and humin nitrogen is formed, as in Experiments 2 and 3, we are unable to state. Various possibilities present themselves, such as the oxidation of tryptophane itself to indol aldehyde, which would in turn unite with more tryptophane to form a deeply colored, insoluble compound,[1] or possibly traces of some other amino acid may be oxidized to the corresponding aldehyde. Isham and Vail[2] have recently shown that ether is readily oxidized to aldehyde by atmospheric oxygen at 110°. A contamination of the protein with a small amount of ether, or of the aldehyde formed from the ether during extraction, would account for this humin formation, if tryptophane were present. We regret that lack of material prevented our trying further experiments in this direction.

Summary.

1. We have shown that in all probability the humin nitrogen of protein hydrolysis has its origin in the tryptophane nucleus.
2. When tryptophane is boiled with mineral acids in pure solution no humin is formed, but when tryptophane is added to a protein, or when carbohydrates are present, an abundance of humin is formed. This humin contains nitrogen which can belong to no amino acid other than tryptophane.
3. The reaction involved in humin formation is probably the condensation of an aldehyde with the —NH group of the tryptophane nucleus.
4. When an abundance of carbohydrate is present nearly 90% of the tryptophane nitrogen remains in the humin nitrogen fraction.

It is suggested that this property be utilized to determine the approximate quantity of tryptophane in proteins.

5. The addition of histidine causes no increase of humin nitrogen, the histidine being quantitatively recovered in the bases. Histidine, therefore, can be eliminated as a factor in the formation of humin nitrogen.
6. Adsorption of ammonia by non-nitrogenous humins formed from carbohydrates is not an important factor in the formation of humin nitrogen.
7. These findings allow us to assign a distinct value to humin nitrogen determinations.

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NOTE.

On Rapid Organic Combustions.—The use of cerium dioxide as contact substance for rapid organic combustions, in place of the more expensive platinum of Dennstedt, has recently been recommended.[3] In trying out the method in this laboratory, it has been found that it is not entirely

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[1] Homer, *Biochem. J.*, 7, 116 (1913).

[2] THIS JOURNAL, 37, 902 (1915).

[3] Julius Bekk, *Ber.*, 46, 2574 (1913).

satisfactory in the hands of beginners. The reasons for this are two: first, part of the substance is carried through the tube unburned if the stream of oxygen is even a little too slow or, on the other hand, so rapid that the vapor of the substance mixed with oxygen is carried too quickly past the catalyst; second, after the asbestos impregnated with cerium dioxide has been used several times, it crumbles to a fine powder and a slight amount of this may be carried into the absorption apparatus if the stream of oxygen is very rapid.

These difficulties can be overcome by the following modification of the method: Instead of the large quantity of asbestos, impregnated with cerium dioxide, recommended by Bekk, a layer of cerium dioxide asbestos only 3 cm. long is placed in the center of a combustion tube of the usual length. Following this is a 20 cm. layer of cupric oxide in wire form, held in place by a cupric oxide gauze plug. The cupric oxide furnishes oxygen for the burning substance in case the supply of gaseous oxygen is insufficient, or if the vapor of the substance has been carried too fast over the catalyst, and prevents the dust of the cerium dioxide from being carried forward in the tube.

In the back end of the tube is the usual 10 cm. cupric oxide gauze spiral. This serves to break the stream of oxygen and does away with the necessity for the "double oxygen" apparatus of Dennstedt and the glass tube surrounding the boat recommended by Dennstedt and by Bekk.

The absorption apparatus described by Dennstedt in an early paper[1] has been found perfectly satisfactory. It consists of the usual calcium chloride U-tube and two 12 cm. U-tubes with ground glass stoppers.[2] The one next the calcium chloride tube is filled with soda-lime, the other contains solid potash with a 2.5 cm. upper layer of fused calcium chloride in each arm. The soda-lime tube can be used for two combustions; the potash tube almost indefinitely.

The procedure differs from that of the usual method in the following points: The combustion boat should be placed not more than 2 cm. from the cerium dioxide asbestos. This is important, as explosive mixtures of gases form if there is any considerable space in which the vapor of the substance and oxygen can mix before they come in contact with the catalyst. As soon as the front end of the tube is hot and the boat in place, a rapid stream of oxygen is turned on and the forward burners are lighted to within about 8 cm. of the boat. If the substance to be burned is very volatile, the stream of oxygen should be less rapid and the cerium dioxide asbestos more cautiously heated by first placing above it hot tiles from the forward

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[1] "Entwickelung der Organischen Elementaranalyse." Sammlung chemischer und chemisch-technischer Vorträge, Ahrens, Stuttgart, 1899, p. 105.

[2] Leakage at the stoppers can be prevented by using the rubber lubricant recommended by Richards (Carnegie Institution of Washington, Publication No. 56, 16 (1906)).

end of the tube. As the vapor of the substance and oxygen come in contact with the hot cerium dioxide, the latter glows brightly. The soda-lime tube becomes very hot from the absorption of carbon dioxide. When the glowing has ceased and *the soda-lime tube cools*, the combustion is ended.

The following results have been obtained:

Succinic Acid, 0.2028 g.
Time, 17 minutes.

Calc. for $C_4H_6O_4$:	C, 40.66	H, 5.08
Found:	C, 40.57	H, 5.12

Salicylic Acid, 0.1975 g.
Time, 11 minutes.

Calc. for $C_7H_6O_3$:	C, 60.85	H, 4.34
Found:	C, 60.66	H, 4.37

Benzoic Acid, 0.1749 g.
Time, 9 minutes.

Calc. for $C_7H_6O_2$:	C, 68.85	H, 4.91
Found:	C, 68.67	H, 5.10

Naphthalene, 0.1888 g.
Time, 13 minutes.

Calc. for $C_{10}H_8$:	C, 93.75	H, 6.25
Found:	C, 93.61	H, 6.31

Sugar, 0.2080 g.
Time. 18 minutes.

Calc. for $C_{12}H_{22}O_{11}$:	C, 42.10	H, 6.43
Found:	C, 42.17	H, 6.44

Methyl Dibenzylidene Phenyl
Glutarate, 0.1585 g.
Time, 14 minutes.

Calc. for $C_{27}H_{26}O_4$:	C, 78.64	H, 5.82
Found:	C, 78.80	H, 6.05

Aside from the great saving of time, the method is satisfactory for beginners, in that it is free from some of the usual sources of difficulty; water does not draw back in the tube nor collect around the forward stopper because of the rapid stream of oxygen, and there is no danger of burning the stoppers, since it is not necessary to heat the tube near the ends.

A disadvantage is that the method cannot be used for the simultaneous determination of carbon, hydrogen and halogens as can the Bekk method where no cupric oxide is used. It is available however, for the analysis of compounds containing nitrogen if a longer empty space is left at the forward end of the tube for the boats of lead peroxide[1] and care is taken to keep that end of the tube fairly cool. The combustion should be run a little less rapidly than with carbon and hydrogen alone.

The following results have been obtained:

Acetamid, 0.1707 g.
Time, 28 minutes.

Calc. for C_2H_5NO:	C, 40.67	H, 8.47
Found:	C, 40.91	H, 8.42

Acetanilid, 0.1788 g.
Time, 24 minutes.

Calc. for C_8H_9NO:	C, 71.11	H, 6.66
Found:	C, 71.01	H, 6.70

Propyl Cyancinnamylideneacetate, 0.1591 g.
Time, 25 minutes.

Calc. for $C_{15}H_{15}NO_2$:	C, 74.68	H, 6.22
Found:	C, 74.46	H, 6.16

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[1] Cf. Dennstedt, "Anleitung zur vereinfachten Elementaranalyse," III Aufl. Hamburg, 1910, p. 66.