

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE HYDROCARBONS OF THE WOOL GREASE OLEINS. FIRST PAPER.

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In 1904 Gill and Mason showed how these hydrocarbons might be distinguished from mineral oil.¹

The hydrocarbons were obtained by saponifying the distilled wool grease oleins with an excess of alcoholic potash. The unsaponifiable matter was extracted with redistilled petroleum ether, treated with acetic anhydride to remove any cholesterol, and if more than 0.2 cc. of 0.5 *N* alcoholic potash per gram of oil were required for the saponification of the neutral oil present, these operations repeated until an oil of this quality resulted.

The oil obtained has the following characteristics (for comparison those of some mineral oils are herewith shown).

Sp. gr. at 15°.	Bromine.		Optical rotation in 200 mm. tube.	Refractive index at 20°.
	Addition.	Substitution.		
0.896	28.8	14.2	+17° 58'	1.4967
Mineral oils 0.848-0.863	4.4-5.9	5.6-8.4	+ 1° 2'	1.4662-1.4750

From the large bromine addition number these hydrocarbons would seem to be unsaturated compounds, and according to the investigations of Smith² to have been formed by the breaking down of an ester, like cetyl palmitate, into the corresponding acid and the double-bonded hydrocarbon of a similar name, $C_{15}H_{31}COOC_{16}H_{33} = C_{15}H_{31}COOH + C_{16}H_{32}$. Between two and three liters of these hydrocarbons were prepared from the olein as above described. Some of this was distilled at a pressure of 17-44 mm. giving boiling points from 270° to 315°; good separations were not obtained, it being impracticable to use a bead tower, five or six inches of vertical height being as much as the liquid could be raised by boiling.

Fractionation under these circumstances being difficult, a rotary vacuum pump, the rotator running in oil, was used; this was similar to those used in evacuating incandescent lamps and afforded a pressure during distillation as low as one millimeter. Richards³ method of heating was used with excellent results, the current being regulated by wire and carbon rheostats. With a coil of platinum wire 0.25 mm. in diameter and 50 cm. long a current of 4-6 amperes at 220 volts was found sufficient to distil the hydrocarbons.

The distilling flask held but 200 cc., consequently many distillations were necessary. Six complete fractionations were made between the

¹ THIS JOURNAL, 26, 665.² *Ann. chim. phys.*, (3) 6, 40 (1842).³ T. W. Richards, THIS JOURNAL, 30, 1282.

following temperatures, 95–100°, 100–110, 110–125, 125–130, 130–140, 145–150, 150–155, 170–176, 176–182, 186–193° and a quantity of each portion of fairly constant boiling point was obtained.

The hydrocarbons were next subjected to purification by crystallization from acetone. Those having boiling points of from 95° to 135° would not separate out in crystalline form even at 0°, coming out of solution simply as oils; but the separation was repeated three times with these as with those of higher boiling point, since any change in composition which might be thereby affected tends toward purification. The remainder of the hydrocarbons were obtained as crystallized white solids from the acetone solutions, and crystallization from fresh acetone was effected three times in each case. The hydrocarbons which were last separated from the acetone were heated on the water bath to remove all traces of solvent. All except the one, crystallizing from acetone, which had the boiling point 130–140° were solid at the ordinary temperatures. The solvent was also distilled from the total mother liquor left from the three crystallizations leaving the hydrocarbon which is soluble in acetone at 0°. All of these soluble hydrocarbons, to the end of the list, were liquid at ordinary temperature.

By this means there were obtained, from the original single series of hydrocarbons, two series, one insoluble after three separations from acetone solution at 0°, and the other soluble in acetone at that temperature.

The molecular weights by the Beckmann method, in benzene, and the iodine absorption values by the Hanus method were now obtained for all the hydrocarbons of each of these series, both solid and residual, these are shown in Tables I and II.

TABLE I.—PURIFIED HYDROCARBONS.

Boiling points at 1 mm.	Molec. wts. after 3rd re-cryst.	Corresponding to	Molec. wts. after 6th re-crystallization.	Corresponding to	Iodine nos. after 3rd re-cryst.	Equal to atoms of iodine.	Iodine nos. after 6th re-cryst.	Equal to atoms of iodine.
95–100°	239	Heptadecylene $C_{17}H_{34}$, 238,	oily, did not		87	1.6
100–110°	252	Octadecylene $C_{18}H_{36}$, 252,	crystallize		95	1.9
110–125°	287	Eicosylene $C_{20}H_{40}$, 280,	..		82	1.9
125–130°	310	Docosylene $C_{22}H_{44}$, 308,	..		74	1.8
130–135°	318	Tricosylene $C_{23}H_{46}$, 322,	..		65	1.6
130–140°	324	Tricosylene $C_{23}H_{46}$, 322,	346	$C_{25}H_{50}$, 350	60	1.5	45	1.2
145–150°	354	Pentacosylene $C_{25}H_{50}$, 350,	378	$C_{27}H_{54}$, 374	57	1.6	43	1.3
148°	348	Pentacosylene $C_{25}H_{50}$, 350,	..		60	1.7
150–155°	367	Hexacosylene $C_{26}H_{52}$, 364,	373	$C_{27}H_{54}$, 374	56	1.6	41	1.2
170–176°	392	Octacosylene $C_{28}H_{56}$, 392,	400	$C_{28}H_{56}$, 406	71	2.2	56	1.8
176–182°	410	Nonacosylene $C_{29}H_{58}$, 406,	412	$C_{29}H_{58}$, 406	72	2.3	67	2.2
186–193°	422	Triacontylene $C_{30}H_{60}$, 420,	424	$C_{30}H_{60}$, 420	80	2.7	72	2.4

¹ Of remarkably constant boiling point but insufficient to recrystallize.

TABLE II.—RESIDUAL HYDROCARBONS.

Boiling points at 1 mm.	Molec. wts. after 3rd re-cryst.	Corresponding to	Molec. wts. after 6th re-cryst.	Corresponding to	Iodine nos. after 3rd re-cryst.	Equal to atoms of iodine.	Iodine nos. after 6th re-cryst.	Equal to atoms of iodine.
95-110°	Insufficient in quantity							
110-125°	284	Eicosylene C ₂₀ H ₄₀ ,	280,	90	2.0
125-130°	305	Docosylene C ₂₂ H ₄₄ ,	308,	85	2.1
130-135°	320	Tricosylene C ₂₃ H ₄₆ ,	322,	80	2.1
130-140°	325	Tricosylene C ₂₃ H ₄₆ ,	322,	332	C ₂₄ H ₄₈ ,	336	83	2.1 66 1.7
145-150°	336	Tetracosylene C ₂₄ H ₄₈ ,	336,	insufficient	79	2.1	..
150-155°	360	Hexacosylene C ₂₆ H ₅₂ ,	364,	"	79	2.3	..
170-176°	366	Hexacosylene C ₂₆ H ₅₂ ,	364,	395	86	2.5 70	2.2
176-182°	382	Heptacosylene C ₂₇ H ₅₄ ,	378,	392	88	2.7 85	2.6
186-193°	402	Nonacosylene C ₂₉ H ₅₈ ,	406,	409	93	3.0 96	3.1

From a study of these tables it would seem that in these distilled wool grease oleins we had hydrocarbons of the olefin series, that is with but a single double bond, and of formula from C₂₀H₄₀ to C₃₀H₆₀.

These hydrocarbons are now under investigation, with the idea of determining some of their physical constants with greater accuracy, more particularly their boiling and melting points, their index of refraction and, if possible, the position of the double bond.

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STUDIES ON AMYLASES. I. AN EXAMINATION OF METHODS FOR THE DETERMINATION OF DIASTATIC POWER.

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The enzymes being known by their activities it is scarcely possible to make satisfactory progress in the isolation of any enzyme for investigation of its chemical nature until we have accurate knowledge of methods and conditions for determining quantitatively the increase of its activity or power with the progress of the purification. This may be illustrated by a reference to the papers of Osborne¹ and of Wroblewski² on the chemical nature of the amylase of malt.

In the case of the amylases there are also extremely important applications, both biochemical and economic, awaiting the development of reliable and comprehensive methods for the measurement of diastatic power. The fact that the salivary digestion of starch may continue

¹ Osborne, THIS JOURNAL, 17, 587 (1895); Osborne and Campbell, *Ibid.*, 18, 536 (1896); Osborne, *Ber.*, 31, 254 (1898).

² Wroblewski, *Ber.*, 30, 2289 (1897); 31, 1127 (1898).