

Resumé.—The experiments cited above seem to show only one point of difference between the caseins from cow's and goat's milk and that is in the equivalent weight. The conductivities for equal amounts of alkali are about the same. The greater equivalent weight in the one case may point to the presence of a small additional complex in the casein molecule, or other small group not readily separated in the preparation, which need not exert any effect on the conductivity or rotation. The possibility of such addition groups is often assumed,¹ and would be in keeping with the general character of the casein as a relatively strong acid. But further investigation will be necessary to settle this point.

CHICAGO, December, 1905.

THE SERIES C_nH_{2n-2} IN LOUISIANA PETROLEUM.²

BY CHARLES E. COATES.

Received January 11, 1906.

DURING the last three years, I have had occasion to examine, with some care, samples of oil from the various Louisiana oil fields. The results of these investigations showed that the oils were of an asphaltic base, with lighter hydrocarbons of the series C_nH_{2n-2} , C_nH_{2n-4} , C_nH_{2n-6} , etc. These series had already been isolated by Mabery, Richardson and others. The various members were saturated, or at least did not add bromine, and had molecular refractions which did not indicate a double union. As the lowest member of this series C_nH_{2n-2} then known was $C_{12}H_{22}$, Mabery suggested that it was dihexahydrodiphenyl and the remaining members were its homologues. This formula seemed to agree with all the properties of these hydrocarbons and was accepted by Richardson in his recent book on the "Asphalt Pavement."

When, however, I began the examination of the crude oil from Jennings, which is the lightest of any of the Louisiana petroleums, I found that there was a small quantity of the very lightest fraction obtained by distillation which gave a molecular weight considerably too low for $C_{12}H_{22}$. From about ten gallons of the crude oil I obtained about 25 cc. of the new fraction in a fair state of purity, and found it to have the formula $C_{11}H_{20}$, and to

¹ See, for example, Raudnitz: *Ergebnisse der Physiologie*, 2, 217.

² Read at the New Orleans Meeting of the American Chemical Society.

possess to a marked degree the odor of turpentine. Moreover, there was a small quantity of a still lighter oil obtained but not enough for analysis. As $C_{11}H_{20}$ can not be derived from dihexahydrodiphenyl, $C_{12}H_{22}$, I undertook the study of these lighter fractions and, as a preliminary step, I endeavored to prepare them in a state of purity and in some quantity. The amount in the crude oil is very little, but through the courtesy of Mr. Alba Heywood I obtained about five gallons of the first distillate from the Jennings refinery, which I found to consist mainly of hydrocarbons of from C_{13} upwards, but to contain enough of the lower members to give a fair amount of $C_{10}H_{18}$, $C_{11}H_{20}$ and $C_{12}H_{22}$. These substances possessed the turpentine odor, which was faint immediately after distillation and became stronger after the flask was allowed to stand uncorked for several days.

It proved exceedingly difficult to get the new members of this series in a state of purity. Indeed, I do not think it can be done by fractional distillation. $C_{11}H_{20}$ boils at about $190-200^{\circ}$, at 60 mm. Possibly a liter of this fraction was collected and purified as usual with fuming sulphuric acid and sodium hydroxide. The resulting oil was clear and water-white, but upon redistillation it broke up into fractions boiling from 180° to 210° and leaving a yellow residue. There had evidently been decomposition, but nevertheless a series of fractional distillations at 760 mm. was instituted. Several hundred distillations were made, but each fraction continued to break up into fractions with a lower and a higher boiling-point, the latter yielding considerable tarry matter to fuming sulphuric acid. In no case could a constant boiling-point be obtained.

In order to determine the effect of heating, a water-white fraction collected from 215° to 220° , corresponding to the substance $C_{12}H_{22}$, was boiled for twenty-four hours with a return condenser. It turned yellow but on distillation gave fractions from 205° to 230° , which was about what the original oil would have done, though possibly there was a larger amount of the higher fractions than usual. Next, a long copper tube was heated to redness for two feet and the remaining portion was cooled by water. A flask was fitted into the hot end with an asbestos stopper and the $215-220^{\circ}$ fraction was distilled slowly through the tube. There was much decomposition and the issuing oil was dark and thick, yielding to fuming sulphuric acid at least

half its volume, a tarry mass being formed. The purified oil, however, boiled at about the same temperature as the original and had about the same physical constants. Evidently superheating and sudden cooling had brought about condensation of a considerable portion of the oil to a semi-asphaltic mass, the remainder being unaffected because it had probably escaped superheating in its passage through the tube.

Distillation under diminished pressure gave less decomposition than at 760 mm., but even at 16 mm. there was some decomposition. I made several hundred distillations at from 16 mm. to 30 mm., but still could not obtain a substance of constant boiling-point. For example, a fraction boiling at 80–85° at 30 mm., was distilled fractionally at least fifty times, at the end of which, the fraction collected from 80–82° gave, on redistillation at 30 mm., fractions from 75° to 90°, these having different specific gravities, etc. Though these yielded considerable tarry matter to fuming sulphuric acid, the resulting oil was not very different from the oil before treatment. A fraction having sp. gr. 0.8199²⁵/₄, molecular weight 139, N_D^{25} 1.4470, gave, after the acid treatment, 0.8197, 142 and 1.4472 respectively.

As the apparent boiling-point did not appear to be an exact index as to the nature of the distillates, these were collected and united according to their refractive indices, but the results were no better. Finally all the available material was fractionated at 760 mm., purified, refractionated, repurified, and then fractionated at 21 mm. a large number of times, using a Glinsky tube.

A series of distillates were eventually obtained which, at 21 mm., boiled inside a range of 5°, the major portions coming over in the middle 2°. The molecular weight of each fraction was determined and those fractions which corresponded to the theoretical formula were taken as representing the corresponding hydrocarbon in a state of as great purity as I was able to obtain. The refractive index, specific gravity and boiling-point at 760 mm. were next determined, then the combustion was made. The results are given in a tabulated form below.

Formula.	Molecular weight calculated.	Molecular weight found.	Carbon calculated.	Carbon found.	Hydrogen calculated.	Hydrogen found.	Sp. gr.	B. P. at 760 mm.	N ^D	Molecular refraction calculated.	Molecular refraction found.
C ₁₀ H ₁₈ ,	138	138	86.95	86.81	13.05	13.01	0.8146 ²² / ₄	168-70	1.4460	43.92	44.96
C ₁₁ H ₂₀ ,	152	151	86.84	87.00	13.16	12.88	0.8378 ²⁶ / ₄	198-200	1.4582	48.53	48.76
C ₁₂ H ₂₂ ,	166	167	86.74	86.68	13.26	13.43	0.8511 ²⁸ / ₄	215-7	1.4640	53.13	53.48
C ₁₃ H ₂₄ ,	180	181	86.67	86.58	13.33	13.42	0.8629 ²² / ₄	235-8	1.4692	57.73	57.93

This table gives only the members from C₁₀ to C₁₃. I hope to be able to supply the deficiencies and to complete the purification of C₁₄ to C₁₇ inside of the next few months. I might add, as to the figures given, that in each case the same hydrocarbon was prepared from fresh material some six or eight times and as the results were concordant they might be taken as fairly well established. I also obtained two fractions with the following constants:

	Mol. wt.	Sp. gr.	N ^D	B. P.	Quantity.
[C ₈ H ₁₄ = 110]	111	7747 ²⁴ / ₄	1.4260	120.5	about 3 cc.
[C ₉ H ₁₈ = 124]	124	7992 ²⁴ / ₄	1.4370	145.7	about 5 cc.

These substances were present in such small quantity that they could not be purified. A combustion of the second gave results between those for C₉H₁₈ and C₉H₂₂. The first was not burned.

I have done very little so far as to determining the purely chemical properties of the oils. The smell of turpentine suggested optical activity, but they were all inactive. Tested with a Hübl and a Harms iodine solution and with an ethereal solution of bromine, there was not the slightest evidence of unsaturation of the ordinary type. Neither have I been able to fit the hydrocarbons into any series of known constitutional formula. Take C₁₀H₁₈ for example, which I purified with particular care. It was inactive and saturated. Being saturated it must belong to a cyclic series, but there is exceedingly little literature on the cyclic series C_nH_{2n-2} and what there is, is rather vague. The various menthenes, hydrocamphenes, etc., have physical properties not far off from those of this C₁₀H₁₈, but they add bromine, mostly, and are generally optically active. A methylbicyclononane¹ has general properties which correspond fairly well with those of C₁₀H₁₈, but the specific gravity is a little too high (0.8416²⁰/₄).

¹ Ber. 37, 1674.

However, an isopropylmethylbicyclononane¹ 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.

CONTRIBUTION FROM THE U. S. DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY, No. 59. SENT BY H. W. WILEY.]

AMERICAN COD LIVER OILS.²

BY L. M. TOLMAN.

Received December 28, 1905.

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.