until all traces of ether have been lost and is then stored in bottles where it is exposed to the vapors of ammonium carbonate. This may be done by protecting each cork with a double sheet of filter paper and placing a lump of ammonium carbonate between the cork and the filter paper.

The yield of cupferron from a given weight of β-phenylhydroxylamine averaged 80 to 90% of that theoretically possible. Since the yield of β-phenylhydroxylamine from nitrobenzene is about 65%, the yield of cupferron from nitrobenzene is about 50% of the theoretical.

Notes.—In the preparation of cupferron, Baudisch and King have recommended that the amyl nitrite be added all at one time. This procedure is satisfactory only when the amount of phenylhydroxylamine used is less than 200 g., otherwise the reaction becomes extremely vigorous and an excessive proportion of ether is lost. The directions given above, on the other hand, should prove adaptable for the preparation of large quantities of cupferron. For the rapid preparation of small quantities of material the amyl nitrite may be added all at one time, provided sufficient excess of ammonia is present. The solvent ether may be replaced by benzene, but this modification offers no advantages for the preparation of cupferron on a laboratory scale.

In the experiments described above, it is found that 75% of the ether and 95% of the amyl alcohol used may be recovered and one man working 6 to 7 hours is able to prepare 800 g. of cupferron. It is found that, even with the present high cost of chemicals and labor, cupferron may be prepared at considerably less than the pre-war price. The present price, moreover, is based on the production in the laboratory where the labor charge is fully 30% of the total cost. It is, therefore, evident that when prepared on a technical scale with normal prices for raw materials, cupferron should be very cheap and may become not only a very common laboratory reagent but also find technical application other than as a precipitant in analytical chemistry.

URBANA, ILL.

[CONTRIBUTION FROM THE KENTUCKY AGRICULTURAL EXPERIMENT STATION.]

THE TRANSLOCATION OF THE MINERAL CONSTITUENTS OF THE JACK BEAN.[1]

BY G. DAVIS BUCKNER.

Received December 5, 1918.

Introduction.

In a previous communication[2] from this laboratory, experiments were described concerning the translocation of the mineral constituents dur-

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[1] Published by permission of the Director of the Kentucky Agricultural Experiment Station.

[2] G. Davis Buckner, "Translocation of Mineral Constituents of Seeds and Tubers of Certain Plants during Growth," *J. Agri. Res.*, **5**, 449 (1915).

ing the growth of garden bean (*Phaseolus vulgaris*) and corn (*Zea mays*) seedlings, grown in distilled water in the light, and concerning the mineral distributed in the sprouted potato (*Solanum tuberosum*), grown in a dark room. These seedlings received only the nourishment stored in their cotyledons and were allowed to grow as long as they would. Their failure to grow further was presumably caused by the lack of food material or by the insufficiency of the mineral content of the partly exhausted cotyledons. The most interesting fact shown in these experiments was that practically 50% of the mineral material remained unused in the cotyledons when the seedling had died, apparently from inanition, and that approximately 50% of the mineral material which had migrated to the separate parts of the seedlings showed a fairly uniform distribution. The containers for the distilled water were paraffined test-tubes and aluminum cups, in the respective cases of bean and corn, but these, for various reasons, proved unsatisfactory. We therefore instituted a similar experiment with the lima bean (*Phaseolus lunatus*), using paraffined paper cups. This, however, had to be abandoned because the several lots of lima beans which were received from various sources proved to be in some way defective, as shown by the beans becoming discolored and being attacked by molds when attempts were made to germinate them. For a bean to fulfil the desired conditions of the series of experiments of which this paper describes a part, it should possess the following qualities: large size with a comparatively high mineral content; a large embryo capable of being dissected out; comparative freedom from the attack of fungus diseases such as anthracnose; and resistance to the growth of molds. While in search of such a bean Dr. E. W. Allen, Chief of the Office of Experiment Stations, Washington, D. C., mentioned to the author that possibly the jack bean (*Canavalia ensiformis*) might possess the desired qualities. The Texas Agricultural Experiment Station kindly furnished a sufficient quantity of these beans for the experiment, for which they proved entirely suitable.

Before studying the growth of the isolated embryo it seemed essential that we first determine quantitatively those elements that the seedling receives from the cotyledons during its early growth, and, at the same time, determine the quantity of these elements remaining unused in the cotyledons after the seedling had died, apparently from inanition.

Experimental.

In order to determine the distribution of calcium, magnesium, phosphorus and silicon in the separate parts of jack bean seedlings grown in distilled water, 2000 perfect jack beans of approximately the same size, were selected and divided into two lots, after being thoroughly cleaned and washed with distilled water. One lot was allowed to germinate in porcelain containers on sterile absorbent cotton which had been previously treated with hydrochloric acid and washed free of chlorides with distilled water.

The germination dishes were kept under properly ventilated bell-jars in order to prevent any contamination from dust. When the integument had broken, from the swelling of the seed, and the radicles had reached 1.2 cm. in length, the integuments were removed and saved to be analyzed after becoming air-dried. The radicle was then wrapped in a small quantity of absorbent cotton, previously treated as described above, and the cotton and radicle placed in a hole in the center of a piece of heavily paraffined cardboard which served as a covering for the paraffined paper drinking cups of ordinary size. The cups were thoroughly washed with distilled water and filled with the same, into which extended the plug of cotton through which the roots passed as they developed. The water was replaced as fast as it was removed by the plant and by evaporation. Since the water contained no mineral matter, it was obvious that any growth must be at the expense of the material stored in the cotyledons. Growth started at once, the cotyledons turned green and a good root system formed, with a corresponding stem and leaf development. As growth proceeded, the cotyledons shriveled considerably and finally the leaves began to etiolate, which was shortly followed by a complete drooping of the seedling. At this point they had reached an average height of 29 cm., in from 21 to 24 days. They were then removed from the containers and divided into the following parts: Leaves, petioles, upper stems, lower stems, exhausted cotyledons and the roots which were carefully separated from the adhering cotton into which they had grown. The water in the paraffined cups was evaporated to dryness with the drainings from the germination dishes and saved, to be analyzed with the separate parts of the seedlings. The growth of these seedlings took place in a basement room which received the proper amount of ventilation and sunlight. It was used solely for this purpose and was entered only when watering was necessary, thereby lessening the chance for contamination from dust. The other lot of 1000 beans was carefully washed with distilled water and analyzed as a control for the seedlings.

In analyzing the separate parts, they were ashed at a dull red heat and, after a gray ash had been obtained, two portions of 0.2000 g. each were weighed. Phosphorus and silicon were determined in one portion according to the official methods of the Association of Official Agricultural Chemists,[1] while in the other portion calcium and magnesium were determined according to McCrudden.[2]

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[1] H. W. Wiley, *et. al.*, "Official and Provisional Methods of Analysis, Association of Official Agricultural Chemists." As compiled by the Committee on Revision of Methods, U. S. Dept. of Agr., Bur. Chem., *Bull.* 107 (revised), 22 (1908).

[2] F. H. McCrudden, (1910), "The Quantitative Separation of Calcium and Magnesium in the Presence of Phosphates and Small Amounts of Iron. Devised especially for the analysis of foods, urine and feces," *J. Biol. Chem.*, **7**, 83 (1910). "The Determination of Calcium in the Presence of Magnesium and Phosphates; the Determination of Calcium in Urine," *Ibid.*, **10**, 187 (1911).

TABLE I.—ANALYSIS OF SEPARATE PARTS OF JACK-BEAN SEEDLINGS AND WHOLE BEANS.

(a) Seedlings.

Part.	Total wt. of air-dried material. G.	Total wt. of ash. G.	Ash in air-dried material. %.	Phosphorus as P_2O_5 in ash.		Calcium as CaO in ash.		Magnesium as MgO in ash.		Silicon as SiO_2 in ash.	
				G.	%.	G.	%.	G.	%.	G.	%.
2000 Cotyledons (exhausted)....	448.3312	19.7955	4.41	5.7981	24.34	0.4394	2.22	0.3978	2.01	0.0594	0.30
1000 Integuments (removed)....	206.2558	5.5895	2.71	0.8490	15.19	1.6388	29.32	0.6495	11.62	0.0212	0.38
1000 Lower stems..............	142.7021	4.8396	3.39	1.2520	25.87	0.1089	2.25	0.2241	4.63	0.0266	0.55
1000 Upper stems..............	61.9031	2.2748	3.69	0.4932	21.68	0.0355	1.56	0.1328	5.84	0.0093	0.41
2000 Leaves...................	137.8190	8.9041	6.46	0.2536	28.48	0.5796	6.51	0.3360	2.65	0.0801	0.90
1000 Roots....................	16.6089	1.2131	7.31	0.2130	17.55	0.0312	2.49	0.0297	2.45	0.0109	0.89
2000 Petioles.................	18.9740	0.7714	4.06	0.1720	22.30	0.0258	3.34	0.0278	3.61	0.0035	0.45
Drain water...................	4.2109	1.3054	30.98	0.2967	22.73	0.1986	15.21	0.0970	7.43	0.0044	0.34
Total weight..................	1036.8050	44.6934	...	9.3276	...	3.0579	...	1.8947	...	0.2154	..
(b) Control Beans.											
1000 Whole beans..............	1462.4560	43.7830	2.99	9.4766	21.64	3.1699	7.24	2.0053	4.58	0.1800	0.41

In Table I will be seen the results of the analysis of the separate parts of 1000 jack-bean seedlings and also the analysis of the 1000 control beans.

The results, as expressed in Table I, show a difference in the total weight of the air-dried material, which possibly may be accounted for by a loss of carbonaceous material which was occasioned by the abnormal conditions governing their growth and by the difference in water content due to unequal drying. The total weight of the ash from the several parts of the seedlings corresponds closely with the control, which, with the total weight of the separate minerals under consideration, falls well within the limits of experimental error.

TABLE II.—PERCENTAGE DISTRIBUTION OF THE MINERAL CONSTITUENTS OF JACK-BEAN SEEDLINGS.

Part.	Ash.	Phosphorus as P_2O_5.	Calcium as CaO.	Magnesium as MgO.	Silicon as SiO_2.
Cotyledons (exhausted)	52.3	70.9	36.0	34.6	31.3
Roots	3.2	2.6	2.6	2.6	5.7
Upper stems	6.0	6.0	2.9	11.5	4.9
Lower stems	12.8	15.3	8.9	19.5	14.0
Petioles	2.1	2.1	2.1	2.4	11.9
Leaves	23.6	3.1	47.5	29.3	42.2

In Table II is given the percentage distribution of these elements which actually migrated from the cotyledons to their final location in the different parts of the seedlings. It will be readily seen that a large percentage of them remained unused in the cotyledons, varying from 31.3% in the case of silica to 70.9% in the case of phosphorus pentoxide. Also it is seen that there is a relatively large amount of those elements under consideration accumulating in the lower stems and, with the exception of phosphorus, even a greater percentage has migrated to the leaves. It is interesting to see the small and even distribution of these elements in the roots and that the distribution of ash in the leaves and stems is proportionately high.

Conclusions.

The jack bean shows a marked retention of calcium, magnesium, phosphorus and silicon in the cotyledons during the growth of the seedlings in distilled water. The large accumulation of these minerals in the leaves is as would be expected, since it is here that we find the greatest metabolic activity and evaporation. The small amount of these elements found in the roots is also as would be expected, since their functions were limited to the taking up of water, which would tend to lessen intracellular activity.

The largest proportion of the translocated elements under consideration, except phosphorus, is found in those parts of the seedling having the greatest external surface and, therefore, capable of the greatest anabolic activity and evaporation, while the large proportion remaining in the cotyledons points to the activity of this part of the mineral matter in promoting the catabolic change occurring therein.

The use of paraffined paper cups has proved very satisfactory for growing seedlings under exclusion of extraneous mineral matter and the method developed seems well suited for the further investigation of this subject.

We hope from this experiment and others in progress to throw further light on the physiology of germination and the nutrition of the embryos of plants and since these figures show that the fixation of carbon was considerably less than the loss apparently caused by oxidation it would be of interest to determine the means whereby they would be made to function normally as carbon fixers.[1]

LEXINGTON, KENTUCKY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE PRESIDENCY COLLEGE AND THE UNIVERSITY COLLEGE OF SCIENCE.]

HALOGENATION. XVII. THE ACTION OF HALOGENS ON THE GRIGNARD REAGENT AND THE REPLACEMENT OF HALOGEN ATOMS BY ONE ANOTHER.

BY RASIK LAL DATTA AND HARAPARBUTTY KUMAR MITTER.

Received December 2, 1918.

The action of halogens on the Grignard reagent has not been much studied. Grignard and Courtot[2] investigated the action of bromine and iodine on α-indenyl magnesium bromide with the formation of α,β,γ-tribromoindane and α,α-diindenyl, respectively, among other minor products. The action of cyanogen haloids on the Grignard reagent has been studied by Grignard and Courtot[3] and also by Grignard, Bellet and Courtot.[4] It has been shown by them that with cyanogen chloride, the nitrite is the chief product, while with cyanogen bromide and iodide mainly the corresponding halogen derivatives are formed. This has led Grignard to conclude that the cyanogen bromide and iodide act in the carbylamine form.

It has been found as a general reaction that one halogen is able to displace the other halogens from the Grignard reagent with the production of the corresponding haloid derivatives. The yield of haloid derivatives is much influenced by the nature of the halogen and also by the conditions of the experiment. These reactions are sometimes accompanied by secondary reactions due to the union of the Grignard residues.

When iodine is added to magnesium phenyl bromide, there are obtained

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[1] Acknowledgment is due Dr. A. M. Peter of this Station for this interpretation of these figures for the loss in weight of the air-dried material.

[2] *Compt. rend.*, **154**, 361 (1912).

[3] *Bull. soc. chim.*, **17**, 228 (1915).

[4] *Ann. chim.*, [9] **4**, 28 (1915).