at least 9 months thereafter, if sprayed with a solution of cysteine hydrochloride when the fruit is first cut.

An interesting application of this principle is based upon the fact that pineapple juice often contains a sulfhydryl compound (probably glutathione) which serves as the natural activator of the bromelin. It should therefore be possible to substitute a pineapple juice of high proteolytic activity for the glutathione and cysteine. Laboratory experiments have indicated that this is the case. Pineapple juice may be fermented, freed from alcohol, and concentrated without losing its property of inhibiting apple darkening.

In these experiments, slices of apple dried after treatment with pineapple juice were always lighter than control slices which underwent no treatment. As a rule they did not look as well as fruit treated with cysteine or glutathione. There was a great difference between various samples of pineapple juice in respect to the color of the dried apples; until the reason for this variation is better understood, it would be unwise for anyone to attempt a technical process depending on pineapple juice to prevent fruit darkening. The underlying principle of such a process, however, seems to be established.

The applicability of peroxidase inhibitors as deterrents of fruit discoloration lays the foundation of many possible processes for the technical handling of those fruits and vegetables whose darkening is partly or wholly accelerated by this ferment.

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Properties of 1-Octadecene, *n*-Octadecane, and Di-*m*-tolylethane

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METHODS of synthesis are recorded for a large number of hydrocarbons whose molecular weights are in excess of 200. However, the data concerning the physical properties of these hydrocarbons of higher molecular weight are quite meager. This investigation was undertaken with two objects: (1) to synthesize a small number of hydrocarbons whose properties would resemble those of lubricating oils of low viscosity and (2) to study the chemical and physical properties of these hydrocarbons in an effort to determine whether or not any of these properties are related to "oiliness."

It is hoped that the work recorded in this report may be of some service in helping to determine which compounds are valuable in reducing friction, and that it may also aid in the identification of some of these compounds which may be isolated from petroleum.

PREPARATION OF HYDROCARBONS

The three hydrocarbons chosen for this study were prepared as follows:

1-Octadecene was prepared according to the method of Krafft (*8*) which consists in distilling octadecyl stearate under a pressure of 120 to 140 mm. of mercury. This distillation caused the decomposition of the ester into 1-octadecene and stearic acid according to the following equation:

$$C_{17}H_{35}CH_2OOCC_{17}H_{35} = C_{18}H_{36} + C_{17}H_{35}COOH$$

Oxidation of the hydrocarbon with potassium permanganate and analysis of the oxidation products indicated that the hydrocarbon was practically pure 1-octadecene. Octadecyl stearate was prepared by treating octadecyl alcohol with stearyl chloride, allowing the reaction product to cool, pulverizing, and washing twice with warm (65° C.) 95 per cent alcohol. Octadecyl alcohol was prepared by reducing ethyl stearate with sodium and absolute alcohol according to the method of Ford and Marvel (*6*).

n-Octadecane was prepared from 1-octadecene by hydrogenation under a pressure of 3 atmospheres of hydrogen. The platinum black–platinum oxide catalyst used for the hydrogenation was prepared according to the method recommended by Adams (*2*). The apparatus used for hydrogenation was similar to that suggested by Adams (*1*).

Di-*m*-tolylethane was prepared by the oxidation of *m*-xylene with potassium persulfate as recommended by Moritz and Wolffenstein (*13*). Di-*m*-tolylethane prepared by this method is identical with that prepared by Carré (*3*), using the reaction between magnesium and *m*-xylyl bromide.

It was desired to include heptadecene in this study, and two attempts were made to synthesize this hydrocarbon. In the first attempt the method of Mai (*11*) was followed, and a fraction distilling between 148° and 153° C. (6 mm. pressure) was obtained. Elementary analysis of this fraction gave the following results:

	THEORETICAL FOR $C_{17}H_{34}$	FOUND	
	%	%	%
Carbon	85.62	85.43	85.42
Hydrogen	14.38	14.45	14.42

Oxidation of this fraction with potassium permanganate and analysis of the oxidation products showed this material to be a mixture of substances and not pure heptadecene. In spite of this fact, its properties were determined and tabulated with those of the hydrocarbons. A second attempt to prepare heptadecene, by the method of Krafft (*8*), gave so small a yield that a determination of properties was not feasible.

In addition to the hydrocarbons, two fractions were prepared from an asphalt-base crude oil; these fractions were prepared with distillation ranges of 160° to 166° C. (10 mm. pressure) and 171° to 177° C. (10 mm. pressure) which have as mid-points the boiling points of di-*m*-tolylethane (163° C.) and octadecene (174° C.), respectively.

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Table I. Molecular Refractivities of Hydrocarbons

	Theoretical	Determined
1-Octadecene	84.89	85.17
n-Octadecane	85.36	85.44
Di-*m*-tolylethane	68.90	69.81

Table II. Iodine Number, Acid Number, and Molecular Weight of Hydrocarbons and Petroleum Fractions

	Iodine No.	Acid No.	Mol. Weight
Mai 148–153° fraction	100.8	Neutral	257.0
1-Octadecene	94.9	Neutral	247.0
n-Octadecane	2.8	Neutral	251.5
Di-*m*-tolylethane	4.1	1.49	206.5
Petroleum 160–166° fraction	20.6	0.94	238.7
Petroleum 171–177° fraction	18.1	0.79	251.3

Table III. Surface Tension and Interfacial Tension of Hydrocarbons and Petroleum Fractions

	Surface Tension	Interfacial Tension[a]
	Dynes/cm.	
	at 22° C.	
Mai 148–153° fraction	28.49	343.3
1-Octadecene	29.20	457.4
n-Octadecane	Solid	Solid
Di-*m*-tolylethane	36.30	Not detd.
Petroleum 160–166° fraction	29.87	850.9
Petroleum 171–177° fraction	29.87	675.1
	at 32° C.	
1-Octadecene	27.63	643.0
n-octadecane	27.58	494.9

[a] In arbitrary units.

Table IV. Specific Gravity and Refractive Index of Hydrocarbons and Petroleum Fractions

	Specific Gravity					Refractive Index	
	5° C.	12° C.	22° C.	32° C.	42° C.	22° C.	32° C.
Mai 148–153° fraction	0.8454	0.8500	0.8447	0.8401	0.8357	1.4565	....
1-Octadecene	Solid	Solid	0.7884	0.7863	0.7823	1.4443	1.4411
n-Octadecane	Solid	Solid	Solid	0.7790	0.7756	Solid	1.4344
Di-*m*-tolylethane	0.9796	0.9756	0.9703	0.9661	0.9623	1.5566	....
Petroleum 160–166° fraction	0.8923	0.8879	0.8818	0.8788	0.8754	1.4911	....
Petroleum 171–177° fraction	0.8980	0.8937	0.8888	0.8854	0.8821	1.4945	....

For the preparation of these fractions, the petroleum was first distilled under atmospheric pressure until the temperature reached 175° C.; the residue was then distilled under a pressure of 1 mm. without the use of a fractionating column. At this pressure the distillate boiling below 125° C. was discarded and two fractions were recovered, one distilling from 125° to 150° C. and the other from 150° to 175° C. These fractions were then fractionated twice, using a fourteen-plate column, to secure the fractions with distillation ranges of 160° to 166° C. and 171° to 177° C. at 10 mm. pressure. The physical and chemical properties of these fractions were determined and are tabulated with the properties of the hydrocarbons.

PROPERTIES OF HYDROCARBONS AND PETROLEUM FRACTIONS

The acid numbers of the hydrocarbons and of the petroleum fractions were determined by dissolving a sample in 100 ml. of neutral solvent (50 parts of benzene plus 50 parts of 95 per cent alcohol), refluxing for one hour, and titrating when cool with 0.1 *N* potassium hydroxide with phenolphthalein as indicator. Iodine numbers were determined by the method of Huebl as described by Scott (*14*).

Surface tension was determined by means of the Traube stalagmometer. Interfacial tension between the oils and water was determined by means of the same instrument by allowing the oil to drop into water; interfacial tensions are recorded in arbitrary units for comparison only.

Specific gravities were determined by the use of a pycnometer of approximately 10 ml. capacity. The Abbé refractometer was used to determine refractive indices. From the refractive index and the specific gravity, the molecular refractivity was calculated according to the equation of Lorenz and Lorentz (*9*). Molecular refractivity was calculated for the hydrocarbons only; fair agreement between theoretical and calculated molecular refractivity was obtained except in the case of di-*m*-tolylethane. Molecular weights were determined by the cryoscopic method, using benzene as the solvent. Viscosity was determined by means of the Washburn modification of the Ostwald viscometer (*12*).

It is not known that there is any relation between the dielectric constant and the "oiliness" of a substance; it was, however, deemed advisable to determine the dielectric constants of the materials studied in order to provide more information concerning them. The dielectric constant was determined by the heterodyne beat method described by Smyth (*15*). The circuit used was essentially the same as that given by Smyth; only minor changes were introduced to secure greater sensitivity:

> The cell used in this determination was composed of two coaxial brass cylinders, a solid inner cylinder of 7.5 mm. radius, and a hollow outer cylinder of 8 mm. inside radius and 12 mm. outside radius. Both cylinders were 60 mm. in length. The inner cylinder was separated from the outer by small pieces of mica set at intervals along both top and bottom of the cell; extreme care was taken to see that the same thickness of mica was used in each spacing so that the inner cylinder was symmetrically spaced from the outer. A small brass rod was threaded into each of the cylinders, and contact was made by means of mercury cups. The entire cell was inserted in a short, close-fitting, glass cylinder; approximately 15 ml. of material were required to fill the cylinder and submerge the cell. The calculated capacitance of the cell was approximately 50 micromicrofarads. The cell was calibrated by use of *n*-heptane ($K = 1.923$). Determinations of the dielectric constant were made at a frequency of 150 kilocycles and at a temperature of 25° C.

The "oiliness" of a lubricant has been defined by Wilson and Barnard (*16*) "as that property by virtue of which one fluid gives lower friction coefficients at low speeds or high loads than another fluid of the same viscosity." Wilson and Barnard preferred to measure the coefficient of friction in the neighborhood of zero velocity, but they found (*17*) that slightly greater reproducibility of results may be obtained at speeds in the neighborhood of 15 cm. per minute. In the present investigation the Herschel machine (*7*) was used.

Table V. Viscosity of Hydrocarbons and Petroleum Fractions

(In millipoises)

	5° C.	12° C.	22° C.	32° C.	42° C.
Mai 148–153° fraction	173.28	132.91	88.51	66.61	48.51
1-Octadecene	Solid	Solid	40.10	33.75	26.34
n-Octadecane	Solid	Solid	Solid	35.57	27.90
Di-*m*-tolylethane	119.15	95.69	63.49	46.88	34.84
Petroleum 160–166° fraction	179.35	129.30	86.03	60.40	43.97
Petroleum 171–177° fraction	272.54	190.36	118.24	79.33	56.69

Table VI. Coefficient of Dynamic Friction and Dielectric Constant of Hydrocarbons and Petroleum Fractions

	Coefficient of Fraction at 22° C.	Dielectric Constant at 25° C.
Mai 148–153° fraction	0.148	3.273
1-Octadecene	0.106	2.246
n-Octadecane	Solid[a]	2.149
Di-*m*-tolylethane	0.230	2.760
Petroleum 160–166° fraction	0.155	2.442
Petroleum 171–177° fraction	0.153	2.442

[a] 0.096 at 25° C. The coefficient of dynamic friction does not change over a range of temperature of 3° C.

This machine measures the coefficient of friction at low speeds and high pressures. Since the hydrocarbons and oils were not all of the same viscosity, the coefficient of friction does not give an exact measure of their "oiliness;" however, since these substances were not widely divergent in viscosity, the coefficients of friction do give a fairly accurate measure of their "oiliness."

The preparation of the friction surfaces for each run with the machine is important:

> The surfaces used in this study were a disk of high-grade babbitt metal and a slider (weight, 129 grams) composed of three steel balls clamped between two aluminum plates. After washing with benzene, the polished face of the disk was rubbed in a thin paste of chromium oxide and water on broadcloth until all scratches were removed. Excess chromium oxide was removed from the disk with moist filter paper. The disk was then moved to another place on the broadcloth and polished until a bright clean surface was obtained; this surface was immediately covered with the oil to be tested. The surfaces of the steel balls were prepared in the same manner. Most of the determinations of the coefficient of friction were made at 22° C., but it was found that this property does not change over a small temperature range (3° C.). It is therefore possible to make a direct comparison between the coefficient of friction and the dielectric constant, although the latter property was measured at 25° C.

The substance designated "Mai 148–153° fraction" in Tables I to VI is the material which was secured in the attempt to synthesize heptadecene by the method of Mai (*11*). The petroleum fractions are designated "petroleum 160–166° fraction" and "petroleum 171–177° fraction." The melting point of 1-octadecene was 18° C. and that of *n*-octadecane 25° C.

Discussion of Results

The number of hydrocarbons studied was not large enough to permit a final decision to be made concerning the "oiliness" of the various series of hydrocarbons. The small difference between the coefficients of friction given by 1-octadecene (0.106) and *n*-octadecane (0.096) indicates that unsaturation is not an important factor in "oiliness." This is in agreement with the results obtained by Dover (*5*) but is at variance with the theory propounded by Deeley (*4*) who believed that the unsaturated compounds were superior in the property of "oiliness." Di-*m*-tolylethane gave a high coefficient of friction (0.230), indicating that probably the diphenyl-substituted paraffins are deficient in the property of "oiliness;" this is in agreement with the ideas of Mabery (*10*) who believed that the members of the C_nH_{2n-14} series are poor lubricants. The viscosity of di-*m*-tolylethane was not enough greater than that of the straight-chain compounds of similar molecular weight to allow us to assume that bicyclic compounds of this type are viscosity carriers.

There was no indication that any physical property is directly related to the property of "oiliness." It is worthy of note, however, that, if we exclude the results for the "Mai 148–153° fraction," there is a parallel between the dielectric constant and the coefficient of friction (Table VI); a high dielectric constant accompanies a high coefficient of friction, and a low dielectric constant accompanies a low coefficient of friction. More work would have to be done along this line before any general relationship could be claimed. Since the straight-chain hydrocarbons gave relatively low coefficients of friction, the petroleum fractions (which were presumed to be largely of cyclic structure) gave higher coefficients of friction, and the bicyclic hydrocarbon gave a much higher coefficient of friction, it seems probable that the straight-chain hydrocarbons possess the property of reducing friction to a greater extent than the cyclic hydrocarbons.

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