The Optical Properties of Some Petroleum Products

by Irvin Wesley Humphrey

1913

Submitted to the Department of Chemistry of the University of Kansas in partial fulfillment of the requirements for the Degree of Master of Science

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I HISTORICAL.

Historical sketches of the development of polarimetry along any line usually begin with reference to Biot, and this is especially true of petroleum, for when the immortal farther of polarimetry published his classical memoir in 1835 upon the circular polarization of light and its relation to organic chemistry, he referred to a carefully rectified sample of naphtha which gave the remarkable rotation of - 15° 21' when examined in red light.[1] Rakusin has since examined petroleum from Biot's native province, Alasce, but found it dextrorotatory, and because the word naphtha was more loosely used then Engler thinks that this sample may have been obtained from bituminous shales, while still others think that Biot may have been mistaken in its rotation. Be that as it may, no other chemist for almost half a century published data upon the optical properties of petroleum except Lentz,[2] who in 1838 examined the white naphtha from Baku, and Biot's own observation and its significance for petroleum chemistry were forgotten until brought to light by Walden in 1900[3]

[1] Mem.de l'Acad.de Sciences,13, 139; 1835.
[2] Mem. Ac.Sci. St.Petersburg III, 3-12.
[3] Natur. Rund., 1900, 198.

When Markownikow and Ogloblin examined crude, white Caucasian naphtha and some petroleum distillates in 1884, they reported both as inactive.[4] But in the following year Demski and Morawski found, among a number of numeral oils, one which had a dextro rotation of 1.2°[5] In fact, during the previous century, most of the German and Russian investigators of petroleum either considered it unnecessary to observe its rotation or else failed to record it.[6]

Soltsien[7] in 1898 examined a number of commercial paraffin oils and found that the amount of rotation increased with their specific gravity:

Sp. Gr.	Rotation ●
.866	+1°14'
	2° 1'
.87	2° 4'
	3°10'
	3°13'
.881	3°23'
	3°49'
.8815	3°51'
	3°53'
.8795	3°54'
.883	4°11'

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4. Journ. Russ.phys-chem.Ges., 15,237; 1884.
5. Dingler's Poly. Jr., 258, 82; 1885.
6. Die Polarimetrie der Erdöle, M.A.Rakusin,P. 13.
7. Zeit. öff.Chemie 4, 223

● 1° circular = 2.88° Ventzke.

Walden[8] was among the first to show that the optical activity of petroleum was doubtless derived from organic matter, thus giving great support to Engler's organic theory of the origin of petroleum. Hence a great deal of work has been done in this new field of petroleum investigation during the past decade by Engler, Albrecht, Marcusson, Rakusin and others, their results showing that the dextro rotation of the plane of polarization by the higher boiling fractions of petroleum is almost universal, although a few are inactive, perhaps because they are racemic mixtures.

Rakusin[8] states that the amount of rotation of the plane of polarization increases, for every fractionated petroleum, with the specific gravity, density, viscosity, boiling point, molecular weight and color, and that the rotation of the crude oil is equal to the sum of the rotations of its constituent fractions when distilled in vacuo, although it may not be when distilled at ordinary pressure because of racemisation and decomposition.

Some petroleums supposed to be inactive have been found to be slightly active after careful examination. For instance, Engler and Bobrzynski[9] took

an oil from Urycz (Galicia), Sp. gr. 0.975,

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[8] Die Polarmetrie der Erdöle, P 62.

[9] Ch. Zeit., 36, 837; 1912.

which was reported inactive, and quickly distilled off the portion below 200°, finishing the distillation at 12 mm. pressure.

These rotations were found:

Fraction	Tube	Rotation (sacch.)
60° - 196°	inactive	
196 - 222°	10 cm.	+ 0.7°
222° - 246°	5 "	+ 0.6°
246° - 275°	5 "	+ 0.7°
275° - 320°	2.5"	+ 1.0°

It has been observed that a maximum rotation is found in the fractions of a given petroleum when distilled in vacuo, say at about 265°, followed by a decrease in rotation beyond 300°. Engler gives this example:[10]

Boiling point at 14 mm.	Rotation (sacch.) 200 mm. tube
106° - 173.5°	+ 0.2°
173° - 208.0°	+ 2.1°
208° - 230.5°	+ 7.3°
230.5° - 278.0°	+ 17.0°
278° - 328.0°	+ 14.6°
328° - 364°	+ 7.8°

and the following maxima[11] of rotation:

Origin	Fraction	sacch.° 200 mm.	mm.press.
Hannoven	235° - 275°	+ 10.4°	12
Baku	230° - 278°	17.0°	12
Galicia	260° - 285°	22.8°	12
Roumania	250° - 270°	22.0°	12
Java	280° - 286°	14.3	17
Pennsylvania	255° - 297°	1.0	14

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[10] Chem-Ztg. 1906, 711.

[11] Cholesterol, the Basis of the Optical Activity of Petroleum.

Engler[12] has examined an Elsässer oil whose fractions show two maxima:

	Boiling Point	Pressure in mm.	Sp.gr. at 20°	Sacch.° 200 mm.
1.	34.0°-45.5°	23.0	0.7922	+ 0.40
2.	45.5°-69.0°	18.0	0.8045	0.45
3.	69.0°-76.5°	17.0	0.8153	0.50
4.	76.5°-84.5°	16.0	0.8231	0.25
5.	84.5°-91.0°	14.5	0.8290	0.15
6.	91.5°-99.5°	12.5	0.8337	0.05
7.	99.5°-215.5°	(ten fractions).		
			0.8445 - 0.8880	0.00
17.	215.5°-235.0°	12.0	0.8737 at 35°	1.32
18.	235.0°-249.0°	12.5	0.8835	2.32
19.	249.0°-265.0°	13.0	0.8918	4.40
20.	265.0°-281.0°	13.0	0.9023	6.40
21.	281.0°-291.0°	13.0	0.9084	6.60

Fraction 17 diluted with benzol 3:1; 18 = 3: 2; 19 and 20 = 1:1; 21 = 1:1.

It might be noted that Engler and his pupils for some reason obtain much larger rotations than Rakusin or ZaloziecKi and Klarfeld do[13] for oils from the same locality. Petroleum from the U. S. seems to show a smaller rotation, as a rule, than European, as may be seen from the following typical examples:

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[12] Zeit. ang. Ch. 1908, 1593.

[13] Die Polarimetrie der Erdöle P. 64.

Pennsylvania oil.[14]

Boiling Point	Rress.	Rotation (sacch.) 200 mm.
100° - 200°	14 mm.	0
200° - 255	14 "	+0.4°
255° - 297°	14 "	+1.0°
297° - 348°	15 "	+0.8°

A Kansas oil from Urbana[15] gave the following rotations:

Boiling Point	Press.	Sp. gr 25°/15°	Rotation in 200mm. tube.
195° - 215°	87 mm.	0.8454	+ 0.10°
215° - 228°	87 "	0.8503	0.11°
228° - 239°	87 "	0.8530	0.15°
239° - 250°	90 "	0.8600	0.23°
225° - 237°	30 "	0.8670	0.34°
237° - 248°	30 "	0.8720	0.46°
248° - 257°	30 "	0.8750	0.54°
250° - 262°	28 "	0.8790	0.61°
262° - 272°	27 "	0.8810	0.76°
272° - 282°	27 "	0.8830	0.98°

Lower boiling fractions of petroleums, which have a laevo rotation, have been obtained from three localities. The fraction boiling from 159° - 283° of an oil from Tartagal Argentine gave a rotation of -0.5° (sacch.),[16] and several oils from Borneo and Java also have laevo rotatory fractions. Jones and Wootton examined a Java oil which gave a rotation of

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[14] Zeit. Ang. Ch. 1908; 1592.

[15] Bushong: Chemical Comp. Of Petroleum.
Univ. Geo.Survey of Kansas, Vol.IX, P.317:1908.

[16] Pet. 1909; 319.

-0.18° in a 200 mm. tube for the portion boiling between 260° - 340°,[17] and Engler has found that the fractionated Java and Borneo oils are first laevorotatory, then inactive, and finally dextrorotatory as is shown in this Roengkoet oil.[18]

Temperature	Pressure mm.	Rotation (sacch°) 200 mm.
- 129°	16.0	0
120° - 150°	14.5	-1.1
150° - 168°	14.0	-2.2
168° - 182°	14.0	-2.0
182° - 242°	14.5	0
242° - 268°	15.5	+1.9
268° - 281°	15.5	+4.1
281° - 290°	15.0	0

This wide spread rotation in petroleum has lead chemists to believe that the optical activity is caused by one and the same substance, but it has not yet been isolated because it comprises only a very small portion of the complex petroleum mixture, and it is exceedingly stable toward reagents. Marcusson has found[19] that the rotation is lessened somewhat by fuming sulphuric acid, and a Russian machine oil ($\alpha_D = + 2.53°$) still retained a rotation of +2.23°

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[17] Jour. ch. Soc. 91,1146; 1907.
[18] Zeit. ang. Chem. 21,1593; 1908.
[19] Ch. Zeit., 1907; 420.

in the 89% portion which remained after treatment with the sulphuric acid and formaldehyde mixture, while the 73.4% portion remaining after treatment with nitric acid still had a rotation of +2.16°. Bobczynski[20] treated strongly active oil with ozone, but the ozonide was inactive and the saturated hydrocarbon mixture still retained its original activity. All these facts indicate that the active principle of petroleum is a saturated substance.

Bobczynski[21] maintains that petroleum gradually loses its activity after a time, but Engler found that four fractions of Baku oil, rotating from +4.0° to +7.2° sacch., did not decrease in activity after heating for many hours at 400°.[22] When a laevorotatory Java oil was heated in a sealed tube for one hour at 300° its activity was not diminished, but at 350° it became dextrorotatory. These results indicate that a racemic compound exists in petroleum, and that the dextro isomer is much more stable than the laevo, as is also indicated by the relative proportions of dextro and laevo petroleums found in nature.

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[20] Ch. Zeit., 1911; 454.
[21] Pet., 6; 438.
[22] Ber., 43; 608.

Albrecht treated strongly active oil with metallic calcium, thereby reducing the sulphur content one-half, but the optical activity remained unaltered. Nor can this activity be ascribed to nitrogen compounds,[23] for the nitrogen content of most oils is very small and exists chiefly in the form of organic bases easily removed by acid treatment.

Many chemists, searching for that elusive asymmetric carbon atom, believe that the substance which causes this optical activity is cholesterol, a highly active laevorotatory alcohol which is widespread in the animal organism, although in minute quantities. Correspondingly,phytosterol is found in somewhat larger quantities in the vegetable kingdom. Now many cholesterol reactions can be duplicated in petroleum. For instance, when rapidly distilled the former gives a dextrorotatory distillate, but if gently distilled it yields first dextrorotatory, then laevo-, then inactive and finally dextrorotatory fractions, therein resembling the laevorotatory Java oils, as it also does in changing from a laevo to a dextro rotation when

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23. Die Polarimetrie die Erdöle, P. 42.
24. Steinkopf, Koss and Liebmann,

heated in a sealed tube above 350°. Steinkopf,[24] however, says that unaltered cholesterol is not volatile in vacuo with petroleum vapors and hence can not cause the laevorotation in the fractionated Java oil. The maximum rotation found in fractionating either petroleum or cholesterol occurs at about the same high temperature, and Windaus[25] obtained from the distillation of cholesterol a substance similar to petroleum. Lewkowitsch,[26] by distilling strongly active Chaulmoogra oil, found a liquid free from acids and glycerine with an odor resembling petroleum, which gave dextrorotatory fractions when distilled in vacuo. Marcusson[27] distilled the unsaponifiable matter from wool fat in vacuo and obtained a liquid, the rotation of which increased with the boiling point, a maximum occurring in the 250° - 275° fraction, which is about the same point where the maximum occurs in many fractionated petroleums.

Albrecht,[28] by repeated fractionation of a crude Galician oil, obtained a fraction boiling fairly con-

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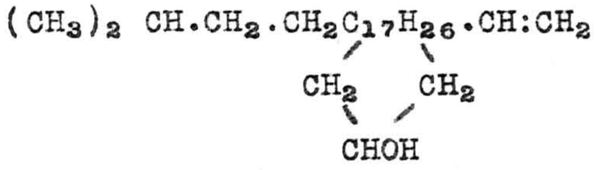
[24] Steinkopf, Koss & Liebmann.
[25] Ber., 37; 2027.
[26] Ber., 1907; 4161.
[27] Ch. Zeit. 1907; 419. No. 33.
[28] Dissertation-Karlsruhe, 1907, p. 77.

stantly at 240° under 10.5 mm. pressure, which amounted to one percent of the original oil. It analyzed: C = 87.76% and H_2 = 12.24%, indicating the formula $C_n H_{2n-6}$. One high boiling member of this series. $C_{25}H_{44}$ has the composition C = 87.12% and H_2 12.88%; another member $C_{30}H_{54}$ has C = 86.86% and H_2 = 13.14%. This shows a compound low in hydrogen, and from what we have seen above, (P. 8) the optical activity is not due to unsaturated compounds. Now according to Windaus[29] cholesterol consists of a complex with several hydrogenized rings, one of which is known to be a pentamethylene ring:



When heated it is probable that some of the rings remain intact, so that Marcusson believes that the activity of petroleum is due to these condensed naphthenes, all of which is in accord with the cholesterol theory.

Neuberg[30] asserts that the quantity of cholesterol found in nature is not sufficient to account for the

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[29] Ber., 1908, 2558; 1904, 2028.
[30] Pet., 2, 750.

optical activity of petroleum and his researches have shown that the decomposition products of proteins give rise to active amino compounds and fatty acids, such as d- valeric and d- caproic acids, as high as 20% of the former being obtained from some decomposing proteins. He distilled a mixture of oleic and d-valeric acids after heating under pressure, and obtained these fractions:

	- 125°	+0.2°	rotation in 200 mm tube
125°	- 230°	+0.5°	" " "
230°	- 320°	+0.7°	" " "

These gave the Salkowski cholesterol reaction caused, Neuberg believes, by condensation of hydrocarbons of high molecular weight formed between the two acids. He also obtained active acids from putrid gelatine and cheese[31] and the acids from the latter, ranging from acetic to hexoic, gave a rotation of +1.2°. Yet it would seem that these fatty and amino acids would be washed out.[27]

Tschugajew showed that lanolin owed its activity to cholesterol[32] which gives a red color with trichloracetic acid as do active animal fats, phytosterol

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[31] Biochem. Zeit., 1906; 368.
[32] Ch. Zeit., 1907; 419.

and cod liver oil, the latter in proportion to its cholesterol content. The intensity of this fleeting color, sensitive to one part in 80,000, has been used by Rakusin[33] to measure the supposed cholesterol decomposition content of mineral oils, for it is roughly proportional to their optical activity. There are some exceptions to this color scheme, however, shown for example in American lubricating oils which give color reactions equal to those of Caucasian oils possessing eight times their optical activity, which Rakusin explains by the presence of racemised cholesterol products in the American oil.[34] Later it was found that the Tschugajew reagent also gave a red color with many organic compounds, such as benzene and phenol, and Charitschkow showed that it gave the same color with naphtha prepared by the Sabatiēr and Senderens reaction.[35] Then the test was modified by the use of formaldehyde, and it gave a bluish color with cholesterol, but no characteristic color with petroleum. Other more or less doubtful color tests have also been used to test for cholesterol in mineral oils.

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[33] Die Polarimetrie der Erdöle, P. 44 ff.
[34] Ch. Zeit., 1906; 1041.
[35] Njeft. Djelo, 1906; 1250, 1388.

Windaus[36] has shown that digitonin forms a crystallin compound when added to cholesterol in alcoholic solution, even if only 0.0001 gram per cubic centimeter is present, and that it also detects any of its derivatives which still retain a hydroxyl group. Steinkopf, Koss and Liebmann[37] found that when slightly less than an equivalent amount of digitonin was added to a 1.33% cholesterol solution (rotation -0.8° in 200 tube, the maximum found in the laevo Java oils) that 89% of the digitonin was precipitated as the double salt of digitonin and cholesterol. But when various dextro-and laevo- rotatory fractions of Java petroleum were tested by digitonin solution, no precipitate was formed. Cholesterol, distilled by them under atmospheric pressure, gave the following fractions, all of which gave the digitonin reaction:

Boiling Point degrees	Length of Tube in mm.	Rotation (diluted with 12.6 parts $CHcl_3$).
380° - 382°	50	- 0.88°
382 - 400	25	- 0.51°
400 - 401	25	- 0.49°
401 - 406	25	+ 0.77°
406 - 421	25	+ 1.88°
421 - 422	25	+ 3.45°
422 - 450	10	+ 0.98°

[36] Ber. 24, 238; 1909.

[37] Ch. Ztg., 36, 653; 1912.

When 0.1 gram of cholesterol was added to 10 cc. of various laevorotatory fractions of Java petroleum, (boiling from 140° - 170°), the optical activity was about doubled, but upon distillation in vacuo at the same temperature the fractions resumed their original activity, and 96.5% of the added cholesterol was found in the residue, but the digitonin test could detect none in the distillates. In fact, cholesterol need not be looked for in fractions of petroleum boiling below 300° in vacuo, although the authors point out that cholesterol, in the course of time, under the influence of catalytic agents, may give rise to the dextro- and laevorotatory substances which cause the activity of petroleum.

It was Rakusin[38] who first observed that a greater rotation was given by the naphthenic acids derived from the residues of Russian petroleum refining than by the petroleum itself. Finding that some naphthenic acids derived from kerosene gave a dextrorotation of +0.55° (sacch.° in 200 mm. tube), he concluded that the optical activity of petroleum might be due to its naphthenic acid content. Later R. Albrecht[39] reported that a

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38. Die Untersuchung des Erdöls und seiner Produkte P.178.

39. Dissertation, Karlsruhe, 1907, P. 82.

sample of cylinder oil, having a rotation of +11.2° (sacch.), still had a rotation of +10.4° after heating for seven hours on a water bath with an equal volume of KOH solution (1:3), while a second sample after treating one hour longer with stronger KOH solution (1:1) had +8.4° rotation.

Marcusson[40] maintained that, since petroleum distillates in general could contain but small amounts of naphthenic acids, the activity of petroleum could not be due to these acids, the activity of which, in fact, must be attributed to the cholesterol derivatives introduced into them by the action of the sulphuric acid during the refining process, or else by the phenols and hydrocarbons which Lidoff had detected in them.[41] On the supposition that the most cholesterol derivatives occur in the higher boiling fractions of petroleum, Marcusson was led to believe that the naphthenic acids separated from lubricating oils would have a greater activity than those which Rakusin obtained from kerosene, and actually found this to be the case in the acids he examined:

[40] Ch. Ltg., 1907, 421.
[41] Ch. Rev., 1902, 134.

	Boiling Point in Vacuo	Percent	Rotation Degrees of arc
1.	- 260°	43.3	+0.77° in 200 mm tube
11.	260° - 350°	36.3	+1.62° " 100 " "

Another source of naphthenic acids is Texas petroleum, and small quantities may also exist in other American oils. R. Albrecht[42] reports that neither Russian nor American naphthenic acids show an appreciably larger rotation than the refined oils from which they were separated, and gives this data for naphthenic acids separated from refined Texas machine oil, having + 9° (sacch.) rotation:

	Boiling Point at 15-18 mm.	Percent	Rotation (sacch.°)
I	145° - 235°	11	-----
II	235° - 275°	30	+ 4°
III	275° - 310°	18	+ 9°
IV	310° - 360°	18	brown
	Residue	23	

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[42] Ch. Revue, 18, 189; 1911.

EXPERIMENTAL.

Recent investigations upon naphthenic acids have been made in the research[43] laboratories of the University of Kansas. Commercial naphthenic acids from Baku, Russia were partially esterified and the most volatile of the resulting esters, after saponification, were freed from hydrocarbons by steam distillation. Then the soap was acidified and the free naphthenic acids, after being converted into their methyl esters, were fractionated twelve times with the aid of a dephlegmator.

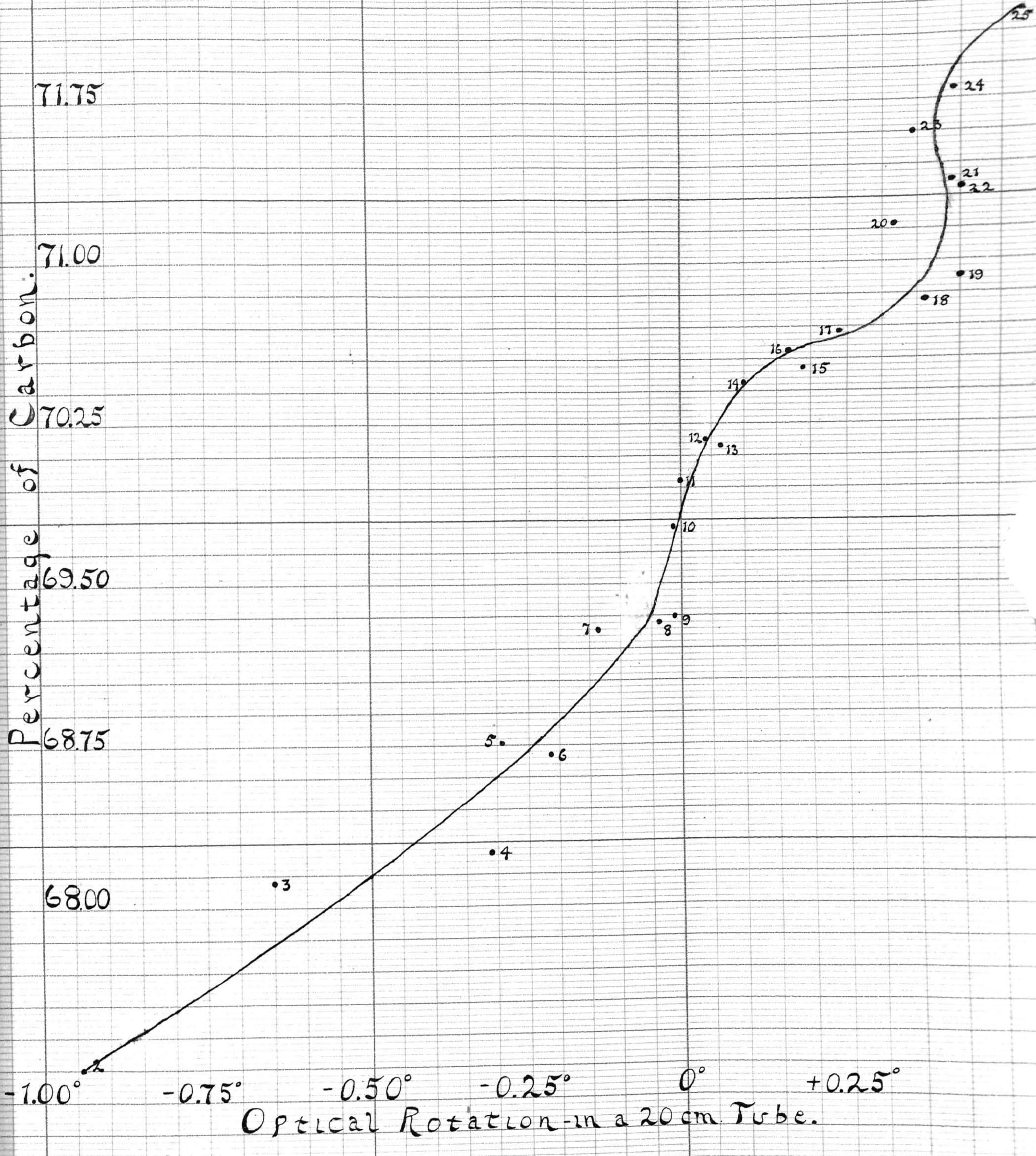
[43] Orig.Com.Internat.Cong.of Appl.Chem., VI,57; 1912.

TABLE I.

Naphthenic Methyl Esters (after 12 distillations).

No.	Boiling Point Degrees	Sp.gr. 23°/15°	Ref. index at 23°	Mol. Wt. in C_6H_6	Opt.rot 20 cm. tube Degrees	Analysis C %	Analysis H %
0	140-148	. . .	1.4048	. . . .	. . . .	. .	. .
00	148-160	. . .	1.4120	. . . .	. . . .	. .	. .
1	160-165	. . .	1.4162	137.1	-0.92	65.64	10.70
2	165-170	0.9070	1.4201	139.5	-0.94	67.25	10.61
3	170-175	0.9158	1.4243	144.7	-0.65	68.14	10.64
4	175-179	0.9195	1.4268	145.8	-0.36	68.25	10.55
5	179-183	0.9213	1.4283	147.0	-0.29	68.76	10.47
6	183-186	0.9230	1.4298	151.6	-0.21	68.71	10.44
7	186-189	0.9245	1.4311	154.9	-0.13	69.29	10.45
8	189-192	0.9262	1.4323	154.1	-0.04	69.32	10.50
9	192-194	0.9252	1.4331	156.4	-0.02	69.35	10.59
10	194-196	0.9255	1.4336	155.8	-0.02	69.77	10.63
11	196-198	0.9235	1.4340	159.7	0.00	69.99	10.59
12	198-200	0.9235	1.4341	158.5	+0.04	70.18	10.65
13	200-202	0.9230	1.4345	161.7	+0.06	70.16	10.72
14	202-204	0.9230	1.4350	162.9	+0.10	70.45	10.73
15	204-206	0.9232	1.4359	164.4	+0.19	70.51	10.71
16	206-208	0.9248	1.4367	165.9	+0.17	70.60	10.86
17	208-210	0.9258	1.4372	170.1	+0.24	70.68	10.79
17	208-210	. . .	. . . .	. . . .	. . .	70.71	10.76
18	210-212	0.9261	1.4383	170.6	+0.36	70.83	10.68
19.	212-214	0.9262	1.4389	170.0	+0.40	70.93	10.67
20.	214-216	0.9269	1.4395	172.6	+0.32	71.17	10.94
21	216-218	0.9269	1.4400	171.9	+0.39	71.38	10.83
22	218-220	0.9276	1.4410	173.3	+0.40	71.36	10.72
23	220-222	0.9279	1.4418	175.2	+0.34	71.60	10.79
24	222-224	0.9284	1.4424	178.6	+0.38	71.79	11.02
25	224-226	0.9290	1.4434	181.6	+0.48	71.99	10.86
26	226-228	. . .	1.4438	. . .	. . .	. . .	. .

Fig. 1.


Percentage of Carbon.
71.75
71.00
70.25
69.50
68.75
68.00
-1.00°
-0.75°
-0.50°
-0.25°
0°
+0.25°
Optical Rotation - in a 20 cm. Tube.
1
2
3
4
5
6
7
8
9
10
11
12
13
14
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25

By the aid of Figure I, the composition of the fractions, represented by carbon percentage, may be compared with the optical rotation. This curve indicates the relationship existing between the optical activities of some isomeric naphthenic esters.

Two minima occur, the first at Fractions 8 and 9, the other near Fractions 18 and 19. Now the analyses show that the latter fractions contain the octonaphthene carboxylic ester (theoretical C 70.53), isolated first by Markownikow and later by Aschan,[44] while the former fractions contain the heptanaphthene carboxylic ester described by both Markownikow[45] and Aschan,[46] who also found the hexanaphthene carboxylic ester contained in Fraction 2. It will be noticed that there are also two maxima; the lower near Fractions 12 and 14, the other near Fractions 23 and 24. Now Fraction 14 has the minimum density in the series of ester fractions, and contains 70.45% C, showing the presence of an isooctonaphthene carboxylic ester, with a density lower than that of either the heptanaphthene or octonaphthene carboxylic esters hitherto known.

[44] Ber., 24, 2723; 1891.
[45] Mr. Praut. Chem., 49, 85; 1894. Ann., 307, 370; 1899.
[46] Ber., 23, 870; 1890.

It is evidently a true homologue of the nononaphthene carboxylic ester in Fractions 23 and 24, which Markownikow has isolated, and this is also shown by the 20^{o} interval between their boiling points, which is about the difference between the boiling points of the hexanaphthene, heptanaphthene and octonaphthene carboxylic esters in the other homologous series. Apparently a difference exists between the optical activities of these isomeric naphthenic esters.

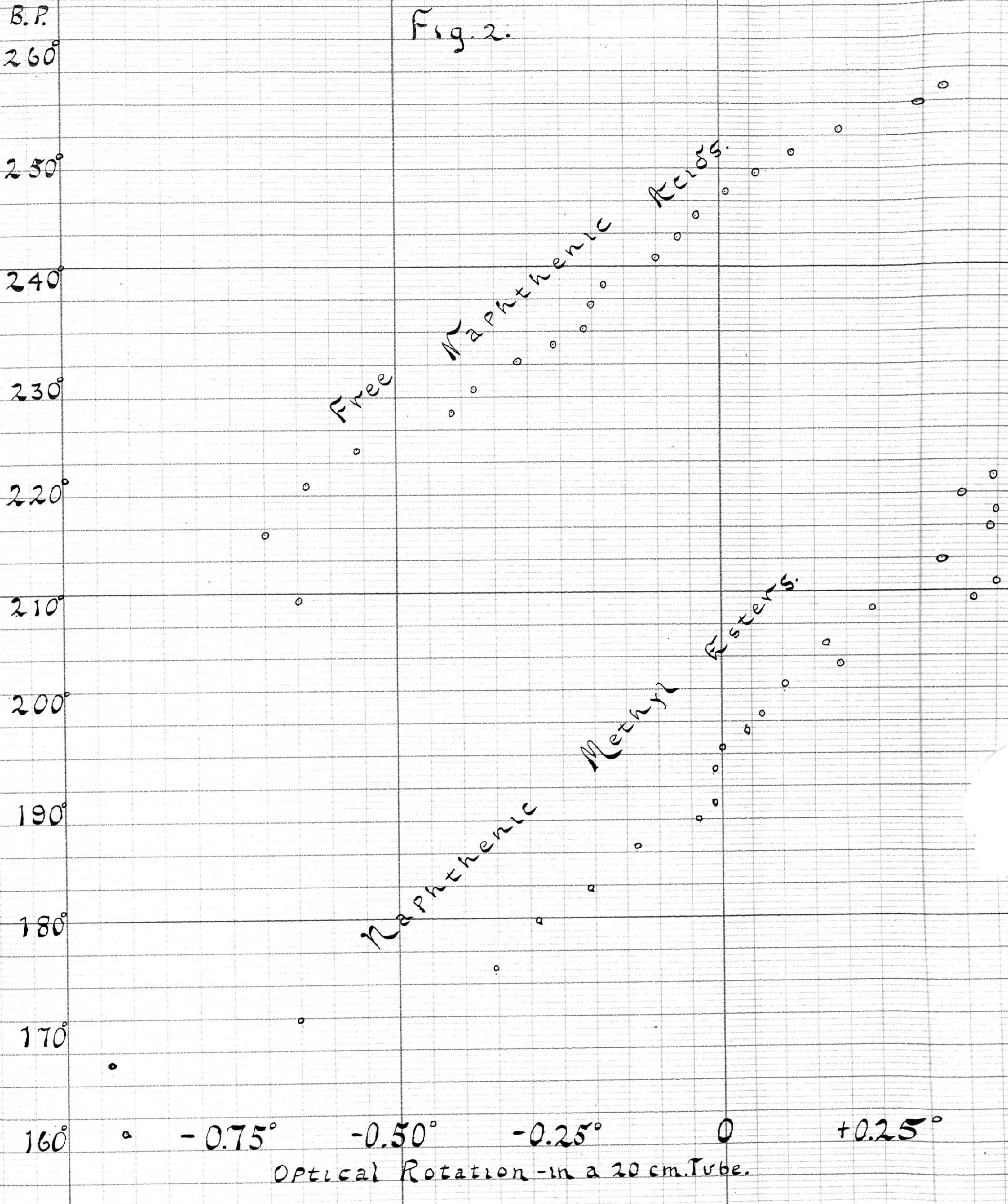
After the more volatile esters above described were separated from the partially esterified naphthenic acids, a quantity of the latter were fractionated three times and then converted into soap, from which the hydrocarbons were removed by steam distillation. This soap was then acidified, and the free naphthenic acids were fractionally distilled twelve time.

TABLE II.

Free Naphthenic Acids (after 12 distillations).

No.	Boiling Point	Sp.gr. 23°/15°	Ref. index at 20.8°	Optical rotation in a 20 cm. tube
	degrees			degrees
00	206-215	0.9246	1.4366	-0.35
0	215-220	0.9369	1.4362	-0.70
1	220-224	0.9467	1.4365	-0.64
2	224-227	0.9519	1.4382	-0.56
3	227-230	0.9565	1.4421	-0.42
4	230-232	0.9580	1.4440	-0.38
5	232-234	0.9615	1.4451	-0.32
6	234-236	0.9630	1.4462	-0.26
7	236-238	0.9627	1.4475	-0.22
8	238-240	0.9627	1.4481	-0.20
9	240-242	0.9629	1.4488	-0.18
10	242-244	0.9623	1.4496	-0.10
11	244-246	0.9626	1.4501	-0.07
12	246-248	0.9625	1.4510	-0.04
13	248-250	0.9617	1.4518	+0.01
14	250-252	0.9620	1.4524	+0.06
15	252-254	0.9622	1.4530	+0.12
16	254-256	0.9624	1.4534	+0.19
17	256-258	0.9623	1.4538	+0.30
18	258-260	0.9624	1.4523	+0.32

Fig. 2.


B.P.
260°
250°
240°
230°
220°
210°
200°
190°
180°
170°
160°
-0.75°
-0.50°
-0.25°
0
+0.25°
Free Naphthenic Acids.
Naphthenic Methyl Esters.
Optical Rotation - in a 20 cm. Tube.

Now when the boiling points and rotations are compared[47] in Figure 2 with those of the methyl esters previously prepared, it is found that the ester fractions boil about 50° lower than the acid fractions with a corresponding rotation. Markownikow and Aschan found that the naphthenic acids which they prepared boiled 49°-50° higher than the methyl esters from which they were made. Such a close parallel between the activity curves of the acids and their corresponding esters leads to the belief that the optically active substances in the naphthenic acids must be of an acid nature since they are esterifiable.

Now investigations of Walden[48] on isomerism in open chains have shown that when the active acid remains the same, and the isomerism is confined to the inactive alcohol, that there is a small difference in the specific rotation as:

$(\alpha)_D$

Methyl - n -butyl malate - 22.44°

Methyl - iso-butyl malate - 22.36°

This is also the case when the active alcohol remains

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[47] Orig.Com.Eighth Int. Cong. Appl.Chem., VI, 64; 1912.

[48] Zeit. Phy. Ch. <u>15</u>, 636; 1894.

the same and isomeric acids are employed:

	$(\alpha)_D$
Amyl - n - butyrate	+ 2.97°
Amyl isobutyrate	+ 2.83°

The iso compounds sometimes show a lower and sometimes a higher rotation than the normal chain compounds.

Walden has also shown[49] that a difference exiats in the rotations of stereoisomeric substances. Thus, the diamylester of fumaric acid has a specific rotation of + 5.93°, while the corresponding ester of maleic acid has + 4.62°. A difference is also found in the specific rotations of the diamylesters of tartaric and mesotartaric acids.

Aschan has proved[50] that naphthenic acids are monocarboxylic derivatives of saturated hydrocarbons known as naphthenes, and the researches of Marknownikow[51] lead to the belief that at least the lower boiling acids are cyclopentane derivatives. Aschan has calculated that there are at least 17 structural isomers of the polymethylene type possible for the acid

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[49] Zeit. Phy. Ch. <u>20</u>, 377; 1896.
[50] Ber., <u>24</u>, 2710; 1891.
[51] Annalen der Ch., <u>307</u>, 367; 1899.

$C_7H_{12}O_{23}$, i.e., eight of the tri-, seven of the tetra- and three of the pentamethylene type.

Zelinsky[52] has found these rotations for cyclic hydrocarbons:

	$(\alpha)_D$
Dimethyl - 1-3 cyclopentane	+ 1.78°
Dimethyl - 1-3 cyclohexane	+ 0.65°
Methyl - 1 - ethyl 3 cyclohexane	- 2.90°
Methyl - 1 - ethyl 3 cyclopentane	+ 4.34°

and the 1- 3 - methylcyclopentane carboxylic acid has the value $(\alpha)_D = -5.89^\circ$

Cyclic compounds with one asymmetric carbon atom in the ring exist in two isomeric active forms. Considering cyclic compounds with two similar asymmetric carbon atoms in the ring, we have cis and trans modifications giving rise to an isomerism resembling that of the tartaric acids. But when these two asymmetric atoms are different, four active forms are possible; for example, all four active isomers of camphoric acid have been isolated. It might be noted that the substitution of a methyl for a carboxyl group in the formulas for the camphoric acids would give rise to some of the structural isomers possible for a naphthenic acid of the formula $C_9H_{17}COOH$.

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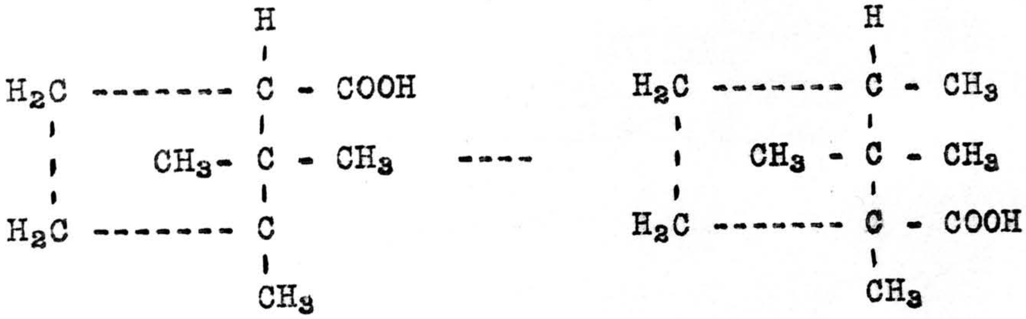
[52] Ber., 35, 2682.

Camphoric Acid.



These examples of optical activity in isomers and in cyclic compounds have been cited to show that naphthenic acids may also be optically active.

The ten fractions of the ethyl esters which were converted into the naphthenic acids described in Table **II**, had smaller rotations because of less complete separation, their rotations being either slightly laevo- or dextro-rotatory. The ethyl esters of the higher fractions have these constants:

TABLE III.

No.	Boiling Point Degrees	Sp. Gr. at 20°	Ref.index at 21°	Rotation to the right. Degrees
8e	220-228	0.912	------	0.00
9e	228-232	0.916	------	0.02
10e	232-236	0.918	------	0.10
11e	236-240	0.921	1.4483	0.14
12e	240-244	0.924	1.4491	0.19
13e	244-248	0.925	1.4506	0.24
14e	248-252	0.927	1.4511	0.26
15e	252-256	0.929	1.4529	0.31
16e	256-260	0.931	1.4540	0.35
17e	260-264	0.933	1.4578	0.36
18e	264-268	0.935	1.4561	0.42
19e	268-272	-----	1.4568	0.46
20e	272-276	-----	1.4578	0.49
21e	276-283	-----	1.4586	0.72

Here too the zero point falls in the region of the nononaphthenic ethyl ester. The point of zero rotation in the methyl esters comes between the octonaphthenic ester of Markownikow and the new isononaphthenic ester, while the zero point for the free acids is also below the nononaphthenic acid.

The naphthenic acids obtained from the ethyl ester fraction XIIe to XXIe were converted into their methyl esters, and, after being distilled five times under reduced pressure and then three times at atmospheric pressure, had the following properties:

TABLE IV.

No.	Boiling Point degrees	Sp. Gr. 16°/W	N 23°/D	Opt. Rot. in 20 cm. tube degrees
1h	196-200	0.9347	1.4364	- 0.36
2h	200-204	0.9337	1.4375	- 0.25
3h	204-208	0.9325	1.4386	- 0.14
4h	208-210	0.9326	1.4390	- 0.03
5h	210-212	0.9323	1.4395	+ 0.02
6h	208-212	0.9321	1.4395	+ 0.02
7h	212-214	0.9316	1.4401	+ 0.06
8h	214-216	0.9319	1.4407	+ 0.11
9h	216-218	0.9320	1.4410	+ 0.14
10h	218-220	0.9323	1.4418	+ 0.18
11h	220-222	0.9326	1.4425	+ 0.21
12h	222-224	0.9329	1.4427	+ 0.25
13h	224-226	0.9330	1.4431	+ 0.30
14h	226-228	0.9332	1.4436	+ 0.32
15h	228-230	0.9332	1.4445	+ 0.36
16h	230-232	0.9340	1.4454	+ 0.42
17h	232-234	0.9340	1.4459	+ 0.42
18h	234-236	0.9344	1.4465	+ 0.48
19h	236-238	0.9345	1.4471	+ 0.49
20h	238-240	0.9354	1.4474	+ 0.54
21h	240-242	0.9357	1.4480	+ 0.53
22h	242-244	0.9364	1.4489	+ 0.56
23h	244-246	0.9363	1.4495	+ 0.57
24h	246-248	0.9367	1.4501	+ 0.62
25h	248-250	0.9370	1.4508	+ 0.63
26h	250-252	0.9372	1.4515	+ 0.63
27h	252-254	0.9382	1.4522	+ 0.65
28h	254-256	0.9382	1-----	------
29h	256-258	0.9405	1.4535	+ 0.71
30h	258-260	0.9420	1.4541	+ 0.71
31h	260-285	0.-----	1.4570	+ 0.70

These fractions contain the higher homologues and isomers of those already known, as is shown by the increase in optical activity and refractive index with the boiling point. A minimum in specific gravity is found in Fraction 7h, but the fractionation of this series was not as effective as that of the other series of methyl esters, partly because they were not fractionated so often, and partly because so efficient a dephlemator could not be used on account of the increase in the boiling point.

The optically active constituents have been found to be very stable. For instance, some crude ethyl esters were highly heated and the distillate, when redistilled, gave the following fractions:

	Temp. of liquid degrees	Temp. of vapor degrees	Sp. gr. at 18°	$N_D/19°$	Rotation degrees
1.	207-275	244-260	0.927	1.4548	+ 0.50
2.	275-298	260-280	0.940	1.4584	+ 0.57
3.	298-360	280-315	0.947	1.4654	+ 0.66

No change in optical rotation has been noticed when the naphthenic esters or acids are distilled under atmospheric pressure instead of in vacuo. For instance, when two liters of crude naphthenic acid, which contained some hydrocarbons, were treated with an excess of dilute sulphuric acid, washed and distilled three times in vacuo, the following fractions were obtained:

No.	Boiling Point at 16 mm. degrees	Sp. Gr. at $18^\circ/15^\circ$	Rotation to the right degrees
IIIa	70-140	0.882	0.02
IIIb	140-160	0.960	0.13
IIIc	160-170	0.967	0.40
IIId	170-175	0.970	0.51
IIIe	175-185	0.972	0.71
IIIf	185-195	0.973	----
IIIg	195-205	0.973	0.92
IIIh	205-225	0.976	1.07

Under this pressure the acids boil about 100° lower than at atmospheric pressure, so it will be seen that their rotations are quite comparable with those of other acids which had previously been esterified, saponified, freed of hydrocarbons by steam distillation and then distilled many times under atmospheric pressure. The hydrocarbons, (which appear to have less optical activity than the naphthenic acids) were not removed by saponification and steam distillation, thus eliminating any influence of alkali on the optical activity. Now the methyl esters in Table IV, which were distilled three times at atmospheric pressure, had rotations ranging from -0.09° to $+ 0.65^{\circ}$ after the second distillation at 42 mm. pressure. When they were finally distilled at atmospheric pressure, five mor fractions were made, which accounts for the wider range in rotation found in the table.

After ethyl ester fraction No. Xe was saponified and the hydrocarbons were removed by steam distillation, the soap was extracted with five successive portions of ether in order to remove any possible cholesterol products, but not more than a drop of extract remained after the evaporation of the ether. The rotations of the naphthenic acids obtained from this fraction agreed with those of the corresponding acid fractions obtained from the preceding ester fraction which was not extracted with ether after saponification.

Through the kindness of Mr. Rhodes, who is investigating the hydrogenation of oils, an attempt was made to hydrogenate 25 cc. of ethyl ester fraction No. 18h. Before treatment it had a specific gravity of 0.9344 at 16°, $N_d/23^0$ 1.4465, and rotation in a 200 mm. tube = + 0.45°. Together with 0.02 gram of palladium chloride and 0.01 gram of potassium carbonate, it was rotated for three hours in an autoclave heated to 80°, and kept meanwhile in an atmosphere of hydrogen under 55 pounds pressure per square inch during most of the time. Under such conditions cottonseed oil is converted into solid stearin, but the properties of the ester were practically unchanged: Sp. gr. 18°/15° 0.9308, $N_D/23^0$ 1.4470, rotation = + 0.42°.

Verrentrapp has shown that when an unsaturated fatty acid is fused with alkali that it is changed into a saturated acid. For example, when oleic acid is fused with alkali, it is changed into palmitic acid, but some acetic and oxalic acids etc., together with free hydrogen are formed. A quantity of high boiling naphthenic acids was fused with NaOH at a temperature of 350° and stirred constantly. No evolution of hydrogen was observed and after the soap was rolled into a cake it was removed from the alkali. The free acids were recovered and converted into their methyl esters which gave the following fractions on steam distillation:

	Rotation degrees	Sp. Gr. 20°/15°	N_D
1	+ 0.52	0.9404	1.4565 at 20°
2	+ 0.63	0.9426	1.4629 at 15°
	Residue	0.9460	

Some investigators have found that the hydrocarbons have about the same optical activity as the naphthenic acids from which they are separated, but we have not found this to be the case. The hydrocarbons separated from the methyl esters in Table I had the following rotations:

	Boiling Point Degrees	Rotation in 200 mm tube Degrees
1.	70-150	+ 0.15
2.	150-162	+ 0.08
3.	162-173	+ 0.05
4.	173-191	0.00
5.	192-203	+ 0.01
6.	204-215	+ 0.00
7.	215-230	+ 0.03

Acids obtained from some of the low boiling ethyl esters had rotations ranging from -0.08° to -0.39°, but the hydrocarbons separated from them had a rotation of but -0.10°, which was changed to + 0.03° upon resaponification. Ethyl ester fraction No. XIe was saponified with alcoholic KOH, freed from alcohol by heating and extracted with ether. After the ethereal extract was freed from ether, the hydrocarbons were washed with water and dried with $CaCl_2$. Hydrocarbons with a specific gravity of 27°/15° = 0.866, were obtained which were inactive in polarized light.

Fractions XIIe-XIVe of the ethyl esters were combined into one portion and Fractions XVe-XXIe into another, and each was separately saponified, and then saturated with carbon dioxide. From the first portion 177 c.c. of hydrocarbons (Sp.gr. at 18°/15° = 0.905, rotation = -0.15°) were obtained by steam distillation; from the second portion 149 c.c. of hydrocarbons,(Sp. gr. 21°/15° = 0.912 and rotation = -0.14°) were separated. These two lots of hydrocarbons were combined, and upon resaponification yielded but 189 c.c. of hydrocarbons (Sp.gr. 18°/15° = 0.908 and rotation = - 0.10°), but the 75 c.c. of naphthenic acids obtained were too dark for polarimetric measurement. The hydrocarbons were then heated to 120°-150° for 10 hours with 100 grams KOH, 100 c.c. ethyl alcohol and 50 c.c. of water. 71 c.c. of hydrocarbons (Sp. gr. 21°/15° = 0.883) were separated, which had a rotation of - 0.07°. The 60 grams of naphthenic acids obtained had a rotation of - 0.24°. The 71 grams of hydrocarbons were then saponified by heating for six hours at 100° with 50 grams of alcoholic KOH, and 54 c.c. of hydrocarbons, (Sp.

gr. $22^{\circ}/15^{\circ} = 0.864$ and rotation $= -0.09^{\circ}$.) were separated. The quantity of naphthenic acids obtained was not sufficient for polarimetric measurement.

It has been pointed out[53] that even though the optical activity of petroleum is not diminished by treatment with alkali, it is quite possible for both dextro- and laevorotatory acids to be removed in equal quantities.

The previous experiment shows that the hydrocarbons have less optical activity than the naphthenic acids which are separated from them, and it also shows how difficult it is to completely free the hydrocarbons from naphthenic acids, because of the solubility of the acids and their soaps in these hydrocarbons.

It will also appear from the above that the dextrorotatory acids are more readily saponified than the laevorotatory, since the latter were last separated from the hydrocarbons.

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A similar behavior was found in the fractional precipitation of the barium soaps from ethyl ester Fraction No. XIe, which before saponification had a rotation of +0.14°. The soap, after extracting with ether, was diluted and poured into a dilute solution of barium chlorid. From the barium soap, five fractions of free acids were obtained, ranging in specific gravity 23°/15° from 0.947 to 0.955 and in rotation from +0.51° to +0.20°. The mother liqour from the barium soap was neutralized and on standing yielded a barium soap, the acid of which had a specific gravity of 23°/15° = 0.970, and a rotation of +0.03°. When the mother liquor from the above soap was acidified, a third crop of barium soap was precipitated, from which naphthenic acids, with a specific gravity of 23°/15° = 0.9815 and a rotation of -0.15°, were obtained.

In order to determine if there were any optically active constituents present in the alcohol used in esterification, two liters of it were concentrated to 50 cc.,⊕ and this gave a rotation in a 200

⊕ A good dephlegmator was used and the residues from the two distillations were combined and then concentrated.

mm. tube of only +0.04°, which is so small as to be entirely negligible.

The first five of the vacuum fractions of the Kansas oil described on page 6, were treated with alcoholic potash in the same way that the naphthenic acids were saponified. After saponification four portions were obtained in the following order:

	Amt. c.c.	Sp.gr. 25°/15°	$N_D/20°$	Rotation 200 mm. tube
A. Separated as an insoluble layer	15	0.860	1.4786	+ 0.11°
B. Distilled from the main portion by steam.	82	0.8488	1.4721	+ 0.07°
C. Not distilled by steam	76	0.8554	1.4750	+ 0.27°

D. Aqueous alkaline solution, from which a very small quantity of acids were obtained, but not enough for examination.

The optical activity of the oil, however, was not appreciably decreased, for since almost equal fractions were taken, the average rotation of the oil before treatment was +0.16°, while the aver- after treatment was + 0.14°.

The molecular refractive power of the methyl esters in Table I is as follows:

Fraction	Ester	MR^2_D calculated	MR^2_D found	Differences	Increase for CH_2
2	$C_6H_{11}COOCH_3$	38.70	39.62	+0.92	
8	$C_7H_{13}COOCH_3$	43.30	43.71	+0.41	4.09
18	$C_8H_{15}COOCH_3$	47.90	48.24	+0.34	4.53
14	$C_8H_{15}COOCH_3$(iso)	47.90	48.08	+0.18	
24	$C_9H_{17}COOCH_3$9iso)	52.50	52.59	+0.09	4.51

Conrady[54] calculated that the refractive power of the CH_2 group for the sodium D line was 4.60.

The octonaphthenecarboxylic ester and its isomer have practically the same refractivity. This, however, is always the case in optical isomers and usually in other isomers of a similar structure and chemical nature. One of the methyl esters described by Petrov[55] had a density at $21.7^{\circ}/21.7^{\circ} = 0.9295$; $N_{D/21.7^{\circ}} = 1.4305$; B. P. $177^{\circ}-178^{\circ}$ at 736 mm., so that it appears to be an isomer of the heptanaphthene carboxylic ester

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[54] Zeit.Phys.Chem.,3,210; 1889.
[55] Jr.Russ.Phys.Chem.Soc.,43,1148;1911.

of Markownikow and Aschan, and a lower homologue of the new iso-octonaphthene carboxylic ester. The molecular refractivity calculated from the above data is 43.40; the calculated value for the same isomer in Table I (Fraction No. 4) is 43.65.

It will be noticed that the molecular refractive power found is uniformily higher than the calculated value. While this may have no significance, it may confirm the belief that these derivatives of the naphthenes are cyclic compounds. It has been observed that the refractivity of trimethylene derivatives is usually greater than the value calculated from the sum of the elements.[56] This increase, in a number of compounds, varies from 0.66 to 1.24 units. Substitution products of other polymethylenes may also have larger observed refractivities than the calculated, but this increase is not so great,[57] and since it never equals that given by the ethylenic linkage, it is

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56. Ber., 25, 1954; 33, 3122; 34, 2859.
57. Relation Between Chem.Consti. and Some Phys. Prop. P. 273.

thought by some to correspond to the tension in the cyclic system.

However Tschitschibabin[58] found the molecular refractivity of methyl-1-cyclopentane carboxylic acid to agree very closely with the calculated value 38.60. Aschan,[59] using the $\frac{n^2 - 1}{n^2 + 2} - \frac{M}{D}$ formula, found the molecular refractivity for octo naphthene carboxylic acid (n = 1.453) to be 43.0 (calculated = 43.4 (, and for heptanaphthene carboxylic acid (n = 1.4486) 37.7, which is just the value calculated by Conrady's method.

Frangopol[60] prepared some methyl esters which had the following properties:

	Boiling Point	Density at 20°	$N_D/25°$
1.	163°-166°	0.9063	1.4418
2.	188°-192°	0.9163	1.4423
3.	210°-215°	0.9398	1.4430
4.	223°-226°	0.9409	1.4485
5.	229°-233°	0.9428	1.4497
6.	238°-241°	0.9443	1.48(?)47

[58] Jr.Russ.Ph.Ch.Soc.,45,184;1913.
[59] Ber., 1891, 2711, 2723.
[60] Revue du Pétrole, 4, 134; 1911.

These esters were converted into the following naphthenic acids:

Naphthenic Acids	Boiling Point degrees	$D_{4^\circ}^{20^\circ}$	$^{N}D/20^\circ$	$\frac{n^2-1}{n^2+2}\frac{1}{d}$	Calculated
Hepta-	216-220	0.9513	---		
Octo-	234-238	0.9761	1.4471	38.81	38.2
Nono-	248-252	0.9836	1.4531	42.85	42.88
Deca-	257-261	0.9851	1.4598	47.11	47.44
Undeca-	263-266	0.9876	1.4706	52.13	52.00
Duodeca-	272-275	0.9884	1.4753	56.43	56.56

The methyl esters in Table I, when examined 21 months later, had the following indices:

Fraction	$N_D/23^\circ$	Increase
I		
2.	1.4208	0.0007
3.	1.4261	0.0018
4.	1.4271	0.0003
5.	1.4302	0.0019
6.	1.4306	0.0008
7.	1.4339	0.0028
8.	1.4331	-0.0008
9.	1.4370	0.0039
10.	1.4346	0.0010
11.	1.4373	0.0033
12.	1.4353	0.0012
13.	1.4368	0.0023
14.	1.4361	0.0011
15.	1.4392	0.0033
16.	1.4377	0.0010
17.	1.4380	0.0008
18.	1.4392	0.0009
19.	1.4402	0.0013
20.	1.4406	0.0011
21.	1.4430	0.0030
22.	1.4430	0.0020
23.	1.4425	0.0007
24.	1.4433	0.0009
25.	1.4442	0.0008

A stick of calcium chloride had been placed in each odd numbered bottle, and the refractive indices of the esters in these bottles show an increase of over twice as much as those without the calcium chloride. This difference is especially noticeable in the lower end of the series, and may possibly be due in part to the removal of traces of water, but more probably to the calcium chloride and calcium soap in solution. The refractive indices were also taken by the light of a mercury vapor lamp. The decrease in refractive index due to the shorter wave length was only 0.0001. There may be more difference by sodium light, however, for all the refractive indices in this paper were made by daylight.

Some chlorides prepared from the more volatile portion of natural gas gasoline had these properties:

	Boiling Point Degrees	Specific Gravity	$N_D/22^0$
I.	75-100	0.979	1.4142
II.	100-135	1.087 at $22^0/15^0$	1.4390
III.	100-135	1.124 " $24^0/15^0$	1.4525
IV.	135-160	1.197 " "	1.4575
V.	135-160	1.134	1.4528

The molecular refractivity of I is 39.14. The calculated value for C_4H_9Cl by the formula of Lorenz and Lorentz, is 41.12; for C_4H_{10} 33.54. Of course this fraction is not one compound, but its average composition is near that of butyl chloride, although it doubtless contains some unchlorinated hydrocarbons.

SUMMARY.

The theory that the optical activity of petroleum is due to the presence of chlosterol or its decomposition products, which has received some support on account of certain color reactions, has recently been shown to be untenable because of the failure of optically active petroleum products to give the digitonin reaction.

The similarity of the optical activity curves for the methyl esters and their corresponding acids; the fact that the methyl ester series starts with a negative rotation which gradually decreases, passes through a point of zero rotation, and then finally becomes dextrorotatory in the higher end of the series, as is the case in some other homologous series; these, and many other facts described above, in the experimental work, indicate that the optical activity of the naphthenic acids is a property belonging to the naphthenic acids themselves.

In conclusion, we wish to thank Dr. Bushong for his many valuable suggestions and for his careful fractionations, without which these optical

properties of the naphthenic acids could not have been discovered.