

Refractive Indices of the Methyl, Propyl, and Isopropyl Esters of the C₆-C₁₈ Saturated Fatty Acids for Various Temperatures Between 20 and 45° C.^{1, 2, 3}

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NUMEROUS references are found in the literature relative to the preparation and purification of the methyl esters of the fatty acids, and the determination of their physical constants (1,2,3,4,5). Similar references are found concerning the ethyl esters of the fatty acids (6,7). However, so far as the authors can determine, no mention has been made of the propyl and isopropyl esters of this series. Consequently the methyl, propyl, and isopropyl esters of the commonly occurring saturated fatty acids were prepared and purified in order that the three homologous series could be compared simultaneously with respect to their physical constants.

Because of its wide application in fat analysis, the refractive index was chosen as the first physical constant to be studied. Although there is an abundance of refractive index data reported in the literature (8,9,10), there is actually little agreement among the values given. As Mattil and Longenecker (10) suggest, these variations in refractive index at any given temperature might be due to a number of factors which include (1) observer error, (2) lack of precise refractometer, (3) poor control of temperature, and (4) poor or complete lack of calibration of the refractometer. Moreover, there has been very little agreement between laboratories as to the temperature at which indices should be determined; each laboratory tending to select the temperature best suited for its apparatus. This is highly undesirable from the standpoint of obtaining indices which are reproducible in other laboratories.

In an effort to report refractive indices in the literature which are readily reproducible, the present authors have (1) eliminated the errors mentioned above and (2) have determined the refractive indices at temperatures from 20-45°C. ± 0.03°C. at five degree intervals.

Experimental

Preparation of Methyl Esters: The methyl esters of caprylic, capric, lauric, myristic, and palmitic acids were prepared by the direct esterification of the respective Neofats with excess methyl alcohol, using concentrated sulfuric acid as the catalyst. In a similar manner, methyl caproate was prepared from caproic acid (Eastman Kodak) and methyl oleate from crude oleic acid which was then converted to methyl stearate by hydrogenation.

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Preparation of Propyl and Isopropyl Esters: The propyl and isopropyl esters of caproic, caprylic, capric, lauric, myristic, and palmitic acids were prepared in two steps. The fatty acids were converted to the corresponding acid chlorides by reaction with thionyl chloride, as outlined by Bauer (11). The esters were prepared by reacting the acid chlorides with propyl and isopropyl alcohol in the presence of pyridine as a catalyst. Propyl and isopropyl stearate were prepared by direct esterification of stearic acid with the alcohols in the presence of dry hydrogen chloride gas.

Purification of the Esters: The iodine number (Wijs) of each ester was determined, and all esters showing any degree of unsaturation were hydrogenated. Each saturated ester was placed in a Claisson flask and rapidly distilled under reduced pressure into three fractions. The "water-white" middle fraction obtained in each case was further purified by fractional distillation through an electrically heated Stedman packed column, at a reflux ratio of better than 50:1.

The various fractions were collected over very narrow boiling ranges. Those which were ultimately selected for the following work were shown to have saponification equivalents very close to the theoretical value (Table 1), and proved by means of their iodine numbers to be completely saturated.

Determination of Refractive Index: A Valentine Improved Precision Refractometer, equipped with a carefully calibrated thermometer, was used to deter-

TABLE 1
Observed Boiling Points and Saponification Equivalents of the Methyl, Propyl, and Isopropyl Esters

Ester	Wt. in gms. of combined fractions	% of total charge	Boiling point °C.	Press. mm. Hg.	Saponification equivalent	
					Observed	Theoretical
Methyl Series						
Caproate.....	13.62	46.6	147	748	130.09	130.11
Caprylate.....	31.74	63.4	187-88	754	158.10	158.14
Caprate.....	36.96	75.1	79	2	186.12	186.17
Laurate.....	34.16	66.5	105	2	214.19	214.20
Myristate.....	41.41	81.5	130	2	242.19	242.23
Palmitate.....	27.01	52.9	151-52	2	270.24	270.26
Stearate.....	35.41	61.7	174	2	298.28	298.27
Propyl Series						
Caproate.....	8.68	34.0	170	753	158.13	158.14
Caprylate.....	6.81	49.7	131-32	40	186.17	186.17
Caprate.....	10.50	62.7	105	2	214.20	214.20
Laurate.....	36.60	68.8	117	2	242.22	242.23
Myristate.....	26.54	53.5	144	2	270.27	270.26
Palmitate.....	10.08	27.0	169-70	2	298.28	298.27
Stearate.....	40.44	23.6	181	2	326.20	326.30
Isopropyl Series						
Caproate.....	8.93	54.8	161	754	158.13	158.14
Caprylate.....	16.13	44.6	124-25	40	186.14	186.17
Caprate.....	25.03	65.1	88-9	2	214.19	214.20
Laurate.....	24.98	52.3	108	2	242.21	242.23
Myristate.....	27.11	61.1	139-40	2	270.22	270.26
Palmitate.....	24.72	51.5	150-51	2	298.29	298.27
Stearate.....	40.76	32.5	177-78	2	326.21	326.30

mine all the indices of refraction. The scale of this instrument is so designed as to allow the observer to read to the fourth decimal place, and to estimate the fifth decimal place with a considerable degree of accuracy. The prism temperature of the refractometer was controlled to $\pm 0.03^\circ\text{C}$. by a Precision constant Temperature Bath and Circulating System.

The refractometer was calibrated with the aid of distilled water and two standard samples of hydrocarbons obtained from the National Bureau of Standards and certified with respect to their indices of refraction at 20, 25, and 30°C .⁵

The refractometer was set for the standard sample, 2,2,4-trimethylpentane (n_D^{20} 1.39145), and allowed to remain at 20°C . for several days to insure that this setting was reliable, before any readings were taken. The two standard samples, distilled water and the twenty-one esters were read at 20°C . by three observers, and the average readings of the observers were recorded. The temperature of the instrument was then changed to 25°C . and, after a twelve-hour interval, the operation was repeated. This procedure was repeated at five-degree intervals up to 45°C .

When all the average readings were recorded, the prism and scale corrections were made as follows:

(1) The observed distilled water values were compared with those reported in the National Bureau of Standards Research Paper No. 1085 (12). The prism correction, thus obtained, was applied to all the readings including the National Bureau of Standards samples.

(2) The observed indices for the National Bureau of Standards samples were compared with the theoretical values as reported on the certificate accompanying the samples. From the values thus obtained, the scale corrections were calculated and applied to the ester indices. (It must be noted that the theoretical values of the standard samples at 35, 40 and 45°C . are extrapolated figures, and are, therefore, not certified values.) The corrected five place readings were reduced to four decimal places with a certainty of ± 0.0001 .

TABLE 2
Corrected Refractive Indices* of the Methyl Esters at Various Temperatures

Esters	20°C .	25°C .	30°C .	35°C .	40°C .	45°C .
M. Caproate.....	1.4053	1.4029	1.4006	1.3983	1.3961	1.3939
M. Caprylate.....	1.4170	1.4148	1.4126	1.4104	1.4083	1.4064
M. Caprate.....	1.4258	1.4237	1.4216	1.4195	1.4173	1.4156
M. Laurate.....	1.4319	1.4298	1.4277	1.4256	1.4235	1.4220
M. Myristate.....	1.4371	1.4350	1.4329	1.4308	1.4288	1.4272
M. Palmitate.....	1.4370	1.4349	1.4330	1.4313
M. Stearate.....	1.4383	1.4362	1.4347

*Corrected to ± 0.0001 .

The refractive indices shown in Tables 2, 3, and 4 indicate that there is an average increment of 0.0004 per degree change in temperature. It will be noted that at 35 and 40°C ., the readings deviate slightly from this average. This deviation may be due to the extrapolated values of the National Bureau of Standards samples used to establish scale correction. The indices at 45°C . show an appreciable deviation which is probably due also to the variation between the extrapolated and correct values of the standards at this temperature plus the fact that at 45°C . a prism correction is necessary for the instrument.

⁵ N.B.S. Standard Sample Number 217 (2,2,4-trimethylpentane) and Number 218 (methylcyclohexane).

TABLE 3
Corrected Refractive Indices* of the Propyl Esters at Various Temperatures

Esters	20°C .	25°C .	30°C .	35°C .	40°C .	45°C .
Pr. Caproate.....	1.4124	1.4101	1.4079	1.4056	1.4034	1.4011
Pr. Caprylate.....	1.4212	1.4191	1.4170	1.4148	1.4127	1.4108
Pr. Caprate.....	1.4281	1.4260	1.4239	1.4218	1.4197	1.4181
Pr. Laurate.....	1.4333	1.4311	1.4290	1.4270	1.4250	1.4234
Pr. Myristate.....	1.4377	1.4356	1.4336	1.4317	1.4298	1.4282
Pr. Palmitate.....	1.4392	1.4372	1.4353	1.4334	1.4319
Pr. Stearate.....	1.4400	1.4380	1.4360	1.4345

*Corrected to ± 0.0001 .

The deviations introduced at higher temperatures may be minimized by determining the refractive indices of the esters in, or as close to, the range of the certified standards as is possible. Thus, it will be noted that the refractive indices of the propyl and isopropyl esters may be determined at 30°C . which is the upper limit of the National Bureau of Standards certified samples. The refractive indices of the methyl

TABLE 4
Corrected Refractive Indices* of the Isopropyl Esters at Various Temperatures

Esters	20°C .	25°C .	30°C .	35°C .	40°C .	45°C .
Is. Pr. Caproate.....	1.4073	1.4051	1.4028	1.4005	1.3982	1.3958
Is. Pr. Caprylate.....	1.4169	1.4147	1.4125	1.4103	1.4081	1.4063
Is. Pr. Caprate.....	1.4242	1.4221	1.4200	1.4179	1.4158	1.4140
Is. Pr. Laurate.....	1.4301	1.4280	1.4259	1.4238	1.4220	1.4203
Is. Pr. Myristate.....	1.4346	1.4325	1.4304	1.4283	1.4266	1.4249
Is. Pr. Palmitate.....	1.4364	1.4344	1.4324	1.4305	1.4290
Is. Pr. Stearate.....	1.4396	1.4376	1.4356	1.4337	1.4321

*Corrected to ± 0.0001 .

esters may be determined at 35°C ., a point close to this upper limit where the extrapolated values are within the limits of reasonable accuracy.

Summary

The methyl, propyl, and isopropyl esters of the $\text{C}_6\text{-C}_{18}$ saturated fatty acids were prepared and purified by fractional distillation.

The refractive indices of the esters were determined by three observers at five-degree intervals between 20 and $45 \pm 0.03^\circ\text{C}$. using a five-place Valentine Improved Precision Refractometer equipped with a Precision Constant Temperature Bath and Circulating System. Prism and scale corrections were calculated through the use of distilled water and two National Bureau of Standards certified samples (2,2,4-trimethylpentane and methylcyclohexane). The corrected indices have been reported to the fourth decimal place with a certainty of ± 0.0001 .

It has been shown that there is an average increment of 0.0004 per degree change in temperature, with an increasing deviation from this average appearing at the higher temperatures of 35, 40, and 45°C .

It has been recommended that the refractive indices of the propyl and isopropyl esters of the $\text{C}_6\text{-C}_{18}$ saturated fatty acids be determined at 30°C . and the methyl esters of the same series at 35°C .

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