

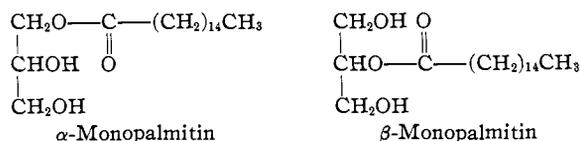
[CONTRIBUTION NO. 399 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

 α - and β -Monopalmitin, Heats of Combustion and Specific Heats at 25^o

BY THEODORE H. CLARKE AND GEBHARD STEGEMAN

In continuation of the program instituted at this Laboratory for obtaining thermal data on compounds of physiological interest, this report contains the first results obtained on the synthetic monoglycerides, α - and β -monopalmitin. Much synthetic organic work relative to the structure of glycerides has been reported in the literature during the past few years but little if any has been published relative to their thermal properties.

Of the glyceride types of fat, the monoglycerides are the simplest in structure, being composed of one acid radical substituted into glycerol. Two isomers are therefore possible and can be illustrated by the structural formulas



In solution the β form exhibits a marked tendency to shift rapidly and completely to the α form.² The presence of very small quantities of acid, base, impurities in solvents, etc., accelerate this shift.^{3,4} Because of a marked change in structure it was thought that a measurable difference might be found in the heats of formation of the isomers.

Method and Apparatus.—The combustion equipment used in these determinations has been described.⁵ The previously reported energy equivalent was corrected for the heat capacity of the benzoic acid pellet in order to secure the energy equivalent of the system ($C_{\text{sys}} = 2769.94 \pm 0.2$ cal. °C.⁻¹) alone. This was done in order to correct for any differences in the heat capacities of the various samples studied.

In order to correct the weight of sample to mass *in vacuo*, the densities of these monoglycerides had to be measured. Since the glycerides are very soft waxy crystals, a sufficiently accurate density measurement was made by forcing the sample into a capillary of known volume in a metal block and then determining the weight of sample used. The densities are probably correct to within 1% or better.

In order to correct for the heat capacity of the sample and also to express the final results at 25°, the heat capacity of the sample must be known at 25°. A small copper calorimeter modeled after that used by Giaque and Gib-

son⁶ and holding between 3 and 4 g. of sample was constructed for these heat capacity measurements. A coil of fine (no. 44) copper wire, having a resistance of 55,498 ohms at 25° and a temperature coefficient of 0.216 ohm per °C., wound on the outside of the calorimeter, served both as thermometer and heater. A set of copper vanes inside the calorimeter aided in the distribution of heat. The calorimeter was suspended in a vacuum jacket which was placed in a thermostat kept at 25°. By rapidly exhausting the jacket, the temperature of the calorimeter could be lowered several tenths of a degree. Heat was then supplied to raise the temperature of the calorimeter to a point several tenths of a degree above that of the jacket. The calculations of the heat capacity were now made in the usual fashion. Measurements on highly purified maltose showed that these specific heat measurements were sufficiently accurate to be used in making the necessary corrections without influencing the precision of the combustion determinations. The energy equivalent of the calorimeter was 1.245 cal. °C.⁻¹ at 25°.

The melting point, density and specific heat data are tabulated in Table I.

TABLE I

	M. p., °C.	Density, g. cc. ⁻¹	C_p , cal. g. ⁻¹ deg. ⁻¹ (25°)
α -Monopalmitin	77	1.04	0.436 \pm 0.001
β -Monopalmitin	69.5	1.03	.439 \pm .001

Preparation of Samples.—The samples were prepared by the methods of Bergmann and Carter⁷ as modified by Daubert and King.⁴ At least two separately prepared samples of each isomer were used for the combustion determinations. These samples were dried at room temperature under a vacuum of 1–2 mm. and were unaffected by the procedures necessary in preparing the samples for combustion. The combustions were clean, no traces of carbon residue being noticeable. The combustion curves were steeper than those of benzoic acid or the sugars reported previously. From this fact it can be concluded that these glycerides ignited and burned more rapidly than either benzoic acid or the carbohydrates studied.

Heats of Combustion.—The values for the heats of combustion are tabulated in Table II. The precision error as outlined by Rossini^{8,9} is used in expressing the results and the defined calorie $\equiv 4.1833$ int. j.⁹ is the unit of energy employed.

Derived Values.—In Table III are listed the derived results: ΔU_B , the heat of combustion in kcal. per gram formula weight under the conditions of an initial oxygen pressure of 30 atm.;

(1) This work was made possible by a grant from the Buhl Foundation, Pittsburgh, Penna.

(2) Fischer, *Ber.*, **53**, 1621 (1920).

(3) Stimmel and King, *THIS JOURNAL*, **56**, 1724 (1934).

(4) Daubert and King, *ibid.*, **60**, 3003 (1938).

(5) Clarke and Stegeman, *ibid.*, **61**, 1726 (1939).

(6) Giaque and Gibson, *ibid.*, **45**, 93 (1923).

(7) Bergmann and Carter, *Z. physiol. Chem.*, **170**, 31 (1927).

(8) Rossini, *Chem. Rev.*, **18**, 252 (1936).

(9) Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, No. 10, Oct. 15, (1939).

TABLE II
 THE COMBUSTION DATA

Sample	Δt , cor. rise, °C.	$C_{8ys} \Delta T$, cal.	$C_{PHI} \Delta T$, cal.	q_{HNO_3} , cal.	Cor. to 25°C., cal. g. ⁻¹	Mass of sample, g.	$-\Delta U_B/M$ 25°C., cal. g. ⁻¹	Δ
α-Monopalmitin								
A1	3.0347	8405.93	1.32	1.90	0.34	0.99938	8410.22	-1.4
2	2.9181	8082.96	1.22	2.71	.35	.96070	8411.71	0.1
3	3.1216	8646.64	1.40	1.87	.42	1.02791	8410.99	-0.6
4	3.0700	8503.72	1.35	1.87	.40	1.01101	8410.20	-1.4
E1	3.1734	8790.13	1.44	1.56	.55	1.04465	8413.76	2.1
2	3.2221	8925.02	1.49	1.30	.57	1.06085	8412.69	1.1
3	3.1995	8862.42	1.47	1.44	.55	1.05350	8411.84	0.2
Precision error = $\pm 0.013\%$						Mean = 8411.6 \pm 1.1 cal. g. ⁻¹		
β-Monopalmitin								
B1	3.2301	8947.18	1.50	1.65	0.56	1.06022	8437.86	-2.5
2	3.2274	8939.70	1.50	1.49	.56	1.05917	8439.74	-0.7
3	3.2253	8933.89	1.50	1.57 (a)	.61	1.05884	8438.17	-2.2
4	3.2219	8924.47	1.49	1.58 (b)	.59	1.05790	8437.24	-3.2
E1	3.2253	8933.89	1.50	1.55	.67	1.05839	8440.30	0.1
2	3.2207	8921.15	1.49	1.56 (c)	.65	1.05644	8444.75	4.4
3	3.2281	8941.64	1.50	1.48	.71	1.05892	8443.62	3.2
4	3.2266	8937.49	1.50	1.47	.64	1.05866	8441.65	1.2
Precision error = $\pm 0.024\%$						Mean = 8440.4 \pm 2.0 cal. g. ⁻¹		

Iron wire corr. = (a) 1.50, (b) 2.00, (c) 1.00 cal.

$-\Delta U_R$, the heat of combustion as if the entire reaction took place at one atmosphere, using the equations of Washburn to reduce the values of $-\Delta U_B$ to this standard state; $-\Delta H_{298.16}^\circ$, the heat of formation of the isomers from the elements by the use of $-68,318.1$ and $-94,029.8$ cal. for the heats of formation of water and carbon dioxide, respectively.

TABLE III

	DERIVED VALUES		
	$-\Delta U_B$, kcal. mole ⁻¹	$-\Delta U_R$, kcal. mole ⁻¹	$-\Delta H_{298.16}^\circ$, kcal. mole ⁻¹
α -Monopalmitin	2780.03 \pm 0.36	2778.78 \pm 0.36	305.83
β -Monopalmitin	2789.54 \pm .67	2788.30 \pm .67	296.31

Discussion of Results

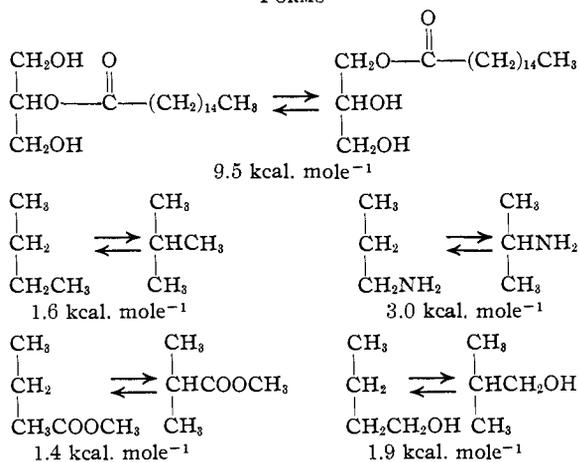
It is not possible to make comparisons with earlier values because no such studies on the glycerides have been reported previously. While the assignment of the precision errors to our measurements is a mathematical process without assumptions, a statement of the limits of accuracy involves factors difficult to evaluate. A conservative estimate might place the accuracy error as 0.025 to 0.035%. No error is stated for the values of $-\Delta H_{298.16}^\circ$ because this would involve the errors on the heat of formation of water and carbon dioxide. Since these errors are smaller than the errors assigned to the glycerides, the uncertainties are probably those of the heats of combustion.

The reaction β -monopalmitin \rightleftharpoons α -monopalmitin is accompanied by a heat evolution of

9.52 kcal. per mole. The direction indicated by the sign of this value is in accordance with the known chemical behavior and also with the melting point data—the α form melting 7.5° higher than the β form. The difference seems large and appears to be unusually so when compared with similar isomeric values reported in the literature, such as a few examples listed in Table IV taken from Kharasch's¹⁰ compilation of combustion values on organic compounds, with the exception of the values for *n*-butane and *i*-butane.¹¹

TABLE IV

DIFFERENCES IN THE HEATS OF COMBUSTION, *n* AND *i* FORMS



(10) Kharasch, *J. Research Bur. Standards*, **2**, 359 (1929).

(11) Rossini, *ibid.*, **12**, 735 (1934); **15**, 357 (1935); **13**, 21 (1934).

While a true comparison should only be made in the vapor state, it is highly improbable that a difference of 9.5 kcal. will be found in the heats of vaporization of this pair of isomeric glycerides.

It is believed that for the solid monoglycerides the heat of combustion will change in a regular fashion with the length of the carbon chain of the substituted fatty acid. Rossini¹² has reported for the gaseous saturated normal hydrocarbons a difference in the heat of combustion per CH₂ group of 157.00 ± 0.08 kcal. per mole. Since the glycerides are composed of a compact head (the glycerol) and a long tail (the fatty acid chain), the possibility is good that the head of the molecule will have little effect on the heat of combustion value upon changing the length of the fatty acid chain by several CH₂ groups. If this is true, α -monomyristin (the fatty acid is two CH₂ groups shorter in chain length than the palmitic acid) would have a calculated heat of combustion of 2464.78 ± 0.36 kcal. per mole. The preliminary values listed below for α -monomyristin give for the heat of combustion 2464.32 ± 0.59 kcal. per mole.

Mean value, $-\Delta U_{B/M} = 8152.1 \pm 1.9$ cal. g.⁻¹ (4 combustions, one sample)

Precision error = ± 0.024%

Density = 1.01 g. cc.⁻¹

$C_p = 0.436 \pm 0.001$ cal. g. deg.⁻¹

$-\Delta U_B = 2465.56 \pm 0.59$ kcal. mole⁻¹

$-\Delta U_R = 2464.32 \pm 0.59$ kcal. mole⁻¹

(12) Rossini, *Ind. and Eng. Chem.*, **29**, 1425 (1937).

Investigations are now under way to determine how far such values can be calculated without exceeding the limits of error on the experimental determinations and will be reported in future publications.

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Summary

1. The heats of combustion of α - and β -monopalmitin reduced to the standard state, $-\Delta U_R$, are reported as 2778.78 ± 0.36 and 2788.30 ± 0.67 kcal. per mole for the reaction carried out at one atmosphere pressure and 25°.

2. The difference in the heats of formation or the heat of the shift of the β form to the α form of -9.52 kcal. per mole is in agreement with the chemical behavior of the isomers but is larger in magnitude than had been expected.

3. As necessary auxiliary measurements, the approximate densities and the heat capacities at 25° of α - and β -monopalmitin are reported.

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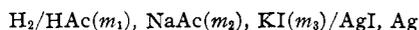
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Silver-Silver Iodide Electrode

BY, ROBERT K. GOULD AND W. C. VOSBURGH

The two most recent determinations of the normal potential of the silver-silver iodide electrode by Owen¹ and Cann and Taylor² led to the values 0.1522 v. and 0.1510 v., respectively. Because of the disagreement, a new determination was undertaken by the method used by Owen, but with an acetate instead of a borate buffer. The cell measured was



in which m_1 , m_2 and m_3 were all either about 0.01 m or between 0.004 and 0.005 m .

(1) Owen, *THIS JOURNAL*, **57**, 1526 (1935).

(2) Cann and Taylor, *ibid.*, **59**, 1484 (1937).

Experimental

Potassium iodide was twice recrystallized as described by Owen¹ and dried at 110°. Potentiometric titration of the iodide by a permanganate solution standardized against arsenious oxide³ showed it to be pure within the error of the analysis, which was about one part in a thousand.

A 0.1 N sodium hydroxide solution was standardized against potassium acid phthalate from the National Bureau of Standards. A 0.1 N acetic acid solution was carefully standardized against the sodium hydroxide solution. Portions of the acid solution containing either 0.02 or 0.01 mole of the acid were half neutralized with the sodium hydroxide solution; then either 0.01 or 0.004 mole of potassium iodide and enough water to make 1000 g. of

(3) Kolthoff, Laitinen and Lingane, *ibid.*, **59**, 430 (1937).