# **Refractive Indices of the Methyl, Propyl, and** Isopropyl Esters of the C<sub>6</sub>-C<sub>18</sub> Saturated **Fatty Acids for Various Temperatures Between 20 and 45° C.**<sup>1, 2, 3</sup>

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TUMEROUS 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.  $\pm$  0.03°C. at five degree intervals.

### Experimental

Preparation of Methyl Esters: The methyl esters of caprylic, capric, laurie, 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.

<sup>2</sup> Condensed from the thesis presented by George W. Hunter to the faculty of the Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Philosophy. <sup>3</sup> Presented at the 20th annual fall meeting, American Oil Chemists' Society, Chicago, Oct. 30-31 and Nov. 1, 1946. <sup>3</sup> Authorized for publication on November 21, 1946, as Paper No. 1348 in the Journal Scriege of the Pennsylvania Agricultural Experiment

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Preparation of Propul and Isopropul 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

fractions         Interfact         Observed         Ical           Methyl Series         13.62         46.6         147         748         130.09         130.11           Caproate	Tropyi, and Isopropyi fisters								
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Estor	Ester gms. of total combined charge		point	mm.				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						Observed	Theoret- ical		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Methyl Series				- ·				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		13.62	46.6	147	748	130.09	130.11		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			63.4	187-88	754	158.10	158.14		
Propyl Series         8.68         34.0         170         753         158.13         158.14           Caproate			75.1	79	2	186.12	186.17		
Propyl Series         8.68         34.0         170         753         158.13         158.14           Caproate			66.5		2		214.20		
Propyl Series         8.68         34.0         170         753         158.13         158.14           Caproate					2		242.23		
Propyl Series Caproate					2		270.26		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Stearate	35.41	61.7	174	2	298.28	298.27		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Propyl Series								
Caprylate         6.81         49.7         131-32         40         186.17         186.17           Caprate		8.68	34.0	170	753	158.13	158.14		
Caprate							186.17		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			62.7	105	2	214.20	214.20		
Source         8.93         54.8         161         754         158.13         158.13           Caproate         16.13         44.6         124-25         40         186.14         186.17           Caprylate         25.03         65.1         88-9         2         214.19         214.22	Laurate	36.60	68.8	117	2	242.22	242.23		
Source         8.93         54.8         161         754         158.13         158.13           Caproate         16.13         44.6         124-25         40         186.14         186.17           Caprylate         25.03         65.1         88-9         2         214.19         214.22			53.5	144	2	270.27	270.26		
Source         8.93         54.8         161         754         158.13         158.13           Caproate         16.13         44.6         124-25         40         186.14         186.17           Caprylate         25.03         65.1         88-9         2         214.19         214.22	Palmitate	10.08	27.0		2	298.28	298.27		
Series         8.93         54.8         161         754         158.13         158.14           Caprotate         16.13         44.6         124.25         40         186.14         186.17           Caprate         25.03         65.1         88.9         2         214.19         214.20	Stearate	40.44	23.6	181	2	326.20	326.30		
Caproate	Isopropyl								
Caprylatc         16.13         44.6         124-25         40         186.14         186.15           Caprate			1						
Caprate									
	Caprylate								
Laurate									
Myristate					2				
Palmitate 24.72 $51.5$ $150.51$ 2 298.29 298.25					2				
	Palmitate		51.5		2				
Stearate	Stearate	40.76	32.5	117 <u>7</u> -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  $\pm 0.03$ °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  $30^{\circ}$ C.<sup>5</sup>

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  $45^{\circ}$ 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  $\pm 0.0001$ .

 
 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 M. Caprylate	1.4170	1.4148	1.4126	1.4104	1.4083	1.4064
M. Caprate M. Laurate M. Myristate	1.4319	1.4298	1.4277	1.4256	1.4235	1.4220
M. Palmitate M. Stearate			1.4370	1.4349	$1.4330 \\ 1.4362$	1.4313

\*Corrected to  $\pm$  0.0001.

The refractive indices shown in Tables 2, 3, and 4 indicate that there is an average increment of 0.0004per 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.

 
 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					1.4197	1.4181
Pr. Laurate	1.4333	1.4311	1.4290	1.4270	1.4250	1.4234
Pr. Myristate					1.4298	
Pr. Palmitate		1.4392	1.4372	1.4353	1.4334	1.431
Pr. Stearate	••••••		1.4400	1.4380	1.4360	1.434

\*Corrected to  $\pm$  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.				}	i	
Caproate	1.4073	1.4051	1.4028	1,4005	1.8982	1.3958
Is. Pr.	1 41 00					
Caprylate Is. Pr.	1.4109	1.4147	1.4125	1.4103	1.4081	1.4063
Caprate	1.4242	1.4221	1.4200	1.4179	1.4158	1.414
Is. Pr.						
Laurate Is. Pr.	1.4301	1.4280	1.4259	1.4238	1.4220	1.4203
Myristate	1 4346	1 4325	1 4304	1.4283	1 4266	1.4249
ls. Pr.	1.4040	1.4020	1.4004	1.4200	1.4200	1.141
Palmitate		1.4364	1.4344	1.4324	1.4305	1.4290
Is. Pr.					1 1000	
Stearate	•••••	11.4396	1.4376	1.4356	1.4337	(1.432)

\*Corrected to  $\pm$  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  $C_{6}$ - $C_{18}$  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  $45 \pm 0.03$ °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  $\pm 0.0001$ .

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  $45^{\circ}$ C.

It has been recommended that the refractive indices of the propyl and isopropyl esters of the  $C_{e}$ - $C_{1s}$  saturated fatty acids be determined at 30°C. and the methyl esters of the same series at 35°C.

### Acknowledgment

The authors wish to express their appreciation to Armour and Company for supplying the Neofats used in this work, and to the General Education Board for the funds which made possible the purchase of the

<sup>&</sup>lt;sup>6</sup>N.B.S. Standard Sample Number 217 (2,2,4 trimethylpentane) and Number 218 (methylcyclohexane).

Precision Constant Temperature Bath and Circulating System.

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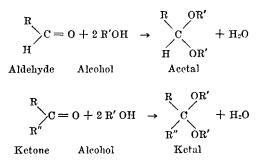
## **Ketals**

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### Structure

**TETALS** are ketone acetals. Just as an acetal is formed by the addition of an aldehyde to an alcohol, so is a ketal formed by adding a ketone to an alcohol.

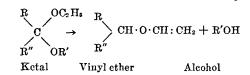


It will be seen that the acetals constitute a special form of the ketals in which one of the substituent groups is a hydrogen atom. The acetals are important in perfumery and have already been described in considerable detail in Soap Perfumery & Cosmetics, June and July, 1945. One of the main reasons for the importance of the acetals is that they provide a means of using the valuable aldehydic perfume constituents without their attendant defects of liability to oxidation and decomposition. In a similar way some of the ketals have found use in perfumery, but they have not yet attained anything approaching the importance of acetals and I think the reason for this is partly that the ketones as a class are so much more stable than the aldehydes. Whereas the danger of the aldehydes decomposing, especially on exposure to the atmosphere, is very great, the ketones are reasonably stable. Consequently whilst some sort of protection is necessary for the aldehydes, and this protection is very conveniently afforded by acetal formation, yet the ketones are stable enough as a rule not to require protection and as a result the development of the ketals has lagged behind that of the acetals.

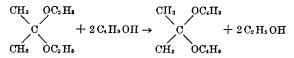
There are, however, special cases where the protection of the ketone is desirable, and there are other cases where the conversion of a ketone to a ketal is accompanied by a change of odour, which may be desirable, and in some cases, indeed, the ketal may have a nuance not otherwise obtainable.

### Properties

As a general rule ketals are colourless liquids with characteristic odours. Acetone dimethyl acetal (CH<sub>3</sub>)<sub>2</sub> C (OCH<sub>3</sub>)<sub>2</sub> boils at 83°C. and the corresponding ketal from acetone and ethyl alcohol which is acetone diethyl acetal (CH<sub>3</sub>)<sub>2</sub> C (OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> boils at 114°C. They lose alcohol when heated and form vinyl ethers



When ketals of the lower alcohols are boiled with alcohols of greater molecular weight exchange of alkyl groups takes place



Monomeric ketals will react with polyvinyl alcohol in the presence of a catalyst such as sulphuric acid and in a substantially anhydrous solvent such as methanol to give polyvinyl ketals (1).

### Preparation

1. Ketals may be prepared by reacting ketones with orthoformic esters in the presence of alcohols. Small quantities of anhydrous acids are necessary to promote the reaction

$$(CH_s)_2CO + H \cdot C(OC_2H_s)_3 \rightarrow (CH_s)_2C + H \cdot CO \cdot OC_2H_s$$
  
acetone orthoformic diethylal ethyl  
ester acetone formate

2. Although British Patent 352,474 (2) is concerned primarily with the formation of acetals by the addition of alcohols to vinyl ethers, the possibility is envisaged in the specification of preparing ketals by the addition of alcohols to substituted vinyl ethers. Whilst vinyl ethyl ether and butanol react to give an acetal known as acetaldehyde-ethyl-normal-butyl acetal

$$CH_2: CH \cdot O \cdot C_2 H_5 + C_4 H_9 OH \rightarrow CH_3 CH$$

$$OC_4 H_9$$

$$Vinyl ethyl ether butyl alcohol acetaldehyde-ethyl-butyl acetal$$

dimethyl vinyl ethyl ether would react with butanol to give a ketal

