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PRESIDENTIAL ADDRESS, 1944.

Dr. R. O. Page.

PROTEINS AND TANNING.

In these days of specialisation many of us find that our own particular field of work is so restricted that a description of it is unlikely to be of interest to our fellow chemists, whose specialised interests are in other branches of chemistry.

I think, however, that a presidential address to the Institute of Chemistry should be on the field in which the speaker is specially qualified rather than on a broad subject with which he has only general acquaintance. Last year, Sir Theodore Rigg was able to speak to us on a special subject which he has made his own and which was also of great interest to all New Zealand chemists. I am less fortunate, in that I feel that leather chemistry is too complicated and specialised to be of general interest, the more so, that the more general aspects of it have been covered quite recently by Dr. Dorothy Jordan-Lloyd in an address that will have been read by many of you.

However, the achievements of the leather industry in New Zealand have been considerable, both on the practical and the scientific side. Thus, as far as leathers from cattle hides, at any rate, are concerned New Zealand's production, per head of population, is probably, at the present time, greater than that of any other country in the world, being approximately twice that of the U.S.A., generally recognised as the world's greatest leather producer.

On the scientific side also, New Zealand leather chemists have made considerable contributions. Thus the second award of the Procter Memorial Scholarship, open to leather chemists from all over the world, went to Dr. Holland who, while holding that Scholarship at Leeds University, made noteworthy contributions to the study of the tanning action of the chromium salts of the dicarboxylic acids. Then, since his return to New Zealand, as well as collaborating with me in work on the nature of the vegetable tanning process, he has made a promising start on the problem of the nature of the 'bound' water in hide and leather. Finally, in the very important and difficult field

of the physical properties of leather White and Caughley have made pioneer investigations on such properties as the tightness of grain, rigidity and abrasive resistance of leather.

Leather chemists do, however, have a common interest with many New Zealand chemists working in other fields in that they are both largely concerned with the chemistry of natural organic products. As a primary producing country, most of New Zealand's special chemical problems have been concerned with such materials and much notable work has been done in this direction. Thus, in recent years, we have had the work done in Auckland by Dr. Briggs on the diterpenes and that of Dr. Hosking on kauri gum, both of whom have gained the Hector prize for their researches. Then there have been the important investigations into the alkaloids of rye grass by the Plant Chemistry Laboratory at Palmerston North and the laboratory of the Department of Agriculture at Wellington, as well as work on alkaloids of native plants at Otago University. Also, at Canterbury College, the plant gums are being studied, while at Cawthron a start has been made on the difficult problem of the organic chemistry of the tobacco leaf, while the war has stimulated work at many laboratories on the vitamin content of our various food products, and much of the work of the Dairy, Wheat, Leather and Woollen Mill Research Associations is on the chemistry of such products.

Probably, of the whole biochemical field, the proteins provide one of the most difficult problems, as well as the one of perhaps the widest interest. This is particularly true in New Zealand. For instance, with the exception of butter, our principal exports, meat, wool, cheese and hides are proteins, and proteins are important constituents of such articles of local consumption as milk and wheat. They play an essential part in the nutrition of man himself and of his farm animals, and many enzymes and hormones are proteins and they are also responsible for virus diseases such as tobacco mosaic. I thought, therefore, that in discussing proteins tonight, with only brief reference to the problems involved in the tanning of one of them, I would be covering ground that might interest a wider field than that of the mere leather chemists. Although I shall find it difficult to avoid considering them from a tanner's point of view, all of us who are interested in proteins have much common ground, as is shown for instance by the fact that vegetable tannins, as well as converting hide into leather, appear also to be able to inhibit the development of the very different protein of tobacco mosaic.

Proteins are built principally and, in some cases, probably entirely of amino acids, but many of them contain other substances as an integral part of the molecule. These components may be carbohydrate in nature, such as the polysaccharide isolated from crystalline egg albumen, or phospholipoids as in

myosin, or phosphoric acid residues as in casein or they may take numerous other forms. Nevertheless, it is the amino acid portion that is specific for all proteins and this is the only field of protein chemistry that I shall attempt to discuss tonight, There are about twenty of these amino acids that have been isolated from proteins and apparently they are all alpha amino (or imino) acids and probably all have the same steric configuration.

The first question, therefore, for consideration is how these amino acids are combined together in the protein molecule. The early work of Emil Fischer produced much evidence that the peptide bond was the principal link involved in joining one amino acid with another. This conclusion is strongly supported by the fact that simple peptides have been isolated from the enzymatic hydrolysis products of proteins and also by the recent findings of Bergmann and his co-workers that peptide linkages in certain synthetic substrates are split by typical proteolytic enzymes. Although it has been suggested that diketopiperazine rings exist in proteins, there is no evidence that any synthetic diketopiperazine can be split by any enzyme found in nature so that it seems unlikely that such rings can be present in proteins. Moreover, it seems most probable that the peptide link is always between alpha amino and carboxyl groups and that such groups as the distal carboxyl groups of aspartic or glutamic acid are free or combined with ammonia as an amide, while the epilson amino group of lysine and the guanido group of arginine are free, for again no enzyme has been found that will split any type of linkage with these groups.

It is of considerable interest to determine accurately the amount of each amino acid in a protein, as this determines the nature of the side groups in a protein chain and, therefore, also its properties. In particular, it is important to know the amino acid content of proteins used as food stuffs for certain acids are apparently essential in nutrition, as they cannot be synthesised in the body from other amine acids. Apparently the body can convert some amino acids into others, but the more complex ones cannot be synthesised by the animal from simpler amino acids and must be obtained from the food. Thus certain natural proteins such as gelatine, and gliadin are incomplete in that they cannot supply all the amino acids required. Gelatine for instance, has no tryptophane and this deficiency can be remedied by adding tryptophane to a diet in which gelatine is the only protein. Similarly, gliadin is deficient in lysine.

Until quite recently there have been few reliable analyses of proteins, due first of all to the uncertainty that the material analysed was a pure chemical individual and secondly to the difficulty of the analysis itself. With proteins which normally

decompose at temperatures below their melting points, the usual melting and freezing point methods cannot be used as criterions of purity, but there are newer physical chemical methods which do give some indication of purity. Thus the determination of the molecular weight of proteins by the sedimentation method, to be discussed later, shows whether there are molecules of more than one size present. Again a pure chemical individual should show constant solubility in a solvent even when the amount of undissolved protein is varied within wide limits.

Once the difficulty of obtaining a pure protein has been overcome there remains the very difficult problem of the separation and accurate estimation of the amino acids obtained by the hydrolysis of the protein material. Many of the amino acids have fairly readily been separated by precipitation, but the monoamino-monocarboxylic acids cannot yet be separated by such methods. The only method available has been to extract them from neutral aqueous solution with butyl alcohol by the method of Dakin and then separate the individual acids by the fractional distillation of the amino acid esters. Because, owing to the presence of polar groups, the increment in boiling point for each CH_2 group is smaller than for the simple paraffins, results obtained by this method could be, even with the most careful attention to details, only approximations. Recently, however, the search for specific precipitants for the amino acids has been successfully prosecuted by Bergmann and his co-workers and they have also developed methods of a new type in which the amount of amino acid is calculated, by means of the solubility product, from the results of two precipitations, in each of which the amount of reagent added is less than is necessary to precipitate all the amino acid. Another recent method which promises very well, involves the addition to the unknown solution of a definite weight of the pure amino acid containing a known amount of an isotope such as deuterium. If a sample of this acid in pure form is then isolated from the solution and its isotope content determined, the amount of the amino acid in the original solution can be readily calculated.

Dr. Page showed a table of the amino acid content of a number of proteins, and discussed the work of Bergmann and Niemann, who suggested a simple formula for the number of amino acid residues in a protein molecule.

This is about as far as the organic chemist can take us at present and for further information we have to use physical chemical methods. One of the most fruitful of these has been the application of X-Ray analysis, particularly to the fibrous proteins. These include such substances as silk fibroin, keratin, myosin and collagen and are found in nature as essential components of long, thin, fibrous structures. Silk fibroin is much the simplest of these chemically and its X-Ray photographs

show many well defined spots and have a considerable resemblance to those obtained on simple crystalline substances. In particular, there is a well marked periodicity of 7.0A° along the fibre axis which, when compared with the results from X-Ray photographs of amino acid crystals suggests that the silk fibre is made up of extended polypeptide chains, the length of 3.5A° per residue being only slightly less than the value of 3.67A° calculated for such a chain and showing, therefore, only slight distortion. The fibrous protein keratin, however, although it also gives well defined, though less sharp fibre diagrams, gives an entirely different one from silk fibroin with a principle spacing along the fibre axis of 5.1 not 7.0A°. Keratin also differs radically from silk fibroin in being reversibly extensible up to twice its original length, the stretching occurring with relative ease when the hair is soaked in hot water or dilute alkalies. The X-Ray diagram of stretched keratin is very similar to that of silk fibroin with a residue length of 3.4A° considerably shorter than the theoretical 3.67A° and, therefore, probably representing a slightly more distorted chain.

A keratin fibre which has been stretched and then immediately released possesses the power of supercontraction to about two thirds of its original length, the further folding involving considerable lessening of the sharpness of the X-Ray photographs. Myosin, the protein of muscle, gives in the relaxed state an X-Ray diagram similar to keratin, contraction involving a transformation to the supercontracted form.

The structure of collagen, the protein of connective tissue was next discussed. The X-Ray investigations of the fibrous proteins suggest the presence of a series of coplanar chains, at an average distance of 4.5A°. At right angles to the plane of the chains, a spacing of 10A° is found, probably due to the side chains, which hold the planes together. In collagen the forces involved are probably electrovalent, between acidic and basic side chains. In keratin there are in addition probably covalent links due to cystine occupying adjacent peptide chains. Such a link would explain the stability of wool, and its ability to regain its original length after stretching. So resistant is the link that the tanner, before he can remove keratin from a hide without destroying its collagen, must first destroy this bond by an alkaline reducing agent.

The association of the side chains with this spacing of about 10A° is made more probable by the fact that it is only this spacing that changes greatly when these proteins absorb water. Silk with few polar side chain groups absorbs little water but keratin can absorb much more with an increase in the side chain spacing up to 11A°. It is probably the presence of the stable covalent cystine side links that prevents a greater increase than this, as collagen, which has no such link, absorbs much more water with an increase in the side chain spacing up

to 16A° while leather into which the tanner has probably introduced such links shows a much smaller swelling. This question of the swelling of proteins in acid or alkaline solutions is of great practical importance, particularly to the tanner, and can be accounted for quantitatively by the application of the Donnan membrane equilibrium, the protein itself, as a non-diffusible ion, acting as a membrane.

The study of the molecule weights of globular proteins, notably by Svedberg's ultra centrifuge method, was next considered. Svedberg concluded that these molecular weights are not distributed at random but fall into groups the weight of the molecules in any group being a multiple of 17,600, the largest number of proteins occuring in the group with a molecular weight of 35,200 (2 X 17,600) and it is of interest in this connection that some of the larger molecules do break up readily and often reversibly into smaller units. However, recent accurate results on highly purified proteins do show variations from multiples of this unit weight which are considerably greater than the experimental error. If there is a factor common to all the molecules in one group, therefore, it cannot be the molecular weight, but it might possibly be that each protein in one group contains the same number of amino acid residues. The analytical work of Bergmann and Niemann suggests that this may be true for certain proteins.

From the rate of movement of the boundry between solvent and protein solution in the ultracentrifuge, together with diffusion experiments, some idea can be obtained of the molecular shape and further information on this subject can be gained from viscosity and dielectric measurements and from X-Rays and the electron microscope. All these methods give similar results and suggest that many of the globular proteins, such as pepsin, insulin, lactalbumen, haemoglobin and many others, are nearly spherical in shape with the greatest diameter not more than two or three times the length of the smallest. On the other hand a protein such as zein has a length of about 320A° twenty times its width of only 16A° and the myosin molecule is also extremely elongated, while tobacco mosaic virus forms a very large rodshaped molecule as has been confirmed by electron microscopy. Apparently no globular protein has a minor axis of less than 16A° so that even the most highly asymmetrical protein molecules have a very considerable thickness and are profoundly different in structure from the threadlike synthetic polymers such as polystyrene and polyacrylic acid with a diameter of from 3 to 6A°. Furthermore, the protein molecule is apparently an essentially rigid structure, orienting as a whole in an electric field.

Further, recent work suggests that many globular proteins when acted on by denaturing agents such as urea appear to uncoil into a relatively elongated form, the completely de-

natured protein resembling the fibrous proteins in structure. Again studies of surface films of proteins show a thickness of the protein monolayer of only 7A° so that a radical change must take place in the structure of a native protein before it can spread on a surface. This change must also be in the nature of an unfolding, although whether the character of the unfolding in surface denaturation, heat denaturation and urea denaturation is the same must be for the present undecided. On the other hand, in the case of long protein molecules, such as myosin, denaturation involves a folding of the molecule rather than an unfolding.

Of fundamental importance, in considering the chemical behaviour of the proteins is the fact that they and the amino acids of which they are composed are amphoteric. The structure of the isoelectric amino acids used to be formulated as the uncharged substances $H_2N.CHR.COOH$, but, in the last twenty years, a consideration of the dissociation constants of the amino acids and of many of their physical properties has shown that in the isoelectric state they exist almost exclusively as dipolar ions with the structure $^{+}H_3N.CH_2R.COO^{-}$. That the amino acids and peptides exist in solution as dipolar ions is shown with particular clarity by studies of infra-red and Raman spectra. For instance, the Raman spectra, in which only groups bound by covalent bonds give rise to Raman frequencies, show lines characteristic of the uncharged COOH group but not of the charged COO^{-} group. Thus acetic acid gives Raman spectra showing this line but sodium acetate does not, but glycine hydro chloride does show the line characteristic of the uncharged CO group while glycine does not. Thus the line near 1700cm, which is characteristic of the unionised C=O group does not occur in glycine, showing very clearly that in glycine the carboxyl group is charged. Other Raman lines show that the amino group also is charged.

There is strong evidence that, in the proteins also, in the isoelectric state, the basic and acidic groups carried on the side chains are fully charged and many of their properties are explained by this assumption. The amino acids for instance form dense crystals with a high melting point, near 300°C and they generally decompose on melting if not before. The polar nature is also the cause of their non-volatility so that Emil Fischer had to convert them into the much less polar esters before they could be separated by fractional distillation. The amino acids and the proteins are also extremely insoluble in all non polar solvents, but are relatively far more soluble in water and salt solutions. Thus the solubility of the proteins in water and both the dissolving and precipitating action of salt which has been used as a means of classification of the proteins, is determined by the nature and amount of their basic and acidic side chain groups and does, therefore, to some

extent at least, show real differences in constitution. Their solutions also, owing to the attractive forces on the dipolar ions, show higher densities than those of most similar organic compounds. The measure of the polarity of a molecule is shown by its electric moment and the high polarity of the amino acids and proteins is shown most clearly in this way. Thus the electric moments of water and alcohols are rather less than 2 Debye units and of organic nitro-compounds between 3 and 4, but glycine, the simplest of the dipolar ions has an electric moment of approximately 15 Debye units. The proteins, because of the large size of their molecules, have huge dipole moments varying from 170 to 1,400 Debye units, so that they form a group, with properties for which there are few analogues in other realms of chemistry. In particular, when dissolved in water, they give solutions with the highest dielectric constants yet known, a saturated solution of alpha amino caproic acid for instance having a dielectric constant near 300. Media with such high dielectric constants offer a new field of research in electro-chemistry, and the biochemical significance of these phenomena may be far reaching, since all living cells contain proteins in concentrations sufficient to affect greatly the dielectric constant within the cell.

Dr. Page then explained the deductions which can be made from the titration curve of a protein such as haemoglobin, and from the heat of ionisation, the interpretation of the two methods leading to the same results.

Finally he offered some observations on the tanning process. It is generally supposed that it is the charged polar groups of the proteins that have the power to attract water molecules and it is found in nature that proteins that have a high water content possess a large proportion of such groups. When, however, a protein is required to function in comparatively dry conditions, nature removes these polar side chains as in silk fibroin, or converts the negative polar groups into amides, as within seed proteins. The tanner, when he has to convert hide into leather, is faced with a similar problem, as he has to change a skin containing 200 per cent of water on its protein content, into a product with similar properties containing only about 15 per cent of water. He has found that this can be done most successfully by blocking some of these polar groups, possibly also linking the parallel peptide chains, and I am going to consider for a few minutes the principles involved in the use of the vegetable tannins for this purpose. These materials are like the proteins, still of largely unknown constitution, but can be classified into two types (a) the gallotannin type of Emil Fischer and (b) the condensed catechin type of Freudenberg. Most of the commercial tannins are of the latter type, but they all have, as a common property, a large number of phenolic OH groups.

There are still considerable differences of opinion as to the nature of the reaction of these complex materials with collagen, the protein of hides and skins, and in order to avoid confusion, I shall give you only my own conclusions and the work on which they have been based, which, however, in general outline at least, have been fairly widely accepted. Of fundamental importance in any explanation of the tanning process is the fact that solutions of the vegetable tannins unlike those of the proteins are polydisperse. This is probably most clearly shown by the decrease in the amount of tannin precipitated by a fixed amount of gelatine in successive precipitations of a tannin solution.

If a molecule of tannin is precipitated by each basic gelatine group, the results suggest that for wattle tannin (and other tannins give similar results) the molecular weight varies from over 2000 to about 600 with a predominence of molecules with molecular weights of 1900 and 1640.

Probably most information as to the nature of the reaction between tannin and collagen has been obtained from a study of the amount of soluble material removed from vegetable tanned leather by successive extractions with equal volumes of water. If the concentration of soluble material in successive extractions of a wattle tanned leather is plotted against the number of extractions, the curve first falls, and then gives two horizontal portions, separated by a break.

The first part of the curve represents the removal of uncombined material, but the two horizontal portions separated by a break show a striking resemblance to the vapour pressure curve of a salt forming two different hydrates and almost certainly show the existence of two different compounds. It is possible, by the controlled extraction of leather to make an approximate determination of the amount of tannin represented by the first horizontal portion of the curve now known as the combined water solubles and the amount corresponding to the second horizontal part, generally called the fixed tannin. These two types of combined tannin show such different characteristics that they almost certainly represent very different types of combination. Thus the blocking or removal of the basic groups of the collagen prior to tanning greatly reduces the amount of fixed tannin but does not affect the amount of combined water solubles. Again the stability of the leather, as measured by its shrinkage temperature, is greatly increased by the fixed tannin but is reduced by the combined water solubles. Also the amount of fixed tannin in leather increases very slowly with increased time of tannage for many years, while the combined water solubles very quickly reaches a constant maximum value.

The simplest explanation of these results appears to be as follows: The combined water soluble material is tannin, the

molecules of which are extended along the protein chains, probably being held by hydrogen bonds between the CO groups of the peptide chains and the phenolic OH groups of the tannin, as tannins which do not contain such groups do not form combined water solubles. An increase in the molecular size of any particular tannin by continued condensation which does not alter the percentage amount of OH groups would not, therefore, alter the amount of tannin held in this way. On the other hand, the fixed tannin is probably combined electrovalently with the positive groups in the collagen chains, the smaller tannin molecules which diffuse faster combining first and being gradually replaced by the larger molecules, thus explaining the slow increase in tannin with time.

When we consider the structure of the fibrous proteins, it is obvious that the distance between the parallel protein chains, or as the tanner would call it, the swelling of the hide must be a controlling factor in determining the amount of tannin that can penetrate in between them. Actually, it seems that the tannin molecules cannot penetrate unswollen hide, i.e. when the maximum distance between parallel chains is only 10 A°, and it is found that the swelling and tanning curves of collagen are extremely similar, thus providing a simple physical reason for the importance of pH on the extent of tannage for which earlier leather chemists sought a chemical explanation.

ANNUAL MEETING OF COUNCIL.

Election of Officers.—The following officers were unanimously elected for the coming year:—

President:—Dr. J. C. Andrews, Auckland.
Vice-President:—Professor F. G. Soper, Otago.
General Secretary-Treasurer:—Mr. W. G. Hughson, Wellington.

The names of the Canterbury and Otago Delegates are not yet to hand but the Auckland and Wellington Delegates to Council are Mr. K. M. Griffin and Mr. D. H. Freeman respectively.

Appointment of Editor.—Dr. H. N. Parton was unanimously re-elected Editor of the Journal and appreciation was expressed of the good work done in past years.

Appointment of Assistant Secretary.—All Branches supported the appointment of Mr. L. Wilkinson of the Dominion Laboratory as Assistant Secretary-Treasurer.

Industrial Chemical Essay Prize.—The recommendation of the examiners was that the prize for 1944 should be awarded to Mr. S. H. Wilson for his Essay entitled, "The Manufacture and Utilization of Calcium Carbide: a possible Electro-Thermal Industry for New Zealand." Council approved the recommend-

ation and extended congratulations to Mr. Wilson who was present at the meeting.

It was decided that the Essay Competition be continued in 1945 and thereafter periodically at the discretion of Council, and that the attention of members be drawn to this fact so that the scope of the Competition might be extended by obtaining more entries.

Detailed regulations governing the Industrial Chemical Essay Competition will be set out in full in the Minutes and may be had from your local Secretary.

Briefly, the Essay is restricted to a length of 6,000-8,000 words and may deal with a single industry or a group of industries or with any consideration affecting chemical industry as a whole in New Zealand. Entries close with the General Secretary-Treasurer on June 30th, 1945.

Salary Survey.—The President, Vice-President and Dr. Dixon were appointed a sub-committee to wait on the Public Service Commissioner to discuss salaries if a favourable reply to our request for a deputation is received.

Employment Register.—The President and Secretary were appointed to confer with the New Zealand Section of the Royal Institute of Chemistry. It was suggested that the two bodies form a central Executive in Wellington and select representatives from the main centres to collect information regarding unemployed chemists, graduates seeking employment and openings offering to chemists and technical staff. Mr. L. Wilkinson has since been appointed Secretary to the Chemists Employment Committee and all information should be forwarded to him, G.P.O. Box 250, Wellington.

Rehabilitation of Servicemen.—It is felt that the information assembled for the Employment Register should be of direct assistance in helping the Rehabilitation Department to place chemists in employment. The information will also be valuable to the Department of Scientific and Industrial Research generally and to the newly formed Manufacturer's Research Committee of the council of the D.S.I.R.

Medical Advertisement Committee.—This committee has been active and has appeared personally before the Board in support of applications relating to (1) Listerine (2) Pulmonas (3) Lactagol (4) Vincent's Tablets (5) Samson's Iodine Belt.

Outstanding Subscriptions.—Attention is drawn to the fact that about £50 is outstanding in overdue subscriptions and members concerned in Wellington and Otago Branches particularly are asked to assist the local committees in righting this position before the end of the year.

Trust Fund.—The Trustees as from November 22nd, 1944, will be Sir Theodore Rigg, Mr. G. A. Lawrence and the Presi-

dent, Dr. J. C. Andrews. £100 has been placed in a special P.O.S.B. Account in accordance with a past resolution of Council. A further £50 was voted to the fund at this meeting.

Australian Chemical Institute.—Mr. Siemon, Canterbury College, brought greetings from the General President of the Australian Chemical Institute. The Secretary has been asked to reciprocate.

Annual Conference.—It has been decided to hold a Conference in August, 1945 in conjunction with the New Zealand Section of the Royal Institute of Chemistry and Palmerston North has been tentatively selected as the most suitable site.

The Secretary was asked to write letters of appreciation to the Departments of Agriculture and Scientific and Industrial Research for their action in deciding that chemists in their employ may attend the Conference "on duty."

It was proposed that symposia of general interest be arranged with an agricultural bias on one day and an industrial bias on the other. Presidential addresses in the evenings will be held.

The following combined committee has now been set up: Mr. P. White and Mr. G. A. Lawrence representing the R.I.C. and Dr. J. C. Andrews, Dr. J. K. Dixon and Mr. W. G. Hughson (Secretary G.P.O. Box 250, Wellington) representing the N.Z.I.C.

Further information will appear in the March Journal.

Rules.—All matters relating to the Rules were held over till the next meeting of Council.

Retiring President.—Dr. R. O. Page, retiring President was thanked for his leadership of Institute affairs during the past year.

BRANCH NOTES

AUCKLAND BRANCH

THE CHEMISTRY AND TECHNOLOGY OF FISH LIVER OILS, WITH SPECIAL REFERENCE TO NEW ZEALAND.

F. B. Shorland, PhD., MSc. 15th June, 1944

The growth of the fish liver oil industry in New Zealand during the war is shown by the fact that production by the two manufacturers has risen from 100 to 150 gallons per annum in 1943. The limit is now set by a shortage of raw materials and if this could be overcome New Zealand would have a substantial exportable surplus.

Science has devised new and more efficient methods of extracting the oil from the livers than by letting them rot when

the oil slowly floated to the top. Now the livers are steam digested, with or without chemicals, and the oil separated centrifugally, or the oil may be solvent extracted from the raw livers. In order to increase the vitamin concentration and also to improve the palatability of the oils they may be distilled in a molecular still.

New Zealand has not a large fishing industry but the oils obtained are richer in vitamin A than those produced in Great Britian and in many other countries. Our potential production is equivalent to 300,000 gallons per annum of cod liver oil in regard to vitamin A content, whereas that of Great Britian is 3,000,000. The best propositions in regard to raw materials here are the livers from swordfish, kingfish, and a few species of sharks, while groper and ling are fairly good. Many of the sharks are useless and even the useful ones give oils having a deficiency of vitamin D in proportion to vitamin A in comparison with cod liver oil. This can be overcome by adding synthetic vitamin D to the finished product without much increase in cost.

There are many peculiar variations to be found in the vitamin contents and other properties of the oils. The seasonal variations can be explained but there are others, such as the variations found between the same species of fish at different places, which are not understood. Nor is the origin of the vitamins known; probably vitamin A is synthesised by the fish themselves although vitamin D may come originally from diatoms.

WELLINGTON BRANCH

"SOME ASPECTS OF MODERN PHOTOGRAPHIC CHEMISTRY"

Mr. K. S. Birrell, Soil Survey Division, Dept. of Scientific and Industrial Research. 27th June, 1944

The speaker began with an outline of the theory of latent image formation put forward by Professors Gurney and Mott of Bristol University. The theory starts by showing how the observed facts of the print out effect, which produces a visible image, can be satisfactorily explained by separating the photographic process into two stages, the first related to the photoconductivity shown by silver halide crystals, and the second dependent on ionic conductivity. Extension of this mechanism to explain the formation of the latent image is made by postulating that the silver sulphide sensitivity specks, discovered by Sheppard, act as nucleating centres. The electrons liberated from the halide ions by the action of light are trapped by the

sensitivity specks. These charged specks then attract the silver ions occupying interstitial positions in the silver halide lattice, and the sensitivity specks, by thus acquiring silver atoms, can grow to a size sufficient to initiate development. The ability of the theory to explain high and low intensity reciprocity law failure, solarisation, kerschel effect, and low temperature effects was pointed out.

An account was next given of the structure and methods of synthesis of the dyes used to make the photographic emulsion sensitive to the green, yellow, red, and infra-red regions of the spectrum. Dyes of the cyanine, carbocyanine and polycarbocyanine series were dealt with in this connection. The impact of these advantages on the motion picture industry, miniature camera photography, modern colour photographic processes, and scientific photography was then described.

The mechanism of the Dufaycolour and Kodachrome transparency processes was then sketched, and also that of the recent Kodacolour print process, some examples of which were shown. The two last-mentioned processes are integral tripack systems, depending on the use of dye-coupling developers of the p-amino dimethyl aniline type, the coupling substances being incorporated in the sensitive emulsion layers with protecting agents to prevent diffusion of the dyes from one layer to another. The coupling substances may be chlorinated phenols, giving on development blue dyes of the indophenol type, but for yellow and magenta aliphatic or heterocyclic compounds with reactive methylene groups are used as couplers. The protective agents to prevent diffusion may be water-soluble resins of the phthalic ester or polyvinyl ester type. Condensation of the coupler with long chain aliphatic groups such as capryl or palmitoyl also overcomes the diffusion difficulty. The history of the dye-coupling development process provides an interesting example of the large amount of work often required to establish a scientific principle as a practical method, the original patent for this method of producing coloured images being taken out as long ago as 1912, whereas Kodachrome was not placed on the market until 1935.

Miss A. E. Lorimer of the Wellington Branch, who is Y.W.C.A. Secretary with the Forces overseas, has received the award of M.B.E.

CANTERBURY BRANCH.

"Plant Gums and Related Polysaccharides" was the title on a lecture by Dr. R. J. McIlroy at the June Meeting.

Plant Gums are polyuronides, that is, polysaccharides which contain uronic acid. In general, polyuronides are constituted of a chain (branched or unbranched) of sugar units

which are more or less easily removed from the complex molecule, leaving behind a resistant acid nucleus. The latter nucleus contains either glucuronic or galacturonic acid residues joined to one or more sugar residues.

There are two major types of polyuronide:—(1) neutral polyuronides, such as hemicellulose, and (2) acidic polyuronides which occur naturally as the calcium, sodium, or magnesium salts. Examples of type (2) are the gums and mucilages, pectin, and alginic acid. A gummy or gelatinous condition seems to be associated with all polysaccharides which contain free acid groups.

Gums and Mucilages:—Gums usually occur as exudations on the bark of trees (cherry gum), on leaves (phormium gum), or on fruits (damson gum), particularly after wounding. Mucilages are extracted from seeds. Physically there is little difference between gums, mucilages and gel-forming substances. There is, however, a constitutional difference between these classes of polyuronide. The acid nucleus of gums contains d-glucuronic acid whereas the nucleus of mucilages contains d-galacturonic acid. Further, a protein-like substance is not infrequently found as part of a mucilage and cellulose may, in some cases, be a component.

Chemical Investigation of Gums:—In the chemical investigation of a gum, the following method is generally adopted. The naturally occuring salt of the gum is dissolved in water, acidified by dilute acid, and the free gum acid precipitated by alcohol. Purification is effected by repeated solution in water and precipitation by alcohol to constant ash content. Dialysis and electrodialysis may sometimes reduce the ash content considerably. The latter method has been used successfully for purification of pectin preparations.

The purified gum is hydrolysed when the main chain sugar units are removed and identified by colorimetric methods or by conversion to crystalline derivatives. The residual acid nucleus is separated as the barium salt which is insoluble in alcohol. Prolonged hydrolysis, frequently under considerable pressure, is necessary for hydrolysis of the barium salt. This drastic treatment is accompanied by degradation.

The mode of linkage of the sugar units in the molecule and the size of the separating unit are determined by the methylation technique. The gum is methylated, hydrolysed by methyl alcoholic hydrogen chloride and the resultant methyl glucosides separated by fractional distillation in high vacuo. The acid nucleus, even after methylation, presents a special problem for which no general method is entirely satisfactory.

The speaker discussed gum arabic at some length, and went on to consider pectin. It is no longer believed that arabinose and galactose, which are associated in the plant with pectin, are integral parts of the pectin molecule. Luckett and Smith hydrolysed fully methylated pectic acid with 2 per cent methyl alcoholic hydrogen chloride to produce 2:3 dimethyl galactofuronoside. Furanose residues may not be present, however, since 2:3 galacto pyruronoside is changed to the furanose form by the above treatment. The high positive rotation of pectic acid and its stability to hydrolytic agents are not in accord with a furanose structure. It may be assumed that the repeating unit in the pectic acid chain consists of 13 residues of d-galacturonic acid in pyranose form joined by 1:4 glycoside linkages.

Mr. Robert Hurst, a member of the Canterbury Branch who has been on leave since 1939, has been awarded the George Medal for bomb disposal work in London during the past four years.

OTAGO BRANCH.

On 10th May, Mr. C. G. W. Mason was the guest lecturer and addressed the Otago Branch on "Chemical Products of Coal Carbonisation in New Zealand".

The speaker introduced his subject with a brief reference to the limited coal reserves in this country, and the necessity for ensuring that maximum use be made of the coal available.

The outline of processes of coal carbonisation was followed by a more detailed description of the products obtained and the methods of converting these products into useful materials. The scope and limitations in the utilisation of sulphur, ammonia coke, benzole and tar products was reviewed. The speaker developed his contention that in the solid and liquid products of coal carbonisation, there existed a field of development in New Zealand, provided that supply, demand and the "Economic Production Unit" were satisfactorily correlated. Conditions under which this could most hopefully be achieved were outlined.

The Institute as a whole is not responsible for statements and opinions appearing in this Journal.

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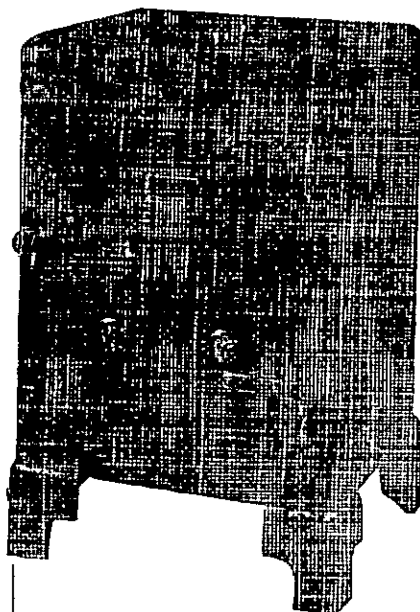

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