JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

VOL. 22. No. 5

OCTOBER - 1958.

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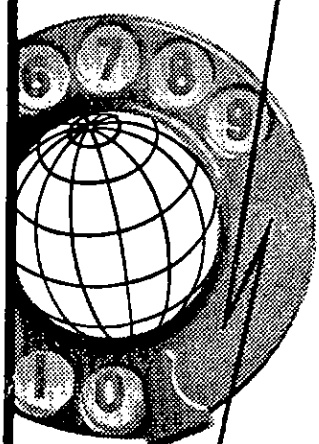

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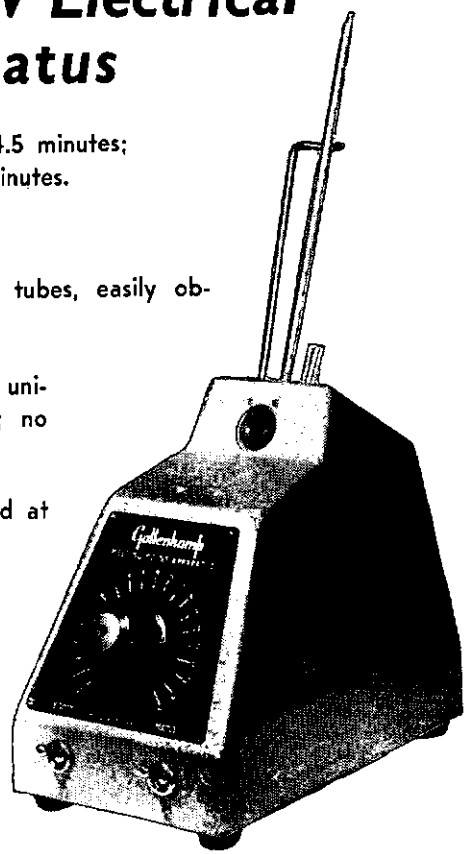

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EDITORIAL

Whither New Zealand?

(Contributed by G. M. Wallace, Massey College, Palmerston North.)

Current marketing difficulties highlight the dependence of the whole of our national economy on our ability to obtain a satisfactory price for a restricted group of primary products. Clearly the situation is most unsatisfactory and a consideration of some of the problems involved raises a number of important questions.

Firstly, are we really making an effort, through research, to supply what the customer wants or are we, through being stifled by unsatisfactory direction and through dearth of information on consumer preference, offering the consumer only what we think he wants? A considerable body of informed opinion is that our consumer relations are very poor, that we are living in the past and are making no more than lip-service effort to give the customer what he wants. We need much more than political representations and pious "it will all come right" statements from the heads of marketing organisations.

How much more do we need proper sales promotion and consumer response studies for our primary products than does the smallest secondary industry manufacturer and yet how does our effort compare with his?

Reliable consumer preference information opens a big field in applied research in food technology. This should give rewarding results if the effort applied is sufficient.

Our second problem is a much more fundamental one. Is the restriction in the range of our primary products wise? We have based our economy on the country's renowned ability to grow grass and on the conversion of this grass, by animals, into milk, meat, hides and wool. A great deal of excellent research has gone into fostering this concept and a great deal still awaits to be done. This is as it should be. But must we always be dependent on animals to convert plant fats and proteins into products that are of greater aesthetic appeal? Remember that this conversion is made only at the expense of a considerable loss of efficiency in land and fertiliser utilisation.

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What then are we doing about this ?

It is time a select research team was looking to our future problems in this field, problems of conversion of plant products into acceptable equivalents of our meat and dairy products, problems associated with the economic production, under our climatic conditions, of better sources of plant fats and proteins than grass, and so on.

We must have men of vision and fortitude to direct our research which will demand an increasing number of pure and applied research workers to implement. Research with the widest horizons is essential for our economic survival. Let us see that it becomes fact.

I.U.P.A.C. SYMPOSIUM ON "THE CHEMISTRY OF NATURAL PRODUCTS" AUSTRALIA, AUGUST, 1960.

During August 1960 a Symposium on "The Chemistry of Natural Products" will be held in Australia under the sponsorship of the International Union of Pure and Applied Chemistry. This will be the first occasion on which an I.U.P.A.C. meeting has been held in Australia. The responsibility for the organisation of this meeting lies with the Australian Academy of Science operating through its National Committee for Pure and Applied Chemistry. It is proposed that the scientific sessions should be held in Sydney and Melbourne with some official functions in Canberra. The programme will be organised under the following general topics —

Aliphatic and homocyclic compounds.

Biological chemistry (that is, topics concerned with chemical structure in relation to biological activity).

Heterocyclic compounds.

Physical methods in the study of the structure of natural products.

It is also proposed that a post-conference excursion to a rain forest area of particular phytochemical interest, either in New Guinea or Northern Queensland, should be held. Dates and locations of the meeting will be finalised within the next few months, so that preliminary information about the scientific and general programme can be made available to all interested scientists. Preliminary inquiries suggest that delegations will be sent by a number of countries, where the proposal for the meeting has been received with some enthusiasm.

The Fifth International Congress on Nutrition will be held in Washington, D.C., in September, 1960. A preliminary announcement only is available at this stage but chemists interested in nutritional fields and wishing to obtain further information should contact the New Zealand representative of the British Nutrition Society, W. A. McGillivray, Biochemistry Department, Massey College, Palmerston North.

THE POLYMERIZATION OF HYDROGEN CYANIDE.

By J. VAUGHAN,

Chemistry Department, University of Canterbury, Christchurch.

(Chairman's address delivered to the Canterbury Branch in March, 1958.)

In 1782 the Swedish chemist Scheele described the odour and taste of hydrogen cyanide, and he must be credited with being the first chemist who lived to record the isolation of prussic acid. Guy-Lussac subsequently prepared fairly pure liquid hydrogen cyanide in 1811. From that time, any chemist who kept hydrogen cyanide in glass vessels must have noticed that it deteriorated with time, first developing colour, then depositing solid, and finally ending as a black amorphous mass called azulmin. Occasionally a sample must have deteriorated rapidly and with explosive force, because the reaction is strongly exothermic. The change, which is a polymerization, only received recorded comment in the second half of the nineteenth century but even then little more than casual interest was displayed in the phenomenon.

Gautier, in 1869, described his attempts to fractionate azulmin. He was not very successful but he also recorded the slow evolution of ammonia from the polymer on standing in moist air and he recognised the possibility of hydrogen cyanide giving rise to more than one polymeric form. Lange, in 1873, extracted azulmin with alcohol and obtained a white crystalline solid which accounted for about 10% of the total polymerization product. Lange assumed that the white compound was a trimer of hydrogen cyanide and that its formula was that of amino-malononitrile

The compound was soon observed by others. Of these, Wipperman deserves special mention because, besides obtaining the white polymer, he made some important observations on the way in which general polymerization of HCN could be brought about. Up to that time, polymerization was almost a matter of chance; epichlorhydrin and cyanogen, for example, were reported as effective additives. Wipperman noticed the marked effect of small additions of alkaline salts, and reached the conclusion that water and base were necessary for the polymerization process. We now regard the reaction as initiated by cyanide ions, and many of the reports before Wipperman's experiments would seem to have originated in impurities.

This century has seen little concentrated effort being made on the general problem, with the exception of a polemic in the 1930's on the structure of the white crystalline material. In discussing the later work, particularly that carried out at Canterbury, there seeem to be three convenient focal points.

1. Attempts to follow the rate of polymerization and attempts to achieve a quantitative comparison of the effects of added materials.
2. The constitution of the crystalline polymer.
3. Speculations on the possible structure of the black azulmin and on the mechanism of polymerization.

1. Polymerization Rates:

Very few quantitative measurements of polymerization rates have been carried out — partly because it has been difficult to know what to measure. When hydrogen cyanide is polymerized, the liquid gradually goes brown in colour, then becomes opalescent, and clears again after coagulation and the start of actual precipitation. Thereafter, the brown-black precipitate of azulmin increases in amount whilst the brown supernatant liquid does not darken appreciably.

If one is concerned with the initial mechanism of polymerization, interest becomes centred in rate measurements made before precipitation of material of presumably appreciable chain-length. There are other, perhaps more practical, reasons why behaviour during this early period should be studied. Commercially the stability of liquid prussic acid is a matter of importance. The material may be stabilised by addition of acidic substances (commonly organic acids) but it would be of advantage to be able to compare with accuracy the effect of various additives on polymerization. The value of an accurate comparison of stabiliser efficiencies springs to mind immediately but a similar comparison of accelerators would be at least as important.

Before precipitation has commenced, however, very little polymerization has occurred and it would appear also that most physical properties of the liquid are insufficiently altered to allow the kineticist to make use of them. In 1950 Sporzynski and Salter, at Imperial College, followed the deterioration of stabilised HCN by conductivity measurements. The temperature was 100°C, the standard material was 98% hydrogen cyanide, and the interest lay generally in the comparison of stabilising effects of added materials and in the effect of water on the stability of the hydrogen cyanide. The effect of water is of much practical importance, because HCN is not marketed in the anhydrous state. Sporzynski and Salter found, among other things, that about 5% water in the cyanide led to very marked accelerative effects on the polymerization. We shall comment on this shortly.

Use may also be made of the development of colour in the early stages of reaction. Measured changes are assumed to be meaningful in terms of the main polymerization reaction, but in the few qualitative experiments which had earlier been attempted, this was a tacit assumption. Lewcock, for example, in examining

the efficacy of added stabilisers, measured (in 1918) the time taken for a discernable colour to appear, and Thomas (1928) compared the colours developed in several HCN samples carrying a variety of additives.

In work at Canterbury, we simply followed the rate of increase in colour at 18°C, using a Spekker Absorptiometer. Pure, dry hydrogen cyanide was the medium into which water or bases could be introduced. Our aim was mainly to arrive at an efficient comparison of the effects of added materials. In the early stages, colour development could be expressed satisfactorily by the simple equation —

$$\log d = kt + \text{constant}$$

where "d" is a measure of the colour, and in more normal analytical procedure "d" would be a measure of the concentration of the material producing colour. This equation appears to hold from zero time, i.e. there is no induction period, and this is in agreement with some analytical work carried out by Sporzynski and Salter in the course of their experiments. However, as polymerization advanced, the rate of increase in colour became progressively greater than that indicated by the simple equation.

In comparing the effects of added materials we compared values for "k" — the apparent " rate-constant." Using piperidine as the standard base, rate of polymerization increased with increase in amount of added base, although the accelerating effect of a given increment of base diminished as the total amount of additive increased.

The effect of water on the polymerization is of much interest.

ml. water per 20 ml. HCN	$k \times 10^2$ (min.$^{-1}$)
0	0.82, 0.81, 0.81, 0.84
0.4	0.53, 0.59, 0.56
0.8	0.49, 0.50, 0.50
1.6	0.49, 0.48, 0.48
4.0	0.43, 0.45

It is clear that water has a retarding influence, in direct contrast to the implications from the experiments of Sporzynski and Salter. The two series of experiments may be reconciled, however, because at 100°C appreciable hydrolysis of hydrogen cyanide, with accompanying instability of the sample, is highly probable and Sporzynski and Salter recognised this. On the other hand, in the Canterbury experiments at about 20°C, such hydrolysis is likely to be negligible.

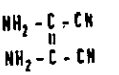
An assessment was also made of the relative effects of a number of organic bases. A constant molarity of base (0.00607 mole per 20 ml. HCN) was maintained and results were:

	$k \times 10^2$ (min.$^{-1}$)
Ethylamine	1.26, 1.26
Diethylamine	1.48, 1.60, 1.30, 1.26
Diethanolamine	0.33, 0.34, 0.33
Diphenylamine	—
Piperidine	0.82, 0.81, 0.81, 0.84
Triethylamine	1.90, 2.03, 1.72.

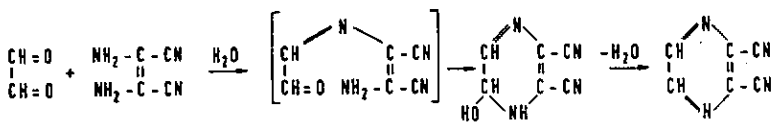
Few conclusions may be drawn. Catalytic activity does not appear to be directly related to basicity, e.g. piperidine is a stronger base than triethylamine which, however, is a much more efficient catalyst for the polymerization. Results on the three ethylamines indicate that catalytic activity increases in the order, primary, secondary, tertiary. Although there is no relationship here again between catalytic activity and basic strength this may be of little significance because nucleophilic activities towards the proton and, for example, towards a positive carbon centre, need not run parallel with each other.

2. Crystalline Polymer of Hydrogen Cyanide:

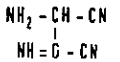
Up to 1923, the crystalline material extracted from azulmin was assumed to be a trimer of HCN, and was assumed also to be aminomalono-nitrile. Bedel, in 1923, carried out some molecular weight determinations which pointed to the compound being a tetramer. This must have been embarrassing for people working on the alleged trimer. The Polish chemist, Grischkevitsch-Trochimovsky, who had earlier been attempting to justify the trimer formula now suggested a formula for the compound as a tetramer without correction to his earlier work. It may be that it is for reasons such as this that certain modern texts still include the trimer as a known compound. But the new formula proposed by Trochimovsky looked quite convincing and with it many of the known reactions could readily be understood. The proposed structure was that of diaminomaleonitrile



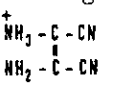
This structure allows us, for example, to explain in a satisfactory manner formation of heterocyclic compounds when the tetramer reacts with nitrous acid or glyoxal:



Following Trochimovsky, Hinkel (in Britain) began work on the chemistry of the tetramer in the late 1920's. Hinkel and his co-workers, however, interpreted all the behaviour of the tetramer in terms of the structure

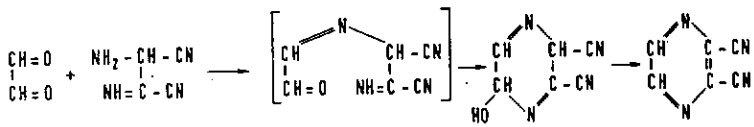


aminoiminosuccinonitrile. In view of the fact that Hinkel finally carried out what he considered to be a decisive experiment, it is worthwhile commenting briefly on some of his early evidence. For example, he regarded as significant the fact that the tetramer forms a monohydrochloride only. But if we inspect the diamino structure of Trochimovsky, the formation of a monohydrochloride, i.e. the addition of a proton to one amino group, should markedly reduce the basicity of the remaining amino group



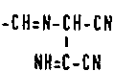
particularly in the presence of two suitably-placed, strongly electron-attracting nitrile groups. Furthermore, monohydrochloride formation is only positive evidence for Hinkel's formula if it be assumed that the imino group is incapable of salt formation. The existence of many ketimine hydrochlorides lends support to the idea that if the imino group in Hinkel's structure is insufficiently basic to form salts, then this is for reasons which would lead us to expect also a lowered basicity of the second amino group in Trochimovsky's structure.

Hinkel and his students formulated the reaction of the tetramer with glyoxal, to give pyrazine derivatives, on the basis of the aminoimino structure

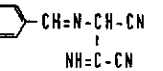


But they placed no weight, apparently, on the fact that ortho phenylene diamines, with an arrangement of amino groups similar to that in Trochimovsky's structure, react with glyoxal in a similar way and give similar intermediates.

Now although the tetramer can be monoacetylated and diacetylated also, its behaviour with monoaldehydes (e.g. benzaldehyde) does not resemble that of normal ortho diamines. Only one aldehyde molecule reacts, and the product is an open-chain compound. Hinkel visualised the structure of the derivative as



There is, indeed, little doubt that one molecule of aldehyde, and one alone, will react with the tetramer. At Canterbury, in experiments in which a monoaldehyde derivative of the tetramer was made to react with a different aldehyde a further aldehyde group could not be introduced, but it was of some interest to find that a series of displacement reactions could be carried out. Thus if the benzaldehyde derivative above was made to react with p-nitrobenzaldehyde, the latter displaced benzaldehyde to give, as the only product,



p-Nitrobenzaldehyde would also displace p-hydroxybenzaldehyde from its tetramer derivative and p-hydroxybenzaldehyde could also be displaced by benzaldehyde itself. Under our conditions it was not possible to reverse these displacements. The displacements do, however, fall into a rational order; the order of displacing powers is the order of di-pole moment values for the aldehydes and it seems reasonably clear that the displacement of one aldehyde by another will occur when the displacing aldehyde possesses a carbonyl carbon atom of greater electron-deficiency than the original aldehyde. It may also be assumed that it is the reversibility of the aldehyde condensation reaction which allows all these apparent displacements to occur.

This takes us a little way from the Hinkel-Trochimovsky polemic. After Hinkel's arguments had been published, Trochimovsky made the suggestion that a tautomeric relationship between the two forms would clear up the points at issue. Hinkel would not accept this. He claimed that there was no evidence for tautomerism, although he had indeed been compelled to assume hydrogen migration and double bond rearrangement in formulating some of his reaction schemes. Hinkel did, however, produce the only conclusive published evidence for one of the two structures. Hinkel's amino-imino structure carries an asymmetric carbon atom and, in 1940, Hinkel and Watkins succeeded in resolving the d-camphor-sulphonate of the tetramer. It should be noted, however, that when they liberated the base, it was optically inactive, suggesting high lability of the key hydrogen atom and this indication of tautomerism was supported by the ready interconversion of the diastereoisomerides on simple solution. To us it seemed that Trochimovsky's suggestion of a tautomeric system was the logical one. Indeed, it would be surprising if such a structure did not display prototropy. With Hinkel sitting on a unique piece of evidence (the only unambiguous one) supporting the

reality of his proposed formula, we then had to decide on a line of approach best calculated to lead to unambiguous evidence in support of the diamino formula, if that also has reality. The chosen approach (Robertson, Thesis 1953) is one similar to that pursued independently by Webb (1955) and by Bredereck (1956).

Of the two structures, the diamino form contains what one can call a triple conjugated system, while in the other formula the conjugated chain is shorter. The ultra-violet spectra of the tetramer and some chosen derivatives could thus be of some interest. Let us start by considering the two forms of the unsubstituted tetramer. For comparison with Hinkel's formula, butadiene has a wave-length of maximum absorption at less than 2200A and the replacement of an olefinic bond by a nitrile or ketimino grouping (e.g. in N-n-butylcrotonaldimine) results in only a very slight change in $\lambda_{max.}$. The highest recorded $\lambda_{max.}$ in such a system (and there are many available for comparison) is 2500 A (propylene cyanide) and it seems reasonable to expect, from the available data, that if the tetramer exhibited the characteristics of Hinkel's formula, $\lambda_{max.}$ would not be above 2500 A. On the other hand, with a triple conjugated system, as in Trochimovsky's formula, recorded values for $\lambda_{max.}$ lead us to expect a value slightly above 2800 A, at which wavelength the closely related maleonitrile displays a maximum. The tetramer gives a simple curve with a well-defined wavelength of maximum absorption at 2980 A. Webb (1955) has also found this and regards it as strong evidence for the diamino structure.

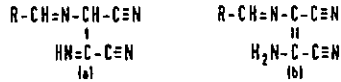
Now on the introduction of an acetyl group into the molecule the three possible structures for the acetyl derivative are:

Structure (1) possesses a more extensive mesomeric system than the original amino-imino structure. We should expect an appreciable shift in the absorption peak. If the acetyl derivative possessed structure (2) or structure (3) it is probable that its spectrum would be similar to that of the tetramer structure from which it is derived. The spectrum is, in fact, closely similar to that of the tetramer, with $\lambda_{max.}$ being very slightly lower (less than 2900 A). This favours the choice of structure (2) or (3).

Consider these two only and assume the introduction of a second acetyl group to give the diacetyl derivative. When the second group is attached to structure (2) we should again expect a marked change in $\lambda_{max.}$, because of more extended mesomerism. With structure (3) little change is probable. The

spectrum of the diacetyl derivative is, in fact, similar to that of the monoacetyl dericative, and hence to the tetramer, with $\lambda_{max.}$ at 2900 A. The implication of these results has received support from the work of Bredereck, who has since established by infra-red examination that both acetyl derivatives in the solid state have the diamino structure.

For us, however, the spectra of aldehyde derivatives of the tetramer proved of greatest interest. There are two possible structures for these derivatives:



In structure (b) the azomethine double bond is linked with the conjugated chain of the tetramer molecule. In (a) it is isolated. It is known (e.g. Braude 1945) that when isolated systems are present in the same molecule, the resultant spectrum is usually the sum of the individual spectra. Thus derivatives of type (a) would be expected to give rise to spectra with peaks corresponding in wavelength (and intensity) to those of both tetramer and azomethine residue.

We prepared a number of these azomethine derivatives and in no spectrum was there an absorption maximum approximating to that of the tetramer. This weighs heavily against the possibility of structures like (a). The introduction of an azomethine group results in a marked increase in the wavelength of the main absorption peak and it is of further interest to note that this effect is progressively enhanced by making R an increasingly long conjugated system:

Substituent		$\lambda_{max.}$
None (Tetramer alone)		2980
	(Isobutylidene derivative)	3150
	(Allylidene derivative)	3430
	(Benzylidene derivative)	3600
	(Cinnamylidene derivative)	3720

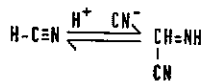
It will be seen that the tetramer and its isobutylidene, allylidene, benzylidene and cinnamylidene derivatives form a series in which the length of conjugated system (and consequently $\lambda_{max.}$) is increasing. It may be noted also that when analogies are drawn with known compounds containing conjugated chains of the same length as in these derivatives (assuming that they are based on the Trochimovsky structure), the main absorption peaks are in agreement.

It would seem reasonable, therefore, to assume that the combination of Hinkel's resolution experiments and the later work of Bredereck, Webb and the Canterbury group indicates fairly strongly that the tetramer has a tautomeric structure.

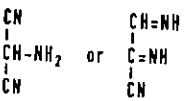
3. Possible Mechanism of Polymerization:

The structure of the black azulmin is not known and no work appears to have been carried out on the way HCN may polymerize. We can suggest a possible, but simplified, structure for the polymer. However, although none of the data at our disposal conflicts with this hypothetical scheme it is well worth emphasizing that circumstantial evidence is unsatisfactory. The scheme requires to be put to the test and convincing tests have yet to come.

It is generally assumed that the polymerization is initiated by cyanide ions. Thus the first step is almost certain to be



This dimer can add a further molecule of HCN in two ways, to form either



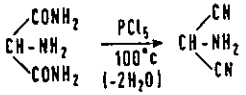
With the formula on the right, the process could be continued but the resulting structure — a polyketimine could not represent the polymer. Apart from the fact that even a simple α, α'-diketimine has never been reported, certain of the properties of the HCN polymer seem incompatible with such a structure.

The formula on the left is of much greater interest. It is the formula of aminomalononitrile, which had originally been assigned to the white crystalline polymer when chemists assumed that the white material was a trimer of HCN. The structure is a disarmingly simple one, but certain facts made us interested in this possible intermediate. For example, patents have been taken out for certain metal powders as inhibitors of the polymerization reaction. In all cases the metals covered by the patents were metals capable of forming complexes with amino groups. The trimer, if produced as indicated, is the first compound in the reaction scheme which possesses a primary amino group and, while other answers are possible, our attention was drawn to the possibility of amino-malononitrile being a key intermediate in the polymerization.

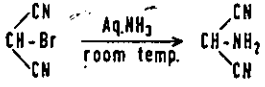
But it would not appear to be a particularly unstable molecule and synthesis should prove relatively easy. However, its preparation has never been reported. We attempted to prepare it and

two of our simple experiments were the following:

First,

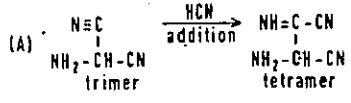


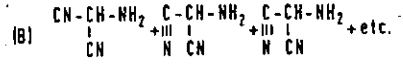
What was obtained on dehydration of aminomalonamide was a black material indistinguishable from azulmin by the means at our disposal. Considering that the conditions may have been too severe, we then carried out another simple experiment

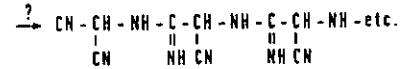


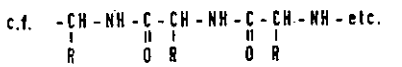
Addition of ammonia led to an exothermic reaction and to a product which again appeared to be azulmin. In neither case could we separate any product other than the assumed "black polymer."

It is possible, then, that aminomalononitrile is an unstable, key intermediate in the polymerization process. It is also possible, judging from the apparent results of attempts to prepare this trimer, that it is the trimer itself which polymerizes. But we must, in addition, account for the formation of the known tautomeric tetramer when HCN is polymerized. A possible scheme is the following:









It will be noted that the hypothetical polymer chain bears certain resemblances to a polypeptide structure. Assuming this scheme, we can look at certain known facts with more purpose. For example, the tetramer decomposes at its melting point and the black residue appears to be azulmin. On part (A) of the above scheme, one would predict a breakdown of the tetramer to HCN + trimer, followed by polymerization of the latter. On decomposition of the tetramer, HCN is, in fact, evolved. We can now

place an upper limit to the amount of HCN likely to be released in this manner. Each molecule of tetramer would be expected to give one molecule of HCN but it is easy to predict that part, at least, of the HCN would itself lead to polymer in the basic medium in which it is formed. Thus we should predict somewhat less than 1 mole HCN per mole of tetramer, but certainly not more than 1 mole. Quantitatively, it is found that the tetramer, on thermal breakdown in an inert solvent, gives rise to 0.65 mole HCN per mole tetramer.

Finally, the proposed polymer structure suggests certain possible experiments. To give one example, in the long chain formula there is a recurring pattern of three nitrogen atoms and it is to be noted that one N atom in three is present as a ketimino group, a group known to be very susceptible to acid hydrolysis. On mild treatment with dilute hydrochloric acid, only this nitrogen atom should be converted into ammonium chloride, and on such hydrolysis the predicted release of nitrogen should be one atom for every three in the polymer. When hydrolysis was carried out until ammonia production practically stopped, the results of three separate experiments gave 0.86, 0.90 and 0.91 atoms of "hydrolysable" N for every three in the polymer. This is very satisfactory agreement with the predicted result. Other reaction schemes for the polymerization are clearly possible, however, and we are a long way from an understanding of this intriguing and somewhat neglected reaction.

VITAMIN A — AN ASSESSMENT OF PRESENT KNOWLEDGE.

By W. A. McGILLIVRAY,

Biochemistry Department, Massey College, Palmerston North.
(Based on Chairman's address delivered to Manawatu Branch in June, 1958.)

Vitamin A is one of our oldest vitamins. In fact, the recognition of a substance in certain foods capable of correcting the inability to see properly at night, dates back several thousand years. An ancient Egyptian medical treatise of about 1500 B.C., recommends roast ox-liver or the liver of a black cock as curative agents, while Hippocrates also advised liver but in a less palatable form — dipped in honey and eaten raw. Then again the prophet Jeremiah gives probably the first description of vitamin A deficiency in animals when he records that, "the wild asses did stand in the high places, they snuffed up the wind like dragons; their eyes did fail, because there was no grass". The identification of vitamin A in the livers, and of carotene in the grass, as the chemical factors responsible had to wait over three thousand years. During the past few years there have been some very significant advances in our

knowledge of vitamin A and in this talk I am going to attempt, very briefly, to high-light some of the areas where real progress has been made against the much wider background where a great deal more work is necessary before a completely clear picture can be presented.

You may wonder, as I have often done, why the old vitamin terminology has been retained for vitamin A whereas it has been replaced by chemical names for all the other vitamins. This is especially surprising when we consider the confusion which may arise when using the term "vitamin A." Do we, for example, mean just preformed vitamin or do we include pro-vitamins? Do we include vitamins A_1 and A_2 or has usage in particular cases limited the term to A_1 only? The lack of a suitable chemical name is not through want of trying on the part of some workers. Karrer has suggested "axerophthol" but as well as being clumsy it suggests that the action of the vitamin is restricted to the eye. "Axerosol" or "axerol" imply a more general action and are better. "Retinol" is gaining favour but again only refers to one function of the vitamin. It also gives "retinal" for the aldehyde, the same spelling as the adjective meaning "belonging to the retina"; hence, as Moore points out, as the aldehyde is frequently discussed in relation to its function in the retina, we could find ourselves talking about "retinal retinal."

These problems will no doubt give international conferences material for many years of deliberations and, in the meantime, we must make the best of "vitamin A."

Vitamin A, like several other vitamins, was dabbled with from about the turn of this century but real progress dates from the classical work of Thomas Moore in the 1920's which culminated in 1929 in his demonstration that the vitamin A appearing in the body was derived from the yellow carotenoid pigments of plant origin.

Carotenoids are widely distributed in plants but as yet we have no precise knowledge of their function. Early suggestions that they were mainly excretory products of unknown metabolites, their water insolubility removing them from active participation in the cell metabolism, seem untenable and most theories regarding their function in plants are based on their two characteristic properties — their ability to absorb oxygen, and their ability to absorb light energy in the blue region of the visible spectrum.

Thus we find that the occurrence together in plants of the carotenoid hydrocarbons, the carotenes, and of their oxygenated derivatives, the xanthophylls, has led to the suggestion that these materials may function as a perfect oxidation-reduction system. The association of carotenoids with chlorophyll in the plastids has been thought to imply some participation in the photosynthetic

process, either actively by a process such as the transfer of excitation energy to chlorophyll, or more passively by being mobilised to act as filters to protect the chlorophyll from intense light which would inactivate photosynthesis. Then again the concentration of carotenoids in pollen grains suggests some intimate association with the reproductive process. Quite convincing evidence has been produced in support of all these suggestions but the action of the carotenoids cannot be regarded as specific in any of these cases since plants appear capable of normal growth and reproduction in the absence of general or localised concentrations of carotenoids.

One function of carotenoids in plants does, however, seem clearly established. This is the part the carotenoid pigments play in photokinetic responses such as phototropic bending and chloroplast migration. Carotenoids are present in all photosensitive structures and their absorption spectra correspond very closely to the photokinetic action spectra which in turn are distinct from the absorption spectra of any other pigments also occurring in photosensitive structure. (Action spectra are constructed by plotting the reciprocal of the energy at different wavelengths required to elicit a constant phototropic response, against these wavelengths.) Thus for example the action spectrum for the bending of seedlings towards light is identical with the absorption spectrum of the mixed carotenoids present and there is a strong body of evidence along similar lines for many forms of plant life and for lower forms of animal life. I am not going to deal with this in any further detail but mention it because the part played by carotenoids in phototropism is of interest in connection with the clearly established role of vitamin A itself in the visual process which I shall be discussing later.

When plants are eaten by animals, the carotenoids may be absorbed, rejected or destroyed. If they are absorbed they may be stored in unchanged forms or they may be converted into vitamin A or into other predominantly animal pigments such as astaxanthin. The mechanisms which control this rejection or modification are characteristic of species or sometimes of varieties within one species. Thus, if we consider different animals on a diet containing various carotenoids, we find that sheep, for example, will accumulate virtually no carotenoids in their bodies. Depending on the breed, the body fat and milk fat of cattle will be coloured to varying degrees mainly with carotene. The ratio of carotene to xanthophyll will depend on the breed of the cow. Humans will non-selectively accumulate all the carotenoids fed. In poultry the fat will be coloured only by xanthophyll.

Mammals, therefore, fall into three classes:

(a) non-specific carotenoid accumulators, e.g. humans.
(b) primarily carotene accumulators,, e.g. cattle.
(c) non-accumulators of carotenoids, e.g. sheep.

Birds on the other hand are primarily xanthophyll accumulators, as also are fish.

The significance of these differences in carotene absorption is not known but the tendency in some species for carotenoids to accumulate in certain organs and to be selectively mobilised would suggest specific functions for these pigments unassociated with their possible conversion to vitamin A. This applies particularly to lower forms of life such as marine invertebrates which possess the unique ability to produce a series of rather interesting, highly-oxygenated carotenoids.

The special ability to convert certain carotenoids to vitamin A is limited to the higher forms of life — mammals, birds, some amphibia and probably fish.

The mechanism of this conversion is one of the major unsolved problems in the vitamin A field. A consideration of the structures of β-carotene and vitamin A would suggest, as a possible mechanism, fission of the central double bond of β-carotene with the addition of two molecules of water to give two molecules of vitamin A, and this was accepted for a considerable time.

There is, however, strong evidence against such a reaction and more recently Glover and Redfearn have presented evidence in favour of the alternative mechanism — the stepwise oxidation of one end of the carotene molecule. Under suitable conditions carotene may be oxidised to retinene (vitamin A aldehyde) by hydrogen peroxide. The attack is initially on one of the terminal double bonds of the carotene molecule. A somewhat similar attack *in vivo* would produce a series of aldehydic intermediates of decreasing chain length. Glover and Redfearn prepared a number of these possible intermediates and showed that they could all be converted to vitamin A in the rat. Thus they suggest a type of β-oxidation of the carotene molecule to form vitamin A aldehyde, as indicated in Figure 1.

Why should the oxidation stop at the vitamin A aldehyde stage? Up to that point the methyl groups are in the α position to the carbonyl group but vitamin A aldehyde is substituted in the β position. Branched chain fatty acids are oxidised *in vivo* when the methyl group is in the α position but not when it is in the β position to the carboxyl group. The picture therefore is one of oxidation to vitamin A aldehyde. This cannot be oxidised further but the enzyme, alcohol dehydrogenase, provides a means for its reduction to vitamin A. Although the conditions are very different

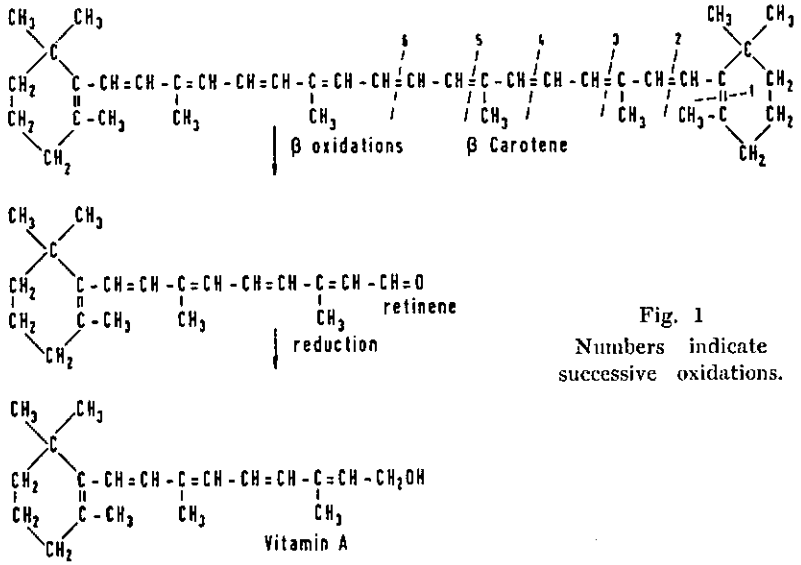


Fig. 1
Numbers indicate successive oxidations.

it is of interest to note that our work in this Department on the utilization of intravenously administered carotene strongly indicates a similar type of reaction. Further evidence in support of this theory of stepwise oxidation is provided by the identification of apo-10- and 12-carotenals in the intestine during the conversion of carotene to vitamin A.

However, this mechanism must still be regarded as a tentative theory only, and it has in fact received something of a setback by the demonstration that a C_{25} homologue of vitamin A could be converted to vitamin A in rats. This homologue, in which the polyene chain is extended by five carbons, has a methyl grouping in a β position to the alcohol group — the same terminal arrangement that we have in vitamin A — and yet this group does not inhibit oxidation. However, vitamin A storage from this compound is much less than from the corresponding alcohol with an α-methyl group so that if the β-methyl group does not completely inhibit oxidation in this type of compound, at least it may retard it sufficiently to allow, in the case of a compound like retinene, some vitamin A formation.

The real problem in connection with carotene-vitamin A conversion work is that it has not been possible to unequivocally demonstrate conversion *in vitro*. There have been plenty of claims to have effected this conversion but it is very difficult to be sure that vitamin A is really formed. Conditions under which vitamin A might be anticipated also favour random oxidation of carotene to yield products which can easily be mistaken for the true vitamin but which have no vitamin A activity when tested

biologically. It must be remembered too that even *in vivo* the yield of vitamin A from carotene is very small, so that *in vitro* it is a matter of separating any traces of vitamin A formed from a mass of unchanged or partly decomposed carotene.

For the identification of vitamin A we have the characteristic absorption curve with a maximum at 325mμ. There is also the reaction with reagents like antimony trichloride which gives coloured compounds with characteristic absorption curves and, perhaps even more useful, characteristic rates of fading. Chromatography is a strong tool for purification of course, and the mixed chromatogram technique is used for identification of products. Biological activity can also be tested. In spite of all these tests many workers, even some very experienced ones, have reported the formation of vitamin A *in vitro* only to find later that the substance identified as vitamin A was possibly only an artifact. A test which we have developed in this laboratory and found most useful is based on esterification by an intestinal esterase. In the presence of this enzyme vitamin A is rapidly converted to the ester but artifacts are not affected. For example, in incubation experiments we obtained a substance which answered all the tests for vitamin A — that is, all the tests we could apply at the concentrations we were able to obtain. Our tissue preparations contained about 10μg vitamin A and incubation of these with carotene consistently appeared to increase this to about 20μg. However, on further incubation with the esterase we obtained only 10μg vitamin A ester and a substance equivalent to about 10μg vitamin A remained in the alcohol fraction. In other words the vitamin A originally present had esterified normally but our product was not vitamin A. Using critical tests of this type Worker has recently repeated many reported *in vitro* conversions of carotene to vitamin A. In every case the result has been negative — conclusive evidence of any vitamin A formation was lacking under the wide variety of likely conditions investigated.

Whatever the mechanism, the intestine is the main site of conversion, and vitamin A, which is absorbed as such or formed there from carotenoids, is transported via the lymphatic system to the systemic blood and thence to the liver where it is stored. Blood and presumably tissue levels of the vitamin are maintained from this liver store. It is fortunate that we can readily distinguish between freshly absorbed vitamin and material which has been released from the liver to maintain blood levels. The former is in an esterified form whereas the latter appears as the free vitamin A alcohol. In the case of carotene accumulators such as cattle, the blood picture appears to be:—

(a) a fairly constant level of vitamin A alcohol in the form of a protein complex and maintained from body reserves.

(b) a similar fairly constant level of carotene and some xanthophyll again in the form of protein complexes.

(c) chylomicrons containing fat, carotenoids and vitamin A ester.

This latter material is all of immediate dietary origin and is variable in carotenoid and vitamin A content depending on the feed of the animal.

I will refer to the significance of this later but let us first look at the vitamin A which is stored in the body. By far the highest concentration is in the liver. Some — about 5% — appears in the blood, kidneys, adrenals, fat deposits and other non-hepatic tissues. A trace — 0.1% of the total — is in the retina of the eye. It is somewhat paradoxical that it is about the function of this trace that our knowledge is most complete. The remaining 94.9% is in the liver and is probably held in passive storage. Despite many theories, we know little about the 5% distributed through the body. I shall deal, therefore, only with the 0.1% which enters into the visual process.

In considering the role of any substance in vision, we must recognise two distinct visual processes—scotopic and photopic vision. The former is concerned with vision in light of very low intensity while the latter mechanism takes over as the light intensity increases and differs from scotopic vision in that there is discrimination of colour as well as of brightness. It is with scotopic vision that we are particularly concerned here since the classical symptom of vitamin A deficiency has always been night-blindness — the inability to see clearly at low levels of illumination particularly at dusk after exposure to bright light during the day.

It has long been known that the retina contains a light-sensitive pigment. Known as "visual purple," although actually it is red in colour, this substance, on exposure to light, undergoes a series of changes producing a number of transitory intermediates before "visual yellow" and finally "visual white." After bleaching, "visual purple" is regenerated in the dark and we have all experienced this as we "become accustomed to the dark" on passing from intense to dim light. The rate of regeneration varies with individuals and does in fact depend on the vitamin A status of the subject. Clearly then, vitamin A is involved in the visual process and the study of the mechanisms involved, mainly by Wald and his associates, has been described as the most fascinating one in the whole field of biochemistry.

Figure 2 indicates the structure of the vertebrate retina. The rods and cones which act as photo-receptors are placed with their free ends directed back on to the pigment epithelium and away from the source of light. The human eye contains about 7 million cones, which are concerned with acute vision in strong light and with the appreciation of colour, and between 70 and

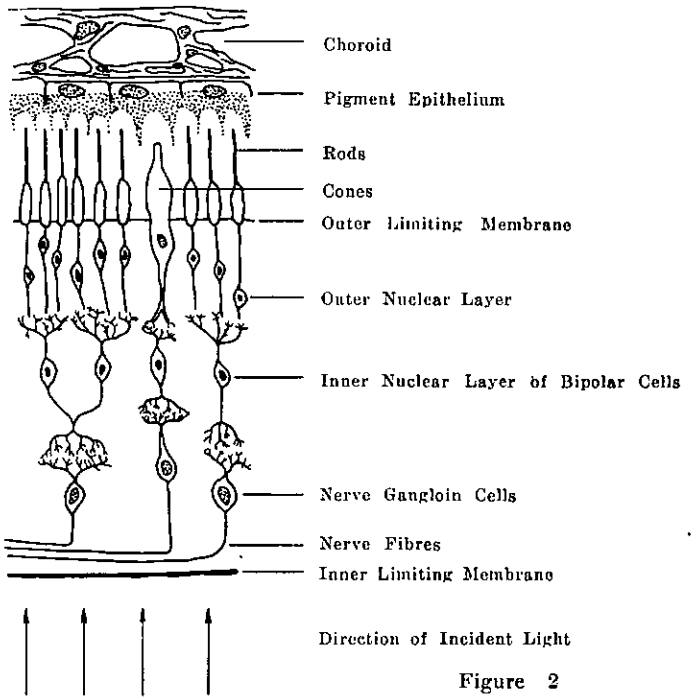


Figure 2

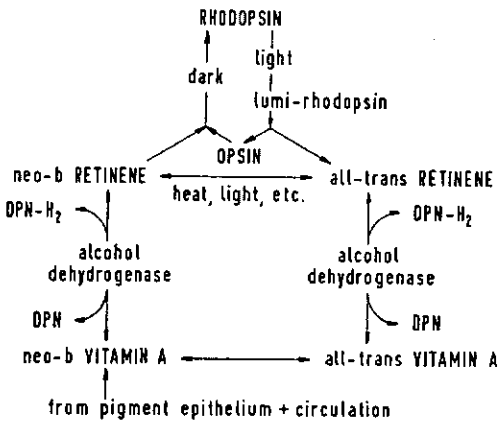
140 million rods. The "visual purple," or rhodopsin as it is now named, is contained in the outer limbs of these rods which are shown in black in the figure. In strong light these rhodopsin containing ends are shielded by pigment of a melanin type protruded from the pigment epithelium. In weak light the pigment covers the cones and the rods are exposed. This change from the visual process involving cones to that involving rods, i.e. from photopic to scotopic vision, shows up as a distinct break in light adaption curves.

To summarise, very briefly, the experimental evidence regarding scotopic vision, the pigment obtained from retinal rods will undergo a series of changes on exposure to light. A protein, opsin, is released and if the retinas are fresh and have not been hardened by materials such as alum, vitamin A is the other end product—"visual white." With old or hardened retinas, retinene is formed—"visual yellow." The rod ends, which contain all the rhodopsin, readily become detached from the wider inner segments during dissection. When a suspension of these rods was bleached, retinene was formed, but when an extract of the rest of the retina was added the retinene was reduced to vitamin A. The retinal extract could be replaced by reduced diphosphopyridine nucleotide, DPN-H_2, or by DPN plus fructose diphosphate to facilitate its reduction to

DPN-H_2. Thus the system for rhodopsin bleaching required, in addition to light, an apo-enzyme, retinene reductase, DPN and fructose diphosphate. The enzyme is present with rhodopsin in the rod outer limbs.

Based on these reactions, Wald was thus able to propose a model system for the break-down of rhodopsin under the action of light and for its reconstitution.

This worked extremely well with natural vitamin A isolated from fish-liver oil but failed when attempts were made to regenerate rhodopsin from opsin and synthetic vitamin A. Wald in his model system had found the regeneration of rhodopsin from bleached retinal extracts a slow reaction and had obtained poor yields. It was also observed that rhodopsin bleached with yellow light would not regenerate as well as that bleached by blue light. Now blue light will promote cis-trans isomerism for which there is ample opportunity in the vitamin A molecule and Wald confirmed the importance of this isomerism by showing that all-trans retinene would not combine with opsin to form rhodopsin. After experiments with various retinene isomers it was found that rhodopsin formation took place successfully with neo-b retinene which is the 2, 4-di-cis isomer. The retinene liberated from rhodopsin by yellow light — the form that will not reconstitute readily — was found to be the all-trans isomer. Thus retinene must be combined with opsin in one form and released in another form. It is in fact combined as the 2, 4-di-cis isomer and released as the all-trans isomer. The complete cycle of events is as follows:—



The vitamin A isomerism required can take place quite readily in the body and the neo-b vitamin A required for the regeneration of rhodopsin is normally supplied from the blood. The rate of regeneration is therefore proportional to the level of vitamin A in the blood and hence to the vitamin A status of the subject.

It is probable that the visual impulse is associated with an initial photochemical transformation of rhodopsin into the orange-red lumi-rhodopsin. The succeeding steps in the bleaching of rhodopsin to "visual white" may provide merely a convenient way of putting the rods completely out of action in bright light.

The key role of opsin in scotopic vision must not be overlooked. The liver, intestinal wall and probably many other tissues contain all the enzyme components necessary for interconversions between vitamin A and retinene. Apparently only the retina contains, in opsin, a suitable aldehyde trapping agent which is capable of stabilizing retinene. Elsewhere in the body the equilibrium is strongly in favour of vitamin A.

Our knowledge of photopic vision is less complete despite the research activity concentrating on it. Nevertheless it does seem that vitamin A again plays an indispensible part in the process probably as a component of the modulators which are responsible for colour perception. The light sensitivity of these modulators corresponds closely to the absorption spectra of certain vitamin A and retinene derivatives.

I am going to pass over the tremendous literature relating to symptoms of vitamin A deficiency, vitamin A requirements in health and in disease, effects of excess vitamin A, vitamin interrelationships, etc. Much of this work, particularly on the clinical side, is confused and rather contradictory and one is left with the feeling that there must be very few clinical symptoms which some one has not claimed are caused by, aggravated by, cured by or otherwise associated with vitamin A.

At the same time we can recognise certain definite symptoms of vitamin A deficiency — xerophthalmia in the eyes, keratinisation in the mucous membranes, defective modelling of the bones, a thinning of the skin, increased clotting time of the blood, resorption of the foetus, congenital abnormalities, etc. Of course these are not all specifically due to a vitamin A deficiency. Other conditions can cause, individually at least, many of these symptoms, but if the vitamin A intake is low, or if some pathological condition has interfered with normal vitamin A absorption or metabolism, we may expect to find any or all of these symptoms showing up. The symptoms are very diverse and could themselves lead to other secondary symptoms so that most workers recognise a very wide spectrum of vitamin A deficiency. It must be remembered too that animals differ in the order in which these symptoms develop and in their severity. Knowing that an animal is deficient in vitamin A and watching for the symptoms to develop is one thing; diagnosing, without a knowledge of the dietary history of the subject, that, for example, the enteritis, which often proves fatal

before more specific symptoms have had time to develop, is due to vitamin A deficiency, is quite another problem. This does lead to the idea that vitamin A therapy is a good thing to try as a routine procedure when no organic disease or other deficiency is indicated. And cures sometimes result. The more sceptical of us will tend to feel that in many of these cases the tissues, subjected to a series of opposing forces including vitamin therapy, have somehow contrived to cure themselves.

At the same time it is interesting sometimes to see how apparently unrelated and unlikely observations come together and I would like to conclude with one recent example from the milk secretion field to show how a series of such observations has been linked into a fairly complete picture.

It is obvious that many milk components, including the fat-soluble vitamins, must derive directly from the blood. We would therefore expect fairly close relationships between the levels of the fat-soluble vitamins in the blood and in the milk. With the carotenoids and vitamin A, the correlation is a reasonable one throughout the year but when there is a sudden change in feed, such as a switch from pasture to a carotene-free diet, the levels in the milk drop sharply whereas the decrease is much slower in the blood. Again, at the onset of lactation the colostrum is very rich in carotenoids and vitamin A but blood levels of these substances are abnormally low at this time. The blood and milk vitamin picture is somewhat similar when there is a diseased condition of the udder, such as mastitis. There is also the fact that milk levels of carotenoids and vitamin A depend very largely on the immediate dietary intake of these substances whereas blood vitamin A, at least, is maintained mainly from liver reserves.

Clearly the picture is not altogether consistent but all these observations can be explained if we assume the uptake by the mammary gland of two different forms of carotenoids and vitamin A from the blood. This brings us back to the point I mentioned earlier about two physically distinct forms of carotene and vitamin A in the blood. Carotene and vitamin A of immediate dietary origin are found in the chylomicrons and it is clear that the uptake of these by the mammary gland provides the main source of milk vitamins. Vitamin A alcohol and some of the carotene in blood occur in protein-bound forms and the proteins to which they are attached are apparently those which can be taken up directly by the mammary gland. During the changes which occur in the cells of the gland, much of the carotene and vitamin A alcohol is dissociated from the proteins and transferred to the fat phase, the vitamin A being esterified in the process. At the start of lactation or in diseased conditions of the udder there is an abnormally high uptake of blood globulins by the mammary gland. These globulins carry with them correspondingly large quantities of

carotene and vitamin A and thus the concentration of carotene and vitamin A in the milk is much higher than normal. Under these conditions transfer from protein-bound state to fat phase is incomplete as is also the esterification of the vitamin A alcohol so that we find the appearance in the milk of protein-bound forms of carotene and vitamin A alcohol very similar to the forms in the blood. These forms are most apparent in pre-partum secretions, decrease through the colostral period and are present as traces only in normal milk.

Nevertheless there is sufficient protein-bound carotene in normal milk to afford a logical explanation for the somewhat unusual observation that carotene is apparently much more concentrated in the smaller fat globules of milk than in the larger ones. Despite the mathematical exactitude with which some workers have calculated the thickness of the surface layers which are supposed to explain these concentration differences, it seems surprising that a non-polar material like carotene should concentrate at an interface more than, say, vitamin A. The presence of protein-bound forms of carotene in the milk affords a more likely explanation since this carotene would be extracted along with the fat. Its effect would be negligible where the fat to milk-serum ratio is high as is the case when larger globules are considered, but it would become important in the case of the smaller fat globules where the fat to serum ratio is very low. Other methods of fat extraction have confirmed that the carotene content does not change with decreasing fat-globule size and that the apparent increase is due to the extraction of protein-bound material with the fat.

It seems clear that the low blood levels of carotene and vitamin A near parturition are the result of the abnormally high uptake of globulins (with their associated fat-soluble material) by the mammary gland and are not due, as had previously been accepted, to any hormonal imbalances connected with parturition. The actual amounts of carotene and vitamin A lost from the blood are very closely related to the extra quantities of these substances secreted in the colostrum, and in the colostrum itself there is also a close correlation between the amount of globulin secreted and the extra amounts of carotene and vitamin A.

Thus the amounts of carotene, vitamin A and probably other fat-soluble vitamins in the milk depend on the ability of the mammary gland to take up proteins and chylomicrons from the blood and on this basis a large number of experimental observations, sometimes apparently unrelated and somewhat anomolous, can readily be explained.

As a final thought, it is interesting to note the occasional use of vitamin A as a marker in following, for example, fat absorption. This is a technique capable of much wider application and in the

milk secretion field it is highly probable that carotene and vitamin A, existing as they do in two distinct forms in the blood, will prove extremely valuable markers with which to follow the uptake of blood constituents by the mammary gland and with which to study the origin of milk fat and milk proteins.

NEWS AND NOTES.

AUCKLAND BRANCH:

The retirement of Mr. K. M. Griffin, a Past-President of the Institute was marked by a complimentary luncheon tendered by the Auckland Branch in the Domain Kiosk. The gathering was presided over by Dr. A. L. Odell, Branch Chairman, and the valedictory speech was made by Emeritus-Professor F. P. Worley, who had been associated with Mr. Griffin since the formation of the Auckland Chemical Society in 1925 when Professor Worley was President and Mr. Griffin Vice-President.

In reply Mr. Griffin touched on various aspects of his career and voiced the opinion that, as the work of the Dominion Laboratory was so closely concerned with the activities of the Police and the Health Departments, it would be better if it was independent of the D.S.I.R. which was primarily concerned with research. He could not help feeling that the very necessary services rendered by the laboratory and its staff might then be much better appreciated, and referred to the situation in Great Britain where the forensic laboratories were administered by the Home Office.

Mr. Griffin will be greatly missed by all the chemical fraternity in Auckland where his co-operation with all other members of the Institute has been a notable feature of his tenure of the office of Government Analyst, a position which he has held for 34 years — believed to be a record for a civil servant in one position in New Zealand. Mr. and Mrs. Griffin are at present in Japan where Mrs. Griffin's brother, the Hon. J. S. Reid, is the New Zealand Ambassador.

MANAWATU BRANCH:

Two members of the staff of the Plant Chemistry Division, D.S.I.R. are leaving shortly for the United Kingdom. Dr. J. L. Mangan has accepted a post in the Department of Biochemistry, Institute of Animal Physiology, Babraham, England, and Dr. R. Bailey has taken up a D.S.I.R. (U.K.) Senior Award Research Fellowship at the Royal Holloway College, University of London.

The September meeting of the Manawatu Branch took the form of a Ladies' Night. The function, which is an innovation for this Branch, was well attended by members and wives and proved a most pleasant and successful one. The guest speaker, Mr. S. G. Brooker of Auckland, chose for his address the rather intriguing title, "A Chemist in the Kitchen." In his opening remarks Mr. Brooker pointed out how appropriate it was for a chemical group to arrange a function of this sort since after all "at heart every chemist is a Lady's Knight."

We offer to Dr. F. H. McDowall, Chief Chemist, The Dairy Research Institute, our congratulations on the award of the Gold Medal of the Australian Society of Dairy Technology. This is the first award of the medal outside Australia and it was made in recognition of Dr. McDowall's contributions to the dairy industry, special mention being made of his text "The Buttermaker's Manual."

WELLINGTON BRANCH:

Mr. J. R. Beck, Wellington Branch Editor, himself provides an item of news this month. He is representing New Zealand Breweries Ltd., at the Annual Convention of the Institute of Brewing, Australian Section, at Perth. He is visiting breweries and laboratories in Sydney, Melbourne and Adelaide on the way.

Mr. I. K. Walker, Dominion Laboratory Wellington has returned from a four month tour of laboratories in Great Britain and the United States.

Mr. J. K. Johannesson, Chief Chemist at the Wellington City Council Laboratory, has been awarded the I.C.I. Prize for 1958. His work was mainly in the field of analytical methods in connection with water supplies.

Mr. A. J. Metson, Principal Scientific Officer, Soil Bureau, D.S.I.R. left in August for a visit of about 2 months to the United Kingdom, France, Switzerland, Germany, Holland, and Spain. He will attend a meeting of the International Society of Soil Science in Hamburg, an International Symposium on Potash in Madrid and visit institutions where work is being done on analytical methods and potassium in soils.

Mr. T. A. Rafter, Director, Division of Nuclear Sciences, D.S.I.R. left in August for Sydney, Bombay, Europe, Great Britain, the United States and Canada. He will attend the 2nd United Nations Conference on the Peaceful Uses of Atomic Energy at Geneva and the Commonwealth Atomic Scientists' Conference in the United Kingdom. After these meetings Mr. Rafter will visit nuclear research institutions and manufacturers of equipment.

CANTERBURY BRANCH:

Mr. R. W. Cawley has resigned from the staff of T. J. Edmonds and Co. Ltd., to rejoin the Wheat Research Institute, Christchurch.

Mr. A. H. Hunt has joined the firm of H. F. Stevens Ltd., Wholesale Druggists, Christchurch.

Mr. H. D. Orchiston formerly of Canterbury Agricultural College, has accepted the position of Agricultural and Scientific Advisor for Australasia to the Chilean Nitrate Corporation. He will be working in Sydney.

New Zealand lost an outstanding agricultural scientist when Professor T. W. Walker left Canterbury Agricultural College in June to take up a Chair of Agriculture at the University of Durham.

Mr. F. Barnes, formerly of N.Z. Forest Products Ltd., Tokoroa, has joined the staff of Fletcher Industries Ltd., Riccarton.

OTAGO BRANCH:

Professor H. N. Parton is at present in Geneva as one of the New Zealand delegates to the Conference on Atomic Energy.

Dr. R. D. Batt, Senior Lecturer in Biochemistry at the University of Otago, and this year's winner of the Morcom Green and Edwards Prize, is due to leave for overseas on Refresher Leave at the end of this year.

At the September meeting congratulations were extended to the firm of Dr. R. Gardner and Partners on the completion of 25 years' service in the consultant field. Dr. Gardner, the founder of the firm, has been a keen member of the Institute over many years.

COUNCIL MINUTES.

MINUTES OF A MEETING OF THE COUNCIL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.) HELD IN THE HAMILTON GIRLS' HIGH SCHOOL ON TUESDAY, 26th AUGUST, 1958.

PRESENT:

Prof. C. R. Barnicoat (President—in the Chair), Prof. L. H. Briggs (Vice-President), Dr. A. L. Odell (Auckland), Dr. E. B. Davies (Waikato), Dr. W. A. McGillivray (Manawatu), P. P. Williams (Wellington proxy), D. J. Hogan (Canterbury), Dr. A. D. Campbell (Otago), Dr. W. E. Harvey (General Secretary) and L. J. Rollo (Registrar).

CHANGE OF RULES:

Resolved.—That in Rule 13.2 the words "30 September" be amended to read "30 June." The Manawatu delegate opposed.

Resolved.—That Rule 13.8 be amended to read "All members of the Council shall hold office until the first day of September of the year following their election to the Council, except the Honorary General Secretary-Treasurer who shall retain his office until the first meeting of Council held after the 1st day of September of each year."

ROYAL CHARTER:

Resolved.—That Council approves of the principle that a referendum of all members be held to determine whether the Institute should apply for a Royal Charter, but that action be deferred until all the necessary information is available.

FLUORIDATION:

The Canterbury Branch suggested that Council should make a public statement of the chemical aspects of fluoridation. In the discussion it was pointed out that the aspects of the controversy concerning fluoridation which are of the greatest public interest are not those concerned with pure chemistry. One of the members of the Royal Commission which investigated fluoridation is a member of the Institute, a fact which members might bear in mind if they are asked to comment on the Commission's Report.

Resolved.—That no action be taken.

PRIZES:

Resolved.—That the sub-committee consisting of the President, the Hon. General Secretary, and the Wellington Delegate be authorised to bring forward an amended series of regulations for the Institute Prizes.

NUCLEAR TESTS:

Resolved.—That no action be taken.

CONFERENCE 1959:

The 1959 Conference will be held in Dunedin and Dr. A. D. Campbell expressed the willingness of the Otago branch to organise the Conference

L.A.C. REGULATIONS:

Resolved.—That Regulation 2.2.2 be amended to read "A candidate may be accredited with passes in Chemistry and/or Physics if he has passed in those subjects . . . . . "

EXAMINATIONS COMMITTEE:

Dr. Campbell has resigned from the Secretaryship of the Examinations Committee.

Resolved.—That Dr. A. D. Campbell be thanked for the good work he has done as Secretary of the Examinations Committee. Carried with acclamation.

Resolved.—That Council approve appointment of T. H. Kennedy as Secretary of the Examinations Committee.

"CHEMISTRY IN ACTION":

The Editor produced several copies of "Chemistry in Action" which will be distributed to post-primary schools, vocational guidance officers, etc. Members expressed warm appreciation of the fine work done by the Editor in producing such an attractive booklet.

LIST OF MEMBERS:

The publication of the new list of members has been delayed because of the tardiness of members who have not yet returned the questionnaire sent out. It is hoped to publish the new list in the near future.

SALARIES SURVEY:

The sub-committee has prepared a questionnaire which will be sent to members soon. It was emphasised that much of the value of the survey is lost if the response to the questionnaire is not as complete as possible.

STANDARDS INSTITUTE:

The President reported that as a result of a request by the Institute's representative on the Standards Institute (G. A. Lawrence), a telegram had been sent to the Director of the Standards Institute supporting the Institute's view that Standard Specifications should not be incorporated in Regulations. This question came into prominence when the Standards Institute learned that the Law Draughtsman wanted to incorporate (as distinct from cite) specifications in Regulations. This appears to be out of line with overseas practice. *Resolved.*—That the action taken by the Standing Committee be endorsed.

MEMBERSHIP:

Elections to Fellowship:—

CARRIE, Maxwell Stuart, M.Sc., F.R.I.C. (Chemist, Canterbury Frozen Meat Co.).

SIEMON, Stanley Robert, B.Sc., M.App.Sc., M.I.Chem.E., A.M.N.Z.I.E., A.R.A.C.I. (Professor of Chemical Engineering, University of Canterbury).

WILSON, Stuart Henry John, M.Sc. (Principal Scientific Officer, D.S.I.R.).

Elections to Associateship:

COCKBURN, Bruce Lindsay, M.Sc. (Assistant Master, Wellington College).

CLARIDGE, Mary Christine, B.Sc. (Chemist, B.A.L.M. Paints (N.Z.) Ltd., Auckland).

JOHNSTON, Alexander Lawrence, M.Sc. (Assistant Master Rongotai College, Wellington.).

McKENZIE, Graham Smith, B.Sc. (Chief Chemist, Southland Cement Co.).

PASTELIDIS, Demetre B.Sc.(Athens), (Chemist, Shell Co.).

SAMPEY, Elizabeth Margaret, B.Sc., Assistant Mistress, Hamilton Girls' High School.

SCHMIDT, Richard Offo, B.Sc. (Chemist, H. F. Stevens Ltd., Christchurch).

SMITH, Michael Francis, M.Sc., (Industrial Chemist, Shell Co.).

SWANTON, Barry Hubert, A.R.A.C.I. (Technical Manager, Lever Bros. (N.Z.) Ltd.).

WHITE, Gwenda Frances, M.Sc. (Chemist, Galloway Laboratory, Hamilton).

WHITE, John Charles Bereford, M.Sc. (Scientific Officer, Dept. of Agriculture).

WILLIAMS, Mary Patricia, B.Sc. (Biochemist, Wellington Public Hospital Laboratory.

Resignations:

Bottomley, G. A.; Christian, K. R.

I.C.I. PRIZE:

Resolved.—That the I.C.I. Prize for 1958, be awarded to J. K. Johannesson, Chief Chemist, Wellington City Council.

MORCOM GREEN AND EDWARDS PRIZE:

Resolved.—That the Morcom Green and Edwards Prize for 1958 be awarded to Dr. R. D. Batt, Senior Lecturer in Biochemistry, University of Otago.

UNIONS:

There was considerable discussion on the substance of the legal opinion and the letter from the Registrar of Industrial Unions concerning union membership. The Wellington Branch was asked to look into this matter and produce a report. The legal opinion and letter from the Registrar of Industrial Unions referred to above will be circulated to Branch Committees.

TECHNICIAN TRAINING:

The detailed syllabus for submission to the Education Department is almost completed but a few details remain to be settled.

Resolved.—That the Institute pay travelling expenses for Dr. Odell to make one trip to Dunedin to confer with the Examinations Committee re the syllabus for technician training.

BOOK REVIEWS.

MECHANISMS OF INORGANIC REACTIONS, by Fred Basolo and Ralph G. Pearson. Published by John Wiley and Sons Inc., New York, 1958. 426 pages. Price: 11.75 dollars.

This volume covers in some detail a field of chemistry that has not yet found adequate coverage in standard textbooks; its appearance is symbolic of the "new look" which has become evident in inorganic chemistry in the last decade or so. It would be as well, however, to notice the sub-title, "A Study of Metal Complexes in Solution," which is a clearer indication of the ground covered than the main title. Thus there is only a brief chapter of twenty-odd pages on oxidation-reduction reactions, the major part of the book dealing with square and octahedral substitutions, and relevant theory. Readers requiring a review of substitution reactions of octahedral cobalt complexes are well catered for; those seeking an appraisal of current knowledge of the mechanisms of permanganate oxidations will certainly be disappointed. The final chapter, a miscellany of topics as diverse and important as absorption spectra and exchange reactions of complexes, leaves an impression of tantalising brevity and perhaps hasty compilation.

Readers whose interests centre on co-ordination chemistry should welcome the appearance of this volume, though in a field which is so rapidly developing, regular revisions will be necessary if the book is to retain its usefulness. —W.E.D.

PRECIS DE CHIMIE ORGANIQUE, 4th Edition. Edited by J. Cologne and Roger Grignard. Published by Masson et Cie., Paris, 1958. 902 pages. Price 8000 fr.

The original edition of this work was written by Victor Grignard before his death in 1935 and was based on his lecture notes to his students at Lyons. Twenty-three years and three editions later it still preserves the spirit of the original work though it has undergone much unobtrusive revision. It is a treatise on well established lines dealing with various classes of organic compounds in turn and devoting only a little space to theoretical aspects. There is a portrait and memoir of Victor Grignard to inspire young French chemists. —S.G.B.

LERBUCH DER ORGANISCHEN CHEMIE, Band III. by F. Klages, Professor of Organic Chemistry at Munich University. Published by Walter de Gruyter and Co., Berlin, 1958. 766 pages. Price D.M. 104 (£9/2/-).

This is the final volume of the work and is divided into eight chapters as follows: Organic minerals (22 pages); Organic colouring matters (156 pages); Macromolecular compounds (44 pages); Carbohydrates (107 pages); Natural products based on isoprene (including steroids) (55 pages); Miscellaneous nitrogen-free natural products (33 pages); Natural products containing nitrogen (177 pages); and Biochemistry-Hormones, auxins, vitamins, antibiotics, enzymes (125 pages). The information is well organised while the printing and illustrations are very good. It should be useful to Honours students and as a general work of reference. The price seems too high. —S.G.B.

THE PETROLEUM CHEMICALS INDUSTRY (Second Edition), by R. F. Goldstein (I.C.I. Ltd.). Published by E. and F. N. Spon, London, 1958. 458 pages. Price 95/-.

Sir Robert Robinson pays a very high tribute to the author in the preface to this book and there is no doubt that it gives a very informative picture of the chemicals derived from petroleum. Well documented and up to date it gives a full description of the simpler compounds derived from petroleum and its by-products by various chemical reactions and much of this information is of general interest in organic chemistry, e.g. the large charts showing products derived from acetaldehyde, acetone, methallyl chloride and 1:4 butanediól. The reviewer did feel however that information on such subjects as detergents and plastics derived from petroleum was sparse, widely dispersed and hard to find. The author could usefully include separate chapters on these topics in future editions. —S.G.B.

CHEMICAL PROCESS ECONOMICS, by John Happel. Published by John Wiley and Sons, Inc., New York, 1958. 291 pages. Price 8.50 dollars.

This book is based on lectures in plant design given to Chemical Engineering students at New York University, and therefore has rather a textbook flavour, although it remains very readable and practical in outlook. It will be of interest not only to Chemical Engineering students but also to those engaged in plant design and to executives of technical background in any process industry.

The principles of the economic balance are developed as a tool for design and decision making, both for whole plants and for specific pieces of equipment. While due prominence is given to rule of thumb methods, more attention is devoted to placing the subject on a firm mathematical basis. While the expressions and techniques used are derived for the mathematically minded, much more stress is placed on their use, and on

the choice and assessment of cost data and other specific information required in using them. Worked examples, which really do illustrate, are extensively used through the text, and serve not only to make the practical use of the techniques clear, but also to relate the economic with the engineering and chemical aspects of design.

Being mainly occupied with the development of economic balance considerations, the book deals with cost estimation rather briefly, and such matters as plant location not at all. For those interested in engineering design and choice of plant alternatives on economic grounds, however, this would be a most useful book. —D.W.K.

AN INTRODUCTION TO THE CHEMISTRY OF FATS AND FATTY ACIDS, by F. D. Gunstone. Published by Chapman and Hall, Ltd., London. 161 pages. Price 32/-.

This is a valuable contribution to the literature of fats and fatty acids. It is primarily intended as a teaching text and is an effort to bridge the gap between the all too frequently inadequate coverage of the subject in standard textbooks of Organic Chemistry and the several comprehensive monographs which, although excellent, are rather too detailed for those not already specialising in the field. In this respect it can to some extent be regarded as a companion volume to Hilditch's "Chemical Constitution of the Natural Fats."

The first four chapters deal with: The Fatty Acids; The Chemical Nature of Fats; The Physical Properties of Fats and Fatty Acids; The Chemical Properties of Fats and Fatty Acids (50 pages). Two further chapters deal briefly with some biochemical and technical aspects of the subject. Throughout the book a considerable amount of useful information is presented in tabular form and structures and equations are well and clearly set out.

The standard of presentation is excellent and the text will be welcomed by teachers of Organic Chemistry and Biochemistry. As well as its value as a student text, it will also provide an excellent introduction to more extensive study of the subjects. —W. A. McG.

BOOKS RECEIVED

PHYSICAL CHEMISTRY OF HIGH POLYMERS, by Maurice L. Huggins. Published by John Wiley and Sons, Inc., New York, 1958. 175 pages. Price 6.50 dollars.

The emphasis in this book is on fundamental principles and it describes in considerable detail the structures of synthetic and natural high polymess.

PHYSICAL CHEMISTRY MADE PLAIN (Second Edition), by J. H. Mandleberg. Published by Cleaver-Hume Press Ltd., London, 1957. Price 16/-.

A very useful text written by an industrial chemist who attempts to provide a new view-point in physical chemistry. This is a marked improvement on the previous edition and can be recommended to the not-so-mathematically inclined.

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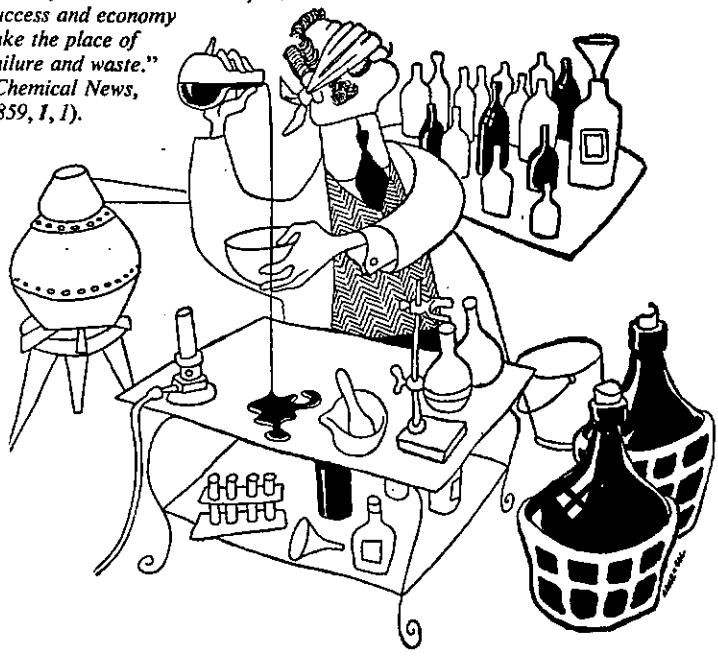

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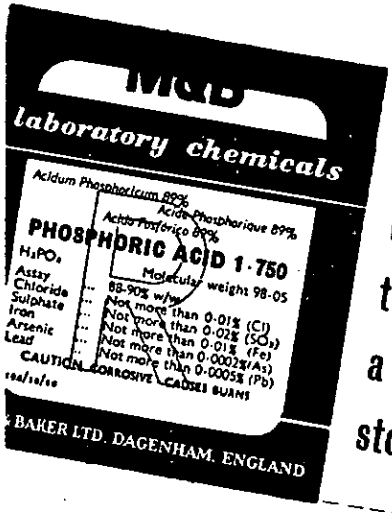

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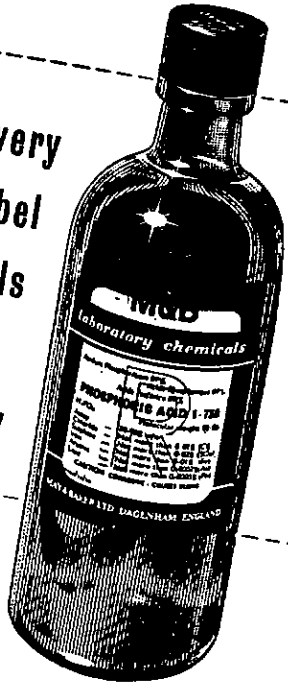

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