LEVULINIC ACID.   II.   THE VAPOR PRESSURES OF ITS ALKYL ESTERS (C₁-C₆)[1]

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In view of the fact that the chemistry of levulinic acid has been the subject of numerous investigations in the past, it is perhaps strange that its esters, with the exception of the ethyl form, have been little investigated until recently.   The most comprehensive previous study of the alkyl esters of this acid has been made by Sah and Ma,[2] who have described the method of preparation, some physical properties, and two derivatives of each of seven of its esters.   Previous to their work, only the methyl, ethyl and n-propyl derivatives had been studied.

The purpose of the present investigation was to study the boiling point–pressure relationships of a series of the alkyl esters of levulinic acid.   In the course of this work, the methyl, ethyl, n-propyl, n-butyl, n-amyl, n-hexyl, isopropyl, isobutyl, and isoamyl esters were prepared and studied.   Of these, the n-amyl and n-hexyl esters have not been described hitherto in the literature.

Experimental

Preparation of the Esters.—The esters were prepared by the direct esterification of levulinic acid[3] (n^{40} 1.4342; b. p. 106–108° (2 mm.).   The alcohols were purified by treatment with lime and subsequent fractional distillation from potassium hydroxide. In all cases the alcohols were made to absorb 3% of their weight of hydrogen chloride immediately before esterification.   Except in the preparation of the n-amyl and n-hexyl levulinates, where acid and alcohol were used in a ratio of three to one, six moles of alcohol were always treated with one mole of acid.   The excess acid in the case of the n-amyl and n-hexyl derivatives was removed after the reaction had reached equilibrium by neutralizing it in a cooled flask with 3.3 N sodium hydroxide solution.   The water-insoluble ester layer was then drawn off from the aqueous layer.

It was found that yields of the esters could be increased if the water formed in the reaction is removed with the aid of carbon tetrachloride by means of a continuous separator.[4]   However, n-butyl and isoamyl alcohols are sufficiently insoluble in water so that a separation can be made without the use of this reagent.   The average yield of ester without separation of water was found to be 74.4%; with separation of water, 84.6%.

Each ester was twice fractionally distilled; the fraction finally retained had, in each case, a maximum boiling range of 2° at 3 mm.   The observed physical constants are set down in tabular form (Table I) and, that they may be readily compared with those reported by Sah and Ma,[2] are also presented graphically (Figs. 1 and 2).

[2] Sah and Ma, THIS JOURNAL, 52, 4880 (1930).

[3] Thomas and Schuette, ibid., 53, 2324 (1931).

[4] Hultman, Davis and Clark, ibid., 43, 366 (1921).

TABLE I

PHYSICAL PROPERTIES OF LEVULINIC ACID ESTERS

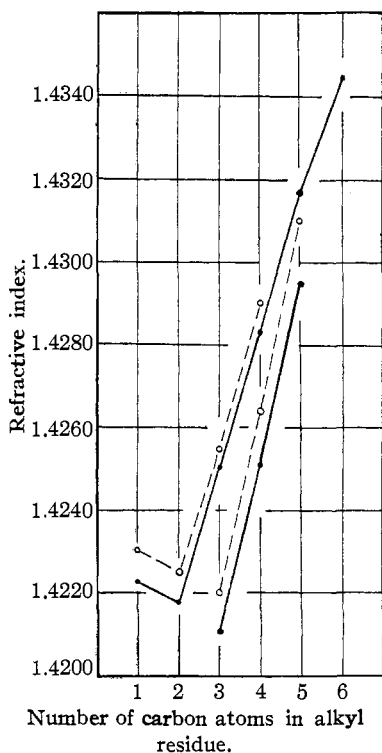|		Specific gravity at 20°/4°			
				Difference	
Alkyl	n^{20}	Obs.	Calcd.	G.	%
Methyl	1.4223	1.05145	1.05015	+0.00130	0.12
Ethyl	1.4218	1.01346	1.00864	+ .00482	.48
n-Propyl	1.4251	0.99007	0.98990	+ .00017	.017
Isopropyl	1.4211	.98005	.....	....	
n-Butyl	1.4283	.97350	.97556	− .00206	.21
Isobutyl	1.4251	.96926	.....	....	
n-Amyl	1.4316	.96357	.96348	+ .00009	.009
Isoamyl	1.4294	.95827	.....	....	
n-Hexyl	1.4343	.95332	.95282	+ .00050	.052

Fig. 1.—Refractive indices of alkyl (straight and branched chain) levulinates.
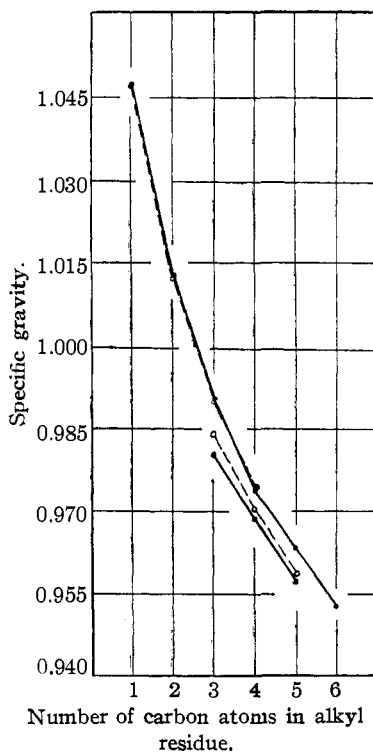

Fig. 2.—Specific gravities of alkyl (straight and branched chain) levulinates.

Specific Gravities.—The variation of specific gravities of the normal esters is sufficiently regular so that this property may be concisely expressed by the equation

$$488.18 \, d^2 - 1029.1 \, d + 543.34 = c$$

in which d represents the specific gravity of the ester and c the number of carbon atoms in the alkyl radical of the ester. It is probable that this empirical expression can be

used to predict with fair accuracy the specific gravities of the higher esters of this homologous series. This formula has been applied to the esters prepared in this investigation and found to give values which vary from the observed ones by less than five-tenths of one per cent.

Vapor Pressures.—An electrically heated modification of the Ramsay and Young[5] type of apparatus was used to determine the vapor pressures of the esters. The electrical method of heating was found to be quite satisfactory as it admits of close and rapid control. Duplicate runs of about twenty-five readings were made for each ester. Temperatures were read to 0.1° with accurate thermometers. The readings are accurate to $\pm 0.1°$ in the lower temperature ranges with the accuracy falling off to $\pm 0.7°$ at the highest temperatures. Pressures were read on a closed manometer which had been corrected by reference to a standard barometer. Pressure readings are accurate to ± 0.2 mm. It was evident that there was some decomposition of the ester during the latter part of each run, as shown by the fact that a small amount of carbonaceous residue was formed at the place of evaporation.

The relation between boiling temperatures and vapor pressures of each ester was shown by calculating the appropriate constants for the Kirchhoff[6] formula, $\log P = A + B \log T + C/T$. The resulting equations (Table II) were used to compute the boiling points of the esters at 760 mm.

By means of these equations and the Clausius–Claperon equation

$$L = [2.303R] [T_1 T_2/(T_2 - T_1)] [\log_{10} P_2/P_1]$$

the molar heats of vaporization were calculated for a vapor concentration of 0.00507 mole per liter following the method of Hildebrand.[7]

TABLE II

PRESSURE–TEMPERATURE RELATIONSHIPS OF LEVULINIC ACID ESTERS

Alkyl	Log P	B. p. (760 mm.), calcd., °C.
Methyl	$55.3575 - 15.350 \log T - 5390.2/T$	197.7
Ethyl	$46.5630 - 12.426 \log T - 4972.5/T$	206.2
n-Propyl	$29.9827 - 6.948 \log T - 4144.4/T$	221.2
Isopropyl	$26.3112 - 5.818 \log T - 3765.8/T$	208.2
n-Butyl	$27.0531 - 5.970 \log T - 4089.1/T$	237.8
Isobutyl	$33.8077 - 8.188 \log T - 4429.5/T$	229.9
n-Amyl	$38.1533 - 9.536 \log T - 4906.6/T$	253.2
Isoamyl	$26.4476 - 5.779 \log T - 4098.4/T$	247.9
n-Hexyl	$32.6214 - 7.699 \log T - 4699.5/T$	266.8

The entropies of vaporization (Table III) derived from these values are higher than the average of 27.3 for normal liquids, pointing to the conclusion that the esters are associated liquids.

    [5] Ramsay and Young, *J. Chem. Soc.*, **47,** 42 (1885).

    [6] Kirchhoff, *Ann. physik. Chem. (Poggendorf)*, **103,** 185 (1858).

    [7] Hildebrand, THIS JOURNAL, **37,** 970 (1915).

TABLE III

ENTROPIES OF VAPORIZATION OF THE ALKYL LEVULINATES

Alkyl	Temperature, °C.	Molar heat of vaporization (cal. mole)	Entropy of vaporization
Methyl	410.7	12213	29.74
Ethyl	419.8	12340	29.39
n-Propyl	436.2	12905	29.58
Isopropyl	422.3	12422	29.42
n-Butyl	451.8	13377	29.61
Isobutyl	443.7	13082	29.48
n-Amyl	465.7	13438	28.85
Isoamyl	460.9	13451	29.18
n-Hexyl	479.3	14129	29.47

Discussion

The deviations of observed pressures from those calculated by means of equations are greatest in the regions of higher pressures (Fig. 3), the maximum of these deviations being about 4%. The mean deviation is about 1.5%.

The boiling points calculated from the equations are, on the average, about 6.5° higher than the experimental values recorded by Sah and Ma.[2] Since the conditions under which they report their data have not been divulged, it is difficult to state whether this discrepancy is due to the fact that readings have been recorded at pressures lower than atmospheric, whether it is due to failure to allow for experimental errors such as would be caused by exposed thermometer stem, or the error on our part in extrapolating values from an equation. The error in the last case would indeed be small because the calculated points are not far removed from the final readings.

The slight decomposition of the esters evidently affected the vapor pressures but little. They distilled undecomposed at low pressures. There is no distinguishable break in the curves (log P plotted against $1/T$) that would indicate the beginning of decomposition.

The decrease in refractive index in passing from the methyl to the ethyl ester, a phenomenon to which Grote and his co-workers[8] first called attention, now has been twice verified, for the data of Sah and Ma[2] also show the same situation. Proceeding from the ethyl ester the increase is regular, however, with ascending molecular weights in the series. That alternate rise and fall with an odd and an even number of carbon atoms so often apparent in other homologous series is not evident here. The ester of a branched chain alcohol has a lower refractive index than the corresponding straight chain derivative.

Specific gravities vary inversely with molecular weight, the decrease, in fact, being so regular that, as pointed out above, it was possible to translate into a mathematical expression the curve obtained by plotting the

    [8] Grote, Kehrer and Tollens, Ann., 206, 207 (1880).

value of this constant against the number of carbon atoms in the alkyl residue.   The ester of a branched chain alcohol has a lower specific gravity than its straight chain isomer.
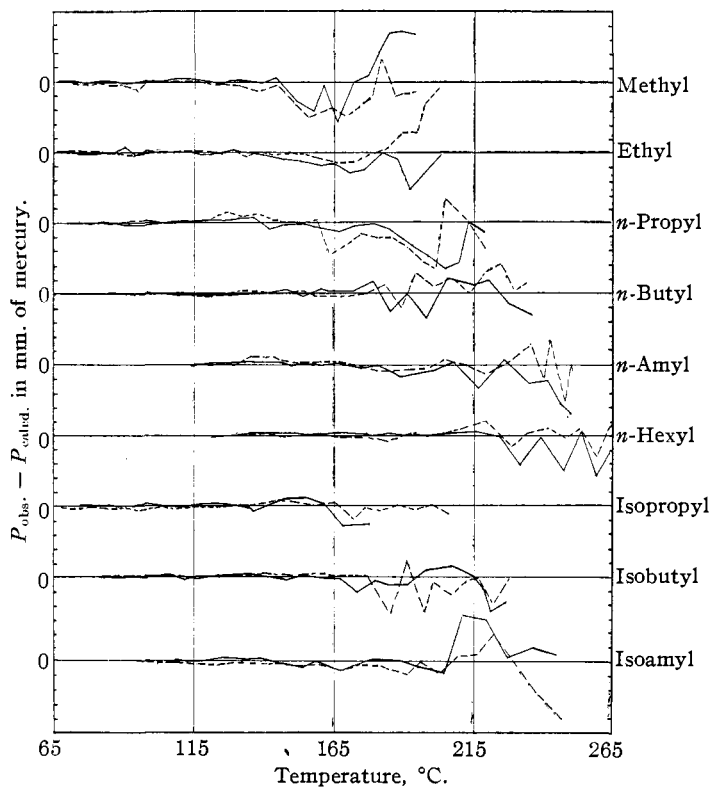

Fig. 3.—Deviation between observed and calculated vapor pressures of alkyl esters of levulinic acid.   Ordinate graduations represent 5-mm. intervals; duplicate runs are indicated by unbroken and broken lines, respectively.

Summary

1.   Nine esters of levulinic acid, of which the n-amyl and n-hexyl derivatives have not been heretofore described, have been prepared and equations derived which express the temperature–pressure relationships of these compounds over a range of 3 mm. to 740 mm.

2.   An equation has been derived to indicate the relationship between specific gravity and the number of carbon atoms in the alkyl radical of the esters.

3.   Entropies of vaporization indicate that these compounds are to some degree associated.

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