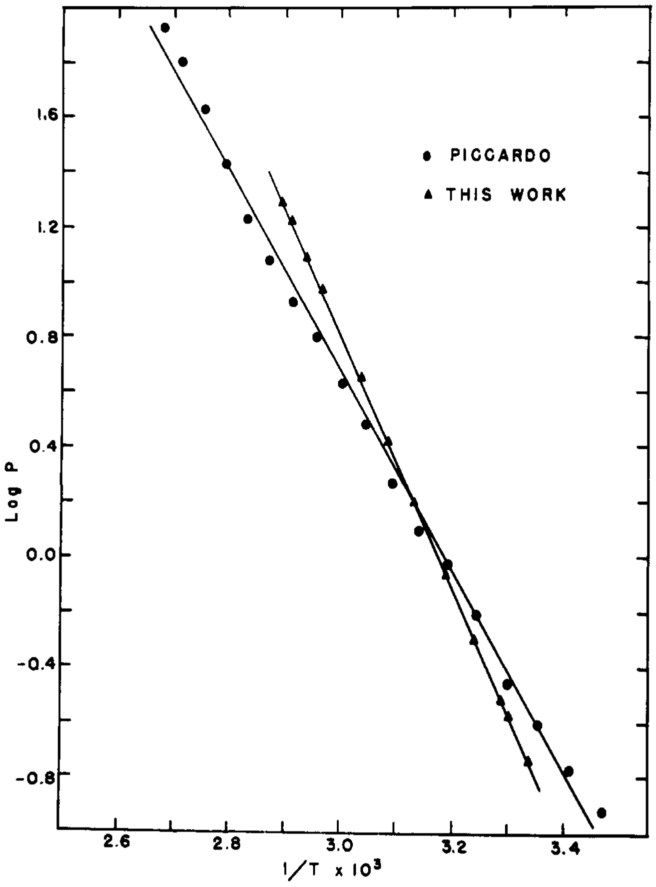

Figure 1. Vapor pressure of metriol trinitrate

Table III. Vapor Pressure Equations, Constants in the Equation $\log p\ (\mu) = A - B/T$

Compound	A	B	Ht. of Vap., Kcal./Mole
Triethylene glycol dinitrate	14.4792	4614.7	21.12 ± 0.03
Metriol trinitrate	14.6237	4603.4	21.07 ± 0.03
Triacetin	14.6673	4285.8	19.61 ± 0.05

the heats of vaporization which were calculated from the slopes of the log *p vs.* 1/*T* plots.

Piccardo determined the vapor pressure of metriol trinitrate over the temperature range 15° to 100° C. by the air saturation method (*2*). Figure 1 shows that the agreement between the two different determinations is not good. By drawing the best line through the data points of Piccardo, a heat of vaporization of 16.58 kcal. per mole is obtained, compared with 21.07 kcal. per mole obtained in this work. Since Piccardo's vapor pressure data for mercury agree within 2% with those obtained in this laboratory (*1*), the lack of agreement in the results for metriol trinitrate is possibly due to the presence of impurities in his sample. Some of these impurities could have been produced by the passage of air through the warm sample inducing some decomposition.

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Acetal Esters of Polyols as Lubricants

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AMONG THE aliphatic esters which have been tested recently as synthetic lubricants, the esters of pentaerythritol (PE) and 2-(hydroxymethyl)-2-methyl-1,3-propanediol (trimethylolethane, TME) have shown promise because of their good viscosity indices and high temperature stability (*3*). Acetals have been ignored as compounds with possible application as synthetic lubricants, even though the acetal grouping might well possess the desired stability. For example, it has been shown that the bis-formal of PE is equal to diethyl ether in its stability to acid hydrolysis (*4*). We, therefore, synthesized some acetal diesters of PE and acetal monoesters of TME by reaction of the monoacetals with the appropriate acid chlorides (Table I). Some of the viscosity properties of these ester acetals were determined according to ASTM procedures (Table II).

SYNTHESES

The preparation of the acetals of PE and TME used in the synthesis of the esters has previously been reported (*2*). The following method for the preparation of the Hexanal dibutyrate of PE (Table I, J) is illustrative of how all the esters were prepared. To a mixture of 21.8 grams (0.1 mole) of the monoacetal of hexanal and PE,

Table I. Acetal Esters of Polyols

		B.P. (Mm.)	Yield, %	Formula	Analyses[a] Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
A	Butyral butyrate of TME	161-163° (16)	52	$C_{13}H_{24}O_4$	63.90	64.44	9.90	9.82
B	Butyral octanoate of TME	143° (0.9)	39	$C_{17}H_{32}O_4$	67.96	68.89	10.74	10.69
C	Valeral octanoate of TME	153-158° (0.6)	58	$C_{18}H_{34}O_4$	68.75	68.94	10.90	11.14
D	Hexanal octanoate of TME	157° (0.7)	57	$C_{19}H_{36}O_4$	69.47	69.51	11.05	11.08
E	Butyral laurate of TME	162-172° (0.4)	48	$C_{21}H_{40}O_4$	70.74	70.78	11.31	11.70
F	Valeral laurate of TME	170-185° (0.2)	40	$C_{22}H_{42}O_4$	71.30	71.58	11.43	11.38
G	Hexanal laurate of TME	172-173° (0.3)	73	$C_{23}H_{44}O_4$	71.83	72.10	11.53	11.68
H	Valeral dibutyrate of PE	162-166° (0.5)	19	$C_{18}H_{32}O_6$	62.76	62.48	9.31	9.42
J	Hexanal dibutyrate of PE	156-162° (0.15)	38	$C_{19}H_{34}O_6$	63.66	64.38	9.56	9.80
K	Valeral dioctanoate of PE	204° (0.5)	58	$C_{26}H_{48}O_6$	68.38	67.95	10.59	10.58
L	Hexanal dioctanoate of PE	190-202° (0.4)	30	$C_{27}H_{50}O_6$	68.90	69.74	10.71	10.72
M	Valeral dinonanoate of PE	211-219° (0.3)	18	$C_{28}H_{52}O_6$	69.38	69.26	10.81	10.83

[a] Microanalyses were performed by Weiler and Strauss Laboratories, Oxfore, England. Melting points and boiling points were uncorrected.

Table II. Viscosity Properties of Acetal Esters

		Kinematic Viscosities, Centistokes 100° F.	Kinematic Viscosities, Centistokes 210° F.	Viscosity Index	ASTM Slope	Pour Points, ° F.
A	Butyral butyrate of TME	6.19	1.68	12.8	0.926	−53
B	Butyral octanoate of TME	9.46	2.26	34.6	0.865	−62
C	Valeral octanoate of TME	11.14	2.53	43.3	0.840	−28
D	Hexanal octanoate of TME	12.58	2.75	49.8	0.829	−69
E	Butyral laurate of TME	15.12	3.23	81.8	0.794	43-46[a]
F	Valeral laurate of TME	16.84	3.52	94.8	0.779	45-59[a]
G	Hexanal laurate of TME	18.82	3.79	99.4	0.768	46-57[a]
H	Valeral dibutyrate of PE	19.74	3.32	−6.39	0.864	−53
J	Hexanal dibutyrate of PE	22.96	3.70	9.25	0.861	−49
K	Valeral dioctanoate of PE	27.11	4.41	65.1	0.795	−46
L	Hexanal dioctanoate of PE	29.33	4.84	92.3	0.767	−22
M	Valeral dinonanoate of PE	30.69	5.00	95.4	0.765	46-66[a]

[a] Melting points.

benzene, 23.4 grams (0.22 mole) of butyryl chloride was added with stirring. A solid formed immediately. The mixture was refluxed for a half hour, 200 ml. of water was added, and the aqueous layer separated and discarded. The benzene layer was dried with $MgSO_4$, the benzene removed in vacuo, and the product distilled.

VISCOSITIES

Viscosities were determined with Cannon-Fenske-Ostwald viscometers calibrated by the Cannon Instrument Co. Viscosities at 100° and 210° F. were determined according to the ASTM procedure (*1a*). From these values, the viscosity index (*1b*) and the ASTM slope (*1c*) were calculated. For the determination of viscosities at 150° F., the viscometer constant was obtained by interpolation of the constants at 100° and 210° F. Pour points were also determined by the ASTM procedure (*1d*).

It is interesting to note that the empirically discovered relationship between viscosity and temperature of petroleum based lubricants applies to these acetal esters. This was ascertained by determining the viscosities of A and G (Table I) at 150° F. (6.51 and 7.86 centistokes, respectively)

22.3 grams (0.22 mole) of triethylamine, and 200 ml. of

and plotting these along with the viscosities at 100° and 210° F. (Table II) on the ASTM chart which embodies this relationship (*1c*). A straight line was obtained. This relationship does not necessarily hold true for all organic compounds, for example, triaryl phosphates (unpublished observations of W.E.C.).

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