[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

n-ALKYL *beta*-HYDROXYPROPIONATES AND *beta*-ACETOXYPROPIONATES

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Several derivatives of hydracrylic acid or *beta*-hydroxypropionic acid, needed in connection with other research, were prepared[2] from readily available starting materials by methods apparently more convenient than those hitherto described (1–5). The preparations of these products, several of which are new, and certain of their physical constants are reported here.

The ethyl, *n*-propyl, *n*-butyl, and *n*-octyl hydracrylates were prepared by passing dry HCl through ether solutions of ethylene cyanohydrin and the appropriate alcohols.[3] The butyl and octyl esters were obtained in approximately 70% yields. The ethyl and propyl esters, which were more difficult to isolate because of their solubility in water, were obtained in lower yields. There was little tendency for the corresponding *beta*-chloropropionates to form under the conditions usually employed, but in one experiment both ethyl hydracrylate and ethyl *beta*-chloropropionate were formed when the reaction mixture was allowed to stand for about 10 days at room temperature.

The butyl ester of dimeric hydracrylic acid, $HOCH_2CH_2COOCH_2CH_2COOC_4H_9$, was isolated as a by-product in the preparation of butyl hydracrylate (Table I). Possibly the dimer ester was formed by self-alcoholysis of butyl hydracrylate[4, 5] or by the reaction of butanol with $HOCH_2CH_2COOCH_2CH_2CN$.

Ethyl and *n*-butyl hydracrylates were made also by saponification of ethylene cyanohydrin (10), acidification of the resulting sodium hydracrylate, and esterification of the free acid. This method resembled that described above in that it was less suitable for the preparation of the water-soluble ethyl hydracrylate.

The acetyl derivates of the *n*-alkyl hydracrylates (Table I) were obtained in approximately 90% yields by acetylation with acetic anhydride. The propionate of methyl hydracrylate had been prepared by earlier workers (3) by acylation with propionyl chloride.

Physical constants. The boiling points given by Drushel and Holden (5) for the ethyl (84°, 12 mm.; 91.5°, 19 mm.; 95.5°, 22 mm.) and *n*-propyl, (102°, 19

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[2] The preparation of hydracrylic esters prior to 1915 has been reviewed by Drushel (4, 5). The interesting synthesis of hydracrylic esters from propiolactone and alcohols was described (6) after the completion of the present work.

[3] Earlier workers prepared related hydracrylic acid derivatives, that is, $C_2H_5OCOOCH_2 \cdot CH_2COOC_2H_5$ (7) and $CH_3C_6H_4SO_2OCH_2CH_2COOC_2H_5$ (8), similarly from 2-cyanoethyl ethyl carbonate and 2-cyanoethyl toluenesulfonate, respectively.

[4] The production of various esters of polymeric hydracrylic acid from β-propiolactone has been described (6).

[5] Esters of polymeric lactic acid have been made by the self-alcoholysis of several alkyl lactates (9).

TABLE I

DERIVATIVES OF HYDRACRYLIC ACID AND 3-CHLOROPROPIONIC ACID[a]

COMPOUND	B.P. °C (10 MM.)	n_D^{20}	d_4^{20}	MOLECULAR REFRACTION		SAPONIFICATION EQUIV.		CARBON, %		HYDROGEN, %	
				Calc'd	Obs.	Calc'd	Obs.	Calc'd	Obs.	Calc'd	Obs.
Methyl hydracrylate[b]	70	1.4228	1.1160	23.85	23.74	—	—	—	—	—	—
Ethyl "	76	1.4222	1.0589	28.47	28.36	118.1	118.9	50.83	50.87	8.53	8.41
n-Propyl "	89	1.4263	1.0243	33.09	33.08	132.2	131.6	54.52	54.62	9.15	9.02
n-Butyl "	101	1.4292	1.0006	37.70	37.67	146 2	146.6	57.51	57.36	9.59	9.40
n-Octyl "	150	1.4405	0.9488	56.18	56.24	202.3	202.1	65.31	65.36	10.96	11.02
Methyl *beta*-acetoxypropionate	81	1.4169	1.1100	33.32	33.10	73.1	73.4	49.3	49.6	6.9	7.2
Ethyl "	88	1.4170	1.0651	37.83	37.81	80.1	80.8	52.49	52.65	7.55	7.82
n-Propyl "	99	1.4198	1.0382	42.45	42.44	87.1	87.2	55.16	55.10	8.10	8.02
n-Butyl "	111	1.4230	1.0179	47.07	47.09	94.1	93.9	57.42	57.64	8.57	8.88
n-Octyl "	159	1.4337	0.9684	65.54	65.64	122.2	122.3	63.90	63.74	9.90	9.86
n-Bu ester of dimeric hydracrylic acid[c]	157 (5 mm.)	1.4432	1.0874	53.31	53.23	109.12	109.0	55.03	55.10	8.31	8.61
Ethyl 3-chloropropionate[d]	60 (15 mm.)	1.4256	1.1035	31.82	31.69	—	—	43.97	44.11	6.64	7.01
" " [e]	60 (15 mm.)	1.4240	1.0962	—	—	—	—	43.97	44.14	6.64	6.79

[a] After this manuscript had been completed, samples of methyl, ethyl, *n*-propyl, and *n*-butyl hydracrylates generously supplied by J. E. Jansen and T. L. Gresham of the B. F. Goodrich Company were redistilled and their physical properties determined: the resulting physical properties of the ethyl, propyl, and butyl esters were in excellent agreement with those given in Table I.

[b] Constants obtained with sample supplied by J. E. Jansen and T. L. Gresham after redistillation.

[c] Hydroxyl groups: theoretical, 7.86%; found, 7.1%.

[d] From 3-chloropropionyl chloride and ethanol; observed chlorine content, 25.74% (theoretical, 25.96%).

[e] This compound and ethyl hydracylate were obtained from ethylene cyanohydrin, ethanol, and hydrogen chloride.

mm.; 120°, 43 mm.) esters of hydracrylic acid are in fair agreement with those observed (Fig. 1 and Tables I and II) in the present work. The hydracrylates

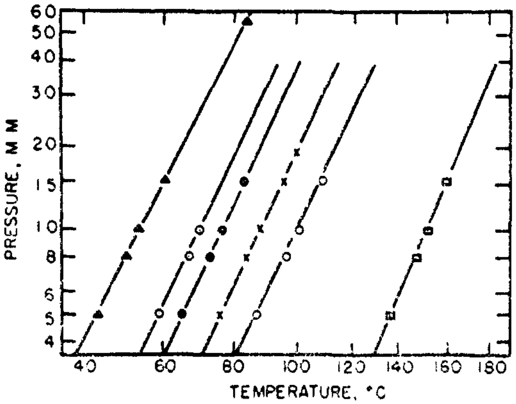


FIG. 1. BOILING POINT OF *n*-ALKYL HYDRACRYLATES AND ETHYL 3-CHLOROPROPIONATE (Et Chloropropionate, ▲. Hydracrylates: Me—⊙; Et—●; Pr—×; Bu—○; Octyl—□.)

TABLE II

BOILING POINTS AND VISCOSITIES OF HYDRACRYLIC ESTERS[a, b]

COMPOUND	BOILING POINT		VISCOSITY (20°)		POISES × 10^6/MOL. VOL.
	°C.	Mm.	Centistokes	Centipoises	
Ethyl hydracrylate	187	754	4.196	4.443	398.26
n-Propyl "	202	760	5.193	5.319	412.26
n-Butyl "	216–218	754	6.208	6.212	425.22
n-Octyl "	276	755	13.076	12.406	581.87
Ethyl *beta*-acetoxypropionate	201	755	2.606	2.776	184.60
n-Propyl "	215	758	2.966	3.079	183.51
n-Butyl "	231	756	3.365	3.425	185.22
n-Octyl "	284	755	6.554	6.347	251.58

[a] Distillation of the *n*-alkyl hydracrylates at atmospheric pressure caused some decomposition.

[b] Dunstan and co-workers (References 15 and 16) observed the value for $\frac{\text{poises} \times 10^6}{\text{mol. vol.}}$, which is under 100 for simple esters, ketones, and alkyl halides, is relatively large for highly associated compounds. Examples are: Water, 500; phenol, 453; glycol, 2750; formic acid, 415; and formamide, 682. The values for the ethyl ethers of ethyl, propyl, butyl, and octyl hydracrylates are, respectively, 82, 86, 89, and 135 (Ref. 17).

and *beta*-acetoxypropionates boiled considerably higher than the corresponding isomeric lactates and *alpha*-acetoxypropionates (Figs. 2 and 3).

Methyl and ethyl hydracrylate resembled *n*-alkanols of comparable molecular weight in that they boiled about 14° lower than their acetyl derivatives (Table

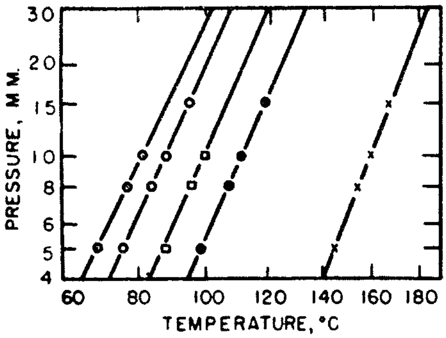


Fig. 2. Boiling Points of n-Alkyl β-Acetoxypropionates (⊙—Methyl; ○—Ethyl; □—Propyl; ●—Butyl; ×—Octyl)

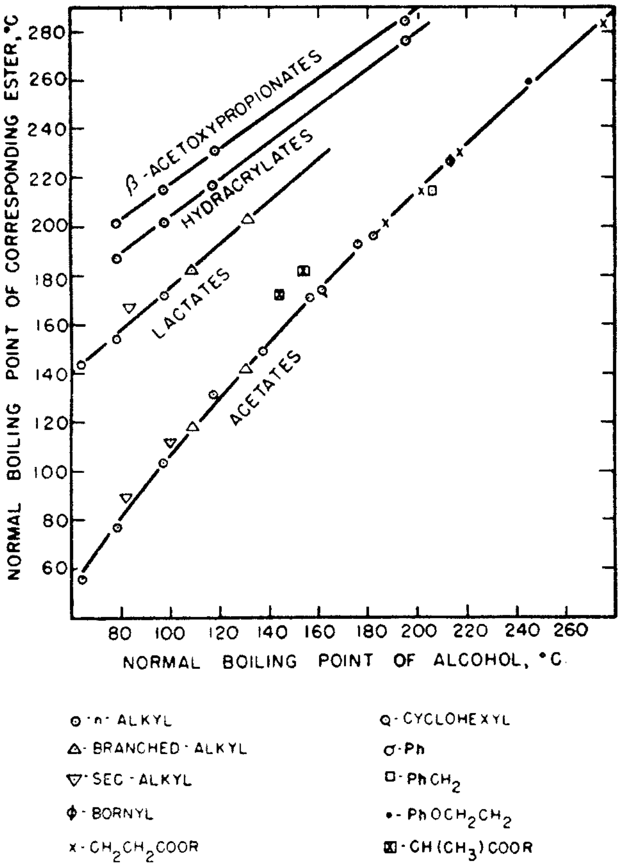
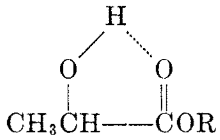


Fig. 3. Relation of Boiling Point of Alcohol to That of the Corresponding Ester

⊙—n-Alkyl
△—Branched—Alkyl
▽—Sec.—Alkyl
Φ—Bornyl
×—CH_2CH_2COOR

Q—Cyclohexyl
σ—Ph
⊡—$PhCh_2$
●—$PhOCH_2CH_2$
⊠—$CH(CH_3)COOR$

II and Fig. 3). The isomeric methyl and ethyl lactates, which (11) exist largely as



have boiling points about 28° lower[6] than their corresponding acetyl derivatives (14).

As is true with many other homologous series (17–20), the square of the absolute boiling points of the *n*-alkyl hydracrylates and *beta*-acetoxypropionates was a straight line function of the number of carbon atoms. The equations below express the relation between boiling point (T = b.p., °K.) and carbon atoms (x):

$$\text{Hydracrylates, 760 mm.} : T^2\,10^{-4} = 1.50x + 13.64$$
$$\text{10 mm.} : T^2\,10^{-4} = 0.96x + 7.32$$

$$\text{Acetoxypropionates, 760 mm.} : T^2\,10^{-4} = 1.42x + 12.56$$
$$\text{10 mm.} : T^2\,10^{-4} = 0.96x + 6.16$$

Since the hydracrylates could be distilled at atmospheric pressure without serious decomposition, apparently the tendency of these esters to dehydrate on heating is less than that of certain more complex *beta*-hydroxy esters (21).

The density (d_4^{20}) and refractive index (n_D^{20}) of the *n*-alkyl hydracrylates of Table I are related to the total number of carbon atoms (x), as shown by the equations:[7]

$$x/d = 1.147x - 1.026$$
$$x/n = 0.686x + 0.093$$

The *n*-alkyl hydracrylates, less viscous than the *n*-alkanols of equal molecular weight, are more viscous than the *beta*-acetoxypropionates, *beta*-ethoxypropionates (Fig. 4), and the isomeric *n*-alkyl lactates (22). Because of their relatively high viscosities and boiling points, it seems likely that the hydracrylates are more associated than the corresponding lactates; this conclusion is in harmony with the generalization of Bingham and Spooner (22) that primary alcohols are more highly associated than the isomeric secondary alcohols.

In harmony with their view are the high viscosity-molecular volume values of the *n*-alkyl hydracrylates (Table II). As would be expected, the acetyl and

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[6] Certain other hydroxy compounds structurally capable of existence in the chelate form also have boiling points (12) considerably lower than those of the corresponding acetates. For example, *o*-nitrophenol (b.p. 214.5°) and eugenol (b.p. 253.5°) boil 37° and 27° lower than their corresponding acetates. Acetoin (b.p. 143°) has a boiling point 28° lower than that of its acetate (13).

[7] The calculated refractive index of ethyl hydracrylate, agreeing poorly with the experimental value, is an exception.

ethyl ether derivatives have much lower values than the corresponding alkyl hydracrylates (Table II).

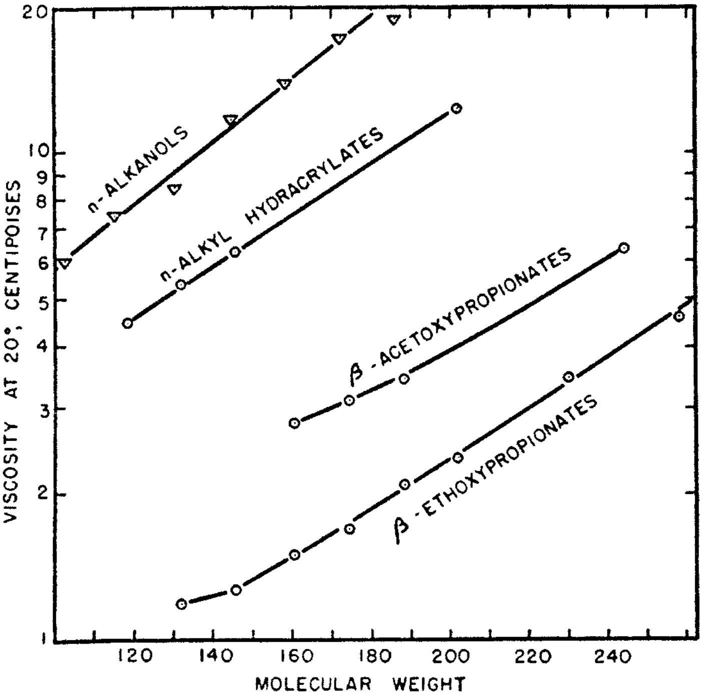

FIG. 4. VISCOSITY OF n-ALKANOLS AND DERIVATIVES OF HYDRACRYLIC ACID

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EXPERIMENTAL

n-Butyl hydracrylate and 2-carbobutoxyethyl hydracrylate. Dry hydrogen chloride was passed into a mixture of 2 moles of ethylene cyanohydrin, 4 moles of n-butanol, and 200 ml. of ethyl ether contained in a 1-liter three-neck flask immersed in ice-water and fitted with a mechanical stirrer.

After the mixture had been saturated with hydrogen chloride, the flask was placed in a refrigerator for two days. During this period a mass of crystals formed. The flask was then attached to a vacuum line (water aspirator) to remove excess hydrogen chloride; this operation was occasionally interrupted so that dry air could be blown through the flask. Benzene (200 ml.) was added, and the mixture was stirred. About 200 ml. of water was then added slowly. The water layer was separated and washed with benzene. The combined benzene solution was washed with water and sodium bicarbonate solution. The benzene-water azeotrope and excess butanol were distilled under water-pump vacuum; the butyl hydracrylate distilled at about 0.1 mm. (The yield was 70%.) The n-butyl ester was much less soluble in water (approximately 0.75 g. per 100 ml.) than the isobutyl ester [given as 1 part in 18 by Drushel and Holden (5)].

The distillation residue from one of the butyl hydracrylate preparations was distilled further, yielding a product (Table I) believed, on the basis of its analysis, to be the butyl ester of dimeric hydracrylic acid.

n-Propyl hydracrylate. (A) When prepared by the method described above for the *n*-butyl ester, but with *n*-propanol instead of *n*-butanol, the yield was 36%.

(B) The following modification was preferable: Approximately 80 g. of dry hydrogen chloride was passed into ether maintained at 10 to 20°. First, *n*-propanol (240 g., 4 moles) and then 142 g. (2 moles) of ethylene cyanohydrin were added (with stirring) to the ether solution. The flask was then allowed to stand at room temperature until the temperature of the contents rose to 40°. After standing for several days, the flask contained an almost solid mass of crystals. By using essentially the isolation procedure described for the *n*-butyl ester, *n*-propyl hydracrylate was obtained from the reaction mixture in 58% yield. In agreement with Drushel and Holden (5), the *n*-propyl ester was observed to be miscible with water.

Ethyl hydracrylate and a fraction that appeared to be impure ethyl *beta*-chloropropionate (Table I) were obtained from ethanol and ethylene cyanohydrin, with the modified (B) propyl hydracrylate procedure. Even after repeated fractional distillations, the constants of the fraction assumed to consist largely of ethyl *beta*-chloropropionate were not identical with those observed with an authentic specimen prepared from ethanol and *beta*-chloropropionyl chloride (Table I). Curtius and Müller (23) also were unable to purify completely ethyl *beta*-chloropropionate obtained as a by-product in the preparation of ethyl hydracrylate.

n-Alkyl beta-acetoxypropionates. Acetic anhydride was added slowly to the alkyl hydracrylates (0.5 mole each), one drop of concentrated sulfuric acid or ten drops of acetyl choride being used as catalyst. After the reaction appeared to be essentially complete, the mixture was warmed on a steam-bath for about one hour. Sodium acetate was added to neutralize the catalyst. The mixture was filtered, and the filtrate was distilled under reduced pressure. Approximately 90% yields of the acetyl derivatives were obtained.

Physical constants. The products were redistilled through 50-cm. Vigreux columns, and middle, narrow-boiling fractions were used for the determination of constants (Tables I and II). Boiling points at about 10 mm. (Fig. 1 and 2) were determined by careful distillation through a similar column, the pressure being read from a Dubrovin gauge (24). The boiling points at atmospheric pressure were less accurate because of some decomposition, but they were only about 4° lower than those calculated by the equation, given below (B_{10} = b.p. at 10 mm.), derived from boiling points of the *n*-alkyl *beta*-ethoxypropionates (17).

$$\text{b.p. at 760 mm.} = \frac{\text{b.p.}_{10} + 84}{0.834}$$

Refractive indices, densities, and viscosities were measured with an Abbé-type refractometer, a 25-ml. Leach pycnometer fitted with a thermometer (similar to 50 ml. size recommended by A.S.T.M. designation D153), and modified Ostwald pipettes that had been calibrated with samples of standard oils furnished by the National Bureau of Standards. The temperature of the baths used in these determinations was controlled within ± 0.05°. Control of pressure at 5.0, 8.0, 10.0, and 15.0 mm. for the data shown in Figs. 1 and 2 was achieved by use of a new-type pressure regulator which allows precise selection and close control of any desired pressure.[8]

Water solubility was determined by a modification of the method of Fordyce and Meyer (25), 50 ml. of water being used instead of 1 liter. The viscosities reported by Müller (26) for the *n*-alkanols were used in the construction of Fig. 4.

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[8] A description of this apparatus has not yet been published.

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