of vinyl stearate with vinyl acetate, which were hard wax-like solids at room temperature. The products containing styrene showed indications of incompatibility, particularly at high contents of long-chain esters. All the copolymers were thermoplastic and colorless, or slightly straw-yellow when styrene was a monomer. They were readily soluble in benzene and amyl acetate, and either slightly soluble or insoluble in acetone and acetic acid, particularly at high contents of long-chain esters. The copolymers were insoluble in water.

The wide range of physical properties attainable in copolymers containing vinyl esters of long-chain fatty acids suggests numerous potential uses for the products.[5,17,18] Furthermore, the polyvinyl esters themselves may be useful as modifying agents for other polymers, particularly where intramolecular modification is either not feasible or is undesirable.

The 2-chloroallyl esters were prepared by direct esterification of the alcohol with the appropriate acid, naphthalene-2-sulfonic acid being employed as catalyst and the water formed during the reaction being azeotropically removed.[2] The results are summarized in Table II. The esters, with the exception of 2-chloroallyl stearate, which decomposed extensively on heating to its boiling point, were isolated in 85 to 95% yields by vacuum distillation of the reaction mixture, and they were substantially pure without further treatment. On redistillation, 60 to 85% yields of pure esters were obtained. The stearate was purified by recrystallization to constant melting point from acetone. The 2-chloroallyl esters were colorless, mobile liquids, with the exception of the stearate, which was a crystalline solid. They were soluble in organic solvents and insoluble in water. The 2-chloroallyl esters were unstable, liberating hydrogen chloride rapidly at elevated temperatures and slowly at room temperature. Products stored for some time gradually became discolored and contained free hydrogen chloride.

(15) Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1943.

(16) Guile and Huston, "A Revised Laboratory Manual of Synthetic Plastics and Resinous Materials," Michigan State College. 1944, p. 99.

(17) Reppe, Starck and Voss, U. S. Patent 2,118,864 (1938).

(18) Fikentscher, Off. Tech. Serv. Report PB A 76327 (1937).

TABLE II

2-CHLOROALLYL ESTERS OF SATURATED ALIPHATIC ACIDS

Ester	Yield,[a] %	Boiling point °C.	Mm.	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	d^{30}_4	n^{30}D(Abbe)[b]	Molecular refraction Calcd.	Found
Caproate	75	80	4.5	56.74	56.90	7.93	7.88	1.0067	1.4389	49.82	49.81
Caprylate	80	107–107.5	4.7	60.40	60.61	8.77	9.05	0.9825	1.4431	59.05	59.00
Pelargonate	75	120	5	61.92	61.85	9.10	9.44	.9719	1.4447	63.67	63.76
Caprate	85	129	4.2	63.27	63.20	9.39	9.46	.9635	1.4458	68.29	68.30
Laurate	80	151–152	4.2	65.55	65.45	9.91	10.16	.9493	1.4484	77.52	77.64
Myristate	75	173	4.0	67.41	67.31	10.33	10.28	.9377	1.4505	86.76	86.75
Palmitate[c]	60	190–191	4.0	68.96	68.17	10.66	10.85	.9291[d]	1.4524	96.00	96.25
Stearate[e]	85	200–202 (dec.)	2	70.25	69.98	10.95	10.96	.9149[f]	1.4497[f]	105.2	105.3

[a] Pure products after two to three distillations with the exception of the stearate, which was purified by recrystallization from acetone. [b] Δn per degree = −0.0004. [c] M. p. 28–29°. [d] d^{40}_4 0.9216. [e] M. p. 36–37°. [f] At 40°. d^{45}_4 0.9112.

TABLE III

METHALLYL ESTERS OF SATURATED ALIPHATIC ACIDS

Ester	Yield,[a] %	Boiling point °C.	Mm.	Sapon. equiv. Calcd.	Found	Iodine no.[b] Calcd.	Found	Carbon % Calcd.	Found	Hydrogen % Calcd.	Found	d^{30}_4	n^{30}D (Abbe)[c]	Molecular refraction Calcd.	Found
Caproate	55	135	100	170.2	170.6	149.1	150.1	70.56	70.40	10.66	10.70	0.8760	1.4250	49.57	49.68
Caprylate	45	147–148	50	198.3	198.6	128.0	129.1	72.68	73.00	11.18	11.20	.8703	1.4308	58.81	59.05
Pelargonate	40	163–164	50	212.3	213.1	119.4	119.8	73.54	73.79	11.35	11.44	.8684	1.4335	63.42	63.60
Caprate	50	175	50	226.3	227.2	112.2	113.1	74.30	74.52	11.58	11.64	.8665	1.4354	68.04	68.15
Laurate	40	165	10	254.4	255.7	99.8	99.4	75.53	75.65	11.88	11.86	.8638	1.4392	77.28	77.45
Myristate	35	164–165	4	282.5	283.1	89.8	90.5	76.53	76.75	12.13	12.36	.8617	1.4423	86.51	86.85
Palmitate	35	186–186.5	4	310.5	311.0	81.7	81.3	77.36	77.49	12.34	12.24	.8604	1.4450	95.75	96.16
Stearate[d]	40	204–205	4.6	338.6	339.2	75.0	76.0	78.03	78.45	12.51	12.73	.8593	1.4471	105.0	105.2

[a] Pure products after two distillations. [b] One hour Wijs method. [c] Δn per degree = −0.0004. [d] This compound solidified only after standing for several months at about 25°. M. p. 30.5–31°.

2-Chloroallyl caprate, myristate and stearate were converted to dark-yellow or brown viscous oils when polymerized in the presence of benzoyl peroxide as catalyst.[16] Copolymers of these esters with vinyl acetate were tough, elastic, colorless products when not more than 10% of long-chain ester was employed. As the proportions of 2-chloroallyl ester were increased, the products became darker and softer, and at the maximum content of long-chain ester (60%) they were yellow to brown viscous oils. The copolymers containing 40% of 2-chloroallyl caprate were readily soluble in hot acetone, acetic acid, amyl acetate and benzene. Those containing 40% of 2-chloroallyl myristate were slightly soluble in hot acetone and glacial acetic acid and readily soluble in the other solvents, and the copolymers containing 40% of 2-chloroallyl stearate were slightly soluble in amyl acetate, acetic acid and acetone but readily soluble in benzene.

Although it has been reported in the literature that methallyl esters of long-chain acids can be prepared by a direct esterification technique in which toluenesulfonic acid is employed as catalyst,[7] we observed that considerable isobutyraldehyde was obtained[19] and that the esters were difficult to purify. For these reasons, we employed the alcoholysis method previously described,[2] and had no difficulty in obtaining the pure esters in fair yields (35 to 55%) from the methyl esters of the acids and methallyl alcohol containing dissolved

sodium. The results are summarized in Table III. The methallyl esters were colorless, mobile, stable liquids, insoluble in water and soluble in organic solvents.

Under the conditions employed in the polymerization of the vinyl and 2-chloroallyl esters, the methallyl esters of the long-chain acids showed little tendency to polymerize. This was demonstrated by the fact that the iodine numbers of the products after polymerization were only about 10% lower than those of the pure monomers In this respect they were similar to the methallyl esters of short-chain acids.[20] Copolymers containing methallyl esters were not prepared.

The allyl, 3-buten-2-yl and crotyl esters were prepared in 80 to 90%, 55 to 85% and 50 to 85% yields, respectively, by direct esterification of the acids with the alcohols, with naphthalene-2-sulfonic acid as catalyst, the water formed during the reaction being azeotropically removed.[2] We also prepared several of the crotyl esters by alcoholysis[2] of the methyl esters, but the yields were considerably lower than by the direct method. The results are summarized in Tables IV, V and VI. The physical properties of a given crotyl ester prepared by either esterification technique were identical, indicating that the acid catalyst did not cause isomerization of the crotyl portion of the molecule. The allyl, 3-buten-2-yl and crotyl esters were colorless, stable, mobile liquids with the exception of allyl stearate, which was a solid melting at 37°. They were insoluble in water and

(19) Hearne, Tamele and Converse, Ind. Eng. Chem., 33, 805 (1941).

(20) Ryan and Shaw, THIS JOURNAL, 62, 3469 (1940).

TABLE IV
ALLYL ESTERS OF SATURATED ALIPHATIC ACIDS

Ester	Yield,[a] %	Boiling point °C.	Mm.	Sapon. equiv. Calcd.	Found	Iodine no.[b] Calcd.	Found	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	d^{20}_4	n^{20}D (Abbe)[c]	Molecular refraction Calcd.	Found
Caproate	80	92.5–93.0	30	156.2	156.4	162.4	161.7	69.19	69.07	10.32	10.28	0.8800	1.4200	44.95	44.93
Caprylate	80	87–88	5.5	184.3	183.7	137.7	137.5	71.69	72.00	10.94	10.79	.8729	1.4271	54.19	54.21
Pelargonate	85	151	50	198.3	198.2	128.0	128.3	72.68	72.80	11.18	11.33	.8702	1.4302	58.81	58.89
Caprate	90	113–114	5.2	212.3	211.8	119.4	118.8	73.54	73.60	11.35	11.03	.8684	1.4326	63.42	63.44
Laurate	90	136	4.5	240.4	239.8	105.6	105.3	74.95	74.71	11.74	11.53	.8648	1.4370	72.66	72.85
Myristate	90	157	4.3	268.4	267.0	94.5	94.7	76.06	75.58	12.02	11.89	.8627	1.4404	81.89	82.00
Palmitate	85	[d]		296.5	294.8	85.6	84.8	76.96	77.25	12.23	12.35	.8609[e]	1.4431	91.13	91.20
Stearate	85	[f]		324.5	323.7	78.2	78.6	77.72	77.71	12.42	12.29	.8524[g]	1.4420[g]	100.4	100.7

[a] Pure products after two distillations, with the exception of the palmitate and stearate, which were purified by recrystallization from acetone at −20° and 0°, respectively. [b] One hour Wijs method. [c] Δn per degree = −0.0004. [d] M. p. 25.3–25.5°. [e] d^{35}_4 0.8581. [f] M. p. 37.1–37.3°. [g] At 40°. d^{45}_4 0.8491.

TABLE V
3-BUTEN-2-YL ESTERS OF SATURATED ALIPHATIC ACIDS

Ester	Yield,[a] %	Boiling point °C.	Mm.	Sapon. equiv. Calcd.	Found	Iodine no.[b] Calcd.	Found	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	d^{20}_4	n^{20}D (Abbe)[c]	Molecular refraction Calcd.	Found
Caproate	55	189	753	170.2	171.4	149.1	150.6	70.56	70.74	10.66	10.56	0.8644	1.4179	49.57	49.59
		123	99												
Caprylate	60	150	75	198.3	197.9	128.0	128.9	72.68	72.61	11.18	11.29	.8609	1.4251	58.81	58.93
Pelargonate	85	173	100	212.3	212.3	119.4	119.8	73.54	74.06	11.35	11.68	.8596	1.4280	63.42	63.63
Caprate	65	185–186	100	226.3	225.8	112.2	112.8	74.30	74.20	11.58	11.70	.8586	1.4308	68.04	68.28
Laurate	80	156–157	10	254.4	254.3	99.8	100.0	75.53	75.70	11.88	12.30	.8567	1.4350	77.28	77.55
Myristate	70	180	10	282.5	281.8	89.8	90.3	76.53	76.40	12.13	12.20	.8556	1.4384	86.51	86.77
Palmitate	70	180	4.3	310.5	310.0	81.7	81.9	77.36	77.34	12.34	12.39	.8546	1.4413	95.75	95.99
Stearate	65	199	4.2	338.6	338.8	75.0	75.7	78.03	77.80	12.51	12.20	.8538	1.4440	105.0	105.3

[a] Pure products after two to three distillations. [b] One hour Wijs method. [c] Δn per degree = −0.0004.

TABLE VI
CROTYL ESTERS OF SATURATED ALIPHATIC ACIDS

Ester	Yield,[a] %	Boiling point °C.	Mm.	Sapon. equiv. Calcd.	Found	Iodine no.[b] Calcd.	Found	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	d^{20}_4	n^{20}D (Abbe)[c]	Molecular refraction Calcd.	Found
Caproate	60	141	100	170.2	170.0	149.1	147.8	70.56	70.87	10.66	10.75	0.8789	1.4279	49.57	49.82
Caprylate	55 85[d]	154–154.5	50	198.3	197.6	128.0	128.4	72.68	72.84	11.18	10.74	.8730	1.4335	58.81	59.08
Pelargonate	85[d]	165	50	212.3	211.7	119.6	118.8	73.54	73.33	11.35	12.02	.8709	1.4358	63.43	63.70
Caprate	65	181	50	226.3	225.0	112.2	112.9	74.30	74.64	11.58	11.48	.8687	1.4378	68.04	68.36
Laurate	65	167–168	10	254.4	254.3	99.8	99.8	75.53	75.79	11.88	12.14	.8656	1.4411	77.28	77.62
Myristate	50	170	4.3	282.5	282.0	89.8	89.7	76.53	76.06	12.13	12.67	.8632	1.4442	86.51	86.94
Palmitate	70	188–189	3.8	310.5	310.1	81.7	81.4	77.36	77.70	12.34	12.28	.8616[e]	1.4466	95.75	96.20
Stearate[f]	35 85[d]	209	4.5	338.6	337.3	75.0	75.2	78.03	77.96	12.51	12.51	.8566[g]	1.4467[g]	105.0	105.5

[a] Pure products after two distillations. [b] One hour Wijs method. [c] Δn per degree = −0.0004. [d] Yield by direct esterification of crotyl alcohol with the fatty acid. All other yields in this table are for the alcoholysis reaction. [e] d^{35}_4 0.8581. [f] M. p. 30.5–31°. [g] At 35°.

soluble in organic solvents. The short-chain allyl esters had fruit-like odors, whereas the long-chain compounds were odorless.

The allyl esters also showed little tendency to polymerize when heated with 0.5% benzoyl peroxide as catalyst,[16] the iodine numbers of the products being only 10 to 20% lower than those of the corresponding monomers. Copolymers of the allyl esters with diallyl phthalate ranged from tough to soft colorless gels as the content of allyl ester was increased from 1 to 20%. These copolymers were insoluble in acetone, amyl acetate, benzene and acetic acid.

Because of the known lack of polymerizability of the 3-buten-2-yl and crotyl esters,[2] their polymers or copolymers were not prepared.

The furfuryl esters were obtained in only 30 to 50% yields by alcoholysis of the methyl esters of the long-chain acids with furfuryl alcohol containing dissolved sodium.[2] The results are summarized in Table VII. They were pale-yellow, mobile liquids, with the exception of the stearate, which was a solid melting at 41°. The furfuryl esters were insoluble in water and soluble in organic solvents. The stearate, isolated by distillation, was pale-yellow when molten. When recrystallized from acetone, it was a beautiful crystalline solid which was colorless when molten and had physical properties identical with those of the product purified by distillation alone, indicating that the discoloration of the products was caused by impurities present only in traces.

Experimental

All the reactions and distillations described were conducted in an atmosphere of nitrogen.

Starting Materials.—Pure caproic, caprylic, pelargonic and capric acids were prepared from the 90% commercial grades of these acids by repeated distillation under vacuum

TABLE VII

FURFURYL ESTERS OF SATURATED ALIPHATIC ACIDS

Ester	Yield,[a] %	Boiling point °C.	Mm.	Sapon. equiv. Calcd.	Found	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	d^{20}_4	n^{20}D (Abbe)[b]	Molecular refraction Calcd.	Found
Caproate	50	149–150	50	196.2	194.1	67.32	66.98	8.22	8.13	1.005	1.4550	53.16	53.10
Caprylate	30	139	10	224.3	222.0	69.58	69.32	8.98	9.24	0.9789	1.4560	62.40	62.32
Pelargonate	40	151.5–153.0	10	238.3	236.0	70.55	70.29	9.31	8.87	.9687	1.4563	67.02	66.88
Caprate	35	167	10	252.3	251.0	71.40	71.08	9.58	9.58	.9600	1.4570	71.63	71.54
Laurate	35	167–168	3.8	280.4	279.1	72.84	72.11	10.07	10.15	.9462	1.4578	80.87	81.00
Myristate	40	187–187.5	3.9	308.5	306.9	74.00	73.85	10.46	10.64	.9352	1.4588	90.11	90.26
Palmitate	30	205–206	3.8	336.5	334.0	74.95	74.75	10.78	10.93	.9226[c]	1.4580[c]	99.34	99.70
Stearate[d]	35	211–213	2.5	364.6	363.2	75.76	75.31	11.06	10.52	.9086[e]	1.4549[e]	108.6	108.9

[a] Pure products after two distillations. [b] Δn per degree $= -0.0004$. [c] At 35°. [d] M. p. 40.7–41.4°. [e] At 45°.

through efficient fractionating columns. Pure lauric acid was prepared from the purest commercial grade by two recrystallizations from acetone (10 ml. of solvent per gram of solute) at −40°, followed by fractional distillation under vacuum. Pure myristic acid was similarly prepared, except that two crystallizations at −20° were employed. Pure palmitic acid was prepared by repeated crystallization of the purest commercial grade from acetone (10 ml. of solvent per gram of solute) at 0° until a constant melting point was obtained. Pure stearic acid was prepared by two recrystallizations from acetone at 0° of the fatty acids obtained from completely hydrogenated soybean oil. The methyl esters were prepared from the acids by refluxing them for six hours with a large molar excess (500%) of anhydrous methyl alcohol containing a small quantity (2% by weight of the acid) of 95% sulfuric acid as catalyst. The reaction mixture was poured with thorough mixing into a large quantity of warm water (40–50°) in a separatory funnel, and the lower aqueous layer was separated and discarded. The esters were washed with warm water until free of sulfuric acid and dried by heating to 100° under moderate vacuum in a stream of inert gas. They were then distilled under vacuum through an efficient fractionating column. The products employed in the reactions described had the theoretical neutralization or saponification equivalents, and their physical properties (m. p., b. p., and n_D [Abbe]) agreed with the best values reported in the literature.[21,22,23]

The unsaturated alcohols were distilled through efficient fractionating columns before use.

Vinyl acetate, styrene and diallyl phthalate, were obtained from the commercial grades by fractional distillation. These substances were used immediately after isolation.

Vinyl Esters.—The procedure of Toussaint and MacDowell[4] was employed. The yield of once-distilled ester was 50 to 70%, and upon redistillation in the presence of sufficient sodium bicarbonate to neutralize the small quantities of free acid which these esters usually contained, 30 to 60% yields of pure vinyl esters were obtained. Negligible residues were obtained on redistillation, with the exception of the distillations of vinyl palmitate and stearate, the two highest boiling vinyl esters prepared. Vinyl stearate was most conveniently purified by recrystallization of the once-distilled product from acetone (3 ml. of solvent per gram of solute) at 0°. It was a crystalline solid, and its physical properties and those of the product purified by redistillation were identical. The results are summarized in Table I.

2-Chloroallyl, Allyl, 3-Buten-2-yl and Crotyl Esters.— The azeotropic method previously described[2] was employed, and refluxing was continued until the theoretical quantity of water was evolved. In the preparation of the 3-buten-2-yl esters, eighteen to twenty-four hours of reflux time was usually required, whereas only three to six hours was required when the primary alcohols were

(21) Dorinson, McCorkle and Ralston, THIS JOURNAL, 64, 2739 (1942).

(22) Pool and Ralston, Ind. Eng. Chem., 34, 1104 (1942).

(23) Markley, "Fatty Acids," published by Interscience Publishers, Inc., New York, N. Y., 1947.

employed. The esters were isolated from the reaction mixture by vacuum distillation, with the exception of allyl and 2-chloroallyl stearate and allyl palmitate, which were recrystallized to constant melting point from acetone (3 to 4 ml. of solvent per gram of solute) after recovery of the unreacted alcohol. Some of the crotyl esters were also prepared by the alcoholysis method,[2] but the yields were much lower than by the direct method. The results are summarized in Tables II, IV, V and VI.

Methallyl and Furfuryl Esters.—The alcoholysis method previously described was employed.[2] The results are summarized in Tables III and VII.

Polymerization of Vinyl, 2-Chloroallyl, Methallyl and Allyl Esters.—Approximately 5-ml. portions of the freshly distilled esters were weighed into test-tubes, 0.5% by weight of benzoyl peroxide was added and the polymerizations were conducted in a thermostatically controlled oven.[16] Solubilities were determined in benzene, acetone, glacial acetic acid and amyl acetate at room temperature, and in the case of those solvents in which the polymers were insoluble, also at 100° or at the boiling point, whichever was reached first. The results obtained have been discussed earlier in the manuscript.

Copolymerization of Vinyl, 2-Chloroallyl and Allyl Esters.—The vinyl esters were copolymerized[16] with vinyl acetate and also with styrene, the 2-chloroallyl esters with vinyl acetate only, and the allyl esters with diallyl phthalate. Benzoyl peroxide (0.5% on a total monomer basis) was employed as catalyst. When vinyl acetate was employed as a monomer, copolymers were prepared containing from 1 to 60% of long-chain ester, on a total monomer basis. When styrene and diallyl phthalate were employed as monomers, copolymers were prepared containing a maximum content of long-chain ester of 40 and 20%, respectively.

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Summary

Vinyl, 2-chloroallyl, methallyl, allyl, 3-buten-2-yl, crotyl and furfuryl esters of caproic, caprylic, pelargonic, capric, lauric, myristic, palmitic and stearic acids have been prepared, and some of their properties have been determined. Modified procedures for the determination of the iodine and saponification numbers of the vinyl esters are described.

The polymerization of the vinyl, 2-chloroallyl, methallyl and allyl esters, with benzoyl peroxide as catalyst, has been studied briefly. The polymerized vinyl esters are soft, colorless, elastic masses, with the exception of polymerized vinyl palmitate and vinyl stearate, which are white, wax-like solids. The polymerized 2-chloroallyl es-

ters are dark-yellow or brown viscous oils. The methallyl and allyl esters display little tendency to polymerize.

The vinyl esters have been copolymerized with vinyl acetate and also with styrene, the 2-chloro-

allyl esters with vinyl acetate only and the allyl esters with diallyl phthalate. The wide range of properties attainable in the copolymers suggests numerous potential uses for the products.

Equilibrium Equations for a Model of Antibody–Antigen Combination

By Manuel F. Morales, Jean Botts and Terrell L. Hill

Application of statistical procedures to models of antibody–antigen combination yields expressions involving certain thermodynamic constants of the equilibrium; such expressions enable the calculation of these constants from conventional measurements, and may therefore be of interest. We wish to present here certain relations of this sort based on a useful model proposed recently by Teorell.[1,2,3]

In Teorell's model, antibody (A) is assumed univalent,[4] and antigen (G) is assumed n-valent; the aggregate compounds have therefore the formulas, A_iG, and the equilibrium is formally similar to that of ampholyte dissociation[5]

$$\left.\begin{array}{l} A + A_{i-1}G \rightleftarrows A_iG \\ K_i = [A_iG]/[A][A_{i-1}G] \end{array}\right\} \quad i = 1, 2, \ldots, n \quad (1)$$
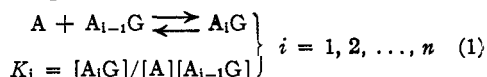
We shall assume in what follows that the total concentrations of antibody and antigen, A_0 and G_0, respectively, are known experimentally. Deferring until later a discussion of the matter, we shall also suppose that the concentration ratio of total bound antibody to total bound antigen in the initial solution

$$R = \sum_{i=1}^{i=n} i[A_iG] \Big/ \sum_{i=1}^{i=n} [A_iG]$$

is measurable (actually this ratio is measurable only in the precipitate which subsequently forms). Clearly, $\lim_{A_0 \to \infty} R = n$, the antigen valence. In certain cases it will be further required to know the amounts of bound A and G. Various assumptions regarding the aggregation will now be considered separately.

I. The reactivity of a vacant reactive site on the surface of an A–G aggregate is assumed to be

completely independent of the remainder of the structure on which it exists. In this case it may be shown that

$$R = \frac{K_1[A](1 + K_1[A]/n)^{n-1}}{(1 + K_1[A]/n)^n - 1} \quad (2)$$

If A_0 and G_0 be given special values, A_0' and G_0' such that [A] becomes equal to n/K_1, then R takes on a special value, $R' = (n/2)/(1 - 1/2^n)$, which is very nearly $n/2$ for $n \geq 4$. Conversely, one may vary A_0 and G_0 experimentally until R becomes, say, $n/2$; at that point [A] equals n/K_1, and one may also show that on this account

$$K_1 = n/(A_0' - R'G_0') \quad (3)$$

K_1 is thus obtainable from the usual concentration measurements. All other equilibrium constants are derivable from K_1 by means of the formula

$$K_i = (K_1/n)(n - i + 1)/i \quad (4)$$

II. The antibody molecules on the surface of the same antigen are assumed to attract or repel one another. It is assumed (rather reasonably) that these interactions can be represented as an A–A bond energy, E_{AA}, and that they operate only between nearest neighbor molecules. To treat this case one must make specific assumptions about the surface lattice formed by the reactive sites on the antigen. We shall here consider three such lattices, corresponding to the contact points on any sphere[6] in the (a) hexagonal closest packing of spheres, (b) cubic closest packing of spheres, and (c) simple cubic packing of spheres. In this case we have

$$R = \frac{\displaystyle\sum_{i=1}^{i=n} \sum_p i(K_1[A]/n)^i W_i^{(p)} \exp(-pE_{AA}/kT)}{\displaystyle\sum_{i=1}^{i=n} \sum_p (K_1[A]/n)^i W_i^{(p)} \exp(-pE_{AA}/kT)} \quad (5)$$

where, for a given lattice, $W_i^{(p)}$ is the number of microscopically different ways in which i antibody molecules may be placed on an antigen molecule in such a manner that among the antibody molecules there will be p nearest neighbor pairs. The calculation of the $W_i^{(p)}$ is considered elsewhere.[7]

(1) Teorell, *Nature*, **151**, 696 (1943).

(2) Teorell, *J. Hyg.*, **44**, 227 (1946).

(3) Teorell, *ibid.*, **44**, 237 (1946).

(4) The unsettled rivalry between this model, which goes back to the concepts of Bordet, and the framework model proposed independently by Marrack and Heidelberger and later greatly elaborated by Pauling (This Journal, **62**, 2643 (1940)) is acknowledged. The same methods here used, however, appear applicable to the latter case, although with more difficulty.

(5) Analogs to our cases I and II below have been given for ampholyte dissociation by Kirkwood in Cohn and Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp.. New York, N. Y., 1943, pp. 290–294. The specific model treated, however, is quite different.

(6) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(7) Morales and Botts, *J. Chem. Phys.*, **16**, 587 (1948).