SUMMARY

Studies of the Water Relations of Dehydrated Foods in Relation to the Diffusion of Simple Constituents.

by

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SUMMARY

The primary object of this work was to study the water-relations of a range of dehydrated foods, in an attempt to define moisture levels which prevent solute diffusion and to examine the effect of molecular size of the solute on the diffusion process.

The work entailed preparation of sorption isotherms for a number of dehydrated foods and examination of diffusion in similar materials stored in equilibrium with different relative humidities, using a carbon 14- labelled solute and the technique of autoradiography.

Results of the sorption experiments show that sorption isotherms for potato, haricot bean, green bean, pea, meat and onion are of the sigmoid type, and that the B.E.T. equation is applicable to these materials. Carrot, tomato, apple and date gave isotherms of the Brunauer type III.

Results of the diffusion experiments show that a relationship exists between the calculated monolayer values for a number of the materials showing isotherms of the sigmoid type, and the moisture levels limiting for solute diffusion. This appears to be the case, for example, with onion, pea, meat and green

bean, in which diffusion was detected at moisture contents little higher than the corresponding monolayer values. However, in green bean, some migration of the tracer was found to occur at moisture contents actually lower than the monolayer value. The results for the materials showing isotherms of the Brunauer type III were entirely negative at the moisture levels tested, except in the case of date, in which a positive result was obtained at a moisture content as low as 4.24 g. water per 100 g. dry solids.

Results of the experiments carried out to study the effect of molecular size of the solute on diffusion have yielded evidence that it is not only the condition of the water in the material which determines the limiting moisture content at which diffusion can occur, but that the latter may vary with the molecular size of the solute.

A further series of experiments was carried out to study the effect of treating materials with liquid glucose, prior to drying, on the rate of drying and on the hydration characteristics of the dried products. The final distribution of the liquid glucose in the dried materials and the effect of this treatment on solute diffusion was also examined.

In addition, the effect of the treatment on the culinary quality of the dried products was considered, using a tasting panel.

Results of the drying curves show that the necessary drying period is not extended; that this treatment has the effect of reducing the initial moisture content and that the rate of drying is greater in the untreated materials during the first 4 hours of drying. Those of the hydration curves and the sorption isotherms show that the water-holding capacity of the treated materials is lower than that of the corresponding untreated materials.

Results of the diffusion experiments suggest that the liquid glucose is present as a dry surface film which prevents contact between the solute and the surface of the tissue.

Results of the tasting tests agree that the treatment results in an improved texture in apple and in a more satisfactory colour in onion.

"Studies of the Water Relations of Dehydrated Foods in Relation to the Diffusion of Simple Constituents"

by

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PREFACE

PREFACE

A proportion of the water present in foodstuffs is considered to be "bound" to the macromolecular constituents of the food. This "bound" water assumes a much greater importance when the moisture level is reduced, as for example, during dehydration. When all the water present is in the bound state, there being no solvent water present, the initiation of chemical reactions in solution is prevented, and the stability of the material is markedly increased.

The purpose of this work is to study the water relations of a range of foods of low moisture content, in an attempt to define moisture levels which will prevent solute diffusion. The method employed is to store dehydrated food materials of different moisture content treated with a carbon 14 - labelled solute, and to measure the diffusion taking place during periods of up to 6 months, by autoradiography. In addition, the influence of molecular size on the diffusion process is examined, and the effects of treating some of the materials, with "liquid glucose", prior to drying, on the rate of drying and on the water relations and culinary quality of the dried products, is considered.

INTRODUCTION

INTRODUCTION

The development of undesirable changes in Food during storage is due to micro-organisms, enzymes and non-enzymic chemical reactions. Dehydration as a method of food preservation has succeeded in controlling micro-biological spoilage by bringing the moisture content of the food to such a low level that micro-organisms cannot grow. Enzymic reactions do not constitute an insuperable problem in dehydrated foods, since the enzymes responsible can be effectively inactivated by suitable scalding treatments. So far, the problem of deterioration due to non-enzymic chemical reactions has not been solved completely, although studies on the effect of moisture content, concentration of solutes, temperature and oxygen and on the use of chemical inhibitors such as sulphur dioxide, have lent valuable information which has resulted in means of minimizing the effects of these reactions. Of these factors, moisture content has perhaps the most pronounced effect on the rate of chemical change.

Salwin[1] has suggested that a moisture content corresponding to a theoretical monolayer of water molecules, as described in the adsorption theory of Brunauer, Emett and Teller [2], confers maximum stability on dehydrated foods.

Water molecules in the monolayer condition may protect polar side-groups of hydrophilic molecules from reactions with one another and with other constituents of the food. On the other hand, at moisture contents above the monolayer value, chemical reactions such as "browning" take place more readily. This latter aspect of the monolayer condition has been a subject of investigation by Duckworth and Smith [3]. These workers have suggested that the initiation and subsequent rate of browning reactions depend on the ability of reactants to move freely. Since the monolayer value is considered as a limit below which all the water is in a "bound" state and above which some water is "free", the browning reactions would be accelerated by the presence of this solvent water. The results of Duckworth and Smith have indicated that the limiting moisture contents for solute diffusion in dehydrated potato and carrot are little higher than the moisture contents corresponding to the monolayer values for these materials. These results support Salwin's [1] suggestion that the monolayer value be used as a guide when determining optimum levels of moisture for stability of dehydrated foods during storage.

The purpose of the present work is to examine the relationships between the calculated monolayer values for a wider variety of foods than has so far been studied, to the respective levels of moisture at which the diffusion of solutes is prevented. A range of freeze-dried, air-dried and sun-dried products is examined in this way, using techniques similar to those employed in earlier work. In addition, experiments to test the effect of the molecular size of the solute on diffusion in such systems will also be described.

A procedure which has recently shown promise in the dehydration of vegetable materials, especially those which are particularly susceptible to loss of flavour due to the removal of volatile constituents during the drying process is to dip the material in "liquid glucose" immediately prior to drying. A few experiments on the effects of this procedure on the rate of drying and on the hydration characteristics and culinary quality of the dried products have also been carried out and the results of these, together with these of diffusion experiments using material treated in this way, will also be included.

PART I

WATER VAPOUR SORPTION AND DIFFUSION IN DEHYDRATED FOODS

LITERATURE REVIEW

Non-enzymic Chemical Reactions

1. "Browning reactions" [4,5]

There are three broad types of browning reaction occurring in foodstuffs. The most common kind, especially in dehydrated foods, appears to result from Maillard-type reactions between carbonyl and amino compounds (this includes the reactions of aldehydes, Ketones, and reducing sugars with amines, amino acids, peptides and proteins). Another type, called caramelization, occurs when polyhydroxycarbonyl compounds are heated to relatively high temperatures in the absence of amino compounds. Both acids and bases are known to catalyze caramelization reactions. A third broad type of browning is the group of oxidative reactions which, for example, convert ascorbic acid and polyphenols into di- or polycarbonyl compounds. In general, browning can be inhibited by the addition of reagents that will combine with or otherwise eliminate reactive carbonyl groups.

In dehydrated foods, the moisture content of the product and temperature are the most important factors determining the rate of browning during storage. Also of importance are the initial sugar content of the product, the method of scalding (whether it tends to increase or decrease the concentration of browning reactants in the product), and the sulphur dioxide content of the material [6].

2. Oxidative reactions

Several kinds of oxidative deterioration occur in dehydrated foods. Unsaturated lipid materials may be autoxidised, resulting in formation of carbonyl compounds which produce rancid off-flavours. Pigment unstability and loss of vitamin C are also due to oxidation. In contrast to the browning reactions, oxidative reactions appear especially to be favoured by low moisture contents. The reason for this is considered more fully in a later section.

3. Effect of dessication on rehydration power

The reconstitutability of certain products is affected by the way the product has been treated prior to drying, by the rate of drying and finally, to an important extent, by the final moisture content to which the material is lowered [7-9]. When drying is rapid, hydrophilic polymers, such as cellulose, may become highly crystalline and the water - imbibing power of the material may therefore be reduced. When drying is less rapid a greater amount of amorphous material is retained, and the swelling capacity on rehydration is greater. In products such as starch and cellulose, the larger the amount of water removed during drying, the greater is the loss of reconstitutability, and in the case of cellulose, further increases in crystallinity have been shown to occur during storage in the dry state.

Bound Water

The term "bound" water is commonly used in the literature with reference to colloidal systems, yet there is no unanimity of definition. Briggs [10] has defined "bound" water as "that portion of the water content of the system which fails to display the normal behaviour of ordinary free water under the particular experimental conditions". There are therefore many possible definitions according to the particular experimental conditions. Kuprianoff [11] has defined it as the part of the water content of a product which remains in it in a bound state after application of the usual drying procedures, such as freezing, chemical dehydration, etc., and which can be expelled only by heating to 100 - 110°C. for a long time. It has also been defined as that portion of water which does not act as a solvent [12]. Determinations of bound water have, for the most part, been based either on the results of freezing experiments or on studies of water sorption by the material concerned.

Freezing Experiments

Many experiments have been performed using different methods and materials. As early as 1916, Foote and Saxton [13], using inorganic hydrogels, attempted to determine unfreezable water by freezing a precipitate of known total water content and measuring the expansion caused by the freezing of the free water. The water bound against freezing was then found by difference. These same authors [14] divide the water present in such systems into three distinct fractions:

1. Free water, which freezes sharply when the material is cooled slightly below 0°C.
2. Water which freezes gradually as the temperature is further lowered.
3. Water which does not freeze, however far the temperature is depressed.

The water which freezes gradually with falling temperature they consider to be capillary water, while the unfreezable water is referred to as combined water. Moran [15] (1926), studying the condition of water in gelatin gels, distinguished more or less the same three categories:

1. Free water separating as ice in the region of 0°C.
2. Water bound to gelatin by osmotic forces and which is gradually frozen as the temperature is lowered to -20°C.
3. Chemically bound water which is not frozen at any temperature.

(St. John [18] (1931) determined the lowest temperature at which all the water in egg white freezes out as -12.5°C.).

Gortner [16], in 1930, studied the freezing out of water, as ice, in biological tissue. By using Theones' [17], equation which depends on the measurement of the heat of fusion of ice, he was able to calculate the amount of frozen water. The total water content was then determined by drying the material to constant weight. The difference between the total and frozen water values gave the amount of bound water in the material.

In 1946, Daughters and Glenn [19] reviewed previous work on the estimation of bound water by freezing. Using calorimetry and a modification of Theones' equation, they were able to obtain values of bound water for different fruit and vegetable materials. These range from 3.8 g. per 100 g. dry solids in rhubarb to 68.4 g. per 100 g. dry solids in samples of green beans. A corresponding value of 4.3 was obtained for cotton, at about the same time, by Magne et al.~~[24]~~[25], who conclude that all the water below this value is hydrogen-bonded to the free hydroxyl groups. Preston [20], in 1956, used the cooling curve method for determining the bound water content of moist synthetic and natural fibres. This method requires no assumption concerning the thermal properties of the components, and thus has an advantage over the calorimetric methods used by earlier workers. Values of between 37.5 and 41 g./100 g. dry solids were obtained with these materials.

Most recently Riedel [21], from studies on meat, has shown that the amount of unfrozen water at low temperatures is independent of the initial water content. If the initial water content is below the value of the unfreezable water, no ice will form. A value of 22.5 g. water per 100 g. dry material was found by this author for the water bound against freezing in meat.

Riedel has attempted to formulate a theory regarding the condition of water in such materials by assuming that a temperature-dependent equilibrium exists between the bound and free water. By evaluating the specific equilibrium constants from measured sorption isotherms, Riedel produced the following isotherm equation:

$$\chi = \alpha + \frac{\Sigma \varphi}{K+\varphi} + \frac{\lambda \varphi^{h}}{1-\varphi}$$

where:

χ = moisture content in Kg./Kg. dry material.

α = a constant representing Langmuir term for a very large binding energy and a very low K value.

K = equilibrium constant.

Σ = a constant representing maximum amount of bound water.

φ = relative water vapour pressure of the air over the system.

λ = a constant representing the ratio of the molecular weight of dissolved particles to the salt content of the material.

$\frac{\Sigma \varphi}{K+\varphi}$ represents chemically bound water as apposed to $\frac{\lambda \varphi^{h}}{1-\varphi}$ which represents capillary water.

Riedel suggests that the validity of B.E.T. theory to water sorption by proteins is very much open to question, but adds that his own suggestions are, at present, hypothetical, and require confirmation by further work on similar materials.

Nemitz [22], working in Riedel's laboratory, obtained a value of 20 g. water per 100 g. dry solids for the content of bound water in desalted egg white by freezing experiments. This value is supported by the results of sorption and heat-denaturation experiments carried out on similar material. Nemitz, like Riedel distinguishes between "molecular bound water" and "capillary bound water". The molecules of the latter are considered to be mobile within the capillaries.

Sorption Experiments

Sorption Isotherms

Modern theory on the adsorption of water by biological material has been based on early work on the adsorption of gases on solid surfaces, a phenomenon best studied by sorption isotherms. A sorption isotherm is a plot of the amount of gas or vapour adsorbed at various pressures by a given solid at a constant temperature. Usually when the adsorbate is a vapour, the amount adsorbed is plotted against the relative pressure rather than the actual pressure. The relative pressure is the actual pressure of the vapour divided by the saturated vapour pressure at the temperature of the experiment. Brunauer[23], divides sorption isotherms into five types, according to the various shapes obtained. Only Brunauer's types II and III will be considered in the present connection and these are represented in Fig. 1. Type II is commonly known as the sigmoid or S-shaped isotherm and can be taken as consisting of three parts:

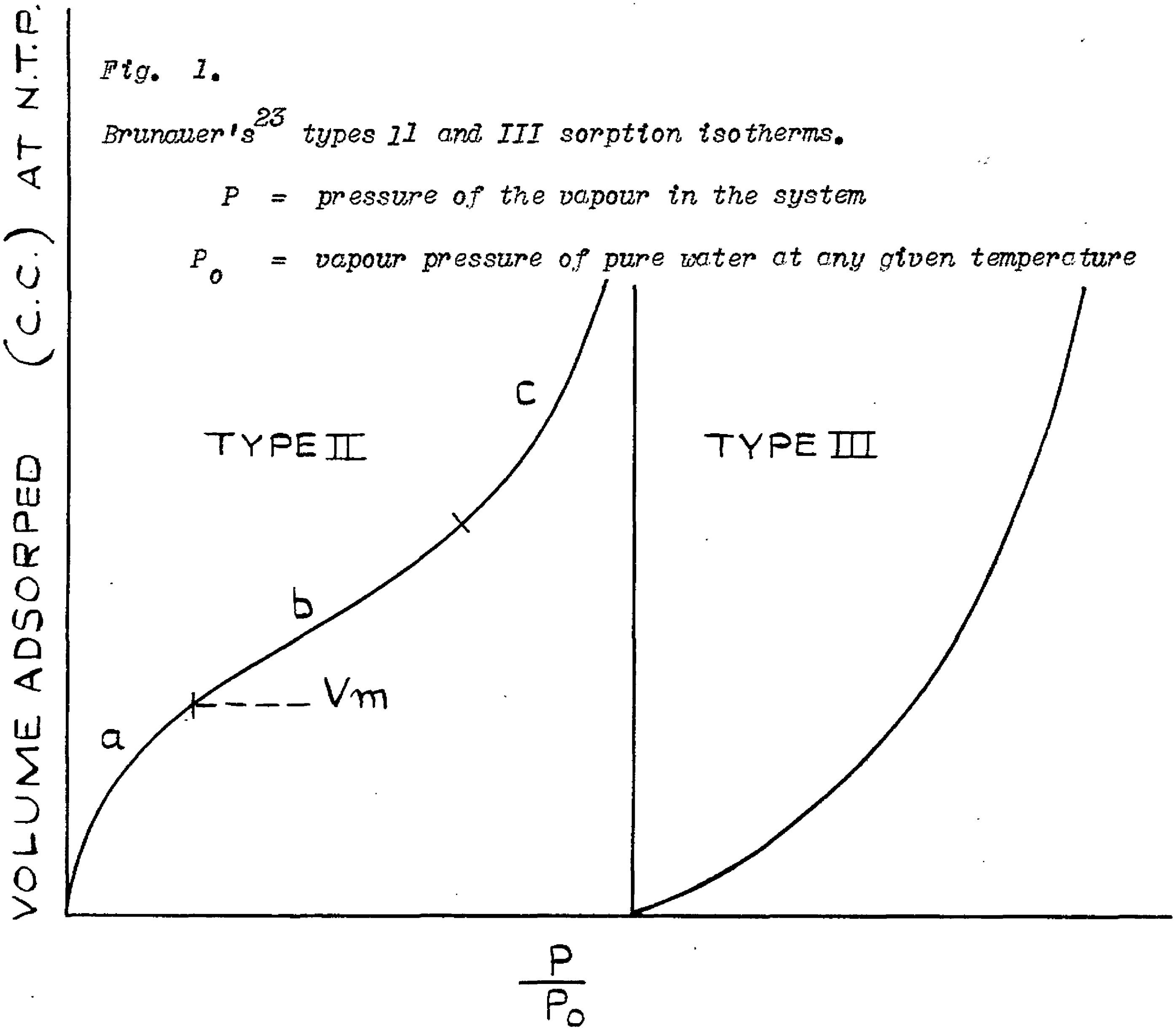


Fig. 1.

Brunauer's[23] types 11 and III sorption isotherms.

P = pressure of the vapour in the system

P_o = vapour pressure of pure water at any given temperature

a. is a low pressure region, concave to the pressure axis, which represents Langmuir adsorption, the amount adsorbed increasing rapidly with increase in vapour pressure and the end of this part corresponds to a completion of a monolayer of gas molecules (Vm).

b. is a linear portion representing multilayer adsorption, the length and slope of which depend on the adsorbate, the adsorbent and the temperature.

c. is a portion showing a sharp increase in the amount adsorbed with increasing vapour pressure and is probably due to capillary condensation.

The type III isotherm is convex towards the vapour pressure axis and this is associated with low heats of adsorption.

There are two characteristic features of sorption isotherms. The first is that, since the adsorption process is always exothermic, the amount adsorbed always decreases with increasing temperature in accordance with the law of Le Chatelier. The second is that the isotherms show hysteresis effects.

The B.E.T. Theory

Many theories dealing with the adsorption of gases and vapours have been introduced, but the most widely used has been that of Brunauer, Emmett and Teller [2] (referred to usually as the B.E.T. theory). This theory enables the surface area and pore structure of solids to be studied and provides an explanation for the five different types of sorption isotherms through the whole range of vapour pressure. The theory assumes that van der Waals' forces are responsible for adsorption of gas molecules on the surface of the solid adsorbent and that these forces are the same forces as those responsible for condensation; that more than one layer of sorbate molecules may be present on the surface of the adsorbent; that the energy of sorption for molecules in all layers except the first is the heat of condensation of pure sorbate; and that the energy of sorption is the same for all molecules in this first layer. The B.E.T. equation is best applied in the region of 0.05 - 0.35 relative vapour pressure. Several workers have applied B.E.T. theory to water sorption isotherms of food. The following is the equation and its modification for moisture sorption [1]:

$$\frac{P}{a(P_0 - P)} = \frac{1}{a_1 C} + \frac{C - 1}{a_1 C} \cdot \frac{P}{P_0} \qquad (1)$$

where:

a = grams of water per 100 grams of dry solids at moisture vapour pressure P.

P_0 = vapour pressure of pure water at the same temperature.

C = a constant related to the heat of adsorption.

a_1 = grams of water equivalent to a monomolecular layer adsorbed on 100 grams of dry solids.

A plot of $\frac{P}{a(P_0 - P)}$ against $\frac{P}{P_0}$ is a straight line with y - axis intercept equal to $\frac{1}{a_1 C}$. In the work carried out by Salwin, vapour pressures are expressed in terms of percent relative humidity, R; thus the following transformation is used:

$$\frac{R}{a(100-R)} = I + S.R \qquad (2)$$

The straight line plot of $\frac{R}{a(100-R)}$ against R, has a y - axis intercept, I, and slope, S. The value of the monomolecular layer can be calculated using equation (3).

$$a_1 = \frac{1}{I + 100S} \qquad (3)$$

The numerical values of I and S can be taken from the plot of equation (2), or can be calculated by solving simultaneous equations which result from substituting into equation (2), numerical values of a and R at two points on the isotherm between approximately 5% and 35% relative humidity.

A number of workers[24-28] have suggested modifications of the B.E.T. equation by applying it to specific systems. Hill's[24] mathematical treatment indicates that there need be no sharp distinction between condensed water and water adsorbed in multimolecular layers, a conclusion also accepted by Magne et al[25]. Hailwood and Horrobin[26], working with natural and synthetic fibres, found the application of the B.E.T. theory in such cases to be only partly successful. By assuming that the adsorbed water exists in two states, one in simple solution and another combined to form a hydrate with definite units of the fibre molecule, they were able to derive a modified equation giving better agreement with their experimental results. Dole and McLaren[27] also expressed doubt as to the applicability of the unmodified equation to proteins and polymers.

The importance of the B.E.T. theory lies in its ability to be used for calculating the amount of adsorbate present at the monolayer condition which, in addition to its use for measuring the surface area of the solid adsorbent[29,30], is of great value in determining the condition of the adsorbate in a particular system. It has been applied by a number of workers studying the state of water in dehydrated foods[31-33].

The Adsorption of Water Vapour by Proteins and Polymers

Several workers have compared the adsorption of gases, such as nitrogen and water vapour, by proteins and polymers [34,-36], and have concluded that water adsorption is different from that of nitrogen in that it takes place at specific sites. A relationship between these sites and the amount of water adsorbed has been established by several workers.

Bull [37] and Shaw [38] both conclude that the area covered by the monolayer is only a small part of the total area of a protein when spread in a thin film, and they therefore suggest that the water is bound locally to certain hydrophilic groups.

Pauling [39] calculates that the number of water molecules adsorbed bears a relationship to the total number of polar side chains in certain proteins and interprets previously published data on the assumption that one water molecule is attached to each polar amino-acid side chain. He maintains that peptide groups do not bind water, because of their mutual interaction involving hydrogen bonds.

Mellon et al.[40] have determined quantitatively the contribution of the amino group to the water adsorbing power of casein. Their study shows that the amino group, which constitutes less than 1% of the weight of the casein molecule, is responsible for about 25% of the total water sorption by casein over the entire range between 6% and 93% relative humidity. The amount of water held at 75% R.H. is consistent with the amount required for complete satisfaction of all hydrogen bonds associated with the amino groups.

The same authors [41] conclude, from studies on polyglycine peptides, that in these cases peptide linkages must be responsible for most of the water absorption. By comparing the absorption of polyglycine peptides with the absorption of proteins, they found that peptide groups were responsible for about 45% of the vapour phase absorption by casein and 70% of the absorption by Zein at 60% relative humidity.

Mclaren and Rowen [42], in 1951, reviewed previous work on the sorption of water vapour by proteins and polymers and noted that, with synthetic polymers, the sorptive capacity of a polar group on a side chain may be different from that of the same grouping in the main polymer chain itself. They suggest that the polar groups in proteins which can bind water include those of serine, threonine, tyrosine, arginine, aspartic acid and glutamic acid. They do not support the idea that peptide bonds play a predominant part in sorption, but suggest that it is necessary in some cases to assume that a certain proportion of the water molecules is bound to peptide groups.

Katchmann et al.[43] conclude from studies on the sorption of water vapour by proteins and polymers that, in trypsin - inhibition, the crystalline material can hold more water at a given vapour pressure than can the amorphous form, and postulate that in addition to water held by polar groups, water may also be held between layers of peptide chains in the crystal. They also maintain that the ability of a polymer to sorb water depends on the nature, as well as the position of the polar groups present in the molecule.

The monolayer water and optimum stability.

The amount of water in the monolayer has been found by Salwin[1] to correspond closely to the moisture values at which a number of foods have the greatest stability (Table 1).

Above these optimum values, browning reactions, caking, and hydrolysis of lipids take place. Below these values, bleaching, loss of vitamin C and rancidity occur, and the ability to reconstitute is affected.

It has been suggested that, at the monolayer value, the reactions are affected as follows:

TABLE 1

COMPARISON BETWEEN THE CALCULATED MONOLAYER VALUES AND THE MOISTURE LEVELS CORRESPONDING TO GREATEST STABILITY.[1]

Material	Moisture content corresponding to greatest stability g./100g. dry solids	Monolayer values from sorption isotherm g./100g.dry solids
Potato dice	6	5.46
Dried whole milk	2.25	1.97
Instant non-fat dried milk	3.50	3.52
Spray-dried cheese	2.20	2.22
Cocoa powder	3	2.37

a) At the monolayer there is no free water and the initiation of browning reactions is thereby inhibited.

b) The monolayer water might offer protection against attack by oxygen on functional groups of proteins and carbohydrates, possibly by excluding adsorption of oxygen directly, possibly by inhibiting the catalytic action of trace metals.[44]

c) The adsorbed water might also inhibit interactions, such as the establishment of hydrogen bonds, between adjacent polar groups, thereby preserving their hydrophilic properties, and facilitating rehydration.

Diffusion Experiments.

During drying there is movement not only of water but also of dissolved solids, and this movement is facilitated by the loss of the semi-permeability of the cytoplasmic membranes which takes place at the death of the cells as, for example, during scalding. This movement of solutes has been studied recently by Duckworth and co-workers.[45, 46, 47.]

Recently Duckworth and Tabasnich[46] using sulphur - 35 - labelled Sodium sulphite and the technique of autoradiography, examined the distribution and movement of sulphite during dehydration of potato and carrot and found a central accumulation of the sulphite in pieces of these materials. More recently Duckworth and Smith[47] studied the movement and distribution of labelled glucose in scalded potato and carrot by soaking carrot and potato strips in solutions of labelled glucose, then obtaining autoradiographs of sections taken at various intervals during drying. Their results indicate that there is a net inward movement and accumulation of labelled glucose at the centres of the strips. These results lend support to the suggestion that the phenomenon of the brown centre in dehydrated potatoes (due to the rapid progress of browning reactions in this central region), might be due to inward diffusion of the browning reactants during drying. These same workers[3,31] also examined the ability of solutes to diffuse at different moisture levels using similar methods. Their results indicate that solute diffusion in these materials is only possible at moisture contents above those calculated to correspond to a theoretical monolayer. When they measured the electrical resistance of these materials, they found a sharp increase in resistance below the point found to be limiting for solute diffusion. The route by which diffusion of these solutes takes place was also examined, and it was found that, in potato, diffusion occurs more quickly through sections of the cell-wall network and of the complete tissue than through sections of starch gel. From this, they conclude that movement in the complete tissue is predominantly along the cell walls, a conclusion which has been supported by autoradiographic evidence.

EXPERIMENTAL

1. Materials

Food materials

The materials used for both sorption and diffusion experiments were:

(1) Freeze-dried onions, green beans and raspberries.

(2) Air-dried potatoes, peas, apples, meat and carrot.

(3) Sun-dried tomatoes, haricot beans and dates. (These were obtained from the Sudan.)

Radioactive material

The radioactive materials used were:

(1) Glucose, uniformly labelled with Carbon 14, obtained from the Radiochemical centre, Amersham, Buckinghamshire. A specific activity of 25 μc/ml. was used. This β - emitting isotope is particularly suitable for autoradiography, having a maximum energy of 0.154 M.e.v., and a half-life of 5,580 years.[51]

Glucose was chosen as a representative of the simple food constituents which may contribute as reactants towards the chemical deterioration taking place in dehydrated foods.

(2) Carbon 14 - labelled urea - specific activity $40\ \mu c/ml$. This was used in work to study the effect of molecular size on diffusion.

2. Sorption experiments

Introduction

The sorption of water vapour by dehydrated foods can best be studied by preparing sorption isotherms showing the equilibrium relationships between the moisture content of the product and the relative humidity of the atmosphere immediately around it. A saturated salt solution held in an enclosed vessel at a certain temperature will produce a constant humidity peculiar to the salt used.[48,49] (See Table 2). Sulphuric acid solutions of known concentration can also be used for this purpose. The exact concentration of the solution can be determined exactly by measuring its density. (Tables relating relative humidity to density and concentration of the acid are given in the International Critical Tables[50]).

The time required for equilibration may be reduced by evacuation, forced circulation of the air above the material or by reducing the particle size of the material used. After equilibrium has been attained the moisture content of the material may then be determined gravimetrically. The humidity of the vapour

TABLE 2

RELATIVE HUMIDITIES CORRESPONDING TO SULPHURIC ACID AND SATURATED SALT SOLUTIONS AT 37°C.[48-50]

Solution	Concentration	Relative Humidity (%)
Lithium chloride	Saturated	12
Potassium acetate	"	20
Sulphuric acid	56.6%	25
Magnesium chloride	Saturated	32
Chromium oxide	"	40
Potassium carbonate	"	43
Sodium bromide	"	58

phase in equilibrium with the sample is expressed as equilibrium relative humidity, $\frac{P}{P_o} \times 100$, where:

P = moisture vapour pressure of the sample.

P_o = vapour pressure of pure water at the same temperature.

The moisture content is expressed as grams of water per 100 grams of dry material.

Preparation of samples

The food materials were powdered in a Glen Creston electric mill, and the powdered material passing a 40 mesh sieve, was used for sorption experiments.

Two methods were used for determining the moisture content of the material at equilibrium. In the first one, and initially dry sample was employed and its equilibrium moisture content at a given relative humidity was calculated from the increase in weight of the sample. In this case initially dry samples were obtained by drying material to near constant weight in a vacuum-oven at a temperature of 70°C. and under a vacuum of 125 mm. Hg. (drying was discontinued when the difference between two successive weighings was less than 2 mg. in a sample of approximately 5 gms.)

In the second method the moisture content determination was made by drying material from the humidity chambers to constant weight over phosphorous pentoxide under vacuum.

Samples of approximately 1 g. were used for each determination of moisture content.

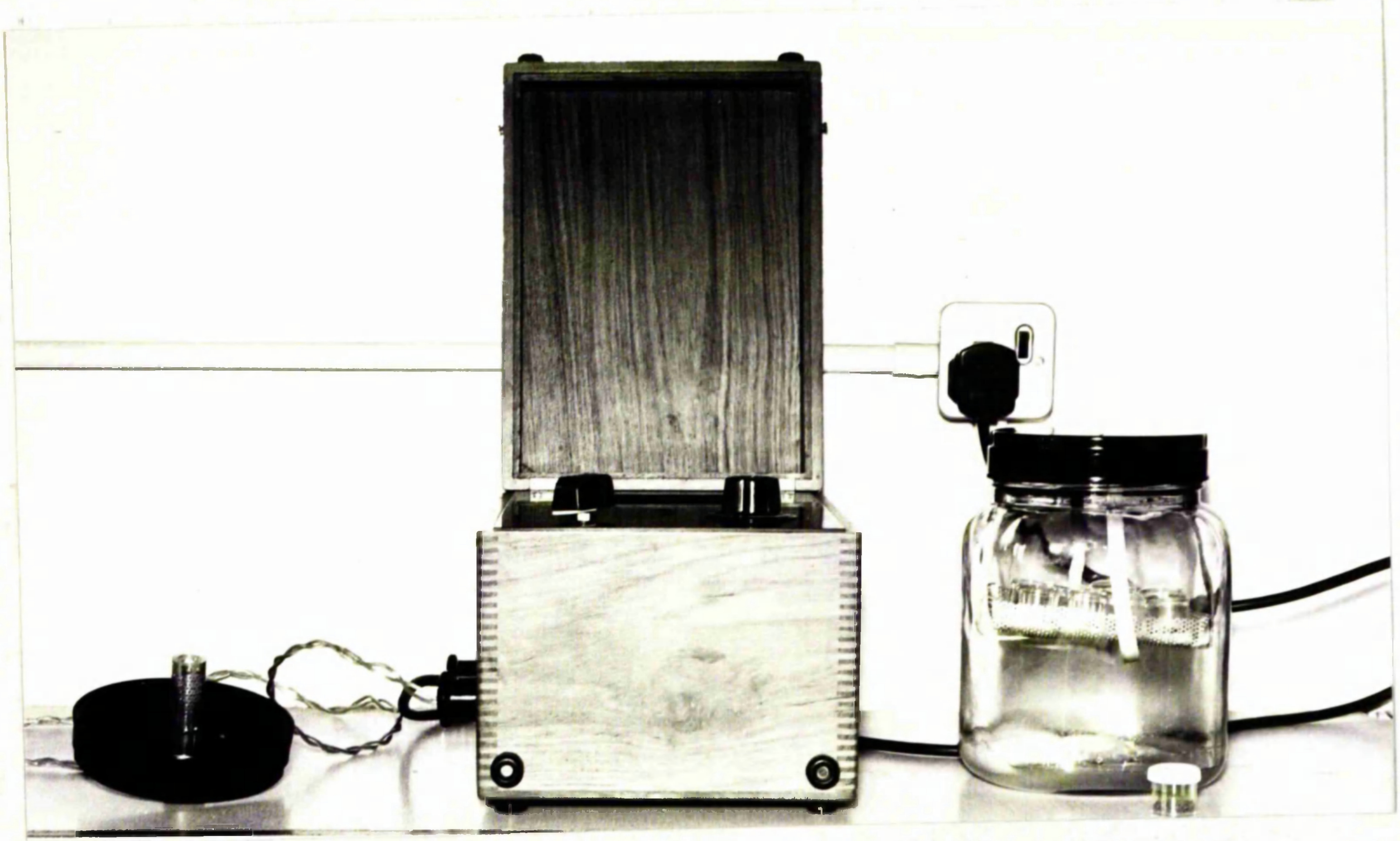
Humidity chambers

Constant relative humidities corresponding to the different solutions given in Table 2, were maintained in closed sweet jars approximately 6" x 6" x 9" in size. In each jar, a perforated zinc platform, supported by aluminium strips attached to the neck of the jar, was used for holding the weighing bottles containing the samples. Relative humidities were measured using a Negretti and Zambra R.H. meter with a lithium chloride cell. (Plate 1).

Equilibration

The weighed samples were placed in the humidity chambers, in which they were stored in an incubator at 37°C. The samples were removed from the chambers at various intervals and weighed. When no significant change in weight occurred between two successive weighings, a sample was considered to have reached

PLATE I. Humidity chamber and R.H. meter.



equilibrium. (In these experiments the samples took 10 - 15 days to reach equilibrium).

Moisture content determination

Many comparisons have been made in the past between different methods of determining the moisture contents of food materials, e.g., 52-57. In common with other authors, Salwin[66] maintains that oven methods are not suitable for foods that are unstable, or which contain volatile materials in addition to moisture, while drying over phosphorus pentoxide under vacuum gives erroneously high results when volatiles are present, unless the temperature is reduced to approximately 40°F. In the present work continued losses were recorded even after drying for 150 hours in the vacuum oven. Moisture content obtained after drying for 6 hours were in good agreement with those obtained by drying over phosphorus pentoxide (Table 3). Potato, haricot bean and meat, being relatively stable materials, showed the least difference in results obtained by the two methods, while date, tomato, apple, carrot and pea showed a relatively larger discrepancy (materials especially rich in sugars (Table 4) or in volatiles.)

TABLE 5

COMPARISON OF MOISTURE CONTENT DETERMINATIONS USING VACUUM-OVEN AND PHOSPHORUS PENTOXIDE METHODS

Material	Moisture content (g. water/100g. dry solids)		Difference
	Vacuum oven (70°C, 6 hrs, 125 mm. Hg)	P_2O_5 (20°C., 30 mm. Hg.)	
Potatoes	8.05	7.85	0.20
H. beans	7.98	7.74	0.24
Peas	5.21	4.61	0.60
Meat	5.42	5.20	0.22
Carrots	5.45	4.85	0.60
Apples	7.09	6.68	0.41
Tomatoes	5.00	4.44	0.56
Dates	5.07	4.24	0.83

TABLE 4

AVERAGE PERCENTAGE SUGARS AND HIGH MOLECULAR WEIGHT CONSTITUENTS PRESENT IN THE MATERIALS USED (CALCULATED FROM AVAILABLE DATA).[70-72]

Material	Carbohydrates other than sugars	Proteins	Sugars
	% dry solids		
Potatoes	86	9	3
H. beans	68	24	3
G. beans	69	17	8
Peas	57	27	7
Meat	0	74	0
Raspberries	39	8	39
Onions	23	12	64
Carrots	27	8	54
Tomatoes	14	15	54
Apples	14	2	70
Dates	10	2	76

Results

Moisture content calculation

Results of measurements were calculated as follows:

$$\text{Moisture content (\% dry weight)} = \frac{(A - B)}{B} \times 100$$

A = weight of sample at equilibria.

B = weight of dry sample.

A - B is very small and is subject to a large percentage error resulting from the relatively small percentage error in the values of A and B.

Each value for moisture content in Table 5 is an arithmetic mean of the results obtained from three samples treated simultaneously under the same conditions.

These values were used to obtain the sorption isotherms shown in Figs. 3-7.

Discussion

Several workers have studied the water relations of different types of dehydrated foods.[31,58-66] It has been shown from these studies that dehydrated foods exhibit S-shaped moisture sorption isotherms. Gane[58] points out that the sigmoid character is most pronounced with foods rich in starch, protein or other high molecular weight polymers, and least for foods high

TABLE 5

WATER RELATIONS OF THE MATERIALS USED.

	Moisture(g./100 g. dry solids) corresponding to % R.H.							Calculated monolayer values (g/100 g. dry solids)	
Material	12% R.H.	20% R.H.	25% R.H.	32% R.H.	40% R.H.	43% R.H.	58% R.H.	*	**
Potatoes	4.43 ± 0.07	6.15 ±0.03	6.17 ±0.12	7.85 ±0.03	8.90 ±0.01	9.15 ±0.03		6.4	5.46–9.6
H.beans	4.75 ± 0.05	6.19 ±0.06	6.05 ±0.18	7.74 ±0.04	8.82 ±0.02	9.30 ±0.07		6.1	5.37
G.beans	1.8 ± 0.03	2.91 ±0.33	3.24 ± .23	4.52 ±0.16	5.30 ±0.09	5.63 ±0.08	6.68 ±0.95	5.52	4.21
Peas	1.93 ± 0.30	2.87 ±0.09	3.45 ±0.01	4.61 ±0.11	6.12 ±0.08	6.60 ±0.15		4.39	3.64
Meat	2.48 ± 0.11	3.57 ±0.06	4.10 ±0.07	5.20 ±0.06	6.40 ±0.08	6.81 ±0.07		4.35	4.0–6.19
Onions	1.88 ±0.13	3.15 ±0.12	3.46 ±0.2	4.80 ±0.03	6.90 ±0.13	8.11 ±0.28		5.29	
Apples	1.60 ± 0.09	3.42 ±0.05	4.80 ±0.14	6.68 ±0.03	9.70 ±0.07	10.80 ± 0.11	15.60 ± .05		
Tomatoes	1.16 ± 0.04	2.34 ±0.26	3.25 ±0.01	4.44 ±0.05	6.40 ±0.06	6.97 ±0.03			
Dates	1.11 ± 0.04	2.24 ±0.03	3.39 ±0.03	4.24 ±0.07	6.86 ±0.03	7.87 ±0.04			
Carrot	1.31 ±0.003	2.62 ±0.12	3.28 ±0.07	4.85 ±0.02	6.78 ± .08	7.20 ±0.2			
Raspberries	1.41 ± 0.12	2.5 ±0.43	2.78 ±0.47	3.51 ±0.03	4.94 ±0.15	5.58 ±0.42			

* Obtained from the present work

** Obtained from other data [31]

in soluable solids. Salwin[66] illustrates four types of isotherms which he maintains cover the moisture sorption behaviour of nearly all dehydrated foods. (See Fig. 2). The first and second are typical for starchy and protein foods respectively. These are both sigmoid and of the type referred to by Brunauer as type II. The third is typical of foods rich in both sugars and constituents of high molecular weight. At low temperature (40°F.) the sigmoid character is pronounced, but at higher temperature (100°F) the curve becomes more convex toward the vapour pressure axis, except at very low vapour pressure. This is due to the solution effects of the sugars being dominant at higher temperatures. The fourth type is typical of foods with especially high sugar content and is similar to the type III of Brunauer.

Recently Giles[67] has discussed type II and type III isotherms in relation to foods. He notes that sugars show the latter type, something which is unexpected for an almost entirely polar surface, as opposed to graphite, which also gives type III water vapour isotherms.

However, he suggests that osmotic effects due to solution of sugar at the surface might be responsible for this phenomenon.

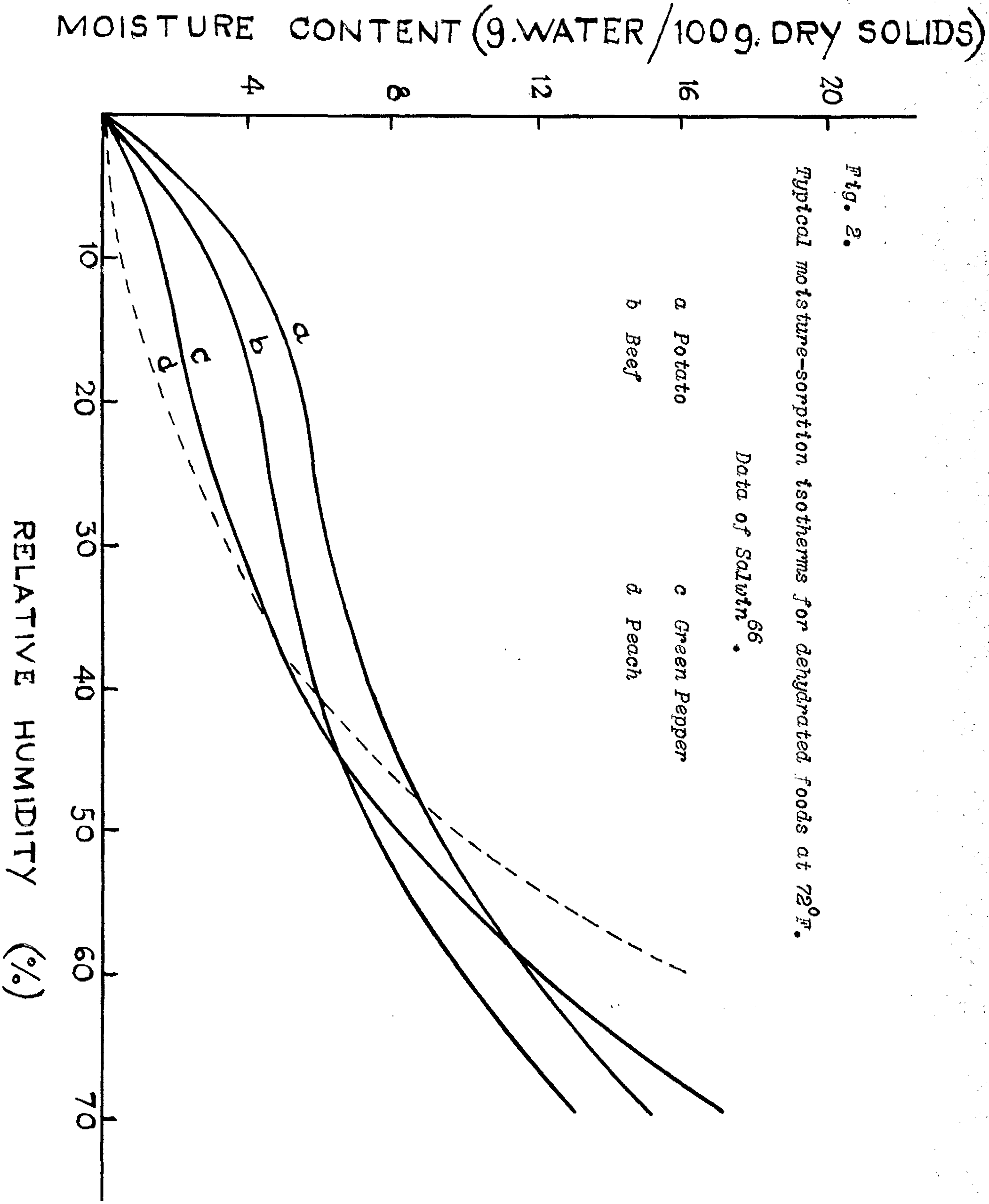


Fig. 2. Typical moisture-sorption isotherms for dehydrated foods at 72°F.

Data of Salwin[66].

a Potato

b Beef

c Green Pepper

d Peach

Figs. 3-7 show the sorption isotherms obtained for the eleven materials studied. Seven of these materials gave sorption isotherms which were concave to the vapour pressure axis at the lower vapour pressure region and would therefore be expected to show typical sigmoid curves, had points also been obtained at higher relative humidities. These are: potato, haricot bean, green bean, pea, meat, onion and raspberry. The remaining materials (carrot, tomato, apple and date) show Brunauer type III isotherms. These results are in good agreement with Salwin's[66] findings in that the first five materials showing the sigmoid isotherms are rich in high molecular weight constituents, while the remaining two are rich both in these macromolecular materials and in sugars (Table 4). The shape of the isotherms for apple and date also agree with expectations since these materials have an especially high sugar content.

The isotherms also show that starchy foods, such as potato and haricot bean, have the greatest water-holding capacity at low relative humidities, while foods rich in protein, such as meat, are intermediate in this respect between the starchy products and the remaining materials.

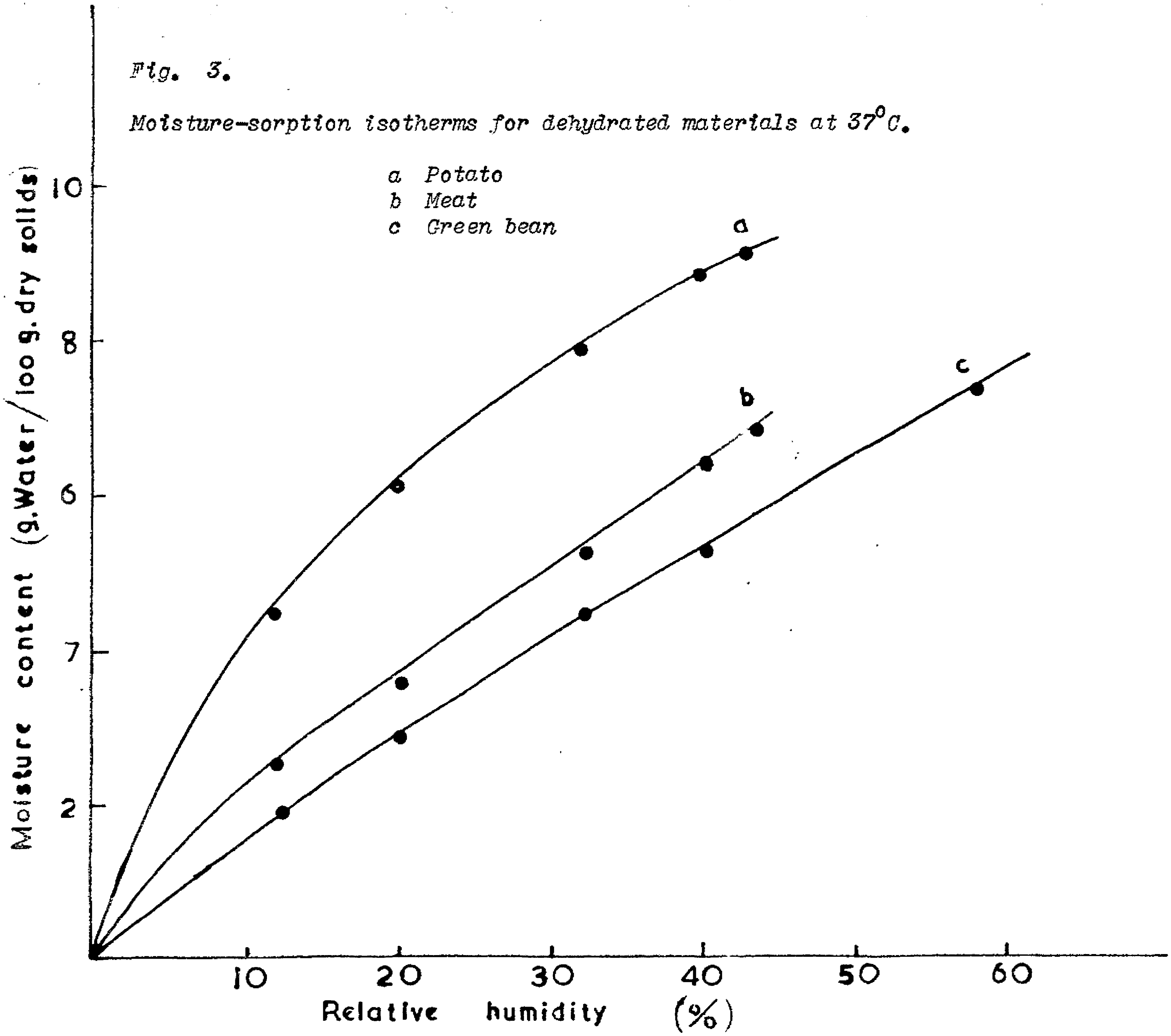


Fig. 3.

Moisture-sorption isotherms for dehydrated materials at 37°C.

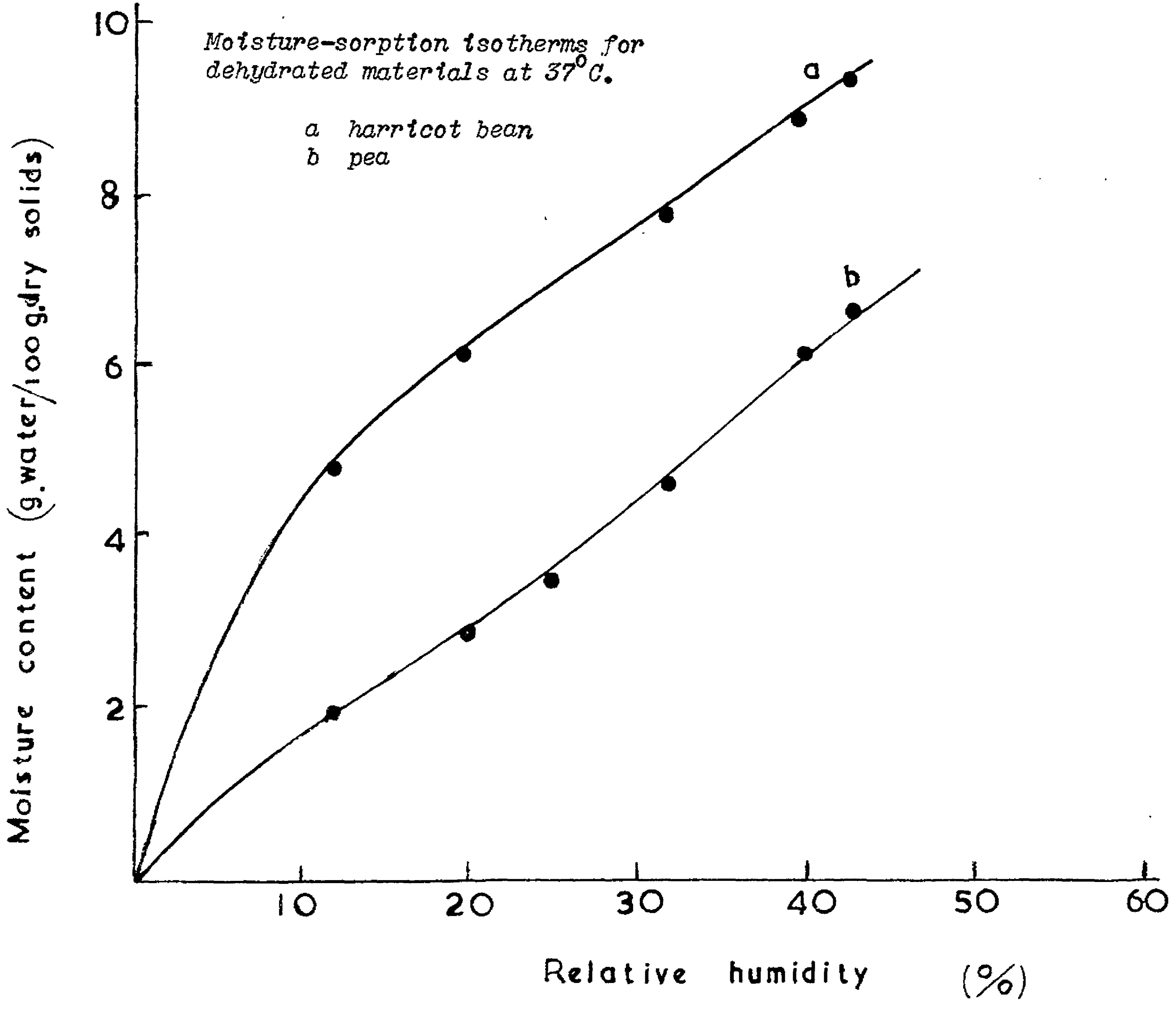


Fig. 4.

Moisture-sorption isotherms for dehydrated materials at 37^{0}C.

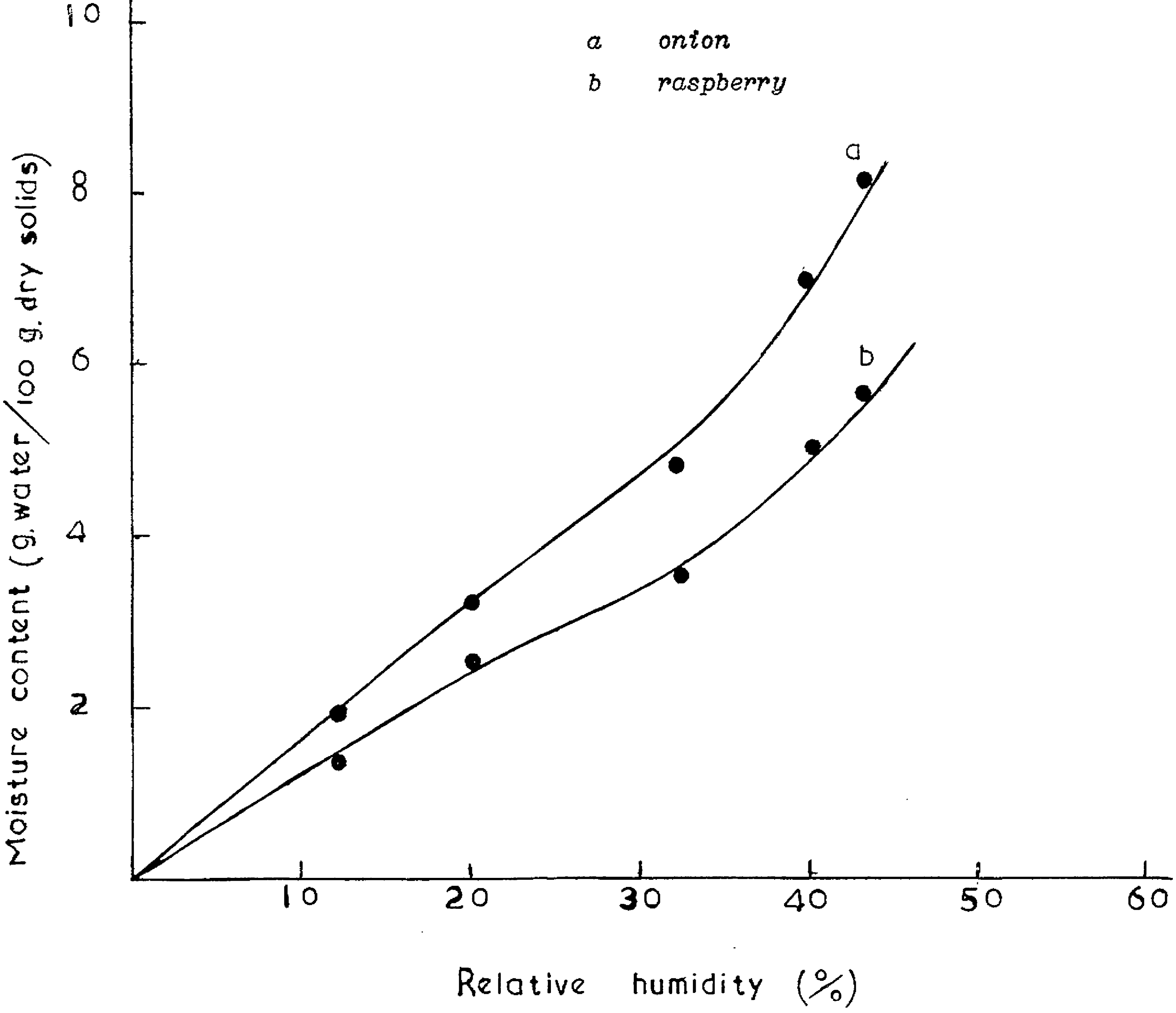


Fig. 5. Moisture-sorption isotherms for dehydrated materials at 37°C.

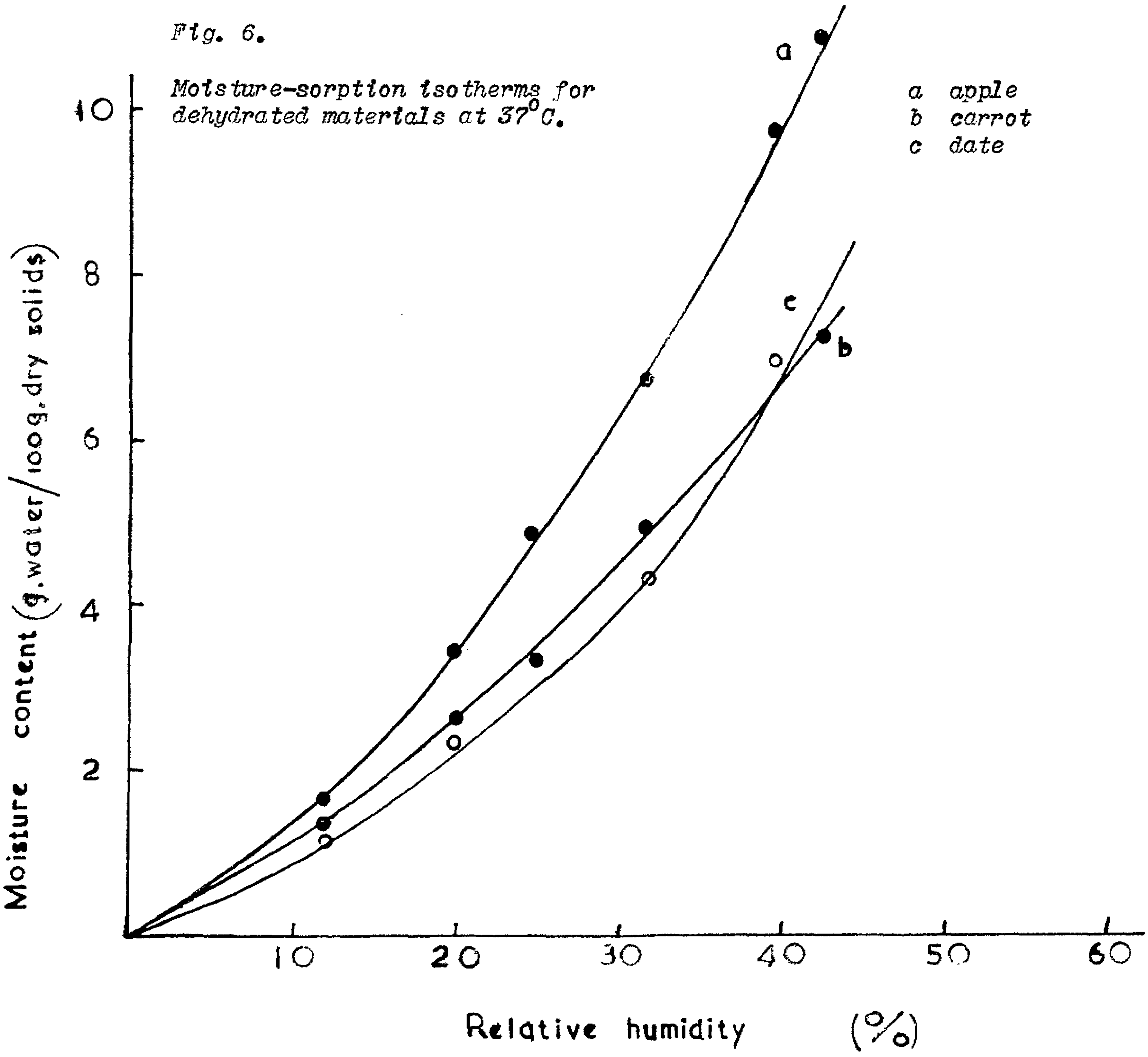
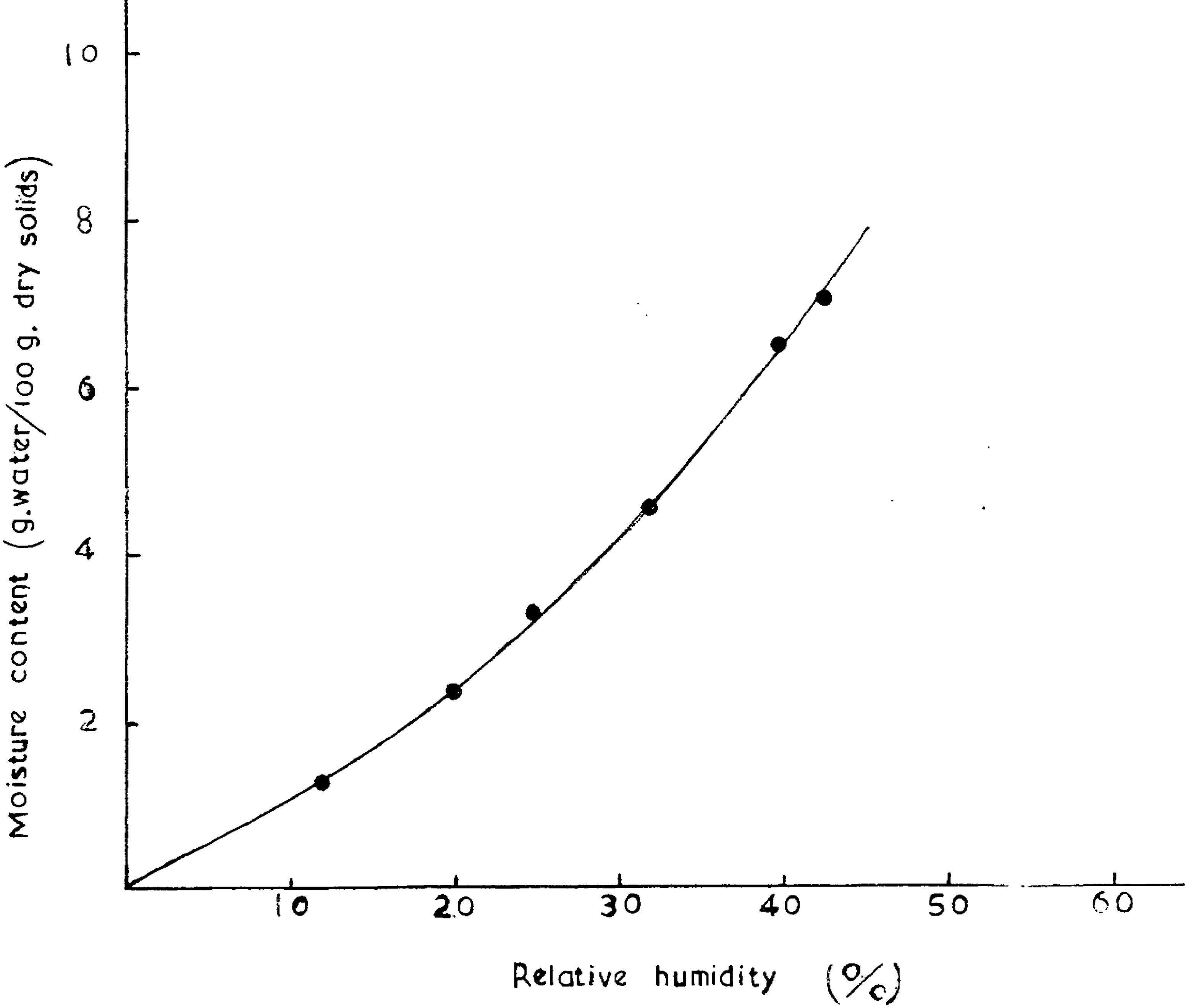


Fig. 6.

Moisture-sorption isotherms for dehydrated materials at 37°C.

Fig. 7.

Moisture-sorption isotherms for dehydrated tomato at 37°C.



Giles[68] attributes the high water-holding capacity of starch to the progressive changes in the available surface of this substance as it becomes swollen by adsorbed water. The foods with very high sugar content, on the other hand, show very low water-holding capacity at low relative humidities, the water present exerting a relatively high vapour pressure.

It is basic to the B.E.T. theory that a plot of $\frac{R}{a(100-R)}$ against R should result in a straight line for values of a and R at two points on the isotherm between 5% and 35% R.H. The values for these are plotted in this way. It will be seen that only in case of potatoes, haricot beans, green beans, peas, meat and onions, do the resulting plots approximate to a straight line (Figs. 8-10). The plots of $\frac{R}{a(100-R)}$ against R for the remaining materials, as expected from the shapes of the sorption isotherms either fail to give a straight line, or produce a line, the slope of which is the reverse of that obtained with the earlier materials.

These results support Salwin's contention that the B.E.T. theory is not applicable to foods with especially high sugar content. With regard to Salwin's intermediate group, the carrot, tomato and raspberry

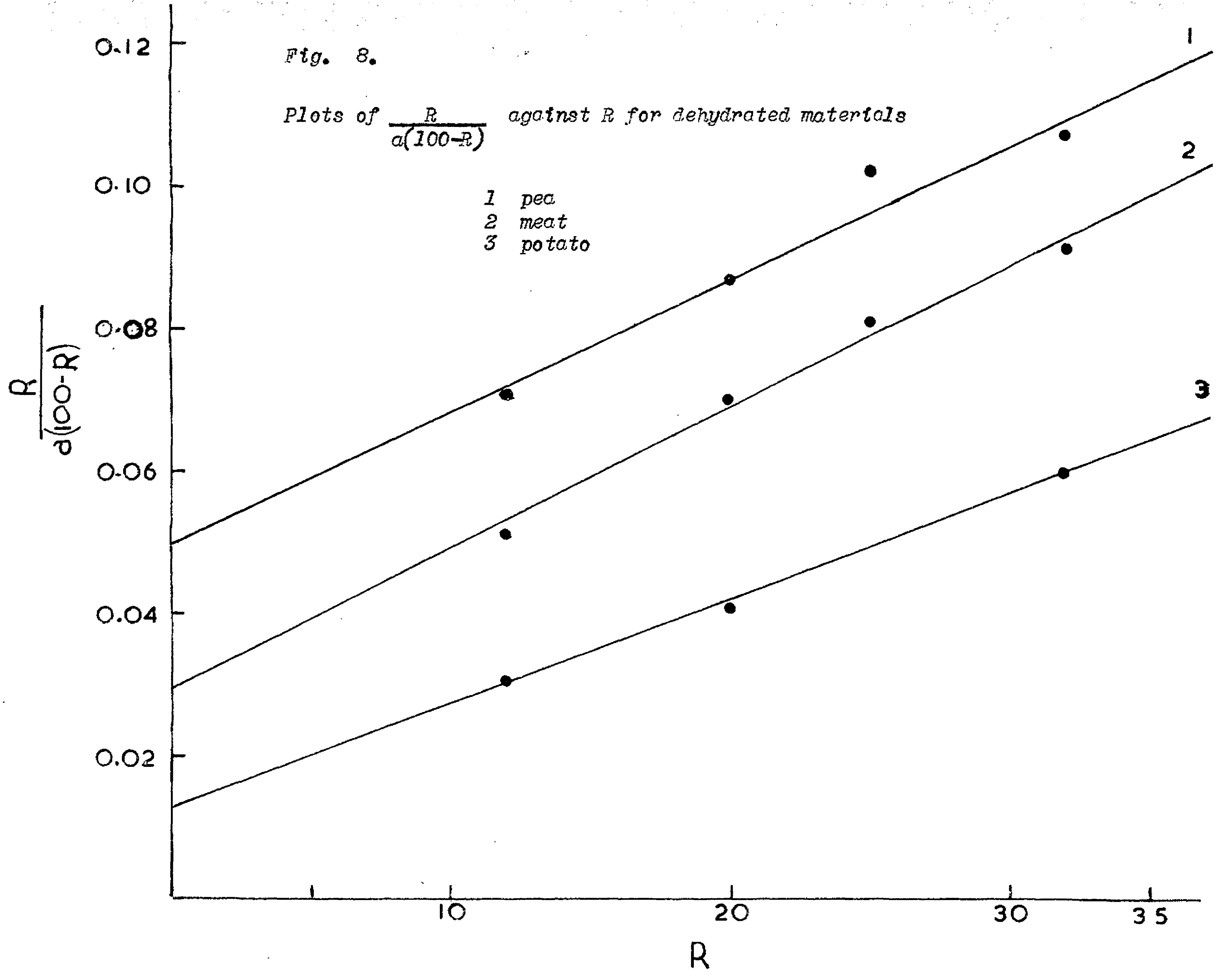
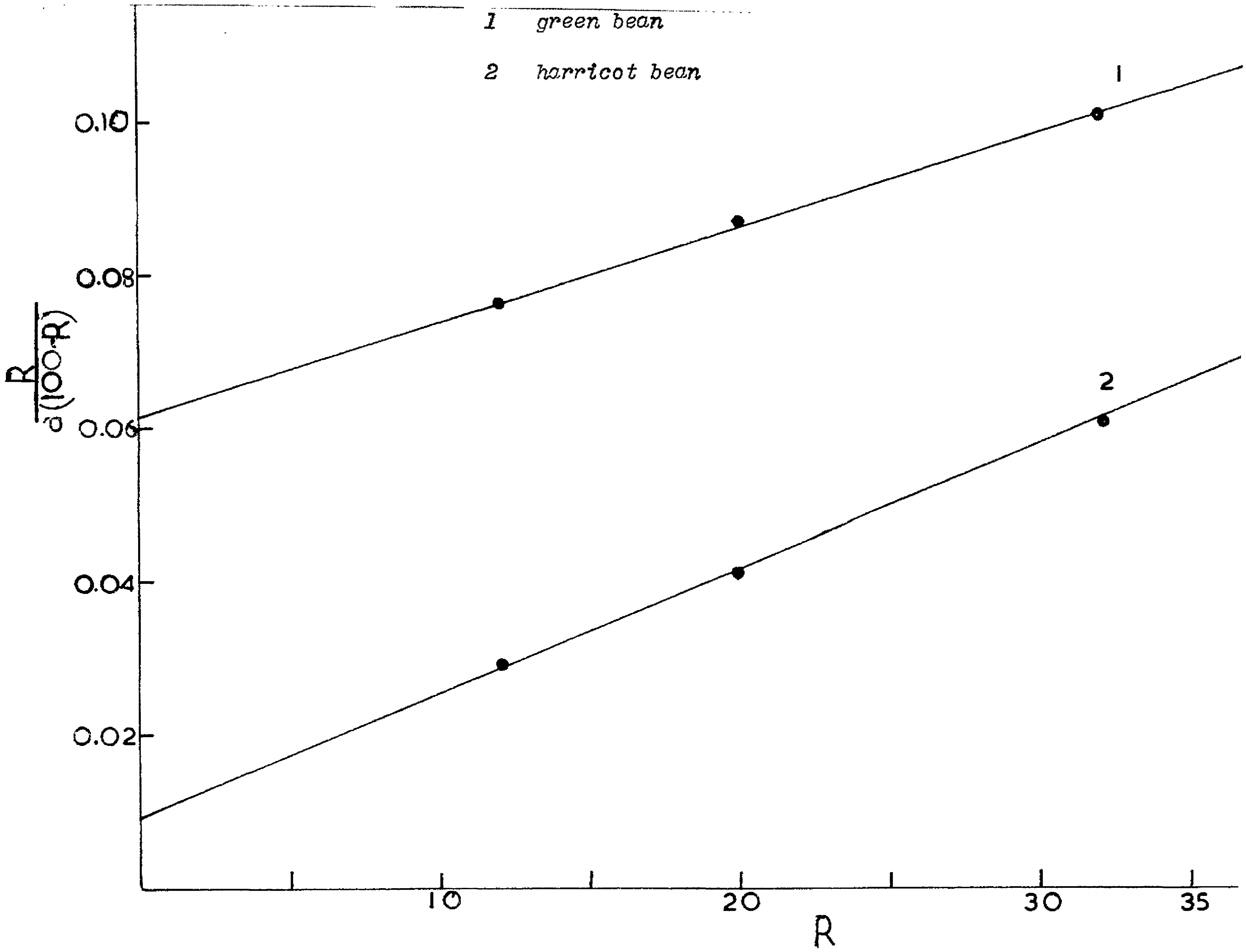


Fig. 8.

Plots of $\frac{R}{a(100-R)}$ against R for dehydrated materials


1 green bean
2 harricot bean
$\frac{R}{a(100-R)}$
0.10
0.08
0.06
0.04
0.02
10
20
30
35
R
1
2

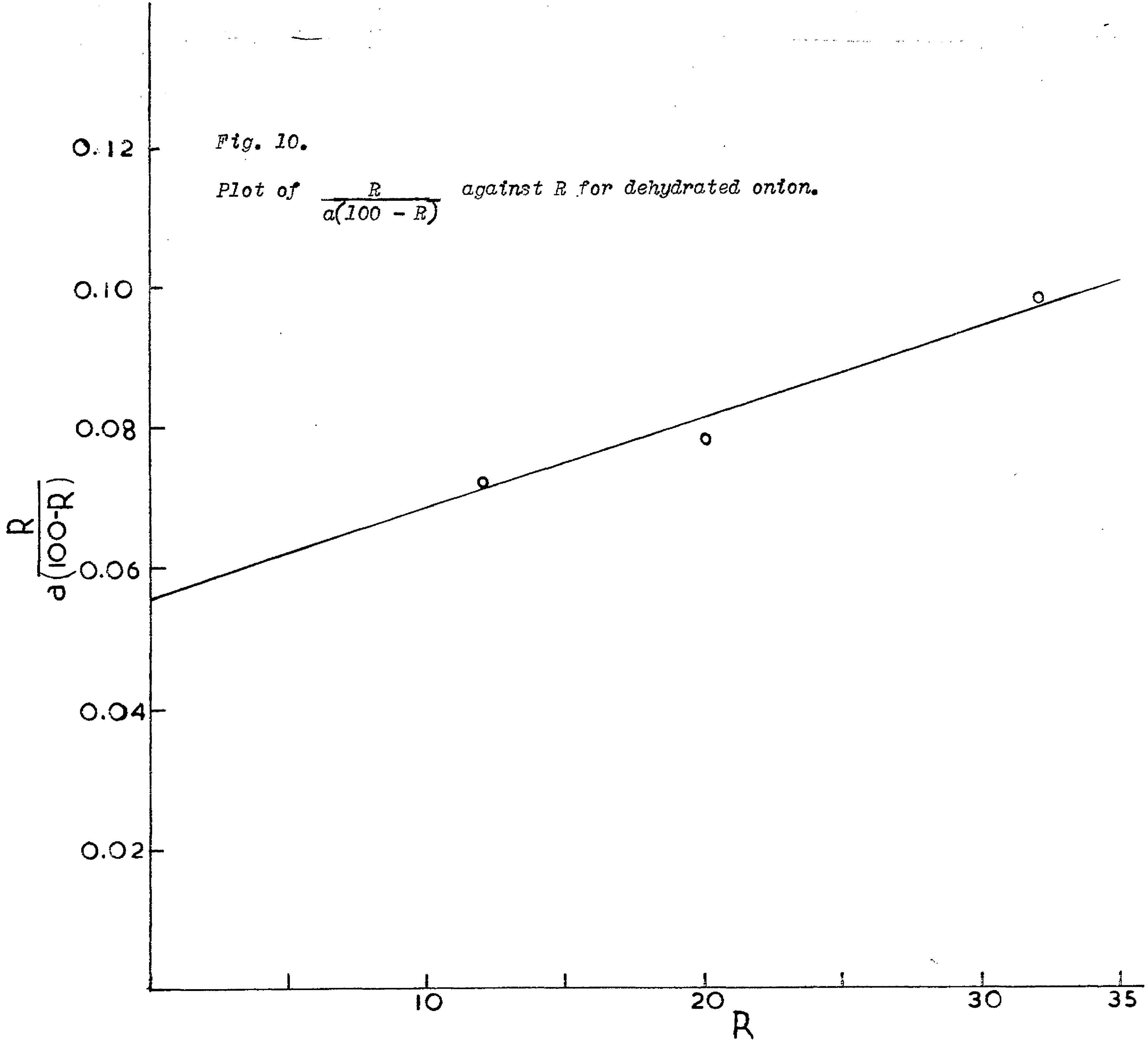


Fig. 10.

Plot of $\frac{R}{a(100 - R)}$ against R for dehydrated onion.

in this case are more similar in their behaviour to products with especially high sugar content, while onion gave a sigmoid isotherm, and a plot of $\frac{R}{a(100-R)}$ against R a reasonable straight line of normal slope.

Table 5 shows the calculated B.E.T. monolayer values for the six materials to which the equation seems to be applicable. These values are in good agreement with values obtained from the results of other workers. The differences are slight and may be attributed to differences in variety, pre-drying treatment, etc.

3. Diffusion experiments

Introduction

The purpose of this series of experiments was to study the diffusion of a simple water-soluable compound (carbon 14- labelled glucose) through pieces of dried material. Solute diffusion requires a continuous phase of solvent water and if such diffusion can be shown to take place, then there must be free water present in the material. It is thus possible to determine the lowest moisture content at which there is a continuous phase of solvent water, by determining whether solute diffusion can take place.

If a radioactive substance such as carbon 14-labelled glucose is applied to the surface of a dry material, migration of this substance can be studied by autoradiography which locates the distribution of the labelled compound by the blackening of an X-ray film due to the action of the emitted ionising radiation.[68]

Preparation of samples

Pieces of material were cut to convenient sizes which varied according to the nature of the individual product. These were first checked to see that their moisture contact was less than the equilibrium moisture content corresponding to a relative humidity of 12%. This was done by placing a weighed sample in the 12% R.H. chamber and examining for any gain or loss of weight.

A square, with sides of approximately 1 cm, was marked with Indian ink on each piece of material to be used. About 0.0002 ml. of a solution of carbon 14-labelled glucose (specific activity 25 μc/ml, glucose concentration 0.025%) was applied to the marked area with a small brush, and this was dried immediately under an infra-red lamp.

The prepared materials were then stored at the different relative humidities (12% - 43% R.H.) at 37°C. A control test was made by examining a number of pieces of each material to confirm that the tracer was initially sharply localised at the surface and confined to the marked area. The method by which the material was prepared for autoradiography is described in subsequent sections.

Freeze-drying[69]

After storing for a definite period, samples of each material were removed from the humidity chambers and freeze-dried, before embedding in paraffin wax. This was done to avoid diffusion taking place during the preparation and autoradiography of the material and to prevent radioactive contamination of the film. Freeze-drying was carried out in an Edwards model 10P freeze-drying unit for a period of 48 hours and under a vacuum of 0.01 mm. Hg. The unit is illustrated in Fig. 11.

Embedding and autoradiography

After the materials were freeze-dried, they were de-gassed under vacuum in molten paraffin wax (melting point 56°C.). This procedure was necessary in order to obtain satisfactory penetration of wax through the tissues so as to facilitate the subsequent preparation of the material for autoradiography. The materials and the molten wax were then poured into petri-dishes and cooled in air so as to prevent any possibility of water getting into the material. A flat surface was then cut through each specimen, at right angles to the labelled side, by means of a microtome, and the cut face applied to X-ray film for autoradiography. The specimen and film were then placed in a light-proof envelope and stored in a cool place for periods of between one and six weeks.

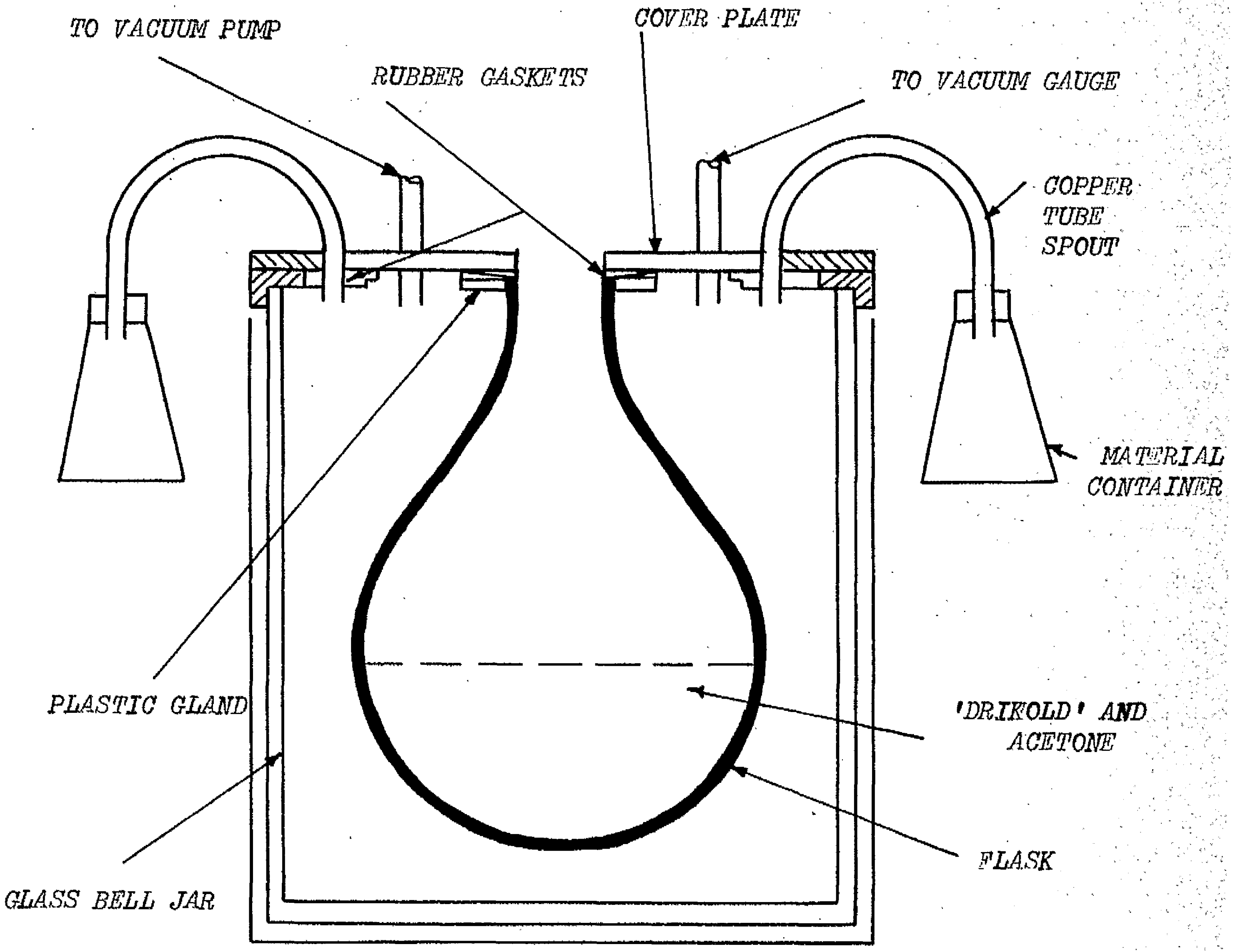


FIG. 11. A SKETCH OF EDWARDS MODEL 10 P. FREEZE - DRYING UNIT.

Development of X-ray film

The X-ray films were developed as follows:

Kodak D.19B developer	8 minutes.
2% acetic acid stop bath	1 minute.
Acid hypo fixer	30 minutes.

These treatments were carried out at room temperature (20°C), using a Kodak 6B safelight. The fixer solution was washed off the film by holding in running water for one hour, and the film was allowed to dry.

Study of the effect of molecular size on diffusion

To study the effect of molecular size on diffusion, two other series of apple pieces were set up and stored, one being treated with carbon 14- labelled urea and the other with carbon 14- labelled glucose in the manner described previously for labelled glucose.

Results

Figs. 12-55 show autoradiographs obtained for the different materials after storage for 6 months in equilibrium with relative humidities of 32%, 40% and 43% respectively. A summary of these results is given in Table 6. Extensive diffusion of a small amount of tracer is shown to occur in date at all the relative

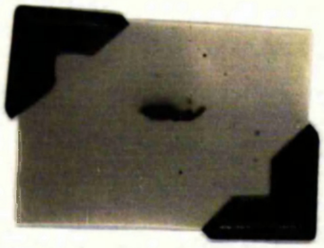
Evidence of diffusion of glucose during storage for 6 months in equilibrium with different relative humidities.

1. Potato

Fig. 12.

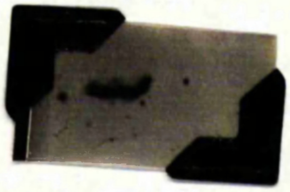
Control

Fig. 13.



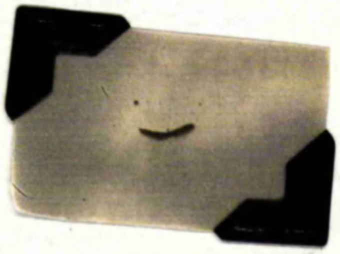
at 32%.

Fig. 14.



at 40%.

Fig. 15.



at 43%.

2. Haricot bean

Fig. 16. **Control.**

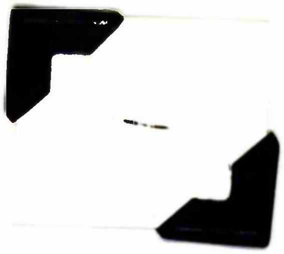


Fig. 17. **at 32%.**

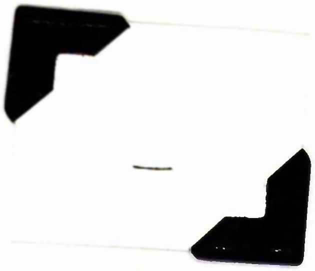


Fig. 18. **at 40%.**

Fig. 19. **at 43%.**

3. Green bean

Fig. 20. Control.

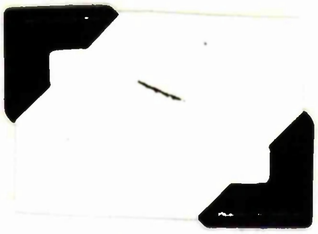


Fig. 21. at 32%.

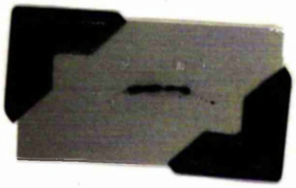
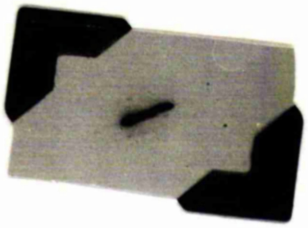


Fig. 22. at 40%.

Fig. 23. at 43%.



4. Pea

Fig. 24. **Control.**

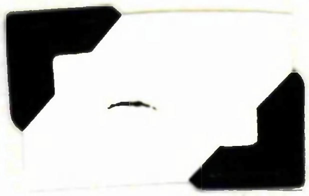


Fig. 25. **at 32%.**

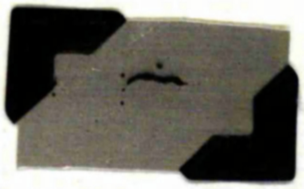
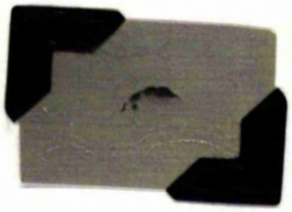


Fig. 26. **at 40%.**

Fig. 27. **at 43%.**



5. Meat

Fig. 28.

Control.

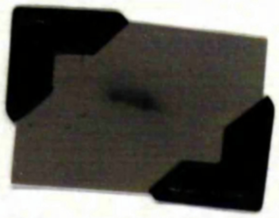
Fig. 29.

at 32%.

Fig. 30.

at 40%.

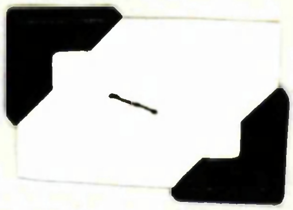
Fig. 31.



at 43%.

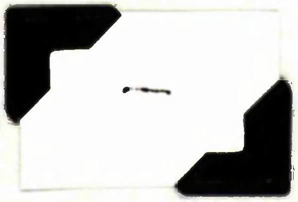
6. Onion

Fig. 32.



Control.

Fig. 33.



at 32%.

Fig. 34.

at 40%.

Fig. 35.

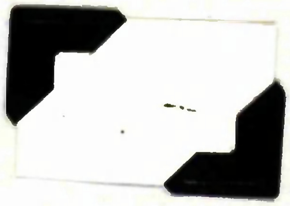
at 43%.

7. Carrot

Fig. 36.

Control.

Fig. 37.



at 32%.

Fig. 38.

at 40%.

Fig. 39.

at 43%.

8. Tomato

Fig. 40.

Control.

Fig. 41.

at 32%.

Fig. 42.

at 40%.

Fig. 43.

at 43%.

9. Raspberry

Fig. 44. **Control.**

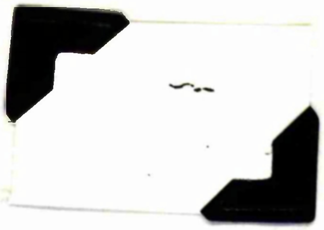
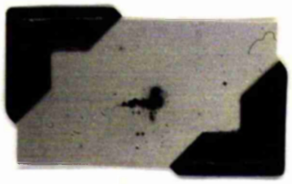


Fig. 45. **at 32%.**

Fig. 46. **at 40%.**

Fig. 47. **at 43%.**

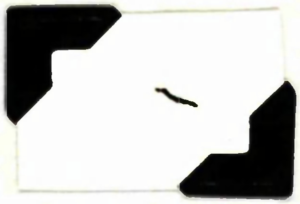


10. Apple

Fig. 48.

Control

Fig. 49.

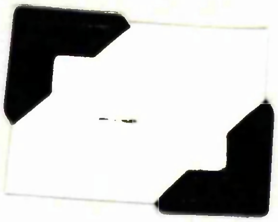


at 32%.

Fig. 50.

at 40%.

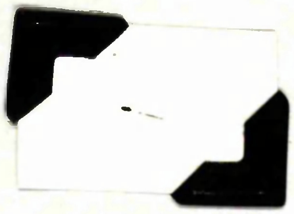
Fig. 51.



at 43%.

11. Date

Fig. 52.

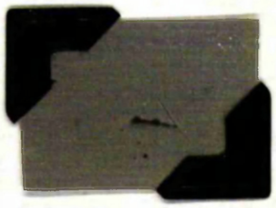


Control.

Fig. 53.

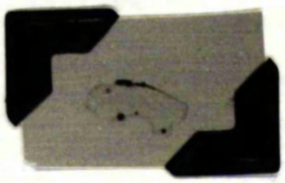
at 32%.

Fig. 54.



at 40%.

Fig. 55.



at 43%.

TABLE 6

EVIDENCE OF DIFFUSION DURING STORAGE FOR 6 MONTHS IN EQUILIBRIUM WITH DIFFERENT RELATIVE HUMIDITIES

Material	Relative humidity and corresponding moisture contents					
	32%	Moisture content g.water/ 100 g dry solids	40%	Moisture content g.water/ 100 g dry solids	45%	Moisture content g.water/ 100 g dry solids
Potato	?*	7.85	?*	8.90	?*	9.15
H. bean	-ve	7.74	-ve	8.82	-ve	9.30
G. bean	?	4.52	+ve	5.50	+ve	5.63
Peas	?	4.61	+ve	6.12	+ve	6.60
Meat	?	5.20	+ve	6.40	+ve	5.81
Onion	-ve	4.80	+ve	6.90	+ve	8.11
Carrot	-ve	4.85	-ve	6.78	-ve	7.20
Tomato	-ve	4.44	-ve	6.40	-ve	6.97
Raspberry	-ve?	3.51	-ve?	4.94	-ve?	5.58
Apple	-ve	6.68	-ve	9.70	-ve	10.80
Date	+ve	4.24	+ve	6.86	+ve	7.87

* The evidence of diffusion in potato is less convincing than that for other materials for which a definitely positive result has been recorded.

humidities and in pea, meat, onion and green bean at 40% and 43% R.Hs. and the results in these cases are regarded as definitely positive. At 32% R.H., date has a moisture content of 4.24 g. water/100 g. dry solids, and at 40% R.H., pea, meat, onion and green bean have moisture contents of 6.12, 6.4, 6.9 and 5.3 g. water/100 g. dry solids respectively. Evidence of less extensive diffusion of the glucose was found in one particular specimen of meat and another of pea, stored at 32% R.H. On the other hand, any diffusion of the glucose in potato has been strictly localised and the results for this material are considered questionable even at the highest R.H. used (at this R.H. (43%) the moisture content of the material was 9.15 g. water/100 g. dry solids). In the case of haricot bean, carrot, tomato and apple, definitely negative results were obtained at all the relative humidities used (at 43% R.H. the moisture contents of these materials were 9.3, 7.2, 6.97, and 10.8 g. water/100 g. dry solids respectively. (In apple, negative results were also obtained at an even higher moisture content - see later.) In raspberry only isolated spots of activity, which are not regarded as valid evidence of diffusion of the tracer during storage, could be detected. This material was unusually brittle in the dry state and the presence of these spots on the autoradiographic film is probably due in this case to the transfer of small active particles from the located surface across the face of the block during the preparation of the material for autoradiography. This material is therefore considered as showing a negative result even at the highest moisture content of 5.58 g. water/100 g. dry solids.

Results of the experiment carried out to study the effect of molecular size on diffusion in apple, are shown in Figs. 56-69 and are summarised in Table 7. These show that while diffusion of urea (molecular weight = 60) was found to occur at a moisture content of 10.8 g. water/100 g. dry solids during storage for one month, no evidence of diffusion has been obtained in the case of glucose (molecular weight = 180) at a moisture content as high as 16 g. water/100 g. dry solids during four months of storage.

Evidence of diffusion of labelled glucose and urea in apple during storage in equilibrium with different relative humidities.

1. Diffusion of glucose during storage for 4 months.

Fig. 56. Control.

Fig. 57. at 32%.

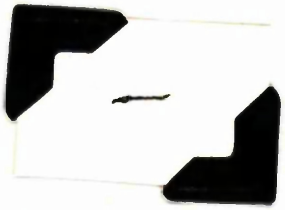


Fig. 58. at 40%.

Fig. 59. at 43%.

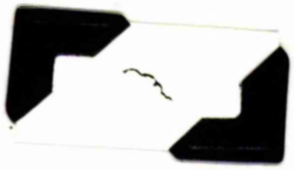
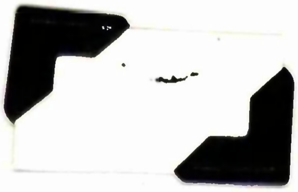


Fig. 60. at 58%.

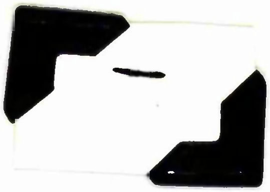


2. Diffusion of urea during storage for 1 month.

Fig. 61.

Control.

Fig. 62.

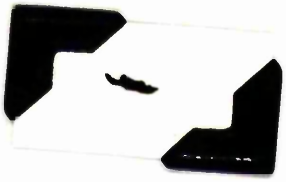


at 32%.

Fig. 63.

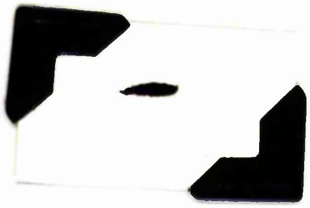
at 40%.

Fig. 64.



at 43%.

Fig. 65.



at 58%.

3. Diffusion of urea during storage for 4 months.

Fig. 66. **at 32%.**

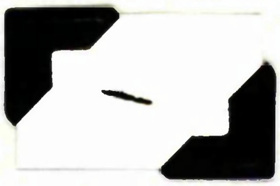


Fig. 67. **at 40%.**

Fig. 68. **at 43%.**

Fig. 69. **at 58%.**

TABLE 7

EVIDENCE OF DIFFUSION OF LABELLED GLUCOSE AND UREA IN APPLE DURING STORAGE FOR 4 MONTHS IN EQUILIBRIUM WITH DIFFERENT RELATIVE HUMIDITIES

Solute	Relative humidity and corresponding moisture content							
	32%	Moisture content g.water/ 100 g. dry solids	40%	Moisture content g.water/ 100 g. dry solids	43%	Moisture content g.water/ 100 g. dry solids	58%	Moisture content g.water/ 100g. dry solids
Carbon 14 - labelled glucose	-ve	6.68	-ve	9.70	-ve	10.80	-ve	15.60
Carbon 14-labelled urea	-ve		-ve		+ve		+ve	

4. Discussion

Previous work has indicated that in some materials which show sigmoid water sorption isotherms (in particular potato and fish), an apparently close relationship exists between the calculated monolayer value and the level of moisture which is limiting for solute diffusion. In other words these earlier results suggest that water in excess of the first adsorbed layer is relatively free of restrictive forces and is capable of facilitating the movement of simple soluable constituents. The primary object of the present experiments was to examine, by extending these investigations to a wider range of materials and solutes, whether this proposed relationship has any general and fundamental significance in regard to the condition of water in dehydrated foods.

The evidence described in the previous section suggests that a similar relationship does in fact exist in a number of additional materials which show isotherms of the sigmoid type. This appears to be the case, for example, with onion, pea, meat and green bean, although in the last material some migration of the tracer was found to occur at moisture contents actually lower than the calculated monolayer value. The results obtained with haricot bean do not conform to this general picture in that no evidence of diffusion of the glucose was found even at the highest moisture content used in the experiment, which at 9.3 g. water/100 g. dry solids was some 3% higher than the monolayer value. Haricot bean is, however, exceptional among the materials used in that the tissues had not been subjected to any prior heat treatment and, though it is doubtful whether the cells would be capable of complete recovery after the extra drying involved in the experimental procedure, the biological membrances would be essentially intact and relatively resistant to the passage of dissolved materials. A disturbing feature of the results in the present case is the doubtful nature of the evidence for diffusion of glucose in potato - the material most exhaustively studied in previous investigations - at moisture contents between 7.85 and 9.15 g. water/100 g. dry solids, the latter being some 2.5% higher than the calculated monolayer value. Although the rate of diffusion of glucose in potato tissue was also found in earlier work to be relatively slow compared with that in other tissues - this has been attributed to the relatively high content of dense homogeneous starch gel - the present results are not in agreement with those of earlier work in which a more extensive movement of the traces was demostrated within this range of moisture content during even shorter periods of storage. No satisfactory explanation of this apparent discrepancy can be offered at the present time.

The results of the diffusion experiments using materials which gave isotherms of the Brunauer type III (non-sigmoid isotherms, showing no clear distinction between the first adsorbed and later adsorbed water) were entirely negative except in the case of date, in which a positive result was obtained at each of the moisture levels tested - down to 4.24 g. water/100 g. dry solids. This latter value is the lowest moisture content at which glucose has been found to diffuse in any of the materials so far examined. Dates differ from the other members of this group (apple, carrot and tomato) in their unusually high level of invert sugar (determination of the proportion of invert sugar to sucrose in date gave a value of 15 parts of invert sugar to 1 part of sucrose) and in the absence of any other explanation for this exceptional result in the diffusion experiments, it may be that the condition of the water of hydration is influenced by this compositional difference in such a way as to facilitate the diffusion of the glucose.

The experiments in which carbon 14- labelled urea was used as a test solute have yielded evidence that it is not only the condition of the water in the material which determines the limiting moisture content at which diffusion can occur, but that the latter may also vary with the molecular size of the solute. The smaller molecules of urea diffused extensively in apple tissue at moisture contents at which movement of glucose appeared to be completely inhibited. This raises the question as to whether the structure of the solid skeleton of the material may not act as a molecular sieve. In this case, the ability of a particular solute to diffuse through the material, though still dependent on the presence of solvent water, would also be controlled by the dimensions of the spaces between the macromolecules, one effect of increasing the moisture content being to increase the size of the latter so as to allow the passage of larger and larger solute particles. Unfortunately, these tests with urea were limited to a single food material, but the results clearly show that the relationships between the degree of hydration of a material and the mobility of its various soluable constituents are more complex than has been suggested by the results of earlier work using a single test solute. This effect of the molecular size of the solute obviously requires more thorough investigation using a representative range of food materials and only then will it be possible to establish more clearly the relationships which exist between the degree of hydration, the effect of the latter on the sub-microscopic structure of the solid skeleton of the material and the ability of solutes to migrate and interact in these dehydrated biological systems.

PART II

VARIOUS EFFECTS OF THE PRE-DRYING TREATMENT OF DEHYDRATED MATERIALS WITH 'LIQUID GLUCOSE'.

Materials

1. The food materials - carrot, apple and onion - used in this part of the work were obtained in the fresh condition from local shops.

2. "Liquid glucose" of 38% dextrose equivalent. This sample was supplied by the Corn Products Company Ltd., and was made by direct acid hydrolysis of maize starch. From this sample two solutions were prepared:

    a) liquid glucose diluted with water (one part of sample to three parts of water).

    b) liquid glucose diluted with carbon 14-labelled glucose - specific activity 5 μc/ml. (one part of sample to three parts of labelled glucose).

Study of the rate of drying and hydration characteristics.

1. Preparation of food materials for drying.

After peeling and trimming as necessary, the materials were cut in a "Suzimatic Chopper" to pieces approximately $\frac{3''}{16} \times \frac{3''}{16} \times \frac{3''}{16}$. The carrot was then blanched in a steam box for a period of seven minutes. Immediately prior to drying half of each lot of prepared material was dipped for half a minute in the liquid glucose solution and subsequently drained for approximately two minutes.

2. Study of the comparative rates of drying.

Samples of approximately 10 g. of control and of liquid glucose treated materials were weighed into aluminium dishes and allowed to dry in an oven at 60°C. for periods of time normally used in commercial drying[73] (ten hours for carrots and apples and eight hours for onions). After following the course of drying during the above periods, the final moisture contents of the samples were determined by further drying in a vacuum-oven at 70°C. and under a vacuum of 25 mm.Hg. for 6 hours. Dehydration curves were obtained by plotting the moisture content of the material (g. water per g. dry solids) against the period of drying.

3. Study of the hydration characteristics.

a) Hydration curves

The treated and untreated materials were dried in the same manner as the samples used for studying the rate of drying (first in the oven at 60°C., then in the vacuum-oven at 70°C.) Samples of about 1g. of the dried materials were weighed in weighing bottles and placed in a humidity chamber containing pure water. The samples were removed and weighed at various intervals during a period of 45 hours. Hydration curves were obtained by plotting moisture content (dry weight basis), against the period of rehydration.

b). Sorption isotherms

Sorption isotherms were obtained by storing material, dried in the same way as described above, at relative humidities of 20%, 32%, 40% and 43%. (See part I).

4. Results and discussion.

Results of drying and hydration experiments are given in Tables 8-10 and are illustrated graphically in Figs. 70-78. This Treatment would be expected to cause the materials to dry less rapidly with a smaller loss in volatile constituents. As may be seen from the results, the necessary drying period is not extended but the treatment with liquid glucose has the effect of reducing the initial moisture content of the materials, and the initial rate of drying is considerably greater in the untreated materials during the first four hours. During later stages of drying, however, the drying rate appears to be similar for the treated and untreated materials. The treated materials are consistently at a lower moisture content, but this difference becomes very small as drying proceeds.

The hydration curves for carrots and onions show the moisture contents of the treated materials at a particular time to be lower than those of the corresponding untreated materials. In the case of apples there is little, if any, difference in this respect. However, the results obtained for carrots and onions are in

TABLE 8

DATA USED IN THE PREPARATION OF DEHYDRATION CURVES FOR TREATED AND UNTREATED MATERIALS

	Moisture (g. per g. dry solids)					
	carrots		apples		onions	
Time (hours)	treated	untreated	treated	untreated	treated	untreated
2	0.96	1.49	1.2	1.8	1.03	1.25
4	0.087	0.09	0.19	0.2	0.068	0.07
6	0.06	0.063	0.13	0.14	0.058	0.061
8	0.046	0.049	0.122	0.125	0.051	0.052
10	0.036	0.039	0.110	0.113		

TABLE 9

DATA USED IN THE PREPARATION OF HYDRATION CURVES FOR TREATED AND UNTREATED MATERIALS

Time (hours)	Moisture (g. per 100 g. dry solids)					
	carrots		apples		onions	
	treated	untreated	treated	untreated	treated	untreated
2	3.8	4.06	4.57	4.7	3.55	5.26
4	6.65	7.56	8.46	8.4	6.64	9.2
21	24.9	26.3	30.25	31.3	25.8	32.1
27	29.5	33.65	35.47	36.34	30.15	36.5
45	40	46.6	48.17	48.08	40.65	48.7

TABLE 10

DATA USED IN THE PREPARATION OF SORPTION ISOTHERMS FOR TREATED AND UNTREATED MATERIALS

R.H.%	Moisture (g. per 100 g. dry solids) corresponding to % R.H.					
	Carrots		apples		onions	
	treated	untreated	treated	untreated	treated	untreated
20	1.4	1.7	2.6	3.0	1.4	2.5
32	2.44	3.42	4.5	5.19	3.29	3.81
40	5.31	6.41	7.7	8.78	6.2	6.89
43	6.19	7.62	8.96	10.34	7.45	7.88

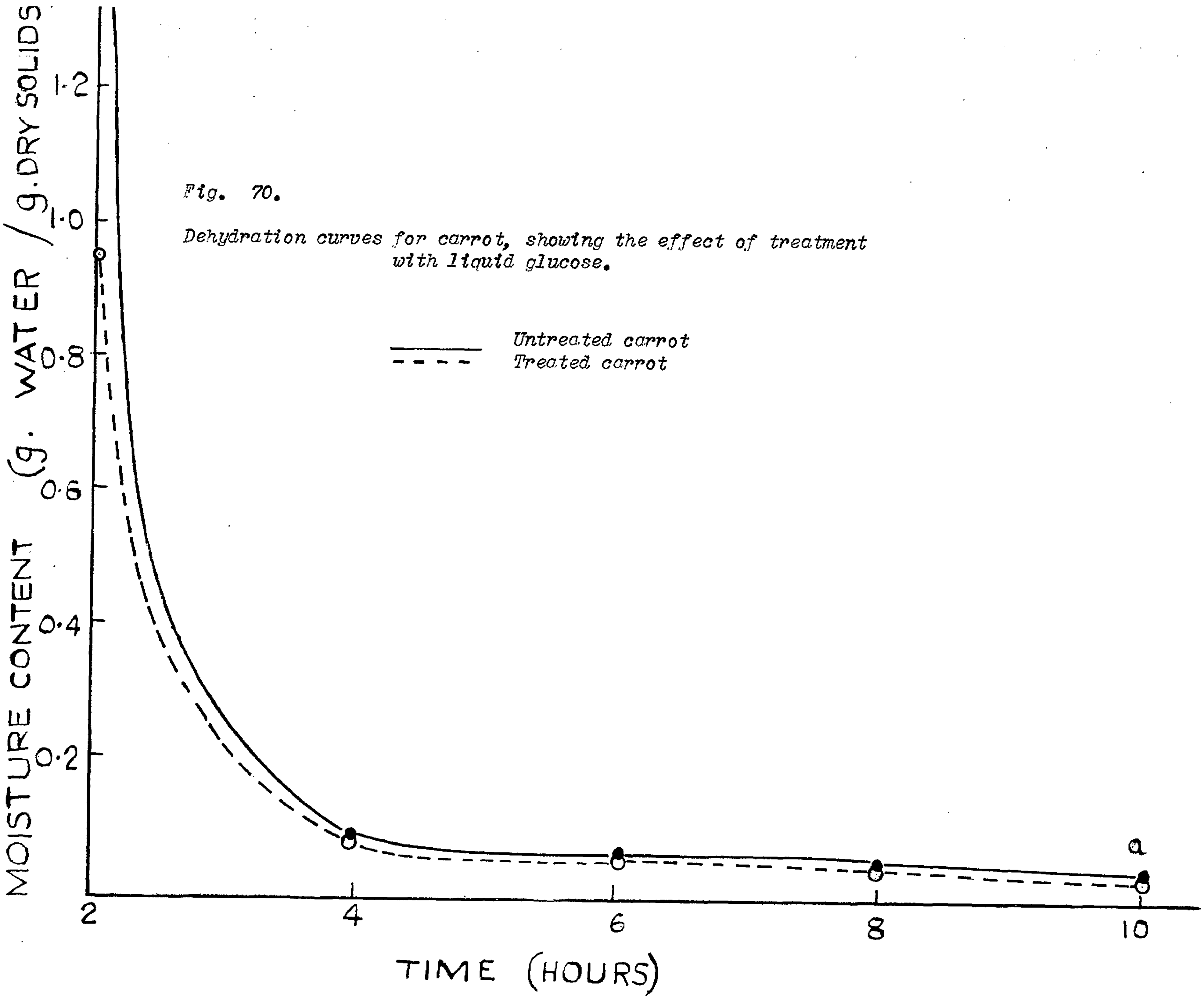
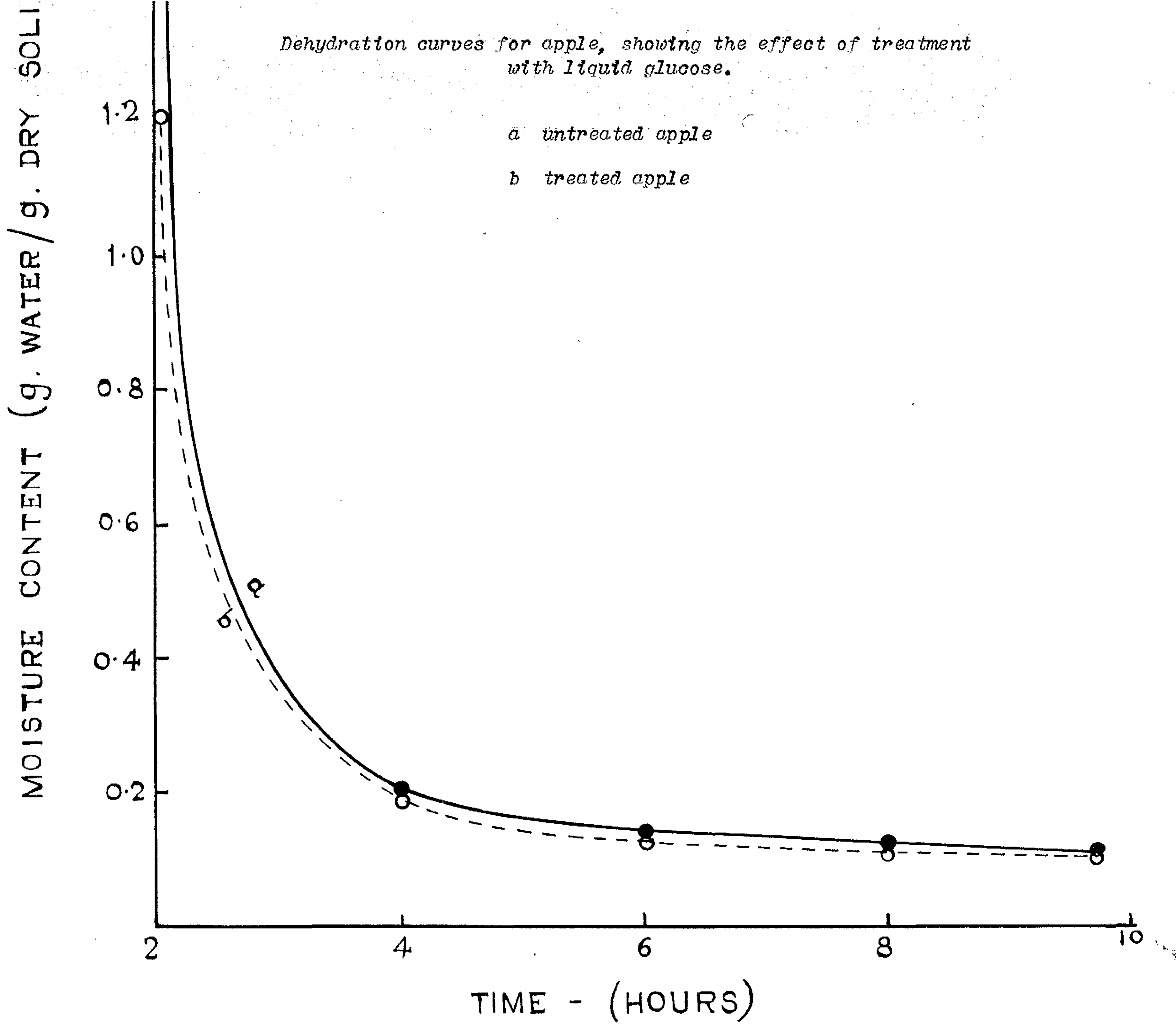


Fig. 70.

Dehydration curves for carrot, showing the effect of treatment with liquid glucose.



Dehydration curves for apple, showing the effect of treatment with liquid glucose.

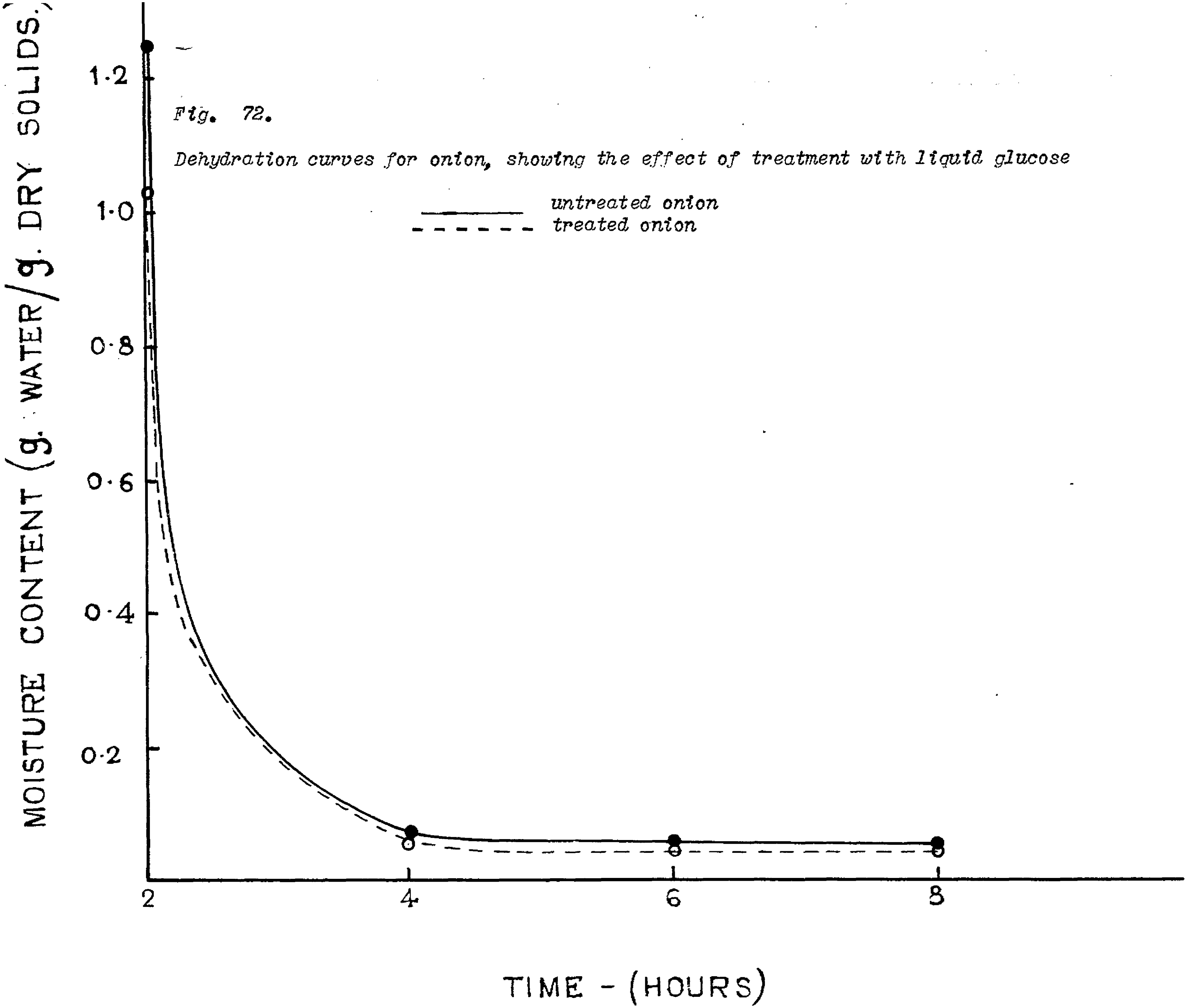
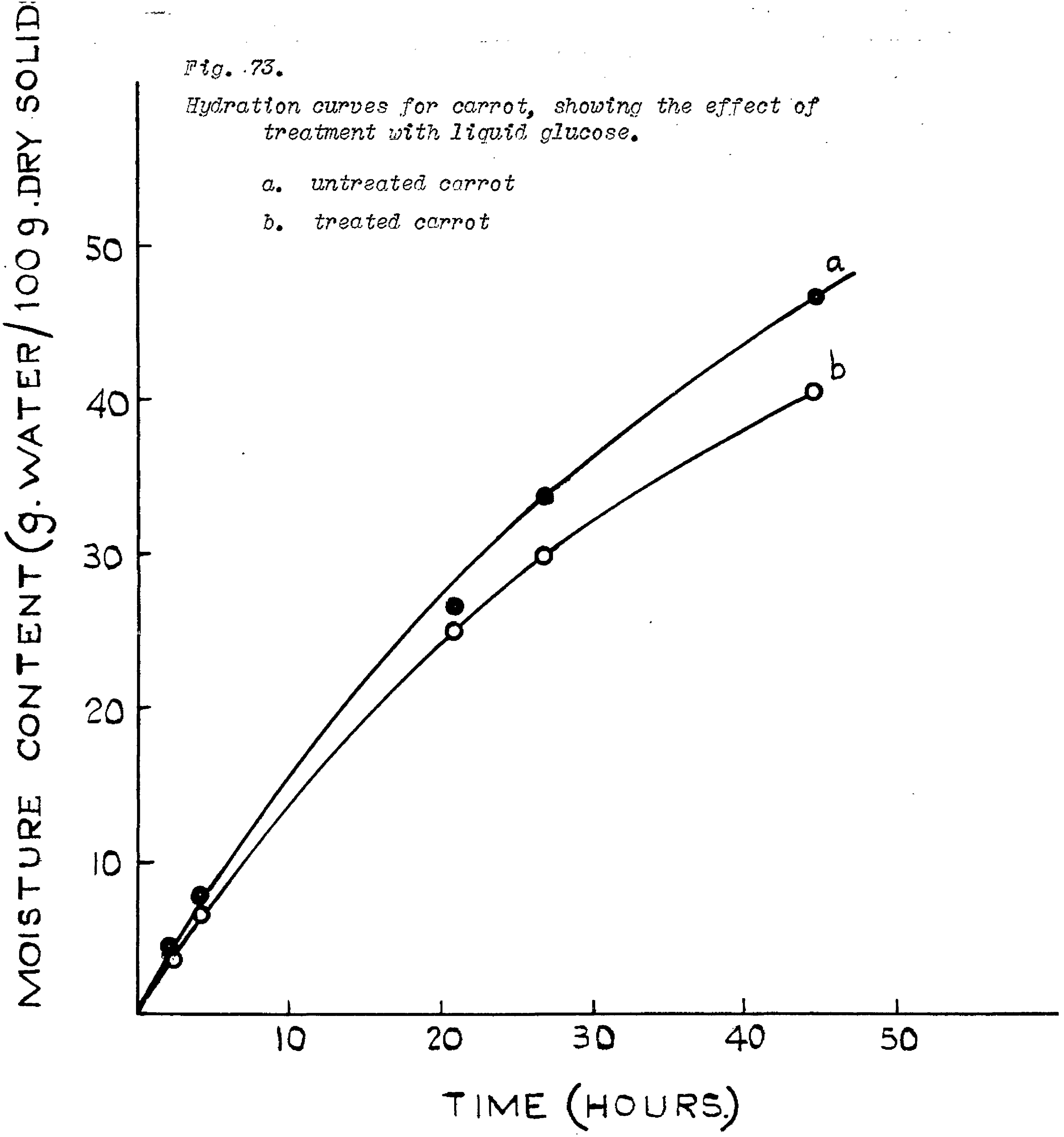


Fig. 72.

Dehydration curves for onion, showing the effect of treatment with liquid glucose

Fig. 73.

Hydration curves for carrot, showing the effect of treatment with liquid glucose.



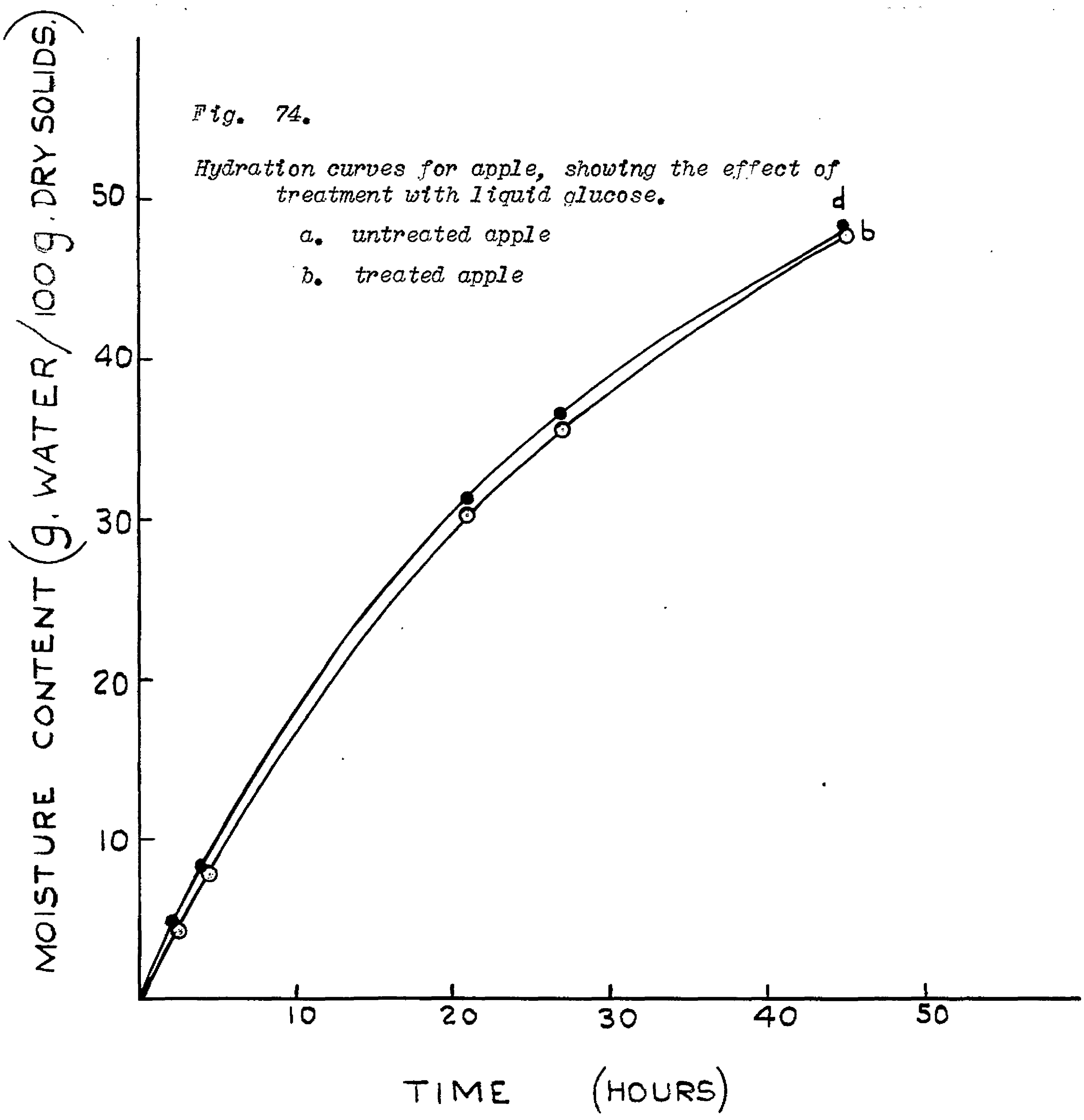


Fig. 74.

Hydration curves for apple, showing the effect of treatment with liquid glucose.

a. untreated apple

b. treated apple

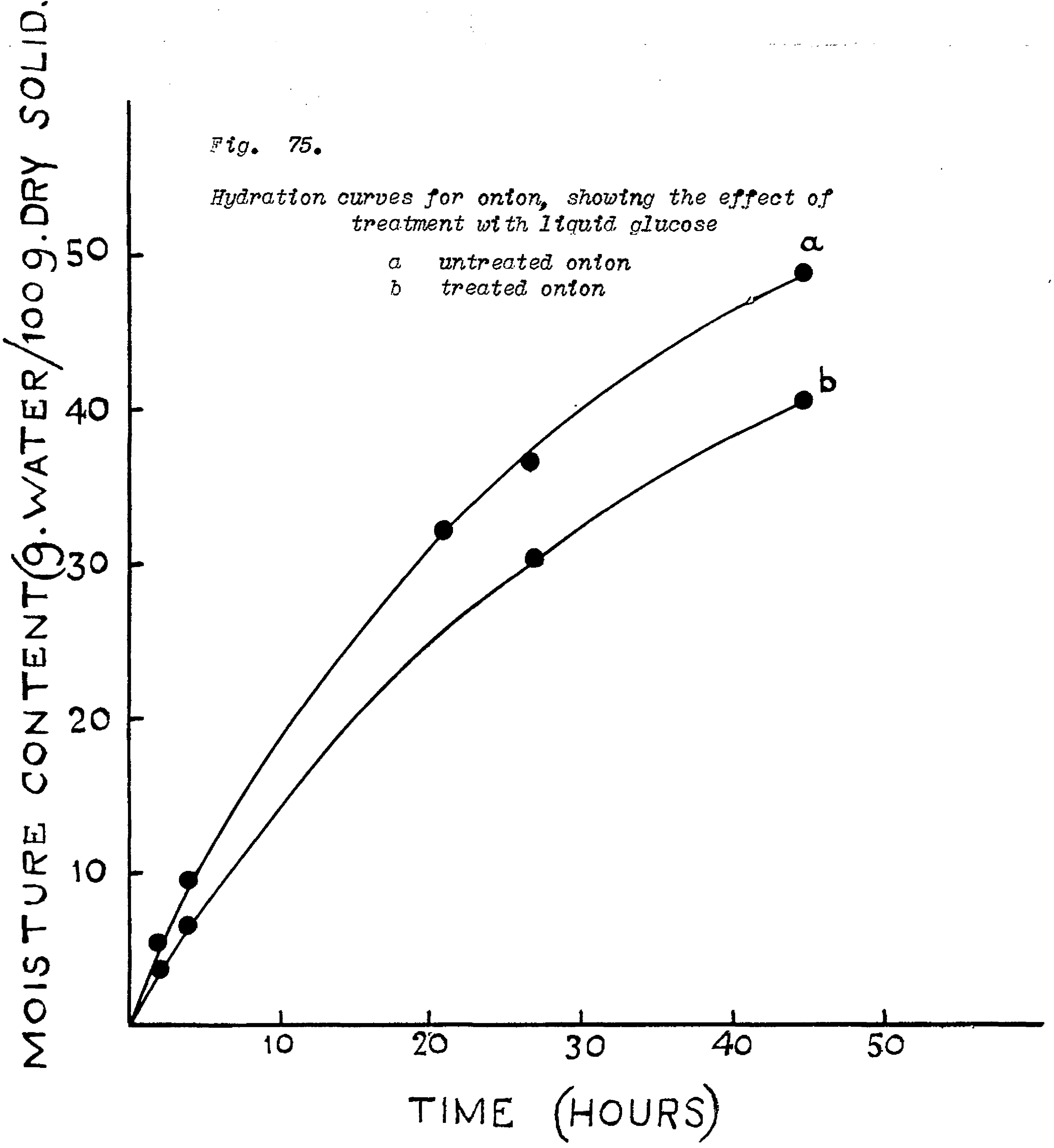


Fig. 75.

Hydration curves for onion, showing the effect of treatment with liquid glucose

a untreated onion
b treated onion

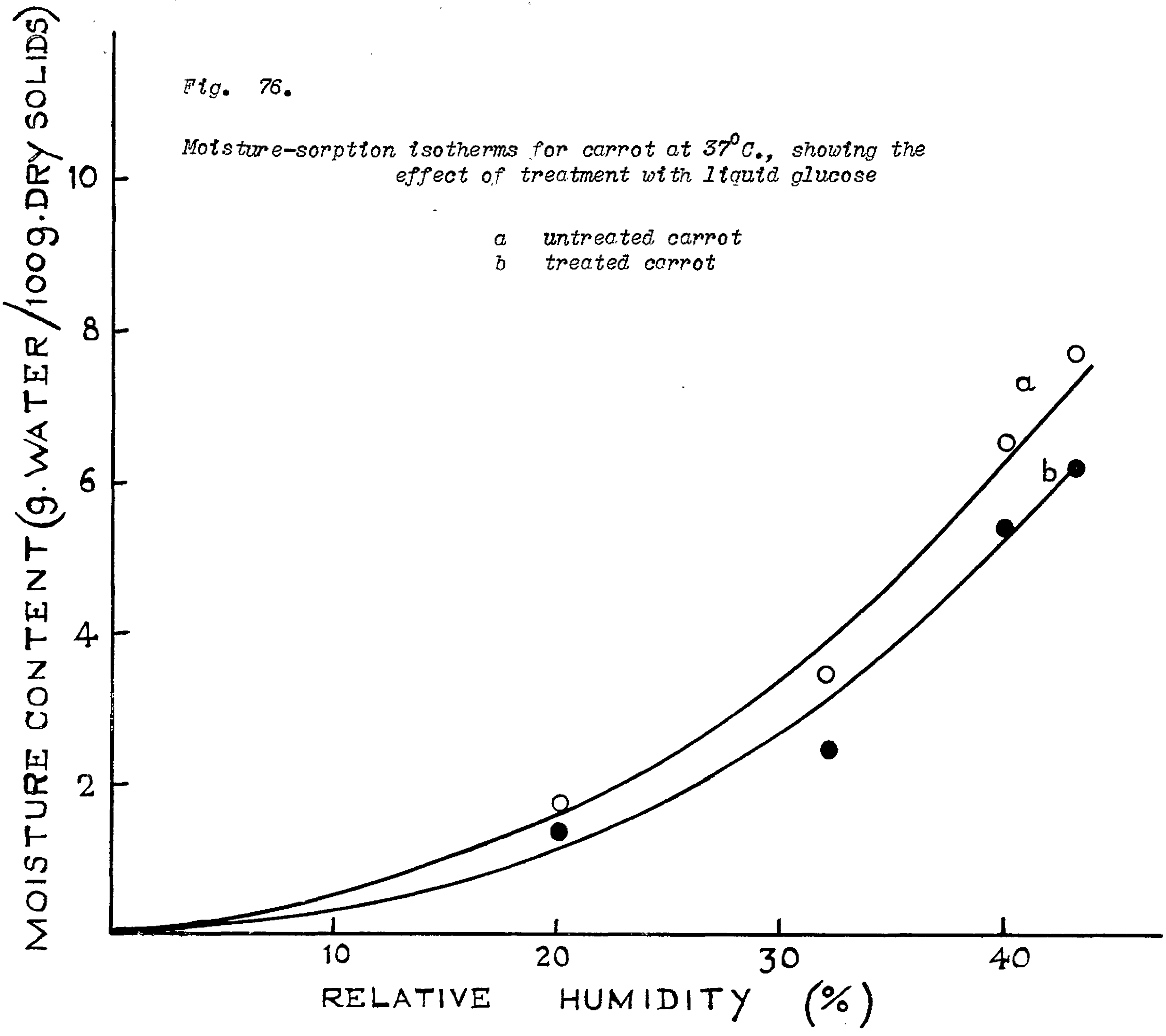


Fig. 76.

Moisture-sorption isotherms for carrot at 37°C., showing the effect of treatment with liquid glucose

a untreated carrot
b treated carrot

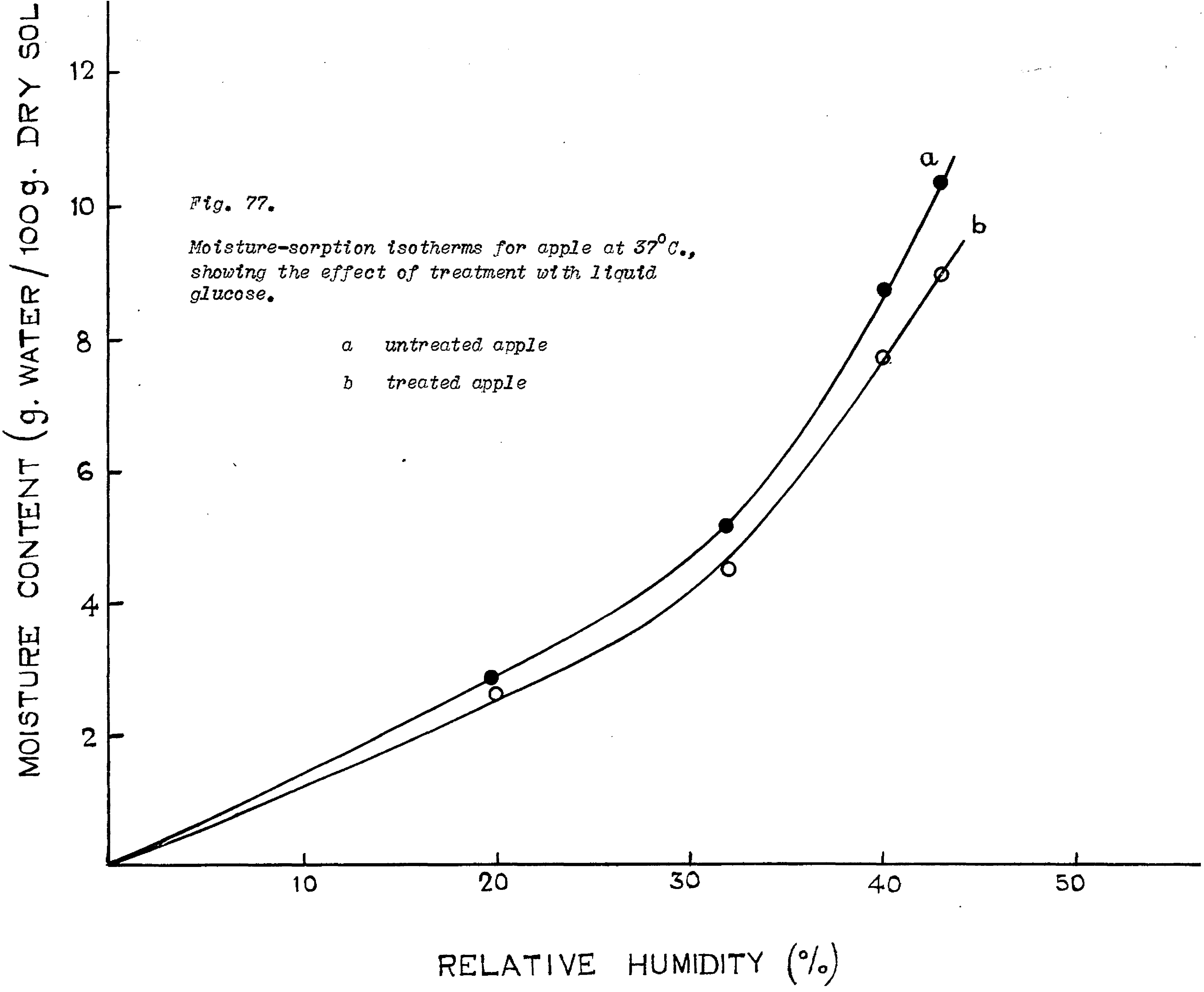


Fig. 77.

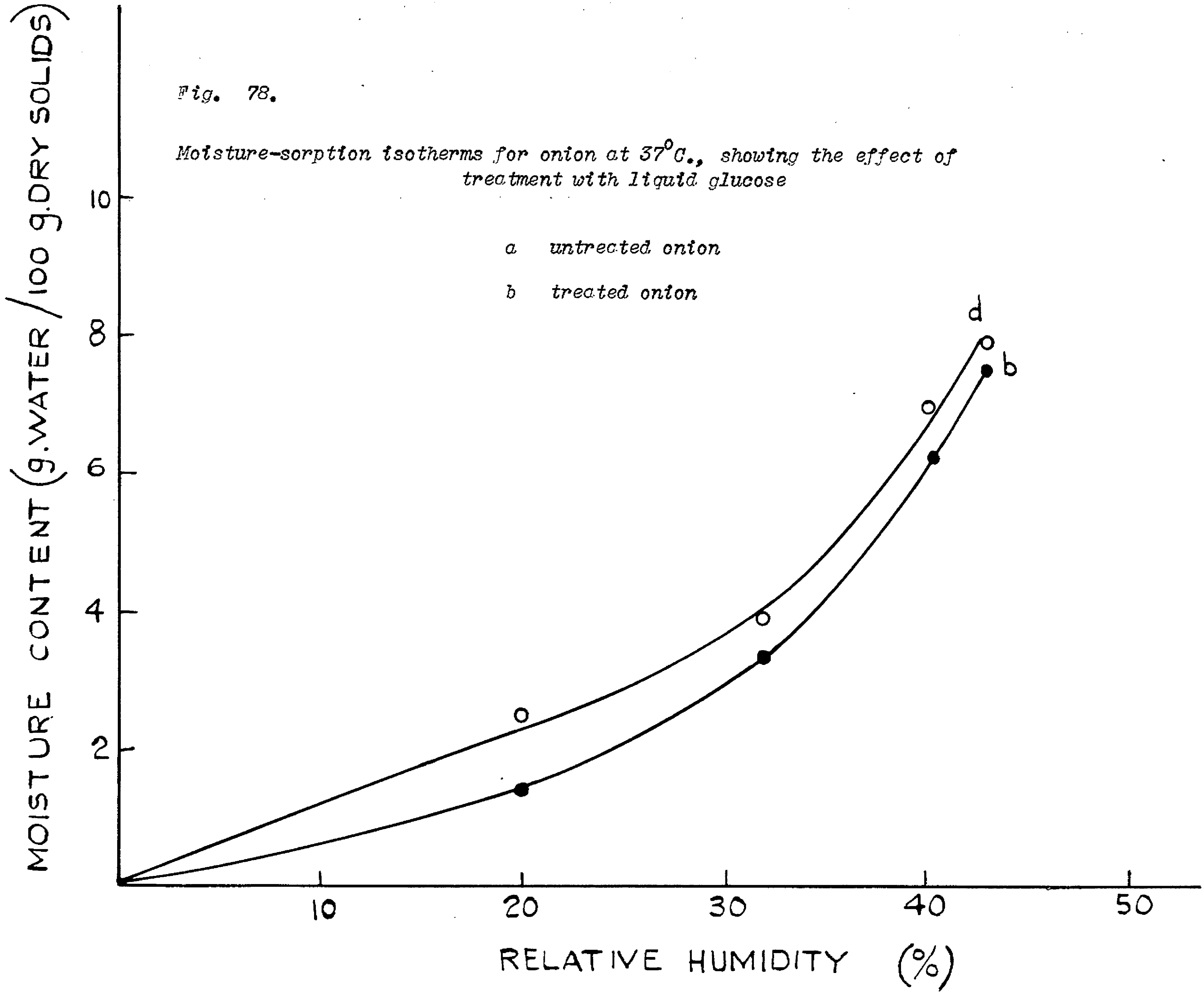
Moisture-sorption isotherms for apple at 37°C., showing the effect of treatment with liquid glucose.

a untreated apple

b treated apple

Fig. 78.

Moisture-sorption isotherms for onion at 37°C., showing the effect of treatment with liquid glucose



general agreement with earlier results (part I) in that they indicate that an increase in sugar content results in a lower water-holding capacity during the earlier stages of hydration.

The results of the sorption experiments show that the treated materials contain less moisture than the corresponding untreated materials when in equilibrium with a particular relative humidity. Treated and untreated carrots and apples and treated onions gave Brunauer type III isotherms, while untreated onions showed a sigmoid curve. These results are in general agreement with earlier results (part I) with respect to both the shape of the sorption isotherms and the effect of sugar content on the water-holding capacity of the materials. In the case of onions, treatment with liquid glucose has the additional effect of changing the sigmoid character of the sorption isotherm into that shown by Brunauer type III isotherms.

This effect of sugar on the shape of the water sorption isotherm is interesting and indicates that natural differences in sugar content between different batches of a given type of material, such, for example, as may be found in material of different varieties, may cause appreciable differences in hydration behaviour, greater intra-specific variations probably exist in this respect in some materials than has been suggested by the published results of earlier work.

Study of the culinary quality of the dried products using a tasting panel.

Preparation of the materials for drying.

After peeling and trimming of the materials, as necessary, carrot and onion were cut in a "Zylyss Pressor" into pieces approximately 1" x ⅓" x ⅓" in size. Carrot was subsequently blanched in a steam box for seven minutes. Apple was cut into ¼" thick slices and immersed for two minutes in a solution of 0.05% sodium sulphite (sulphur dioxide inhibits both enzymic and non-enzymic browning). Half of each lot of prepared material was then dipped in the liquid glucose solution for half a minute and subsequently drained for approximately two minutes. The treated and untreated materials were then dried in an oven at 60°C. for the periods used in the earlier experiments. The dry materials were then stored in a dessicator until they were reconstituted.

Reconstitution.

To reconstitute the materials, six parts of water were added to one part of the dry material. The carrot material was soaked overnight, the onion for half an hour and the apples for five minutes. The reconstituted carrot and onion were then boiled for fifteen minutes and salted; the apple was brought to boiling and allowed to simmer for three minutes. These were then placed in an oven at 50°C. until they were served to members of a tasting panel.

Presentation to the tasting panel.

The taste panel members were selected from the staff and students in the Food Science Department of the Royal College of Science and Technology, Glasgow. Two different series of tests were carried out. In the first, a number of triangular tests was used. In each test, two samples of treated and one of untreated material were presented to the panel and the judges were asked to identify the odd sample and to comment on the differences between the odd and the other two samples. In the second, a number of paired comparison tests was carried out. In each case, one sample of treated and one of untreated material were presented and the judges were asked to describe the differences between the two samples in flavour, texture and colour.

Results

Results of the triangular and the paired comparison tests are given in Table 11 and 12. In the triangular tests all but one of the judges were able to correctly identify the odd sample with each of the materials - a highly significant result (Probability = 0.001) - indicating a clearly recognisable difference in culinary quality. The majority of judges considered the texture of the treated apple to be smoother and the colour of the treated onion to be lighter than those of the corresponding untreated materials. The majority considered the flavour of the untreated onion to be stronger than that of the treated material. In the paired comparison tests the majority considered the treated apple to be stronger in flavour and smoother in texture than the untreated. In the case of onion, the majority considered the treated material to have a smoother texture and a lighter colour than the untreated.

TABLE 11

RESULTS OF TASTING PANEL (TRIANGULAR TESTS)

	Number of judges ascribing characteristics					
Product	flavour of treated		texture of treated		colour of treated	
	Stronger than control	Weaker than control	Smoother than control	Tougher than control	Lighter than control	Darker than control.
Carrots	4	-	5	-	4	-
Apples	3	1	7	1	-	5
Onions	-	8	-	-	7	-

TABLE 12

RESULTS OF TASTING PANEL (PAIRED COMPARISON TESTS)

Product	Number of judges ascribing characteristics					
	Flavour of treated		Texture of treated		Colour of treated	
	Stronger than control	Weaker than control	Smoother than control	Tougher than control	Lighter than control	Darker than control
Carrots	2	5	4	4	4	1
Apples	8	2	6	5	5	5
Onions	5	5	7	2	8	1

Discussion

It has been said that dipping vegetable materials in liquid glucose immediately prior to drying helps to preserve the flavour of the dry product by decreasing the loss of volatile constituents. While the results of the paired comparison tests lend support to this contention with respect to apple, the triangular tests results suggest that this procedure might even adversely affect flavour as, for example, in the case of onion. Results of both the triangular and paired comparison tests suggest that this treatment has resulted in an improved texture in apple. In the case of onion, according to the results of the paired comparison tests, this treatment has resulted in an improved texture and the results of both types of tasting test suggest that the treatment produces a more satisfactory colour in the reconstituted product. In both these cases, the textural improvement due to the treatment is attributable to the surface film of dextrin which in some way facilitates the more complete rehydration of the material. According to the results of the tasting tests, treatment with liquid glucose appears not to have affected the culinary quality of dehydrated carrot.

Diffusion experiments

Procedure

The materials used for the diffusion experiments were prepared and dried in the same manner as those used for the tasting panels. The ability of carbon 14-labelled glucose to diffuse in these materials was studied using the techniques already described in Part I, using relative humidities of 32%, 40% and 43% during a storage period of six months. The results obtained with materials treated with liquid glucose were compared with those of earlier storage experiments with comparable untreated materials (see Figs. 32-39, 48-51) The ability of the liquid glucose to diffuse into the materials was also studied. In this case, instead of dipping the materials in the liquid glucose solution used earlier, the materials were dipped in a solution prepared by diluting liquid glucose with carbon 14-labelled glucose (1 part of liquid glucose to 3 parts of labelled glucose of specific activity of 5μc/ml.) and dried as before. These were then prepared for autoradiography in the same manner as that described earlier.

Results and discussion.

Figs. 79-87 show autoradiographs obtained for the treated materials. These show that no measurable diffusion of the tracer has taken place in any of these materials at any of the humidities used. Since similar results have been obtained with untreated carrot and apple, no conclusions can be drawn with regard to the effects of this treatment on the ability of the glucose to diffuse in these materials over the range of moisture content obtained. In the case of onion, while a negative result has been obtained with the treated material at a moisture content of 7.45 g. water/100 g. dry solids, diffusion of the tracer was found to occur in the untreated material at a moisture content of 6.9 g. water/100 g. dry solids. A possible explanation of this difference is that diffusion of the tracer in the treated material might have been impeded by presence of a dry film of liquid glucose on the surface of the material which has prevented contact between the tracer and the surface of the tissue itself. The presence of such a film has been demonstrated by the results of the experiment carried out to study the final distribution of the liquid glucose in the dried material. (See Figs. 88-90). Since glucose is the constituent of lowest

Diffusion of labelled glucose in materials treated with liquid glucose during storage in equilibrium with different relative humidities.

1. Carrot

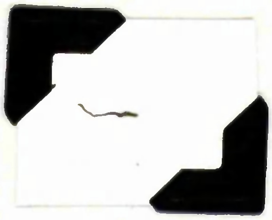


Fig. 79. at 32%.

Fig. 80. at 40%.

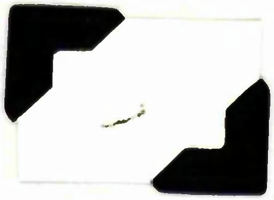


Fig. 81. at 43%.

2. Apple

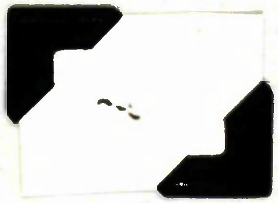
Fig. 82. at 32%.

Fig. 83. at 40%.

Fig. 84. at 43%.

3. Onion

Fig. 85.

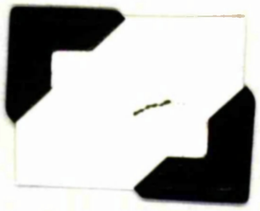


at 32%.

Fig. 86.

at 40%.

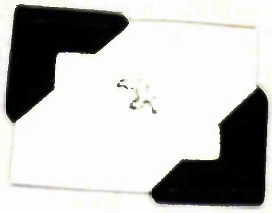
Fig. 87.



at 43%.

Evidence of diffusion of liquid glucose into the materials.

Fig. 88.



Carrot.

Fig. 89.

Apple.

Fig. 90.

Onion.

molecular weight in the liquid glucose preparation, which also contains maltose and dextrins of a wide range of molecular size, the maximum penetration of the preparation into the material is shown by the distribution of the labelled glucose. The extent of penetration even of the glucose is very limited and the bulk of the higher molecular weight materials must clearly remain as a surface film.

SUMMARY AND CONCLUSIONS

Summary and Conclusions.

1. Water sorption isotherms for potato, haricot bean, green bean, pea, meat, onion and raspberry, have been shown to be of the sigmoid type. Those for carrot, tomato, apple and date are found to be of the Brunauer type III.

2. Modified B.E.T. plots ($\frac{R}{a(100-R)}$ against R) for potato, haricot bean, green bean, pea, meat and onion have given a reasonable straight line of normal slope. Those for the remaining materials, as expected from the shapes of the isotherms, either fail to give a straight line, or produce a line, the slope of which is the reverse of that obtained with the earlier materials. These results generally support Salwin's contention that the B.E.T. theory is not applicable to foods with especially high sugar content.

3. Diffusion of labelled glucose has been shown to take place in pea, meat and onion at moisture contents little higher than the corresponding calculated monolayer values for these materials. In green bean, some migration of the tracer

was found to occur at moisture contents actually lower than the calculated value. The evidence for diffusion in potato is doubtful even at a moisture content 2.5% higher than the calculated monolayer value. In the case of haricot bean no evidence of the tracer was found at a moisture content 3% higher than the calculated monolayer value. Raspberry gave a negative result at all the moisture levels tested - up to 5.58 g. water/100 g. dry solids.

4. The results of the diffusion experiment using materials which gave isotherms of the Brunauer type III were entirely negative, except in the case of date in which a positive result was obtained at each of the moisture levels tested - down to 4.24 g. water/100 g. dry solids.

5. The experiments in which carbon 14- labelled urea was used as a test solute with apple have yielded evidence that it is not only the condition of the water in the material which determines the limiting moisture content at which diffusion can occur, but that the latter may also vary with the molecular size of the solute.

6. The drying curves for materials treated with liquid glucose and control materials show that the necessary drying period is not extended; that this treatment has the effect of reducing the initial moisture content of the materials and that the initial rate of drying is greater in the untreated materials during the first 4 hours of drying. During later stages of drying, the drying rate is shown to be similar for the treated and untreated materials. The treated materials are shown to be consistently at a lower moisture content but this difference becomes very small as drying proceeds.

7. The hydration curves for carrot and onion show the moisture content of the treated materials to be lower than those of the corresponding untreated materials. In the case of apple there is little, if any, difference in this respect.

8. The results of the sorption experiments show that the treated materials contain less moisture than the corresponding untreated materials when in equilibrium with a particular relative humidity. Treated and untreated carrot and apple and treated onion gave Brunauer type III isotherms, while untreated onion gave a sigmoid curve.

9. Results of the tasting tests agree that treatment with liquid glucose has resulted in an improved texture in apple and in an improved colour in onion. According to results of the triangular tests this treatment has adversely affected the flavour of onion and according to results of the paired comparison tests, the treatment resulted in an improved flavour in apple and an improved texture in onion.

10. Results of the diffusion experiment in treated and untreated materials show that diffusion of the tracer in the treated onion was not possible even at a moisture content about 0.5% higher than that at which diffusion of the tracer was found to occur in the untreated material. This has been attributed to the presence of a dry film of liquid glucose in the untreated material. Results of the experiments carried out to study the ability of the liquid glucose to diffuse into the material show that such a surface film is indeed present.

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