halides and liquid ammonia on the one hand and between the halides and the metal salts on the other.

Polyhydroxy compounds may be alkylated.

The naphthols are reduced by sodium in liquid ammonia to tetrahydronaphthols.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF McGILL UNIVERSITY]

THE CONSTITUTION OF KEROGEN[1]

BY J. W. McKINNEY[2]

RECEIVED NOVEMBER 24, 1923

Introduction

Kerogen is the name given to the organic matter which occurs in pyrobituminous shale.[3] It is a mixture of complex compounds which is very difficult to work with, because it is largely insoluble in organic solvents, it cannot be separated from the inorganic mineral constituents which always accompany it, and its composition varies over a wide range, so that not much is known about the real nature of this material, although a certain amount of empirical data has been obtained.[4]

The pioneer in this field is Robertson,[5] who worked with some Scotch shales. By the action of nitric acid he obtained complex acidic bodies containing nitrogen, similar to those previously obtained by Anderson[6] from bituminous coal in the same manner. He found the carbon-hydrogen ratio of his shales, and attempted to establish a relation between it and the yield of oil. He found that pyridine was the best solvent, giving as much as 5% of extract, but could not get much information as to the nature of this material.

Other workers have extracted shales with a great variety of solvents invariably removing a small quantity of material, but have never attempted a detailed examination of the extracts. Many other methods of attack have also been tried, but the information gained is empirical and haphazard. The work described in this paper was an attempt to get a systematic knowledge of the action of solvents on pyrobituminous shale, and to work up the extracted material in detail.

---

[1] Abstract of a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, McGill University, 1923.

[2] Fellow of the Advisory Research Council of Canada, 1922.

[3] Commonly called "oil-shale," which is a misnomer and should be reserved for shales from which all or most of the organic matter can be extracted by carbon disulfide.

[4] Gavin, "Oil-Shale," Bur. Mines, *Bull.*, **210** (1922).

[5] Robertson, *Proc. Roy. Soc. Edinburgh*, **34**, II, 190 (1913).

[6] Anderson, *J. Soc. Chem. Ind.*, **17**, 1018 (1898).

Experimental Part

The Action of Solvents

The sample of shale used in this work was taken from an outcrop of curly shale near Albert Mines, New Brunswick, weathered shale being rejected. This was crushed to pass a 10-mesh sieve, and samples were ground in a ball mill to 100 mesh for the analyses and preliminary extraction work. Table I gives the analysis of this shale, together with that of some other samples for comparison. Oil yields are reported as imperial gallons per short ton.

TABLE I

ANALYSES IN PERCENTAGES

Sample	C	H	C/H	N	S	Yield of oil
New Brunswick shale....	19.44	2.18	8.92	1.3	1.18	30.1
Same, acetone extr'd.....	18.43	1.94	9.51	...	..	..
Scotch shale (Dunnet)[5]...	19.51	2.48	7.86	0.7	1.36	20.8
Nevada shale[7]..........	37.65	5.43	7.21	.4	1.08	72.4
Colorado shale[7].........	13.37	1.80	7.42	.4	0.27	14.0

Samples of shale No. 1 (100 mesh) were extracted with several solvents in an ordinary Soxhlet apparatus, in each case until no further color was removed in the flask. The shale was dried in the thimble at 105°, the percentage loss calculated, and the percentage of moisture (0.8) in the original shale deducted, giving the net percentage of extract. The results are given in Table II, the percentages being reported on the basis of the original shale.

TABLE II

EXTRACTION OF SHALES

Solvent	B. p. °C.	Time of extr. Days	Net % extr.	% Sol. in $CHCl_3$	% Sol. in petr. eth.
Alcohol..........................	78.0	5	1.5	100	...
Ether...........................	35.0	8	2.2	100	...
Carbon disulfide.................	46.2	8	2.8	100	...
Acetone.........................	56.5	9	2.6	100	1.7
Chloroform......................	61.2	9	2.2	100	2.1
Carbon tetrachloride.............	76.0	8	2.6	100	2.5
Benzene.........................	80.4	6	3.2	100	2.7
Pyridine........................	115.0	11	2.6	2.0	1.3
Acetic acid.....................	118.1	27	6.9	2.8	1.0

The dilute solutions of the extracts all showed a strong greenish fluorescence, the colors ranging from light red to black. Most of the solvent was distilled (the pyridine and acetic acid under reduced pressure) and the residue was then heated in an evaporating dish on a steam-bath for some hours. This left a reddish-black oil containing considerable solid material. On treatment with chloroform all of the extracts dissolved

---

[7] U. S. Geol. Surv., *Bull.*, **641F**, 139 (1916).

completely except those from the pyridine and acetic acid, which left a black powder. After driving off the chloroform the extracts were treated with petroleum ether,[8] and in every case a brown powder remained. When the petroleum ether solution was evaporated there was left a clear red oil.

Following Jones and Wheeler in their separation of coal extracts,[9] the portion soluble in chloroform corresponds to the truly resinic, as opposed to cellulosic, constituents. Of course it includes hydrocarbons as well, and the proportion of these present is indicated by the amount soluble in petroleum ether. It will be seen that only pyridine and acetic acid remove any cellulosic substances, and they in very small amount, for most of the acetic acid extract was a water-soluble, inorganic salt.

In comparing the action of solvents, the most striking point is the great similarity in the amounts extracted. The larger amount removed by acetic acid is due to its chemical action on the inorganic part of the shale. It is noteworthy that pyridine dissolves no more than any of the other solvents and less than from the Scotch shale.

It was found that the red petroleum-ether solutions could be decolorized by filtration through fuller's earth, and when the solvent was evaporated there remained in all cases a clear, straw-colored oil, which solidified at about 0°. This oil was completely saturated, and on combustion proved to consist entirely of hydrocarbons: C, 85; H, 15. It was decided to extract the shale on a large scale in order to obtain enough of this material to examine in detail.

Recently the results of a systematic extraction of American shales have been published, six of the solvents listed above being employed on five samples of shale.[10] It is interesting to note that each shale yields a characteristic amount of extract, which varies little from solvent to solvent, exactly as with the New Brunswick shale. The amounts extracted also are quite similar, excepting in the cases of the California and Kentucky shales, which belong to quite different and comparatively rare types.

Large Scale Extraction and Filtration

Acetone was chosen as solvent for the large scale work, and some preliminary experiments made to find the effect of fineness of grinding and temperature of extraction. The extraction of 10-mesh shale at room temperature yielded less total extract than was at first obtained, but practically the same amount of material soluble in petroleum ether. This

---

[8] The petroleum ether used throughout this work was specially prepared from commercial "86° gasoline," by distillation through a long Hempel column, the portion from 30–55° being collected.

[9] Jones and Wheeler, *J. Chem. Soc.*, 103, 1704 (1913); **109**, 707 (1916).

[10] Gavin and Ayedelotte, Bur. Mines, *Ser.*, **1922**, 2313.

made it possible to use a simple apparatus, of the percolation type, holding 40 kg. of shale; by means of this extractor 217 kg. of shale was extracted.

The extracted oil was then separated by the method of Marcusson[11] into asphaltenes, resins and hydrocarbons, the approximate proportions being 10%, 5% and 85%, respectively. The method is one of wide application and great value in simplifying the study of these complex mixtures, and is carried out as follows. After being freed from solvent the extract is poured into twice its volume of petroleum ether, when the asphaltenes separate and are filtered off as a cocoa-brown powder. The resulting solution is repeatedly filtered through freshly ignited fuller's earth until it is colorless, showing that all the resins are absorbed. After the filtration the fuller's earth is washed free from oil with petroleum ether, then the resins may be extracted with chloroform. The clear petroleum ether solution when distilled leaves the hydrocarbons.

Since the asphaltenes and resins were present in such small amounts, only the hydrocarbons were examined. This filtered oil was heated for one hour in a vacuum (10 cm.) on a water-bath, to remove traces of petroleum ether, and then was almost colorless, slightly fluorescent, and had a kerosene-like odor. It was not acted on by dil. potassium permanganate solution or bromine water, and was optically active: $[\alpha]_D = +0.76$. Table III gives the results.

TABLE III

EXTRACTED OIL

Crude extract	3440 g.	1.58%	d., 0.874
Filtered oil	2943 g.	1.36%	d., 0.833

Fractionation in a Vacuum

An attempt was made to distil the oil in a vacuum, using a water-pump, first at 40 mm., then at 13 mm., but this failed because of bumping and decomposition. The pressure was then reduced to 1 mm. by means of a Maass sulfuric acid pump, which is an automatic Toepler pump, using sulfuric acid instead of mercury,[12] and it was found that distillation was uniform and quiet, with no sign of decomposition.

For the fractionation special Pyrex distilling flasks were used, having long necks filled with glass beads, a small condenser being fitted directly on the side-arm. To permit the receivers to be changed without interrupting the distillation, a Bruehl apparatus was used for the liquid fractions, and a "distilling triangle" for the solid fractions. By means of a second side arm sealed into the neck of the distilling flask, fractions were introduced with very slight loss in pressure, and a complete fractionation was thus carried out without opening the flask. Pressure was measured by a mercury manometer and a differential sulfuric acid manometer.

---

[11] Marcusson, *Z. angew. Chem.*, **29**, 346 (1916). Abraham, "Asphalts and Allied Substances," D. van Nostrand Co., New York, **1920**, p. 545.

[12] Maass, THIS JOURNAL, **42**, 2571 (1920).

Using this apparatus, the oil was distilled between 20° limits up to 290°. After a second fractionation of the oil in these limits, the specific gravities of the fractions were measured, and the results are shown in Table IV. The fractions up to 150° were mobile liquids, from 150° to 210° solids of low melting point, and above 210° very viscous liquids. A slight yellow color appeared about 160°, which gradually increased in intensity with rise of boiling point, the last fraction and the residue being blue.

Table IV

Specific Gravities of Fractions

Range °C.	Amount Cc.	% by vol.	D.	
50	100	2.8	0.796	15°
50– 70	200	5.6	.804	
70– 90	300	8.5	.810	
90–110	300	8.5	.819	
110–130	400	11.3	.822	
130–150	400	11.3	.825	
150–170	300	8.5	.826	30°
170–190	200	5.6	.839	
190–210	200	5.6	.854	
210–230	225	6.3	.899	
230–250	200	5.6	.908	
250–270	75	2.0	.913	
270–290	50	1.5	.915	
Residue	50	1.5	.917	

The portion up to 150° was taken first, and separated into 5° fractions, then systematic fractionation was continued in these limits, using the Bruehl apparatus. At the end of each fractionation the residue was treated with concd. sulfuric acid to remove traces of decomposition products. Up to the fourteenth fractionation there was no definite separation into compounds; the fractions did not vary much in amount and the variation was quite gradual. From then on, however, distinct "heaps" began to collect, some of the fractions increasing at the expense of the rest, until at the end of the twenty-first fractionation these heaps stood out very distinctly, being three or four times the size of the intermediate fractions. The twenty-second fractionation did not alter the relative sizes of the fractions, showing that the separation was as complete as it could be made. The nine heaps which had collected were examined for the presence of compounds.

The solid portion from 150–210° was next separated into 5° fractions as before, then fractionated, using the distilling triangle. The condenser jacket was removed to keep the distillate liquid until it reached the receiver. The residues were purified by treatment with concd. sulfuric acid as before, the material being first dissolved in an equal volume of carbon tetrachloride. As before, the amount of the impurity removed was too small to estimate. After twenty-one fractionations, six heaps had collected, and these were examined for compounds with the others.

The portion above 210° was not worked up, due to lack of time, and in any case the amount of material left was too small to fractionate successfully. Given enough material there would be no difficulty in completing the fractionation, especially if the pressure were reduced to 0.1 mm., which is quite possible with the pump used.

Identification of Compounds

These fifteen large fractions were analyzed, the nine liquid fractions being first purified as follows. The oil was washed five times with concd. sulfuric acid, twice with dil. sodium hydroxide solution and twice with water, then dried over calcium chloride and finally metallic sodium. Before treatment the fractions all had a slight disagreeable odor, afterwards they were practically odorless. The solid fractions had a faint yellow color and an oily odor; no attempt was made to purify them. The molecular-weights were determined by the cryoscopic method in benzene, with the modified apparatus proposed by O. Maass,[13] in which supercooling can be greatly reduced and accurately controlled. The results of the analyses, together with the melting points of the solid fractions, are given in the first part of Table V. The calculated results are for the series C_nH_{2n}, except Nos. 14 and 15, which are for C_nH_{2n-2}.

Each fraction was then separated into two parts. In the case of the liquid members, this was done by cooling until a solid separated, then filtering by suction, the flask and funnel being cooled as low as —20°. The lowest members had to be cooled in a bath of solid carbon dioxide and ether before they solidified, and it was found impossible to filter Nos. 1 and 2 at the atmospheric temperatures available. The solid members were melted, allowed to cool somewhat and then filtered before they had solidified completely. In every case the process was repeated several times, cooling to a lower temperature each time, and in this way the seven highest fractions were separated almost completely. The separation of Nos. 3 to 8 was not quite so complete, on account of the low melting point of the solids. On the average, the amount of solid material removed was about 15% of the original fractions.

The solids thus removed were pure white waxes, melting to colorless liquids at a low temperature; the five lowest members were liquid at room temperature. These five had a faint sweet odor; the rest were quite odorless. The eight solid members were purified by recrystallization from benzene, the melting points taken, and they were then all analyzed in the same manner as the original fractions. The highest four members were found to be nearly insoluble in benzene, acetophenone and bromoform at

---

[13] Maass, *Proc. Roy. Soc. Canada*, **13**, III, 97 (1919).

the freezing point, so that their molecular weights were not determined. However, it will be seen that the melting points increase in a very regular manner, so there can be no doubt as to the identity of the compounds. The analyses of this series, together with those calculated for paraffins, C_nH_{2n+2}, are given in the second part of Table V.

Table V

Analytical Results

No.	B. p. (1 mm.) °C.	M. p. °C.	Found C	Found *H*	Found Mol. wt.	Calculated C	Calculated *H*	Calculated Mol. wt.
1	55- 60	..	85.99	14.26	170	85.62	14.38	168.3
2	65- 70	..	85.82	14.29	183	85.62	14.38	182.3
3	80- 85	..	86.00	14.11	197	85.62	14.38	196.3
4	90- 95	..	85.69	14.06	211	85.62	14.38	210.3
5	100–105	..	85.90	14.34	222	85.62	14.38	224.3
6	115–120	..	85.53	14.41	234	85.62	14.38	238.4
7	125–130	..	85.70	14.12	252	85.62	14.38	252.4
8	135–140	..	85.83	14.24	265	85.62	14.38	266.4
9	145–150	..	86.08	13.86	284	85.62	14.38	280.4
10	155–160	22.8	85.98	13.92	294	85.62	14.38	294.4
11	165–170	27.0	86.08	13.98	312	85.62	14.38	308.5
12	175–180	30.2	86.01	13.82	326	85.62	14.38	322.5
13	185–190	31.8	86.28	13.88	336	85.62	14.38	336.5
14	195–200	32.0	86.40	13.50	355	86.12	13.88	348.5
15	205–210	31.8	86.58	13.44	366	86.10	13.90	362.5
23	80- 85	..	84.86	15.08	199	84.75	15.25	198.3
24	90- 95	..	84.80	15.01	214	84.81	15.19	212.3
25	100–105	..	84.93	15.10	223	84.86	15.14	226.4
26	115–120	..	84.94	14.92	235	84.90	15.10	240.4
27	125–130	..	85.21	14.84	252	84.94	15.06	254.4
28	135–140	27.1	84.98	14.79	266	84.98	15.02	268.4
29	145–150	32.2	85.16	14.90	286	85.01	14.99	282.4
30	155–160	36.8	84.93	14.86	298	85.04	14.96	296.5
31	165–170	40.0	85.22	14.73	312	85.07	14.93	310.5
32	175–180	44.1	85.33	14.72	...	85.09	14.91	324.5
33	185–190	48.4	85.52	14.66	...	85.11	14.89	338.5
34	195–200	52.3	85.28	14.52	...	85.14	14.86	352.5
35	205–210	54.9	85.36	14.60	...	85.16	14.84	366.6

The residual fractions, after removal of the paraffins, were oils, the highest members having quite high viscosities. They were not analyzed, since the analyses of the original fractions indicate their identity clearly. Their physical constants were determined, however, as were those of the paraffins, and the identities of all the compounds proved by means of the molecular refractive power. The figures are given in Table VI.

The molecular refractive power is calculated from the Lorentz-Lorenz formula, $M = n^2-1/n^2 + 2.m/d$, where n is the refractive index, d the specific gravity, and m the (theoretical) molecular weight. This gives the observed M, which is independent of temperature provided n and d

are measured at the same temperature. The calculated M is a summation of the values for the number of carbon and hydrogen atoms in the compound, taking carbon as 2.418 and hydrogen as 1.100, since the measure-

TABLE VI

PHYSICAL CONSTANTS

No.	Formula	D.	n	M obs.	M calc.	Δ	CH_2
23	$C_{14}H_{30}$	0.7820^a	1.4370	66.49	66.85	−0.35	
							4.84
24	$C_{15}H_{32}$	.7825^a	1.4380	71.33	71.47	− .14	
							4.68
25	$C_{16}H_{34}$	.7835^a	1.4379	76.01	76.09	− .08	
							4.67
26	$C_{17}H_{36}$	.7839^a	1.4379	80.68	80.71	− .03	
							4.47
27	$C_{18}H_{38}$	.7916^a	1.4423	85.15	85.32	− .17	
							4.50
28	$C_{19}H_{40}$	.7833^b	1.4356	89.65	89.94	− .29	
							4.43
29	$C_{20}H_{42}$	.7848^b	1.4370	94.08	94.56	− .48	
							4.55
30	$C_{21}H_{44}$	.7871^c	1.4363	98.63	99.18	− .55	
							4.66
31	$C_{22}H_{46}$	.7939^c	1.4400	103.29	103.80	− .51	
							4.39
32	$C_{23}H_{48}$	.7953^c	1.4410	107.68	108.41	− .73	
							5.03
33	$C_{24}H_{50}$	.7872^d	1.4370	112.71	113.03	− .32	
							4.35
34	$C_{25}H_{52}$	.7907^d	1.4380	117.06	117.65	− .59	
							4.79
35	$C_{26}H_{54}$	.7948^d	1.4408	121.85	122.29	− .44	
1	$C_{12}H_{24}$	.8032^a	1.4458	55.93	55.42	.51	
							4.63
2	$C_{13}H_{26}$	.8075^a	1.4487	60.56	60.03	.53	
							4.73
43	$C_{14}H_{28}$	.8187^a	1.4560	65.29	64.65	.64	
							4.57
44	$C_{15}H_{30}$	.8203^a	1.4570	69.86	69.27	.59	
							4.53
45	$C_{16}H_{32}$	.8270^a	1.4600	74.39	73.89	.50	
							5.13
46	$C_{17}H_{34}$	.8133^a	1.4539	79.52	78.51	1.01	
							4.38
47	$C_{18}H_{36}$	.8200^a	1.4569	83.90	83.12	0.78	
							4.50
45	$C_{19}H_{38}$	.8257^a	1.4601	88.40	87.74	66	
							4.08
49	$C_{20}H_{40}$	.8538^a	1.4751	92.48	92.36	12	
							4.62

TABLE VI (*Concluded*)

No.	Formula	D.	*n*	*M* obs.	*M* calc.	Δ	CH_2
50	$C_{21}H_{42}$	.8569[a]	1.4771	97.10	96.98	.12	
							4.50
51	$C_{22}H_{44}$	.8643[a]	1.4811	101.60	101.60	.00	
							4.44
52	$C_{23}H_{46}$	.8732[a]	1.4860	106.04	106.21	− .17	
							4.40
53	$C_{24}H_{48}$	.8819[a]	1.4906	110.44	110.83	− .39	
							3.56
54	$C_{25}H_{48}$	.8877[a]	1.4922	114.00	113.25	.75	
							3.82
55	$C_{26}H_{50}$	.8964[a]	1.4943	117.82	117.87	− .05	

[a] At 25°. [b] At 40°. [c] At 50°. [d] At 60°.

ments were made in daylight. The column headed Δ gives the difference between them. The calculated value for the CH_2 group is thus 4.618, and the last column gives the observed increment.

It will be observed that the agreement is quite close, the observed values of *M* being uniformly a little lower for the paraffins, and with three exceptions, a little higher for the other two series. According to Cohen,[14] simple ring formation produces no perceptible change in *M*, whereas a double bond gives a rise of about 1.8. Also, Smiles[15] shows that while *M* for cyclohexane is normal, the value for its methylated derivatives shows a small increase. This proves conclusively that these compounds belong to the three series to which they have been assigned, and have the empirical formulas given above.

From the combustion analyses and the sudden change in the specific gravity, Nos. 49 to 53 might also be placed in the series C_nH_{2n-2}, but if the molecular refractive power is calculated on that assumption, the results are widely divergent, as is shown in Table VII. So the change in properties at No. 49 must be assumed to be due to the greater purity of it and the succeeding members.

TABLE VII

MOLECULAR REFRACTIVE POWER

No.	Formula	*M* obs.	*M* calc.	Δ
49	$C_{20}H_{38}$	91.97	90.16	1.81
50	$C_{21}H_{40}$	96.55	94.78	1.77
51	$C_{22}H_{42}$	101.16	99.40	1.76
52	$C_{23}H_{44}$	105.57	104.01	1.56
53	$C_{24}H_{46}$	109.90	108.63	1.27

Thus it will be seen that 28 compounds have actually been identified, and it is quite certain that two others are present (the paraffins $C_{12}H_{26}$ and

---

[14] Cohen, "Organic Chemistry," Edward Arnold, London, **1921**, vol. 2, pp. 17–27.

[15] Smiles, "Chemical Constitution and Physical Properties," Longmans, Green and Co., London, **1910**, pp. 267 and following.

$C_{13}H_{28}$). In addition there are probably ten compounds in the higher-boiling portion, five paraffins and five hydronaphthalenes, which could be isolated, given sufficient material. No attempt was made to determine the structure of any of these compounds, for that would be a research in itself.

Paraffins similar to those obtained above have been isolated from various sources by several investigators: by Krafft[16] from lignite, by Mabery[17] from Pennsylvania and Japanese petroleums, and by Francis[18] from paraffin wax obtained from Scotch shale-oil. The melting points given by these workers are approximately the same, and correspond quite closely to those given above, so that all these compounds must have the same structure, but what that is has never been definitely determined. Krafft assumed without experimental confirmation, that his compounds were the normal paraffins, but Francis is studying the constitution of his compounds by auto-oxidation methods, so that this question may be settled before long.

Naphthenes having the same empirical formulas as those given above have been isolated by Mabery from Ohio, Canadian, Japanese and South American petroleums, also from distillates from grahamite, gilsonite and bituminous coal; by Markownikow[19] from Baku petroleum; and by Seyer[20] from bituminous sand. None of these workers has determined the structure of any of his compounds. The structures of some of the lower members have been worked out, however; for example, $C_{11}H_{22}$, was obtained by all the above-mentioned investigators, and also by Pictet[21] from Loire coal. He proved that his compound was the symmetrical pentamethylcyclohexane.

Compounds having the general formula C_nH_{2n-2}(homologs of dekahydro-naphthalene) have been obtained by both Mabery and Seyer, but apparently the two members isolated as described above have never been obtained before. No work has ever been done on the structure of these compounds.

The Action of Acids

An attempt was made to investigate the action of nitric acid and also a mixture of nitric and sulfuric acids on pyrobituminous shale. In both cases heating on a water-bath for a week with an excess of the reagent

---

[16] Krafft, *Ber.*, **40**, 4779 (1907).

[17] Mabery, *Proc. Am. Acad. Arts Sci.*, **25–41**; THIS JOURNAL, **39**, 2015 (1917); **41**, 1690 (1919).

[18] Francis, *J. Chem. Soc.*, **121**, 496, 1529, 2804 (1922).

[19] Markownikow and Ogloblin, *Ber.*, **16**, 1983 (1873); *J. Russ. Phys. Chem. Soc.*, **15**, 335 (1883).

[20] Krieble and Seyer, THIS JOURNAL, **43**, 1337 (1921).

[21] Pictet and Ramseyer, *Ber.*, **44**, 2486 (1911). Pictet and Bouvier, *Ber.*, **46**, 3342 (1913).

seemed to dissolve most of the organic matter, and on dilution this was precipitated as a brown, amorphous mass, free from inorganic matter. This product was a rather unstable material, very soluble in ammonia from which it was precipitated by hydrochloric acid, and it contained nitrogen but no sulfur. Thus it falls into the class of humins. On account of the extreme difficulty in working with this material, nothing further could be accomplished.

Extraction under Pressure

Some of the 10-mesh shale was heated with benzene to 200° in a sealed tube for three hours. When the tube was opened there was a slight outrush of gas, in which hydrogen sulfide could be detected. The shale was then placed in a Soxhlet apparatus and extracted completely with benzene. A second tube with only shale in it, open at one end, was heated at the same time, and the shale extracted in the same way. The percentage of extract in the first case was 7%, and in the second case 2%. The first extract was a black limpid liquid, with a slight odor of decomposition, which contained less asphaltenes than the normal extract, but a much greater proportion of resins; the second extract was a thick, red liquid with the characteristic hemp-like odor, which behaved in every way like the extract from unheated shale.

This proves conclusively that the higher amount of extract obtained in pressure extraction is not due merely to the elevated temperature, for heating without pressure has absolutely no effect. Evidently there is some specific action on the part of the solvent under these conditions, more dependent on the pressure than the temperature.

The thanks of the author are due to Dr. R. F. Ruttan, Director of Chemistry, under whose direction this research was carried out.

Summary

It has been shown that a considerable extract is obtainable from pyrobituminous shale, which may be separated by a standard method into three empirical parts—asphaltenes, resins, and hydrocarbons. The amount of hydrocarbons obtained on the large scale was 1.36% of the original shale, which is about 4% of the kerogen. This mixture contains only traces of compounds boiling below 200° at atmospheric pressure, but by fractionation at low pressures compounds may be isolated. In this way 28 compounds belonging to the paraffin, naphthene and hydronaphthalene series have been identified. Two of these have never been obtained before, the rest are probably identical with compounds which have been isolated from very varied sources. The asphaltenes and resins were not examined further; they form only about 15% of the total extract and are difficult to work with, but that problem must be solved later in order to complete the study of these extracts. This method is especially

valuable since it involves no alteration of the kerogen—it is absolutely certain that the products obtained existed as such in the original shale.

By the action of benzene in a sealed tube at 200°, the amount of extract obtainable from pyrobituminous shale is more than trebled. As this amounts to 20% of the kerogen, it will be very interesting to find its constitution, and evidently this can best be done by the method described above.

By the action of nitric acid the kerogen may be completely removed from the shale, though in a highly altered condition. The products obtained are humins.

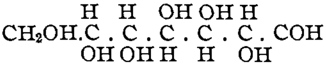
Montreal, Canada

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. IV. TWO ISOMERIC CRYSTALLINE HEXA-ACETATES OF DEXTRO-ALPHA-MANNOHEPTOSE

By C. S. Hudson and K. P. Monroe[1]

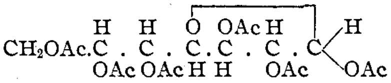
Received November 28, 1923

Fischer and Passmore[2] prepared from *d*-mannose by the cyanohydrin synthesis a sugar, *d*-α-mannoheptose, the configuration of which was established later by Peirce[3] to be



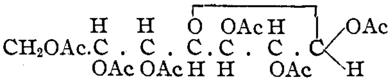
$$\begin{array}{rcccccl} & H & H & OH & OH & H & \\ CH_2OH. & C & .\,C & .\,C & .\,C & .\,C & .\,COH \\ & OH & OH & H & H & OH & \end{array}$$

It is to be expected that a sugar of this structure will yield, like glucose, two fully acetylated derivatives of configurations



$$\begin{array}{rcccccl} & H & H & O & OAc & H & \;/H \\ CH_2OAc. & C & .\,C & .\,C & .\,C & .\,C & .\,C\langle \\ & OAc & OAc & H & H & OAc & \;\backslash OAc \end{array}$$

and



$$\begin{array}{rcccccl} & H & H & O & OAc & H & \;/OAc \\ CH_2OAc. & C & .\,C & .\,C & .\,C & .\,C & .\,C\langle \\ & OAc & OAc & H & H & OAc & \;\backslash H \end{array}$$

($Ac = CH_3.CO$)

We attempted to prepare these compounds by the usual methods, with the result that we have crystallized two isomeric hexa-acetates and have obtained good evidence of the existence of a third form in an amorphous state. The *first hexa-acetate of d-α-mannoheptose* was prepared by acetylating the sugar with boiling acetic anhydride and sodium acetate. The melting point of the pure crystalline substance is 106° and its rotation in chloroform solution is to the right, $[\alpha]_D^{20} = +24.2°$. When a solution of this hexa-acetate in acetic anhydride containing a small quantity of

---

[1] This work was done in 1918 in the Carbohydrate Laboratory of the Bureau of Chemistry, U. S. Department of Agriculture. Part 3 of this series was published in This Journal, **46,** 483 (1924).

[2] Fischer and Passmore, *Ber.,* **23,** 2226 (1890).

[3] Peirce, *J. Biol. Chem.,* **23,** 327 (1915). The proof of the configuration consists in Peirce's demonstration that *d*-α-mannoheptitol is antipodal to *d*-α-galaheptitol and that the same relation holds between the corresponding heptaric acids.