

ORGANIC ANALYSIS.

The Characteristics of Oleo-distearin. R. Henriques and H. Kühne. (*Berichte*, 1899, xxxii., 387-394.)—Heise (*Arbeit. a. d. Kaiserl. Gesundheitsamt.*, 1896, 540) found that Mkani fat, which is derived from the seeds of the East African tallow-tree (*Stearodendron Stuhlmanni*), consisted essentially of a mixed glyceride containing two stearic acid radicles and one oleic acid radicle. As doubt has since been thrown on the correctness of Heise's conclusions, the authors have made a number of experiments on the subject.

By crystallizing a large quantity of the fat five times from a mixture of ether and alcohol they obtained a substance melting at 44.5° to 45.5° C., but which, having once been melted, had a melting-point of 38.5° to 39.5° C. As no further alteration could be brought about by continued crystallizations from absolute alcohol and from glacial acetic acid, the conclusion was arrived at that Heise's oleo-distearin was a definite chemical substance notwithstanding the fluctuations in its melting-point. Its iodine value was 28.6, and its molecular equivalent 295.2, the theoretical values for oleo-distearin being 28.6 and 296.0 respectively.

On treating the glyceride with Waller's iodine solution, or by dissolving it in ether and adding an alcoholic solution of iodine chloride, the chlor-iodo addition compound crystallized out almost quantitatively. This had the same appearance and almost the same solubility in various solvents as the oleo-distearin. It melted at 44.5° to 45.5° C., and after having once been melted and again solidified, had a melting-point of 41.5° to 42.5° C. It was very stable, and retained about two-thirds of its chlorine after repeated boiling with alcoholic potassium hydroxide. Boiling with quinoline or aniline, however, was found to remove the whole of the halogens.

Oleo-distearin yielded an elaidin, but with less readiness than olein. This had only one melting-point (61° C.). It readily formed a chloro-iodide, which melted at 57° to 58° C., and, like the elaido-distearin, did not change its melting-point after fusion.

The authors consider that it may be possible to isolate similar mixed glycerides from other fats and oils in the form of their chloro-iodides, and have already obtained crystalline compounds in this way from butter and from linseed oil, which appear to have properties similar to the substance described above (*cf.* Hehner and Mitchell, *ANALYST*, xxiii., 317).

C. A. M.

On the Saponification Value of Fish-Oils. W. Fahrion. (*Chem. Rev. Fett-u. Harz-Ind.*, vol. vi., pp. 25-29.)—The following values were obtained by the author in a new series of investigations:

	Iodine Value.	Henriques' Cold Saponification Method.		Hot Saponification Method.	Saponification according to Becker.	Inner Saponification Value by the Fahrion Method.
		24 hours.	2-8 days.	Henriques' Reagent.		
Sardine-oil ...	191.7	189.5-195.9	192.5-216.8	190.9-193.8	196.2-200.3	185.2-186.4
Stickleback-oil ...	162.0	183.2-190.7	184.5-209.9	186.6-189.9	190.6-192.6	181.1-181.5
Seal-oil ...	146.2	186.0-190.4	186.7-197.4	190.7-192.9	189.8-193.5	184.4-186.0
Haddock-oil ...	166.2	182.3-183.3	183.5-185.5	182.5-183.0	187.8-188.3	181.6-181.9
Japan fish-oil ...	108.5	186.0-186.8	186.1-189.2	186.6-186.8	189.3-191.4	180.0-180.9
Whale-oil ...	106.1	184.0-185.1	184.5-188.0	184.5-185.5	191.2-193.5	174.8-175.7
Linseed-oil ...	172.0	187.0-187.7	187.0-188.6	187.6-189.1	188.8-192.3	186.8-187.9

The abnormally high values furnished by the first three oils in the longer period cold method are due to the formation of low molecular volatile fatty acids under the prolonged influence of alkali on these oils. That oxy-fatty acids, insoluble in petroleum spirit, are also formed has now been ascertained by the author, who obtained from 10 grammes of sardine-oil 0.0413 gramme of liquid and 0.0079 gramme of solid oxy-acids, together with 0.0448 gramme of volatile fatty acids (m.w. 73.9), and also succeeded in isolating oxy-acids from saponified stickleback-oil; and it is to this partial oxidation of the fatty acids that he ascribes the irregularities in the saponification value of these fish-oils, though the temperature of the reaction directly affects the results. The conditions causing these irregularities disappear for the most part when the test is performed without any excess of alkali, as is the case in determining the inner saponification value. The evaporation of the fatty-acid solution in petroleum spirit or alcohol should, however, be effected on the water-bath, and not in a drying-oven, at 100° C., since under the latter conditions the acids undergo a modification which falsifies the results.

In the hot method of saponification the proportion of water in the alkali has an influence on the results, Becker's reagent, with about 16 per cent. of water, giving higher values and requiring longer time to react than that of Henriques, which contains only 3 to 4 per cent. The author recommends the latter, as giving results more in accordance with the cold method, and he agrees with Henriques as to the advisability of dissolving the alkali direct in 96 per cent. alcohol in place of the usual procedure.

C. S.

On the Reduction of Chromic Acid by Acetic Acid, and its Effect in Anthracene Testing. H. Bassett. (*Chem. News*, vol. lxxix., p. 157.)—Owing to certain irregularities in the results obtained during a series of experimental tests on anthracene, the acetic acid employed (crystallizing at 56° F.) was subjected to examination and compared with the best acid, crystallizing at 62° F., the solutions being prepared exactly as in the ordinary test for anthracene (with chromic acid of 98 per cent.). It was found that after twenty-four days the loss of chromic acid by reduction amounted to 0.87 gramme (out of 15 grammes taken) in the case of the

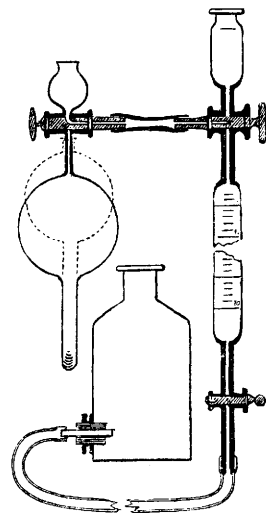
inferior acetic acid, and to 0.16 gramme in the other, owing to the presence of aldehyde, acetone, etc., in the former. Under the usual conditions of the anthracene test, a blank experiment gave, after four hours' boiling, a loss of 6.45 and 4.44 grammes respectively. The reduction, however, fell to almost *nil* when equal volumes of acid and water were used.

The use of inferior acid leads to results higher than the truth, the difference in the present instance being equal to about 0.4 per cent. of anthracene; and a similar error (of about 0.3 per cent.) arises from the use of a reagent that has been stored for about a month. It is therefore advisable to employ pure acetic acid, and an oxidizing mixture not more than fifteen days' old.

C. S.

Analysis of Illuminating Gas. O. Pfeiffer. (*J. Gasbeleucht.*, 1899, xlii., 209; through *Chem. Zeit. Rep.*, 1899, 129.)—The author has abandoned absorption methods except for the carbon dioxide and the heavy hydrocarbons; he prefers processes of gradual combustion. His absorption apparatus is figured herewith; and for the explosions he uses a burette, which holds 110 c.c., fitted with stoppers at both ends. After explosion and removal of carbon dioxide, the excess of oxygen is absorbed with phosphorus, thus leaving the nitrogen of the original sample. A complete analysis of coal-gas can be carried out in forty-five minutes, the formulæ employed being the same as those quoted by Dennis and Hopkins (*ANALYST*, vol. xxiv., p. 106, Nos. 7, 8, and 9).

F. H. L.



The Use of Silico-tungstic Acid as a Reagent for Alkaloids. G. Bertrand. (*Bull. Soc. Chim.*, 1899, xxi., 434-439.)—Silicotungstic acid ($12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and its alkaline salts give precipitates with alkaloids in sufficiently concentrated solution, which can be readily collected on a filter. The precipitates are white, pale yellow, buff, or salmon coloured. They are insoluble, or nearly so, in cold water, but are somewhat soluble in boiling water. When dried at 30°C . to constant weight they retain a certain proportion of their combined water, the amount varying with the alkaloid. A further part, at least, of this water is liberated at 120°C .

These neutral alkaloidal silicotungstates generally contain four equivalents of alkaloid to one of silico-tungstic acid:



They resist the action of concentrated mineral and organic acids, and on calcination leave a fixed residue of silicic and tungstic acids.

The pyridine salt ($12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot 4\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O}$) is a white crystalline powder, which becomes anhydrous at 120°C . It is slightly soluble in boiling water, from which it crystallizes on cooling in small colourless prisms.

Morphine silicotungstate ($12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot 4\text{C}_{17}\text{H}_{19}\text{NO}_3 + 9\text{H}_2\text{O}$) forms an amorphous salmon-coloured mass, which retains two molecules of water at 120°C .

The strychnine salt ($12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot 4\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2 + 8\text{H}_2\text{O}$) resembles the morphine compound, but is of a buff colour, and only retains one molecule of water at 120°C .

On heating an alkaloidal silicotungstate in the liquid in which it was precipitated, it immediately loses a portion of its water. This body is also obtained in the form of a fine precipitate, which is not readily filtered, by adding the reagent to a hot solution of the alkaloid.

The silicotungstates of morphine and strychnine thus obtained have the following composition when dried at 30°C .:

Morphine silicotungstate ... $12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot 4\text{C}_{17}\text{H}_{19}\text{NO}_3 + 8\text{H}_2\text{O}$.

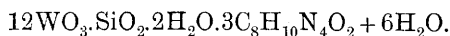
Strychnine silicotungstate ... $12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} \cdot 4\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2 + 7\text{H}_2\text{O}$.

When testing a solution qualitatively for an alkaloid, it is preferable to attempt to form the salts containing the smaller amount of water, since these are often more perceptible than the salts precipitated from cold solutions. Thus, if 1 or 2 drops of the reagent be added to 5 c.c. of a solution of aconitine sulphate (1 : 50000), there is only a very slight opalescence; but on warming the liquid to the boiling-point, it becomes clear, and then on cooling a fine powdery precipitate appears. This difference is still more pronounced in the case of veratrine, it being possible to detect one part in 130,000 by warming the solution after the addition of the reagent.

The author has determined the limits of sensibility of this reaction with the principal alkaloids, and finds that they can be classified into two groups, viz., those whose silicotungstates are equally perceptible in hot and cold liquids, and those whose silicotungstates become more visible on warming the solution to 100°C . and then cooling.

I.				II.					
			One part in :				One part in :		
Pyridine	3,000	Aconitine	80,000		
Coniine	8,000	Veratrine	130,000		
Morphine	16,000	Brucine	150,000		
Theobromine	18,000	Strychnine	}	...	200,000		
Nicotine	20,000	Narcotine					
Quinoline	}	...	30,000	Quinine	}	...	500,000		
Narceine				Quinidine					
Codeine	40,000	Cinchonine					
Atropine	}	...	50,000	Cinchonidine					
Caffeine									
Cocaine	200,000						

Caffeine and theobromine are exceptional in requiring the addition of a sufficient quantity of free acid (*e.g.*, 3 to 4 per cent. of hydrochloric acid) if their full limit of sensibility to the reaction is to be reached. The caffeine silicotungstate formed under these conditions has the formula :



Notwithstanding their stability, the silicotungstates of alkaloids are attacked by

certain reagents, noticeably by oxidizing bodies. It is thus possible in certain cases to obtain the characteristic colour reaction of the alkaloid directly with the precipitate—as, for example, in the case of strychnine with sulphuric acid and bichromate, and of morphine with Fröhde's reagent.

The alkaloids can be recovered from the precipitates by treating the latter with an alkali, which instantly decomposes them, and the alkaloid can then be extracted from the liquid by the usual methods.

The author has also made experiments to determine the action of silicotungstic acid on a number of glucosides, such as arbutin, coniferin, digitalin, ouabain, salicin, etc.; on certain bitter principles, such as picrotoxin, santonin, and quassin; on amides, such as urea, asparagine, leucine, and tyrosine; and on tannin, gum arabic, and other bodies which are often found accompanying alkaloids in plants. With the exception of albuminous substances, however, no precipitate was obtained with any of them, either in neutral or in acid solution.

C. A. M.

A Modification of Denigés Method of Estimating Uric Acid. (*Ann. de Chim. Anal.*, 1899, iv., 82, 83.)—The method described below combines the methods of Denigés and of Hopkins. The phosphates are first removed by adding to 100 c.c. of the urine 10 c.c. of a solution of 160 grammes of anhydrous sodium carbonate in a litre of water; 82 c.c. of the filtrate are taken, and the uric acid rendered insoluble either by the addition of 30 c.c. of a mixture of 10 c.c. of Fehling's solution with 20 c.c. of sodium bisulphite solution (36° to 40° Bé), as proposed by Kluger; or, as described by Denigés, by the addition of 5 c.c. of a solution of copper sulphate (40 grammes per litre) and 20 c.c. of a solution containing sodium thiosulphate, 100 grammes, and sodium potassium tartrate 100 grammes, in a litre of water.

The mixture is shaken and filtered, and the filter washed with water until free from alkali, and thrown into 500 c.c. of water acidified with 5 c.c. of sulphuric acid. After the liquid has been well shaken for several minutes in contact with the air, decinormal permanganate solution is added drop by drop until a permanent pink tint is obtained.

If n c.c. be used in the titration, the amount of uric acid in a litre of the urine can be calculated by the formula,

$$\frac{n \times 0.00745 \times 1000 \times 110}{82 \times 1000} = n \text{ decigrammes};$$

or, in other words, the number of c.c. used gives directly the decigrammes of uric acid.

The relation between decinormal permanganate and uric acid (1 c.c. = 0.00745 gramme) was obtained experimentally with a specimen of that acid purified by means of sulphuric acid.

C. A. M.

Note on Kjeldahl's Method of Determining Nitrogen. Maquenne and Roux. (*Bull. Soc. Chim.*, 1899, xxi., 312-314.)—Referring to the precipitation of mercury by means of sodium sulphide, the authors point out that there are two main

objections to this course. Firstly, volatile sulphur compounds are formed, which distil with the ammonia, and interfere with the sharpness of the subsequent titration, especially when turmeric is used as indicator; and, secondly, the mercuric sulphide formed is not completely insoluble in alkaline sulphides, and there is nothing to prevent the formation of compounds of ammonia and mercury, which are not readily decomposed by alkalies, with the result that the yield of ammonia may be too low, as is shown by the figures in the subjoined table.

These drawbacks are obviated by precipitating the mercury from the acid solution by means of sodium hypophosphite. About 1 gramme of this salt is introduced into the acid solution while still warm, the whole heated to 60° to 70° C., then cooled, sodium hydroxide added, and the ammonia distilled in the usual manner.

The comparative results obtained by this modification, by the ordinary method, and by the soda-lime method were:

KJELDAHL'S METHOD.					
Material.			Precipitation with Hypophosphite.	Precipitation with Sulphide.	Soda-lime Method.
Cotton-seed cake	4.45	4.39	4.48
Colza cake	6.84	6.70	6.87
Wheat flour	1.86	1.89	1.91
Bean flour	5.24 ; 5.25	—	5.29
Powdered horn	14.31 ; 14.28	14.12 ; 14.11	14.30
Dried blood	7.73 ; 7.78	7.69 ; 7.79	7.78
C. A. M.					