Table VI. Data to Show that Same Degree of Extraction is Obtained for Each Treated Crude and Its Treated Fractions

(Using Groennings procedure calculated as micrograms per gram of original crude, p.p.m.)

Crude	Oil Phase		Water Phase	
B. C. Prescott	Ni	V	Ni	V
Asphaltenes	1.0	2.7	0.76	0.78
Oil fraction	0.88	6.96	2.60	5.54
Total	1.88	9.66	3.36	6.32
Crude	3.28	12.75	2.63	7.25
14-T				
Asphaltenes	10.0	38	10.5	20.0
Oil fraction	1.29	8.5	7.75	11.5
Total	11.29	46.5	18.25	31.5
Crude	6.0	46.0	18.0	36.0
Venezula				
Asphaltenes	13.6	57.0	42.6	66.0
Oil fraction	1.0	8.0	30.0	36.0
Total	14.6	65.0	72.6	102.0
Crude	14.5	58.0	77.0	92.0

The deviation for the sum of the metal content in the asphaltenes and the oils compared to the metal content of the whole crude was from 0.3 to 14%. Duplicate results on a single sample varied from 0.2 to 5.4% and parallel results on similiar samples varied from 0.2 to 10%, the B. C. Prescott oil excepted. Many of the values for this oil ran below 10 p.p.m. Standard curves yielded an accuracy of about 25% in this range.

For these reasons, the experimenters feel sure that there are at least three classes of metallic complexes in crude petroleum: (1) the metallic porphyrins, (2) metallic compounds—nonporphyrins which are easily decomposable by glacial acetic-hydrobromic acid mixtures, and (3) metallic compounds—nonporphyrins which are not readily decomposed by glacial acetic-hydrobromic acid mixtures.

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Some Physical Properties of Certain C_9 and C_{10} Aliphatic Acids and Their Methyl Esters

2-Ethylheptanoic and Pelargonic Acids, and Methyl Esters of 2-Ethylpentanoic, Pelargonic, 2, 5-Diethyladipic, 2-Ethylsuberic, and Sebacic Acids.

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THE COMMERCIAL process for the manufacture of Isosebacic acid produces a mixture of 2,5-diethyladipic acid (12 to 18%), 2-ethylsuberic acid (72 to 80%), sebacic acid (6 to 10%), and small amounts of pelargonic and 2-ethylheptanoic acids. The data recorded herein are concerned with two of these five acids and the methyl esters of all five acids.

Scattered data are available in the literature on pelargonic acid, 2-ethylheptanoic acid, methyl pelargonate, and dimethyl sebacate. The most recent data on pelargonic acid are those given by Mumford and Phillips (*6*). They recorded the freezing point as 12.0° C., boiling point as 254° C. at 760 mm. of mercury, specific gravity as 0.9052 at 20° C. referred to water at 0° C., and refractive index as 1.4322 at 20° C. with sodium *D* line. Eggenberger and others (*3*) give a value of 12.52° C. as the melting point of pelargonic acid. Dorinson, McCorkle, and Ralston (*2*) report the refractive index of pelargonic acid at temperatures from 20° to 80° C. and the density as 0.8570 gram per ml. at 80° C. Pool and Ralston (*7*) give the boiling point of pelargonic acid at different temperatures from a vapor pressure of 1 mm. of mercury to the boiling point at 1 atm. The values cited by Pool and Ralston for vapor pressure are generally lower than those given in this article over the temperature range studied. The purity of the compounds was established by chromatography, so the values reported here may be considered as taken on compounds of known composition.

Methyl pelargonate was prepared by the Gartenmeister method (*5*), and its boiling point established as 213.5° C. at 760 mm. of mercury. Walbaum and Rosenthal (*11*) reported the specific gravity as 0.8799 at 15° C. *vs.* water at 4° C. and the refractive index as 1.42135 at 20° C. using the sodium *D* line.

Royals and Covington (*9*) describe the preparation of

2-ethylheptanoic acid and give its boiling point as 121-2° C. (6 mm. of mercury) and its refractive index as 1.4255 using the sodium *D* line.

Literature data on dimethyl sebacate which are related to this work are as follows: specific gravity of 0.9432 at 78° C. *vs.* water at 4° C. (*4*); melting point 27.5° C. (*8*); and refractive of 1.41364 at 78° C. using the sodium *D* line (*4*).

EXPERIMENTAL

The C_9 acids were prepared by fractional distillation of large volumes of the crude acids obtained from the commercial process of synthesis. The fractionation was carried out in a Podbielniak Helipak column 36 inches by 13 mm. at 10 mm. of mercury pressure with a reflux ratio of 60 to1. The purity of the acids, checked by gas chromatography, was as follows: pelargonic 99.7% and 2-ethylheptanoic acid, 99.6%.

The methyl esters of both the C_9 and C_{10} acids were prepared either by esterification of the acids with methanol or by reaction of the appropriate acid with diazomethane. The purity of the esters, measured by gas chromatography, was as follows: methyl pelargonate, 99.9%; methyl 2-ethylheptanoate, 99.8%; dimethyl 2,5-diethyladipate, 99.9%; dimethyl 2-ethylsuberate, 99.9%; and dimethyl sebacate 99.8%. The diazomethane was prepared by the deBoer and Backer procedure (*1*) with the esterification carried out in a diethyl ether solution.

The density was measured by a pycnometer. The boiling points and vapor pressures of 2-ethylheptanoic and pelargonic acids were measured with a Swietoslawski-type ebulliometer (*10*). The gas heating element was replaced with an internal electrical heating element. The pressure was maintained constant by a mercury manostat, and the temperatures were measured with an iron-constantan thermocouple. 2-Ethylheptanoic acid decomposed at atmospheric pressure (753 mm. of mercury) in air with the evolution of water. The refractive indices were measured with a Bausch and Lomb precision laboratory model refractometer while the temperature was controlled to ±0.03° C.

RESULTS AND DISCUSSION

Table I summarizes the physical data on boiling points, refractive indices, and densities of 2-ethylheptanoic acid and the methyl esters of pelargonic, 2-ethylheptanoic, diethyladipic, sebacic, and suberic acids. The melting point of dimethyl sebacate was found to be 26.8° C. at atmospheric pressure, lower than Rennkamp's value (*8*). Even though the purity of the diemthyl sebcate was established by chromotography, a cooling curve was also run on the compound, and no evidence of any impurity was found. The authors feel that the purity of the compound is well established and thus, the value for the melting point of the ester is correct.

Table I. Boiling Points, Refractive Indices, and Densities of 2-Ethylheptanoic Acid and the Methyl Esters of Some C_9 and C_{10} Aliphatic Acids

Compound	B. P., ° C. (at Reduced Pressure, Mm. Hg)	Refractive Index n_D^{25}	Density, G./Ml. 25° C.
2-Ethylheptanoic acid	153.0 (31)[a]	1.42470[b]	0.8916[c]
			0.8935
			0.8969[d]
Dimethyl 2, 5-diethyladipate	146.5 (20)	1.43162	0.9860
Dimethyl 2-ethylsuberate	151.5 (15)	1.43412	0.9888
Dimethyl sebacate	175.0 (20)	1.43416	0.9944
	157.0 (9.5)		
Methyl 2-ethylheptanoate	108.0 (45)	1.41607	0.8644
Methyl pelargonate	122.0 (45)	1.41395	0.8655

[a] Number in parenthesis indicates pressure.
[b] Refractive index at 30° C.
[c] Density at 30° C.
[d] Density at 20° C.

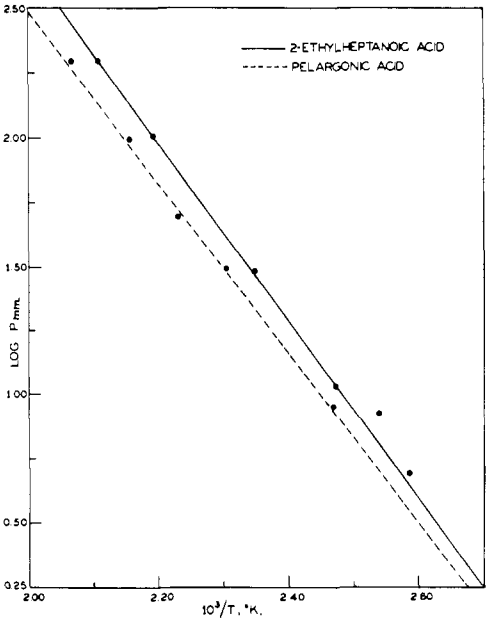

Figure 1. Vapor pressure-temperature curves for 2-ethylheptanoic and pelargonic acid

The results of the vapor pressure data on 2-ethylheptanoic acid and pelargonic acid are shown graphically in Figure 1. The lines were fitted by the method of least squares. The vapor pressure equations for the two acids were established graphically and are found to be

$$\text{2-Ethylheptanoic: } \log P_{(\text{mm.})} = \frac{-3314}{T} + 9.28 \quad (386.66 \leq T \leq 474.66)$$

(Standard deviation: 1.28 mm. Hg)

$$\text{Pelargonic: } \log P_{(\text{mm.})} = \frac{-3351}{T} + 9.23 \quad (386.66 \leq T \leq 483.16)$$

(Standard deviation: 2.66 mm. Hg.)

From these data, one calculates the latent heat of vaporization of 2-ethylheptanoic acid to be 16.0 ± 0.5 kcal. per mole (426.2 ≦ T ≦ 474.7). Further data on C-10 acids and their methyl esters will be available later.

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