These melted at 132°. Since this acid has already been fully characterized,[1] the experiment was not repeated.

The hydrocarbon was obtained in an amount too small for study, its presence being indicated by the odor. It was doubtless isolaurolene.

Summary.

In conclusion the results of this investigation may be stated as follows:

1. The method of preparing isoaminodihydrocampholytic acid has been improved.
2. The free acid and the hydrochloride have been studied. The physical constants have been determined. A trans anhydride is not formed when the hydrochloride is heated with acetic anhydride and sodium acetate, but a rearrangement occurs to form the anhydride of the isomeric-*d*-aminodihydrocampholytic acid.
3. Decomposition of isoaminodihydrocampholytic acid with nitrous acid yields a hydrocarbon, *d*-campholytic acid, and *l*-*trans*-hydroxydihydrocampholytic acid. The Walden inversion occurs to only a slight extent in this decomposition, owing, probably, to a favored configuration.
4. A direct proof of the relation of *l*-isocamphoric acid to *d*-camphoric acid has been obtained.

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THE DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS.

[SECOND PAPER.]

BY MAITLAND C. BOSWELL.

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A direct method for the determination of oxygen in organic compounds was described in the first paper of this series.[2] In the case of compounds of high oxygen content this gives satisfactory results, but if the oxygen is less than 30–40%, depending on the nature of the compound, the results are too high. In some cases, as anthraquinone, the results exceed the true value to the extent of several per cent., owing to the formation of reaction products other than water and carbon dioxide, which condense in the absorption apparatus. The method can hence be used with security only in the case of compounds containing at least 40% of oxygen. The present paper describes a method applicable to compounds, irrespective of the amount of oxygen present in them. It consists in heating a weighed quantity of substance in a quartz combustion tube in a current of nitrogen, causing the vapors to pass over a small quantity of heated copper oxide of known oxidizing value distributed over a long layer of asbestos, weighing the water and carbon dioxide formed, and determining the oxidizing

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[1] Noyes and Knight, *Loc. cit.*

[2] *J. Am. Chem. Soc.*, **35**, 284 (1913).

value of the copper oxide remaining unreduced. The copper is then oxidized in the tube without disturbance, under definite conditions, by a current of oxygen, and is again ready for another determination.

Let x grams = oxygen in weighed amount of substance.
Let a grams = total oxygen available from the copper oxide in the tube.
Let b grams = oxygen available from the copper oxide remaining after the combustion.
Let c grams = oxygen in the water formed.
Let d grams = oxygen in the carbon dioxide formed.

Then $x + a = b + c + d$.

$$x = b + c + d - a.$$

The hydrogen content of the substance is also calculated from the weight of water formed.

In this method two possible difficulties and sources of error are at once apparent. Will the vapors of the substance be completely burned by the necessarily small amount of copper oxide used, and is it possible to so oxidize the copper and reduce the resulting copper oxide that a constant quantity of oxygen is available for each analysis? By a measurement of the rate of oxidation of the copper and of the reduction of the copper oxide, it was found that both of these processes, after proceeding for a definite determinable time, continue at velocities so small that it is practicable to obtain a definite amount of copper oxide, of definite available oxygen content, by allowing oxidation and reduction to proceed for definite intervals of time, and that an error as great as five minutes in timing makes no appreciable difference in the oxygen available. No difficulty was experienced in effecting complete combustion of the vapors distilling from the substance. As the boat containing the substance is heated finally to a white heat, no oxygen compound can remain undecomposed.

Description of Apparatus.—A quartz tube, 12 mm. internal diameter and 980 mm. long, is filled for a length of 570 mm. (starting 110 mm. from one end) with asbestos, which has been impregnated with a solution of approximately 4 grams of copper in nitric acid, by evaporating the solution and heating the residue until all the nitrate has been transformed into oxide. This leaves a space 300 mm. long at one end of the tube, which, during the analysis, is partly occupied by a quartz boat containing the substance. The tube rests in a combustion furnace of the usual form, except that the iron trough and tiling supporting the combustion tube are removed, so that in an analysis the whole of the oxide may be brought to a red heat before the substance has begun to distil. The nitrogen is made by carefully warming in an Erlenmeyer flask, a mixture of 75 grams sodium nitrite, 115 grams ammonium sulfate, 75 grams potassium bichromate and 225 cc. water. Heat is applied only to start the reaction. The evolution of nitrogen proceeds with rapidly increasing velocity, owing to the heat of the reaction, and, unless controlled by immersion of the flask for a few seconds at a time in water and ice, may become explosive in violence. The gas holder containing the nitrogen is connected with a purifying apparatus, consisting of a quartz tube 360 mm. long containing a tight roll of copper gauze 130 mm. long, which is heated in a small gas furnace of two wide, flat flames. This removes any traces of oxygen in the gas. This is followed by a U-tube containing calcium chloride and two sulfuric acid washers of special form[1] which give very thorough contact of gas and acid with small friction and pressure head. The absorption apparatus which is attached to the other end of the tube, consists of a U-tube with bulb containing concentrated sulfuric acid on pumice, to absorb water, and a U-tube containing soda lime followed by a U containing sulfuric acid on pumice, for the determination of carbon dioxide.

Measurements were first made to determine the conditions of oxidation of the copper and reduction of the oxide in order that a constant amount of oxygen shall be available for each analysis. The details of this procedure will be given presently The following results were obtained:

	a.	*b.*	*c.*		*a.*	*b.*	*c.*
1	—	5	0.9538	8	45	25	0.9235
2	—	90	. .	9	45	30	0.9240
3	0	5	0.8116	10	90	30	0.9247
4	0	45	0.8168	11	90	40	0.9256
5	45	0	0.9170	12	90	30	0.9241
6	45	5	0.9198	13	90	40	0.9250
7	45	20	0.9226				

a is the time in minutes of heating of the copper in oxygen after the glow has ceased.

b is the time in minutes of the reduction with hydrogen after the hydrogen is running freely from the combustion tube.

c is the weight in grams of water formed.

All the copper at the outset is present as oxide. This is not true subsequently, for after reduction in hydrogen and oxidation of the copper, only a portion of the reduced copper is oxidized, the remainder being protected by the external layer of oxide, so that the velocity of oxidation becomes very slow. This is clearly shown in the above results, the amount of oxygen available from the original oxide (experiment 1) being greater than in any subsequent reduction. The results also indicate that the hydrogen penetrates the layer of oxide more effectively than the oxygen, for in 5 minutes (experiment 1) the hydrogen has removed more oxygen from the original oxide than a subsequent reduction (experiment 12) lasting 30 minutes, the oxidation prior to this last reduction having lasted 90 minutes. This indicates that it is first necessary to reduce the original

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[1] *Trans. Faraday Soc.*, **6**, 10 (1910).

oxide very thoroughly. This is accomplished by passing hydrogen over the heated oxide for 90 minutes. Experiments 8, 9 and 11 show that in 45 minutes the copper is almost as effectually oxidized as in 90 minutes, and experiments 9, 10 and 12 show that in 45 minutes the copper is almost as effectually oxidized as in 90 minutes. Experiments 8 and 9, 10 and 11, 12 and 13 show that, at the end of 25 minutes, the reduction is proceeding at such a low rate that in 5 minutes only 0.0005 gram of water are formed. Hence, if the copper is each time oxidized for 45 minutes and the oxide formed reduced for 30 minutes, a constant amount of oxygen will always be available. The rate of passage of the gases has probably no influence in either the oxidation or reduction, provided there is always an excess of gas present in both cases, and provided the velocity is sufficient to carry off the water vapor immediately it is formed, and thus prevent any equilibrium between copper, copper oxide, and water vapor. Although the temperature may have greater influence on the rates of oxidation and reduction, it is probable that, at the high temperature at which these are conducted, a considerable change of temperature would be necessary to seriously alter them. No special precautions were taken to secure either constant gas flow or constant temperature, beyond turning the furnace on fully in each operation. This, along with the direct play of the flames against the quartz tube, secured a very high temperature almost immediately.

Method of Procedure.—0.2 gram of substance is weighed out in a quartz boat and inserted in the combustion tube about 60 mm. from the asbestos carrying the copper oxide. A rapid stream of nitrogen is sent through the tube for 20 minutes. The rate of nitrogen flow is considerably diminished, and the absorption tubes are attached. The whole layer of copper oxide is now heated to the highest temperature attainable in the furnace, and three burners lighted at the other end of the tube. The flow of nitrogen is further diminished to about 1 bubble per second, and the substance heated very gently. The rate of flow of gas in the purifying apparatus and also the absorption vessels is carefully observed, and at the first indication of either too rapid flow through the latter, or a diminution of rate through the former, due to a sudden generation of pressure in the combustion tube, the heating of the substance is discontinued until the normal rate is reëstablished. After all the burners have been turned on full, the heating is continued for 20 minutes longer, with a somewhat more rapid flow of nitrogen in order to sweep over all products of combustion. The absorption apparatus is disconnected, the contained nitrogen displaced by air, the end of the combustion tube is closed and the furnace allowed to cool. Another weighed U-tube, containing conc. sulfuric acid on pumice, is now connected to the tube and a rapid stream of purified hydrogen, generated electrolytically, by means of the apparatus described in the first paper, is caused to pass; the hydrogen generator being connected by a T tube to the same purifying apparatus used for the nitrogen. The flames are lighted two at a time, starting with those nearest the absorption tubes. The hydrogen is so rapidly oxidized that none escapes the action. When the bubbles commence again to pass through the absorption tube the next pair of burners is lighted. These operations are continued until all the copper oxide is heated and hydrogen is running freely through the tube. The rate of passage of hydrogen is now reduced somewhat, and the heating continued for 30 minutes longer. The U-tube is now detached, and the hydrogen displaced by air. The other absorption tubes from the first operation can be weighed during this 30-minute interval. In order to prepare the copper oxide for a second analysis, oxygen is passed through the tube, all the burners are lighted, and the oxidation continued for 45 minutes after the bright glow, which passes rapidly through the tube, ceases.

The following results were obtained in the analysis of carefully purified compounds:

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Succinic acid.............	0.2018	0.0825	0.1789	0.6687	0.1087	53.9	54.2	5.1	5.1
Cane sugar..............	0.2020	0.0993	0.1051	0.7230	0.1060	52.5	51.5	6.1	6.4
Phthalic anhydride.......	0.1658	0.0322	0.1398	0.7046	0.0552	33.3	32.4	2.4	2.7
α-Naphthol..............	0.1909	0.0797	0.2846	0.4775	0.0204	10.7	11.1	5.2	5.5

Column 1 gives the number of grams of substance taken.

Column 2 gives the number of grams of oxygen corresponding to the water formed in the combustion.

Column 3 gives the number of grams of oxygen corresponding to the carbon dioxide formed.

Column 4 gives the number of grams of oxygen corresponding to the water formed in the reduction of the copper oxide remaining.

Column 5 gives the number of grams of oxygen in the substance obtained by adding the corresponding weights in columns 2, 3 and 4 and subtracting 0.8214 gram, the total weight of oxygen available from all the copper oxide.

Column 6 gives the determined percentage of oxygen in the substance.

Column 7 gives the calculated percentage of oxygen in the substance.

Column 8 gives the percentage of hydrogen in the compound determined from the weight of water formed in the combustion, and corresponding to the oxygen given in column 2.

Column 9 gives the percentage of hydrogen in the compound calculated from the formula.

On comparing the results in columns 8 and 9, it is seen that the agreement of the hydrogen determined by the method, with the hydrogen calculated from the formulas, is about as close as that usually obtained in the ordinary carbon-hydrogen method. The oxygen percentages determined, given in column 6, differ from the calculated values, given in column 7, by amounts varying from 0.3% to 1%. In view of the indirectness of the oxygen determination a greater degree of accuracy could scarcely be expected.

Summary.

A method has been worked out for the simultaneous determination of hydrogen and oxygen in organic compounds, giving results differing by 0.3% from the calculated values in the case of hydrogen, and by 0.3% to 1% from the calculated values in the case of oxygen.

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[FROM THE LABORATORIES OF THE REFEREE BOARD OF CONSULTING SCIENTIFIC EXPERTS AT THE UNIVERSITY OF PENNSYLVANIA.]

A COPPER BALANCE ON SEVEN[1] EXPERIMENTAL SUBJECTS TO DETERMINE THE EFFECT OF EATING COPPERED VEGETABLES.

BY CARL L. A. SCHMIDT.

The following work constitutes part of the investigation on the "Action of Coppered Vegetables on the Health and Nutrition of Man" conducted under the general direction of Dr. A. E. Taylor of the Referee Board, the general results of which have appeared in Report No. 97 of the United States Department of Agriculture. Since Taylor's conclusions as to the harmfulness of the ingestion of vegetables colored with copper sulfate are almost entirely based on the fact that copper was apparently retained by the individuals eating coppered vegetables, it was thought important to publish the work in detail as a separate article.

The subjects, all of them medical students, were put on a constant diet previously determined by them in an experimental period. A certain amount of peas constituted a part of the daily menu for each individual. The diet was altered in some cases during the course of the experiment by substituting for part or all of the vegetables an increasing amount of peas or string beans so as to increase the amount of ingested copper. The coppered vegetables were purchased in large lots on the open market. For serving, the vegetable was steamed in the can, thrown on a colander, thoroughly mixed, and a sample taken for analysis at the same time that the portions were weighed out by the men. The experiment was divided into three parts—a foreperiod of two weeks during which time the men were given uncolored peas; an experimental period of nine weeks, during which coppered peas and string beans were eaten; and a two weeks' after- or controlperiod of uncolored peas and string beans. One subject was

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[1] There were eight experimental subjects. Subject No. 1 was a poor subject for experimentation, being strongly influenced by psychological factors. For this reason the results obtained from him are omitted.