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Soil, Organic Constituents of - Zymurgy

With an index by M. Le Pla, B.Sc.,
J. G. Cockburn, M.Sc., Ph.D., and J. Bird

WITH ILLUSTRATIONS

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FOREWORD

THIS Volume completes the text of the Fourth Edition ; it will be followed shortly by a final Index Volume providing a consolidated index to the whole Edition.

A number of articles in this Volume were planned for earlier publication and have unavoidably been held over on account of editorial and production difficulties ; it is due to our contributors that this fact should be stated.

We record with particular regret the untimely death of Miss Margaret Le Pla, who prepared much of the material for the index to this Volume and for the forthcoming general index. The thanks of the Board are due to Dr. J. G. Cockburn and Mr. J. Bird, of the Chemical Society, who at quite short notice have completed the work begun by Miss Le Pla.

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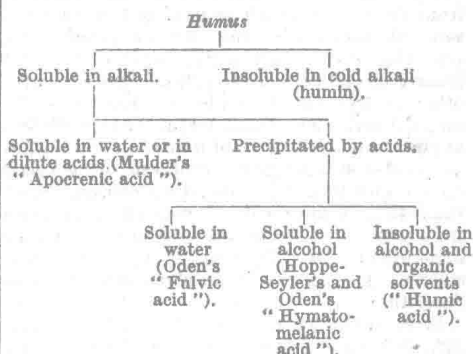
SOIL, MINERALOGY OF (v. Vol. VIII, 150 c.)

SOIL, ORGANIC CONSTITUENTS OF. The organic matter of soil is primarily derived from the decomposition products of plants and from the products of autolysis of the vast microbiological population which develop at the expense of substances of plant origin. A dynamic equilibrium exists in the soil between the immense number of bacteria, protozoa, yeasts, fungi, etc., that inhabit the soil and the organic matter continually being supplied by the decaying animal and vegetable tissues. This equilibrium is such that the ratio of carbon to nitrogen in soil organic matter keeps remarkably constant, *i.e.*, about 10. Autotrophic bacteria which gain their sustenance from atmospheric carbon dioxide and the nitrogen fixers, such as *Azotobacter*, play a fundamental part in withdrawing carbon dioxide and nitrogen from the air into the organic matter of soil.

Soil, therefore, normally contains a whole range of substances commonly classed as metabolites of animal and plant tissues. The speed of change of these substances may be very great, the rate depending on the temperature, hydrogen concentration, aeration, water availability, and mineral content of soil. A number of substances, derived from animal, plant, or microbiological life, are, however, relatively resistant to breakdown and these substances make up for the most part what is commonly known as soil organic matter. Such substances have physical and chemical properties which together help to determine the structure of a soil and to influence greatly its fertility. These substances are also in a continuous state of change, but an equilibrium is achieved so that their total quantity remains fairly constant in any one *locale*, the amount being largely dependent on climate and geographical conditions and the type of plant life being supplied.

Among the most characteristic of the products making up soil organic matter is the black colloidal material, having high hydrophilic power, known as humus, the presence of which helps to make possible the crumb structure of soil so

necessary for its fertility. Humus is a complex mixture which has been resolved in the following manner (E. J. Russel):



Humic acid has been a favourite object of study. It is apparently formed in at least the following ways: (a) by bacterial attack on cellulose; (b) by chemical transformations of lignin; (c) from fungal mycelia. Humic acid from soil is stated to contain about 5% nitrogen; it cannot therefore be wholly a lignin or cellulose condensation product. Oden believed it to be a tetrabasic acid with an equivalent weight of about 300.

Many of the characteristics of soil organic matter are in harmony with the view that lignin, or lignin derivatives, represent a major constituent. This is made more likely by the fact that lignin is very resistant to microbiological attack. Lignins from various biological sources vary in composition; thus, the lignin from grass roots is not identical with the lignin of oak leaves or pine needles.

Humus

It was originally thought that humus is formed from cellulose in the soil. Thus V. A. Beckley (J. Agric. Sci. 1920, 11, 69) found that sugars on treatment with acids gave rise to hydroxymethylfurfuraldehyde which readily condenses

to form a substance closely resembling humus. He found indications of the presence of this aldehyde in a dunged soil and in rotting straw in which humus was being formed. An alternative view was put forward that humus was derived from the oxidation of quinones (W. Eller and K. Koch, Ber. 1920, 53 [B], 1469).

F. Fischer (Brennstoff-Chem. 1924, 5, 132) advanced the view that lignin is the parent substance of humic acid.

Bray and Andrews (J. Ind. Eng. Chem. 1924, 16, 137) had shown that during the bacterial decay of wood, the cellulose almost disappeared within 3 years whereas the lignin suffered but little diminution in that period. Other work showed that lignin and humic acid have, chemically, much in common (F. Fischer and H. Tropsch, Ber. 1923, 56 [B], 2418). From a study of the fractionation of organic matter in mineral soils, C. W. B. Arnold (Chem. Soc. Annual Rep. 1924, p. 173) obtained results indicating the origin of humic matter of soil from lignin, and other evidence showed a correlation between the formation of humic acid, and loss of lignin but not that of cellulose or pentosans. Oden (Trans. Faraday Soc. 1922, 7, 288) showed that humic acid of soil was a true acid, this being obtained from diverse soils such as peat and agricultural soil. It readily gives rise to colloidal solutions. Its salts with alkali metals are soluble and behave as colloidal electrolytes. The salts with other metals are insoluble. J. Marcussen (Z. angew. Chem. 1925, 38, 339) regarded oxycellulose as the parent substance of humic acid, his argument against the lignin hypothesis being based on the fact that sphagnum peat contains more than 40% humic acid whereas the sphagnum from which it is derived is said to contain very little lignin. He, later (*ibid.* 1926, 39, 898), considered lignin also to be involved in humic-acid formation.

S. A. Waksman (Soil Sci. 1926, 22, 123, 323, 395, 421) has emphasised the lack of satisfactory methods of characterising humic matter and has pointed out that many of the products referred to as humus and humic acid are not homogeneous. It is pointed out that of the various constituents of straw, lignin is most resistant to microbiological attack and tends to accumulate in soil organic matter. If, in fact, lignin is added to soil it is recovered, after incubation, as "humus." According to Waksman (Trans. Intern. Soc. Soil Sci. Copenhagen, 1933, Vol. A, pp. 119-132) the chemistry of humus is not that of its individual constituents. "It must be first of all studied as a whole. Humus must be looked upon as a natural body, as a natural system. It may vary in composition; it may consist of various derivatives of lignin, proteins, certain hemicelluloses and even cellulose, as well as other plant and animal constituents; it may even contain numerous newly synthesised bodies, all of which go to make it a complex system." Waksman uses the term humus to designate "organic residues which have undergone extensive decomposition by micro-organisms whether in peat bog or in compost, in forest soil or in mineral soils. . . . The chemical composition of humus varies considerably, depending on the nature of the plant residues,

on the conditions of decomposition, on the extent of decomposition and the micro-organisms active in the decomposition process. Humus is not in a static condition but undergoes continuous change, the rate of change depending upon the above conditions. Humus is therefore not constant in chemical composition."

Waksman has published (*loc. cit.*) the figures given in Table I, showing analyses of soil humus derived from a variety of biological sources.

TABLE I.—CHEMICAL NATURE OF SOIL HUMUS.

Nature of humus.	Per cent. of total humus in ash-free material.		
	Carbohydrates.	Lignins and lignin-like derivatives.	Proteins.
Hardwood—spruce forest, F-layer	27.16	43.18	9.11
Hardwood—spruce forest, H-layer	17.00	57.00	8.49
Lowmoor peat, Newton	11.85	44.08	25.84
Lowmoor peat, Florida	7.48	51.24	25.62
Highmoor peat, young sphagnum	37.04	34.72	5.33
Highmoor peat, old sphagnum	21.70	53.25	5.85
Alpine humus	17.95	35.18	35.77
Chernozem soil, Kansas	13.88	40.81	34.74
Prairie soil (Carrington loam)	11.85	49.29	30.38

The results given in this table show that, with certain exceptions, natural humus formations tend to be low in carbohydrate and have a high lignin and protein content. The sphagnum peats are exceptional because (a) the carbohydrates of the sphagnum plant are more resistant to decomposition than those of the grasses; this in turn produces a low protein accumulation as insufficient carbon is released to build up the protein of the micro-organisms; and (b) the highly acid conditions of sphagnum bogs reduce the rate of decomposition by micro-organisms. Constituents of the carbohydrate group, e.g., hemicelluloses of the uronic acid type, are also contained in the resistant fraction of the humus. Soil humus, after a variety of transformations proceeding at different rates on the manifold plant products, tends, according to Waksman, to have the following composition: (a) lignin-protein complexes 60-80%, (b) certain resistant hemicelluloses and waxy substances 5-12%, (c) cellulose, and other products in an active state of transformation, 5-25%. When the humus is treated with alkali, a large part of groups (a) and (b) are brought into solution leaving group (c) undissolved, the latter being "humins." When the alkali extract is acidified, the major part of (a) and some of (b) are precipitated giving the "humic acids" whilst a part of group (b) and possibly a part of (c) are left in solution, to be termed the "fulvic acid" fraction. F. G. Tenney and S. A. Waksman (Soil Sci. 1929, 28, 55; 1930, 30, 143) show

that the decomposition of plant products on the soil proceeds much more slowly under anaerobic conditions than under aerobic. This is true especially of the lignins and organic nitrogenous complexes, when compared with the decomposition of celluloses and hemicelluloses.

Although in the fresh plant residues the ratio of carbon to nitrogen is from 200:1 to 50:1, the humus in the soil shows a narrow carbon to nitrogen ratio approximating to 10:1, with variations depending on the nature of organic residues, extent of decomposition, etc. The relatively high nitrogen content of the humus makes it likely that the organic nitrogenous complexes in the humus are either not of a protein nature or that they are not in a free state, or they would decompose as quickly as plant and animal proteins usually do (S. A. Waksman and K. R. N. Iyar, *J. Washington Acad. Sci.* 1932, 22, 41). According to these authors "ligno-proteinates form the most essential constituents of the soil humus, or the nucleus of the humus." They are accompanied by pectins, uronic acids, fats, waxes, etc. Thus organic matter of the soil may be divided, according to Waksman and Iyar, into two groups:

1. The humus nucleus, consisting of ligno-proteins combined with bases, giving H-ligno-proteinates, Ca-lignoproteinates, Fe-lignoproteinates, Al-lignoproteinates, and probably also with silicates and phosphates. These ligno-proteinates, possibly combined with the hemicelluloses, form the fraction designated as humic acid and are responsible for the characteristic colour and organic colloidal properties of soil.

2. The remaining constituents of humus, consisting of cellulose, hemicelluloses, waxes, fats, starches, etc., in various amounts and proportions according to the location, e.g., forest soils, highland peats, etc. These together form the fraction known as "humin," but this may include substances designated as "orenic," "apocrenic," "fulvic," "humal," and other so-called acids.

The lignoprotein complexes are not completely resistant to decomposition and may be broken down by a variety of fungi including the mycorrhiza associated with the roots of trees.

Lignin (*v.* Vol. VII, 307c-311a).

There seems to be agreement that, in the plant, lignin is attached to carbohydrates, possibly polyuronic acids. Presumably such complexes exist in the soil, for they are only very slowly broken down by micro-organisms.

Lignin is attacked by hypodite and this reagent has been used by A. G. Norman and W. J. Peavy (*Soil Sci. Soc. Amer. Proc.* 1939, 4, 183) for the estimation of a fraction of soil organic matter which contains lignin. They point out, however, that the attack by hypodite may depend on the state of combination of the lignin. (See also A. G. Norman and J. E. Moody, *ibid.* 1939, 5, 171.)

A review of the methods of proximate analysis of humus, including the lignin fractions, is given by S. A. Waksman (*Trans. Intern. Soc. Soil Sci.*, New Brunswick, 1939, Vol. A, p. 101).

Polyuronic Acids.

It is now apparent that polyuronides, and uronic groupings, are widely distributed in plants, composts, and soils. Methods of estimation depend on the fact first shown by K. N. Lefèvre and B. Tollens (*Ber.* 1907, 40, 4513) that prolonged boiling with 12% hydrochloric acid liberates carbon dioxide from uronic acids. W. V. Bartholomew and A. G. Norman (*Iowa State Coll. J. Sci.* 1941, 15, 253) have worked out a method of estimation of uronic acids in soils based on this observation. Some of their results are given in Table II. There is some error due to carbon dioxide evolution from hexosan groups.

TABLE II.—URONIC CONTENT OF VARIOUS SOILS
EXPRESSED AS CARBON DIOXIDE YIELD.

Soil type.	Depth, in.	G. CO ₂ per 100 g. air-dry soil.
Edina silt loam	0-4	0.082; 0.084
Edina silt loam	16-19	0.016; 0.016
Weller silt loam	0-14	0.114; 0.118
Weller silt loam	10-13	0.028; 0.030
Ames very fine sandy loam	0-24	0.232; 0.238
Webster silty clay loam	0-6	0.162; 0.162
Leon fine sand	0-14	0.108; 0.110
Leon fine sand	14-3	0.019; 0.021

The polyuronides, the content of which in soil seems to have a direct relation to the fertility of soil, contribute greatly to the water retention and crumb structure of soil. J. H. Quastel and D. N. Webley (*J. Agr. Sci.* 1947, 37, 257), using a new manometric technique, have shown that the addition of sodium alginate to a soil improves its crumb stability and water-holding power. It was demonstrated that the addition of 0.1 g. sodium alginate to 100 g. of the air-dried standard soil used in their investigations had an effect equivalent to a 11% increase in the water-holding power of the soil. It was suggested that alginate confers hydrophilic properties on soil by its combination as an ion with one or more constituents of the soil particles, thereby presenting new surfaces with high water-holding powers.

Polyuronides present in soil, and which are important in determining soil structure and soil fertility, include pectic acid and alginic acid, as well as a variety of bacterial polysaccharides. Pectic acid is composed of D-galactopyruonic acid units mutually united by 1:4 α -linkages. Alginic acid, on the other hand, is composed of a chain of D-mannopyruonic acid residues joined by 1:4 β -linkages. The formulae of both polyuronides resemble that of cellulose, but X-ray measurements show that the period along the fibre axis for alginic acid is 8.7 Å. as against 10.3 Å. for cellulose.

The specific polysaccharide of *Pneumococcus* Type III is a polyuronic acid, containing cellobiuronic acid residues formed by β -linkages through the 1:3 positions. Precise knowledge, according to Percival (*Proc. Biochem. Soc.* 1946), of the ill-defined polyuronic hemicelluloses is almost non-existent owing to the difficulty of isolating homogenous products. In many cases,

he points out, the uronic acid constituent has not been identified with certainty, e.g., the methoxyuronic acid of the hemicellulose of cotton wood, even though the proportion of uronic acid is relatively high in this instance, the polysaccharide consisting of a chain of 7-9 xylose residues.

Many mucilaginous polysaccharides contain uronic acid units. Seed mucilages of the plantains may have a high proportion of xylopyranose end-groups and a smaller proportion of galactopyranose end-groups. The work of F. Smith and E. L. Hirst has given information on the complex polyuronides present in gum arabic and other plant gums, that may be found in soils containing decaying vegetable matter. There seems to be little doubt that the metabolism of both micro-organisms and plants contributes greatly to the store of polyuronic acids in soil.

Other polysaccharides which are metabolic products of bacteria, and which increase the hydrophilic properties of a fertile soil, are the levan polysaccharides. These substances, which on hydrolysis yield fructose, are formed from sucrose by commonly occurring soil organisms such as *B. subtilis*. These organisms are able to secrete an enzyme that accomplishes the synthesis (S. Hestrin and S. Avineri-Shapiro, *Biochem. J.* 1944, 38, 2).

Cellulose Decomposition in Soil.

The major part of the cellulose of plants is deposited on the land, or in the forest, as post-mortem material or as waste matter. It is destroyed either directly by soil micro-organisms or after passing through the digestive systems of animals. Animal manures, rich in cellulose, find their way ultimately to the soil. A great variety of organisms attack cellulose (see S. A. Waksman, *Bot. Rev.* 1940, 6, 637), including anaerobic and aerobic bacteria and fungi. *Actinomyces*, and the filamentous fungi including *Fusarium*, *Aspergillus*, *Penicillium*, *Trichoderma* are all involved. According to Waksman, in the breakdown of wood by fungi, three stages may be distinguished: (a) attack by *Uredineæ* and *Ustilagineæ* that decompose sugars and starches; (b) attack by fungi belonging to the genera *Mucor*, *Penicillium*, and *Aspergillus*, that bring about destruction of sugars and starches and decompose hemicelluloses and polyuronides; and (c) development of the true wood-destroying fungi, belonging to the *Polyporaceæ* and *Agaricaceæ*, that attack both cellulose and lignin. Apart from these organisms, protozoa and a variety of wood boring insects (termites, cockroaches, etc.) are involved in cellulose decomposition in soil. The products of cellulose decomposition may be, besides carbon dioxide, organic acids (chiefly acetic, butyric, and valeric acids) and alcohols, methane, and hydrogen; these are usually produced by anaerobic organisms. Aerobic bacteria and fungi seem to bring about a complete destruction of cellulose. Among the final products of aerobic decomposition, the formation of slimy materials and pigments is usually noted. Winogradsky suggested that the slimy material might be oxy-

cellulose, but it is more likely to be composed of uronic acids.

The major product of cellulose breakdown is bacterial matter, the rate of its formation being determined by the availability of nitrogen that must enter into bacterial synthesis and growth. It is estimated that 40-70% of the carbon of the cellulose decomposed is transformed into microbial cells.

Soil as a Biological System.

Soil may be considered as a complex biological system in which hosts of organisms are competing with each other often for a limited supply of nutritional material. They exercise profound effects on the development and chemical activities of each other, and establish between themselves a dynamic equilibrium which is constantly changing with changes in the physical and chemical environment of the soil. Studying the soil as a biological whole, it is possible to investigate its metabolic events, under defined experimental conditions, in a manner similar to the method of exploration of the metabolism of other complex systems of living cells such as those presented by isolated animal and plant tissues. This has been carried out by H. Lees and J. H. Quastel (*Biochem. J.* 1946, 40, 803, 815, 824) and by J. H. Quastel and P. G. Scholefield (*Nature*, 1949, 164, 1068), in their studies of nitrification of inorganic and organic constituents of soil, and by P. J. G. Mann and J. H. Quastel (*ibid.* 1946, 158, 154) in their studies of manganese metabolism of soil.

Some conception of the enormous population of micro-organisms in soil is provided by the fact that there may be as many as 5,000 million bacteria per g. of soil. This corresponds to a weight of over 4 tons of bacterial substance per acre of soil. The numbers fluctuate greatly, depending on availability of food supply, moisture, aeration conditions, temperature, hydrogen-ion concentration of the soil, the types of plants growing in the soil, etc. Results given in Table III (taken from S. A. Waksman, "Principles of Soil Microbiology," Williams and Wilkins, Baltimore, 1927) show how the micro-organisms of soil vary in number according to the treatment of the soil.

TABLE III.

Treatment of the soil.	Hydrogen-ion concentration of the soil.	Micro-organisms found.*		
		Bacteria.	Actinomycetes.	Fungi.
Unfertilised and unlimed	4.6	3,000	1,150	60
Lime only added	6.4	5,410	2,410	23
Salts and ammonium sulphate added	4.1	2,690	370	112
Salts, ammonium sulphate, and lime added	5.8	6,990	2,520	39
Stable manure and salts added	5.4	8,800	2,920	78

* In thousands per g. of soil, determined by plate method.

Results given in Table IV, taken from R. C. Starkey (Soil Sci. 1938, 45, 207), show how the properties of micro-organisms in soil vary according to their proximity to plants.

TABLE IV.

Plant.	Sample of soil taken.	Micro-organisms found.*		
		Bacteria.	Actinomycetes.	Fungi.
Rye	Near roots	28,600	4,400	216
	Away from roots	13,200	3,200	162
Sugar beet	Near roots	57,800	15,000	222
	Away from roots	32,100	12,200	176
Alfalfa	Near roots	93,800	9,000	268
	Away from roots	17,800	3,300	254

* In thousands per g. of soil.

The bacteria range in numbers usually from a few hundred thousand to several hundred million per g. of soil, though many species do not develop by the ordinary plating technique. P. H. Gray and H. G. Thornton (Nature, 1928, 122, 400), with an improved counting technique for bacteria, obtained direct counts of the order of 4,000 million bacteria in a g. of manured arable soil. Such figures were over a hundred times greater than those obtained by the plating technique (see also P. C. T. Jones and J. E. Mollison, J. Gen. Microbiol. 1948, 2, 54). Protozoa may reach figures of the order of one million per g. of soil (Amoebæ 280,000; flagellates 770,000; ciliates 1,000; estimated on a neutral manured arable soil at Rothamsted). Algae may exceed 100,000 per g. of soil. According to S. A. Waksman and R. C. Starkey ("Soil and the Microbe," Wiley, New York, 1931, pp. 67, 110, 157), the numbers of actinomycetes range from a few thousand to many millions per g. of soil, while the numbers of fungi may exceed one hundred thousand per g.

In such a complex microbiological population there exist numerous chemical inter-relationships affecting metabolic behaviour and cell proliferation. Symbiotic associations take place and antibiotic developments occur. Thus S. A. Waksman and H. B. Woodruff (Soil Sci. 1942, 53, 233) have shown that by the use of a proper extractant (e.g., ether), it is possible to demonstrate that soils contain substances of the actinomycin type which inhibit the growth of certain bacteria in culture media. Such substances may be both bacteriostatic and bacteriocidal; their effects may be considerably modified by soil constituents. (See S. A. Waksman, "Microbial Antagonisms and Antibiotic Substances," The Commonwealth Fund, New York, 1945, and A. C. Thaysen, Nature, 1950, 166, 93, for a discussion of the subject.)

Considerations such as these, together with increasing knowledge of the phenomena of cell adaptations as a function of the environment, make it necessary to investigate soil as an integral biological whole. Its organic matter may be,

according to the circumstances, largely that of living tissue similar in many fundamental respects to that of plant or animal, or it may be largely that of the lignoprotein-polyuronide system of complexes with relatively little living material present. The usual proportion of micro-organisms is about 5% of the total organic matter. The investigation of all such material—living and non-living—is proper to the study of soil organic matter.

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J. H. Q.

SOLANINE (v. Vol. VI, 966; X, 1596).

SOLANOCAPSINE (v. Vol. VI, 96c).

SOLANUM ALKALOIDS. Alkaloids have been extracted from a large number of *Solanum* species (see, e.g., Heiduschka and Sieger, Arch. Pharm. 1917, 255, 18) but only a few bases have been closely examined and ascertained as individual alkaloids. They are all steroid bases and belong to the small group of gluco-alkaloids, the best-known of which are listed in the following table:

Plant origin.	Gluco-alkaloid.	Formula of aglucone.
<i>S. tuberosum</i> (potato)	Solanine, $C_{45}H_{73}O_{15}N$	$C_{27}H_{43}ON$
<i>S. nigrum</i> (woody night-shade)		
<i>S. lycopersicum</i> (tomato)	Solasonine, $C_{45}H_{73}O_{16}N$	$C_{27}H_{43}O_2N$
<i>S. sodomaeum</i> , <i>aviculare</i>		
<i>S. zanthocarpum</i>	Solaucine, $C_{45}H_{73}O_{16}N$	$C_{27}H_{43}O_2N$
<i>S. auriculatum</i>		
<i>S. angustifolium</i>	Solanguine, $C_{33}H_{53}O_7N$	$C_{27}H_{43}O_2N$
<i>S. demissum</i>	Demissine, $C_{50}H_{83}O_{20}N$	$C_{27}H_{45}ON$
<i>S. pseudocapsicum</i>	?	$C_{26}H_{44}O_2N_2$ (?) $C_{26}H_{44}O_4N_2$

An excellent review on the *Solanum* alkaloids has been given by T. A. Henry ("Plant Alkaloids," Churchill, Ltd., 4th ed., London, 1949, pp. 661 *et seq.*) where also historical data are given.

Solanine, $C_{45}H_{73}O_{15}N$, $[\alpha]_D^{20} -59.45^\circ$ (pyridine), crystallises with water in needles, and after drying at 100° shrinks at 235° and melts at varying temperatures between 235° and 295° . Solanine is sparingly soluble in water, almost insoluble in ether and chloroform, has a bitter taste, and is hardly alkaline to litmus. Most of its salts are amorphous. Solanine is best prepared from potato (*S. tuberosum*); fresh potatoes should not contain more than 10 mg. per 100 g. fresh weight, but the content varies within wide limits, as much as 300 mg. having been found in a sample. Fresh potato shoots are specially rich in alkaloids, and contain up to 290 mg. per 100 g. of fresh shoots. (For preparation of solanine from this material, see Soltys and Wallenfels, Ber. 1936, 69 [B], 817. For the estimation of solanine, see Bömer and Mattis, Chem. Zentr. 1923, iv, 736). If solanine is

treated with warm dilute hydrochloric acid it is hydrolysed into solanidine, small amounts of "solanthrene," and a mixture of the sugars, D-glucose, D-galactose, and L-rhamnose. Zemplén and Gerecs (Ber. 1928, 61 [B], 2294) have hydrolysed peracetylsolanine with hydrogen bromide in glacial acetic acid and have obtained an acetylated solanidine-glucoside and an acetylated rhamnoside-galactose. (For a similar hydrolysis, see Oddo and Caronna, *ibid.* 1934, 67 [B], 446.)

Solanidine, $C_{27}H_{43}ON$, $[\alpha]_D^{21} -28.5^\circ$ (alcohol), m.p. 219° , contains a secondary hydroxyl group (monoacetyl derivative, m.p. $206-208^\circ$), a tertiary nitrogen atom, no methyl group being attached to it (methiodide, m.p. 280°), one double bond and three terminal C-methyl groups. If solanidine hydrochloride is heated *in vacuo*, one molecule of water is split off, "solanidene," $C_{27}H_{41}N$ (m.p. $166-167^\circ$) being formed. This compound is identical with "solanthrene" (*v. supra*) and should better be called *solanthrene* (cf. also Bergel and Wagner, *ibid.* 1933, 66 [B], 1093); it contains two double bonds, apparently in conjugation, although no spectrum was measured (but *v. infra*, solasodine) and can be hydrogenated to tetrahydrosolanthrene (*solanidane*), $C_{27}H_{45}N$, $[\alpha]_D^{17} +30.4^\circ$ (chloroform), m.p. 164° . All attempts to effect a Hofmann degradation on solanidine have given negative results.

Solasonine and Solasodine.—*Solasonine* has been isolated from *Solanum sodomæum*, *S. aviculare*, and *S. xanthocarpum* (Briggs *et al.*, J.C.S. 1942, 1). It is $C_{45}H_{73}O_5N$, and crystallises from methanol with $\frac{1}{2}H_2O$, m.p. $275-280^\circ$, $[\alpha]_D^{25} -53$ to -68.7° (alcohol). Solasodine differs from solanine only by an extra oxygen atom and on hydrolysis with acids yields the same sugars and an aglucone *solasodine*, $C_{27}H_{43}O_2N$, containing one oxygen more than solanidine. Solasodine crystallises from 80% alcohol with $1H_2O$, m.p. $197.5-198.5^\circ$, $[\alpha]_D^{25} -97.1^\circ$ (methanol) (Bell and Briggs, *ibid.*, p. 2); it contains two active hydrogen atoms, but only monoacyl derivatives are formed. The nitrogen is tertiary, no methyl group being attached to it, and a double bond is present. Dehydration with alcoholic hydrogen chloride yields $\Delta^{3,5}$ *solasodiene*, $C_{27}H_{41}ON$, m.p. 170.5° , $[\alpha]_D^{25} -86.9^\circ$ (chloroform), with an ultra-violet spectrum characteristic of double bonds in different rings (Briggs *et al.*, *ibid.*, p. 3; Rochelmeyer, Arch. Pharm. 1939, 277, 329).

Solauricine and Solauricidine.—*Solauricine*, $C_{45}H_{73}O_5N$, was isolated from an alcoholic extract of the dried berries of *S. auriculatum* (Bell, Briggs, and Carroll, J.C.S. 1942, 12). By acid hydrolysis, *solauricidine* (possibly isomeric with solasodine), m.p. $213-217^\circ$, rhamnose, galactose, and glucose are obtained.

Solangustine and Solangustidine.—*Solangustine*, $C_{33}H_{53}O_7N$, was isolated from *S. angustifolium* by Tutin and Clewer (*ibid.* 1914, 105, 559). On hydrolysis it yields *solangustidine*, $C_{27}H_{43}O_3N$ (amorphous) and glucose. A similar gluco-alkaloid with one sugar molecule only is *solmargine* from *S. marginaum*. It is

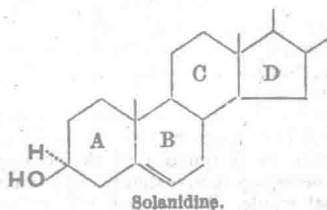
probably a rhamnoglucoside of a hydroxylated solasodine of still uncertain structure (Briggs, private communication).

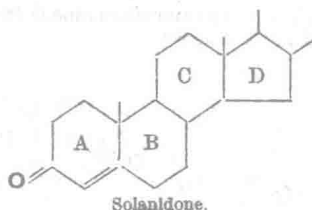
Demissine and Demissidine.—The gluco-alkaloid demissine, $C_{50}H_{83}O_{20}N$, m.p. $305-308^\circ$, $[\alpha]_D^{20} -20^\circ$ (pyridine) was obtained by Kuhn and Löw (Ber. 1947, 80 [B], 406) from *S. demissum*. On hydrolysis it yields dihydrosolanidine, D-xylitol, D-galactose, and 2 mols. of glucose (see also *idem*, *ibid.* 1948, 81, [B] 552).

Solanocapsine and Solanocapsidine.—Alkaloids have first been isolated from *S. pseudocapsicum*, by Berger and Fränkel-Conrat (J.C.S. 1936, 1537), but it is doubtful whether solanocapsine ($C_{30}H_{44}O_4N_2$) and solanocapsidine ($C_{28}H_{42}O_4N_2$) are genuine, because during the extraction the basic material has been treated with dilute hydrochloric acid. The two formulae (*v. supra*) are questioned by Rochelmeyer (Arch. Pharm. 1945, 282, 92). Only solanocapsine is well defined; it differs from all other solanum alkaloids by having two nitrogen atoms, one of which is a primary amino-group removable with nitrous acid. For alkaloids from other *Solanum* species, see Henry (*op. cit.*, p. 671).

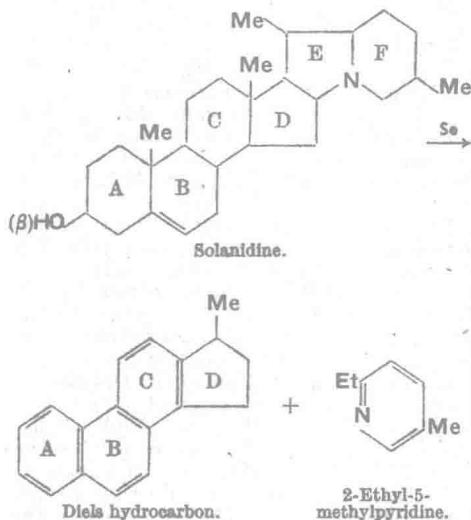
Constitution of the Aglucones.

With the exception of solanocapsine and solanocapsidine, all aglucones of the *Solanum* alkaloids contain twenty-seven carbon atoms which make feasible a relationship with cholesterol. By selenium dehydrogenation of solanidine, Dieterle and Rochelmeyer (*ibid.* 1935, 273, 532) obtained phenanthrene, chrysene, and a 'basic moiety which seemed to be a higher homologue of pyridine. Soltsy and Wallenfels (Ber. 1936, 69 [B], 811) succeeded in definitely connecting the *Solanum* aglucones with the sterols by isolating 3'-methyl-1:2-cyclopentenophenanthrene (the "Diels-hydrocarbon") from the dehydrogenation mixture (see also Craig and Jacobs, J. Biol. Chem. 1943, 149, 461). The secondary hydroxyl group of solanidine must be in position 3 of the steroid skeleton; it is easily oxidised to a keto-group (*solanidone*, $C_{27}H_{41}ON$, m.p. 218° , oxime m.p. 228°) by the usual reagents. Since all of the aglucones, with the exception of those of *S. pseudocapsicum*, give precipitates with digitonin, the hydroxyl group in position 3 must have the β -configuration. The double bond is in a β : γ -position to this hydroxyl group, and when the aglucones are oxidised to the corresponding ketones, the double bond shifts, as usual in the steroid field, into the α : β -position relative to the newly-formed keto-group as shown by its characteristic absorption spectrum. This reaction is represented as follows:





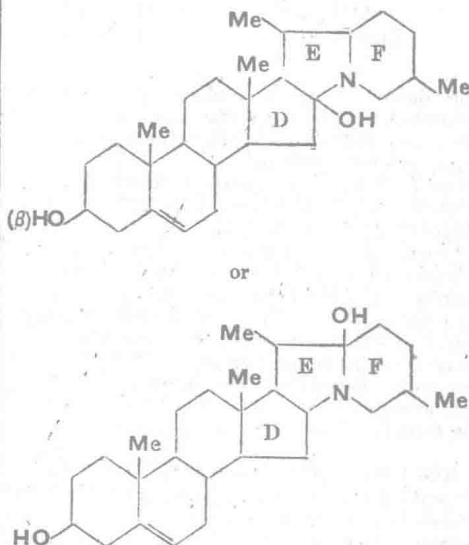
Nothing definite is known about the function of the second oxygen atom in solangustidine and solanocapsine, but the work of Briggs *et al.* has clearly shown that in solasodine the second hydroxyl group is not attached to any of the four rings of the steroid skeleton, but to the nitrogen-containing moiety of the molecule. The elucidation of this part of the molecule has been difficult. The first positive evidence as to the nature of the heterocyclic part was provided by Prelog and Szpilfogel (Helv. Chim. Acta, 1942, 25, 1306), who, by dehydrogenating solanidine at 300–320° isolated 2-ethyl-5-methylpyridine, a compound which had been previously isolated from the dehydrogenation of the veratrum alkaloid cevine (*see, e.g.,* Jacobs and Craig, J. Biol. Chem. 1938, 124, 659). The identification of this degradation product provided a strong indication that the nitrogen atom, which is tertiary, occupies a bridgehead position in a terminal six-membered ring. The following structure for solanidine has been proposed by Prelog *et al.* (Helv. Chim. Acta, 1942, 25, 1306); it also explains the cleavage of the molecule under the conditions of the selenium dehydrogenation:



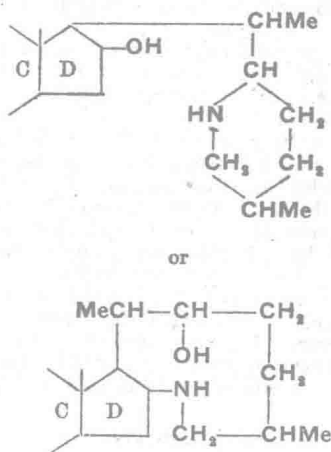
Mention must be made of Prelog's work on the stereochemistry of ring A in solanidine (*ibid.* 1944, 27, 390) where all four possible solanidanols (solanidanol-3β and -3α and *allo*-solanidanol-3β and -3α) have been prepared. This work set the foundation for the brilliant work of Uhle and Jacobs (J. Biol. Chem. 1945, 160, 243), who, by a series of reactions, transferred the steroid

sapogenin sarsasapogenin into the corresponding dihydrosolanidine (*allo*-solanidanol-3β), thus proving the correctness of above formulation for solanidine.

Solasodine contains two hydroxyl groups, one of which must be attached to the ring system E-F; either of the following formulae is proposed by Briggs, but it is supposed that the second formula is the more likely:

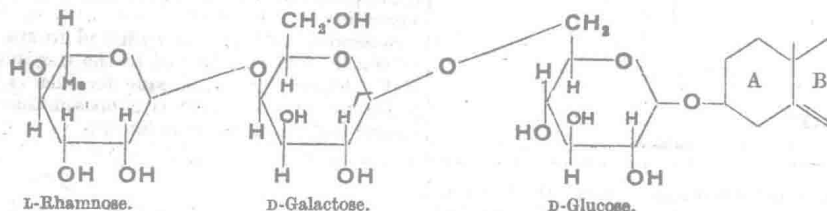


Solasodine behaves differently from solanidine in that hydrogenation with different means opens the ring system E-F, and the following chain-compounds may be obtained from the above two formulae (Briggs, private communication), of which again the second is the more likely:



As already mentioned, the sugar moiety of the gluco-alkaloid is attached to the steroid part through the oxygen atom in position 3. In solanine the sequence of the sugars (D-glucose, D-galactose, L-rhamnose) has been proved.

periodate oxidation, Briggs (private communication) has shown that the mode of linkage of the sugars in solanine and solasonine is through 1, 1:4, and 1: 6-linkages:



The glucose linkage is probably β , like most natural glucosides, but so far no evidence as to the α - or β -linkage of the rhamnose or galactose sugars has been obtained.

Colour Reactions of Solanum Alkaloids.—See Rochelmeyer, Arch. Pharm. 1939, 277, 329, and Briggs *et al.*, J.C.S. 1942, 11.

Pharmacological Action.—Therapeutically, no solanum alkaloid is used, and their effects are usually only encountered in cases of poisoning by potatoes, if they contain more than the usual traces of solanines. Solanine causes vomiting, nausea, headache, and cramps, but fatal cases are rare. Berries of the different *Solanum* species contain more alkaloid and severe poisoning from an overdose may be possible.

Schl.

SOLDERS AND BRAZING METALS.

In soldering and brazing a joint is made between metals by a molten alloy which is caused to flow between the parts to be joined at a temperature at which they are still solid. The solder or brazing alloy acts simply as a cementing material, and for any specific application it must (i) melt at a temperature below the softening point of the metals to be joined but above the temperature which the joint must withstand in service, (ii) wet and flow freely over the surfaces of the metals to be joined, (iii) adhere firmly when solid, and (iv) have reasonable inherent strength. "Soldering" or "soft soldering" is the term generally applied to the operation of jointing with lead-tin alloys at temperatures below about 300°C. Brazing originally referred to the use of 50:50% copper-zinc "brazing spelter," melting at about 870°C.; but large numbers of other alloys, including the silver brazing alloys or silver solders, with melting-points in the range 595–780°C., are now in use for making joints of greater strength than can be produced by soft soldering. Copper brazing, using copper as a solder, and heating the work in a reducing atmosphere, is widely employed for jointing ferrous materials, tungsten, and molybdenum. There are apparently no alloys that melt between about 310° and 595°C. that are sufficiently ductile to be of any value as solders.

SOFT SOLDERING.

The alloy traditionally used by the tinsmith, tinman's solder, was made from 2 parts of tin and 1 part of lead, and was very close in composition to the eutectic (63% tin). A solder of this composition is generally slightly easier to use than the cheaper alloys containing less

tin, as it becomes completely molten and free flowing at the lowest possible temperature (183°C.).

In all soft soldering operations, the surfaces to be joined must be carefully cleaned and a flux must be applied to dissolve any surface films of oxide and to serve as a protection against re-oxidation during heating. The flux should preferably be fluid at the temperature of soldering and should be displaced from the solid metal by the solder. The most vigorous flux, effective on iron, copper, and most non-ferrous metals and alloys, is zinc chloride, conveniently employed as a 30% solution of the commercial fused salt in water. The "killed spirits" of the tinsmith was made by adding an excess of zinc to hydrochloric acid. The melting-point of zinc chloride (262°C.) is, however, undesirably high, and the 70:30 eutectic mixture of zinc chloride and ammonium chloride, melting at 180°C., is a better flux. For soldering stainless steel, a mixture of (30%) zinc chloride solution and hydrochloric acid in equal proportions is often recommended. Flux pastes containing zinc chloride as the active ingredient are widely marketed, a popular paste comprising petroleum jelly 75, zinc chloride 20, and ammonium chloride 5%, with a small amount of water as an emulsifying agent.

It is important to recognise that the flux residues remaining on the joint after soldering with zinc chloride fluxes are extremely corrosive. Wherever possible the articles should be washed at once in hot water containing a few drops per gallon of hydrochloric acid (to prevent the formation of an insoluble crust of zinc oxychloride) and finally in water made faintly alkaline.

For all electrical work, the use of zinc chloride in a flux is absolutely prohibited, since it is impossible to wash the soldered assemblies effectively. The most usual flux for this work is resin, which melts at about 125°C., and may be applied as a solution in industrial spirit or as a powder sprinkled on the joint. More usually, the resin is incorporated as a core in the solder wire. Solid resin residues are quite inactive, but when molten, the resin acids have a slight solvent effect on the common metal oxides. The activity of resin as a flux may be increased by the addition of such substances as the amine hydrochlorides, which largely decompose at the temperature of soldering and thus tend to become non-corrosive. Activated resin fluxes of this type are permitted by many electrical users, and appreciably increase the speed of soldering. Typical activated resin fluxes contain 1–2% of aniline hydrochloride or hydroxylamine hydro-

chloride. Additions of mannitol and lactic acid have also been proposed.

Soft Solders.—The soft solders commonly used are essentially tin-lead solders, varying in composition from 18 to 70% of tin, and may be divided into two groups, non-antimonial and antimonial. The antimonial solders contain up to 3% of antimony, added mainly to reduce their cost; they can be prepared from the ternary eutectic alloy of tin, antimony, and lead obtained from the refining of scrap white-metals. Antimonial solders are suitable for most industrial purposes, with the exception that they will not form satisfactory joints on zinc or galvanised-iron articles.

The following tables give the compositions of the solders listed in British Standard Specification No. 219 (1949) and indicate their principal uses.

COMPOSITION OF B.S. SOFT SOLDERS.

Antimonial solders.			Non-antimonial solders.		
B.S. solder.	Tin, %.	Antimony, %.	B.S. solder.	Tin, %.	Antimony, %.
B	49-50	2.5-3	A	64-65	<0.6
M	44-45	2.3-2.7	K	59-60	<0.5
C	39-40	2.0-2.4	F	49-50	<0.5
L	31-32	1.7-1.8	G	39-40	<0.4
D	29-30	1.0-1.7	J	29-30	<0.3

MELTING CHARACTERISTICS AND TYPICAL USES OF B.S. SOLDERS.

B.S. solder.	Approximate limits of melting range, °C.		Characteristics.	Uses.
	Liquidus.	Solidus.		
A	185	183	Lowest melting - points of series.	Electrical, radio, and instrument assemblies and machine soldering of can end-seams.
K	188	183		
B	204	185	Moderately low melting-point and short melting range.	Coppersmiths' and tin-smiths' bit soldering and general machine soldering.
F	212	183		
M	215	185		
C	227	185	Somewhat higher melting - point and longer melting range.	Blowpipe soldering. Soldering of side seams on high-speed body-forming machines.
G	234	183		
L	243	185	Long melting or plastic range.	Wiping of cable and lead-pipe joints. Dip soldering.
D	248	185		
J	255	183		

In all the above solders, it is necessary to limit the amounts of zinc, aluminium, and cadmium present as impurities, as these elements, even in amounts of 0.001%, are generally believed to impair the adhesion and free-running characteristics of the solders.

Resin cored solder is usually made from Grade F or Grade A.

In addition to the above alloys, pure tin is sometimes used as a solder, particularly for pre-tinning small non-ferrous parts. When soldered joints are required to withstand heating to temperatures near 180°C. (at which temperature all lead-tin alloys commence to melt) the following high melting-point solders are sometimes used. These solders are particularly useful for jointing the armature binding wires of small electric motors.

SOLDERS FOR SERVICE AT HIGHER TEMPERATURE.

Composition.				Approximate limits of melting range.	
Lead, %.	Tin, %.	Silver, %.	Antimony, %.	Liquidus, °C.	Solidus, °C.
—	95	—	5	243	236
98.5	5	1.5	—	301	296
97.5	1	1.5	—	309	310

For such applications as boiler plugs and the control mechanism of fire extinguishers, low-melting fusible alloys may sometimes be used as solders. These alloys, however, do not wet metal surfaces readily and are often difficult to apply, possibly on account of the low activity of all fluxes at temperatures below about 180°C. The Table below gives the compositions and melting-points of some typical fusible alloys.

Alloy.	Melting-point, °C.	Composition, %.				
		Bismuth.	Lead.	Tin.	Cadmium.	Zinc.
Lipowitz's alloy	70	50	26.7	13.3	10	—
Wood's metal	73	50	24	14	12	—
Darcey's alloy	93	50	25	25	—	—
Newton's alloy	95	52.5	32	15.5	—	—
Rose's alloy	100	50	28	22	—	—
—	102.5	54	—	26	20	—
—	130	56	—	40	—	4
—	144	60	—	—	40	—

All soft solders are usually obtainable as cast ingots, bars, or sticks, as well as in the form of wires. For electrical instrument work, economies in the amount of solder used in each joint may sometimes be made by using thin wires of solder. Solder pastes or creams, consisting of powdered solder mixed with a flux, are also available.

Methods of Soldering.

Soldering with a Copper Bit.—The use of a copper bit to heat the work and apply molten solder to the joint is widely practised. It should be emphasised that it is always desirable to employ a bit which is sufficiently massive to

heat the work to a temperature above the melting-point of the solder; molten solder will not adhere to a cold surface. Bits may be heated in a coke fire, by gas jets, or in a gas-heated stove, or they may be continuously heated by built-in gas burners or electrical heating elements. However they are heated, they must be kept free from scale and the faces must be "tinned" with a continuous layer of solder. Solders containing 50-70% of tin are readily applied by a copper bit; with less tin difficulties may arise unless a very massive bit is used and the working temperature is kept sufficiently high.

Blow-pipe Soldering.—The blow-pipe is occasionally used for soft soldering when it is necessary to confine the heating to a very small area, in which case a small hot flame may be of service. Zinc chloride is the best flux to use for blow-pipe work; resin tends to char. Large blowlamps are used for applying solder to motor-car bodies to fill in dents before painting.

Dip-soldering.—Dip soldering is the method of joining assemblies by immersing them in a bath of molten solder. It has been widely used for "pre-tinning" small parts which are subsequently to be joined by soldering; but its most important application is in the manufacture of automobile radiators. The radiators, assembled from copper tubes or strips, are immersed in a bath of molten solder (covered with molten flux), allowed to remain in the bath until they have reached a steady temperature, removed, and allowed to drain. The 30:70 tin-lead solder is usually used for soldering radiators. Eutectic solders and even pure tin are often used for "tinning" electrical parts by dipping, but with tin-rich alloys it is necessary to limit the upper temperature of the bath and renew the alloy frequently, otherwise rough gritty coatings will be produced as a result of solution of copper with the formation of tin-copper compounds in the bath.

Machine Soldering.—Machines are used on a large scale for producing can-bodies and for soldering these to their ends. In making the cylindrical bodies, the solder is applied to the prefluxed longitudinal seams by a roller which is half immersed in molten solder and acts as a bit to heat the work and apply the solder alloy where it is required. The ends are soldered to the bodies by rolling the assemblies, tilted at an angle in guides so that the rims pass along a shallow trough filled with molten solder. For machine soldering, tin-lead alloys containing at least 50% of tin are preferred, as it is desirable that they should be free-flowing and should drain well at as low a temperature as possible. Antimonial solders are considered to behave in a gritty manner and are not used.

Electrical Heating.—In factory assembly operations, electrical methods may often provide a neat means of applying heat to the joint. In *electrode soldering* a carbon rod, shaped to fit the work, is brought in contact with the assembly; a current is then passed through the rod, which, owing to its high electrical resistance, becomes heated and in turn heats the joint. In *resistance soldering* a current is passed directly through the joint. With both these methods of heating, the

solder is conveniently applied as paste or foil. *Eddy-current heating* methods, using a high-frequency source of energy, have also been used for soldering on mass-production lines.

Pre-tinning.—Whatever method of soldering is adopted, it is usually advantageous to "pre-tin" the surfaces to be joined, particularly if resin is to be used as a flux. It is usual to employ the same solder as is to be used in making the joint, and this may be applied by dipping or by an iron. Small articles are often coated with pure tin by electrodeposition, but if this is done it is essential that the coating should be at least 0.0005 in. thick (on brass articles) or 0.0002 in. thick on steel, otherwise adhesion of the solder may be poor owing to diffusion of the tin into the base metal, and particularly to surface oxidation.

Wiped Joints.—A special soldering technique, depending on the use of a solder having a long plastic range, is practised by plumbers and cable jointers for joining lead pipes. The solders used for this purpose are antimonial or non-antimonial solders containing 28-32% of tin. The pipes to be jointed are butted together, and molten solder poured from a ladle over the joint or melted on to the joint with a blow lamp. The solder running off the pipe is caught on a buckskin cloth and wiped repeatedly round the joint, the plastic mass being moulded round and finally wiped to the familiar smooth contour. In this operation, tallow is used as a flux.

Soldering-Power of Solders.—In choosing a soft solder, the ease with which it wets the surfaces to be joined and penetrates the joints is usually the deciding factor. The mechanical strength of the joint is more often a secondary consideration, since in most applications the parts are folded or interlocked before soldering. Many methods of evaluating the soldering-power have been proposed, but the results are difficult to interpret and often contradictory. "Spread of drop" tests, in which measurements are made of the area coated by a weighed pellet of solder when heated under standardised conditions have been reported by McKeown¹ and many others. Good reproducibility is usually obtained in any given set of conditions, but, as McKeown notes, "there is some difference of opinion as to whether the information obtained is directly related to the soldering power of the solder tested. More informative results might be given by measuring, in addition to the total spread in a given time, the rate of spread, especially in the first few seconds of the test, by means of a cine-camera, but experiments of this kind have not yet been made." The complexity of the problem is well illustrated by the observations of Schumacher, Bouton, and Phipps,² who proposed to measure "solderability" in terms of the height of climb of solder up a pair of twisted copper wires dipped in a pot of the molten alloy. They noted that the composition of the solder changed as it travelled up the wire; in progressing to the cooler surfaces, the higher-melting phase became frozen out and the eutectic penetrated the farthest. Latin³ has attempted to measure "solderability" in terms of the speed at which the solder penetrates the gap between two strips mounted horizontally and separated at the edges