However, an isopropylmethylbicyclononane[1] corresponds almost exactly with the new $C_{13}H_{24}$, the constants being, sp. gr. $0.8645^{20}/_{4}$; N_D 1.4660. The homologue of tetrahydrobenzene, $C_{10}H_{18}$, would probably add bromine, though this is perhaps doubtful, but it would show a double union, which is not indicated by the molecular refractions in the series under discussion. All things considered, a bicyclic formula seems the most probable, but as yet the data do not permit of a definite determination of this point. It does seem clear, however, that we have here a homologous series beginning at least as low as $C_{10}H_{18}$. This would make the dihexahydrodiphenyl theory proposed by Mabery and by Richardson untenable. The question is of considerable interest for there is undoubtedly a connection of some sort between this series and asphaltum, and despite the importance of asphaltum, we know almost nothing of its chemical composition. I hope to continue the study of the lower members, C_9 to C_{12}, as soon as I am able to purify enough to work with.

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AMERICAN COD LIVER OILS.[2]

BY L. M. TOLMAN.

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A STUDY of American cod liver oils was begun about a year ago by the Bureau of Chemistry of the United States Department of Agriculture, with the coöperation of the United States Bureau of Fisheries. The facilities of the Bureau of Fisheries, and especially the coöperation of Dr. H. M. Smith, has enabled us to obtain for our study a collection of fish liver oils which are of extraordinary interest and value in the following particulars: First, the large number and variety of the oils obtained; second, the data regarding the source and history of the samples; third, the oils were prepared from the fish as soon as they were caught, thus assuring oils which had undergone no decomposition; and fourth, the condition of the fish from which the oil was prepared was carefully noted. This last condition is of special importance,

[1] Ber. 37, 1666.

[2] Read before the Lewis and Clark Pharmaceutical Congress, Portland, Oregon, 1905.

as it explains, to a certain degree, the extraordinary variation in composition of oils from the same variety of fish.

This investigation was begun at the suggestion of Mr. L. F. Kebler, chief of the Drug Laboratory of the Bureau of Chemistry, and the work has been done in collaboration with him. The primary object of the investigation was to make a thorough study of American cod liver oils to find if they differed in any way from Norwegian oils, and whether the difference in market price was due to any actual difference in value or only to the reputation of the Norwegian article.

The investigation includes a study of the chemical composition of the oils, the methods and conditions of manufacture, and the condition of the fish used, as well as a comparative test of the actual medicinal value of the different oils. A number of other objects of no less importance were, however, in mind, such as the study of methods for the detection of adulteration, which in recent years has probably increased, owing to the scarcity and accompanying high price of pure cod liver oil; a study of the other fish liver oils to see if they differ from cod liver in chemical composition or in medicinal value; and finally, an examination of the tests required by the U. S. Pharmacopoeia to see if pure American cod liver oils can conform to the requirements to which they will be subjected.

The latter investigation, which is perhaps as important as any to the American producer, will be the subject of this article, including, however, a discussion of the value of these tests as a criterion of purity. The tests as laid down in the U. S. Pharmacopoeia are based on the reactions and composition of Norwegian oils, and the difference in conditions of production and manufacture in this country might affect many of the purely qualitative reactions which are often due to substances which in no way affect the quality or value of the oil. Especially is this true of the numerous color tests, which of late have fallen into bad repute not only in this country but in England, where a number of cases have occurred in which they have proved of little or no value in judging of purity.

The cod liver oils examined were twenty-one samples furnished the Bureau of Fisheries; two Alaskan oils of undoubted purity, four Newfoundland oils obtained by the American consul at St. Johns, three samples of Norwegian oils obtained by the American

consul at Bergen, ten commercial Norwegian oils taken from the original packages in which they were imported, by the United States custom officials, and two commercial American oils.

The cod liver oils supplied by the Bureau of Fisheries were prepared from fish caught at different seasons of the year and on different fishing grounds, and so represent the extremes of variation liable to occur in oil. They were from fat fish caught early in the fall long before the spawning season, and from fish taken just before, during, and after the spawning season, and the results show that the composition of the oil varies to an extraordinary degree, depending on the condition of the fish.

These variations are much wider than obtains with the Norwegian product, which is prepared from fish caught in a very short season and which are in about the same condition. This means that one may expect that constants and tests based on Norwegian oils will not be satisfactory when applied to the American oils, and it would be unjust to the American producer to compel him to comply with them. Especial attention was called to this fact by an American producer who was unable to place upon the market a medicinal oil of undoubted purity and of a high grade because it failed to respond to one of the color tests prescribed.

Beside the cod liver oils a number of other fish liver oils were obtained for comparison. These are the oils most likely to be used as adulterants. The list of other fish liver oils[1] examined is as follows:

Cusk, *Brosmius brosme* (Müller); Hake, *Urophycis tenius* (Mitchell) and *Urophycis chuss* (Walbaum); Haddock, *Melanogrammus aeglifinus* (Linnaeus); Pollock, *Pollachius virens* (Linnaeus); Sunfish, *Mola mola* (Linnaeus); Dogfish, *Squalus acanthius* (Linnaeus).

The oils from the above-named fish were furnished by the Bureau of Fisheries, having been prepared from fish freshly caught and all the data as to the condition of the fish, etc., recorded. Two samples of Norwegian fish liver oils liable to be used as adulterants of cod liver oil were obtained by the American consul at Bergen, namely, coal fish, *Pollachius virens* (Linnaeus)

[1] The writer is in debt to Barton W. Evermann, of the Bureau of Fisheries, for the scientific names of the different fish.

the same as the pollock, and ling, *Brosmius brosme*, the same as the cusk.

The U. S. Pharmacopoeia requires that the oil must have a specific gravity of 0.918–0.922 at 25° C. The following table shows the determinations made on twenty American oils:

AMERICAN COD LIVER OILS.

Serial number.	Sp. gr. at 15.5° C. / 15.5° C.	Sp. gr. at 25° C / 25° C.	Index of refraction 15.5° C.	Iodine number.
14273	0.9224	0.9174	1.4783	135.4
11307	0.9230	0.9180	1.4783	135.5
11372	0.9232	0.9182	1.4795	144.4
11302	0.9232	0.9182	1.4796	147.8
11274	0.9239	0.9189	1.4801	145.4
11275	0.9245	0.9195	1.4805	152.4
14305	0.9245	0.9195	1.4801	150.4
14309	0.9246	0.9196	1.4802	152.9
14308	0.9248	0.9198	1.4802	153.6
14306	0.9249	0.9199	1.4806	154.1
14326	0.9250	0.9200	....	....
14310	0.9251	0.9201	1.4806	157.8
14303	0.9254	0.9204	1.4812	158.2
11271	0.9256	0.9206	1.4806	157.3
14263	0.9260	0.9210	1.4814	162.5
14327	0.9265	0.9215	....	....
14324	0.9265	0.9215	....	....
14325	0.9266	0.9216	....	....
14272	0.9268	0.9218	1.4803	157.7
11596	0.9270	0.9220	1.4814	172.6

This table shows that only one out of the twenty samples examined was below the minimum allowed, which would indicate that the limits set are satisfactory for American cod liver oil, although other oils may show wider variation.

Little value can be placed on this determination as separating or indicating mixtures of other fish liver oils, as can be seen when it is noted that all the other oils come within these limits with the exception of dogfish liver oil, additions of which might easily be detected by the low specific gravity and index of refraction.

QUALITATIVE TESTS OF THE PHARMACOPOEIA.

Test No. 1.—"If one drop of the oil be dissolved in 20 drops of chloroform and the solution shaken with one drop of sulphuric acid, the solution will acquire a violet-red tint, rapidly changing to rose-red and finally to brownish yellow."

It is the experience of the author that the colors obtained depend to a great extent on the size of the drop of sulphuric acid added. If a small drop is added, the change of colors is comparatively slow, and one obtains at first instead of the violet-red a beautiful blue and then a violet-red and finally a red or reddish brown.

If, however, a large drop is added the change of colors is so rapid that the blue color is hardly apparent, the violet-red developing almost instantly, and at no stage does the rose-red color, which shows so beautifully in the nitric acid test, develop.

If carbon bisulphide is used as the solvent instead of chloroform, as described by the German Pharmacopoeia, the blue color does not develop and we have a red-violet changing almost at once into a brown. This test, however, is unfortunately given by all fish liver oils. The author applied the test to all the fish liver oils used in this work and found that they gave identical results, so that this test is of no value in identifying cod liver oil as distinguished from the other fish liver oils. Even the oil from the liver of the dogfish, a species of shark, gives this test. It was also found that cod liver oils which had been exposed to the action of light and air for a considerable time give instead of the blue only a reddish color.

Test No. 2.—"If a glass rod moistened with sulphuric acid be drawn through a few drops of the oil on a porcelain plate, a violet color will be produced."

This color reaction is undoubtedly due to the presence of the same substance which produces the blue-violet color in the previous test and has the same value and the same limitations. All the fish liver oils gave this test in just as marked a manner as cod liver oil, and the oils which had been exposed to the light and air and failed to give the other test failed also when this test was applied.

Test No. 3.—"If 2-3 drops of fuming nitric acid be allowed to flow along side of 10–15 drops of the oil contained in a watch-glass, a red color will be produced at the point of contact. On stirring the mixture with a glass rod the color becomes a bright rose-red, changing to a lemon-yellow. (Distinction from seal oil, which shows at first no change of color, and from other fish oils, which become at first blue and afterwards brown and yellow.)"

This is known as the nitric acid test and has been considered the

Color Reactions of Fish Liver Oils with Nitric Acid of Different Strengths.

		Acid sp. gr. 1.40.		Acid sp. gr. 1.46.		Acid sp. gr. 1.49.	
		Color developed at once.	Color developed on standing half hour.	Color developed at once.	Color developed on standing half hour.	Color developed at once.	Color developed on standing half hour.
2447	High-grade Norwegian oil	Red to rose-red.	Lemon-yellow.	Red to rose-red.	Lemon-yellow.	Purple at point of contact, changing to rose-red.	Lemon-yellow.
11226	Alaskan cod liver oils, high grade	Little color.	Brown.	Purple at point of contact, changing to brown.	Deep brown.	Very strong purple, changing to red and brown.	Black.
11227	Alaskan cod liver oils, high grade	Brownish.	Brown.	Purple at point of contact, changing to brown.	Brown.	Very strong purple, changing to red and brown.	Black.
11337	Newfoundland cod liver oils, American consul at St. Johns..	Little color.	Brown.	Brownish red.	Orange.	Purple at point of contact, changing to red-brown.	Brownish yellow.
11338	Newfoundland cod liver oils, American consul at St. Johns..	Red to rose-red.	Lemon-yellow.	Red to rose-red.	Yellow.	Purple at point of contact, changing to red.	Yellow.
11339	Newfoundland cod liver oils, American consul at St. Johns..	Red to brown.	Brown-red.	Red to rose-red.	Yellow.	Purple at point of contact, changing to red.	Orange.
11340	Newfoundland cod liver oils, American consul at St. Johns..	Red to rose-red.	Orange.	Red to rose-red.	Yellow.	Purple at point of contact, changing to red.	Orange-yellow.
11372	American cod liver oil from U. S. Bureau Fisheries	Slight red.		Purple at point of contact, changing to red.	Yellowish brown.	Strong purple, changing to red.	Orange.
11596	American cod liver oil from U. S. Bureau Fisheries	Red to rose-red.	Yellow.	Red to rose-red.	Yellow.	Purple to rose-red.	Yellow.
14273	American cod liver oil from U. S. Bureau Fisheries	Red to rose-red.	Red.	Purple at point of contact, changing to red.	Yellow.	Purple to rose-red.	Yellow.
14274	American cod liver oil from U. S. Bureau Fisheries	Red to rose-red.	Deep brown.	Purple at point of contact, changing to red.	Brown.	Purple to rose-red.	Blackish.
14275	American cod liver oil from U. S. Bureau Fisheries	Red to rose-red.	Brown.	Purple at point of contact, changing to red.	Brown.	Purple to rose-red.	Brown.
14302	American cod liver oil from U. S. Bureau Fisheries	———	———	Purple at point of contact, changing to red.	Brown.	Deep purple to red.	Black.
14303	American cod liver oil from U. S. Bureau Fisheries	———	———	Purple at point of contact, changing to red.	Black.	Deep purple to red.	Black.
14305	American cod liver oil from U. S. Bureau Fisheries	———	———	Purple at point of contact, changing to red.	Yellow.	Deep purple to red.	Dark brown.
14306	American cod liver oil from U. S. Bureau Fisheries	———	———		Yellowish brown.	Deep purple to red.	Orange.
14307	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose-red.	Yellowish brown.	Deep purple to red.	Yellow-brown.
14308	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose-red.	Yellowish brown.	Deep purple to red.	Yellow-brown.
14309	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose-red.	Yellowish brown.	Deep purple to red.	Yellow-brown.
14310	American cod liver oil from U. S. Bureau Fisheries	———	———	Purple to rose-red.	Yellowish.	Deep purple to red.	Orange.
14324	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose-red.	Yellow.	Deep purple to red.	Yellow.
14325	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose-red.	Yellow.	Deep purple to red.	Yellow.
14326	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose-red.	Yellow.	Deep purple to red.	Yellow.
14327	American cod liver oil from U. S. Bureau Fisheries	———	———	Red to rose-red.	Yellow.	Deep purple to red.	Yellow.
11371	American hake liver oil from U. S. Bureau Fisheries	Slight reddish.	Yellow.	Purple at point of contact, changing to red.	Yellow.	Deep purple to red.	Orange-yellow.
11373	American cusk liver oil from U. S. Bureau Fisheries	Slight reddish.	Yellow-brown.	Slight red, changing to rose-red.	Reddish brown.	Purple, changing to red and brown.	Brown.
11376	American sunfish liver oil from U. S. Bureau Fisheries	Red to rose-red.	Yellow.	Red to rose-red.	Yellow.	Deep red.	Orange.
11594	American pollock liver oil from U. S. Bureau Fisheries	Red to rose-red.	Yellow.	Red to rose-red.	Yellow.	Purple to rose-red.	Yellow.
11595	American haddock liver oil from U. S. Bureau Fisheries	Red to rose-red.	Red-brown.	Red to rose-red.	Reddish brown.	Purple to red.	Red-brown.
11597	American dogfish liver oil from U. S. Bureau Fisheries	No action.	Brown.	Brown.	Brown.	Purple to brown.	Brown.
11556	Norwegian ling liver oil from American consul at Bergen	Red to rose-red.	Yellow.	Red to rose-red.	Yellow.	Purple to rose-red.	Yellow.
11557	Norwegian coalfish liver oil from American consul at Bergen	Red to rose-red.	Yellow.	Red to rose-red.	Yellow.	Purple to rose-red.	Yellow.

best test for cod liver oil and is used to a greater extent than any other.

The author has found that a great difference in the test is brought about by the variation in strength of the fuming nitric acid used. A series of experiments was made on the various oils with acids of different strength. Three acids were used: First, ordinary acid, sp. gr. 1.40; second, fuming acid, sp. gr. 1.46; and third, fuming acid, sp. gr. 1.49. The acid of sp. gr. 1.40 was evidently too weak to be satisfactory, although it gave the characteristic rose-red with many of the oils, but with some of the oils it failed to react.

The preceding table shows the difference of color produced by the different acids:

The first oil in the table is a high-grade Norwegian oil and the test as applied to it is typical, the results agreeing exactly with the description given in the method of the colors formed and the different changes in color during the reaction. All the Norwegian oils examined reacted in very much the same manner. The only point, however, to be noted with this sample is the fact that with the fuming acid, sp. gr. 1.49, instead of a red color being produced at the point of contact between the acid and oil a purple color is developed. This, however, quickly changes to red and rose-red and finally to yellow, but when the American oils are examined a very different condition is noted. Very few give the marked typical reaction given by the Norwegian oil. The two Alaskan oils gave with the acid sp. gr. 1.46 a purple color which changed to brown on standing, and in fact a considerable proportion of the American oils gave a brown color on standing.

There seems to be more of the substance present in American oils which gives the blue color with nitric acid. This is shown by the fact that nearly all give a purple color at the point of contact between the oil and the acid with the acid sp. gr. 1.46, while none of the Norwegian oils gives this color with this strength of acid. However, with stronger acid, sp. gr. 1.49, most of the Norwegian oils showed the purple at the point of contact.

The color obtained is practically the same in all cases except in quantity, rose-red being a mixture of blue and red, while purple is also a mixture of these same colors but in different proportions. The most important point, however, to be noted is the brown color which develops in so many of these oils, which,

according to the last section of the method, would classify them as "other fish oils."

There is a question, however, as to what is meant by the phrase "other fish oils." Probably other fish *liver* oils, as the fish oils, such as menhaden and herring do not give the blue color so characteristic of the liver oils. In fact this nitric acid test is a general test for fish liver oils and is coming to be so considered and not as a specific test for cod liver oil, as will be seen from the reactions given by the other fish liver oils shown in the table. Hake, pollock, haddock, ling, coalfish, and cusk liver oils give reactions which can in no way be distinguished from cod liver oil. Even dogfish liver oil gives the reaction, although not quite so strongly.

From these results, therefore, practically all that we can say is that this is a test for fish liver oils and should be given by cod liver oil, but that American oils do not react exactly like Norwegian oils, giving often a purple color changing into a brownish yellow. Also the strength of the fuming nitric acid used makes a great difference with the colors produced.

Another point which must be taken into consideration is the age of the oil and the conditions to which it has been exposed. Oils which have been exposed to light and air do not react as strongly as fresh oils and in some cases fail entirely, but this only takes place when the oil has been very badly treated. Some experiments made, allowing oils to stand in the light in tightly corked bottles for nearly a year, showed that the color reactions of the oil were not affected. When, however, the same oil was exposed in an uncorked bottle for a much shorter time it was very much changed and failed to give the proper color tests. Oils which are properly handled should give the proper tests after long standing.

The range of iodine number of 140–150 as given in the Pharmacopoeia seems to be exceedingly narrow. The method for the determination of iodine number given by the U. S. Pharmacopoeia has been largely abandoned of late because of the rapid change which a mixture of the test solutions of alcoholic iodine and alcoholic mercuric chloride undergoes in the first few hours. Under the conditions of the analysis the blank determination is liable to greater change on account of the larger amount of iodine present, and results obtained by this method are lower than they should be.

The Hanus solution, iodine monobromide, dissolved in glacial acetic acid, has many advantages as a reagent in this determination on account of its stability and permanence. Using this solution for determining the iodine number of the cod liver oils examined, a much wider variation was found than is suggested in the U. S. Pharmacopoeia. This is due, however, to the same reason as was noted in the discussion of the variation observed for the specific gravity and other constants.

In conclusion, the writer would say that the standards and tests of the U. S. Pharmacopoeia which are satisfactory for Norwegian oils are not applicable to the American oils, which are liable to show more variation, and the color tests as laid down are not characteristic of cod liver oil but only of fish liver oils. Further, the nitric acid test is liable to give misleading results with many pure cod liver oils of American origin.

THE PREPARATION OF ALDEHYDE-FREE ETHYL ALCOHOL FOR USE IN OIL AND FAT ANALYSIS.

By Frederick L. Dunlap.

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One of the most common reagents in the analysis of oils and fats is alcoholic potassium hydroxide. In the preparation of this reagent, it is necessary to remove the aldehyde from the alcohol before the potassium hydroxide is dissolved in it, otherwise the solution obtained is more or less dark colored, according to the amount of aldehyde present. There are cases in which the dark color of the alcoholic potassium hydroxide offers no obstacle, but where the solution is a standard, it is necessary that it be water-white. Especially is this true where a titration is made in a solution which is itself dark colored and in which the end-point is, at best, not of the sharpest. Cases of this kind are by no means infrequent in determining the saponification value of oils and fats.

In the preparation of aldehyde-free alcohol, it is desirable that the method be fairly rapid, and that the yield be as nearly quantitative as possible. The most common method is to treat the alcohol with potassium hydroxide (10 grams per liter) and let stand for ten days to two weeks; or, in lieu of this, to boil this alcoholic solution for three hours. The dark colored solution