

JOURNAL OF THE NEW ZEALAND
INSTITUTE OF CHEMISTRY

Vol. 27 No. 2
April, 1963





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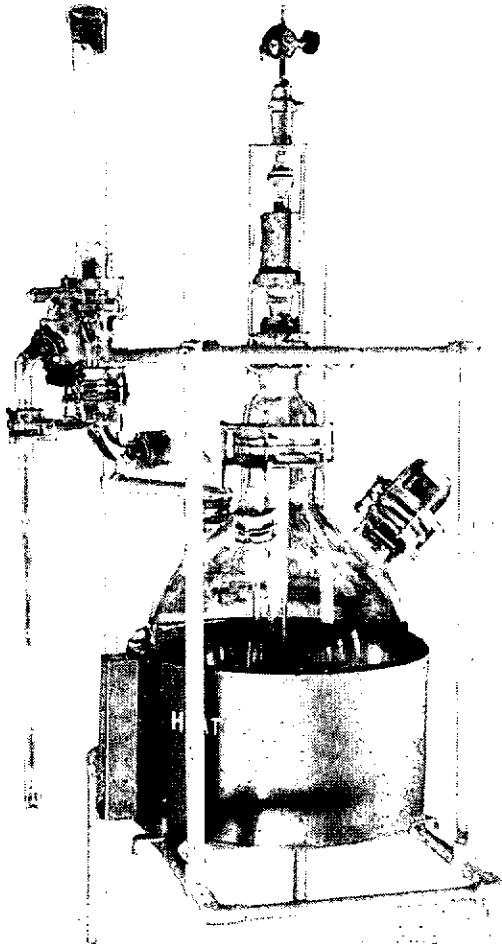
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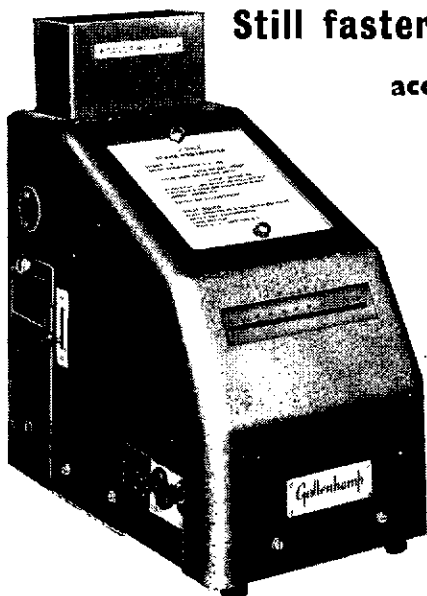
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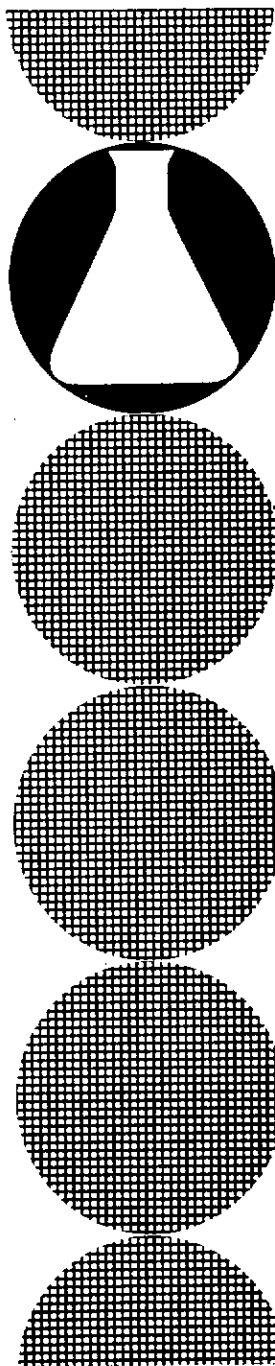
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JOURNAL OF THE NEW ZEALAND INSTITUTE OF CHEMISTRY

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METABOLISM AND MIGRATION

*Who wonder, 'mid our fern, why men depart
To seek the Happy Isles!*

KIPLING: *Song of the Cities* — Auckland

The item from *Svensk Kemisk Tidskrift* that is reprinted on page 59 of this issue was chosen originally because it amused us. Obviously it is not entirely applicable to *Homo scientificus* var. *N.Z.* For example, the lack of Nobel laureates amongst us suggests that there is some deficiency in the post-Rutherford academic pabulum, or a toxic factor in the diet or environment which blocks an important enzyme process. (The award of a Nobel Prize to a New Zealand-born scientist last year indicates that the defect is not in the genotype.) It seems that there is scope for a local millimicrosubmolecular biologist to carry out a parallel investigation on endemic material.

Yet it is not only for the laugh that we have included this item, for behind the distortion of caricature lies a cynical discernment of truth. The research which leads to a similar metabolic map for New Zealand conditions might shed some light on alleged defects in the organization of science here. In particular it might reveal those factors in the biochemistry of *H. scientificus* var. *N.Z.* which give this curious organism a lemming-like urge to migrate. There have been several recent assessments of the loss of New Zealand scientists to other countries, and the most obvious reason, the lure of higher salaries, has generally been offered to account for this loss; but we have yet to see a thorough examination of the motives of those who depart. We suspect that these are complex and that salary, although very important, is only one of many. Such an examination (organized perhaps a little more factually than the Ragland metabolic map) would provide valuable material for submission to an enquiry into the organization of scientific services, if one is ever conducted.

One point that might emerge is that emigration of scientists is not limited to New Zealand. A recent newspaper article and comments by visitors indicate that England is becoming increasingly concerned about loss of scientists to the U.S.A.

If, as a result of these suggested researches, there arises any mechanism for inhibiting the migratory impulse in New Zealand scientists, it is equally important not to block it altogether. That curiosity which is the mainspring of research is commonly associated with an urge to see other places and to obtain stimulus from other minds, so that freedom of exchange between countries is part of the normal development of a scientific community. The evil lies in one-way migration. We do not want our scientists to emulate Wordsworth's lark ("Type of the wise, who soar but never roam, True to the kindred points of Heaven and Home"), but rather the pipiwharauroa, although preferably with a sabbatical instead of an annual migratory cycle. (Any imitation of the socially irresponsible behaviour of this bird towards its offspring would no doubt be curbed by several Government departments.)

At this point recollection of Wordsworth's description of the European cuckoo as "but a wandering voice" prompts us to silence ours and to commend more serious consideration of such matters to someone (or a Committee) not dogged by a date-line for an editorial.

COURSES IN ANALYTICAL CHEMISTRY

VICTORIA UNIVERSITY OF WELLINGTON

The Chemistry Department, Victoria University of Wellington, is arranging a series of instruction courses in analytical chemistry. The first, on "Chromatographic Methods of Analysis", will be held from August 15 to 17 inclusive. This course will consist of a series of lectures on various aspects, including adsorption, partition, gas, paper and thin layer chromatography, and the application of these for analysis and production. The leading speaker will be Mr R. Dewar, Assistant Research Manager of I.C.I.A.N.Z., Melbourne, who is visiting Wellington especially to assist in this course, by arrangement with I.C.I. Mr Dewar was primarily responsible for the development of the flame ionization detector, which he will demonstrate. Other speakers will be Dr W. E. Harvey and Dr A. T. Wilson from V.U.W.; Mr I. R. C. McDonald (terpenes), Mr T. Gerson (gas chromatography) and Dr F. B. Shorland (application to fats), all from D.S.I.R.; and Miss J. M. Mattingley (Wellington Hospital) will describe electrophoretic separation of proteins. The fee for the course, including social activities, is £5. 5s. 0d. Further information may be obtained from the Director of Adult Education, Box 196, Wellington. A further course later in the year on "Instrumental Methods of Analysis" is planned.

PROPIONIC ACID*

A. T. JOHNS

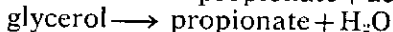
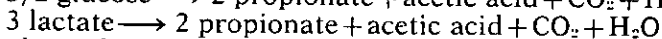
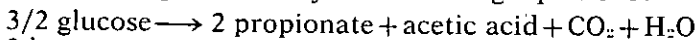
Plant Chemistry Division, D.S.I.R., Palmerston North

Propionic acid was once considered to be of importance only in being responsible for the characteristic appearance and flavour of Gruyère and Emmenthaler cheese. Now it is known to play a major role in ruminant metabolism and has become of particular interest from the point of view of the biochemistry of its formation and oxidation.

The first work of importance on the chemistry of the propionic acid fermentation was reported in 1878 by Fitz who found that the fermentation of lactate and malate yielded propionate, acetate and CO₂.

The association of micro-organisms producing propionic acid with the eyes in Emmenthaler cheese was studied by Orla Jensen in 1898. Von Freudenreich and Orla Jensen succeeded in isolating pure cultures of propionic acid organisms in 1906. Although the role of these organisms in Swiss cheese-ripening has received much attention, the bulk of the fermentation data was obtained by Van Niel and presented in his Ph.D. thesis in 1928 and added to later by Werkman and his associates.

The stoichiometry of the better known fermentation reactions is represented by the following equations:



However, the proportions of the acids shown in the above equations were achieved only in the roughest sense. In fact Wood and Werkman in 1936 and Van Niel in 1928 showed that the ratios of propionate to acetate varied from 7.8 up to 14.8. These equations also do not account for the fact that in 1923 Virtanen found that, when glucose was fermented, succinic acid could on occasions account for as much as 20 to 25% of the sugar fermented.

Virtanen tried to explain the formation of succinate by a scheme whereby succinate and a 2-carbon compound were produced by splitting the glucose molecule between carbons 4 and 5. This 2-carbon compound was supposed to be acetaldehyde.

An observation not explained by Virtanen's theory was that succinate can also be formed from lactate, a C₃ com-

* This paper was read by Dr Johns as the Chairman's Address to the Manawatu Branch in 1962.

pound. Van Niel found in his fermentations of lactate that there was usually some succinate formed and the ratio of propionate to acetic was always less than 2. Van Niel explained the production of a C_1 compound during the fermentation of a C_2 substrate by assuming that the succinic acid arose from aspartic acid in the yeast water used in the medium to grow the organisms.

Van Niel found a carbon recovery of 100% from lactate excluding succinate which was in good agreement with the suggestion that succinic acid was being produced from a source other than lactate. Indeed Van Niel, in almost all his dextrose fermentations, found that the amount of volatile fatty acid + succinic acid surpassed the amount of fermented dextrose. These results were later confirmed in 1936 by Wood and Werkman who interpreted them differently.

In 1934 Wood and Werkman in studying the fermentation of glycerol by the Propionibacteria first introduced the concept of heterotrophic utilization of CO_2 . They observed in some experiments that the end products contained more carbon than had been added in the form of glycerol and showed that CO_2 was utilized. Wood and Werkman at this stage believed that succinate arose as a result of a condensation of two molecules of acetic acid.

In 1938 they proposed that succinic acid was formed in the fermentation by Propionibacteria by the combination of a C_3 and a C_1 compound. Pyruvic acid was suggested as the C_3 compound since it could be isolated from the fermentation liquid and this combined with CO_2 to form oxalacetic acid. This condensation has come to be called the Wood-Werkman reaction.

In 1940 the stable isotope of carbon C^{13} and the short life radioactive isotope C^{11} (half life 21 minutes) became available and work was commenced using both of these tracers to investigate the mechanism of CO_2 utilization in the propionic acid fermentation.

Carson and Ruben (1940) employed C^{11} while Wood, Werkman, Hemingway and Nier (1940) using C^{13} confirmed that fixation occurred. It was found that the labelled CO_2 was indeed assimilated and appeared in the carboxyl group of the propionic and succinic acids.

The experiments provided striking evidence for the view that the fixation of CO_2 is not limited to photosynthesis in green plants but is a more general biochemical phenomenon. In fact Krebs and Eggleston (1940) obtained evidence that the step, pyruvate + $CO_2 \rightarrow$ oxalacetate, occurred as the primary step in the synthesis of α -ketoglutaric acid by pigeon

liver and demonstrated that it occurred in animal tissues as well.

In 1941 both Carson, Foster, Ruben and Barker and Krebs and Eggleston put forward the scheme shown in Fig. 1 to account for the formation of carboxyl labelled propionic and succinic acids in the presence of isotopic CO_2 .

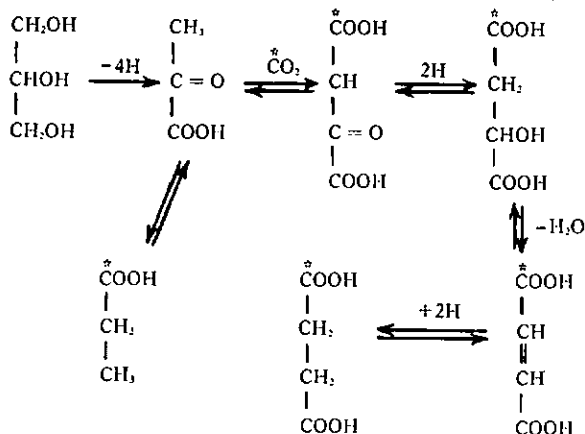


Fig. 1

This scheme was in agreement with the following experimental findings:

- Both propionic and succinic acids formed from CO_2 are radioactive.
- The acids contained the labelled carbon only in the carboxyl groups.
- Pyruvic acid is an intermediate in the propionic acid fermentation (Wood and Werkman 1934).
- A radioactive α -keto-acid besides pyruvic acid is formed during the fermentation of pyruvate in the presence of CO_2 .
- The set of reversible reactions from oxalacetate to succinate were found to occur in the propionic acid bacteria by Krebs and Eggleston in 1941.
- It was suggested that succinic acid could be decarboxylated to give propionic acid but Krebs could not demonstrate this either of succinate alone or in the presence of glucose, pyruvate or glycerol.

In 1946 the author (Johns, 1946) isolated *Viellomella gazogenes* from the rumen of sheep and from the human mouth. This organism was found to produce propionic acid, acetic acid, CO_2 and hydrogen. It did not ferment any sugars but only organic acids such as tartrate, pyruvate,

malate, etc. No succinate was found to accumulate and isotope experiments showed that CO_2 is fixed in the carboxyl group of propionic acid. Washed suspensions of *Viellomella* decarboxylated succinate very readily with an almost theoretical yield of CO_2 . It was shown that CO_2 tension affected the ratio of acetate to propionate, the higher the CO_2 tension the greater the proportion of propionate formed.

Contrary to the observations of previous workers it was found that Propionibacteria would decarboxylate succinate slowly with a pH optimum of 5.2, with no activity at 6.8. This low pH optimum explained most of the variable results obtained by many previous workers on this subject. The variations found by other workers in the amount of succinate formed and the variable ratios of acetate to propionate were due to the fact that many had used CaCO_3 or Na_2CO_3 in the medium to neutralize the acids formed from glucose glycerol. The greater the amount of CO_2 the greater the amount of succinate formed. The amount of succinate remaining in the final medium depended on the final pH. If it fell to near 5.2 most of the succinate was decarboxylated to propionic acid and CO_2 .

With the lactate fermentation there is little change in pH as 3 molecules of lactate are converted into 3 molecules of fatty acid. The amount of succinic acid was usually lower as no CaCO_3 or Na_2CO_3 was added.

The rate of decarboxylation was not increased by the addition of an exogenous supply of energy.

It seemed at this stage to be fairly well proved that propionate arose by the decarboxylation of succinate formed by the pathway outlined in Fig. 1. At this time the mood of biochemists was governed by the idea of unity of nature as regards metabolic pathways. It was becoming appreciated that the Krebs' cycle was common to micro-organisms and higher plants and animals. It was therefore felt that it was most unlikely that there would be more than one mechanism for the formation of propionic acid in nature.

One hypothesis of long standing as to the mechanism of propionate formation involved dehydration of lactate to acrylate to propionate. For the Propionibacteria this was eliminated when Barker and Lipmann found that sodium fluoride inhibited lactate fermentation but not that of pyruvate. In addition acrylate was not fermented.

However, Cardon and Barker (1947) isolated an organism, *Clostridium propionicum*, that formed propionic acid from

lactate and some amino acids, and was able to reduce acrylate to propionate.

The author was able to show that this organism neither utilized CO_2 nor decarboxylated succinate. Also in contrast to the other organisms lactate -3C^{14} was fermented to acetate and propionate labelled almost exclusively in either the methyl or methylene carbons. Randomization between the α and β carbons of propionate was not observed. Further work by Stadtman has confirmed this direct reduction pathway with *Cl. propionicum*.

A coccus termed LC was isolated by Elsden from the rumen which forms acetate, propionate, butyrate, valerate and caproic from the glucose or lactate. It has also been shown to form propionate by the direct reduction pathway.

There are thus at least two separate mechanisms by which propionic acid may be formed by bacteria, something that was considered highly unlikely a few years ago.

A side issue of interest in rumen biochemistry is the mechanism by which propionate is formed in the rumen. Elsden and the author independently showed a number of years ago that the decarboxylation of succinate is very rapidly carried out by washed suspensions of rumen bacteria so this pathway seemed highly likely for propionate formation in the rumen. There is also the question of whether formation of propionate is a two-step process involving two groups of organisms or only one group. Is most of the propionate formed directly from cellulose by cellulose fermenters, or is the greater part of the carbohydrate fermented first by lactobacilli to lactic acid and then to propionic and acetate by lactate fermenters?

To answer the second question first, studies by Hungate on the turnover of lactate in the rumen indicated that it functioned only to a very small extent as an intermediate in the production of propionate in the rumen. However, more work on a number of diets will be needed to settle this point.

The contributions of the dicarboxylic acid (randomizing) pathway and the acrylate (non-randomizing) routes to propionate formation have recently been investigated by Michigan State University workers by determining the randomization produced when glucose -1-C^{14} -2-C^{14} and -6-C^{14} and lactate -2-C^{14} -3-C^{14} were fermented to propionate by rumen fluid. The propionate and acetate were isolated and the C^{14} in each carbon determined. The randomization in acetate — a measure of the randomization in pyruvate or lactate entering the lactate routes — was very low (5%).

The labelling pattern obtained indicated that when glucose was fermented the predominant route for propionate formation was via the randomizing route, *i.e.*, via succinate. When lactate was fermented it was calculated that 60% of the propionate came via the acrylate route. When the diet of the animals contained increasing amounts of starch there was a greater participation of the acrylate route. With glucose fermentation it increased from 0 to 20% and with lactate from 60 to 90%. The acrylate route becomes more prominent as the carbohydrate availability of the diet increases, presumably because of greater lactate production and selection of lactate fermenters with the acrylate route. This is all the more surprising as a large number of rumen organisms have been shown to produce succinate. It appears that the organisms that actually form the bulk of the propionate in the rumen remain to be isolated as none of those studied so far occur in large numbers under normal feeding conditions.

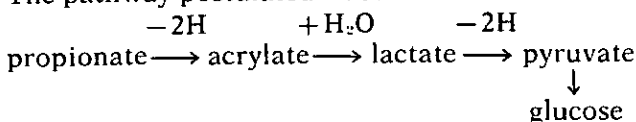
Before considering the latest work on the formation of propionic acid, advances in our knowledge of the pathway by which it is metabolized will be described.

METABOLISM OF PROPIONIC ACID

In the ruminant, carbohydrates are converted to volatile fatty acids and absorbed into the bloodstream. The question as to what extent fatty acids are precursors for organic substances synthesized by the animal, such as glucose or glycogen, was studied before isotopes became available as metabolic tracers.

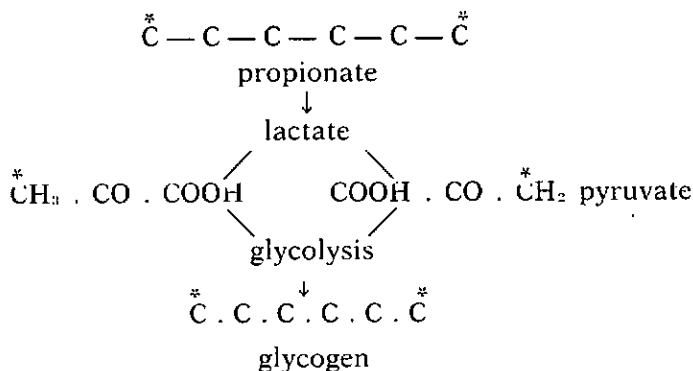
Based on measurements of glucose formation in dogs with phlorhidzin diabetes, Ringer as early as 1912 concluded that propionic acid is completely converted into glucose. Reviewing results obtained by measurements of increase in glycogen content of liver, Deuel and Morehouse concluded that the animal readily transfers fatty acids with odd-numbered carbon chains to carbohydrate, and that, in contrast, fatty acids with even-numbered carbon chains are not available for carbohydrate synthesis.

The pathway postulated was:



Feeding animals with isotopically labelled lactate and propionate did not support this hypothesis. On the assumption that lactate enters into metabolism via pyruvate, rever-

sal of the glycolytic reactions will lead to the following type of isotopic glucose if β -labelled lactate is fed



When labelled propionate and lactate were fed to animals it was found that the labelling patterns in the resulting glycogen were different. Calculations showed that about 1/6 of the lactate was converted to glucose directly via pyruvate and the remainder underwent randomization via the Krebs cycle. With propionate there was a complete randomization of the α and β carbons to give glucose



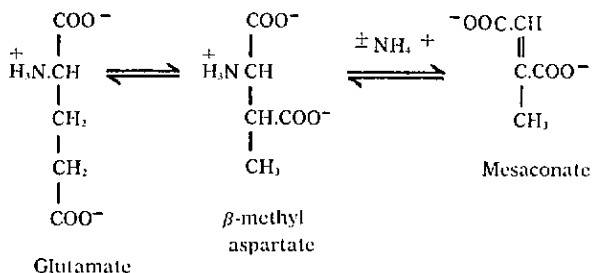
What mechanisms could account for this. Wood *et al.* (1950) said that carboxylation of the methyl group of carbon to give succinate would account for it but there was no evidence for such a reaction. Moreover, Haennekens, Mahler and Nordman in 1957, on the basis of enzymic studies with liver preparations, still claimed that the pathway of propionate oxidation is via lactate.

About this time Lipmann discovered a dialyzable cofactor named coenzyme A which is most important in the metabolism of fatty acids. It is involved in what is known as the formation of active compounds which take part in many metabolic steps. The first step in the oxidation of fatty acids involves the activation of the acid by formation of the coenzyme A derivative. Active "acetate", acetyl CoA, is utilized directly by combination with oxalacetic to form citric acid in initiating the citric acid cycle.

CoA is a derivative of the vitamin pantothenic acid. The sulphur bond of acetyl CoA is a high-energy bond equivalent to the high energy phosphate bonds of ATP and other high-energy phosphorylated compounds.

The formation of these high-energy bonds requires, therefore, a source of energy, either from a coupled exergonic

coenzymes from microbial sources. They were discovered in searching for the factors concerned in the conversion of glutamate to β -methyl aspartate or mesaconate by cell-free extracts of *Clostridium tetanomorphum*.



Although it had been suspected that vitamin B₁₂ functions as a coenzyme in metabolism, such a function was only proved by the isolations made by Barker. The coenzymes are inactivated and converted to vitamin form by visible light or by cyanide ion, the adenine nucleoside being removed or replaced by the cyano group. The methods used previously to extract the vitamin included heating in weak acid, addition of cyanide ion and exposure to light. As a result the coenzyme was converted to the inactive vitamin form.

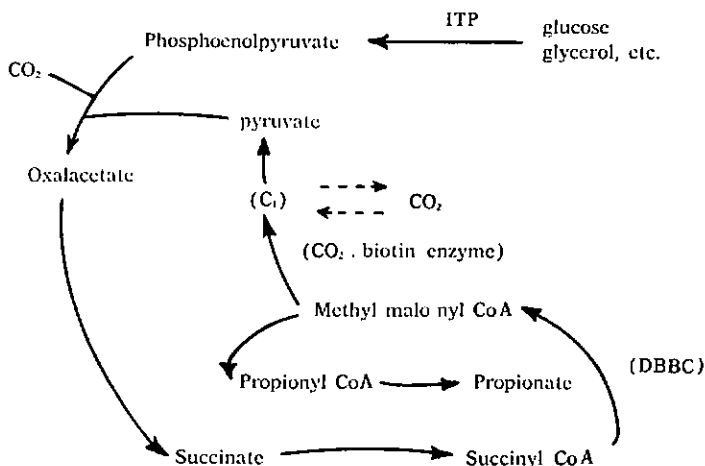
The best source of the vitamin yet found is in a culture of *Propionibacterium shermanii*.

It has now been established by Wood and co-workers that the di methylbenzimidazole-B₁₂-coenzyme is necessary for the interconversion of succinyl-CoA to methylmalonyl-CoA while biotin is involved in the carboxylation reaction.

RECENT STUDIES ON THE BACTERIAL FORMATION OF PROPIONATE

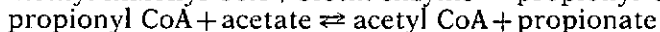
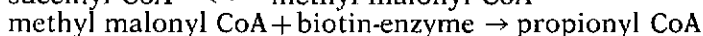
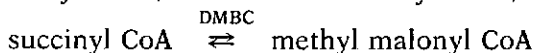
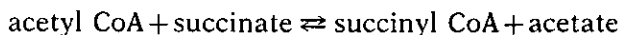
In our scheme for the formation of propionate by decarboxylation of succinate, because succinate is symmetrical, half of the CO₂ released would be derived from the original fixation and the other half from pyruvate. However, in isotope experiments designed to measure these reactions the observed CO₂ labelling was insufficient to account for the propionate formed and it was concluded that a one carbon unit other than free CO₂ was a product of the cleavage. Also the discovery of the pathway of propionate metabolism in animal tissues raised the question of whether succinate is directly decarboxylated or whether methylmalonate is an intermediate in the formation of propionate by the propionic acid bacteria.

Results obtained in 1960 by Swick and Wood show that methylmalonate is involved. The results show that succinyl CoA is not decarboxylated but is first converted to methylmalonyl CoA, and that it is the latter which is first converted to propionyl CoA. This cleavage occurs with the transfer of the carboxyl carbon to pyruvate, forming oxalacetate, and the C₁ unit does not equilibrate with free CO₂. Thus it is not CO₂ as such but a C₁ unit which combines with pyruvate to form oxalacetate, while the fixation of CO₂ *per se* may occur with phosphoenolpyruvate.



DBBC = dimethylbenzimidazole-B₁₂ coenzyme

The function of biotin as the CO₂ converter in the interconversion is indicated by the complete inhibition of this step by avidin (avidin is the biotin-binding protein of egg white).



The mechanism involves a new concept termed trans-carboxylation in which one compound, a carboxyl donor, is decarboxylated and a second compound, a carboxyl acceptor, is carboxylated. Thus it is possible to accomplish a direct carboxylation without the intervention of CO₂ or the expenditure of energy to activate the CO₂ as the transfer appears to be accomplished without the intervention of ATP. It involves a CO₂ and a CoA cycle. Recent work suggests that such a cycle may be present also in animal tissues.

It can be seen, therefore, that studies on propionate formation and metabolism have been of interest from a number of points of view:

- (1) The first biochemical investigation employing isotopes was carried out with the Propionibacteria.
- (2) The first demonstration of the heterotrophic utilization of CO₂ was demonstrated with them.
- (3) It was one of the first clear demonstrations of a product being produced by two distinct metabolic pathways.
- (4) After a long period of time the role of cobalt in ruminant nutrition has been at last at least partly elucidated. It is required for both the production and utilization of propionate by the animal. This appears to be a reason for the high amount of B₁₂ in propionic acid producing bacteria.

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SOME CHEMICAL ASPECTS OF LUBRICATING OILS

(Concluded from previous issue)

WALTER FREITAG

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The interpretation of test results on used lubricating oils falls into three categories:

- (1) Interpretation of an individual, or set, of results.
- (2) Comparison of results obtained prior to and during use.
- (3) Comparison of a series of results with a pattern established for a particular application.

The interpretation is governed by:

- (a) The nature and origin of the sample.
- (b) The nature and accuracy of the test.
- (c) Other available (mechanical) data.

Used lubricating oils have diverse compositions; fully representative samples are essential to the avoidance of misleading results.

Viscosity: The opposing effects of fuel dilution and heavy oxidation products upon viscosity, during use, necessitate interpretation in conjunction with flash point, fuel dilution, and extent of oxidation. A pattern commonly followed by internal combustion engine lubricants during use, and representative of many such samples examined in the writer's laboratory, is depicted in Fig. 2 (9).

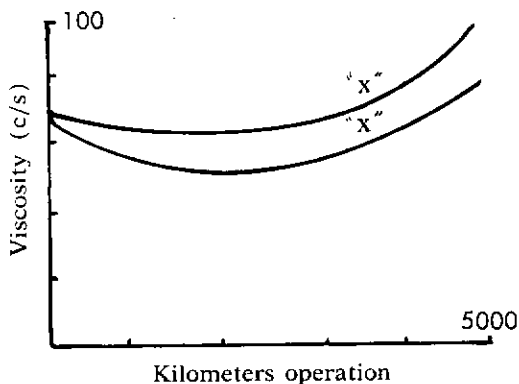
INTERPRETATION OF TEST RESULTS ON USED LUBRICATING OILS

Fig. 2

Initial operation, particularly under cold conditions in a worn engine, is accompanied by fuel dilution, continued operation permitting evaporation of the volatile components and promoting oxidation, as indicated by an increase in viscosity. Values around point "X" can thus be misleading.

The addition of certain additives during use (*e.g.*, graphite) and the presence of finely-divided solids will also give anomalous results.

Generally, oils subjected to oxidizing conditions without excessive heat give rise to heavier agglomeration products which raise viscosity, whereas oils subjected to extreme heat will have their viscosities reduced by lighter "cracked" products. Reduction in viscosity due to fuel dilution can usually be attributed to excessive wear, inadequate fuel, or faulty fuel supply.

Viscosity Index: The viscosity index of an oil is reduced during use by the formation of low viscosity index polynuclear compounds and decomposition of "viscosity index improvers". Fuel, or low molecular weight "cracked" products, on the other hand, because of their greater effect upon low temperature viscosity, give anomalously high values. A knowledge of fuel dilution or flash point is therefore necessary in interpreting viscosity index changes occurring during use.

Flash Point: Since low values indicate either fuel or "cracked" products, identification of the volatile material by fuel additive (*e.g.*, Pb from TEL) or a product of cracking (*e.g.*, naphthenic acids), may be necessary.

Fuel Dilution: Accurate interpretation is impeded by the factors outlined under test methods. The method is used to indicate excessive dilution and is checked by flash point, viscosity and identification as previously outlined.

Carbon Residue: For given molecular weight range, carbon residue distinguishes between "paraffinic" and "aromatic" oils. Comparison with results obtained on the new oil may be made to indicate the extent of dehydrogenation during use. Increasing values during use can usually be associated with excessive temperatures, incorrect ventilation, and soluble or suspended contaminants.

Water Content: Values below approximately 0.5% can usually be ascribed to normal condensation; figures in excess of this warrant further investigation. Analysis of

centrifugally separated water (e.g., hardness, salinity, coolant inhibitor) will frequently identify its source as either excessive condensation associated with "cold" operation, coolant leakage or extraneous. Evaporation at elevated temperatures may result in misleading figures.

Acidity: High total acidities necessitate resolution, by aqueous extraction, into organic and inorganic constituents. Excessive sulphuric acid results from fuel exhaust gas condensation, indicating (a) too low operating temperature (b) use of a fuel of too high sulphur content under these conditions, (c) engine wear or incorrect fuel combustion, allowing excessive ingress of exhaust products into the oil. Other inorganic acids or alkalis may similarly arise through contact with products of an industrial process (e.g., NH_3 , SO_2 , from refrigerator units). Organic acids remaining in the oil after extraction, usually accompanied by an increase in viscosity and carbon residue, are products of oil or additive decomposition, indicating either prolonged use or too severe operating conditions. If required, these acids may be separated by acidification of a KOH extract and then identified. In interpreting acidity, the acidic or basic nature of any additive used must be considered.

Saponification Value: This includes the total acid content; positive values must therefore be corrected for acidity as well as for additives known to react under the test conditions. True saponifiable matter arises from certain intermediate oil oxidation products containing olefinic, aldehyde or ester compounds; or from fatty material present either as contamination or additive. In the latter case, the test provides useful means of assessing the rate of depletion of the additive. Excessive saponifiable matter in straight mineral oils usually points to extraneous contamination and if required, this can be separated and identified (IP-136-B).

Sulphated Ash: Ash residues contain (a) normal and spent metal-containing additives, (b) non-combustible air-borne and local contaminants. Chemical analysis of the ash will usually establish inadequate air filtration, the locality of excessive wear or certain abnormalities in operation. (e.g., Cr is associated with piston rings; Zn, Pb, Cu with bearings; Al with pistons, etc.) If it is accepted that metal-containing additives, upon decomposition, yield oil-insoluble residues, the ash from a filtered sample will originate entirely from unspent additive. Comparison with the result obtained on the new oil indicates the extent of

its depletion. Similar comparison with the result obtained on an unfiltered sample will show the extent of contamination with non-combustible matter.

Total Insoluble Matter: The material precipitated from a *n*-pentane suspension includes decomposed additive carbon, air-borne impurities, products of wear, and asphaltic oil decomposition products. The latter may be estimated by difference following extraction with benzene, the difference between *n*-pentane and benzene insolubles thus indicating the extent of oil decomposition. The loss in weight by ignition of benzene insolubles is due to carbon. The remaining residue may be submitted to analysis as under "Ash". The examination for solid contaminants and additive depletion is summarized in Table 1, combinations of groups permitting separation of almost every type of solid contaminant.

Pour Point; Foaming Tendency; Demulsification Characteristics: These properties can be interpreted only by reference to values obtained on the new oil and the magnitude and direction of changes related to operation. Generally, decomposition products increase these values.

Chromatographic Spot Techniques: These are used to assess oil condition during use by comparison with a series of patterns established for a given oil type and application. Provided these conditions remain unchanged, the extent of oil deterioration may be monitored without further examination.

Hydrocarbon Type Analysis: Increase of unsaturates during use indicates thermal "cracking", whilst an increase in aromatics and naphthenes indicates the extent of dehydrogenation and cyclization of paraffins under oxidizing conditions. Time-consuming experimental procedures favour the use of indirect methods of evaluating these phenomena.

Tests for Specific Additives: The effects of decomposition products upon the property of an additive under investigation may cause misleading results. Structural changes in the additive, which may or may not affect its properties, may escape detection by elemental or functional group analysis.

Examination of Extraneous Substances: Although perhaps not immediately associated with lubrication, any accumulated deposit (sludge, scale, etc.) should be examined with the object of elucidating its composition and source, so that

steps can be taken to arrest a process which, if allowed to continue, may lead to premature failure. Such examinations must be interpreted individually and in conjunction with mechanical observations. Examples of this type of occurrence include:

- (1) Petrol engine valve deposits arising from (a) leaded fuel — indicating faulty fuel or valve systems; (b) oil additive — indicating excessive valve gear wear.
- (2) Crankcase oil-ways deposits due to excessive oil or additive decomposition, or accumulation of excessive wear products.
- (3) Oil-originating deposits on piston crowns, indicating excessive bore or ring wear.
- (4) Accumulation of extraneous contaminants.

RECLAMATION AND RECONDITIONING OF USED LUBRICATING OILS

The steps necessary for rendering used lubricating oils suitable for further use will be evident from a study of the degradation processes previously referred to. Briefly, oil reconditioning consists of the following steps (not necessarily in order):

- (1) Removal of water, fuel-dilution and volatile decomposition products by slow heating preferably under vacuum.
- (2) Removal of suspended matter by filtration or centrifuging.
- (3) Precipitation and removal of asphaltic decomposition products.
- (4) Neutralization of acidic oxidation products.
- (5) Removal of remaining soluble dark-coloured impurities by clay treatment.
- (6) Blending to correct viscosity.
- (7) Restoration of additive to correct level.

The need for any particular reclamation process and its severity can be determined by the tests already described, which, when applied to the reclaimed product, will assess the efficiency with which reclamation has succeeded.

CONCLUSION

By intelligent application of the available test methods — both prior to and during use — the severity of degradation processes may be minimized, and their extent related to operation. It is impossible to establish universally accept-

able limits beyond which an oil should be withdrawn from use. For example, whilst the presence of 0.5% of insoluble material may not seriously impair operation of a heavy industrial engine fitted with a good oil filter, this amount could be disastrous in a sensitive hydraulic mechanism or precision machinery; each case must therefore be treated individually. In order to derive maximum value from the tests applied, it is clearly desirable to institute regular test programmes for each type of application in order to establish a typical pattern of the rate of degradation. Such a programme will soon reduce the number of necessary tests to those involving major variables only and facilitate the detection of unusual operating circumstances. The development of better quality lubricants will tend to reduce the number of available grades and thus make test series of more universal application. The present rate of development in industrial lubrication demands serious consideration of investment in more costly spectrochemical equipment, the use of which will replace many of the current tests — as has already been strikingly demonstrated overseas.

The chemist, together with the engineer, can thus play an important part in choosing the correct lubricant for each application, establishing its useful life and reconditioning it for further use; factors which are so necessary in the efficient utilization of a commodity costing New Zealand valuable overseas funds.

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ANOTHER NEW ZEALAND PINE PRODUCT

G. A. NICHOLLS

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The first commercial plant in Australia or New Zealand to recover and process crude sulphate turpentine, referred to as pulp mill liquor (PML) in the U.S.A., went unobtrusively into operation at Kinleith towards the end of 1962. This was a milestone marking the contribution made by a number of N.Z. Forest Products Ltd. employees to a project initiated some time ago to develop both an appropriate refining technique and market outlets for a locally available raw material.

In the early stages of this project laboratory work indicated the amount of turpentine to be expected. During 1958 it was confirmed, by a series of direct measurements spread over a year and based on a composite production sample of 2,500 tons of kraft pulp, that a little more than one gallon of crude turpentine could be recovered per ton of pulp. Up to three times this amount of turpentine would be obtained from some pines in the U.S.A.

Essentially sulphate turpentine is derived from pine chips. When these are converted to pulp by kraft cooking liquor in digesters such as those used at Kinleith, which hold about 12 tons oven dry weight of *Pinus radiata* chips, the pressure is generally relieved continuously to a separator and condenser through an orifice under one half inch in diameter. Any liquor carried over is removed by the separator. A mixture of water and crude turpentine is discharged from the condenser and non-condensable gases containing sulphur compounds escape to the atmosphere to become "the essence" of a kraft pulp mill.

INITIAL INVESTIGATION

Refining of the decanted crude turpentine from Kinleith began over four years ago at Penrose in a laboratory pilot plant conceived as a result of bench-scale experiments and designed around an industrial glass steam distillation unit based on a 20 litre flask. With experience a consistent quality vegetable turpentine meeting the appropriate standard specification was produced from this pilot plant. It became the basis on which the project grew to the point where the Kinleith unit was brought into operation last year, by which time 20,000 gallons of vegetable turpentine had been sold from the pilot equipment and a realistic assessment of market acceptability obtained.

In the U.S.A. crude sulphate turpentine output is roughly 16 million imperial gallons a year, whereas in New Zealand the total amount potentially available from established pulp mills is round 200,000 gallons, but currently only about half is being collected and it is anticipated that until further market outlets are developed the yearly amount refined would not exceed 50,000 gallons. Although this is a relatively insignificant volume when compared with the volume processed in the U.S.A., it means in effect that New Zealand will have vegetable turpentine available either for more extensive local use or for export. In addition the potential volume of crude raw material available in New Zealand and the established refining plant allow for growth to the point of at least tripling a refined output of 50,000 gallons per year by working additional shifts.

PRODUCTION PLANT

To produce vegetable turpentine at Kinleith the condensate from the digester relief gases is run into a decanter from which crude turpentine automatically passes into a storage tank and from this there is a gravity feed to a conical bottomed batch reaction tank. After batch chemical treatment, turpentine is pumped to a head tank, then gravity fed to an industrial glass unit where it is steam distilled at atmospheric pressure. The turpentine phase of the condensate is decanted, dried, fed into a collection vessel and pumped into a holding tank prior to release for shipment.

In designing the crude turpentine decanter it was necessary to make the volume large enough to ensure sufficient dwell time for breaking of the emulsion that tends to accumulate at the interface of the two liquid phases in the relief gas condensate, especially when there is significant carry-over of cooking liquor from the digester. It was also necessary to take into account the corrosive nature of the condensate in which the aqueous phase is alkaline, whereas the gaseous phase above the crude turpentine is comparable in its acidity to wet hydrogen sulphide. To meet these conditions the same approach was used in both the decanter and the storage tank for crude turpentine. These tanks were constructed of mild steel, the relatively small vent and outlets pipes were made of stainless steel, and the top portions of the tanks exposed to acidic vapours were spray coated inside with stainless steel. When the storage tank was being designed the crude turpentine outlet was put near the top. The amount stored above this outlet is sufficient

to fill the batch reaction tank and only that part of the tank enclosing this volume is spray coated. To remove the substantial volume of crude turpentine from the lower part of the tank, the water-immiscible liquid is pushed up through the outlet by temporarily running water in at the bottom. Later on, as further crude turpentine passes into storage overnight or during a week-end, the water is automatically displaced through a decanter leg until ultimately the storage tank is full of crude turpentine. This then begins to go out an overflow pipe right at the top. Compared with having a tank from which crude turpentine is removed at the bottom, this arrangement avoids the need for one pump and reduces the area inside the tank that must be sprayed with stainless steel because it is exposed to acidic vapours.

To produce distillate free from the foul odour of low molecular weight organic sulphur compounds, crude turpentine is mixed in a conical bottomed reaction tank with aqueous sodium hypochlorite made in an adjacent plant from chlorine and caustic soda obtained by the electrolysis of salt. The reaction tank was lined by an Auckland firm with "liquid glass", a phenolic resin, that was found to provide very satisfactory protection against corrosion in the pilot plant. When going through this part of the refining process variation in the reactivity of different batches of crude turpentine with respect to hypochlorite is taken into account by altering the treatment conditions, but this is the only point at which the refining process is varied. The conical bottom of the reaction tank facilitates removal of the aqueous layer prior to pumping the upper phase to a head tank.

From this tank turpentine is continuously fed for at least one shift through a ballcock level controller into a 200 litre five-necked flask, constituting part of the industrial glass unit. At the same time steam injected into this flask carries turpentine vapour through an entrainment separator to the condensers. Additional heat is supplied for the distillation by two external boiler-type heat exchangers attached to the flask and heated with steam at 50 lb/sq. in. The steam distillation proceeds very smoothly and almost without attention, a significant contributing factor being a neck at the bottom of the flask through which any water droplets fall to a pipe below so that the main cause of bumping is eliminated. Not more than once in eight hours the residual fraction in the flask is drained out which means that, although the distillation is discontinuous, the unit at least operates continuously for a working day. An automatic

decanter, cooler, coalescer column and drying tower constitute the other parts of the industrial glass unit. As the turpentine distillate flows up the appropriate leg of the decanter, it passes over cooling coils so that most of the dissolved water separates before it begins to pass up a three feet long column 12 inches in diameter that is packed with glass fibre. In this column practically all of the very small entrained droplets of water are coalesced into large enough droplets so that they no longer flow with the turpentine stream. The latter subsequently passes up a drying tower comprised of an anhydrous calcium chloride packed column the same size as the coalescer column. The dried distillate goes into a collection vessel where it joins a stream of turpentine that constantly flows from and is pumped back into an overhead holding tank, to ensure complete mixing of the accepted cut from each steam distillation.

The unique design of the industrial glass unit was developed in consultation with the manufacturers, and is based on the experience obtained in operating the pilot plant which incorporated a number of ideas arising out of a first-hand knowledge of bench-scale steam distillations. Pressure gauges on the steam and water lines, and a thermometer in the pocket of one boiler comprise the instruments used in the whole plant, which is readily run by one operator.

EQUIVALENT NAMES OF SOME COMMON INDICATORS

The following table was prepared by Mr J. R. L. Walker, Cawthron Institute, Nelson, during a comparison of methods for the estimation of calcium. Although this Table is not intended to be exhaustive it

<i>Chemical Name</i>	<i>British Drug Houses Ltd.</i>
Ammonium purpurate	Ammonium purpurate
Fluorescein-iminodiacetic acid	
<i>o</i> -Cresolphthalein- <i>bis</i> -methyl-iminodiacetic acid	Phthalein-complexone
Pyrocatechol sulphone-phthalein	Catechol violet
2-(1-Hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulphuric acid	Calmagite
2-Hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid	Full chemical name
(4-Chlorophenol)-(2-azo-2)-(1:8-hydroxy-naphthalene-3:6-disulphonic acid), Na ₂ salt	
1-(1-Hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonic acid, Na salt	Solochrome black
1-(1-Hydroxy-2-naphthylazo)-2-naphthol-4-sulphonic acid, Na salt	
1-(2-Hydroxy-1-naphthylazo)-2-naphthol-4-sulphonic acid, Na salt	Solochrome dark blue

POSSIBLE USES FOR PRODUCT

Vegetable turpentine derived as described above from *Pinus radiata* is unusual in that it consists mainly of pinenes, the amount of *beta*-pinene being about 65%. At present most of the Kingleith product is used as a solvent for which purpose high pinene content is superfluous and prices are keen because there is considerable sales competition on world markets from turpentine with chemical constituents that make them less sought after for chemical conversion. Products that are mainly pinene generally command a premium price for the manufacture of synthetic chemicals, hence this field offers the more promising outlet for New Zealand turpentine. For the manufacture of household cleaning fluids large quantities of synthetic pine oil are produced, sometimes from only one pinene and sometimes from a mixture of *alpha*- and *beta*-pinene. The insecticide toxaphene is obtained from pinene by chlorination. Terpene resins which are of value in the manufacture of paint are also produced from pinene on a commercial scale. Today there is a revolutionary development in the perfume industry based on the commercially practical syntheses of myrcene from *beta*-pinene and terpene alcohols from myrcene. These are some of the established synthetic chemical processes that seem to point to the use of this new local product as a chemical raw material at some future date.

USED IN COMPLEXOMETRIC (EDTA) TITRATIONS

should be of assistance to other workers who have found their reading of compleximetric chemistry rendered more complex by synonyms.

<i>Hopkins & Williams Ltd.</i>	<i>L. Light & Co.</i>	<i>E. Merck, A.G.</i>	<i>Other Names</i>
Murexide Calcein	Murexide Calcein	Murexide	Fluorexon Cresolphthalein-complexone
Metalphthalcin I Catechol violet	Phthalein purple Pyrocatechol violet	Phthalein purple Pyrocatechol violet	
	Calmagite		Patton & Reeder's indicator. HHSNNA
Full chemical name		Calcon carboxylic acid	
Eriochrome black T	Eriochrome black T	Eriochrome blue SE Eriochrome black T	Erio black T, W DFA
Eriochrome blue-black B	Eriochrome blue-black B	Eriochrome blue-black B	Solochrome black 6B
Eriochrome blue-black R	Eriochrome blue-black R		Calcon

MASSEY UNIVERSITY COLLEGE OF MANAWATU

The following notes describing teaching and research activities in chemistry at Massey University College have been contributed by members of the Manawatu Branch. Further articles will be published in the June and August issues in order to provide members attending the 1963 Conference in Palmerston North with information on the work of chemists and chemical laboratories within the territory covered by the Manawatu Branch.

RECENT DEVELOPMENTS IN TEACHING

Considerable attention has been focused on university teaching in Palmerston North recently, with the establishment of Massey University College of Manawatu, the widening of its teaching activities, and the forecast that the roll of the College is likely to be in the vicinity of 3,000 by 1975.

The first university lectures were given in the area in 1928, the year Massey Agricultural College was formally opened. Providing both degree and diploma instruction, the Faculty of Agriculture then established was enlarged in 1948 to form a Faculty of Agriculture and Horticulture. In 1958 the College offered its own courses in Botany, Chemistry, Physics and Zoology for the first examination of the B.Agr. Sc. degree. More recently, in 1962, these subjects were also offered at Stage I level. Thus, in addition to providing the first year course towards the B.Agr.Sc., B.Food Technology and B.Vet.Science degrees, the College is now able to cater for students taking these science units towards a pure science degree, or for the first year of the Medical, Dental, Architectural and Engineering degrees.

A Faculty of Food Technology was formed in 1961 and a Dean appointed in the same year. For many years the University of New Zealand had granted the degree B.Agr.Sc. (Dairy Technology), which was taught at Massey, but the course leading to this degree was terminated in 1961 and replaced by the B.Food Technology degree. The dairy manufacturing and processing industry is now treated as part of the wider food industry, a natural development that is in line with the policies of many overseas universities. One quarter of the Bachelor degree is devoted to chemistry and biochemistry together with their application to foods. Graduates may proceed to the degree of M.Food Tech. which can include a specialized study of food chemistry. Tenders are to be called shortly for the Riddet Building which will house the Food Technology Department. The building of 14,500 sq. ft will contain a processing laboratory and cool stores, as well as lecture rooms, service and teaching laboratories, instrument rooms and staff offices.

Following the decision of the Government in 1961 to site a Faculty of Veterinary Science at the College and the subsequent appointment of a Dean, preliminary planning has reached the stage where students may start their professional training in the new Faculty at the start of 1964. Applications have been invited for three chairs — in Animal Health, Veterinary Biology and Veterinary Clinical Sciences — and for a number of other staff.

While many of these developments were progressing at Massey College, the Victoria University of Wellington established a Branch College in Palmerston North during 1960, to provide opportunities for extra-mural and local students to proceed to a degree in Arts. On January 1, 1963, this Faculty of General Studies joined with those faculties already established at Massey College to form the Massey University College of Manawatu. With this expansion of university teaching in Palmerston North and the consequent increase in the student roll, a considerable building programme will have to be faced. In the case of future science teaching alone it is envisaged that about 150,000 sq. ft of space will be required.

RESEARCH IN CHEMISTRY AND RELATED SUBJECTS

As one would expect, having regard to the present teaching role of Massey University College, much of the research activity of both staff and graduate students is in agricultural and related fields.

SOIL AND INORGANIC CHEMISTRY

For a number of years, most of the work in soil chemistry has been connected with soil phosphate and the forms in which it is present. Recent and current work has been concerned with the applicability of alkaline NH_4F extraction for the determination of aluminium-bound soil phosphate in soils containing allophane and crystalline iron and aluminium oxides as their predominant clay minerals. Further work concerns the influence of added phosphate on the amounts of various chemical forms of phosphate in soil. The study of the effect of fertilizer treatment on the minor element composition of soils which is also being carried out has been made possible by the acquisition of an automatic spectrograph and accessories through Nuffield funds.

ORGANIC CHEMISTRY

Reactions between aldehyde and amino groups are being studied in a number of chemical systems. These include

lactose and casein, glyceraldehyde and ammonia, and lactose and polylysine. In the disaccharide-protein system the formation of 1-amino-1-deoxy-2-ketoses is accompanied by the disappearance of amino-N, which conforms with the initial formation of a lactose-protein complex followed by an Amadori rearrangement. Glyceraldehyde and ammonia interact to yield sugars and imidazolic compounds. Among the later, 4(5)-methylimidazole and 4(5)-hydroxymethylimidazole have been isolated.

Work on the distribution of fatty acids between the α' - and β -positions of milk phospholipids (phosphatidylcholine and phosphatidylethanolamine) has shown that the ratio α'/β for the major fatty acids is similar for the two classes of phospholipid. This similarity lends support to the transformation of phospholipids during biosynthesis.

BIOCHEMISTRY, NUTRITION AND FOOD CHEMISTRY

Much of the work at the College on lipid metabolism is concerned with the effect of dietary lipids on the ruminant. Relationships between the amount and the composition of grass lipids and the composition of the milk fat of cows have been followed. Variability in the lipid content of grasses would seem to be sufficient to result in changes in milk fat composition. Triglycerides are hydrolysed in the rumen to give monoglycerides and diglycerides as well as the products of complete hydrolysis. There appears to be some selectivity in the hydrogenation of these hydrolysis products because the mono- and diglycerides are less saturated than the fatty acids. Currently the enzymic hydrolysis of galactolipids in the rumen is being studied.

Initial investigations into the origin of methyl ketones in steam distillates of butterfat have led to a study of the metabolism of fatty acids by *Penicillium roqueforti* and in particular their conversion to methyl ketones.

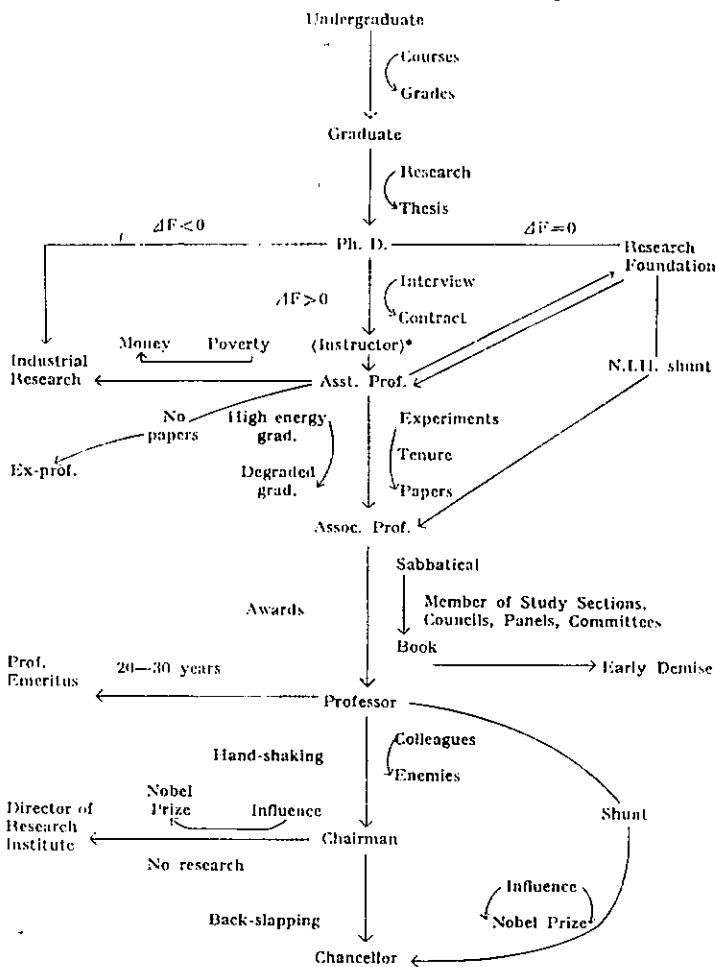
The hydrolytic effect of commercial rennet, rennin and other enzymes on casein as a pure substrate, and also in cheese, is being followed using urea starch gel electrophoresis. Confirmation of the specific sites of rennin attack on casein has been obtained.

The possibility of obtaining a chemical index of the value to animals of meatmeals as a source of protein is being investigated. For the limited number of samples studied, a good correlation has been found between the "available" lysine as measured by reaction with 2,4-dinitrofluorobenzene, and the gross protein value calculated from the growth rate of chickens.

ACADEMIC METABOLISM IN THE U.S.A.

The following metabolic map appeared in *Svensk Kemisk Tidsskrift*, 74: 546 (1962), with an explanatory note, a translation of which reads:

"After extensive investigation Tom Ragland, of Indiana University, Indianapolis, has mapped out the course of academic metabolism in the U.S.A. The results are presented as a metabolic map in the biochemical style. The short curved arrows represent coupled reactions. As apparent from the terms ' ΔF ' (change of free energy) and 'N.I.H.' (National Institute of Health) the system is relevant only to American conditions. The map is reproduced from 'Manual of millimicrosubmolecular biology' with the author's permission."



* Hypothetical Unstable Intermediate

BRANCH NEWS AND NOTES

AUCKLAND BRANCH

At the first meeting for 1963, Dr G. A. Wright, a former Rhodes Scholar who is at present lecturing in physical chemistry at the University of Auckland, addressed the branch on the subject of "Chemistry of bismuth ions".

Dr R. K. Ralph and Professor R. E. F. Matthews, who heads Auckland University's Department of Microbiology, have jointly received a \$39,300 grant from the U.S. Public Health Service, with the co-operation of the U.S. State Department, to aid their work on viruses, nucleic acids and virus inhibition. Part of this grant will be used for the purchase of a recording spectrophotometer and a liquid scintillation spectrometer. Professor Matthews has also received £11,000 from The Wellcome Trust, London, for a high resolution electron microscope.

To commemorate the visit of the Duke of Edinburgh to N.Z. Forest Products Ltd., Penrose, a sum of £1,000 p.a. for five years has been made available for a fellowship to be awarded by the University of Auckland in either engineering or science (including the building sciences) for research work to be carried out in New Zealand.

To aid work in chemistry at the University of Auckland the research committee of the New Zealand University grants committee has made available £2,000 for X-ray equipment, £5,000 towards an IBM 1620 computer and £11,000 for a nuclear magnetic resonance spectrometer.

Professor D. R. Llewellyn has advised that there are twenty-seven students for the one year's chemistry honours course at Auckland and a few of these graduates will probably remain in New Zealand.

Polymers (N.Z.) Pty. Ltd., chemical manufacturers, and N.Z. Forest Products Ltd. have announced their intention to jointly produce high quality coated papers in Auckland. A coating material of primary interest is polyvinylidene chloride, thin films of which, unlike polyethylene, act as a gas transfer barrier. Thus P.Vi.C. coated papers find application in packaging such goods as coffee, castor oil, etc., where either loss of aroma and/or odour transfer may be undesirable.

Miss C. Bishop, the previous branch secretary, will be leaving shortly for London, where she will work with Dr Bunton who is known for his reaction mechanism studies.

In January the University of Auckland announced that Professor D. R. Llewellyn has been appointed to the position of assistant vice-chancellor with special responsibility for buildings. The active part played by the new appointee in bringing forward details of the new chemistry building, estimated to cost £750,000, was undoubtedly taken into account when assigning responsibility.

WAIKATO BRANCH

Following a discussion at a monthly meeting last year, the Branch decided to appoint a committee to consider the operation of the Technician Certification Authority courses in chemistry and to make suggestions for any changes considered desirable. The convener of this committee is Mr N. H. Law. Several Branch members are again co-operating with Hamilton Technical College by conducting evening classes for technicians.

Miss J. M. Gumbley, of Ruakura Animal Research Station, left for England in March, on leave from the Department of Agriculture.

She will take up a position in the Department of Biochemistry at Cambridge University.

The announcement that the projected steel industry for New Zealand is likely to be sited in the Waikato raises the possibility of future increase in the numbers of chemists in this district with some reduction of the agricultural bias in the present branch membership.

MANAWATU BRANCH

The Council of Massey University College includes four members of the Manawatu Branch—Dr J. C. Andrew (who is Chairman of the Council), Dr A. T. Johns, Dr C. V. Fife, and Dr W. A. McGillivray.

Dr G. W. Butler (Plant Chemistry Division) returned in December from the United States. He had been working recently at Berkeley, California.

OTAGO BRANCH

Professor H. N. Parton, Dr G. N. Malcolm and Dr A. M. Kennedy attended the First Australian Conference on Electrochemistry held in Sydney and Hobart from February 13 to 20. Professor Parton was chairman of the session on Non Aqueous Electrolytes at Hobart.

Dr C. G. Pope has been appointed Lecturer in Chemistry at Otago University.

Dr J. G. Blackman, who has spent three years at Edinburgh on an I.C.I. Fellowship, has returned to take up the post of Senior Lecturer in Pharmacology in the newly formed department of Pharmacy at Otago University.

Mr J. Robb is at present overseas for three months.

DR. RUTH ALLCROFT

Dr Ruth Allcroft, O.B.E., who is well known for her work on the biochemistry of animal diseases, spent three weeks visiting friends and former colleagues in New Zealand. Dr Allcroft was educated at Otago University and Victoria University College and worked for three years in the Chemistry Section of the Department of Agriculture in Wellington, under Mr B. C. Aston. After a period at the Rowett Research Institute, Dr Allcroft worked with Dr H. H. Green, a pioneer of the application of biochemistry to animal disease problems, at the Veterinary Laboratory of the Ministry of Agriculture and Fisheries, Weybridge. She is now Senior Research Officer in the Biochemistry Section at Weybridge. Although her recent visit was primarily on holiday, she spent some time at Wallaceville, Ruakura and Rukuhia Research Stations discussing trace element and magnesium metabolism and mycotoxins. In this latter field recent work on the ground-nut toxicity problem, including extraction and assay of the active principle, aflatoxin, from *Aspergillus flavus*, was of particular interest to workers on sporidesmin and facial eczema.

R.I.C. MONOGRAPHS FOR TEACHERS

The Registrar has a few copies of the R.I.C. Monographs for Teachers, Nos. 4 and 5, still available. These monographs (*Principles of Metallic Corrosion* by Chilton, and *Principles of Chemical Equilibrium* by Ashmore) were reviewed in the *Journal* for August, 1962, page 112. Interested members may obtain these from the Registrar for ten shillings per set.

**THE NEW ZEALAND POTTERY AND CERAMICS
RESEARCH ASSOCIATION (INC.)**

DIRECTOR OF RESEARCH

The Council of the New Zealand Pottery and Ceramics Research Association invite applications for the position of Director of the Research Association.

The Research Association, an independent organization financed jointly by the ceramic industry and the Department of Scientific and Industrial Research, has laboratories at Gracefield, Lower Hutt, and employs a staff of ten.

The ceramic industry in New Zealand includes manufacturers of whitewares, structural clay products and refractories. The primary functions of the Research Association are the investigation of scientific and technical problems relating to raw materials and processes used in the industry and the utilization of the manufactured products.

Applicants should have a university degree, preferably in physical chemistry or physics, and considerable research experience. Some industrial experience would be an advantage. It is essential that the appointee be able to lead and direct a research team and maintain liaison with industrial members of the Association.

The Director will be given the opportunity and will be expected to undertake research himself, and in addition will be responsible to the Council for the preparation of research programmes, organization and direction of work, and for submitting reports.

A commencing salary up to £2,500 per annum will be paid in accordance with the appointee's qualifications and experience. Superannuation benefits on a subsidized contributory basis are available. Reasonable travelling expenses incurred in taking up the appointment will be paid by the Association.

Applications should be sent by May 15, 1963, to:

**President,
New Zealand Pottery and Ceramics Research Association,
Inc.,
Private Bag,
Lower Hutt.**

NEW ZEALAND MEDICAL RESEARCH COUNCIL

A vacancy exists for the position of Senior Chemist with the Dental Research Unit, New Zealand Medical Research Council. The successful applicant would be employed in the laboratories of the Dental Research Unit, Wellington, and would be expected to work on the analytical programme relating to an investigation of micro-elements in soils and dental caries. Salary for the position is £1,750 to £2,000 p.a., commencing salary to be dependent on qualification and experience. Annual leave is 3 weeks, study leave is available after not less than 6 years' service, and superannuation benefits are available. Applications, describing age, marital status, qualifications and experience should be forwarded to the Director, Dental Research Unit, P.O. Box 3155, Wellington.

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Qualifications: University degree in chemistry with interests in mineralogy or analytical chemistry.

Duties: Assistance with geochemical investigations on N.Z. rocks, minerals, and thermal waters.

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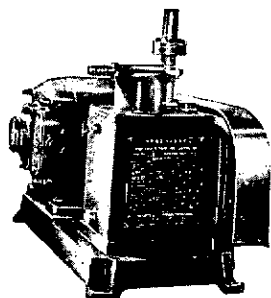
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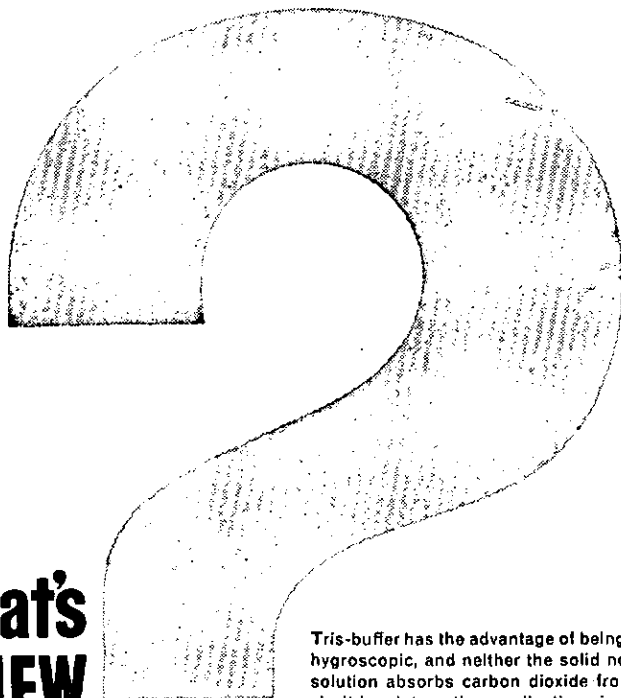
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2. Williams, T. R. and Harley, J. D., *Chemist-Analyst*, 1961, 50, 114.
3. Davies, M. T., *Analyst*, 1959, 84, 248.

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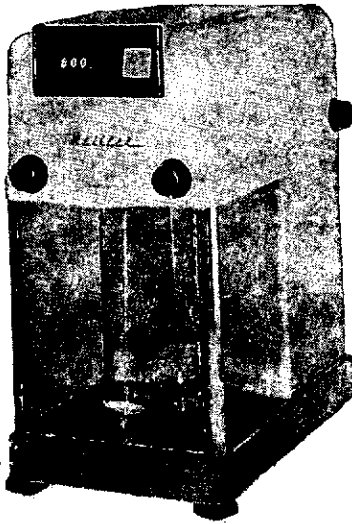
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