Physical Characterization of a) a Series of Ethyl Esters and b) a Series of Ethanoate Esters[1,2,3]

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THE CHARACTERIZATION of the naturally occurring C_6-C_{18} saturated fat acid esters through various physical constants has been the subject of immediate concern in this laboratory for a number of years. This paper presents data for the physical characterization of (1) the ethyl esters of the aforementioned acids and (2) the ethanoate esters of the saturated monohydric alcohols obtained through the reduction of the respective acids.

Preparation and Purification

Ethyl Esters. The ethyl esters of caproic, capric, lauric, myristic, and palmitic acids (of varying degrees of purity) were furnished by the Kessler Chemical Company. These compounds were purified by repeated fractional distillations, using either a column packed with glass curls or a column packed with single-turn glass helices.

Ethyl caprylate and ethyl stearate were prepared by refluxing Armour's Neo-Fat 7 and 1-65, respectively, with an excess of ethyl alcohol in the presence of concentrated sulfuric acid (5% by weight). The esters were purified by repeated fractional distillations.

Ethanoate Esters. Methyl esters of the naturally occurring saturated fat acids from caprylic to stearic were prepared by reacting the crude acids with an excess of methyl alcohol in the presence of concentrated sulfuric acid (5% by weight). The esters were purified by repeated fractional distillation. The esters from laurate to stearate were also hydrogenated as a part of the purification procedure. The refractive indices of the purified methyl esters corresponded to those reported by Althouse, Hunter, and Triebold (1).

The saturated alcohols having the same carbon content as the above-mentioned acids were prepared by the reduction of the methyl esters with lithium aluminum hydride ($LiAlH_4$). The detailed procedure for this reduction is given by Bonhorst (3).

The crude preparations of octanol, decanol, and dodecanol were purified by fractional distillation. Benzene solutions of each of the alcohols were treated with ethanoic anhydride. The ethanoate esters were purified by fractional distillation.

Benzene solutions of the crude preparations of tetradecanol, hexadecanol, and octadecanol were treated with ethanoic anhydride. The ethanoate esters were purified by fractional distillation.

Hexyl ethanoate was prepared by treating practical n-hexanol (Eastman) with ethanoic anhydride. The ester was purified by fractional distillation.

Physical Characterization

Refractive indices were measured with a Valentine precision refractometer, the prism temperature of which was controlled to ± 0.05° C. The instrument was calibrated by three observers according to the method outlined by Althouse, Hunter, and Triebold (1). The values obtained for the ethyl esters and the ethanoate esters are reported in Table I.

TABLE I

Refractive Indices[a] at Various Temperatures

	20° C	25° C	30° C	35° C	40° C
Ethyl caproate	1.4072	1.4050	1.4029	1.4007	1.3985
Ethyl caprylate	1.4178	1.4157	1.4136	1.4116	1.4095
Ethyl caprate	1.4254	1.4235	1.4215	1.4195	1.4173
Ethyl laurate	1.4315	1.4295	1.4275	1.4255	1.4235
Ethyl myristate	1.4361	1.4340	1.4321	1.4302	1.4282
Ethyl palmitate	....	....	1.4363	1.4343	1.4324
Ethyl stearate	....	....	....	1.4375	1.4355
Hexyl ethanoate	1.4091	1.4068	1.4046	1.4023	1.4002
Octyl ethanoate	1.4193	1.4171	1.4150	1.4128	1.4108
Decyl ethanoate	1.4268	1.4247	1.4227	1.4206	1.4186
Dodecyl ethanoate	1.4326	1.4306	1.4286	1.4265	1.4246
Tetradecyl ethanoate	1.4373	1.4352	1.4332	1.4312	1.4293
Hexadecyl ethanoate	....	....	1.4370	1.4350	1.4332
Octadecyl ethanoate	....	....	....	1.4381	1.4362

[a] Accuracy ± 0.0001.

Density determinations were made with modified Sprengel type pycnometers of about five milliliters capacity. The temperatures of the large water baths were thermostatically controlled to ± 0.05° C. Using distilled water as a standard, and literature values (7) for the absolute density of water in grams per milliliter, volume calibrations of the pycnometers were determined at 35°, 50°, 65°, 80°, and 95° C. The density values for the two series of compounds are shown in Table II. Figures 1 and 2 show a plot of these data.

TABLE II

Densities (grams per milliliter) at Various Temperatures

	35° C	50° C	65° C	80° C	95° C
Ethyl caproate	0.8569	0.8426	0.8284	0.8141	0.7998
Ethyl caprylate	0.8541	0.8410	0.8279	0.8148	0.8017
Ethyl caprate	0.8523	0.8399	0.8275	0.8151	0.8026
Ethyl laurate	0.8506	0.8389	0.8271	0.8153	0.8035
Ethyl myristate	0.8496	0.8383	0.8270	0.8156	0.8042
Ethyl palmitate	0.8489	0.8379	0.8268	0.8158	0.8047
Ethyl stearate	0.8487	0.8378	0.8270	0.8161	0.8053
Hexyl ethanoate	0.8594	0.8454	0.8314	0.8175	0.8036
Octyl ethanoate	0.8558	0.8431	0.8302	0.8174	0.8044
Decyl ethanoate	0.8545	0.8415	0.8293	0.8172	0.8051
Dodecyl ethanoate	0.8520	0.8404	0.8289	0.8173	0.8057
Tetradecyl ethanoate	0.8510	0.8398	0.8286	0.8175	0.8063
Hexadecyl ethanoate	0.8502	0.8393	0.8284	0.8175	0.8066
Octadecyl ethanoate	0.8494	0.8388	0.8282	0.8176	0.8068

Viscosity determinations were made with modified Ostwald viscosimeters of the Cannon-Fenske type which had been calibrated previously under the supervision of M. R. Cannon. The method followed was in accordance with that proposed by the A.S.T.M. in "Standards on Petroleum Products and Lubricants" (2).

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[1] Based in part on dissertations presented by J. W. Shigley, C. W. Bonhorst, and C. C. Liang to the faculty of the Graduate School of Pennsylvania State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Authorized for publication on *December 22, 1953* as paper No. 1848 in the Journal Series of the Pennsylvania Agricultural Experiment Station.

[3] Presented at the 27th fall meeting, American Oil Chemists' Society, Chicago, Nov. 2-5, 1953.

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By using the density values of Table II, the absolute viscosities in centipoise units were calculated for the various compounds. These values are reported in Table III.

TABLE III
Absolute Viscosities in Centipoises at Various Temperatures

	35° C	50° C	65° C	80° C	95° C
Ethyl caproate	0.8182	0.6734	0.5665	0.4832	0.4174
Ethyl caprylate	1.212	0.9780	0.7954	0.6691	0.5867
Ethyl caprate	1.739	1.353	1.087	0.8974	0.7490
Ethyl laurate	2.444	1.854	1.463	1.177	0.9677
Ethyl myristate	3.318	2.433	1.869	1.489	1.231
Ethyl palmitate	4.459	3.208	2.415	1.892	1.516
Ethyl stearate	5.689	4.041	2.986	2.292	1.831
Hexyl ethanoate	0.9102	0.7390	0.6154	0.5233	0.4491
Octyl ethanoate	1.377	1.084	0.8767	0.7275	0.6137
Decyl ethanoate	2.059	1.574	1.239	0.9963	0.8147
Dodecyl ethanoate	2.820	2.080	1.608	1.285	1.047
Tetradecyl ethanoate	3.850	2.792	2.100	1.639	1.326
Hexadecyl ethanoate	5.114	3.581	2.652	2.053	1.634
Octadecyl ethanoate	6.680	4.542	3.301	2.513	1.976

Vapor pressures were determined by a semi-micro method based upon restricted gas flow which was developed by Bonhorst (4, 5) and improved by Liang (6). Details for the calibration of this instrument have been reported by Bonhorst (4) while the exact operating procedure is described by Liang (6). Table IV lists the boiling points of the two series of compounds at various pressures.

Discussion

Density. A previous paper (4), which reported the densities of the methyl, propyl, and isopropyl esters of the C_6-C_{18} saturated acids, showed that for any one series (methyl, propyl, isopropyl) there was an intersection of the density-temperature curves. It can be seen from the present data that the ethyl esters and the ethanoate esters follow this pattern. Whether this intersection occurs at a definite temperature or over a narrow temperature range has yet to be determined. Regardless of the above statement however, it is obvious that density determinations should be made at a temperature as far removed as feasible from the intersection temperature in order to be most useful in characterizing a compound. The approximate intersection temperatures for the various ester series are as follows: methyl 105° C. (4), ethyl 71° C., propyl 75° C. (4), isopropyl 40° C. (4), ethanoate 80° C. The densities of any one series of esters decrease with increase in molecular weight at temperatures below the intersection temperature while at temperatures greater than the intersection temperature the densities increase with increasing molecular weight.

A study of the data for the ethyl esters (Table II) would seem to show that the ethyl stearate values do not behave in exactly the same fashion as the other members of the series. This may indicate that the ethyl stearate is slightly impure or that possibly the ethyl palmitate is slightly impure. Since the density values for ethyl palmitate and ethyl stearate are so close together, it is difficult to differentiate the two esters by means of density measurements. (The density values for ethyl stearate are not shown in Figure 1 because the line would be too close to that for ethyl palmitate to make a clear figure.)

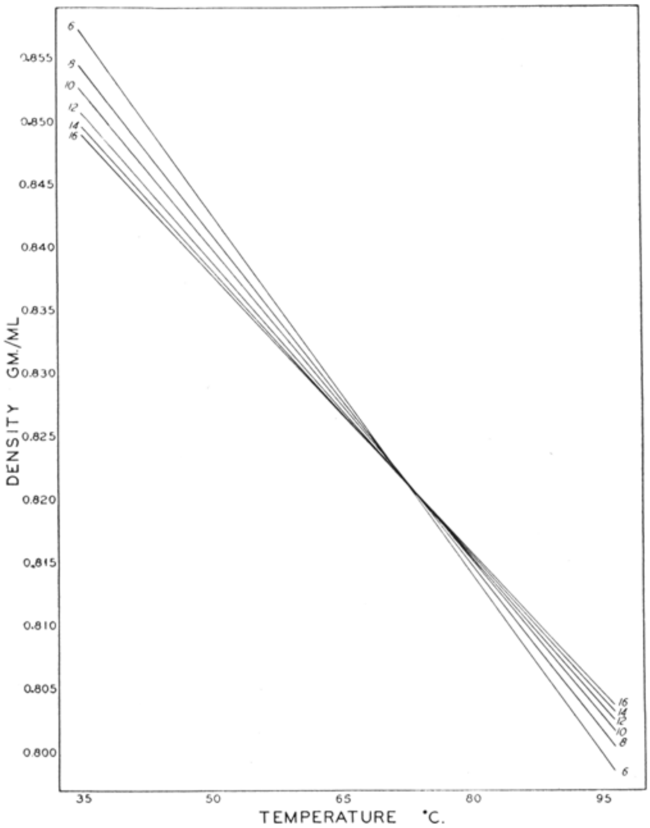

FIG. 1. Relation between Density and Temperature of the Ethyl Esters of Some Saturated Fat Acids. (Numbers correspond to number of carbons in acid portion of ester.)

The densities of the ethanoate esters are slightly higher than those of the corresponding ethyl esters. However the values for compounds of equal carbon content are quite close. The slight difference in values

TABLE IV
Boiling Points at Various Pressures (mm. Hg.)

	2	5	10	20	40	100
	°C	°C	°C	°C	°C	°C
Ethyl caproate	27.1	42.2	54.5	67.7	82.2	103.0
Ethyl caprylate	57.4	73.7	87.0	101.8	117.6	140.8
Ethyl caprate	86.8	103.8	117.9	133.1	149.7	174.0
Ethyl laurate	113.8	131.3	146.0	161.5	178.4	....
Ethyl myristate	134.8	153.3	168.7	184.8	....	....
Ethyl palmitate	156.5	176.2	192.6	....	....	....
Ethyl stearate	181.1	195.6	....	....	....	....
Hexyl ethanoate	31.0	45.6	58.1	71.4	86.1	107.4
Octyl ethanoate	61.5	77.6	91.0	105.5	121.2	144.0
Decyl ethanoate	90.5	107.4	121.3	136.0	152.1	175.9
Dodecyl ethanoate	125.9	133.9	148.3	164.0	180.6	....
Tetradecyl ethanoate	138.5	157.5	172.7	189.0	....	....
Hexadecyl ethanoate	158.0	178.4	196.0	....	....	....
Octadecyl ethanoate	177.2	....	....	....	....	....

might be attributed to the position of the ester linkage with respect to the rest of the molecule. (The density values for octadecyl ethanoate are not shown in Figure 2 because the line would be too close to that for hexadecyl ethanoate to make a clear figure.)

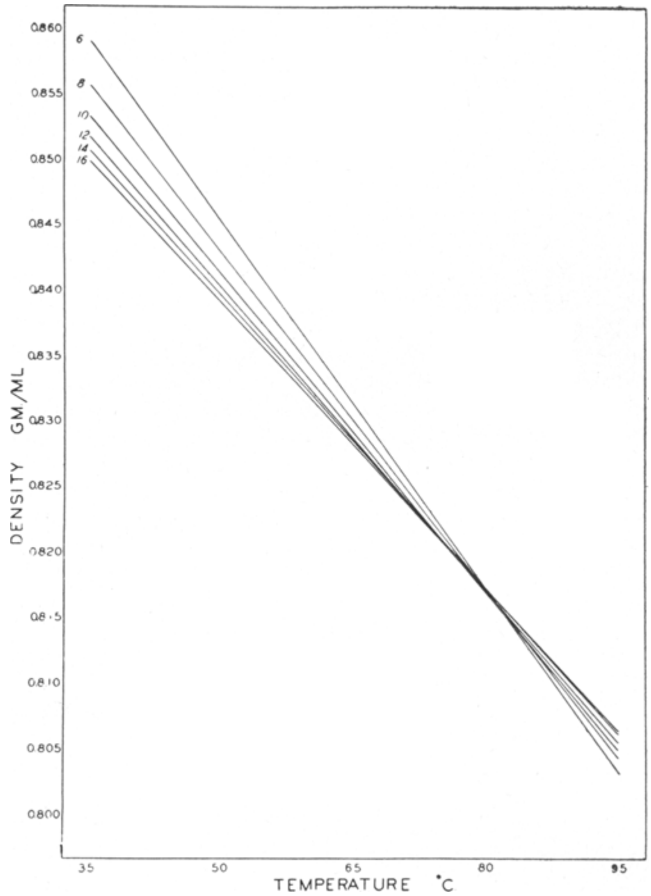

FIG. 2. Relation between Density and Temperature of the Ethanoate Esters of Some Saturated Alcohols. (Numbers correspond to number of carbons in alcohol portion of ester.)

If at some future date it is found that the density-temperature curves for a series of esters intersect at a definite temperature, that fact might possibly be used as a criterion of purity for any member of the series.

Refractive Index. The ethyl esters show a lower refractive index than the corresponding ethanoate esters at all temperatures used in this study. Here again the difference in values between the two series might be attributed to the position of the ester linkage with respect to the rest of the molecule.

By using the Lorentz-Lorenz equation for the calculation of molar refraction, it can be shown that molar refraction is of little practical value as a criterion for the purity of fat acid esters. For example, it is possible to calculate the molar refraction of ethyl laurate, using the refractive index of ethyl laurate and the density value of any of the other esters in the series, and still obtain a value for molar refraction that is close to the calculated theoretical value.

Since refractive index and density are thought to be related properties, it would be interesting to determine the possible effect on refractive index for any one series of esters at the temperature where the density-temperature curves intersect. For any one series the refractive index-temperature curves are close to being parallel straight lines in the temperature range used. It would be of interest therefore to determine refractive indices at higher temperatures than were used in this study. This would indicate whether a gradual change or a sharp change in refractive index occurs as one approaches the temperature where the density-temperature curves intersect.

Viscosity. In each of the two ester series there is an increase in viscosity with increase in molecular weight. There is a decrease in viscosity however with increase in temperature. This decrease is more pronounced at lower temperatures than at higher temperatures. Where compounds of equal molecular weight are considered, the ethanoate esters show a higher viscosity than the ethyl esters.

It should be pointed out that the difference in viscosity values of adjacent members of a given series at the same temperature is large in comparison with the other properties. This property may be especially valuable in differentiating members of any given series of esters.

Boiling Points. As should be expected, in each of two ester series there is an increase in boiling point with increase in molecular weight. When compounds of equal molecular weight are considered, the ethanoate esters exhibit a slightly higher boiling point than do the ethyl esters.

It has been shown throughout this study that, with respect to physical characteristics, the ethanoate esters exhibit higher values than the corresponding ethyl esters. This might be explained on the basis of the position of the ester linkage in connection with the remainder of the molecule. Further studies along this line are in progress.

Summary

Physical characterizations of (1) the ethyl esters of the naturally occurring C$_6$-C$_{18}$ saturated fat acids and (2) the ethanoate esters of the saturated alcohols corresponding to the above acids have been made. They are a) refractive indices at 20°, 25°, 30°, 35°, and 40° C., b) densities and viscosities at 35°, 50°, 65°, 80°, and 95° C., and c) boiling points at several pressures.

The physical characteristics exhibited by the two series of esters are quite similar. However the actual values obtained for the ethanoate esters are slightly higher than those obtained for the corresponding ethyl esters.

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