CLXXXIV.—*The Boiling Points of Some Higher Aliphatic* n-*Hydrocarbons.*

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The long-continued fractionation of Scotch paraffin wax led to the isolation of seven fractions of constant boiling point (J., 1922, **121**, 1529), and later (*loc. cit.*, p. 2804), evidence was advanced for the belief that these fractions were pure hydrocarbons. Piper and his students (J., 1925, **127**, 2194) submitted these hydrocarbons to *X*-ray analysis, and finding that the spacings coincided with those obtained by Müller and Saville for synthetic hydrocarbons (*loc. cit.*, p. 600), concluded that " the hydrocarbons obtained from paraffin wax are identical in constitution with the synthetic *n*-hydrocarbons."

Certainly, then, as regards the material obtained from shale in Scotland fusing between 55° and 56°, and most probably paraffin from all sources, the view that has been held since Krafft's work in 1888 has been proved finally to be correct. The number of hydrocarbons present in different paraffins is still an open question, but if Scotch wax is at all typical, the number is not so large as Krafft stated, and is much nearer 10 to 12 than the 35 (18 of which were considered to be pure) that he believed to be present in the specimen he investigated (*Ber.*, 1907, **40**, 4779).

In Piper's communication, the question was raised of the untrustworthiness of the molecular magnitudes of some of the hydrocarbons from paraffin wax as determined by the ordinary ebullioscopic methods.

We thought it most probable that a direct comparison of the boiling points of synthetic *n*-docosane, $C_{22}H_{46}$, with fraction B over a range of pressures would show either that these two substances were identical, which Piper states to be the case, or that B was $C_{23}H_{48}$, the deduction from a series of very concordant molecular-weight determinations by the ebullioscopic method. *n*-Docosane was synthesised by the electrolysis of a solution of potassium laurate " Kahlbaum " (Petersen, *Z. Elektrochem.*, 1906, **12**, 141) and purified by three crystallisations from benzene; it fused at 44·5° and the specimen used for this work boiled at a constant temperature.

A boiling-point graph drawn from the data (Table I) for this synthetic material showed that all the boiling points at different pressures of the hydrocarbon B isolated from paraffin fell on that curve. There can therefore be no doubt that the two substances are identical, that one of the constituents of paraffin is *n*-docosane, and that the molecular-weight determination of this hydrocarbon from that source was too high by about 4%.

TABLE I.

Boiling points at various pressures (uncorr.).

Fraction.

B ($C_{22}H_{46}$).		C ($C_{24}H_{50}$).		E ($C_{26}H_{54}$).		F ($C_{28}H_{58}$).	
27·1 mm.	236°	27·6 mm.	255·5°	26·5 mm.	269°	28·0 mm.	288°
16·0	224	13·3	238·5	14·2	257	12·1	267·5
9·9	212	4·4	210·5	8·4	245·5	7·1	258·5
4·8	199·5	2·5	202	4·4	233	3·6	244
2·0	189	1·5	195	2·1	223·5		

Fraction.

G ($C_{29}H_{60}$).		C.O. ($C_{24}H_{50}$).		F.O. ($C_{28}H_{58}$).	
19·0 mm.	290·5°	24·6 mm.	253°	26 mm.	287°
13·6	279·5	12·5	236·5	14·9	274·5
8·3	270·5	7·3	221	7·1	258·5
4·1	254	3·7	209	4·5	247
2·5	248			2·2	234

Synthetic Hydrocarbons.

$C_{16}H_{34}$.		$C_{22}H_{46}$.		$C_{30}H_{62}$.		$C_{34}H_{70}$.	
19·5 mm.	161·5°	24·7 mm.	233·5°	30·5 mm.	311·5°	30 mm.	337·5°
13·8	156	18·3	226	20·5	300	19·5	325
9·0	145	11·2	215	14·5	291	15·0	319
5·3	137	5·0	198	6·2	268	4·6	297·5
				1·7	241·5	2·4	285

The synthetic hydrocarbons (C_{24}, C_{25}, C_{26}, C_{28}, C_{29}, C_{31}) required to make a similar direct comparison between the other six hydrocarbons isolated from paraffin were not available.

Consequently we synthesised *n*-hexadecane, *n*-triacontane, and *n*-tetratriacontane in order to obtain the relationship between the boiling points at 15 mm. of these hydrocarbons and their respective carbon contents. This would enable a comparison to be made with the boiling points under the same pressure of the hydrocarbons isolated from paraffin.

Hexadecane was prepared by the reduction of cetyl iodide and purified by treatment with concentrated sulphuric acid; it showed a constant boiling point of 156°/13·8 mm. Triacontane and tetratriacontane were synthesised by the electrolysis of the potassium salts of palmitic and stearic acids, respectively, these acids being the purest obtainable from Kahlbaum. Each hydrocarbon was purified by three crystallisations from benzene and the specimens used in this investigation had constant boiling points.

From the data for the synthetic hydrocarbons in Table I, the boiling points at 15 mm. can be obtained by interpolation, and when these were plotted against their respective carbon contents a smooth curve resulted.

On this curve, within an experimental error of between 1° and 2°, lay the boiling points at 15 mm. of the following hydrocarbons isolated from paraffin : $C_{24}H_{50}$, $C_{26}H_{54}$, $C_{28}H_{58}$, $C_{29}H_{60}$. We had insufficient amounts of the hydrocarbons $C_{25}H_{52}$ and $C_{31}H_{64}$ from paraffin to determine the boiling points with any degree of accuracy.

As these results are in entire agreement both with the molecular weights of these paraffin hydrocarbons as determined by the Menzies and Wright apparatus (J., 1925, **127**, 2194) and with those obtained by *X*-ray analysis, there can be no doubt that the paraffin wax investigated in these laboratories contains in addition to *n*-docosane, the *n*-hydrocarbons tetracosane, hexacosane, octacosane, and nonacosane. The two (pentacosane and hentriacontane) whose boiling points at 15 mm. have not been determined had been analysed by *X*-rays and can clearly be added to this list.

It has been shown (J., 1922, **121**, 2808) that on the oxidation of the seven hydrocarbons obtained from paraffin, in each case the small amounts which escaped this process were identical with the hydrocarbon used, and this fact was taken as a criterion that pure specimens had been isolated. Sufficient amounts of the unchanged hydrocarbons from the oxidation of tetracosane and octacosane (from paraffin) were available for the purpose of determining their boiling points at different pressures; in both cases these lay on the graphs for the parent hydrocarbons (see Table I, Fractions C.O. and F.O.). This constitutes a further proof of their identity and an additional support for the view that the two hydrocarbons are pure materials.

All the boiling points given in Table I were determined in an apparatus similar to that used for the fractionation of wax (J., 1922, **121**, 1529), but the data obtained were not corrected for the exposed stem of the thermometer.

Krafft prepared a large number of synthetic *n*-hydrocarbons in 1882 and 1886 (*Ber.*, **15**, 1687, 1711; **19**, 2218), and we found that the boiling points at 15 mm. recorded by him for the ten hydrocarbons $C_{15}H_{32}$ to $C_{24}H_{50}$ fell on the graph (connecting b. p. and carbon content) constructed from our more limited data. Even in the case of $C_{27}H_{56}$, $C_{31}H_{64}$, $C_{32}H_{66}$, and $C_{35}H_{72}$, the difference was only $+ 2°$.

This correspondence with our uncorrected data was so striking that we concluded that Krafft's boiling points at 15 mm. could not have been corrected for the exposed stem of the thermometer. It appeared to us that the corrections, certainly necessary for our own data, were equally applicable to his.

On the thermometer used in this work and with the same apparatus the boiling point of naphthalene at 744·2 mm. was 211·1°, and of benzophenone 293·5° at 749 mm. Dimmer's formula for the correction (Landolt-Bornstein, ii, 1212) being applied, these data become 216·9° and 305·9° at 760 mm., which are in agreement with the recorded boiling points of these substances, *viz.*, 217·2° and 305·9°. The correction amounts to 1·7° at 150°, 4·5° at 200°, 8·3° at 250°, and 12·3° at 300°.

In Table II are the most probable corrected boiling points at 15 mm. of Krafft's hydrocarbons and those described in this communication; the error, we believe, does not exceed ± 1·5°.

TABLE II.

Boiling points of n-*hydrocarbons* (*corrected*) *at* 15 *mm.*; *probable accuracy* ± 1·5°.

$C_{15}H_{32}$	Synthetic K	144°	$C_{25}H_{52}$	Interpolated	259°
$C_{16}H_{34}$	,, K, F	158	$C_{26}H_{54}$	Paraffin F	268
$C_{17}H_{36}$	,, K	171	$C_{27}H_{56}$	Synthetic K	277
$C_{18}H_{38}$	,, K	184	$C_{28}H_{58}$	Paraffin F	286
$C_{19}H_{40}$	,, K	196	$C_{29}H_{60}$	,, F	295
$C_{20}H_{42}$	,, K	208	$C_{30}H_{62}$	Synthetic F	304
$C_{21}H_{44}$	,, K	219	$C_{31}H_{64}$	,, K	312
$C_{22}H_{46}$	,, K, F	230	$C_{32}H_{66}$	,, K	320
	and paraffin		$C_{33}H_{68}$	Interpolated	328
$C_{23}H_{48}$	,, K	240	$C_{34}H_{70}$	Synthetic F	336
$C_{24}H_{50}$	,, K, F	250	$C_{35}H_{72}$	,, K	344
	and paraffin				

K = Krafft. F = present communication.

The observed b. p. of our specimen of hexadecane on the thermometer used in this investigation was 278° at 764·8 mm.; correction for exposed stem raises this to 288·6°. Within the experimental error, this agrees with Krafft's determination, *viz.*, 287·5° at 760 mm.

Since the boiling point at 760 mm. recorded by Krafft for this hydrocarbon, and also those of $C_{17}H_{36}$, $C_{18}H_{38}$, and $C_{19}H_{40}$, all lie on a smooth curve connecting boiling points and carbon content, there can be no doubt that, as far as these hydrocarbons are concerned, Krafft's data at normal pressure were corrected for the exposed stem of the thermometer.

Our warmest thanks are due to Professor Sydney Young of Trinity College, Dublin, for the great assistance he has given us in considering and comparing our results with those of Krafft. In Krafft's communications to the *Berichte* there are many cases in which it is not possible to be certain whether the data recorded have or have not been corrected in the manner discussed in this communication.

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