VIII.—*Spinacene: A New Hydrocarbon from certain Fish Liver Oils.*

By A. CHASTON CHAPMAN.

IN September, 1915, a sample stated to consist of cod-liver oil was submitted to me with the request that I would report on its genuineness. In the course of its examination, the following results were obtained:

Specific gravity (15°/15°)	0.8666°
Saponification value	22.5
Iodine value (Wijs)	358
Unsaponifiable matter	89.1 per cent.
Iodine value of unsaponifiable matter	376.2
Free fatty acid (as oleic acid)	0.42 per cent.
Bromine precipitate insoluble in ether	76.5 " "

I reported that the sample consisted of a mixture of approximately 89 parts of some unsaturated hydrocarbon oil with approximately 11 parts of some fish oil. Whilst it was clear that I could not have arrived at any other conclusion as to the general composition of the sample, the analytical numbers perplexed me very greatly. I knew of no hydrocarbon or other unsaponifiable substance having the iodine value and the other properties which this appeared to possess, and I began to wonder whether the sample might not be an abnormal, and not an adulterated, specimen of oil. I therefore decided for my own satisfaction to submit it to a systematic investigation.

As bearing on the origin and authenticity of this sample, it is necessary to follow the history of the oil a little further before describing the results of its chemical investigation.

Some weeks after the work had commenced, I received a copy of a report which greatly stimulated my interest in the matter. The vendors of the oil in Lisbon repudiated the suggestion that it was not genuine, and submitted a sample to Dr. Hugo Mastbaum of

that city, who obtained results similar to mine and expressed the same opinion. As the vendors were still not satisfied, they submitted portions of the fish livers to Dr. Mastbaum, who again obtained similar results with the expressed oil. Finally, Dr. Mastbaum witnessed the actual extraction of the livers of two different species of fish from which the oil in question had been derived. These fish, which will be referred to more fully below, appear to be known in Portugal as "Barroso" and "Carocho" respectively.

The fish, according to Mastbaum, were about 1 metre in length, were quite fresh, and the livers were "smooth and oily, and when pricked with a knife, considerable quantities of oil immediately separated, the bulk of the liver substance being transformed in the course of a few hours into an oily liquid."

In a subsequent communication (*Chem. Zeit.*, 1915, **39**, 139, 889), the following results are given by Mastbaum for these two samples of oil:

	"Barroso."	"Carocho."
Specific gravity (15°/15°)	0.8637°	0.8711°
Butyro-refractometer at 25°	102	93
Polarisation in 200 mm. tube	-0.3	-2.33
Solidification point	{ still liquid at -7°	becomes turbid at -7°
Saponification value	15.4	36.7
Free acids (calculated as oleic acid)	0.097 per cent.	0.165 per cent.

Until quite recently I was unaware that Dr. Mastbaum had published this note, and I therefore wrote to him pointing out that I had completed the first part of an investigation of the oil and asking him to give me any information he could in reference to its origin. He replied informing me that the oil in question was obtained from the two species of fish above referred to, and added the information that, according to a standard Portuguese dictionary, the scientific descriptions of the above fish are *Centrophorus granulatus* and *Scymnus lichia* respectively. He also informed me that these fish are caught in deep water off the Moroccan coast, and that they have only come into the Portuguese market since the employment of steam trawling in those fishing grounds. He suggests that it is owing to this fact that the existence of fish-liver oils containing so large a proportion of unsaponifiable matter has hitherto escaped observation.

Assuming that the fish in question were not in any way abnormal, the existence of liver oils containing nearly 90 per cent. of an unsaturated hydrocarbon is a matter of very considerable interest both from the analytical and from the physiological points of view. The fact that samples of oil having approximately the same composition were derived from fish which had been caught during periods extending over several weeks, and the fact that the

consignment represented by the sample submitted to me amounted to nearly 5000 litres, must, I think, be regarded as tending to negative any suggestion of abnormality.

It may be recalled that cod-liver oil rarely contains more than 2 per cent. of unsaponifiable matters, and that, according to Lewkowitsch, liver oils obtained from coal-fish, tunny, skate, ling, haddock, and hake rarely contain more than about the same amount. On the other hand, shark-liver oil appears to contain in some cases as much as 20 per cent., which has been stated to consist largely of cholesterol. In this connexion, it is of interest to note that the two fish above referred to belong to the Spinacidæ or Squalidæ, a family of the Selachioidei, or sharks.

EXPERIMENTAL.

The sample of oil, weighing 330 grams, was heated on the water-bath with sufficient sodium hydroxide dissolved in alcohol to effect the complete saponification of the saponifiable portion. After evaporating the alcohol, the residue was heated for some time with water, and the unsaponified oil extracted by shaking with ether. The ether was distilled off, and the remaining oil was heated in a current of steam until the aqueous distillate was free from odour. The oil, which did not show any tendency to distil with the steam, was again extracted with ether, the solution dried over calcium chloride, and the ether removed by distillation. The residual oil was then submitted to fractional distillation under a pressure of 10 mm., with the following results:

264—268°	...	...	...	...	50 grams
268—269°	...	...	...	...	235 "
269—270°	...	...	...	...	5 "

The residue in the flask, weighing about 10 grams, was very viscous and dark coloured.

From the first fraction there separated on keeping a small quantity of solid, which proved to be cholesterol.

The main fraction gave, on analysis, numbers which indicated that it was a hydrocarbon with a small quantity of some oxygen-containing impurity, the percentages of carbon and hydrogen amounting to 99.6. A preliminary experiment having shown that metallic sodium was without action on the hydrocarbon, this fraction was distilled over sodium under diminished pressure. There was a little action at first, but this soon ceased, and the melted sodium remained quite bright throughout the distillation.

The main fraction so obtained consisted of a colourless and fairly mobile oil having a faint and pleasant odour suggestive of

lemon oil terpenes. It burned with a smoky flame, producing a terpene-like odour. It boiled at 280° (corr.)/17 mm.:

0.1381 gave 0.4438 CO_2 and 0.1555 H_2O . $\text{C}=87.63$; $\text{H}=12.51$.

0.135 ,, 0.4344 CO_2 ,, 0.154 H_2O . $\text{C}=87.74$; $\text{H}=12.67$.

The following results represent the average of five analyses:

$\text{C}=87.75$; $\text{H}=12.45$.

$\text{C}_{30}\text{H}_{50}$ requires $\text{C}=87.80$; $\text{H}=12.20$ per cent.

The average of four series of estimations by different observers of the molecular weight as determined by the depression of the freezing point in benzene solution was 375, whilst $\text{C}_{30}\text{H}_{50}$ requires 410. It will be seen, therefore, that the determined molecular weight agrees more closely with the formulæ $\text{C}_{27}\text{H}_{44}$ or $\text{C}_{28}\text{H}_{46}$, with which the analytical results would also correspond. On the other hand, the analyses of the crystalline hexahydrochloride and of the bromine derivative are in better agreement with the higher molecular formula. Assuming that the results obtained by the cryoscopic method as applied to this hydrocarbon are normal, there would appear to be a discrepancy which cannot at present be explained. I would point out that the saturated hydrocarbon gives numbers agreeing better with one of the lower molecular formulæ than with the higher.

This hydrocarbon does not appear to be identical with any known hydrocarbon, and I propose for it the name *spinacene*, since both *Centrophorus granulatus* and *Scymnus lichia* belong to the natural family of the Spinacidae. It is optically inactive, and does not solidify when cooled to -20° .

Its specific gravity at $15^{\circ}/15^{\circ}=0.8641$, and at $20^{\circ}/20^{\circ}=0.8616$.

The following are the results of determinations of its index of refraction at 20° :

$$n_H\alpha=1.4932$$

$$n_D=1.4967$$

$$n_H\beta=1.5054$$

$$n_H\gamma=1.5130.$$

At 15° , its index of refraction for the D -line is 1.4987. Its specific refraction, calculated by the $\frac{n^2-1}{(n^2+2)d}$ expression, is 0.3394, and the molecular refraction 139.1.

Taking Conrady's average numbers for the atomic specific refractions (D -line), $\text{C}_{30}\text{H}_{50}$ with six ethenoid linkings requires 137.7.

Employing the n^2 formula, the specific dispersive power of spinacene, $r\gamma - r\alpha$, is 0.0114, and its molecular dispersion $(r\gamma - r\alpha)M$, 4.67. Taking Eisenlohr's numbers for the atomic dispersions for the α - and the γ -hydrogen lines, the calculated number is 4.33. It

will be seen, therefore, that the molecular dispersion, like the molecular refraction, is high. In this connexion, it is worthy of note that both the molecular refraction and the molecular dispersion of the saturated hydrocarbon obtained from spinacene, and described later, agree well with the calculated numbers.

Viscosity (Time of Efflux).—Fifty c.c. of spinacene required 78 seconds to flow through the aperture of a Redwood viscometer at 21° as compared with an average of 370 seconds for rape oil.

Absorption of Oxygen.—1.662 Grams of spinacene were exposed in a flat-bottomed glass dish to an atmosphere of oxygen at the ordinary temperature. At the end of two months the hydrocarbon had absorbed 0.397 gram of oxygen, and had become so viscous that it would not flow. Thin films of the hydrocarbon when exposed to the air formed a hard skin similar to that given by linseed oil.

Action of Hydrogen Chloride. Spinacene Hexahydrochloride,
 $C_{30}H_{50}, 6HCl$.

Dry hydrogen chloride was passed into a well-cooled solution of spinacene in dry ether until the liquid appeared to be saturated. After remaining for some hours, a quantity of a well crystalline, colourless solid separated. This was collected, washed with ether, and dried in an exhausted desiccator over sulphuric acid and solid sodium hydroxide.

More of the solid separated from the filtrate after keeping for twenty-four hours, and when this was removed, a further quantity formed on remaining for several days. When heated with any of the liquids ordinarily employed for purposes of purification, the substance appeared to undergo decomposition, but it could be crystallised from a cold mixture of benzene and alcohol. From this solvent it separates in well-defined plates, together with some needles, the substance being polymorphous:

0.1058 gave 0.2242 CO_2 and 0.0847 H_2O . C=57.78; H=8.89.

0.20 ,, 0.2727 AgCl. Cl=33.81.

0.25 ,, 0.3402 AgCl. Cl=33.75.

$C_{30}H_{50}, 6HCl$ requires C=57.23; H=8.90; Cl=33.86 per cent.

When heated, the hexahydrochloride commences to shrink at 108°, and begins to melt at 110°. On raising the temperature to about 140°, hydrogen chloride is freely evolved.

In a future communication I hope to deal with the nature of the hydrocarbon left when the elements of hydrogen chloride are removed from the compound, either by heating or by the action of reagents.

I propose also to investigate more closely the properties of spinacene from the point of view of its saturation with other elements or groups. In particular, the action of ozone is being studied, as it is expected that this will throw considerable light on the constitution of the hydrocarbon.

Spinacene Trihydrochloride, $C_{30}H_{50}, 3HCl$.

A current of dry hydrogen chloride was passed through a thoroughly cooled solution of spinacene in ether. As soon as the hydrogen chloride appeared to be in excess, the solution was set aside for twenty-four hours, and the resulting crystalline hexahydrochloride removed by filtration. The ethereal filtrate was shaken with sufficient aqueous solution of sodium carbonate to remove the excess of hydrogen chloride, and was then washed with water, dried, and evaporated under diminished pressure without the application of heat. A viscous oil remained, together with a little of the crystalline hexahydrochloride. The residue was dissolved in the smallest possible quantity of dry ether, and filtered in order to separate the crystals.

The ethereal solution, after treatment with a little charcoal, was transferred to a desiccator, and the ether allowed to evaporate under diminished pressure. The residue consisted of a pale yellow, viscous oil having a specific gravity $18^\circ/18^\circ = 1.0137$. It is of interest to note that when in one experiment the ethereal solution was treated with sodium carbonate solution immediately after its saturation with hydrogen chloride, the resulting oil contained but little chlorine. It is evident, therefore, that the formation of even the trihydrochloride requires some appreciable time for its completion:

0.2607 gave 0.2408 $AgCl$. $Cl = 22.90$.

$C_{30}H_{50}, 3HCl$ requires $Cl = 20.5$ per cent.

The excess of chlorine is due to the impossibility of separating the hexahydrochloride completely, as on keeping a little of the crystalline substance always separates from the oil. When the trihydrochloride is dissolved in ether and the liquid saturated with hydrogen chloride, the crystalline hexahydrochloride is formed.

Action of Bromine.

The action of bromine on spinacene is somewhat complicated, since not only does the saturation of the double bonds appear to take place in two stages, but substitution derivatives are simultaneously formed. Even when a dilute solution of bromine in dry ether or in carbon tetrachloride is added slowly to a dilute

solution of spinacene in the same solvents at a temperature of -10° , hydrogen bromide is formed in considerable quantity from the very beginning.

The following experiments will illustrate this behaviour. A solution containing 0.445 gram of bromine in 25 c.c. of carbon tetrachloride was added to 20 c.c. of a solution containing 0.1996 gram of spinacene in the same solvent. Both solutions were well cooled in a freezing mixture, and immediately after the addition the excess of bromine was determined by titration with sodium thiosulphate after the addition of potassium iodide in the usual way. It was found that 0.39 gram of bromine had entered into the reaction, corresponding with 10 atoms of bromine for one molecule of spinacene.

This experiment was repeated, with a similar result.

In the next experiment, 50 c.c. of the bromine solution (0.89 gram of bromine) were added to the same volume (20 c.c.) of the spinacene solution, and the excess of bromine determined after keeping for three hours at the ordinary temperature. 0.1996 Gram of spinacene had reacted with 0.566 gram of bromine, corresponding with rather more than 14 atoms for one molecule.

In these experiments, hydrogen bromide was given off in apparently considerable quantities.

The following experiments were then made with the object of differentiating between the bromine uniting directly with the hydrocarbon and the bromine existing as hydrogen bromide formed during the operation as the result of substitution.

The well-cooled bromine solution was run, as before, into the well-cooled solution of spinacene in carbon tetrachloride in an apparatus so arranged as to permit of the estimation of the hydrogen bromide formed. To 0.2007 gram of spinacene 0.557 gram of bromine was added. Immediately after the addition, it was found that 0.427 gram of bromine had reacted, of which 0.0673 gram existed as hydrogen bromide. From this it will be seen that the weight of spinacene taken has united directly with $0.427 - (0.0673 \times 2) = 0.2924$ gram of bromine, which corresponds with rather more than 7 atoms for one molecule.

In a further experiment, still more carefully arranged so as to prevent the loss of any hydrogen bromide, it was found that the amount of bromine with which one molecule of spinacene united directly corresponded with 6.7 atoms.

The above results show that under the conditions obtaining in the last two experiments, that is to say, when the temperature was kept low, when the solutions of the hydrocarbon and of the bromine were dilute, and when the titration of the uncombined

bromine was made at once, only three of the six ethenoid linkings are saturated. This fact, coupled with the existence of the trihydrochloride and of the other tri-derivatives referred to below, appears to indicate that three of these linkings are differently situated in the molecule from the remaining three. The fact that the above results are slightly in excess of the six atoms corresponding with three ethenoid linkings may be due to the commencement of the saturation of the remaining linkings or to the union of the spinacene with some of the hydrogen bromide at the moment of its formation. The most probable explanation of this behaviour with bromine is that three of the ethenoid linkings are in the open chain and the remaining three in some ring system. This view is supported by the way in which spinacene reacts with hydrogen chloride and by some other considerations, which will be referred to later.

Spinacene Dodecabromide, $C_{30}H_{50}Br_{12}$.

When a solution of bromine in dry ether is added to a solution of spinacene in the same solvent, the colour of the bromine rapidly disappears, and after a time a white, finely crystalline substance commences to separate. This was filtered, washed with ether, and purified by the cautious addition of alcohol to a solution in tetrachloroethane, when it separated in a crystalline condition. From the filtrate, which contained an excess of bromine, a further quantity of the same compound separated on keeping for some days, and when this was removed some more crystallised on further keeping:

0.1252 gave 0.123 CO_2 and 0.0416 H_2O . $C=26.79$; $H=3.69$.

0.150 „ 0.2453 $AgBr$. $Br=69.7$.

$C_{30}H_{50}Br_{12}$ requires $C=26.27$; $H=3.64$; $Br=70.07$ per cent.

When heated, the substance commences to darken at about 160° , and melts and decomposes at about 185° .

It is not appreciably soluble in alcohol or ether, is sparingly soluble in acetic acid, carbon tetrachloride, or chloroform, and is moderately soluble in pyridine or trichloroethylene. It was found that a portion of the bromide which separates from the ether was insoluble in tetrachloroethane, the remainder being freely soluble. This contained the same percentage of bromine as the soluble portion, so that it would seem that the dodecabromide exists in two modifications.

The compound soluble in tetrachloroethane exhibits the phenomenon of polymorphism, the same microscopical preparation often showing needles, plates, and nodules. In some cases, the transformation of one form into the other, as, for example, the forma-

tion of needles from spherical nodules, can be observed. When solutions in carbon disulphide are allowed to remain for some time they become converted into a jelly.

The filtrate from the above insoluble bromine derivatives was shaken with a slight excess of an aqueous solution of sodium hydroxide. The ethereal liquid was washed with water, dried, and evaporated under diminished pressure without the application of heat. A viscous oil remained which, on the addition of a mixture of light petroleum and alcohol, and stirring with a glass rod, gradually solidified. It was purified by crystallisation from a mixture of ethyl acetate and alcohol, or from a mixture of benzene and alcohol. From the latter solvent it forms colourless, spherular masses of radiating needles.

This contained 63·7 per cent. of bromine, corresponding almost exactly with nine atoms of bromine, but owing to the complex character of the reactions involved and to the impossibility of distinguishing by analysis between additive compounds and those in which there has been some substitution, it is inadvisable at the moment to assign a definite formula to this derivative. The study of this and of other compounds formed during the action of bromine is being continued.

Spinacene Trinitrosochloride, $C_{30}H_{50}(NOCl)_3$.

Two grams of spinacene were mixed with 5 c.c. of amyl nitrite, and to the liquid, cooled to -15° , a mixture of 6 c.c. of hydrochloric acid (D 1·19) and 12 c.c. of glacial acetic acid was added. The mixture when vigorously shaken became green, and in a very short time almost solid. It was allowed to remain in the freezing mixture for one hour, and was then treated with water and filtered.

An attempt was made to crystallise the air-dried substance from various solvents, but the heating necessary to bring about solution invariably caused decomposition. It was finally obtained in a roughly crystalline form by dissolving it in cold tetrachloroethane, and gradually adding light petroleum, in which it is insoluble.

It forms a pale, buff-coloured substance, which, when dry, is moderately stable. The above conditions must be closely followed if the solid nitrosochloride is to be obtained, and, as is the case with the majority of the compounds of spinacene, the best results are got by working with small quantities of substance:

0·2533 gave 0·1889 AgCl. Cl=18·48.

0·252 „ 16·4 c.c. N_2 at 20° and 752 mm. N=7·36.

$C_{30}H_{50}O_3N_3Cl_3$ requires Cl=17·50; N=6·92 per cent.

So far as I am aware, this is the first instance of the preparation of a nitrosochloride containing three NOCl groups. The excess of chlorine is due to the impossibility of obtaining this compound free from a little of the hexanitrosochloride, these compounds being unstable, and consequently difficult to purify.

Spinacene Dinitrosochloride Mononitrolpiperidide,
 $C_{30}H_{50}(NOCl)_2NOC_5NH_{10}$.

When piperidine was added to the solid spinacene trinitrosochloride, the latter dissolved readily with development of heat. After heating the solution gently in order to avoid decomposition, cold water was added. The precipitated substance was collected, dissolved in dilute sulphuric acid, and precipitated by the cautious addition of dilute sodium hydroxide solution. It was then purified by dissolving it in cold alcohol and precipitating by the gradual addition of water. When dry, it formed a buff-coloured substance, which was very readily soluble in dilute acids and in the ordinary organic solvents. When heated, it commenced to shrink at about 110°, and melted and decomposed at about 146°:

0.2140 gave 17.0 c.c. N_2 at 15° and 758 mm. $N=9.10$.

$C_{35}H_{60}O_3N_4Cl_2$ requires $N=8.60$ per cent.

This substance forms a crystalline hydrochloride.

In the above preparation, although the amount of piperidine was in excess of that required to react with the three NOCl groups, it will be seen that only one was attacked.

Spinacene Trinitrolpiperidide, $C_{30}H_{50}(NOC_5NH_{10})_3$.

In the preparation of this compound, the nitrosochloride was added to a quantity of piperidine in excess of that required to react with the three NOCl groups. As before, there was considerable development of heat, but in this case, as soon as the reaction had slackened, the liquid was heated nearly to the boiling point of piperidine. From the resulting dark brown liquid, water precipitated a gummy substance, which was purified by dissolving it in dilute sulphuric acid and precipitating with a dilute solution of sodium hydroxide, this operation being repeated three times. The resulting substance, which had a pale brown colour, was very readily soluble in alcohol, and, unlike the mononitrolpiperidide, was not precipitated by the addition of water:

0.2041 gave 20.4 c.c. N_2 at 15° and 758 mm. $N=11.52$.

$C_{45}H_{80}O_3N_6$ requires $N=11.20$ per cent.

When dry hydrogen chloride was passed into a solution of this

compound in ether, a crystalline substance separated, which, however, became gummy when attempts were made to dry it.

Spinacene Dinitrosochloride Mononitrolbenzylamide,
 $C_{30}H_{50}(NOCl)_2NO \cdot NH \cdot CH_2 \cdot C_6H_5.$

Spinacene nitrosochloride was added little by little to benzylamine, the latter being in excess of the quantity required to react with the three NOCl groups. There was a vigorous reaction, and when this had subsided, the mixture was gently warmed and allowed to remain at the ordinary temperature for an hour. On treating the resulting pasty mass with cold water, a plastic, brown substance remained undissolved. This was purified by dissolving it in cold alcohol and precipitating it by the gradual addition of water, the process being repeated several times. Finally, the substance, after drying, was obtained as a buff-coloured powder:

0.2027 gave 15.4 c.c. N_2 at 20° and 752 mm. $N=8.59$.

0.1696 „ 0.076 AgCl. $Cl=11.11$.

$C_{37}H_{58}O_3N_4Cl_2$ requires $N=8.27$; $Cl=10.50$ per cent.

Spinacene Trinitrolbenzylamide, $C_{30}H_{50}(NO \cdot NH \cdot CH_2 \cdot C_6H_5)_3.$

Spinacene nitrosochloride was treated with an excess of benzylamine as in the preparation of the preceding compound, but after the first reaction had subsided, the mixture was heated to the boiling point of benzylamine for a few minutes. On the addition of water to the resulting dark red solution, a viscous substance separated. This was purified by repeated solution in alcohol and precipitation with water, and finally by dissolving it in glacial acetic acid, diluting with water, and precipitating with ammonia.

The substance thus obtained had, when dry, a pale yellow colour, dissolved readily in dilute acids, and appeared to form a crystalline hydrochloride:

0.1653 gave 15.8 c.c. N_2 at 21° and 740 mm. $N=10.58$.

$C_{51}H_{74}O_3N_6$ requires $N=10.27$ per cent.

It will be seen that the action of benzylamine on the nitrosochloride is similar to that of piperidine, that is to say, one molecule of NOCl is much more readily attacked than the remaining two.

Spinacene Hexanitrosochloride, $C_{30}H_{50}(NOCl)_6.$

In the preparation of the trinitrosochloride as described above a substance was obtained on one occasion which on analysis was

found to give the following results, corresponding approximately, as will be seen, with the composition of a hexanitrosochloride:

0.2381 gave 22.4 c.c. N_2 at 21° and 754 mm. $N=10.62$.

0.2305 „ 0.255 AgCl. $Cl=27.42$.

$C_{30}H_{50}O_6N_6Cl_6$ requires $N=10.46$; $Cl=26.52$ per cent.

The experimental conditions attending the preparation of the above compound did not differ intentionally from those which in other cases resulted in the formation of the trinitrosochloride. The percentage of chlorine is high, but the compound is not very stable and is difficult to purify.

Spinacene Nitrosate, $C_{30}H_{50}(NO \cdot NO_3)_3$.

A mixture of spinacene with twice its volume of amyl nitrite was cooled in a freezing mixture to -15° , and to this solution a well-cooled mixture of nitric acid and glacial acetic acid was added little by little, with constant shaking. After remaining at the above low temperature for one hour, the mixture, which had become viscous, was poured slowly into cold water. A yellow substance separated, which could not be satisfactorily recrystallised from any of the ordinary organic solvents. The substance is practically insoluble in light petroleum, sparingly soluble in ether or carbon disulphide, somewhat more readily soluble in alcohol, benzene, chloroform, or carbon tetrachloride, and very readily soluble in acetic acid, tetrachloroethane, or acetone. When heated, it decomposes at 85° , with the formation of a considerable volume of gas.

When prepared as above described, it consisted of a yellow powder, but when kept in a specimen phial for several weeks at the ordinary temperature, it underwent gradual decomposition, becoming converted into a dark brown, spongy mass:

0.2704 gave 31.0 c.c. N_2 at 19° and 739 mm. $N=12.80$.

$C_{30}H_{50}O_{12}N_6$ requires $N=12.30$ per cent.

Many attempts were made to prepare a nitroso- or an isonitroso-derivative of spinacene, but without success. When to a solution of spinacene in light petroleum cooled to -15° a concentrated aqueous solution of sodium nitrite was added, followed by the addition of acetic acid, the mixture acquired a bright green colour, indicating the formation of a nitroso-compound, but no crystalline substance could be obtained.

Hydrogenation of Spinacene.

Fifteen grams of spinacene were introduced into a test-tube together with rather more than 1 gram of freshly prepared and

very active platinum black. The tube was supported in an air-bath, which was so heated that the contents of the tube could be maintained at a temperature of 180° to 190° throughout the experiment. A slow current of dry purified hydrogen was passed through the heated spinacene by means of a piece of glass tubing drawn out to a fine orifice, and passing to the bottom of the tube, so as to keep the platinum black in a state of suspension.

The iodine value, which at the commencement of the experiment was 350 (Wijs's method), fell rapidly at first and then more slowly until, after the hydrogen had been passing for about thirty hours, it had fallen to 18, at which point it remained almost stationary. The contents of the tube were separated from the platinum black and fractionally distilled over metallic sodium under 18 mm. pressure. Almost the whole of the liquid passed over at $274\text{--}275^{\circ}$ (corr.) as a perfectly colourless, odourless oil, which burned with a smoky flame and a slightly resinous odour:

0.138 gave 0.431 CO_2 and 0.1822 H_2O . $\text{C}=85.23$; $\text{H}=14.67$.

$\text{C}_{30}\text{H}_{62}$ requires $\text{C}=85.30$; $\text{H}=14.70$ per cent.

It will be seen that the above formula is that of a paraffin. That this hydrocarbon is not a normal paraffin is shown by the fact that it remains liquid when cooled to -20° , and for several reasons it seems improbable that it is one of the *isoparaffins*.

The specific gravity of the hydrocarbon at $20^{\circ}/20^{\circ}=0.8172^{\circ}$. The following are the results of determinations of its index of refraction at 20° :

$$n_{H\alpha}=1.4525$$

$$n_D=1.4547$$

$$n_{H\beta}=1.4607$$

$$n_{H\gamma}=1.4655.$$

Employing the n^2 formula, the specific refraction of this compound is 0.3318 and its molecular refraction 140.0. The theoretical number for a saturated hydrocarbon having the formula $\text{C}_{28}\text{H}_{58}$ is 140.1.

Its specific dispersion, $\gamma\gamma-\alpha\alpha$, is 0.0082, and its molecular dispersion 3.46. Taking Eisenlohr's numbers for the specific atomic dispersions of carbon and hydrogen for the α - and γ -hydrogen lines, the calculated value is 3.47.

The nature of this hydrocarbon, like that of spinacene itself, must for the present remain a matter for conjecture. That spinacene is a chain compound containing a ring system is exceedingly probable, but more than this can scarcely be said until the oxidation products have been thoroughly studied. As soon as the opportunity occurs, I hope to deal as fully as possible with this

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aspect of the subject. I would merely remark that some preliminary experiments in this direction tend to strengthen the view that this hydrocarbon may prove to be in some way related to the terpenes.

Since this communication was submitted to the Society, I have seen a recent paper (*J. Ind. Eng. Chem.*, 1916, **8**, 889) by M. Tsujimoto dealing with an unsaturated hydrocarbon obtained from the livers of certain Japanese sharks, to which he has given the name "squalene," and which, if not identical with spinacene, resembles it closely.

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8, DUKE STREET, ALDGATE, E.C. [Received, November 25th, 1916.]