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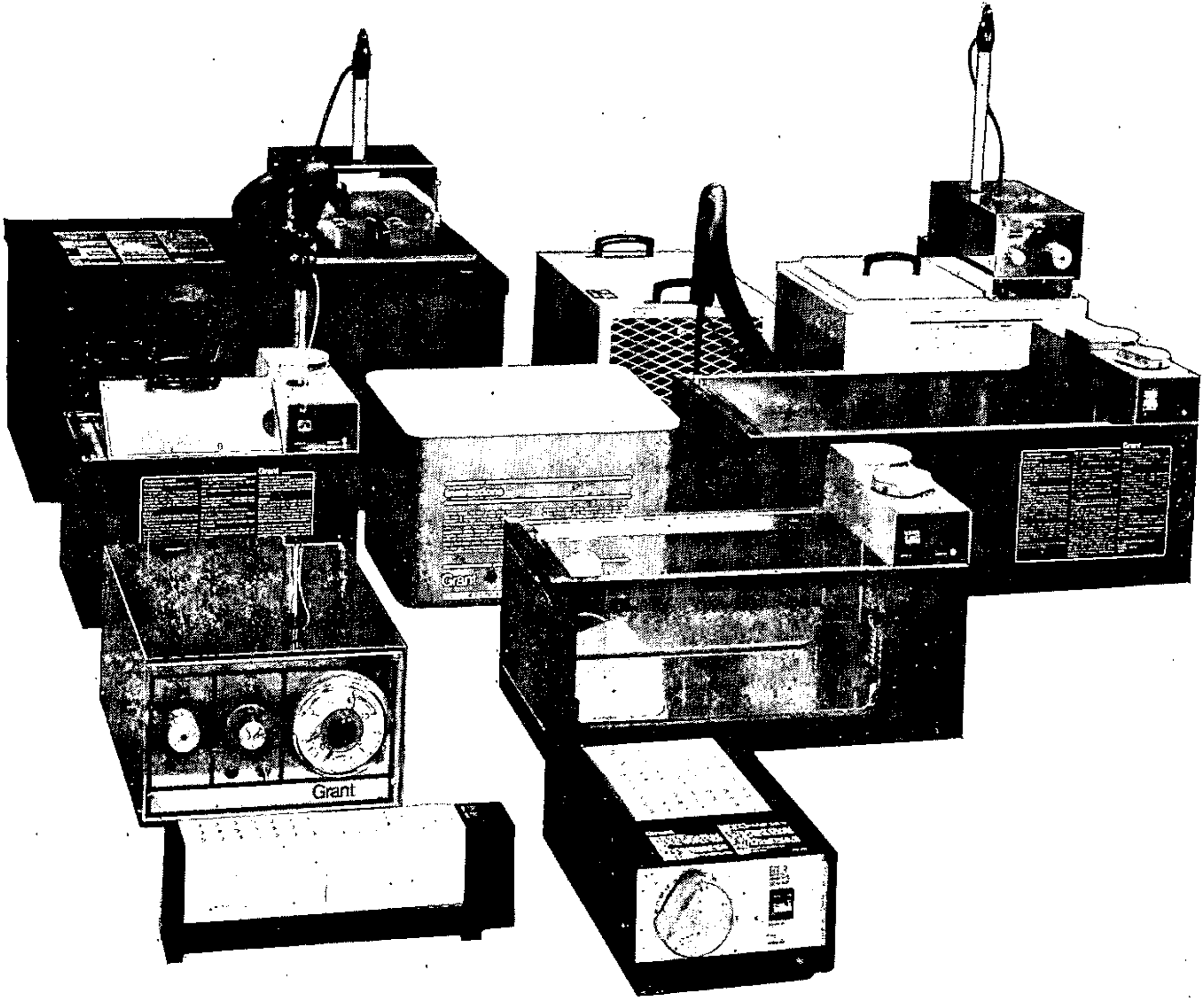
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LOOKING INWARD

John Pollard, President, 1975-76

For many years it has been my privilege to be associated with administrative aspects of the Institute. Always I have been impressed by the organisation's tolerance and kindliness, but increasingly I have also become aware of both its strength and its fragility. These latter features are not widely appreciated so I think it might help members understand our Institute the better if I spend a page or two in the not very fashionable activity of looking backward and inward.

The Institute owes a considerable debt to its first Secretary, Mr W. A. Joiner and its first President, the late Professor W. P. Evans. These two prepared the first draft rules which have given us a constitution which I believe is unique. I know of no other professional body in which it is the Council rather than the Annual General Meeting which confirms the major constitutional matters such as rule changes, nor do I know of another which so carefully guards the rights of branches.

Each branch, irrespective of size, sends only one delegate to the Council, thereby ensuring that representation is by region, not by numbers. There are considerable differences in the attitudes and interests of regions so this provision is an important safeguard against the regional view being swamped by the sheer size of another branch.

In 1944 the Council was given added stability by adopting the concept of a vice-President who was effectively a President-elect. This was later extended to the concept of a second vice-President who was in turn effectively a first vice-President-elect. In parallel with the necessary rule changes the custom grew up for each branch in turn to be the sole nominator of a new second vice-President.

The resultant "presidential pipeline" has ensured that by the time each President takes office he has already had two years involvement in current Council business. This pool of experience safeguards the orderly transfer of ultimate administrative responsibility whilst removing the need for the post of immediate past-President—a grey shadow that has haunted the authority of many a president in other institutions.

To no less a degree is it also desirable that Branch Delegates acquire a thorough knowledge of Council activities if they are to represent properly their branch and report to it. It is, therefore, desirable for branches to give their representative not less than a two year term.

Between the rules and the customs there has evolved a strong experienced Council. It is moreover, a Council of branches. Each of the six branches has direct representation but in addition three of the six also have their nominee in the presidential sequence. Only the General Secretary, the tenth voting member present at the Council, is outside this strong branch tie. Most Council resolutions need a simple majority but in the important matter of rule changes the decision requires the assent of four of the six branches.

The rules also provide checks and balances to preserve the democratic rights of all the members. Any six members if they saw fit could challenge the presidential sequence by putting forward their personal nominee for any of the three presidential offices. Any 20 members may demand an extraordinary general meeting, whilst at any general meeting any 10 members present may demand a postal ballot. But note that the members must be corporate. By these means the Institute is safeguarded from packed or irresponsible councils, packed or irresponsible meetings, whilst always the ultimate decisions reside with the corporate members.

Because the rules say little about detailed procedural matters, the Council, the subcommittees, and the branch committees have considerable flexibility in freedom of interpretation and action.

These are the things which give the Institute its strength, stability and tolerance. They also contain the seeds of a weakness that was not obvious in the beginning when all the members were at least acquainted; when the unwritten rules were yet to be evolved, the customs yet to be established. Even though the Council meetings were infrequent, and travel onerous, most knew what things were done, and why they were done. After all even in 1946 the membership was only 300.

Presidents have come and gone, so too have Branch delegates; there is only one member of the first Council to remind me of why things were organised the way they are. Within the active membership there are only two with a proper claim to understand the collective customs of the Institute. We have been singularly fortunate in that the holder of the General Secretaryship has changed but infrequently. In 34 years the office has been tended faithfully and well with only one change. Now that Dr W. E. Harvey has been elected to the post of second vice-President we are in the process of losing the one voting member of Council who remembers in detail all the functions of the Institute.

The second person who fully understands the Institute is Mr D. J. Hogan. He has been associated with Council meetings firstly as Branch Delegate and then as Registrar for some 18 years. Successive Presidents have looked to these keepers of the Institute's heritage for guidance on procedure and custom. Wish though we may, we cannot assume they will be free to advise indefinitely. This year for the first time a start has been made in committing to paper their collective knowledge. The intent is a guide for incoming Council members.

It is not easy for a new Council member to become familiar with Institute affairs. There are but three meetings a year, a very full agenda, plus travel limitations for the times of start and finish. There have been various attempts to speed or prune the Council business but nothing has produced the leisure time needed for members to talk informally or become properly acquainted with one another. This is a major reason for suggesting that Branch Delegates should have at least two year appointments.

More frequent Council meetings would assist; but a Council meeting costs at least $600, about 50 cents from every member of the Institute. The solution I think lies in more Council business being transferred to small committees charged with presenting the Council with firm recommendations for action. This transfers the communication to a more easily assembled group at a lower travel cost. It is essential that such committee members do meet for I have found nothing substitutes for person to person discussion.

This is an immediate solution, less costly than additional full Council meetings, but it does not assist the more diffuse need to improve regional communication. I have already referred to the differences in branch interests. To me they have sometimes seemed considerable. A Council meeting with a full agenda is not the best forum for branches to seek common ground. There needs to be a greater interchange of branch views and comparison of attitudes independent of Council meetings if the Council is to reflect properly the wishes of all members. This need was apparent during discussions on technician entry, it is again apparent in regard to the future of Institute publications.

To aid communication between Council and members a journal was published as far back as 1936. The conception was preceded by much discussion. The birth began a love-hate relationship which continues to this day, still attended by much discussion.

The early issues were bedevilled by cost. So much so that in 1939 there was no issue. A further 37 years of progress have again brought us to near crisis because of costs. In fact the history of the journal is remarkable in the degree to which the same complaints, the same remedies, have been voiced over and over, each new voice seemingly oblivious that it is but an echo of voices past.

Professor Parton stated in 1955 that the journal "helps to combat New Zealand's difficult geography, in which Cook Strait separates productivity from culture, or so it is held in some parts. It expresses the vigour of a growing profession, and its growth to maturity measures the development of the Institute it serves. Its status in 1955 justifies the faith of those who began it nearly twenty years ago, and New Zealand chemistry moves into the second quarter century of its institutional life, well equipped on the publication front to match its achievements in other fields."

His words are no less true today, but the economic facts are harder. We are not the only professional organisation to be in financial straits over publications. Between the May and June issues of "New Zealand Engineering" the Institution of Engineers has been forced to cut the text from 31 pages to 16 along with a change of printer. This is the fate of a long established magazine with a printing run in the order of 5000. "Chemistry in New Zealand" is proportionately more expensive because there are fewer issues and a printing run of only 1500 copies. The overall budgets for publications are similar, 21% for the NZIE; 27% for the NZIC. The NZIE is currently seeking comment from its members to determine the future of "New Zealand Engineering."

Within the institute opinions regarding "Chemistry in New Zealand" range from indifference through to a desire for 12 issues and no "NZIC Bulletin." I think the current compromise of three journal issues in combination with six bulletins is a good one. Any further reduction in the number of journal issues would sever a link hard forged over the years. The journal and the bulletin are complementary, the more so now that Dr Creamer has consented to edit both.

Regular journal issues provide a permanent record of the Institute's interests, administration and growth. It is our show case, something that needs to be collated, dressed and displayed with loving care. Miss Mattingly has done just this for us over many years—"Chemistry in New Zealand" is an outstanding achievement. This standard of publication takes time to plan and such is the progress of commercial printing, longer and longer to progress from copy to publication. (This article is being written against a September 23 deadline for a November publication.)

The "NZIC Bulletin" is intended to fulfil a different communication need, that of rapid dissemination of news, comment, information, without too much heed to format or style, with a minimum of delay in the transformation of copy to publication. Currently there are delays whilst the bulk packages await branch distribution with their monthly newsletters. This could be avoided if—if—members were willing to pay for postage under a separate cover; say 50 cents per person per year plus some volunteers.

Herein is the crunch — services, convenience, standards, style, all cost money. My total subscription in 1970 was a trivial $9.25. This year it is an apparently substantial $20. In reality it is now a slightly lower fraction of my gross salary which has more or less kept pace with inflation over the same period. It is unfortunate that for several years we did not increase the subscription in pace with both costs and salary increases. The result was a run down on reserves coincident with a time when the membership had at last grown large enough to warrant a part-time administrative secretary.

It has taken stringent budgetting to hold expenditure in line with income. That the situation has been held is testimony to Mr Hogan's skill and understanding as Registrar. Even so I doubt if we can ever again revert to the highest quality of publication — the old format for the "List of Members" has already gone — nor can we be as generous as we would wish in our encouragement of visitors.

In spite of austerity, subscriptions will have to be raised if only to keep pace with inflation. On this issue one again finds differences between branches. No doubt a return to tax deductions for actual reasonable professional expenses would make the increases a little more palatable. The true intentions of the present Government still await clarification.

One thing is certain, members get rather more than they pay for in subscriptions. There was professional surprise at the journal quality achieved with a volunteer editor, there was administrative surprise at the membership we cover with a part-time secretariat. Nor should we forget the subtle subsidies from the organisations which employ our various volunteer officers, house our meetings, welcome our conferences.

The Conference, the third national link in Institute affairs is currently successful, self-supporting, and therefore non-controversial. Less popular is the local link, the branch meeting. I have had some experience with programme organisation. I suggest that there is no certain formula for ensuring attendance, nor do I think it correct to equate attendance at branch meetings with the real interest of individuals or with the health of the body corporate.

It is no longer fashionable to attend regular meetings of any form, a fact causing concern in many technical societies. Fortunately there remain individuals who are willing to work for organisations with enthusiasm, without thought of reward beyond personal satisfaction. Let us be grateful to them but also let us be aware that these activities do bring personal satisfaction. There is no reason for us to expect the majority to share in these efforts, nor to expect them to come to applaud. Closer scrutiny will show that the majority too have their special interests and causes. We should be grateful that members are concerned with things beyond Institute affairs, perhaps bringing the chemist's specialist approach to bear on other efforts in the community. It is sufficient that these members accept the efforts of those who labour for the Institute.

Nevertheless I should be disturbed to see any curtailment of branch programmes for those who still enjoy the fellowship of scientific colleagues. Many chemists of my generation are now far removed from the practice of chemistry, we rely heavily on the journal, branch meetings and conference programmes to give us at least some inkling of progress in fields well beyond our deeper understanding.

During each branch visit I mentioned that the Institute means different things to different people. I think it combines its functions remarkably well. That it has done so from the beginning is no small tribute to the skill and foresight of those who were the architects of the structure. It has been my honour to have been allowed to care for it for a little time.

HONORARY FELLOW

Mr. S. G. Brooker was earlier this year elected by Council to Honorary Fellowship of the N.Z.I.C. Mr. Brooker obtained his M.Sc. from Victoria University College, graduating with honours in 1933. After a period (1930-35) in the Department of Agriculture chemical laboratory in Wellington he moved to Auckland as a research student at Auckland University College and thence to Abels Ltd. as Chief Chemist, a post he held from 1936 until his retirement in August this year. He joined the N.Z.I.C. as an Associate in 1942 and was elected a Fellow in 1948.

Mr. Brooker has served us as Editor (1949-53), Librarian (1959-76); and President (1963-64). He was one of the founders of the N.Z. Institute of Food Science and Technology, being President (1971-73), and holding other offices and awards. He was President of the Auckland Institute and Museum (1964-67), Secretary of the Eighth N.Z. Science Congress (1954), Council member of the Royal Society of New Zealand (1956-66) and has held many other important positions on national and international scientific bodies.

Mr. Brooker has an outstanding record as an industrial chemist, and in his contributions to scientific organisations. He is widely known as an authority on the science and technology of fats and related products and has been responsible for many technical innovations in this field. He has written two books, and many technical papers. His contribution to food science was recognised by his election as the first Honorary Fellow of the N.Z. Institute of Food Science and Technology, and his election to Honorary Fellowship of the N.Z.I.C. is a fitting tribute to a distinguished career in chemistry.

PERSPECTIVE ON CHEMISTRY

H. N. PARTON

In the forty-five years of its life, the Institute of Chemistry has maintained a close relationship at both national and regional levels with the university system, to the satisfaction of many people and the benefit of both institutions. It is worth noting that the first four of the Institute's Presidents were professors (W. P. Evans, T. H. Easterfield, H. G. Denham, F. P. Worley); also that the disciphighest level of university administration with three Vice-Chancellors, F. G. Soper (Otago), F. J. Llewellyn (Canterbury) and D. R. Llewellyn (Waikato), and with Sir Malcolm Burns serving as Principal of Lincoln College for more than two decades. My colleague, Professor Soper, quoted me as describing the conversion of a professor of chemistry into a Vice-Chancellor in terms which may seem to denigrate it. On the contrary, along with Otago University, I was a major beneficiary of his inter-disciplinary transformation.

The University of New Zealand to which Dr Soper came as a professor in 1936 received me at a more humble level eleven years earlier as a first year student at Canterbury College (then an 'affiliated institution'). 1925 was a notable year for the University for other reasons, as will be shown below. The University was a peculiar institution — to borrow a phrase applied to slavery in the southern United States. All countries have peculiar institutions. England sometimes appears as made up of them, with Trooping the Colour, beating the bounds — and swan upping on the Thames; the Warden of the Cinque Ports (not all ports today) and the Chiltern Hundreds; public schools which are private, and designed, according to Chesterton, for the fathers of gentlemen; and Carnaby St where boy can meet girl without realising it, and vice versa. New Zealand cannot challenge the rich eccentricity of England. But it did have the University of New Zealand, and now it has been without it for fourteen years we only have the Rugby Union to remind us of the 19th century.

Its peculiarity arose in its foundation years and was the product of the strife which accompanied them. It was embalmed in Clause 4 of the 1874 Act which laid down the University's functions. "It is hereby expressly declared and enacted that the University hereby established, is so established not for the purpose of teaching but for the purpose of encouraging . . . the pursuit of a liberal education, and ascertaining, by means of examination, the persons who have acquired proficiency in literature, science and art, by the pursuit of a liberal education." To govern, to encourage, to examine, but not to teach, these were its limitations. It was given no power to establish professional schools, which thus became a major battle ground for much of its life, with parochial interests mixed with national needs in the ardent pursuit of "Special Schools." Its last Vice Chancellor, Sir George Currie, described it as consisting of "An Act and a brass plate." The Act has been deactivated and the brass plate now needs cleaning. It was born the examining university and remained so until its last years, which became it more than most of its earlier years as it devolved its powers to its constituent colleges and prepared its own dissolution.

In its first years the University was content to use the professors in Otago and Canterbury as its examiners, but late in the seventies took a decision which dominated the university scene, and especially the teaching staffs in the colleges, for sixty years. The Senate decided that its examinations should be conducted by "eminent authorities overseas." A case could be made for the decision if the teachers in New Zealand had been involved in some way. But the justification for the system which became an article of faith with successive Chancellors was pure mythology. They believed, and frequently announced their belief, that the system gave the New Zealand degree a uniquely high standing. The thought that examinations adapt to the teaching, even when conducted 12,000 miles away by eminent scholars, seems to have been overlooked. One eminent professor (later Chancellor of the University) had no failures in the examinations set overseas in nineteen years. His method was simple. He failed in the annual college examinations, ("Terms") everyone likely to fail in the finals, and no doubt some who would have passed. He was not unique. The Royal Commission of 1925 (this was the other notable event of that year) stated that whereas the overall performance of part-time students was much below that of full-time students, the two groups had almost identical success in the examinations set overseas. The Commisioners drew the obvious conclusion — the standards were set in New Zealand by the terms examinations. In these however, as in other fields of human endeavour, the establishment of facts, even when they can be established, has little effect on deep-rooted prejudices. The Royal Commission also invited the students of the day to answer a questionnaire. It was very old fashioned — nothing about our sex life or drug habits as would be de rigueur now — just questions on the sporting and intellectual clubs we joined, and an invitation to estimate our weekly effort at "private study." I was delighted to find, 50 years later, that Canterbury students made the most inflated claims in the

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Based on a Review Lecture given at the N.Z.I.C. Conference, August, 1975.

latter estimate. I have been sceptical of questionnaires ever since.

So much for the university. What of chemistry in the 1920s? As taught to me at school, it was very much the subject described by J. D. Bernal —"the old chemistry was largely a matter of memory, a set of cookery book recipes that had, for no apparent reason but to worry the students, to be learnt by heart." I found it uninteresting until my last year, when the need to study it for scholarship purposes changed my view; so much for the tyranny of the scholarship examination. Then when I went to Canterbury College, H. G. Denham's first year course completed my conversion. He had experimented (in Queensland) with introducing the Periodic Law much earlier in his course than was usual then. I realised for the first time that chemistry possessed broad generalisations from which predictions could be made and tested in the laboratory. In later terminology it is a theoretical generalising science, not a collection of facts. Advanced lectures (apart from John Packer's organic chemistry most of which I missed when he was on leave in 1926) were much less stimulating, though Denham was very good on heterogeneous equilibria (Gibb's phase rule). So we had to read a lot, and I used W. C. M. Lewis's *System of Physical Chemistry, Vol I Kinetic Theory, Vol II Thermodynamics, Vol III Quantum Theory.* Unhappily the eminent overseas scholars did not think we were up to Quantum Theory, and from the standpoint of examinations I "wasted" a lot of effort. The 1920's were revolutionary times in physical science. We chemists are fairly simple souls, accepting atoms and molecules, and a very simple theory of valency on which the remarkable structure of organic chemistry was built. Physicists were less happy with the sharp clash between particle theory and field theory, and the best of them looked for some unified field theory from which particles could emerge as singularities in a natural way. Quantum mechanics (1926) was a compromise, and in 1928 Dirac stated that "in principle, all of chemistry and a large part of physics can be derived by application of quantum mechanics to a few basic properties of electrons, protons and neutrons." As we all know, to say that something can be done in principle means it can't be done. The effect in chemistry of the development of quantum mechanics was swift and far reaching. We already had Bohr's explanation of chemical periodicity (1922) and the underlying principle (Pauli 1924). In 1927 came Heitler and London's theory of the covalent bond in hydrogen and three years later London's explanation of Van der Waals forces in non-polar molecules. 1929 saw Bethe's crystal field theory, the forerunner of ligand field theory. With Goldschmidt's lecture to the Faraday Society on the significance of ion size and polarisation for the structure of ionic crystals — the most exciting lecture I ever read — 1929 was a seminal year in the renaissance of inorganic chemistry. Then in 1930-31 Eyring and Polanyi developed the transition state theory of reaction rates.

When I joined the Canterbury staff in 1930 (Denham remarking "better the devil you know than the devil you don't know"), I was given a free hand with M.Sc. lectures (fourth year) in both physical and inorganic chemistry. I earned my keep with Intermediate Organic and Stage III Inorganic. I wanted to lecture on the sort of questions I have mentioned above. I believed, perhaps naively though I still believe it, that universities are concerned with the advancing front of understanding, much more than accumulated knowledge. Here is where my discussion above of examination procedure in the University of New Zealand is justified. Like many of my colleagues I was frustrated by external examiners. Inorganic and physical chemistry suffered more in the B.Sc. course than organic, which was normally done at Stage II and examined in New Zealand from 1927. John Packer however returned from Imperial College excited about reaction mechanisms and had to wait a long time before he could make full use of his enthusiasm for them. In recollection I doubt if more than half the lectures I gave at the M.Sc. level were of any help to the students, assuming any of them were. How then, did they cope? Very well; partly because they were of high average ability, with a number of quite outstanding ones, and partly I suspect by the help of Samuel Glasstone. His *"Recent Advances"* books of the 1930's were obviously read by the external examiner in physical chemistry, and guided his setting of questions in some degree. Then his text book of 1941 became a rock on which many students found refuge, though by this time external examiners were no longer with us. I was never fond of the book. I agree with the judgement passed on it in a famous (or notorious) review in the *Transactions of the Faraday Society* signed E.A.G. The book lacked perspective, and so did not teach physical chemistry as I had learned it from Lewis. I was however surprised recently to see how descriptive it was, compared with a modern text such as that of Walter Moore. I should however add that when I visited E.A.G. in 1949, I found Glasstone's text in his reading list but marked "for reference only." The standard in physical chemistry demanded by our external examiners was not high. One of them tried to "soup up" a simple question in thermodynamics by giving an enthalpy of transition in mechanical units instead of calories (or joules). He made an error of 10^5 and a candidate who got his sum right found that a change of pressure of one atmosphere (the commonest unit among the multifarious pressure units of the dav) was alleged to change a transition point by 2000°C. It is the good student who suffers from such errors.

In 1940 even the University of New Zealand had to give up its overseas examiners. I hasten to add that it would be wrong to attribute the outbreak of World War II to frustrated academics in New Zealand, even though we knew that nothing less than a world conflagration would destroy the myth. We had a few years of common examinations among the four constituent colleges, and then in 1948 were freed from our shackles, and internal examining with external assessors came in. The trouble about reforms (and revolutions) is that they never fulfil the reformers fondest dreams. By the time we achieved freedom, increasing student numbers were met with increased staffs. Over the years I found myself firmly and politely levered out of my favourite parts of my subject. My consolation today is that the guilty parties have now themselves reached the age when they will (I hope) be levered out too, politely but firmly. A much more important effect of larger staffs was increasing specialisation, and it was this, more than anything, which raised standards. I found the situation of physical chemistry in my last years increasingly baffling. Ideally a course could be devised to proceed deductively — from atoms and molecules (quantum mechanics) through to matter in bulk (by the averaging methods of statistical mechanics) and then to the relations between the properties of bulk systems (thermodynamics, an unsatisfactory name). The historical order is the reverse and learning must proceed by compromise. I wonder if the majority of chemistry students are well enough grounded in physics and mathematics. If they are not, a Glasstone type text, with or without perspective, might be all that many can manage.

So I come to education in chemistry as part of education in general. Anything I say about that is of course mere prejudice — only the young have opinions. Whatever may be said about the "permissive society," I find permissiveness with the English language deplorable. One word must not be used where six will do. So "now" or "at present" becomes "in this day and age" and "at this point in time" — pretentious rubbish. Adverbs ("hopefully" is the main sufferer) appear in sentences which lack a verb they can properly modify. An "examination result" is now "an achievement profile"; homework is "individual pupil activity"; cramming is "reinforced cognitive development"; and a timetable is "a factor in curriculum strategy"! At least we can be grateful for the French Academy and hope it will maintain one language as an instrument of clear thinking.

"Communication" is the current fetish. Just as production is surely prior to distribution and consumption, I think the acquisition of knowledge and understanding precedes communication. Pop musicians are effective communicators — it is a pity they have nothing to communicate except phony sentiments and trivial emotions.

Sophistication of equipment has profoundly altered chemistry and of course chemical research. Chemists have always owed much to glassblowers; now like the pop singers, they are in thrall to the electronic technicians. Problems can be tackled which seemed impossible 30 years ago. Are we heading for the Elimination of the Experimenter, with data being logged direct on to computers? Teaching aids are also a boom industry — are we also about to eliminate the lecturer? Once upon a time a certain professor found himself involved with important activities outside his university, as professors will. Being a conscientious man, as professors are, he decided that when he was away his lecture should be recorded on tape and played to his class by his head technician. One day he found the airport closed and was back in his department at the hour when he would have been lecturing. So he decided to check-up and listened at the lecture room door. All was well — his voice could be heard dropping the pearls of the day one by one. Then he peeped in the door. The recorder was playing away, and so were a number of small recorders scattered round the room. The students, like the professor, were absent. Why then, do we still lecture? The practice has an ancient lineage, from the time when students were prepared for learned controversy. It persisted after the production of cheap books — some say through the patience and tolerance of the students and the self-esteem of their teachers. It is an economical method, and contributed largely to keeping the university system in New Zealand among the cheapest in the world. There is always at least one person who benefits from a course of lectures — the person who prepares and gives it. I am, from this point of view, grateful to those who tolerated me. Most of us will agree that there is at the university level some kind of transaction between "masters" and "scholars" to which the name teaching can be applied, at least for convenience. But a university is concerned with learning, and the scholars are of an age at which their basic needs are guidance and stimulation. I could never see that "a good set of notes" had much to do with university education. If they are not available in a book, there is still the typewriter and machinery for reproduction. So among possible objectives of lecturing, the transfer of subject matter, "covering the course," seemed to me to rank very low, whatever the students might think. The demonstration of skills is more important—how to read around a subject, how information and evidence is marshalled, how experimental procedures are designed, how logical conclusions are drawn from evidence. Some university teachers succeed in influencing students by the example of their attitude to their discipline — their enthusiasm for it and their understanding of its part in the whole process of growing knowledge. Of course the objectives a teacher sets are not mutually exclusive. There may be one somewhere who excels in all facets of the art. But university teaching should, I believe, guide, stimulate and help students to develop their own subsequent learning. There is no "best" method for this, and I am by no means clear that the capacity to do it can be achieved except by trial and error in the lecture room, with a tolerant audience. Probably a good teacher is the one who renders his task unnecessary.

Examining, like teaching, is under fire today. I am very old fashioned about it. Examinations are part of the university's public responsibility. If the process of judging and classifying those who will become professional men, not only in the traditional "learned professions" but in all disciplines, is given up by the universities, then other institutions of society (such as the professional societies) will take the task over, (or take it back in many cases). Examinations endeavour to judge students by their merits, to put them roughly in some order — this one is a little better than that one; this one is the poorest of those who qualify; these are so poor they must be failed. But they need to be tailored to the objectives the teacher is pursuing. This was why those of my generation objected to the external examiner, whom we saw as obstructing, distorting, nullifying and even corrupting our teaching. Final examinations which determine the standing of the degree a student earns need complementing by the personal knowledge of his teachers. A lone examiner can be a menace — perhaps a group of too like-minded examiners is a danger also.

At a recent conference of the Chemical Society and the Royal Institute of Chemistry on the shortage of chemists in the United Kingdom a number of reasons were put forward to explain a trend which we must, as chemists, be troubled about. Among them were the cut in graduate recruitment by industry three years ago; a shortage of good teachers in the schools; a reaction of young people against the physical sciences, seen as materialistic and inhuman; the intellectual demands of modern chemistry. One that found an echo in my mind came from Lord James, sometime chemist, grammar school head, and Vice-Chancellor (of York). He was critical of the emphasis being laid on the vocational rather than the educational value of chemistry, summing it up with the remark that students are being given the latest detergent rather than "intellectual adventure." While the phrase repels me a little—perhaps it is a bit pretentious — it does describe what attracted me to chemistry 50 years ago, as I have tried to indicate early in this talk. Science is an intellectual adventure, and no lesser concept of it is appropriate to a university. Such is my simple minded belief. The task of the university teacher is to encourage and guide those who will solve problems, many of which we cannot even formulate at present. I do not entirely agree with an opinion expressed by Sir Ian Wark some years ago that "in a university the subject is all important, in industry the problem transcends the subject or discipline." At the research level the problem transcends our arbitrary division of scientific knowledge into disciplines in a university as elsewhere. But a further point Wark made is one which must concern us. He observed that 90 percent of Australian Ph.D. chemists wanted to carry on with the problem of their last year of formal training, and added "it is appalling. Their Ph.D. studies have failed to develop a spirit of adventure, a desire to accept a challenge such as industry presents." This is a valid and serious indictment. Of whom? Probably of timid students, staff lacking breadth of vision, industry with similar limitations. I say again, science is an adventure in ideas; that is how it seemed to me 50 years ago and how it remains today.

INTERNATIONAL CO-OPERATION AT THE UNIVERSITY OF CANTERBURY

C. H. L. KENNARD

For a number of years, the Australian Research Grants Committee has funded a scheme whereby research students from the Department of Chemistry, University of Queensland have used the Hilger-Watts X-ray diffractometer at the University of Canterbury. This machine is under the control of Professor Bruce Penfold and Dr Ward Robinson. The research students were Terry DeLacy, Rodney Seccombe, John Tillack, Kelvin Shields, Graham Smith and Janette Whitnall. This arrangement has been extremely profitable, and as a result a number of interesting structures have been determined. This paper is a summary of the joint program.

A major part of the crystallographic research at Queensland has been to try and develop mode of action theories for insecticides, weedicides and analgesics. In a general attack on DDT-type compounds, the structure of the *o,p'*–DDT was determined[1] (Fig. 1). The structures of two cyclodienes, endrin and aldrin, have also been determined[2], as well as the analgesic, pethidine hydrochloride.[3]

Other work has included studies on the stereochemistry of flexible chelate metal complexes, such as dihydrogen ethylenediamine tetra-acetatostannate (II)[4] (Fig. 2) and 1, 2, 4-triazoles (guanazine hydrobromide)[5]. A number of other structures have been solved but most of this work has still to be written up for publication. DDD, a DDT break-down product belongs to this group.

This scheme has allowed a continual exchange of views, ideas and computer programs across the Tasman on a laboratory to laboratory basis. Although most of the students had collected data using similar equipment within Australia, for all of them it was their first experience in a different country, and they all took advantage, of course after data collection, of exploring the country.

On their behalf, I would like to thank those involved in New Zealand Chemistry for the help given to the group and in particular to those staff and students at Christchurch. This type of international co-operation has really helped our research.

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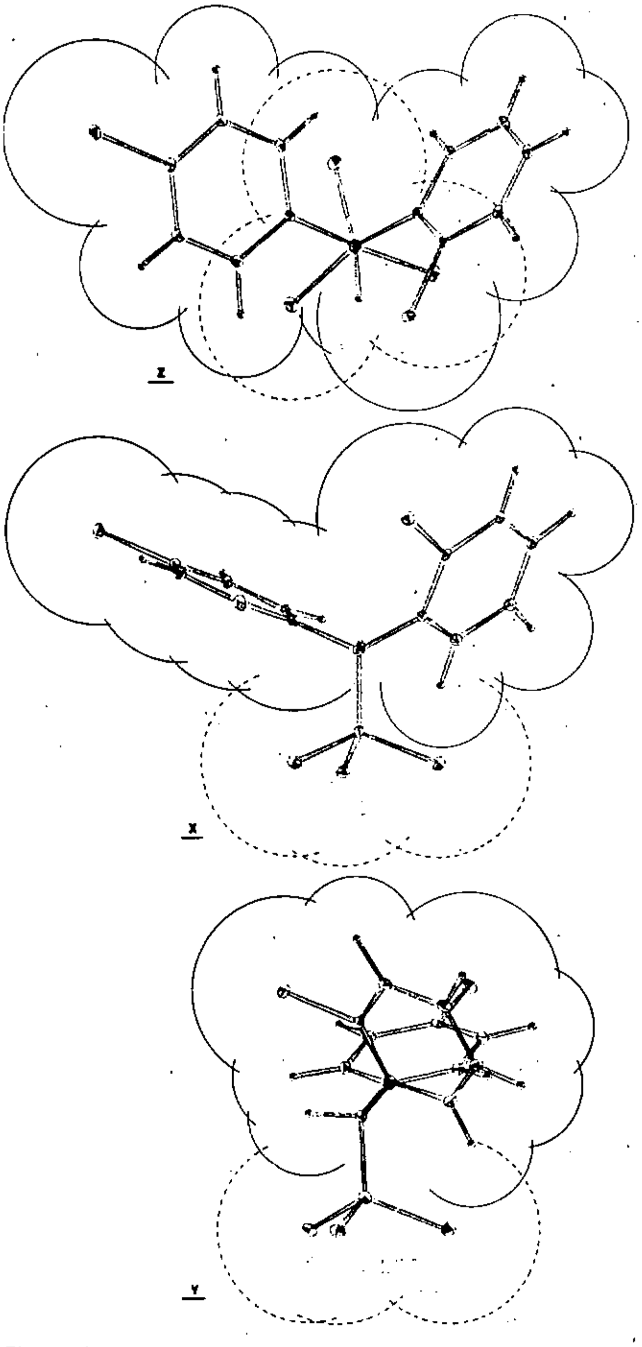

Figure 1

Three plane projections of *o,p'*–DDT.

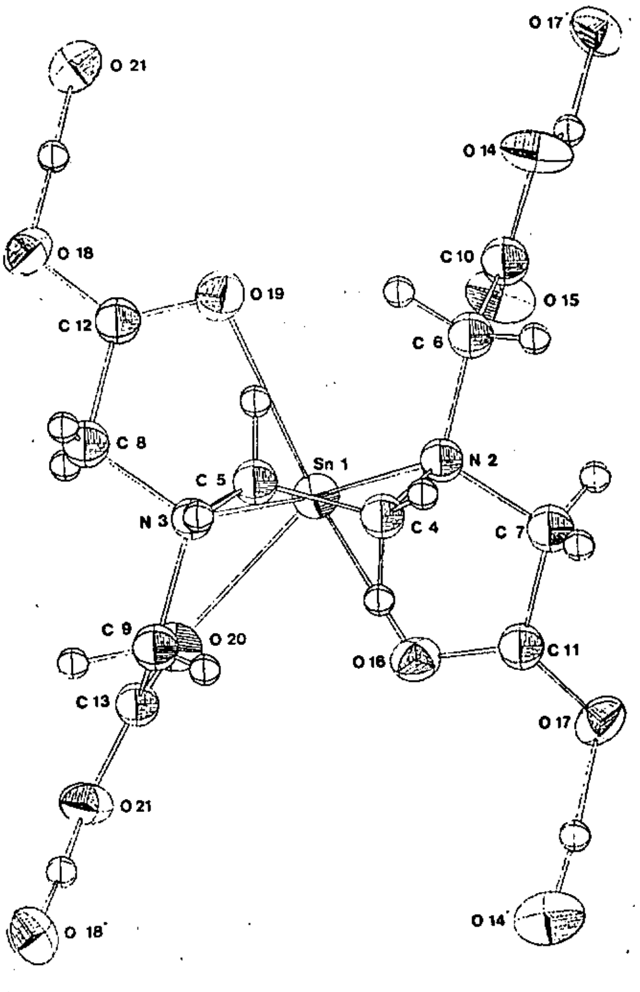

Figure 2

Structure of dihydrogen ethylenediamine tetra-acetatostannate (II).

SOME CHEMICAL AND BIOCHEMICAL OBSERVATIONS ON CERTAIN β-GLUCAN COMPONENTS OF PLANT CELL WALLS

B. A. STONE

In this survey I hope to illustrate, by reference to specific examples of β-glucans, the relationship between their chemical structure and biological functions, and to examine some current concepts concerning their depolymerization and biosynthesis.

Structure-Function Relationships Among β-Glucans

The basic structures and occurrence of β-glucan polymers from natural sources are shown in Table 1. All are composed of glucopyranose monomers in which the anomeric hydroxyl is in the β-configuration so that all bonds joining substituents to the pyranose ring, other than hydrogens, are equatorial (Fig. 1).

TABLE 1

OCCURRENCE OF β-GLUCANS

(L = linear, B = branched)

1,4-	Cellulose	L	Cell walls
	Amyloids (xyloglucans)	B	Cell walls
1,3-	Paramylon	L	Intracellular inclusions
	Pachyman	L	
	Callose	L	Cell walls
1,3-; 1,6-	Laminarins (~10% 1,6-)	L	Intracellular inclusions
	Leucosins (~10% 1,6-)		
	Curdlan (~0.5% 1,6-)	L	Extracellular
	Yeast glucan (~10-20% 1,6-)	B	Cell walls
	Claviceps-type glucans (~25% 1,6-)	B	Extracellular
1,2-	Crown gall polysaccharide	L	Extracellular
1,6-	Lutean (esterified with malonic acid)	L	Extracellular
	Pustulan	L	Intracellular
1,4-; 1,3-	Barley glucan	L	Cell walls
	Oat glucan	L	Cell walls
	Lolium glucan	L	Cell walls
	Cereal leaf and stem glucans	L	Cell walls
	Lichenin	L	Intracellular
	Monodus glucan	L	Cell walls

The differences between the β-glucans relate to the position of the glucosidic linkage between the anomeric (hemiacetal) hydroxyl at carbon 1 on one monomer and the hydroxyl on the next sugar residue. All possible positional types have been found, viz: 1,2; 1,3; 1,4; and 1,6; and several of the β-glucans possess linkages of more than one type. Many of the glucans are linear molecules with degrees of polymerization usually of several hundred, and in the case of cellulose over 8000.

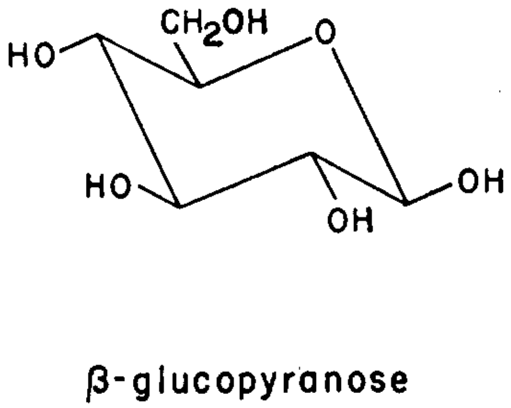

Fig. 1. β-glucopyranose (chair form).

The basic chemistry of these polymers has been established and it is now possible to attempt to relate their structures and functions. In doing so it is necessary to examine the spatial configurations or conformations of the polymers. This leads to an understanding of the molecules at a level intermediate between the chemical constitution on one hand and the macroscopic properties of the polymer on the other.

Rees and others[1,2] have been able to compute "average conformations" for each of the linear β-glucans. In principle this method involves exploring all conformations systematically, and exhaustively rejecting those involving steric compression. From the computed average conformations it is possible to depict one regular conformation for each polymer as shown for the 1,4- and 1,3-β-glucans in Fig. 2.

In agreement with results from physical measurements on fibrous cellulose, 1,4-β-glucans have an extended ribbon-like conformation. The structure-function relationship for this conformation is immediately understandable since the extended, ribbon-like molecules readily pack together to form aggregates which are recognized at the level of resolution of the electron microscope as microfibrils. The inter-molecular forces are strong and the molecular aggregates are ideal structural units for their supportive role in plant cell walls.

The linear 1,3-β-glucans, on the other hand, have a flexible, helical conformation but it is not easy to relate this organization to their role as readily

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(Based on a lecture given at the N.Z.I.C. Conference, Massey University, Palmerston North, on August 22nd, 1975)

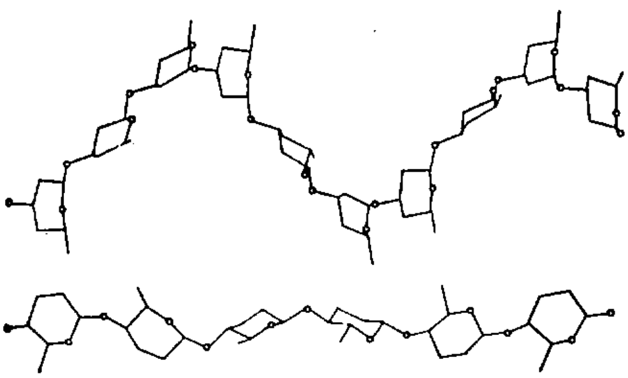


Fig. 2. Regular β-glucan conformations in projection corresponding to 'average conformation" deduced from computer output.

(a) 1,4-β-glucan
(b) 1,3-β-glucan
From Rees and Scott[1]

mobilized storage polysaccharides such as paramylon[3], or callose which occurs as deposits, often of a transitory nature, on cell walls[4]. Presumably the wide, helical form makes them easily accessible to the active sites of their specific depolymerizing enzymes. It is relevant here to note that 1,4-α-glucan chains in starch and glycogen storage molecules also have a flexible helical conformation[1].

Another series of β-glucans possess both 1,3- and 1,4-linkages in linear chains. One of these mixed-linkage glucans, lichenin, which is found in the fronds of Iceland moss, has 30% 1,3-links and 70% 1,4-links. Similar molecules have been found in cereal grains and in the leaves and stems of grasses. The cereal grain β-glucans, like lichenin, also have approximately 30% 1,3- and 70% 1,4-linkages and are readily extracted by water from ground endosperm to yield very viscous solutions.

The molecules of these glucans are assembled from runs of 1,3- and 1,4-linked glucose residues of variable length yielding an interrupted, non-regular conformation. Such molecules do not readily aggregate, and their high water solubility compared with the extreme insolubility of the linear β-1,3- and β-1,4-glucans as exemplified by paramylon and cellulose is readily explicable.

If one is interested in structure-function relationships it is essential to know the sub-cellular location of the molecule under investigation. Polysaccharide chemists have in the past used a "lucky dip" approach in isolating molecules for structural study, but such an approach tells nothing about the location within the cell.

We have investigated this aspect for the mixed-linked glucans and other polysaccharides in several cereal endosperms including the endosperm cells of *Lolium multiflorum* (rye grass) grown in tissue culture as cell suspensions[5,6].

Cell walls have been studied by Dr. Meryl Smith[7] and more recently by Mrs. Robin Anderson[8]. When examined under the electron microscope, walls which had not been extracted in any way showed an amorphous matrix material into which was embedded a fibrillar phase[9]. In this respect the walls have an organization typical of the primary plant cell wall and are very similar in appearance to walls obtained from wheat endosperm[10]. Since these walls have been isolated in a medium of 70% ethanol, polysaccharide and other polymeric components should have been retained so that it is possible to extract differentially the wall with various solvents and examine the composition of each fraction. The results obtained for *Lolium* walls are shown in Table 2.

Water at 40° extracts only a very minor polysaccharide fraction. However 8M urea extracts a major component which is almost entirely composed of glucose. Methylation and periodate analysis show this material to be a mixed-linked β-glucan. The residue after 8M urea extraction is still rich in glucose, and further extraction with alkaline solutions of increasing concentrations results in dissolution of components containing glucose, arabinose and xylose. Ultimately a residual polysaccharide is obtained which is composed almost entirely of glucose.

Methylation analysis of alkali soluble fractions shows that the glucose residues are both 1,3- and 1,4-linked, and in the 2.8% KOH and 24% KOH extracts the proportion of 1,3- to 1,4-linkages is similar to that in the urea-soluble material. It is noteworthy that in all cases the glucan extracted

TABLE 2
MONOSACCHARIDE COMPOSITION OF *LOLIUM* ENDOSPERM CELL WALLS

Fraction	*Percentage of Total Wall (by weight)*	*Relative Monosaccharide Composition (% by weight)*				
		Ara	*Xyl*	*Man*	*Gal*	*Glu*
Whole walls		23.8	18.4	trace	6.7	52.0
Water soluble	1.2	40.0	trace	—	1.9	58.3
8M Urea soluble	10.3	trace	trace	—	—	100.0
2.8% KOH soluble	41.4	27.5	22.3	—	5.8	44.5
24% KOH soluble	28.7	34.2	26.1	—	13.2	26.6
24% NaOH-5% H_3BO_3 soluble	5.9	35.3	28.9	trace	9.2	26.8
Residue	13.4	—	—	—	—	100.0

From Anderson[8]

from the wall with either urea or alkali was then soluble in water.

The remaining polymers in the alkaline fractions are composed of arabinose and xylose and were shown by methylation analysis to be typical arabinoxylans with a linear 1,4-xylan backbone substituted by arabinofuranosyl residues.

The results for *Lolium* are compared with those from similar studies for wheat[10] and barley endosperm[11,12] cell walls in Table 3.

TABLE 3

COMPARTIVE COMPOSITION OF ENDOSPERM CELL WALLS

Fraction	*Wheat*	*Barley*	*Lolium*
	Mares & Stone[10]	Costello & Stone[11] Fincher[12]	Smith & Stone[7] Anderson[8]
water-soluble	arabinoxylan	β-glucan arabinoxylan	minor fraction
8M urea soluble	minor fraction	β-glucan	β-glucan
alkali soluble	arabinoxylan	β-glucan arabinoxylan	β-glucan arabinoxylan
alkali residue	glucomannan cellulose	*arabinoxylan glucomannan cellulose	cellulose

*Insoluble in 1M NaOH. This arabinoxylan may have been extracted by more concentrated alkaline solutions.

It is noteworthy that wheat endosperm walls lack mixed-linked β-glucan although both water and alkali extractable arabinoxylan is present. In barley the β-glucan is found in the water, 8M urea and alkaline extracts. The other predominant polysaccharide is in each case an arabinoxylan. *Lolium* lacks the water soluble β-glucan but otherwise is similar to barley.

The basic polysaccharide composition of these walls is simple. In each case a portion of the polysaccharide is extractable with water or chaotropic agents, whilst further fractions can be extracted with alkaline reagents.

The arrangements and interaction of the polymers in the matrix phase of the cell wall, i.e. the phase which is not amenable to fine structural examination by electron microscopy can now be considered.

The water and 8M urea extractable components are presumably only loosely held in the matrix and may conceivably constitute a special layer. Electron microscopy shows that the remaining matrix material surrounds the cellulose microfibrils as cement surrounds the reinforcing rods in the walls of buildings. The important question to be answered relates to how this material is organized in the wall.

Two possibilities exist:

(i) that the alkali extractable fractions, which in the case of wheat, are physically and chemically difficult to differentiate from their water extractable counterparts,[13] represent a spectrum of molecules which are held in the walls by non-covalent forces of variable strengths. A possible intertwining of β-glucan molecules with themselves or with arabinoxylans is conceivable. The alkaline conditions might, through partial ionization of hydroxyls, contribute to a loosening of the associations allowing solution.

(ii) The second possibility is that the molecules not extracted by water or urea solution are associated by covalently linked bridging molecules ,or by covalent bridges between the molecules themselves. A candidate for this might be a uronic acid residue on one polymer joined in ester-linkage with a hydroxyl contributed by another polymer. Alternatively, the polymers may be cross-linked by bifunctional molecules which could interact with two adjacent chains and form a bridge between them. Such a molecule is diferulic acid which has been suggested by Neukom and Geissman[14] to be important in the cross linking of molecules of wheat endosperm pentosans.

The alkali extractability of part of the wall polymers might then rely on the cleavage of alkali labile linkages, either of the ester type or of some other type. Ester bonds are certainly found in endosprem cell walls as judged by the hydroxylamine-ferric chloride test[13]. Dilute alkaline buffers extract some of the polymers and neutral hydroxylamine also releases polysaccharides from wheat endosperm cell walls. There is thus presumptive evidence that ester type linkages may be involved in cross linking these polymers in the wall. However in the case of *Lolium* this cannot be the only linkage involved, since alkaline solutions of varying concentration remove different polysaccharide fractions from the wall, and one must anticipate that there may be a variety of cross-linkages between wall polysaccharides[15,16] including the non-covalent associations mentioned earlier.

In summary, the endosperm cell walls contain a fairly small quantity of the fibrillar cellulose phase (<10%). The bulk of the polysaccharides are found in the matrix phase and are partly soluble in water or 8M urea, the remainder being soluble to varying degrees in alkaline extractants.

It is possible now to speculate on the relationship between the chemistry and organization of these cell walls and their physiological roles. During the formation of the grain the developing endosperm is a very fragile structure requiring support from the surrounding non-endospermic tissues and from within through the skeletal framework given by the cell wall materials[17]. Here, the fibrillar cellulosic material would be of utmost importance in reinforcing the matrix polysaccharides which make up most of the wall.

As the grain develops starch granules and protein bodies are deposited, so that at maturity each endosperm cell is packed tightly with protein and starch[18]. Under these circumstances the structural role for the endosperm wall in the mature grain is slight. At germination however, access to the endosperm by hydrolytic enzymes formed in the aleurone layer is important, and it is clear from the work of Dickson & Shands[19] with barley and our our work with wheat[18] that one of the first events in germination is the removal of the endosperm cell wall. There is progressive removal of the wall structures in a centripetal fashion consistent with the release of enzymes from the aleurone. However, it is also possible that latent enzymes in the endosperm are activated and participate in this digestion process. The pattern of digestion would be the same in both cases. The essential point here is that the hydrolases for endosperm cell wall polysaccharides are not confronted with a highly organized cell wall as found for example in a woody plant cell.

On the contrary, in the endosperm wall most of the polymers are loosely organized and their structures are such that they are easily accessible to the hydrolytic enzymes.

The endosperm cell wall has a transient structural role during maturation of the grain, but it is also composed of polymers organised in such a way that it can be readily demolished. We can see in this a very nice tuning of structure to function.

Depolymerisation of β-Glucans

A large number of hydrolases which depolymerize β-glucans are known from plant, microbial and invertebrate sources. A number have been purified, and studies with them have led to the accumulation of comparative information concerning their specificity[20]. This has been made possible by the use of β-glucan substrates with known structures. Among these the mixed-linked glucans have been particularly valuable. However because the arrangement of linkages in the naturally occurring mixed-linked glucans has not been clearly specified, Mrs. Marilyn Anderson has prepared a glucan with alternating 1,3- & 1,4-linkages by reduction of the pneumococcal type 3 polysaccharide[21] in which the repeating unit is cellobiuronic acid polymerised through 1,3-β-linkages. Using this and other substrates it has been possible to extend the information on the substrate specificity for a group of closely related hydrolases. The specificity ranges and the apparent minimum specificity requirements are shown in Tables 4 & 5. The subtle differences in specificity of this closely related group of enzymes are apparent and other variants may be predicted. With this range of substrates available it will be possible to search for and detect new enzymes.

The use of well characterized hydrolases in studies on polysaccharide structure is well known in the starch and glycogen field[22] but they have also been, and will continue to be, of considerable importance in studies on structures of β-glucans[22].

Biosynthesis of β-Glucans

The variety of structures found in β-glucans pose interesting problems concerning the pathways and reactions involved in their biosynthesis. Especially interesting is the mechanism controlling the organization of 1,3- and 1,4-linkages in linear glucans.

It is now generally accepted that all syntheses of glycosidic linkages in polysaccharides ultimately involve a reaction in which a nucleoside diphosphate or monophosphate sugar is the donor of the glycosyl residues as shown in the equation:-

NPP-glycose + HO-acceptor → glycosyl-0-acceptor
+ NPP
where N = uridine, guanosine, thymidine, cytidine
or adenosine residues.
= Phosphate residue.

TABLE 4

Comparison of hydrolysis products from three β-glucan hydrolases acting on their β-glucan substrates. From Anderson & Stone[21].

Glucan substrate	*Streptomyces*	*Bacillus*	*Rhizopus*
β-1,3- (Laminarin)	Not hydrolysed	Not hydrolysed	●3●3● ●3●
β-1,4- (Cellulose)	○4○4○ ○4○	Not hydrolysed	Not hydrolysed
β-1,3; 1,4- (Lichenin or oat glucan)	○3●4○4○ ○4○3●4○ ○3●4○ ○4○	○4○4○3● ○4○3●	○4○4○3● ○4○3●
Alternating β-1,3; 1,4- (RS III)	Not hydrolysed	(○3●4○3●4○3●4○3● ○3●4○3●4○3● ○3●4○3●)* ○3●	(○3●4○3●4○3●4○3● ○3●4○3●4○3● ○3●4○3●)* ○3●

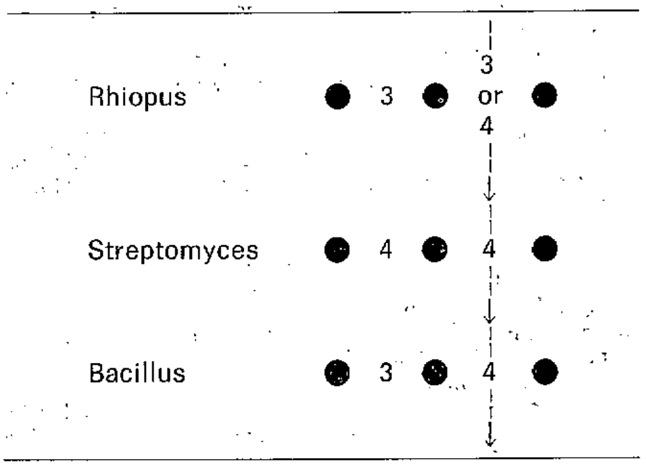
* Transient products

TABLE 5

Minimum structural requirements for hydrolysis of β-glucans by three β-glucan hydrolysases. The reducing end of the glucan is to the right.

● β-glucopyranosyl residue

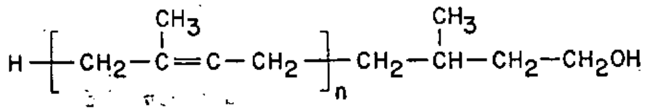
↓ point of hydrolysis.



Glucose is the ultimate precursor for all monosaccharides found in polymers and these arise by a series of enzyme catalysed reactions involving epimerization, oxidation and decarboxylation of monosaccharides, either as their sugar phosphate or nucleoside diphosphate derivatives.

In many cases the sugars from the NPP-glycose derivatives are directly transferred to acceptors but there are now a number of well documented examples involving bacterial and yeast cell wall polymers and mammalian glycoproteins where intermediate lipid-sugar compounds are implicated[23]. In each case membrane bound transglycosylases are involved and the lipid carriers are of the prenol (polyisoprenoid alcohol) type (Fig. 3) linked through orthophosphate or pyrophosphate bridges to sugars.

Recently there has been special emphasis on the possibility that the synthesis of cell wall polymers in plants, e.g. cellulose and the mixed linked glucans may involve membrane bound enzymes and that this might imply the operation of lipid intermediates. To date no clear-cut, rigorous demonstration that this is the case has emerged. We have found lipid-like compounds containing phosphate and glucose in *Lolium* tissue cultures that are labelled in pulse-chase experiments and appear to be rapidly turned over[8]. Evidence for similar compounds has been presented for *in vitro* systems but at present the postulated pathway must be regarded as not proven[24,25].



$$H\left[CH_2-\overset{CH_3}{\overset{|}{C}}=C-CH_2\right]_n CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_2OH$$

Fig. 3. Structure of polyisoprenoid alcohol molecule implicated in glycosyl transfer during polysaccharide biosynthesis.

In vitro experiments using membrane fractions which incorporate glucose from uridine diphosphate glucose into β-glucans have been used by a number of workers to study the characteristics of the synthetic reaction. Working with cell-free preparations from *Lolium* Dr Meryl Smith[26] showed that the concentration of UDPG in the incubation mixture markedly affected the proportion of 1,3- and 1,4-linkages in the β-glucan reaction products (Fig. 4). This was also evidenced by the solubility properties of the products (Table 6). The specific β-glucan hydrolases, especially the *Bacillus* enzyme (see Table 4), were employed in characterizing the products and showed that at high UDPG concentrations the predominant product was a water-soluble, mixed-linked glucan.

The intriguing question which remains unanswered for the present is how the proportion of linkages in the products is actually controlled. Before this can be answered we will need to know much more about the organization of the synthetase enzyme complex in the membrane, whether lipid intermediates are involved and the nature of the acceptor molecules. Fig. 5 summarises some of the postulated routes to the formation of polysaccharides and indicates the complex nature of the problem.

TABLE 6

SOLUBILITY CHARACTERISTICS OF β-GLUCANS SYNTHESIZED *IN VITRO*

Fraction	*UDPG concentration in Reaction Mixture* 3.9 μM	100 μM
Water-soluble	28	91
1M NaOH-soluble	22	4
1M NaOH-insoluble	49	5

From Smith and Stone[26]

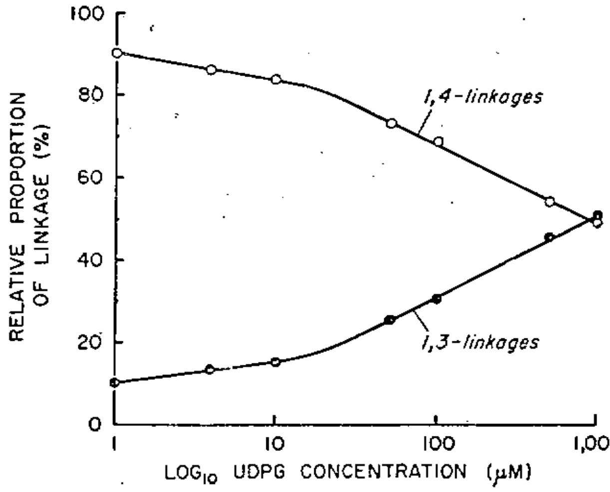


Fig. 4. Relative proportion of 1,3- and 1,4-linkages in β-glucans synthesized by cell free extracts from *Lolium multiflorum* endosperm cells at varying UDPG concentrations. Data from Smith and Stone[26].

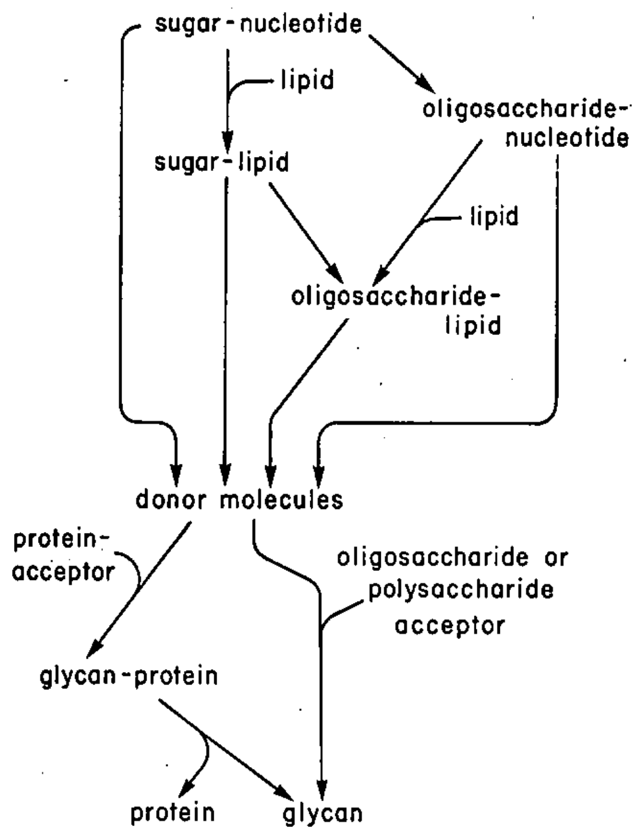


Fig. 5. Postulated biosynthetic routes from sugar nucleotides to polysaccharides.

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Owing to a misunderstanding, this paper was received too late by the Editor for inclusion in the IUPAC issue of Chemistry in New Zealand.

CHEMISTRY IN NEW ZEALAND INDUSTRY

S. G. Brooker and A. F. Wilson

In discussing this aspect of local chemistry it is appropriate to begin with the food industry. Not only does it account for more than a third of total industrial production, but also the first industrial chemist in New Zealand was Alfred Carter, appointed to the Gear Meat Company in Wellington in 1890, nearly a decade before that city had its own university. He and his employers were truly pioneers: chemists only really came into their own in the food industry with the advent of the Second World War, and before long their position began to be challenged by the first graduates in food technology from Massey University in 1965.

Meat and dairy products comprise by far the largest part of the output of the food industry, and both are served by vigorous research institutes whose work is discussed elsewhere in the IUPAC issue of "Chemistry in New Zealand." However, chemists outside these institutes have made useful contributions, such as the Murray "Vacreator" for deodorising cream, well known outside New Zealand; new techniques for the extended holding and transport of chilled beef; pioneering continuous drum curing of hides and skins; centrifugal fractionation of fats; and continuous fermentation in the brewing industry, to name only a few. Tasman Vaccine Laboratory Ltd., after a co-operative research programme with the staff of Massey University, have established a plant, N.Z. Pharmaceuticals Ltd., to process gall for recovery of cholic and deoxycholic acids. The output of 20 tonnes per year of these products is sold to Collectorgane Ltd. of France. It is noteworthy that in his address at the plant opening in 1975 the Chairman said that interest in this development was initially stimulated by members of the NZIC.

While the products of the pastoral industry, for which New Zealand is ideally suited, have pre-eminence, other industries have shown very rapid growth in recent years. Since the forest products industry first began to make wood pulp in the 1940's, production has risen to over 900,000 tonnes per year. Large tonnages of chemicals such as chlorine, sodium hydroxide, sodium chlorate, chlorine dioxide, sodium sulphide and calcium oxide are produced for utilisation in the chemical pulping and bleaching operations. Close to 100 graduate chemists or chemical engineers are employed in the industry, including the managing directors of the two largest companies, N.Z. Forest Products Ltd. and Tasman Pulp and Paper Co. In addition to manufacturing such basic forest products as timber, fibreboards, pulp and paper, the kraft chemical pulping operations at Kinleith and Kawerau produce approximately 5500 tonnes per year of tall oil and 2000 tonnes of turpentine. These useful chemical raw materials are currently exported as crudes, but consideration is being given to upgrading them in New Zealand.

New Zealand possesses very large reserves of iron ore in the titaniferous ironsands on the West Coasts of both islands. As far back as 1848 John Perry produced a small quantity of iron from this source before his furnace blocked up with titanium nitride. His failure to make the process a commercial success was the first of many subsequent disappointments, and it was therefore something of a triumph of chemistry when the N.Z. Steel Co., at its plant at Glenbrook, near Auckland, started production of sponge iron from the ironsands in 1969. This sponge iron is subsequently converted into steel. The company also concentrates the iron ore in the sand for direct export in bulk at Taharoa on the South-west Auckland coast, and one of the many products of the staff chemists has been the corrosion protection of the undersea pipeline used. N.Z. Steel Co. also has a galvanising plant supplying one-third of the local market. A $400 million expansion plan has recently been announced.

Aluminium was first produced in New Zealand in 1971 when N.Z. Aluminium Smelters Ltd. began production at their Tiwai Point plant near Bluff. The raw material, bauxite, is mined at Weipa, near the northern tip of Queensland. Alumina is extracted from it at Gladstone, further south on the Queensland coast, and shipped to Tiwai Point. This site was chosen for the plant because of its nearness to power supply from Lake Manapouri power station, deep harbour water, level terrain, and the sound infrastructure provided by the city of Invercargill. Production of aluminium is currently being expanded from 112,000 to 150,000 tonnes per year.

One of the most remarkable purely chemical developments on the local scene is the operation of Ivon Watkins-Dow Ltd. at New Plymouth, where various weedkillers, herbicides, insecticides and surfactants are produced by synthetic organic reactions, many of them scaled up from research in the company's own laboratories. Examples of chemicals produced are the sheep dip insecticide Dichlofenthion (O,O-diethyl 0-2,4-dichlorophenyl phosphorothioate), and triazine herbicides such as Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine). These products are manufactured both for the local market and for export, and their ready availability in New Zealand has been of valuable assistance to our primary industries.

In 1964 the first major petroleum refinery was opened at Marsden Point near Whangarei and it now produces the major proportion of New Zealand's motor spirit. An associated oil burning plant provides 6 percent of our electricity requirements. Off-shore prospecting for petroleum is being actively prosecuted, and has been successful in discovering the Maui gas field off the Taranaki coast, estimated to have a reserve of 2 x 10^{11} cubic metres of high quality methane. It is expected that condensate from the field will supply 10-15 percent of crude petroleum feedstock requirements, and proposals for a petrochemical industry are mooted.

A further 6 percent of our electricity requirement is provided by the geothermal plant at Wairakei, in the centre of the North Island, which is worth a visit by any scientific visitor to New Zealand. The establishment of this plant has involved chemists in many unusual problems, particularly related to corrosion.

The fertiliser and leather industries are major sites of chemical activities in New Zealand. In 1881 T. W. Kempthorne won a Government bonus of £1500 for the production of 150 tons of sulphuric acid over three years, and his name is still associated with the fertiliser industry. While major research in these areas is conducted at research institutes, much pioneer work is being carried out by chemists in the works. They have come together recently in the production for the leather industry of chrome tanning salts, using locally produced sulphuric acid.

Passing to general issues, the total value of industrial production in New Zealand is of the order of $5000 million. In volume it is increasing about three times as fast as agricultural and pastoral production, which means increasing work for chemists. Approximately one quarter of the country's exports are from secondary industry. Government has provided financial support for industrial research since the Industrial Research and Development Grants Act was passed in 1970. In the financial grant year 1974/75, 127 grants totalling $1.36 million were approved. Any company doing industrial research or development work can apply for grants, based on increased costs on approved work in the grant year, compared with a base period two years previously. To date there is little evidence that companies have taken on new research projects to capitalise on the scheme, due mainly to the fact that any new research is effectively supported for only two years.

Education of chemical staff for industry is catered for by the usual courses provided at universities for students majoring in chemistry, and courses in chemical engineering at Christchurch and Auckland. The New Zealand Certificate in Science — a three-year, post-sixth-form qualification available through the Technical Institutes — is now nationally recognised as a desirable avenue for industrial laboratory staff. The fact that it is a part-time course which dovetails in with knowledge gained by the students in the laboratories where they are employed is a strong feature. Since 1963 over 280 people have been awarded the certificate. The Technicians' Certification Authority also awards a diploma in science to those with N.Z. Certificate in Science who study applied chemistry in depth at a Technical Institute. This means that New Zealand will have a range of qualifications suitable for all levels of careers in chemistry.

New Zealand does not have a large chemical industry, and the work of the industrial members of the Institute of Chemistry is fairly varied. Often they choose to join the technical associations of their own industries rather than the Institute. There are technical associations for workers in the forest products industry, the food industry, and the paint industry, to name only a few. Many chemical engineers are members of the Institute, but usually retain a stronger relationship with the N.Z. Institution of Engineers. Some potential N.Z.I.C. members are separated geographically from local branch meeting places. Despite all these limitations restricting membership, the number of industrial chemists joining the Institute continues to increase. Undoubtedly the main reasons for this healthy sign are the interest and benefits that members have in maintaining an association with their scientific colleagues working in other fields of chemistry.

CORRECTION

L. H. BRIGGS MEMORIAL PLAQUE

Readers of the caption of the cover photograph of the February issue of this journal may have gained the impression that the commemorative plaque shown was to mark the fiftieth anniversary of the founding of the Auckland Chemical Society. (The Auckland Branch was celebrating its Golden Jubilee not its Diamond Jubilee — apologies from the Auckland Branch Editor.) This was not the case and as reported on p. 23 of that issue and in the November, 1975, number the plaque was to the memory of the late Emeritus Professor L. H. Briggs. This plaque is now mounted in the main foyer of the Chemistry Department of the University of Auckland, and the inscription reads:

> LINDSAY HEATCOTE BRIGGS (1905-1975),
> D.Phil(Oxon), D.Sc.(N.Z.), F.R.S.N.Z., F.N.Z.I.C., F.A.N.Z.A.A.S.
> This plaque was presented by the Auckland Branch
> of The New Zealand Institute of Chemistry to
> honour the memory of Emeritus
> Professor L. H. Briggs
> Professor Briggs held executive office in the Institute from 1933-1960 and gave outstanding service
> to chemistry and to the Auckland Branch.
> He became first I.C.I. medallist of the Institute in
> 1949, was elected President in 1959 and was made
> an Honorary Fellow in 1970.

OBITUARIES

MAX HUMPHREY PANCKHURST (1929-1976)

The sudden death of Professor M. H. Panckhurst on August 8th is a severe loss to chemistry and administration in the university system in New Zealand. At the time of his death he had come back to his research interests, following three years of heavy involvement in administration for the University of Otago, and a year of refresher leave in the United States.

Max Panckhurst was a West Coaster, educated first in Reefton, and then for a year at Christchurch Boys' High School. His academic career at Canterbury College was a distinguished one, overshadowed in some measure by that of Michael Spiro in his undergraduate years. Panckhurst's first research was with S. R. Siemon, building an adsorption balance for gas-solid studies. His Ph.D. research, with the writer as supervisor, used adsorption spectroscopy to study ion interactions (ion-pairing), and in 1953 he was awarded a Shell Scholarship, which he took up at Oxford University, in R. P. Bell's laboratory. He spent almost four years there, holding an I.C.I. research fellowship after the Shell Scholarship. He graduated D. Phil., and then spent two years in R. L. McIntosh's laboratory at Toronto, as an N.R.C. post-Doctoral fellow, returning temporarily to his early interest in the gas-solid interface. Before going to Oxford he was briefly assistant lecturer at Auckland University College. When appointed lecturer at Otago (1959), he returned to the study of the thermodynamics of electrolyte solutions and continued in this field, interrupted through the recognition of his outstanding administrative gifts. The growth of university staffs, consequent on the explosion of student numbers in the 1960s led, happily, to the end of the dominance of the one-professor department in New Zealand, and in 1966, Dr. R. E. Corbett (now Mellor Professor of Chemistry), and Panckhurst were appointed professors of chemistry at the University of Otago.

Panckhurst's view of his commitment as a university teacher was, in his own words, "to the teaching of chemistry, which in my view presupposes an active research interest, and also an interest in administration to help to ensure the proper atmosphere for University activities." He carried out this commitment with all the very considerable ability at his command. It led him into a variety of responsible posts both at Otago and more widely; sub-Dean of the Faculty of Science (1965-7), chairman of the committee on Student Services (1969-73), member of the U.G.C.'s Curriculum Committee (1970-72), chairman of the Vice-Chancellor's sub-committee on graduate employment (from 1972), member of the Council of the Christchurch Clinical School (from 1972), and, from 1972 to 1974, Pro Vice-Chancellor of the University of Otago. In this last post he was Chairman of the Academic Staffing Committee, member of the University Council, and of its Finance and Budget Committees, and on a number of occasions acting Vice-Chancellor. Outside the University, he was subject convenor in chemistry for the University Entrance Board, chairman of the Academic Committee of Dunedin Teacher's College (1969-74), and chairman of the organising committees for Otago and Southland for the Educational Development Conference. He was chairman of the Otago Branch of the Institute of Chemistry in 1966. Finally in 1976 he became one of the three academic members of the University Grants Committee.

Many people serve on many committees. Few bring to all of them the clear thinking, the articulation in speech and the natural diplomacy in dealing with colleagues (including student colleagues), which Max Panckhurst brought to those on which he served.

Success with one led inevitably to his being sought for others; finally to a greater degree than he wished for. He was glad, in 1975, to take well-earned leave to spend a year with Dr R. G. Bates in Florida, to get back to electrolyte solutions. The two papers which he published (with J. B. Macaskill, one of the ablest of his associates), on the difficult problem of multi-ionic solutions, were clear evidence that the "very limited attention" (his own words) which he had been able to give to it for three years, had in no way reduced his capacity to contribute to his field.

Panckhurst was a first-rate physical chemist and a very gifted teacher of university students, both graduate and undergraduate. He also showed unusual administrative gifts. But he was more than these. He was an all round acadamic of the kind a university community needs, and fortunately for its own health, is able to recognise and use. The involvement of good academics in administration is both proper and inevitable, but it has its price. Max Panckhurst was willing to pay the price, for that was his commitment.

H.N.P.

RAYMOND WALTER OLLIFF

Dr. Raymond Walter Olliff, Senior Lecturer in Chemistry at Auckland University, died suddenly on 17 September 1976. Ray first entered the University as an undergraduate in 1950, from Auckland Grammar School, with a University National Scholarship. He completed his M.Sc., (1st Class Hons) in Chemistry in 1953 and held the Duffus Lubecki Research Scholarship and a University Research Scholarship in 1954, before joining the staff in 1955. He was elected a Member of the N.Z.I.C. in 1956.

His interests in chemistry were wide, and centred around studies of structure and reactivity of co-ordination compounds. His special love was Quantum Chemistry and he spent two periods of leave with the late Professor C. A. Coulson at Oxford University. He taught Quantum Chemistry to second and third year students, and also at Masters level for a number of years, establishing himself as a most popular teacher of this topic. He was associated with the Urey Radiochemical Laboratory from its establishment in 1959, and in recent years was responsible for the organisation of the teaching work of this laboratory.

He was a fine chemist, an able mathematician, a gifted teacher, an excellent sportsman, and a delightful colleague. His death leaves a great gap in the Chemistry Department.

A.L.O.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)
FORTY-SIXTH ANNUAL REPORT
For the Year Ending July 31, 1976

OFFICERS:

President: Mr. J. S. Pollard
First Vice-President: Prof. G. N. Malcolm
Second Vice-President: Prof. G. A. Wright

Delegates:

Auckland: Dr. A. F. Wilson
Waikato: Dr. W. P. Judd
Manawatu: Dr. W. B. Sanderson
Wellington: Dr. R. J. Furkert
Canterbury: Dr. W. S. Simpson
Otago: Dr. G. W. Emerson

Editor: Miss J. M. Mattingley
Bulletin Editor: Dr. L. K. Creamer
Journal Bus. Manager: Mr. R. C. Turner
Employment Officer: Mr. C. L. H. Stonyer
Hon. Librarian: Mr. S. G. Brooker
Registrar: Mr. D. J. Hogan
Admin. Secretary: Mrs. N. E. Wignall
General Secretary: Prof. W. E. Harvey

MEMBERSHIP:

During the year the following changes in membership have taken place:

New Fellows	0
Members elected to Fellowship	8
New Members	29
Graduate Members elected to Membership	22
New Graduate Members	22
New Technician Member	1
Resignations	31
Deaths	4
Deleted	12
Reinstated	2

Consolidated membership figures for the last four years are as follows:

	1973	1974	1975	1976
Auckland	302	311	335	343
Waikato	85	94	97	97
Manawatu	138	133	131	128
Wellington	273	292	299	310
Canterbury	169	174	182	180
Otago	94	95	105	104
Overseas	128	139	146	140
	1189	1238	1295	1302

OBITUARY:

We record with regret the deaths during the year of the following members: D. Bradwell, J. A. Bruce, A. R. Browning, Miss M. N. Ward.

HONOURS:

Mr. S. G. Brooker was elected as Honorary Fellow of the Institute.

Dr. J. E. Ferguson has been elected to Fellowship of the Royal Society of New Zealand.

Professor J. F. Duncan has been awarded the O.B.E.

ROYAL SOCIETY OF NEW ZEALAND SUB-COMMITTEES:

The following members are currently serving on various National Committees:

The National Committee for Chemistry: Dr. T. A. Rafter, Mr. J. S. Pollard, Prof. R. C. Cambie, Dr. A. J. Ellis, Dr. W. A. McGillivray, Mr. K. Seal, Prof. G. N. Malcolm, Prof. C. J. Wilkins, Dr. H. C. Sutton.

The National Committee for Biochemistry: Prof. J. N. Smith, Dr. R. W. Carrell, Dr. L. K. Creamer, Prof. G. B. Petersen, Dr. D. E. Wright.

The National Committee for Nutrition: Dr. W. A. McGillivray.

The National Committee for Crystallography: Dr. P. P. Williams, Dr. A. G. Freeman, Prof. B. R. Penfold, Dr. W. T. Robinson, Dr. Sylvia V. Rumball, Dr. J. M. Waters, Prof. T. N. Waters.

Member Bodies Committee: Prof. G. N. Malcolm, Dr. P. P. Williams.

REPRESENTATIVES ON OTHER BODIES:

Technicians Certification Authority: Executive Committee for Science: Prof. W. E. Harvey.

Standards Association of New Zealand: Mr. J. Gilmour, Dr. P. K. Foster.

UNESCO: Mr. J. A. D. Nash.

PRIZES:

The I.C.I. Prize for 1975 was awarded to Associate Professor Charmian O'Connor of the University of Auckland.

No entries were received for the Chemical Essay Prize.

The prize for the best student paper at the 1975 Conference was awarded to Miss T. E. Smith-Palmer of the University of Auckland.

Council gratefully accepted the offer of Tasman Vaccine Laboratory Ltd., to offer two prizes in industrial chemistry, which will be open to competition for the first time in the forthcoming year.

CONFERENCES:

The 1975 Conference was held at Massey University, 19th-22nd August, and was attended by a total of 299 delegates, 32 of whom were students. These numbers, although lower than those for the previous year's conference in Auckland, show that the annual conference still attracts a very high proportion of the total membership.

The Conference Guest Lecturer was Mr. T. R. Hitchings, Headmaster of Riccarton High School, and the Biochemical Guest Lecturer was Professor B. A. Stone, La Trobe University, Australia. A Memorial Address to the late Professor L. H. Briggs was delivered by Professor R. C. Cambie, and Professors F. G. Soper and H. N. Parton also presented special lectures.

As has been the practice in recent years much of the programme was divided into sessions appropriate to the various Specialist Groups within the Institute, and as an innovation a poster session was held one afternoon.

Trade exhibitors as usual made a significant contribution to the success of the Conference, not least because of their provision of appropriate refreshments in the trade display area.

OVERSEAS VISITORS:

In addition to the Biochemistry Guest Lecturer at Conference the Institute provided financial assistance for a visit by Prof. E. Matijevic. With the increase in costs faced by the Institute it seems inevitable that it will be increasingly difficult to provide financial assistance for overseas visitors and the Council has laid down guidelines for requests for this purpose.

GRADES OF MEMBERSHIP:

As the culmination of several years of discussion the Rules were amended to provide for non-corporate membership of the Institute being made available to technicians who are holders of the N.Z.C.S.

At the same time other amendments were made to the Rules, some of a tidying up nature, but others of greater significance such as the change making a professional interview obligatory before admission to corporate membership.

RELATIONSHIPS WITH OTHER BODIES:

The Institute has continued its close relationship with the Royal Society of New Zealand through its membership of the Member Bodies Committee and the National Committee for Chemistry. Although it is now clear that some restructuring of the Royal Society committee system will take place it is clear that the Institute as one of the larger Member Bodies will continue to play a significant role in R.S.N.Z. affairs, and to this end the Council resolved that one of its representatives on the Member Bodies Committee will be the First Vice-President of the Institute.

The Institute has become increasingly aware of the need to provide expert assistance to Government, Royal Society and ad hoc committees concerned with such matters as Energy Resources and the environment and has taken steps to ensure that, where it appears desirable, the Institute or individual members are brought to the attention of the appropriate authorities.

The N.Z.I.C. continues to be represented on such organisations as S.A.N.Z. and the T.C.A. where its presence is long established.

PUBLICATIONS:

The Publications Committee established last year has continued to advise Council in this very contentious area. The increasing costs of publications of all kinds have placed considerable strain on the Institute budget and it is unlikely that this situation will change materially in the near future. In an effort to stem the rising tide of costs and to provide a better service to members the number of issues of the Journal published annually has been decreased and a new Bulletin has appeared to carry topical news and comment.

The list of members will probably next appear in a modified form taking advantage of computer data processing techniques.

ADMINISTRATION:

With the increasing diversity of Institute affairs the time appeared opportune to review the administrative structure which has grown up — rather like Topsy—over the years. This exercise, commenced last year, has continued and although it would be fair to say that no major changes are envisaged it is clear that much greater use will be made of ad hoc committees than has been the case in the past.

LIBRARY:

The N.Z.I.C. Library of forty-five Chemical Journals painstakingly built up by Mr. S. G. Brooker, who has been Hon. Librarian since its inception, has been housed by the Auckland Museum who now require the space. Negotiations are completed to deed the collection (with the exception of twelve journals from sister organisations which will remain with the Auckland Museum) to Massey University which is prepared to finance the transportation and much needed binding of the journals.

We acknowledge with gratitude the offers of assistance of the Royal Society librarian in Wellington and the librarian of the Philson Library, Auckland, and all the past care and assistance of the librarian of the Auckland Museum.

FINANCE:

Although the further increase in subscriptions has prompted a higher level of resignations, the Balance Sheet to April 30th, 1976, shows an excess of Income over Expenditure of more than $1,300. In spite of inflation expenditure has been closely watched to keep it slightly under the estimated amount.

THANKS:

It is a pleasure once again to express thanks to the many individuals, committees and groups who have assisted the Council and the Institute throughout the year.

For and on behalf of the Council,
J. S. POLLARD, President.
W. E. HARVEY, General Secretary.

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

INCOME AND EXPENDITURE ACCOUNT FOR YEAR ENDED 30th APRIL, 1976

1975 $	**EXPENDITURE:**			
	Administration Expenses:			
4,566	Honoraria less Proportion charged to Journal		4,617.02	
2,799	Printing, Stationery, Postages, Tolls, etc.		2,240.58	
1,561	Travelling Expenses		1,664.73	
900	Branch Expenses Allowances		900.00	
345	Audit Fees		400.00	
350	Conference Costs, paid by Institute		251.93	
70	Donations: S.A.N.Z.	70.00		
—	Water Pollution Research	150.00		
27	Other		—	
			227.00	
—	Interest—Bank of New Zealand		19.24	
8	Depreciation		7.00	
20	Royal Society of N.Z.—Fee		10.00	
74	Prizes		—	
(10,720)				10,337.50
	PUBLICATIONS:			
9,127	Cost of Journal		7,078.77	
—	"An Invitation"		717.09	
—	Bulletin Costs		315.00	
(CR2)	Monographs		152.97	
—	Journal Binding		48.00	
—	Chemistry 13 News		20.73	
510	Sundry		—	
(9,635)			8,332.56	
	Less Revenue from			
3,123	Advertising and Journal Subscriptions	2,340.76		
(DR)68	Proceeds of Publications—Environment in Industry	.50		
(DR)73	Education in Chemistry	347.13		
(DR)17	Chemistry	13.87	2,702.26	
(6,670)				5,630.30
—	Excess of Income over Expenditure			1,377.60
$17,390				$17,345.40

1975 $	**INCOME:**		
14,155	Subscriptions—Annual		17,052.01
	Interest Received:		
301	Bank of New Zealand	149.63	
196	Local Body Stock	143.76	
(497)			293.39
2,738	Excess of Expenditure over income For Year		—
$17,390			$17,345.40

OVERSEAS VISITORS TRAVELLING FUND

1975 $		
826	Travelling Expenses Paid During Year	708.25
675	Balance 30/4/76	381.65
1,501		$1,089.90

1975 $		
688	Balance 30/4/75	675.39
813	Conference Surplus	414.51
1,501		$1,089.90

EASTERFIELD FUND

129	Expenses—Powell	—
271	Balance 30/4/76	634.86
400		$634.86

400	Balance 30/4/75	270.66
—	Royal Institute of Chemistry	364.20
400		$634.86

THE NEW ZEALAND INSTITUTE OF CHEMISTRY (INC.)

BALANCE SHEET AS AT 30th APRIL, 1976

1975 $			
	CURRENT LIABILITIES:		
1,831	Bank of New Zealand	—	
175	Sundry Creditors	548.47	
(2,006)	**TOTAL CURRENT LIABILITIES:**		548.47
	SPECIAL FUNDS:		
140	Education Fund (School Bulletin)	140.00	
675	Overseas Visitors Travelling Fund	381.65	
271	Easterfield Fund	634.86	
(1,086)	**TOTAL SPECIAL FUNDS:**		1,156.51
	TRUST FUNDS:		
2,598	Balance 30/4/75	2,601.44	
3	Plus: Interest Credited	3.03	
(2,601)			2,604.47
	ACCUMULATED FUNDS:		
5,690	Balance 30/4/75	2,951.95	
2,738	Excess of Income over Expenditure for year (DR)		1,377.60
(2,952)	**BALANCE 30/4/75:**		4,329.55
8,645			$8,639.00

1975 $				
	CURRENT ASSETS:			
—	Bank of New Zealand		2,663.07	
—	Cash on Hand		90.96	
2,006	Subscription in Arrears		2,300.00	
651	Sundry Debtors		750.50	
349	Publications on Hand		200.00	
(3,006)	**TOTAL CURRENT ASSETS:**			6,004.53
	TRUST FUND INVESTMENTS: (At Cost)			
102	Post Office Savings Bank		104.47	
—	North Canterbury Hospital Board Stock		1,000.00	
1,500	Lyttelton Harbour Board Loan		1,500.00	
(1,602)	**TOTAL TRUST FUNDS INVESTMENTS**			2,604.47
	GENERAL FUND INVESTMENT:			
1,000	North Canterbury Hospital Board Stock		—	
3,000	Bank of New Zealand Ltd. Term Loan		—	
(4,000)				—
	FIXED ASSETS: (At Cost)			
	Office Equipment	317.80		
	Less Depreciation	289.80		
35			28.00	
	Addressograph Plates	62.35		
	Less Depreciation	60.35		
2			2.00	
(37)	**TOTAL FIXED ASSETS**			30.00
8,645				$8,639.00

We have audited the books of the New Zealand Institute of Chemistry (Inc.) for the year ended 30th April, 1976, and have received all the information and explanations we have required. In our opinion, according to the best of our information and the explanations given to use as shown by the books of account, the Balance Sheet, Income and Expenditure Account, and Trust Fund Account are properly drawn up so as to give a true and fair view of the state of the Institute's affairs as at 30th April, 1976.

SHANAHAN AND WINDER
Chatered Accountants.
M. P. Winder

BOOK REVIEW

Chemistry and the Needs of Society —The Chemical Society London 1974. 249 pp. ca $6.00 ($4.50 to N.Z.I.C. members).

This book is based on a Symposium organised by the industrial division of the Chemical Society. It contains the texts of 17 lectures by representatives of a wide range of interests within the field of Chemistry. Material resources, energetics, pharmaceutical chemistry, biochemistry, polymers and plastics, environmental chemistry, economics and chemical education are all discussed. The main emphasis is on applied aspects of chemistry and presumably for this reason most of the authors are from industrial concerns or government establishments.

The promise of exciting reading contained in the title and the table of contents is unfortunately not sustained in the text. Despite the excellent choice of topics and the fact that the content of the individual chapters is in the main good, I found that I finished the book mainly because I was reviewing it. I gained the impression that many of the authors were writing as apologists for their companies or agencies and that the general tone of the text was too serious.

Nowhere did I get the feeling that the authors enjoyed their work as chemists. The thought of all these chemists stolidly dedicating themselves to the good of mankind is rather depressing.

The book contains much of interest to those already committed to the study of chemistry but I think its tone would be boring for a non-chemist, and I certainly wouldn't offer it to a senior schoolboy trying to make up his mind whether or not to become a chemist.

A.G.W

The Registrar is not holding stock copies but would order from the Chemical Society on request.

THE SEA AS A SOURCE OF FINE CHEMICALS

R. J. FERRIER

In the late 1960s the sea could be considered largely unexploited as a source of specific organic natural products, whereas in 1974 the numbers of new substances isolated from marine species rivalled those from terrestrial sources. An awareness of this burst of activity and of the apparent absence of a proportionate response in New Zealand led to the collection of the material for this paper. Perhaps the drawing of attention to the intense interest being taken overseas in marine natural products, particularly those of potential pharmacological value, may assist with the exploitation of the obvious opportunities offered by New Zealand's coast-lines.

Although until this century man appears largely to have ignored the sea as a source of raw materials—except of course for food—there are a few early records of his exploiting marine resources for more sophisticated purposes. Thousands of years ago the Chinese used clams in treatment of cancer patients, and Tyrian purple (derivable in tiny amounts from a mollusc) was a dye prized by the ancients of the Eastern Mediterranean. By the year 1000 B.C. it had become one of the most expensive commodities known, and as the first commercial marine natural product was the basis of a thriving wool and silk dyeing business.

In more recent times seaweeds have been used as sources of polysaccharide materials put to a wide range of uses varying from textile sizes to food additives of many types; cod-liver oil has enjoyed the status of panacea; iodine, bromine, magnesium and potassium are amongst the inorganics which have been isolated on a commercial scale from marine sources. However, none of these is a "fine" chemical in the sense that the adjective will here be used, nor will reference be made to the possible products of the topical sea-based gas-oil industry. Main attention will be given to discrete organic substances of plant or animal origin, especially those with physiological activity. Before inorganic materials are further disregarded, it should be pointed out that amongst the trace elements in the sea there are several which certainly qualify for the category "fine". As early as the years following the First World War, Fritz Haber in Germany carried out a feasibility study on gold extraction, and concluded that at a concentration of 10^{-6} ppm it was effectively inaccessible. It seems that the situation is currently unaltered, but the opposite conclusion has been drawn for uranium, the concentration of which is 3×10^{-3} ppm, and it appears that technology is ready to exploit marine sources when the terrestrial availability declines. Looked at more positively, these tiny concentrations mean that there are about 3×10^{9} tons of uranium and 10^{6} tons of gold in the sea (Wellington Harbour's share of the latter having a value of about $10,000), and for further encouragement it can be noted that algae can concentrate strontium, zinc and cobalt by factors as large as 10^{4}, and some sea squirts can achieve a concentration factor for vanadium of 3 or 4 orders of magnitude higher. Other species efficiently concentrate niobium. With efficiencies of this sort to aim at, and with co-ordination chemistry developing as it is, it seems perhaps not altogether impossible that one day organic chemists will provide the means for extracting valuable trace elements from the sea.

The success of searches for marine natural products of medicinal value are related to the ecology of the search areas, and depend upon such factors as the accessibility of the raw materials and the extractability, purification and stability of the isolated substances. At the present state of development of the subject prudent new explorers have also to assess the types of organisms most likely to yield the kinds of materials they are pursuing, or conversely the substances likely to be found in any plant or animal they aim to examine. Absorption of sunlight ocurs mainly in the upper 20 fathoms of the sea, so it is in this layer that primary food is produced photosynthetically; favoured coastal water can be a hundred times more productive than the open oceans. It is in the fertile in-shore regions that the majority of about 10,000 plant species and 400,000 dependent animal species have their natural habitat; particularly densely populated are the west coasts of continents at sub-tropical latitudes where there are prevailing off-shore winds and where surface waters are replaced by nutrient-rich deeper waters. Such areas are the coasts of California and Peru, North-West and South-West Africa, the Arabian coast, parts of west-facing coast-lines in Australia and northern parts of New Zealand's shores. In these relatively shallow waters innumerable algae, sponges, coelenterates (e.g. jellyfish, sea anemones and coral), echinoderms (e.g. starfish, sea urchins and cucumbers) and molluscs live, and on them depend the more advanced crustacea, fish, reptiles and mammals. Current attention is being paid, by natural product and pharmaceutical chemists, almost exclusively to the simpler organisms.

Hardly surprisingly, tropical islands and associated coral reefs are also happy hunting grounds, and a feature of their ecology is particularly interesting from the chemical point of view. Their inhabitants live in close proximity to each other in a relatively immobile state which has caused them to develop a complex communication system based to some degree on organic chemicals. Sessile algae, coral and sponges share space with sedentary creatures such as worms, bivavles and crustacea, and more mobile species even seem to prefer

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Review paper given at N.Z.I.C. Conference, August 1975.

a fixed locale. The anemone fish, for example, remains associated throughout its life with the same anemone, and it ventures no great distance from it. In these densely populated, relatively static circumstances each creature is especially vulnerable to predators and parasites (including microorganisms), and in response, chemical protective mechanisms have been developed so that such places are potential sources of defensive antibiotics and toxins and of many other chemical messengers associated with the prosperity of individual organisms and species. It is particularly worth recognising that organisms which utilise filter systems for the collection of food material are likely to have effective means of dealing with potentially harmful bacteria, and may therefore be possible sources of antibiotic substances.

Chemical defences are sometimes more subtle than is obvious. The octopus as well as using its ink as a crude defence mechanism excretes with it a substance which affects the olfactory sense of predators, so that e.g. the Moray eel can no longer detect the octopus after swimming through the ink. Not all secreted substances are defensive in nature; some species use chemical lures to attract prey, and in some circumstances the situation is reversed with the receiving organism gaining the advantage in the form of notification of danger or, on the other hand, of food. Some molluscs can detect a saponin exuded by the predator starfish in concentrations as low as 10^{-9} M, and conversely mussel extracts can elicit exploratory feeding behaviour on the part of fish. Other known chemical messengers stimulate responses associated with mating behaviour, epidemic spawning and aggregation of fish, so there are analogies in the sea to the insect phermones; the parallelism becomes very close in the case of the crab, the male of which is attracted to the premoult female by a steroidal substance which is closely related to an insect moulting hormone. A characteristic feature of such messengers is their enormous biological potency, crustecydysone being detectable by the male crab at 10^{-13} M. A more complex set of chemical messengers is involved in the sex life of a water mould, in that the male responds to a hormone secreted by the female by itself secreting a reciprocating hormone, and both compounds initiate sexual development in their respective receivers.

As is to be expected, the chemical natures of the available substances are characterised by their diversity, and there are few worthwhile generalisations to be made, except, for example, that the algae have yielded many brominated terpenoids and aromatics, that molluscs seem to be a source of brominated indoles, and echinoderms and sponges of steroids, carotenoids and alkaloids. A brief survey of some of the substances already referred to will indicate this chemical diversity. Examination of the sea clam in Szent-Gyorgyi's laboratory has shown that it does indeed contain a tumour inhibiting material, now called mercenene, which is a glycopeptide and therefore extremely difficult to characterise structurally. Much simpler is the member of the indigo family upon which the structure of Tyrian purple is based. Marine products which posses antibiotic activity range from sulphated polysaccharides to acrylic acid, but many of those which have been isolated from sponges are terpenoid in character and some show broad spectrum activity as might be expected of components of filtering organisms. Several exotic antibiotic compounds have been reported, one having a bromine content of 72% which surely must be the highest figure recorded for an organic natural product.

Antiviral activity of sulphated polysaccharides was suggested by observations that agar used for culturing virus-infected tissues permitted tissue culture while inhibiting viral growth, but the most significant antiviral compounds are 1-*β*-*D*-arabinofuranosylthymine and -uracil which were first isolated in 1950 from a Caribbean sponge. Not only do these "spongonucleosides" have interesting biological activity through their interference with nucleic acid biosynthesis, but they served as models for many synthetic nucleosides of which the cytosine analogue is best known, being used clinically as an antitumour drug.

The subject of marine toxins contains several extraordinary stories, some of which are centred around extraordinary compounds. The puffer fish is a delicacy in Japan, but it produces a toxin a thousand times more poisonous that sodium cyanide, so only trained and licenced people may handle the fish in the market. Despite this precaution however, 294 fatalities from poisoning occurred in Japan in 1959. Tetrodotoxin, which is thought to be associated with the sexual cycle of the puffers and which is found in highest concentrations during the prespawning winter months, can be isolated and crystallised, and it soon became evident that it presented a structural problem of Woodwardian dimensions. With the aid of X-ray diffraction analysis of a derivative, it was shown in his laboratory to have a most unusual dioxa-adamantane structure with various hydrophilic groups, including a guanidine moiety, attached.

Saxitoxin is the substance responsible for "paralytic shellfish poisoning" known on the North Atlantic coasts of Europe and America, the Pacific coast of North America and in Japan and South Africa. Outbreaks occur when the sea count of the causative dinoflagellate reaches 200 per ml, at which stage mussels which ingest the microorganism are too toxic for human consumption; when the count reaches 20,000 per ml the well known "red-tide" phenomenon becomes apparent. Use of the red tide, therefore, as an indication of danger is much too insensitive. The involved toxin is one of the most poisonous non-protein substances known, and is a complex tetracyclic guanidine derivative, the chemistry of which has been examined for several years—notably by Rapport in Berkeley.

Not all toxins are molecularly complex. The boxfish, a colourful relative of the puffer, found in the reefs of the Hawaiian Islands, secretes pahutoxin which is a choline ester of β-acetoxypalmitic acid. Nereistoxin, a simple monocyclic disulphide, 4-dimethylamino-1,2-dithiolane, is synthesised by a particular worm which was noticed by Japanese fishermen to be toxic to insects (in consequence "padan" has been developed to rival pyrethrum as an insecticide). Octopus ink is a polymerised form of a catechol derivative, whereas the compound which affects the olfactory senses of predators is the quinonoid form of the monomer. A fish attractant recently reported is a simple alanine derivative; the starfish exudate which serves as a warning signal to molluscs is a glycosidic derivative of marthasterone; and crustecdysone is the 20-hydroxy derivative of the insect hormone. The range of available structures is therefore enormous.

All of the above substances are of considerable biochemical significance, but there are also available from marine organisms organic compounds which might be considered to be of more interest to non-natural-product organic chemists—substances such as cyclohepta-1,3-diene, oxygenated benzpyrenes and innumerable terpenes, acetylenes etc., some with remarkable structures which often contain bromine but, strangely, seldom chlorine.

Special mention must be made of the attempts currently under way to find anti-cancer drugs from the sea. A screening of 4,400 extracts from marine organisms at the U.S. National Cancer Institute revealed that about 200 had activity, and at the University of Oklahoma a survey of nearly 2000 marine species of tropical and subtropical origin showed an 8.1% positive result. These figures are very much more encouraging than any to be expected from a random screening of synthetic substances, and may well reflect the need for some marine species to elaborate chemical defences to invaders, notably viruses, which have metabolic similarities to cancer cells. Interest in this field is currently strong, and active substances which have their origins in algae, sponges, coelenterates, echinoderms and chordata are being examined.

Lastly and especially significantly, comes a remarkable story relating to the prostaglandins, a family of monocyclic diterpenoids present in tiny amounts in many body fluids, known since the 1930s but largely unstudied until the 1960s. There are several closely related members, all differing slightly in chemical structure but having highly specific and immensely potent physiological activity. As a group they affect the activity of smooth muscles, the blood flow and the control of various body secretions. Prostaglandin A_2 has a dramatic blood pressure lowering effect, the E_2 compound stimulates uterine contractions and can be used orally to induce labour in women in a total dose of 15 micrograms, and F_2 has potential as a fertility drug and a contraceptive. The Upjohn Company in the United States invested many millions of dollars in prostaglandin research before their synthetic E_2 and F_2 compounds ultimately reached the pharmaceutical market in September 1973. Quite unexpectedly, while the synthetic work was proceeding a Caribbean soft coral called "sea whip" was found to contain the A_2 compound in 1.5% concentration, and to contain also the E_2, both identical with the hormones of mammalian cells. These findings caused considerable stir in the pharmaceutical industry, but Upjohn's current assessment is that synthetic methods are more promising for production purposes than large scale operations involving the culturing and harvesting of coral. Nevertheless, the finding of these "ultrafine" compounds has highlighted the potential of marine sources of pharmaceuticals.

Considering the vast promise held out by the examples mentioned above, progress towards the utilisation of marine products in the pharmaceutical industry has been slow in the extreme. The difficulties to be faced however, are substantial. Sources can be inaccessible, and culturing can be fraught with problems; the pharmaceutical industry is not equipped to tackle the collection, storage, dissection and extraction of unattractive and intractible raw materials; finance has been a problem exacerbated by the psychological barrier to funding expeditions to exotic tropical islands. To add to these, climatic, seasonal and other natural and unnatural factors can make the sources unreliable. For example, the New England clam registers its protest at the pollution of its aquatic habitat by cutting off its synthesis of its anti-cancer component.

While "big" industry (with the highly significant exception noted below) has not responded to the challenge in a dramatic way, the opposite is the case with academic organic chemists. Recent conferences exemplfy this: a series of international meetings on "Drugs from the Sea" was initiated in 1967 by the University of Rhode Island and was continued in 1969, 1972 and again in 1974; the First Gordon Conference on "Marine Natural Products" was held in July 1975 in Santa Barbara, and the first Chemical Society—I.U.P.A.C. meeting on the same subject was held in Aberdeen in September 1975. Evidence of high activity is apparent from the programmes of many other meetings and from the open literature as chemists set about tackling the last big source on earth of new natural products. The August I.U.P.A.C. Symposium on Natural Products in Dunedin will provide further evidence of this enthusiasm.

There is some indication that granting authorities, research organisations and industry are recognising the opportunities, but there is only one very significant recent development. By setting up in 1974 the Roche Research Institute of Marine Pharmacology in Dee Why, New South Wales, Roche Products have ensured that they will be the commercial leaders in the field for the next several years. In the first few months chemists there isolated several dozen new compounds, identified a good proportion of them, and are working currently on a material which shows juvenile hormone activity, two tranquilisers, an anti-inflammatory agent and several microbiologically active materials. Success, however, does not come quickly or cheaply in the pharmaceutical industry, and the next few years will reveal the scope of the opportunities which currently seem to be offering.

While is it obvious that there are scientists galore in New Zealand interested in marine phenomena of most sorts, it seems that marine natural product chemistry is under study by very few. Professor Berquist of the Zoology Department, Auckland, is a sponge expert who works with their steroidal constituents, Drs Blunt and Munro in Canterbury have a project under way on antibiotic materials from algae, and D.S.I.R. scientists are examining the green mussel and are known to be interested in expanding their interests in related sea-based topics. No further activity has come to notice but, like the author, others are known to have hypothetical interests with perhaps ambition to enter the field.

To the writer's knowledge there has been only one commercial venture in New Zealand into this area; this followed the discovery by Americans, who were looking for anti-cancer activity, that the New Zealand green mussel contains an anti-inflammatory agent. A preparation from them is on the market under the name "Seatone" which is being used by sufferers from arthritis.

The author thanks Dr R. J. Wells and Mr P. Tortell for assistance with gathering information.

SOME SEPARATIONS AND MASKING AGENTS IN INORGANIC ANALYSIS

H. GREEN

Synopsis

In a solution containing complex mixtures of metal ions, very little selectivity is achieved by addition of reagents, such as ammonium hydroxide or ammonium benzoate, to precipitate and separate the metal ions. Addition of complexing and masking agents, particularly ethylene diamine tetra-acetic acid (E.D.T.A.), imparts a useful degree of selectivity under the right conditions. This article presents a few of the most useful separations gathered from the chemical literature involving precipitation with ammonium hydroxide or benzoate. In addition, a number of examples are given when the same principles of selectivity can be employed using E.D.T.A. as titrant.

Introduction

It has been the practice for many years to teach chemistry students to separate complex mixtures of metal ions in solution into 'groups' employing reagents such as ammonium hydroxide and hydrogen sulphide. Although these separations are useful for qualitative analysis they are often unsuitable for quantitative analysis. For example, the elements which one finds in the old 'group 2' acid hydrogen sulphide precipitation include antimony, arsenic, bismuth, cadmium, copper, lead, and tin (omitting to mention the many other elements such as mercury, molybdenum, tungsten, and platinum which precipitate under these conditions). These very same elements, in varying proportions, make up all the white-metal alloys that are used today. There is, therefore, nothing to be achieved by employing the old group separation system with such alloys.

However, some very useful separations are obtained when one or more masking agents are present in the solution capable of forming compounds with some of the metals which have high-stability constants, so that they do not react with the particular precipitant. Some of the more generally useful separations which can be achieved, particularly with the two common reagents, ammonium hydroxide and ammonium benzoate ,are given here. This should enable the analyst to achieve separations of the metallic ions into groups with which he can deal much more competently than with those obtained by the earlier reagents.

A corollary of this work is the use of E.D.T.A. as a titrant in the presence of other masking agents, which enables specific ions, or groups of ions, to be titrated in the solutions containing complex mixtures of metal ions. This latter technique is widely used, and a few examples are included to demonstrate the potentialities it possesses.

1. Separations in the presence of E.D.T.A. as Masking Agent:

Ammonium hydroxide will precipitate a large number of metal ions from aqueous solution, but, in the presence of E.D.T.A., many of these ions remain in solution. In solutions containing ions of aluminium, beryllium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, tin, titanium, vanadium, zinc, and zirconium with E.D.T.A. present, beryllium, stannic tin, titanium, and zirconium are quantitatively precipitated. Vanadium may contaminate the precipitates, and if phosphate ions are present, the beryllium will precipitate in part as ammonium beryllium phosphate. Trivalent chromium ions will precipitate, but this may be avoided by oxidation to the chromate state.

In solutions buffered with acetate and containing E.D.T.A. many metal ions, which would normally precipitate with 8-hydroxyquinoline (oxine), may be retained in solution. Metals which do precipitate under these conditions include molybdenum, titanium, tungsten, uranium, and vanadium. Any beryllium present will precipitate as the hydroxide or, if phosphate is present, as ammonium beryllium phosphate.

In a similar manner if sodium diethyldithiocarbonate (NaDDC) is added, in the presence of E.D.T.A., many ions which are normally precipitated may be retained in solution. Selectivity is usually achieved by having other masking agents present in addition to the E.D.T.A. Thus in solutions containing E.D.T.A. and cyanide as masking agents, antimony, bismuth, and tellurium may be quantitatively precipitated by NaDDC. If the cyanide is omitted, copper will also precipitate, but cobalt, lead, nickel, and zinc will not. If citrate is present bismuth will not precipitate, but, in the presence of sodium potassium tartrate at pH 11, the bismuth is quantitatively precipitated by NaDDC.

Cupferron reacts only with a comparatively small number of metal ions, and masking with E.D.T.A. finds little application. One separation which can be used is that of vanadium from copper. Addition of E.D.T.A. to a solution containing copper and pentavalent vanadium ions complexes both metals. If the pH of the solution is then adjusted to 0.5 and cupferron is added, vanadium cupferrate is quantitatively precipitated. When filtering off the vanadium precipitate it is necessary to wash with 2 percent E.D.T.A. solution, adjusted to pH 0.5, to ensure a satisfactory separation.

Titanium may be determined spectrophotometrically, using 1, 2-dihydroxy-3, 5-benzenedisulphonic acid (tiron) in the presence of iron and pentavalent vanadium. Both iron and vanadium form almost colourless complexes with E.D.T.A. at pH 6 and below, while quadrivalent titanium will react with tiron to give a colour suitable for quantitative measurement.

The direct precipitation of cacium as the oxalate can be achieved without preliminary separation of aluminium, antimony, arsenic, beryllium, bismuth, cadmium, cerium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, tungsten, uranium, zinc, and phosphate. The precipitation is made from an acetic acid/ammonium acetate solution in the presence of sufficient E.D.T.A. to complex all the metal ions present.

In slightly acid tartrate medium (pH 5.8), in the presence of E.D.T.A. and cyanide as masking agents, it has been shown that pentavalent niobium may be reacted with bromopyrogallol red to give a solution suitable for spectrophotometric measurement. (Refer to Belcher, R., Ramakrishna, T. V., and West, T. S. *Chemistry & Industry*, 1963, No. 13, pp. 531-532.) Ions of arsenic, barium, bismuth, cadmium, trivalent chromium, cobalt, copper, calcium, trivalent cerium, ferrous and ferric iron, lead, magnesium, manganese, nickel, strontium, quadrivalent tin, quadrivalent vanadium, zinc, and zirconium do not interfere. Addition of fluoride will overcome the interference of aluminium, while hexavalent uranium can be masked using phosphate. The blue-coloured solution, stabilised with gelatin, may be measured at 610 nm.

2. Separations using Ammonium Benzoate

From hydrochloric acid solutions a number of metal ions may be precipitated using ammonium benzoate. Table 1 shows the reactions of some of the more common ions.

TABLE I

Metal Ion	Reaction with Ammonium Benzoate
Al	Precipitates
Sb	Incompletely precipitates
Ba	No precipitate
Be	Precipitates
Bi	Precipitates
Cd	No precipitate
Ca	No precipitate
Cr^{3+}	Precipitates
Cr^{6+}	No precipitate
Cu^{2+}	Incompletely precipitates
Cu^{1+}	No precipitate
Fe^{3+}	Precipitates
Fe^{2+}	No precipitate
Mg	No precipitate
Mn	No precipitate
Ni	No precipitate
Sr	No precipitate
Sn^{2+}	Incompletely precipitates
Sn^{4+}	Precipitates
Ti^{4+}	Precipitates
U	Precipitates
V^{4+}	No precipitate
V^{5+}	No precipitate
Zn	No precipitate
Zr	Precipitates

If complexing agents are present, or the pH of the solution is carefully controlled, a number of very useful separations may be made. In the presence of thioglycollic acid, ferric iron is reduced to the ferrous state and will not be precipitated by ammonium benzoate. This makes possible the separation of the group 3 metals into two further groups; elements such as cerium, trivalent chromium, and iron do not give rise to insoluble benzoates in the presence of thioglycollic acid, but aluminium, beryllium, titanium, and zirconium do give precipitates. If phosphates are present the aluminium will precipitate as aluminium phosphate.

In the presence of salicylic acid, ammonium benzoate will not precipitate aluminium, beryllium, chromium, and ferric iron. At pH 7 titanium is completely precipitated, but any cerium or zirconium will precipitate as salicylates but not as benzoates.

Trivalent cerium will precipitate as benzoate from sulphuric acid solution, but not from hydrochloric acid. The precipitation of chromium with ammonium benzoate does not go to completion unless the solution is boiled for 30 minutes. In the presence of acetate and hydroxylamine hydrochloride, copper does not precipitate. This is very convenient when the determination of aluminium is required in copper base materials. The alloy is dissolved in nitric acid and filtered, if necessary, to remove the metastannic acid. The bulk of the acid is neutralised with ammonia until any precipitate just redissolves; then 8 g of sodium acetate are dissolved in the solution, and 5 ml of hydrochloric acid and 15 ml of 5 percent hydroxylamine hydrochloride solution are added. The solution is brought to the boil for one minute to reduce the copper, and 20 ml of 10 percent ammonium benzoate solution, freshly prepared and filtered, is added. The solution is allowed to stand in a warm place for about 15 minutes. The precipitate is removed by filtering through a paper pad and washed with hot, 1 percent ammonium benzoate solution. The determination of the aluminium is then completed by dissolving the precipitate in a hot solution containing 2.5 g of tartaric acid, 0.5 g of potassium cyanide, and 12 ml of concentrated ammonia per 100 ml; the aluminium can then be precipitated as the oxinate and the determination finished by titration with standard bromate/bromide solution or spectrophotometrically if the aluminium content is not too high. For optimum conditions it is recommended that the aluminium content of the solution, before precipitation, should lie between 5 and 10 mg.

Separation of aluminium and beryllium can be achieved by careful control of the pH of the solution. Aluminium benzoate precipitates quantitatively between pH 3.5 and 4.0, but beryllium benzoate does not begin to precipitate from pure solution until the pH value rises above pH 6.5. However, if a solution containing both aluminium and beryllium ions is adjusted to pH 3.5 and ammonium benzoate is added, up to 5 percent of the beryllium will be carried down by co-precipitation. If a re-precipitation is made the separation is virtually complete.

All precipitates obtained with ammonium benzoate will contain benzoic acid, probably by adsorption; if desired, the precipitates can be ignited to give the appropriate metal oxides. The precipitates will peptise if washed with water so they should be washed with benzoate solutions.

3. The Masking of Cations in Solution before Titration with E.D.T.A.

Many metal ions can be determined by titration with E.D.T.A., and the usefulness of this type of titration may be greatly increased by the use of selective masking agents. If cyanide is added to solutions containing cadmium, divalent cobalt, monovalent copper, divalent manganese, nickel, and zinc these ions are complexed. The complexes formed with these ions, with the exception of manganese, are more stable than the corresponding E.D.T.A. complexes. This makes it possible to determine elements such as magnesium and calcium in the presence of any of these metals, except manganese. In addition to this type of masking it is possible to 'unmask' ions, such as zinc and cadmium in the presence of cyanide, by the addition of formaldehyde or chloral hydrate. This makes possible the titration of these ions in the presence of copper, nickel, iron, and cobalt. Because copper in large quantity tends to interfere with the end-point of E.D.T.A. titrations (when present as the complex cyanide) it is usually advisable to remove the bulk of this element by electrolysis or by shaking with powdered aluminium until the copper is completely replaced and the solution becomes colourless. The copper and excess aluminium can then be removed by filtration. In a solution containing nickel, zinc, and magnesium, for example, it is quite simple to employ the selective masking and de-masking techniques and determine the three elements by titration with standard E.D.T.A. solution. Two aliquots are taken from the solution, and ammonium chloride - ammonium hydroxide buffer (60 g of ammonium chloride and 550 ml of ammonium hydroxide dissolved in water up to one litre) is added to both solutions until a pH of 10 is obtained. The first solution is titrated directly with standard E.D.T.A., using eriochrome black T as indicator, to give the sum titre of nickel, zinc, and magnesium. Potassium cyanide is added to the second solution until a clear, yellow colour is obtained and any white precipitate due to the zinc has re-dissolved. This solution is then titrated with standard E.D.T.A., using eriochrome black T, as indicator, to give the magnesium titre alone. A few ml of 10 percent formaldehyde solution is added to unmask the zinc:

$$\mathrm{Zn\,(CN)_4^{2-} + 4HCHO + 4H_2O \rightarrow Zn^{2+} + 4H_2C(OH)CN + 4OH^-}$$

The titration is then continued, and the second end-point gives the titre of zinc plus magnesium. From these results it is an easy matter to calculate the amount of each metal present in the solution. Alternatively, the solution, after addition of the ammonium chloride/ammonium hydroxide buffer, may be treated with an excess of standard E.D.T.A. and back titrated with standard magnesium sulphate solution, using eriochrome black T as indicator. The difference between the titres is the sum titre of the three ions. A few ml of a 20 percent solution of 2, 3-dimercaptopropanol in ethyl alcohol is added to form a complex with the zinc. The colour of the solution will change from red to blue because of the liberation of the E.D.T.A. originally combined with the zinc. The solution is then titrated with the standard magnesium sulphate solution as before, and this new titre is equivalent to the zinc. Addition of cyanide to the solution will complex the nickel and liberate the equivalent quantity of E.D.T.A. This can then be titrated with the standard magnesium sulphate solution, and this titre will be equivalent to the nickel originally present.

This example, complexing with 2, 3-dimercaptopropanol, opens up the possibility of selective titration of many mixtures of metal ions. The reagent forms complexes with antimony, arsenic, bismuth, cadmium, cobalt, copper, lead, tin, and zinc, which are more stable than the corresponding E.D.T.A. complexes. In weakly acid solution many metal ions form precipitates, but these are readily soluble in ammonium hydroxide. In the case of cobalt, copper, iron, manganese, and nickel the complexes are deeply coloured; this necessarily places a limit on the quantity of these ions which may be present in a solution to be titrated with E.D.T.A. if a reasonable end-point is to be obtained using a colour indicator.

Triethanolamine is another reagent which can be used for complex formation. Strong complexes are formed with aluminium, iron, and manganese. Because the manganese complex is highly coloured only small concentrations may be present if other ions in the solution are to be titrated with E.D.T.A. The manganese complex will oxidise eriochrome black T, unless hydroxylamine is present, so murexide is usually used as indicator. Triethanolamine is used as complexing agent for aluminium when the other ions in the solution are to be titrated with E.D.T.A., but, because not many ions are complexed, the reagent is mainly useful in such mixtures as Al + Mg + Ca and Al + Zn + Cd. The widest use of the reagent is in conjunction with other masking agents such as cyanide. In the example previously given for the determination of magnesium, nickel, and zinc if aluminium is present triethanolamine is added to mask the aluminium, and the procedure is then the same as before.

Aluminium, beryllium, iron and titanium may be masked by the addition of ammonium fluoride to the solution to be titrated with E.D.T.A. This enables ions such as cadminium, copper, nickel, and zinc to be titrated, but not calcium and magnesium which form precipitates with ammonium fluoride.

BOOK REVIEW

Structure and Properties of Orientated Polymers—edited by I. M. Ward 1975 (50 pages). Price £18.00. Materials Science Series. Applied Science Publishers.

In the realms of physics and physical chemistry this book must rank high in dealing with the ever increasing scope of orientated polymer structure and mechanical property relationship.

The editor has been shrewd in his choice of co-authors and has provided an up-to-date spectrum under 13 main headings ranging from the general to the specific with chapters which include the latest approaches and techniques now being used in the field.

Taking some of the topics at random they include molecular aspects of orientated polymers, U.V., visible and I.R. dichroism, polarised fluorescence and Raman spi-spectroscopy, stiffness of polymers, creep behaviour, orientation of films and fibrillation.

Of course there are other recent publications available which deal with certain aspects in each chapter, as, for example, the subject of composite structures of fibrous materials, but often it is found that the author is then the same one as has contributed to this collection of papers.

As might be expected there are some complex mathematics involved in understanding some of the topics, e.g. physico-chemical approaches to anisotropy measurement and anisotropic yield behaviour, but the general polymer chemist is well catered for with graphs, tables, spectra and structural formulae in other chapters.

Although the proof checking appears to be meticulous it is perhaps unfortunate that the references given in Chapter 2 are incomplete (in the Reviewer's copy anyway!)

There is a good index to the book but curiously it only contains one trade name selected apparently at random from the few trade names which have been considered necessary to include in the text. One might have expected that none or all the trade names used would have been found in the index.

With the inclusion of the missing references this book can be recommended to all polymer scientists who have an interest in the relationship between the structure and properties of orientated polymers. At a cost of approximately $1.00 per contributor the book is not overpriced.

A. Kennet.

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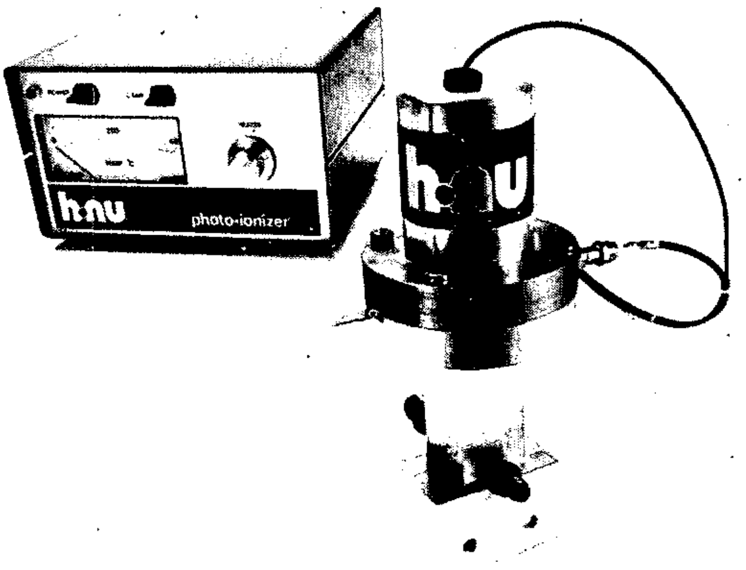


TO: New Product Editor
SUBJECT: Model PI51
Photoionization Detector
for Gas Chromatography

A unique design photoionization detector (PID) for gas chromatography has just been developed which provides 10 times to 50 times greater sensitivities than flame ionization detectors (FID's). The new photoionization detector employs a sealed ultraviolet lamp adjacent to an ionization detector and uses ultraviolet photon energy for ionization of the species. The new detector has a wide dynamic range ($>10^7$) and is extremely versatile, responding to most organics including aromatics, chlorinated hydrocarbons, amines, organic sulfurs, ketones, high molecular weight compounds such as pesticides, and some inorganics including hydrogen sulfide, hydrogen selenide, organometallics, ammonia, iodine and phosphine. The detector does not respond to several commonly used solvents such as methanol, or extraction solvents such as methylene chloride, dichloroethane, carbon tetrachloride or acetonitrile.

The principle of operation is termed photoionization since the absorption of ultraviolet light by a molecule leads to ionization via:

$$R + hv \rightarrow R^+ + e^-$$

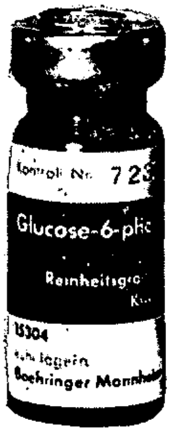
where R^+ is the ionized species and h is a photon which has an energy $\geqq$ the ionization potential of the species.

The sensor consists of a sealed ultraviolet light source that emits photons which are energetic enough to ionize many trace species (particularly organics) but do not ionize components such as O_2, N_2, CO, CO_2, H_2O, or He. A chamber adjacent to the ultraviolet source contains a pair of electrodes. When a positive potential is applied to one electrode, the field created drives any ions formed by absorption of the UV light to the collector electrode where the current (proportional to concentration) is measured.

In addition to providing a state-of-the-art improvement in sensitivity, the detector has several other important characteristics. Since the photoionization technique is nondestructive, the sample can be run in series with a destructive or element selective detector. The detector sample can be recovered for further analysis and quantification by mass spectrometry or IR. The detector has been designed with a built in heater that allows operation from abient temperatures to 250°C. The fundamental simplicity of the detector also makes it easy to install and operate. There is only one gas (carrier) required for operation. The photoionization detector is useable on any gas chromatograph.

For further information, contact:

WILTONS



analytical bio chemistry

For the solution of a variety of considerably complex questions, many analytical methods are employed by the biochemist. An almost classical method of analytical biochemistry came into existence from biochemistry itself, viz. the enzymatic analysis.

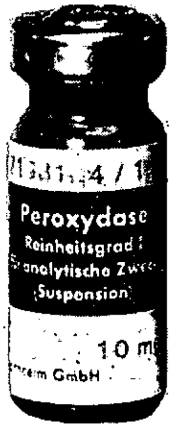
Enzymatic analysis means determination of metabolite concentration with the aid of enzymes, measurement of activities and study of the characteristics of enzymes in vivo and in vitro, and analysis of the control and regulatory functions within the cell and in organ metabolism.

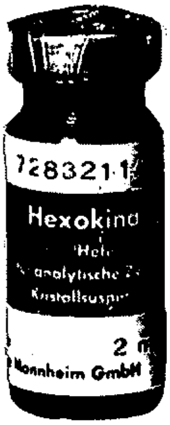
molecular biology

The research fields of protein and nucleic acid biosynthesis are nowadays lumped together – unfortunately – under the term "molecular biology." In our program we offer enzymes, substrates, templates, primer, inhibitors and auxiliary reagents, all of which are indispensable for the study of molecular action mechanisms.

enzymology

Enzymologic research revolutionizes biology not only because of the mushrooming number of newly-discovered enzymes. To the extent to which the biologist advances into cellular regions, he will become an enzymologist; to the extent to which the enzymologist interprets biological functions of cell components enzymatically, he will become a biologist. Thus, enzymology has become one of the main pillars of all biological disciplines.





clinical chemistry

This program is noted for its search for ever more specific and predictable test methods for medical research and routine diagnosis while adhering to the rising requirements for precision and accuracy of laboratory data. On the other hand, such a program must also take into consideration the requirements for simplification and rationalization. The ideal requirement is reached when simplification of actual labour allows, at the same time, for an increase in precision.

Our program for clinical chemistry offers numerous examples of this ideal.

food analysis

The first knowledge of biochemical processes, of the role enzymes play in them and the first experiences with enzymatic analytical methods were gained with foods. Analyses with the aid of enzymes have many advantages in food analysis: enzymatic methods are fast, safe and reproducible. The measurement of enzyme activities as a criterion of the condition of foods is supplemented more and more by enzymatic analysis of the components of foods.

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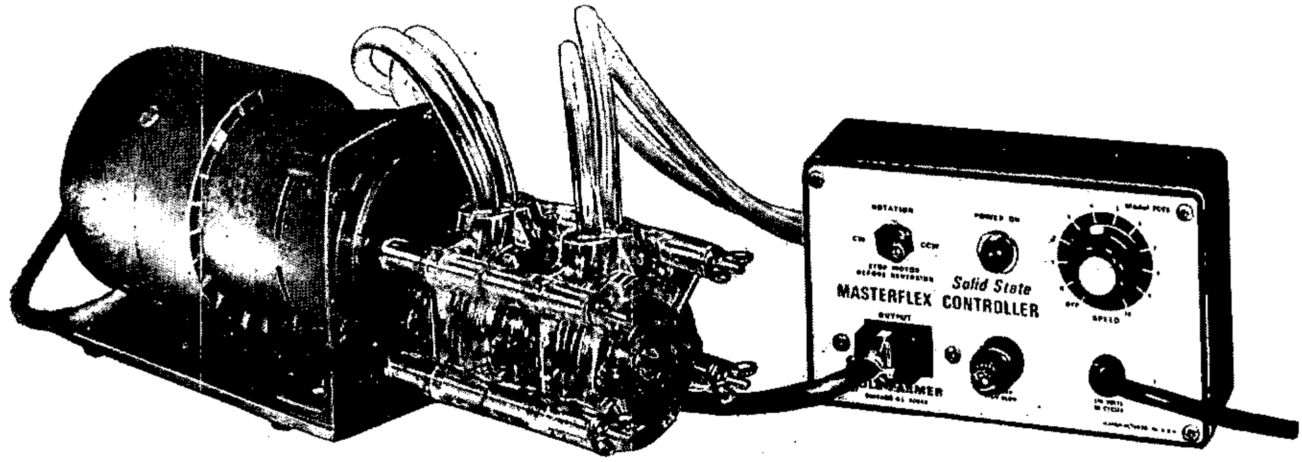

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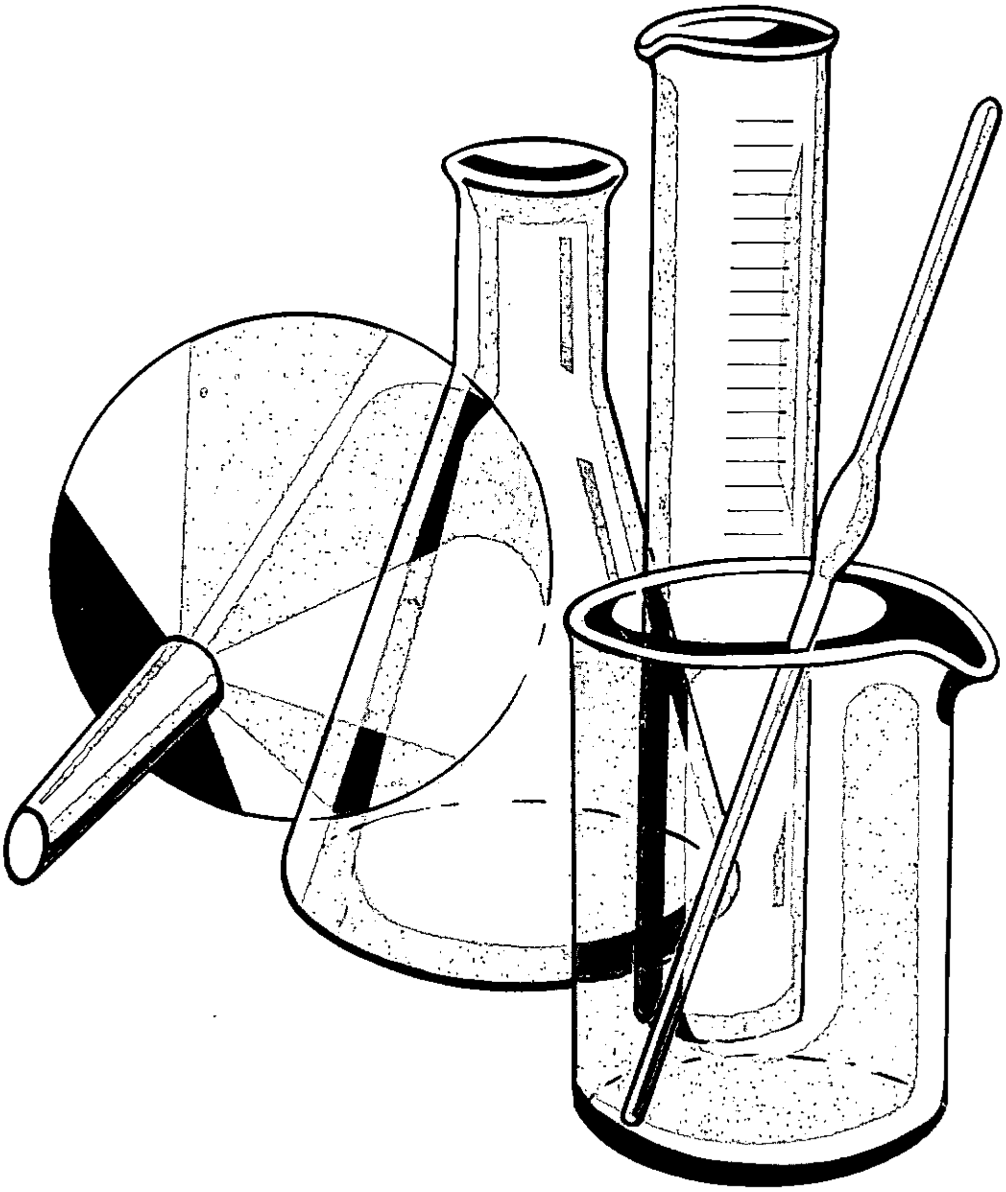

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