A Chromatographic Investigation into the Reactions of Urea and Formaldehyde

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ABSTRACT

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A literature survey showed that very few studies into the chromatographic separation of urea formaldehyde resins have been made. Those that have been undertaken are of doubtful or limited value.

A rapid reproducible method for investigating the molecular mass distribution of urea formaldehyde resins by size exclusion chromatography has been developed. By using lithium chloride in dimethylformamide as the solvent for chromatography, solubility and molecular association problems have been overcome.

A novel liquid chromatographic procedure using an aminopropyl bonded silica column,having 8,000+ plates and acetonitrile/water as eluant has been developed. Using this technique some twenty simple low molecular mass urea-formaldehyde reaction products have been separated efficiently and quickly.

Using the novel chromatography, investigations of the reactions of urea and formaldehyde in the pH range 5.5 to 8.3 and molar ratio 1:1.5 to 1:2.5 demonstrated that dimethylene ether linkages were formed to a greater degree than simple methylene linkages.

It has been shown that the ammonia formed by hydrolysis of urea was converted fistly into methylamine and subsequently into 1,3,5-triazin-4-ones structures.

Tetrahydro-1,3,5-oxadiazin-4-ones (urons) have been shown to be formed very readily at high and low pH values (<2 and >10)

Dimethyloluron has been obtained in the solid state for the first time and its physical properties studied. Four new uron compounds have been isolated and completely characterised.

The reactions of dimethyloluron with urea and formaldehyde have been studied.

The lack of reactivity of formaldehyde, when stabilised with a small amount of urea has been shown to be due to the formation of dimethyloluron.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my two supervisors firstly Dr R.M. Anderson of Dorset Institute of Higher Education for his academic guidance and his unfailing support throughout this course of study and secondly, to Mr B.Vyse of Borden (U.K.) Limited for his many helpful suggestions and day to day involvement.

Likewise, I would like to thank my advisors, Dr R. Cowdell of Dorset Institute of Higher Education and Dr M. Sainsbury of Bath University, for their help and useful suggestions.

I am most grateful to the management of Borden (U.K.) Limited, especially Mr P. Lemon, for permission to undertake this programme of research.

Sincere thanks are due to Mr J.King of Borden (U.K.) Limited, who has a genuine and deep interest in urea-formaldehyde chemistry. He has helped considerably in both the practical and theoretical fields, especially during the development of the chromatographic techniques.

Crucial to this study have been the several nmr spectra, often on very small amounts of some quite novel compounds and I would like to thank Mrs J. Street of Southampton University for obtaining excellent spectra and making a significant contribution to their interpretation.

A CHROMATOGRAPHIC INVESTIGATION INTO THE REACTIONS OF UREA AND FORMALDEHYDE

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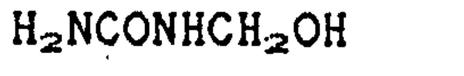
I. INTRODUCTION

The reaction of urea and formaldehyde in aqueous solution proceeds initially with the formation of the monourea methylol addition compounds, monomethylolurea, (MMU; I), dimethylolurea, (DMU; II), and trimethylolurea, (TMU; III) and these reactions are reversible as was shown by De Jong and De Jonge[1]. The methylol compounds so formed can then condense together to produce diurea compounds linked with methylene groups >N-CH_2-N< such as methylenediurea, (MDU; IV), monomethylolmethylenediurea, (MMMDU; V) and dimethylolmethylenediurea, (DMMDU; VI). A second series of condensation products can also be formed where the linking group is dimethylene ether, >N-CH_2-O-CH_2-N<. The simple members of this series are oxymethylenediurea, (OMDU; VII), monomethylololoxymethylenediurea, (MMOMDU; VIII) and dimethyloloxymethylenediurea, (DMOMDU; IX). Cyclic ethers, (the so-called urons), derivatives of tetrahydro-1,3,5-oxadiazin-4-one, (uron; X), are also formed under some extreme conditions such as high molar ratio (4:1) of formaldehyde to urea and with high (>9) or low (<5) values of pH. Simple formaldehyde derivatives of uron, (X) are monomethyloltetrahydro-1,3,5,-oxadiazin-4-one, (MMuron; XI) and dimethyloltetrahydro-1,3,5,-oxadiazin-4-one, (DMuron; XII). The presence of ammonia added as coreactant or formed from the hydrolysis of urea can complicate the reactions further by forming derivatives of tetrahydro-1,3,5,-triazin-4-one, (triazinone; XIII) notably monomethyloltetrahydro-1,3,5,-triazin-4-one (MMtriazinone; XIV) and dimethyloltetrahydro-1,3,5-triazin-4-one (DMtriazinone; XV). Primary amines likewise react, forming even more complicated mixtures containing derivatives of the 1-nitogen atom in the triazinone structure.



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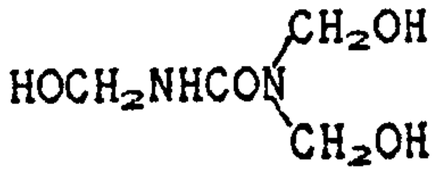

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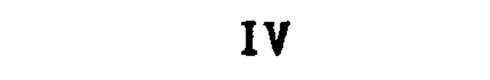

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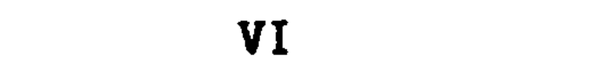

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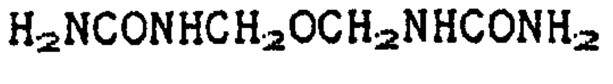

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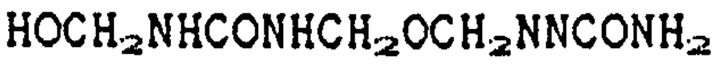

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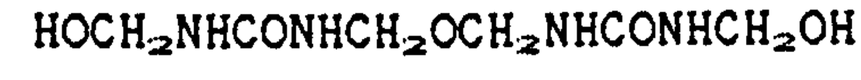

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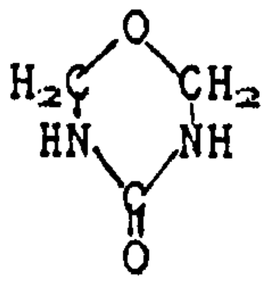

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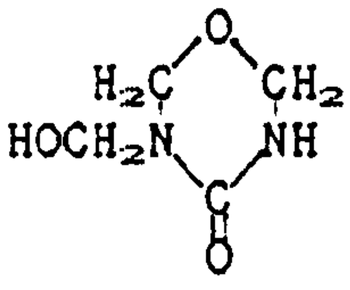

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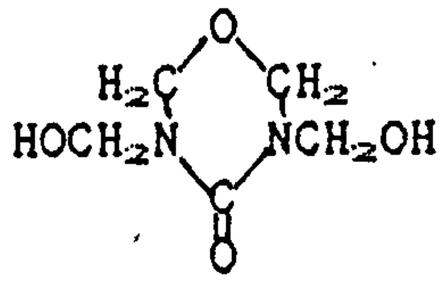

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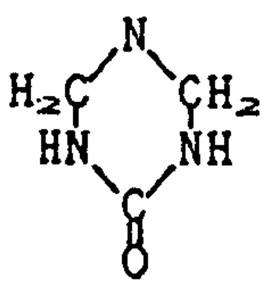

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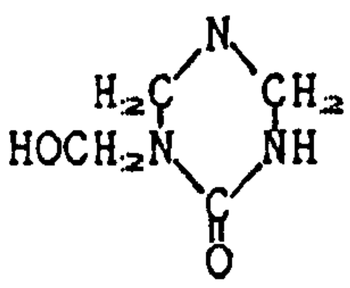

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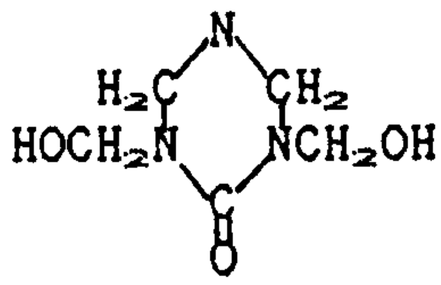

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Condensation can continue, forming molecules having relative molecular masses of several thousand and until the present study was commenced, no method had been published which would give realistic mass distribution figures. The reversibility of all of the reactions mentioned (except possibly uron formation) leads to complicated mixtures. Thus dimethylol-urea (DMU; II) in aqueous solution will on the one hand lose formaldehyde to give monomethylolurea (MMU; I) and urea and at the same time react with itself and its daughter molecules to produce such high molecular mass compounds that they are no longer water soluble. An immediate consequence is that changes, albeit slight, in the physical condition of the urea-formaldehyde condensate during analysis or in preparation for analysis can change the molecular constitution to such a degree that the analysis is meaningless.

A further phenomenon which complicates the chemistry of urea-formaldehyde compounds is their low solubility in water and other simple solvents. Urea itself is extremely soluble in water and its simple methylol derivatives although noticeably less soluble than urea, pose no problem. Methylenediurea (MDU; IV) is, however, markedly less soluble in water and its methylol derivatives can for most purposes be considered insoluble. This fact is remarkable when it is appreciated that these compounds are relatively low in molecular mass and the increase in molecular mass from the parent compound is achieved for the most part by adding methylol groups which would be expected to confer high solubility in polar solvents. It seems quite possible that the insolubility of urea-formaldehyde compounds is caused by hydrogen bonding and the addition of lithium salts, which may be expected to reduce the hydrogen bonding effect, does indeed lead to greater solubility in water. It can be

immediately appreciated that the analysis of urea-formaldehyde compounds is fraught with difficulties. Methods, often most exacting, have been developed to determine bulk properties such as free formaldehyde content, methylol content, and linear ether content. A more sensitive and revealing technique for obtaining an insight into bulk properties of mixtures of urea-formaldehyde compounds such as the commercial products used as adhesives etc. is ^{13}C-nuclear magnetic resonance, but if information on the occurrence and formation of individual molecules is required then the various chromatographic techniques have to be used. There are certain chromatographic techniques which seem to offer more potential than others for analysing urea-formaldehyde compositions. Obviously in order to obtain information on molecular mass distribution, size exclusion chromatography (SEC) has to be used.

Much interesting work was carried out a few decades ago on paper chromatography especially by the Japanese[2-6]. This technique however has severe limitations, time probably being the most obvious since a typical run can take several hours. Another major drawback is the effective resolution of the technique, and the fact that most of the visualising procedures destroy the nature of the compounds under investigation makes it very difficult to determine the composition of the materials once they have been successfully separated.

The advent of thin layer chromatography (TLC) made the task of chromatographing urea-formaldehyde compounds somewhat easier. The author produced a method in 1973[7,8] which would separate a few of the low molecular mass compounds and enable them to be determined semi-quantitatively. The acidic nature of the absorbent used in this study

and the difficulties encountered in devising a system which would adequately separate the low molecular mass compounds made it imperative to use the methyl ethers of the methylol compounds for the analysis.

Although the method was somewhat complicated, one advantage gained was that the methyl ethers were comparatively stable and solutions used for quantitative standards would store satisfactorily for several months. TLC plates with much improved resolving power are available now but it is not likely that this area of chromatography would be so fruitful as high performance liquid chromatography (HPLC) where there are many different packing materials available and columns having 30,000 plates per metre are not uncommon. HPLC is fast, a typical run taking half the time of a TLC run and unknown peaks can be isolated and possibly identified by spectroscopic techniques. Normal phase liquid chromatography on silica columns is not likely to be successful because of the total insolubility of urea-formaldehyde compounds in the solvents of low polarity which have to be used to give flexibility to the approach and theoretically highly polar compounds like the urea-formaldehyde derivatives should be separated in the reverse phase mode.

Some efforts have been made to investigate urea-formaldehyde reaction products and other amide-formaldehyde compounds by liquid chromatography but to date, a simple, rapid, efficient and universal method has not been reported. For instance Kumlin and Simonson[9,10] studied urea-formaldehyde condensates using a large particle size cation exchange resin in the Li^+ form and although a separation of about 10 compounds was achieved, the efficiency of the column was low as might be expected and a full analysis run took some 120 minutes to complete. Beck and coworkers[13] used the

cation exchange resin in the Li^+ form to examine durable press finishes and textile finishes were studied by Kottes Andrews[14] using a reverse phase column. Murray *et al.*[11] used a reverse phase column to separate biuret (XVI), triuret (XVII) and methylenediurea (IV) which occur as impurities in fertilizer grade urea and Davidson[12] in a similar fashion separated urea, methylenediurea (IV) and dimethylenetriurea (XVIII) in urea-formaldehyde fertilizer compositions.

$H_2NCONHCONH_2$ **XVI**

$H_2NCONHCONHCONH_2$ **XVII**

$H_2NCONHCH_2NHCONHCH_2NHCONH_2$ **XVIII**

Reverse phase chromatography of urea-formaldehyde compounds has many limitations for even using the weakest solvent which is water, the elution time of some compounds e.g. urea is very short and the separation of urea, MMU (I) and DMU (II) is very difficult. Materials such as the urons are likely to elute at the solvent front and any chromatographic separation will be impossible.

Once a method for separating low molecular mass urea-formaldehyde compounds has been developed then the parameters which are varied to produce the large range of commercial resins currently being marketed can be investigated. Such parameters include molar ratio of urea to formaldehyde, pH and reaction time. During the formation of urea-formaldehyde products many reactions that hitherto have not been investigated will need to be studied. These include the formation of urons, the reactivity of urons, the formation of ammonia from urea hydrolysis and the fate of the ammonia in the formaldehyde rich reaction mixture.

To summarize, the main aims of the research are as follows:

i. To devise a size exclusion chromatographic procedure which is simple and fast and will give accurate and reproducible molecular mass distribution figures for all types of urea-formaldehyde compositions.

ii. (a) To devise a chromatographic procedure which is capable of separating low molecular mass reaction products of urea and formaldehyde taking into account the fact that in reaction mixtures of this type coreactants such as methanol and ammonia can be present. Novel columns and eluants will be investigated

(b) To use this procedure to understand the synthetic pathways which are followed as the high molecular mass compounds are formed from the low molecular mass compounds, which are themselves formed from the parent monomers.

(c) To determine the influence and importance of reaction parameters such as pH, molar ratio (urea:formaldehyde), time and temperature.

(d) To discover new synthetic pathways which will enable novel urea-formaldehyde compositions to be developed and exploited in the market place.

II. DEVELOPMENT OF THE CHROMATOOGRAPHIC TECHNIQUES

A. Size Exclusion Chromatography

1. INTRODUCTION

During the past 15 years, a substantial effort has been made to study the molecular mass distribution of urea-formaldehyde resins by size exclusion chromatography (SEC)[16-27]. A rapid, reproducible and accurate procedure which will classify all urea-formaldehyde resins including the most highly condensed types, however, has not been reported. Serious difficulties arise due to the poor solubility of high molecular mass material in any simple solvent or combination of solvents and a urea-formaldehyde resin of high molecular mass will not dissolve completely in the most effective solvent, i.e. dimethylsulphoxide (DMSO). Strong intermolecular hydrogen bonds form betwen the polar sites on the molecules, producing a supermolecular structure.

For many years it has been realised that urea-formaldehyde resins even when condensed to a high degree will dissolve in strong aqueous solutions of lithium chloride. Hope *et al.*[17] in an early article on the subject referred to this approach for sample preparation and it is clear that in some way lithium chloride eliminates the hydrogen bonds which are responsible for the association effect. The solutions obtained are clear, are of low viscosity and can be infinitely diluted with solvents such as dimethylformamide (DMF) and DMSO. The chemical nature of the resins is not altered and the solute in solution remains unchanged for 24 hours at room temperature.

It has been appreciated for some time that the addition of lithium halide to DMF shows advantages over DMF alone when used as a solvent for the SEC of thermoplastic polymers. Cha[28] investigated the chromatography of polyacrylonitrile containing some sulphonate groups using lithium bromide in DMF as solvent. He found that the salt caused an increase in the elution time of the polymer from the column and attributed this effect to charge neutralization and thus a reduction in the effective molecular size. Coppola *et al.*[29], however, working with uncharged polyacrylonitrile considered that the effect on the solute molecular size was too great to be explained by this effect and they suggested that the lithium salt prevented the molecules associating together thus allowing the polymer to elute at its true position. DMF containing lithium salts has been used by a variety of other workers as a solvent for the SEC of polymers. For example, Kenyon and Mottus[30] studied a variety of thermoplastic polymers while Hann[31] worked with polyurethanes and Connors *et al.*[32] found that the addition of lithium bromide to DMF simplified the chromatograms of lignins. Cathodic electrodipping primers were examined successfully by Nomayr *et al.*[33] who also studied the effect of varying the strength of lithium salt in the solvent, establishing that concentrations in excess of 0.5% produced essentially the same chromatogram as obtained when using 0.5%.

In the present study, evidence has been obtained which indicates that there is a strong association between some of the lithium salt used in the preparation of the solution and the dissolved solute. This occurs to such a degree that the salt will pass with the urea derivative through the chromatographic column.

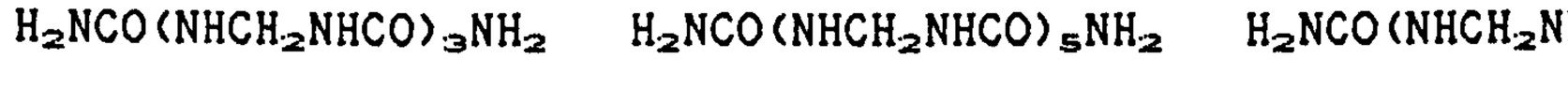
Calibration of the chromatographic columns for the analysis of urea-formaldehyde resins has caused problems for previous workers[28-33]; however, when polyethylene glycol and urea-formaldehyde standards are used in a solvent containing a lithium salt, a logical relationship is apparent.

2. EXPERIMENTAL

The chromatography equipment used in this investigation consisted of a Waters 6000A pump, a Rheodyne 70-10 injection valve fitted with a 100µl loop and Model 70-11 filler port, Polymer Laboratories PL GEL 10µm columns, porosities 10^4, 500 and 50A all 300 x 7.7mm, housed in a Waters column oven, a Waters R-401 Differential Refractometer and a Waters Model 730 Data Module with GPC integration option.

Calibration Standards

Polyethylene glycols were obtained from Polymer Laboratories (Calibration Kit PEG 10), urea (AR grade from BDH Limited) and monomethylolurea (MMU; I), dimethylolurea (DMU; II) and methylenediurea (MDU; IV) were prepared as described elsewhere[7]. Crude trimethylenetetraurea (XIX) containing some hexaurea (XX) and octaurea (XXI) compounds was prepared as detailed below.



XIX XX XXI

Preparation of Trimethylenetetraurea

Methylenediurea (IV; 22.5g, 0.17mol) was dissolved in water (250ml) warmed to about 45°C and 50% aqueous formaldehyde solution (1g, 0.017mol)

was added followed by 1 drop of 90% phosphoric acid. The solution was allowed to stand overnight and the precipitated material was filtered off and washed well with water. A chromatographic examination showed the material to be free from methylenediurea (IV) and to contain higher molecular mass oligomers (6 and 8 urea units), which could also be used for calibration.

Preparation of Samples

Many resin samples are only partially soluble in DMF unless a high initial concentration of lithium chloride is present. This causes the intermolecular hydrogen bonds to break, resulting in the resin dissolving completely and once in solution the resin sample is infinitely dilutable with DMF. The salt concentration in the sample solution was adjusted to the same strength as that in the chromatographic solvent using one of the following two procedures. The first method, used with relatively low molecular mass resins, was to dissolve the sample (0.2g) in 1M lithium chloride (anhydrous GPR grade, BDH Limited) solution in DMF (1ml) (GPR grade, BDH Limited) and then to dilute tenfold with DMF. With more difficult samples including semi-solid materials, solid lithium chloride (0.04g) was added to the sample (0.2g) and mixed vigorously with a small volume of DMF (up to 0.5ml). After the sample had dissolved completely (warming to about 45°C was occasionally necessary), DMF was added to give a final volume of 10ml. To protect the columns, any insoluble particles which may have been present were removed by passing the sample solution through a 0.5µm filter.

Chromatographic Procedure

The SEC columns were thermostatted at 25 ± 1°C and equilibrated by passing the solvent (0.1M lithium chloride in DMF) at a flow rate of 1ml min^{-1} until the retention times of the polyethylene glycol standards were constant and identical with the retention times used in the calibration of the columns. If this could not be achieved, the columns were recalibrated. The sensitivity of the detector was set to a suitable value (X16) and 100µl of sample solution was injected onto the columns via the sample loop.

Samples

Many samples of urea-formaldehyde resins have been examined by this technique and two typical resins illustrating the various aspects of the chromatography are considered in detail.

Resin A. A moderately condensed resin of high molar ratio (urea:formaldehyde 1:1.8) with no end urea addition.

Resin B. A moderately condensed resin with a very high initial molar ratio (urea:formaldehyde 1:2.0) but with a second urea addition to give a lower final molar ratio (1:1.4).

Both resins were tested when fresh and after storing for three months at 21°C. These resins were further used to demonstrate the reproducibility of the method and to examine the effects of varying the salt concentration both in the sample solution and in the mobile phase.

3. RESULTS

Calibration Standards

Urea-formaldehyde condensation products and polyethylene glycols of known molecular mass were chosen as calibration standards since the former can

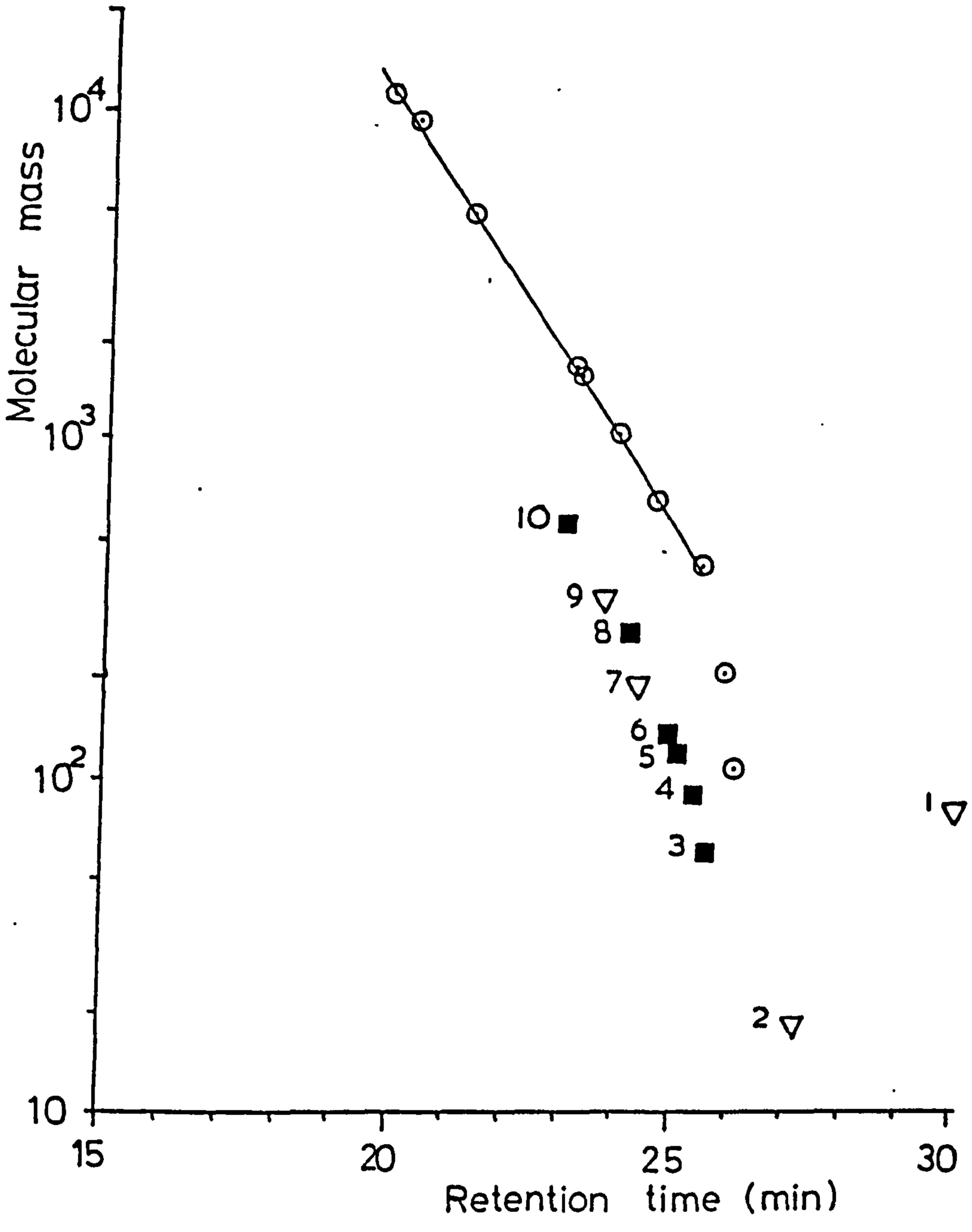


Fig.1. Calibration plot of all standards using raw molecular masses (o) poly(ethyleneglycol) standards; (■) urea derivatives; (3) urea (4) MMU (I); (5) DMU (II); (6) MDU (IV); (8) TMTU (XIX); (10) HMOU(XXI) (▽) other standards; (1) DMSO; (2) water; (7) glucose; (9) sucrose.

be directly related to the resins and the polyethylene glycols should behave similarly due to their polar nature. It was found, however, that although the plot of the polyethylene glycol standards was linear over a large part of the range (Fig.1; P.13), there was poor resolution and non-linearity at the low molecular mass end. Furthermore, the retention times of the urea derived standards did not correlate with the polymeric standards. Other polar materials such as sucrose, glucose and water showed unexpectedly short retention times, i.e., they behaved in a similar manner to the urea compounds. Since SEC strictly separates by molecular size rather than molecular mass, a possible explanation was that total solvation of the molecules was occurring at hydroxyl (-OH), amino ($-NH_2$) and imino ($>NH$) groups. This would explain both the short retention times and the poor resolution since the relative differences between the effective masses would then be small.

There is indeed strong evidence that solvation does occur at all active hydrogen sites and a plot of the retention times of all materials so far considered against their molecular mass plus one associated solvent molecule per active hydrogen atom does fall on, or is very close to, a straight line (Fig.2(A); P.15). It seems justified therefore to base all calculations on the assumption that the molecules are fully solvated and, to allow for the solvent molecules which are associated with the resin, an average structure has to be assumed. The most important factor governing this structure is the molar ratio of urea to formaldehyde. Commercial products are normally manufactured with a molar ratio varying from 1:1.0 to 1:2.0, but a value of 1:1.5 would be considered a typical value. If chain branching, ether linkages, and cyclic structures can be ignored, then a very simplified structure such as:

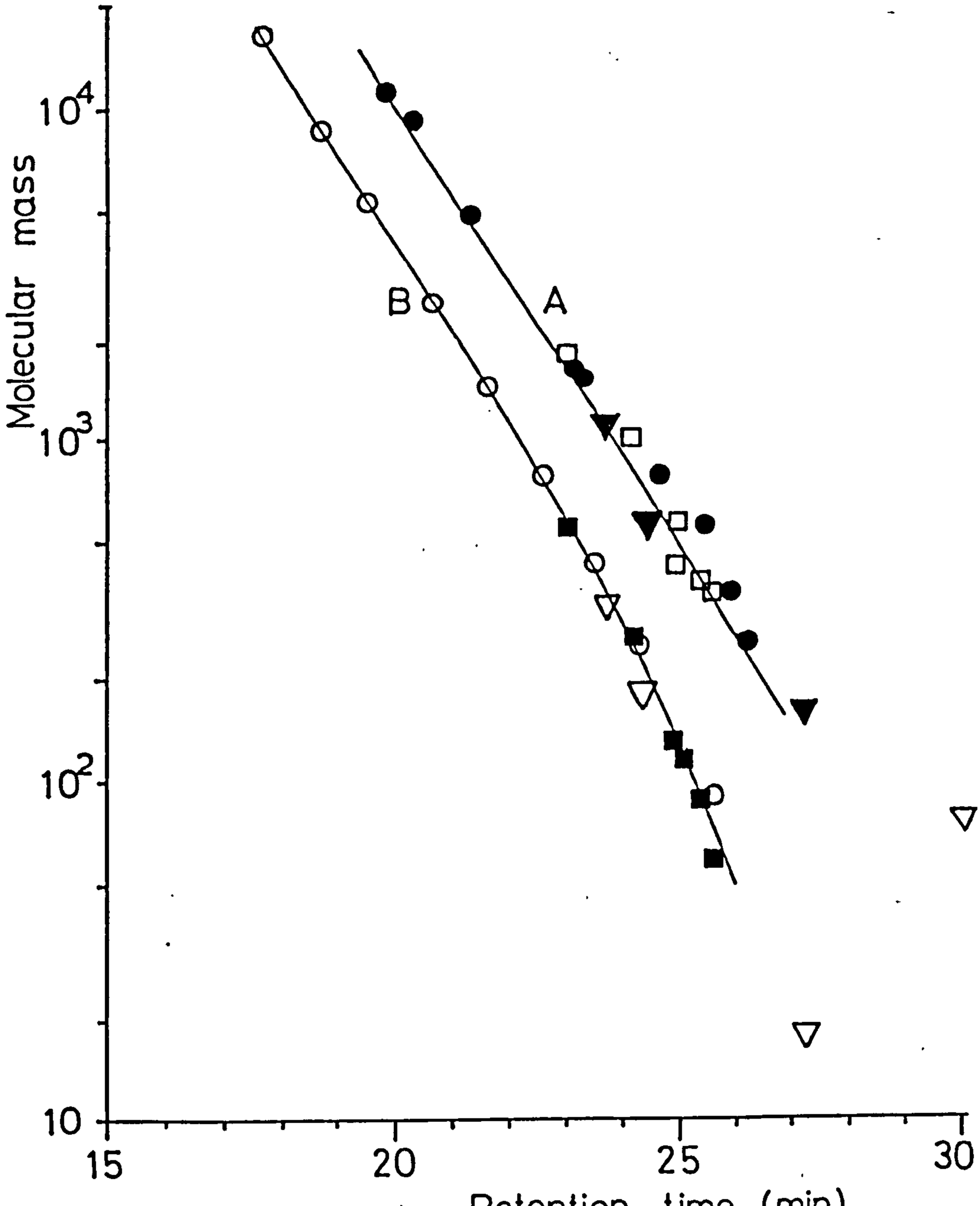
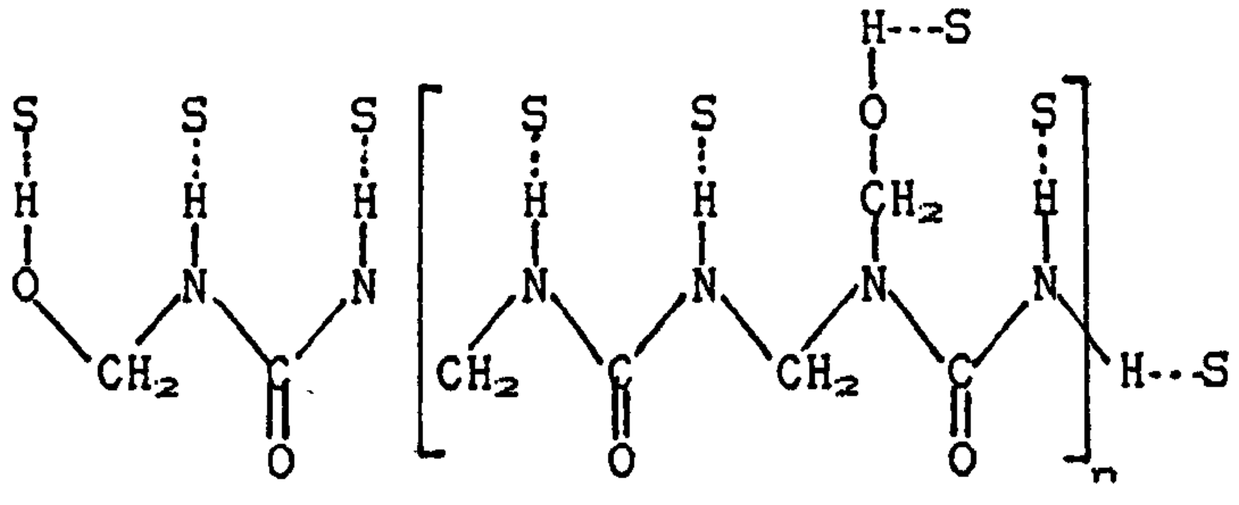


Fig.2. (A) Calibration plot of all standards as their totally solvated masses: (●) PEG standards assuming terminal -OH groups solvated; (□) urea derivatives assuming all-NH and -OH groups solvated; (▼) other standards assuming all -OH groups solvated; (B) Calibration plot adopted for urea-formaldehyde resin measurements; (o) urea standards calculated assuming structure shown in text (P.16); (▽) other standards as in Fig.1 (P.13).



where S = possible sites for solvation, can serve as a basis for calculating the contribution made by the solvent molecules to the molecular mass. Thus by assuming various values for n (the number of repeating units in the urea-formaldehyde molecule) it is possible to replot the calibration curve (Fig.2(A); P.15) in terms of the unsolvated species. For example, taking an average value for n of 30, the totally solvated molecule has an effective mass of 14,362. Using this mass, a retention time of 19.5 minutes was obtained from Fig.2(A); P.15. This retention time was then plotted against the corresponding mass of the unsolvated molecule (calculated as 5310) to give a point on the new curve (Fig.2(B); P.15). The calculated figures were in agreement with the experimentally determined points, and this calibration plot enabled direct determination of the molecular mass averages of urea-formaldehyde resins to be accomplished.

Effects of Lithium Chloride

When urea derivatives were dissolved in the mobile phase and chromatographed, a large negative peak was produced due to a deficiency of lithium chloride. This indicated that some of the salt was carried through the chromatographic columns in a form that is closely associated with the urea derivative and further examination of this phenomenon revealed that the addition of an equimolar amount of lithium chloride to urea and DMU (II) solutions in the mobile phase was sufficient to exactly

neutralize the negative peak, whereas with MDU (IV) two moles of lithium chloride were required to cancel out the negative peak.

The effect of altering the lithium chloride concentration in the sample solution was examined, and it was found that variation over a large concentration range had very little effect on the molecular mass averages. Samples prepared without lithium chloride and with a large excess of lithium chloride did, however, give significant variations in the values obtained. (Table I; P.20).

An exhaustive investigation of the effects of varying the lithium chloride concentration in the mobile phase was not made since this aspect has been examined previously by Nomayr *et al.*[33]. If a sample was run in DMF without added lithium chloride but using DMSO to improve the sample solubility there appeared to be some very high molecular mass material which was excluded, and a somewhat variable pattern of peaks was produced, the position and intensity of which seemed dependent on the method of sample preparation and the age of the solution. An example of this type of chromatogram is shown in Fig.3a (P.19). Using lithium chloride in DMF as the eluting solvent for the analysis of about fifty urea-formaldehyde samples, only one, which was partially gelled, showed any signs of exclusion.

Reproducibility

Five samples of resin were prepared for analysis using the methods described previously (P.11), four using 1M lithium chloride and diluting, the fifth using solid anhydrous lithium chloride. The molecular mass figures obtained are given in Table I (P.20) and the results obtained on samples prepared using different procedures are included for comparison

purposes. The samples were prepared at the same time and were run one after another, and once in solution, samples were found to be stable for up to twenty four hours. After three days however, some increase in molecular mass figures was noticeable.

Resin Samples

Two resin samples A and B were studied for changes in molecular mass distribution on storage for a period of about six months and chromatograms of fresh and old resins are shown in Fig.3b and c (P.19) and Fig.4 (P.21). It can be seen that resin A with no end urea addition shows a fairly even distribution when fresh, the low molecular mass end altering only slightly on ageing while the medium to high molecular mass region becomes much more extended. Resin B containing the end urea shows a large low molecular mass peak when fresh which diminishes considerably on ageing, producing a large increase in medium molecular mass materials while the high molecular mass end is relatively slow to change.

4. DISCUSSION

The objective at the outset of this work was to develop a method of determining the molecular mass distribution of urea-formaldehyde formulations which was rapid, reproducible, and applicable to all types of samples. Since the introduction of semi-rigid microparticulate crosslinked polystyrene gels, analysis times of thirty minutes or less have been commonplace. Columns packed with these gels therefore show a considerable advantage over the types previously used in this field, which were usually composed of large soft particles often based on a polysaccharide or a polyester.

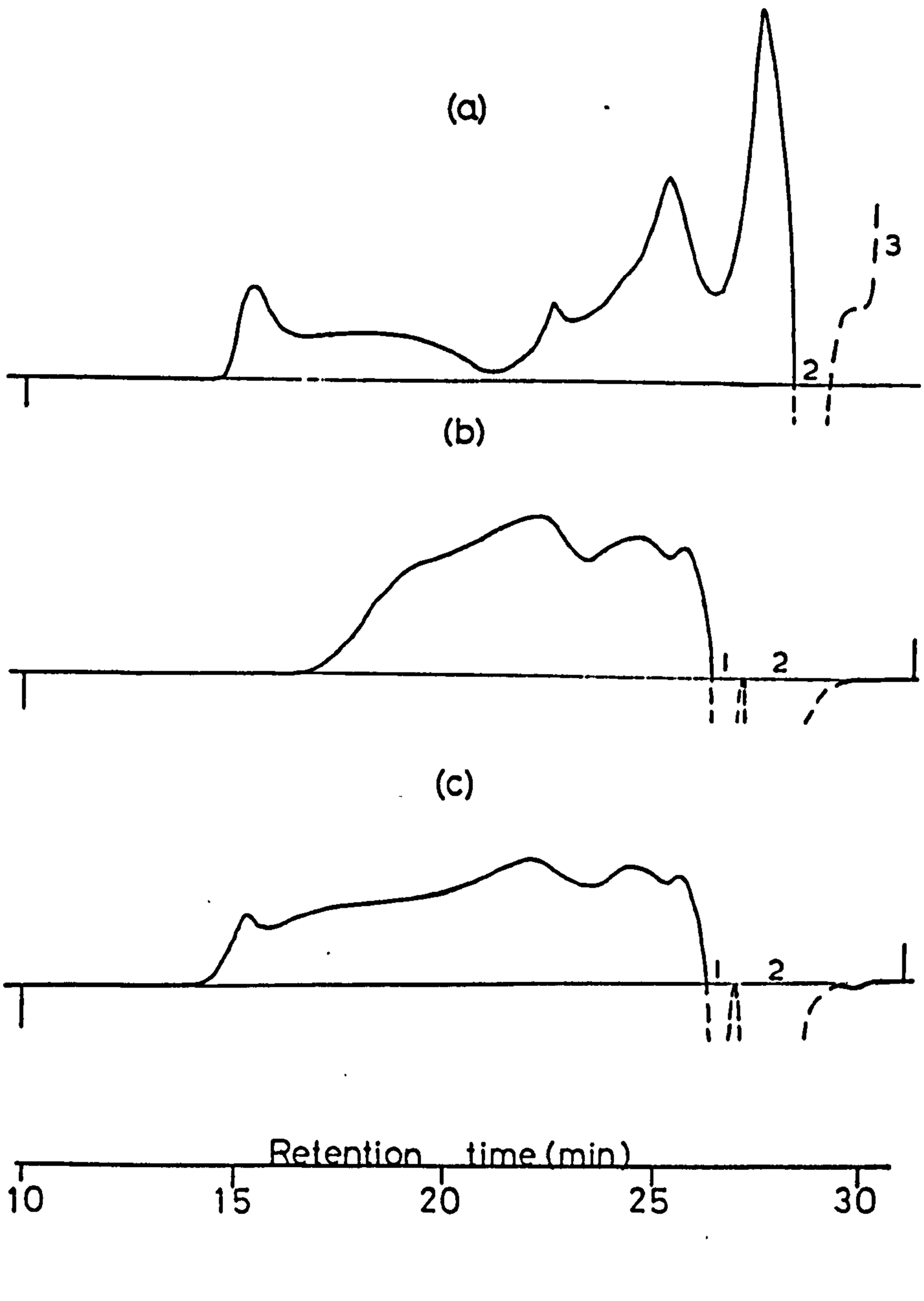


Fig.3. Resin A: (a) fresh sample dissolved in DMSO/DMF (1:10) and run in a mobile phase of DMF alone; (b) fresh sample dissolved and run in 0.1M LiCl in DMF; (c) six month old sample, stored at 21°C, dissolved and run in 0.1M LiCl in DMF. Peak identification: (1) LiCl; (2) water; (3) DMSO.

Sample number	Method of preparation	M_n	M_w	M_z	Dispersity
1	1ml 1MLiCl-10ml	146	1395	5559	9.53
2	1ml 1MLiCl-10ml	147	1419	5675	9.63
3	1ml 1MLiCl-10ml	144	1368	5456	9.48
4	1ml 1MLiCl-10ml	146	1397	5584	9.60
5	0.04g LiCl-10ml	144	1397	5620	9.68
6	No LiCl	163	1270	4451	7.80
7	0.5ml 1MLiCl-10ml	152	1464	5812	9.60
8	1.5ml 1MLiCl-10ml	145	1399	5525	9.65
9	2.0ml 1MLiCl-10ml	137	1347	5508	9.85
Standard deviation for samples 1-5		±1.2	±16	±73	±0.07
Coefficient of variation for samples 1-5		0.83%	1.15%	1.31%	0.73%

M_n, the number average molecular mass, $= \Sigma N_i M_i / \Sigma N_i$

M_w, the weight average molecular mass, $= \Sigma N_i M_i^2 / \Sigma N_i M_i$

M_z, the Z average molecular mass, $= \Sigma N_i M_i^3 / \Sigma N_i M_i^2$

where N_i is the number of molecules of molecular mass M_i for every species i

Dispersity $= M_w / M_n$

Table 1. Molecular mass figures for a urea-formaldehyde resin prepared for chromatography in several ways (samples 1-4 are replicate runs)

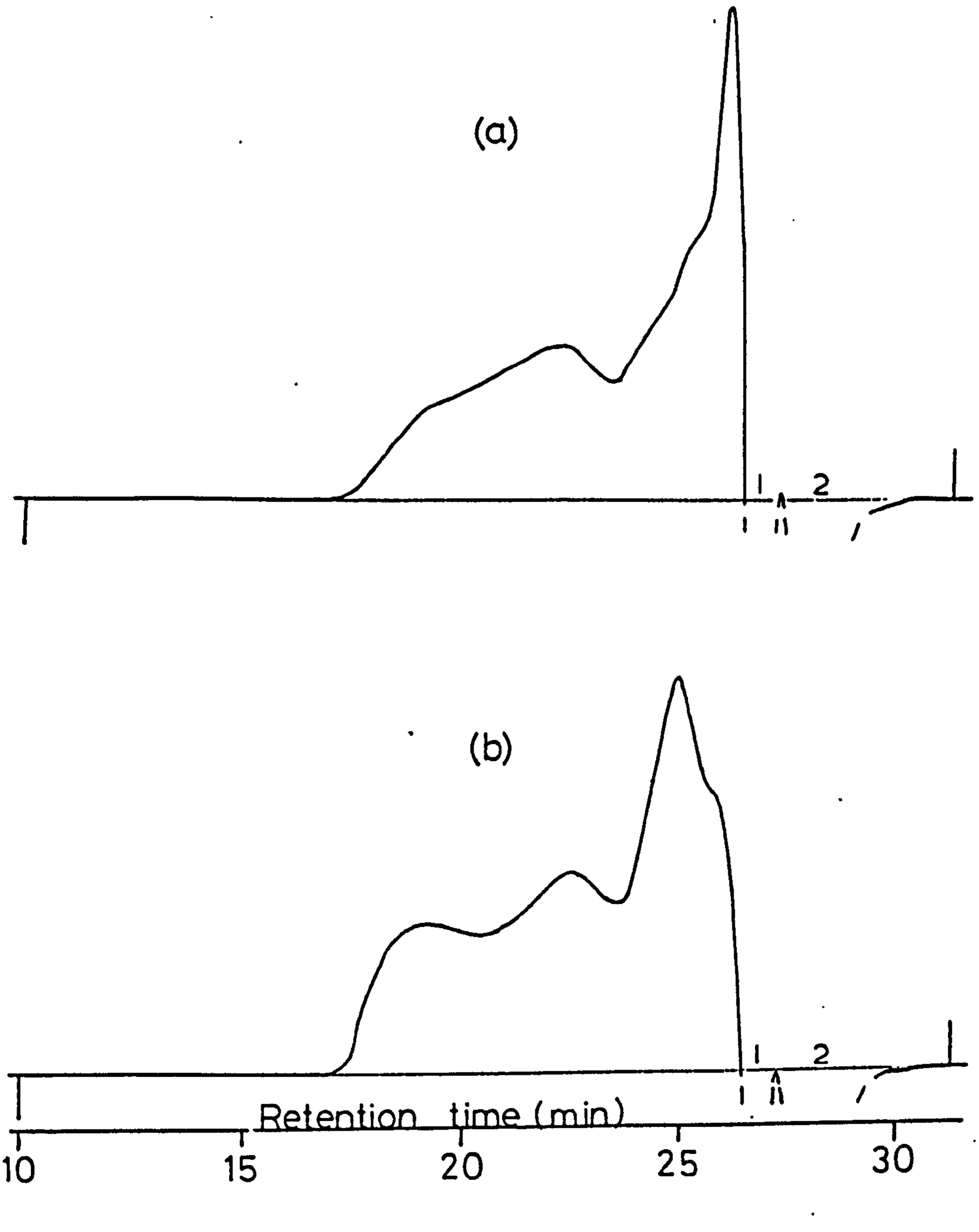


Fig.4. Resin B: (a) fresh sample; (b) six month old sample, stored at 21°C. Both samples dissolved and run in 0.1M LiCl in DMF.
Peak identification; (1) LiCl; (2) water.

The set of three SEC columns which was employed gives a separation time of about thirty minutes using a flow rate of 1ml min^{-1} of DMF containing lithium chloride (0.1M). The columns were stored in this solvent when not in use and proved stable and reliable over a period of many months and there was no significant change in the calibration plot during this period.

The choice of the solvent has proved crucial to the success of this investigation since it eliminated the hydrogen bonding in the solute and allowed complete solvation of the molecules to occur. As a consequence, a rational calibration curve has been obtained leading to meaningful values for Mn, Mw, Mz, and polydispersity. In the absence of lithium salt the degree of molecular association was variable, rendering all results thus obtained virtually meaningless.

Obviously some assumptions have had to be made about the structure of the polymer chain, but this is invariably the case when calibrating SEC columns for molecular mass determinations. These assumptions are only likely to cause significant errors in samples having final urea: formaldehyde molar ratios of about 1:2 and commercial materials of this type are rare.

The action of the lithium salt in rendering urea-formaldehyde polymers soluble is not completely understood. It has been shown experimentally (P.16) however, that lithium salt is transported through the SEC column with the urea derivative and that each urea group is associated with one molecule of lithium chloride probably via the carbonyl oxygen, $>C=O--Li^{+}Cl^{-}$.

The lithium salt not only confers solubility on the polymer but also provides a secondary beneficial effect in that there is an increased detector response to the urea compounds compared with that observed in DMF alone. Since a lithium ion is associated with each urea unit, this effect is shown over the whole molecular mass range but the high degree of solvation of the urea derivatives means that there is very little relative difference in the molecular size of the low molecular mass components, causing poor resolution of these materials. The complete separation of these materials however, is not necessary for the purposes of determining average molecular masses, and they are better separated, using other techniques such as high performance liquid chromatography.

The actual values obtained at Borden U.K.Ltd. for the molecular mass averages of commercial samples have varied widely. Typical figures found for freshly prepared materials were: Mn between 140 and 500, Mw between 800 and 3000, Mz between 3000 and 25,000, polydispersity between 5 and 20 and these values can increase substantially on storage at 21°C for six months (Fig.3; P.19 and Fig.4; P.21).

It can be concluded that this approach to SEC[15] of urea-formaldehyde compositions is a viable method of quality control and it is also a powerful procedure for investigating the formation of the urea-formaldehyde polymers and not least their ageing characteristics.

B. Liquid Chromatography

1. INTRODUCTION

The published work on liquid chromatography of urea-formaldehyde compounds is very scanty due mainly to the problems discussed earlier (P.3). Probably the most important investigation has been conducted by the Swedish workers K. Kumlin and R. Simonson who published a series of papers[10,25,34,35] under the general title "Urea-Formaldehyde Resins". These workers used a cation exchange resin of large particle size in the Li^+ form as column packing material and although a separation of about ten compounds was achieved, the efficiency of the column was low as might be expected and a full analysis run took some 120 minutes to complete.

As mentioned previously (P.6), Murray *et al.*[11] used a reverse phase column to separate biuret (XVI), triuret (XVII), methylenediurea (IV) and dimethylenetriurea (XVIII) in urea-formaldehyde fertilizer compositions, Beck and coworkers[13] used the cation exchange resin in the Li^+ form to examine durable press finishes and textile finishes were also studied by Kottes Andrews[14] using a reverse phase column.

The limitations of these liquid chromatographic procedures are discussed and a method presented which is quite unrelated to any chromatographic approach used to date and which will separate urea-formaldehyde condensation products efficiently and quickly. Some progress has been made also in the characterisation of several little known compounds notably dimethyloltetrahydro-1,3,5,-oxadiazin-4-one (dimethyloluron or DMuron; XII).

2. PRELIMINARY INVESTIGATIONS

In order to separate the many compounds formed when urea and formaldehyde react together and to ensure that the analysis was complete in as short a time as possible, it was decided to investigate the potential of reverse phase silica columns rather than the ion exchange columns used by Kumlin and Simonson[9] as these were reported to be inefficient and slow to use.

In the course of the investigation, several 5µm octadecylsilane (ODS) reverse phase packing materials from various manufacturers were examined, for example Zorbax ODS, Lichrosorb ODS and Spherisorb ODS. A mixture of urea, monomethylolurea (MMU; I), dimethylolurea (DMU; II), and methylene-diurea (MDU; IV) was used as a simple test solution and not unexpectedly, it was found that the elution patterns were slightly but significantly different. With Zorbax and Lichrosorb, DMU (II) and MDU (IV) were not separated and with Spherisorb the resolution of urea and MMU (I) was not adequate. By coupling a Zorbax column to a Spherisorb column, however, complete resolution of the test mixture could just be achieved and although the analysis time was long and the separation was barely adequate, this column configuration was used for several months at Borden (U.K.) Limited to estimate low molecular mass compounds in urea-formaldehyde compositions. Attempts were made to improve the analysis, by using a column packed with Hypersil C_{22} Super in the hope that the longer carbon chains would retain the molecules of interest to a greater degree but the results were disappointing, showing little improvement when compared to the usual ODS packings.

Severe limitations of chromatographing urea-formaldehyde compounds in the conventional reversed phase mode were observed and are listed below.

1. Resolution of the most simple compounds was very difficult to achieve and with more complex mixtures considerable peak overlap occurred so that the chromatography became meaningless.

2. Many compounds such as uron (X) and its methylol derivatives (XI) and (XII) eluted at the solvent front even using the weakest solvent and it did not seem likely that this difficulty could be overcome.

3. The analysis time was quite long being about twenty five minutes for a typical mixture.

It was thought that a better separation of the methylol compounds (typically MMU (I) and DMU (II)) could be achieved by using a more polar column and furthermore the increased interaction between the polar stationary phase and the urea-formaldehyde compounds could possibly give greater flexibility with the eluting solvent. A column was therefore packed with a hydroxy terminated material (Lichrosorb Diol) and the test solution of urea, MMU (I), DMU (II) and MDU (IV) was chromatographed using water as the eluting solvent. The elution pattern was markedly different to that obtained using the hydrophobic ODS columns, the hydroxy compounds DMU (II) and MMU (I) eluting first, followed by urea and MDU (IV). It was apparent that the -OH---NH- hydrogen bonding effect was more powerful than the -OH---OH- interaction and compounds were eluting according to the -NH content. This order of elution from the column was contrary to the ideal pattern and it was considered likely that on such a column, the chromatography of urea-formaldehyde mixtures would be most complicated. The possibility of reversing this elution pattern by using an amine column seemed attractive and worth investigating.

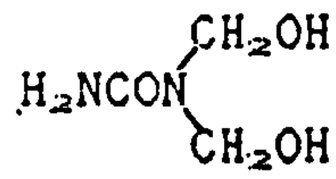
An aminopropyl terminated phase, Techsil NH_2 (5µm) was examined and using the aqueous solvent as before, all the test compounds eluted at the solvent front. Since an amino column has characteristics of a "normal" phase, water is likely to be the strongest solvent available and by using methanol as a potentially weaker eluant, a partial separation was achieved and the order of elution obtained was as follows; parent compound, monomethylol compound (I) and dimethylol compound (II), which seemed most encouraging. Methanol was replaced by acetonitrile in the hope that the absence of solvent/solute hydrogen bonding would firstly accentuate differences between the dimethylol, monomethylol and unsubstituted compounds thus giving better separation of the test mixture and secondly, increase the elution time. This indeed was so, and after an adjustment of the solvent strength to give a 9:1 ratio of acetonitrile to water, an almost ideal system for separating the test mixture was obtained.

The flexibility of the system was demonstrated when less polar compounds such as uron (X) and its methylol derivatives (XI and XII), hitherto eluting at the solvent front, were completely separated by reducing the solvent strength to a 19:1 acetonitrile to water mixture.

Thus a system that seemed almost ideal for the chromatography of simple urea-formaldehyde compounds was developed in which the column had high efficiency (8,000 plates), peak shape under normal conditions was good, analysis time was short, being apprximately ten minutes for the test mixture of urea, MMU (I), DMU (II) and MDU (IV) and the elution pattern was favourable.

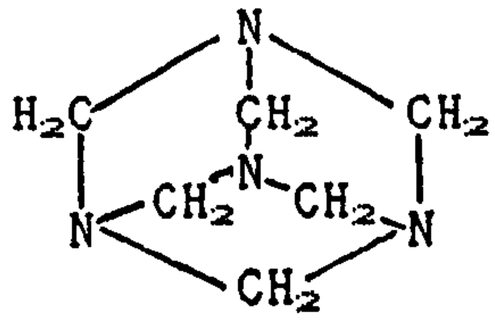
3. EXPERIMENTAL

The chromatographic equipment used in this investigation consisted of a Waters 6000 A pump, a Rheodyne 70-10 injection valve fitted with a 100µl loop and Model 70-11 filler port, a Waters R401 differential refractometer and a Waters Model 730 Data Module. A 2µm inline filter was positioned between the injector and the column. The analytical columns employed were made from 250mm x 4.6mm stainless steel tubing with zero dead volume fittings and were packed using the slurry technique developed by Kirkland[37]. Initial upward displacement with methanol was followed by downward displacement and "slamming" to improve the stabilisation of the bed. The slurry used for packing the 5µm aminopropyl bonded silica to produce the columns used for the majority of this work was prepared by dispersing, by ultrasonic agitation, Techsil NH_2 (5µm) packing material (3.5g) in a 3:1 chloroform:methanol mixture (70ml). The aminopropyl bonded silica columns normally have an adequate life but when used for the analysis of materials with a high proportion of free formaldehyde, they can deteriorate quite quickly. This is possibly due to irreversible amino-aldehyde interaction taking place and is indicated by shortening retention times and lack of resolution of methylenediurea (MDU; IV) and N,N-dimethylolurea (asymDMU; XXII).



XXII

In an attempt to offset this problem, a small amount of ammonia (0.01M) was added to the eluting solvent to convert the free formaldehyde to the less troublesome hexamethylenetetramine, (hexamine; XXIII).



XXIII

Addition of ammonia to the solvent approximately doubled the life of a column but depending on the type of sample under investigation the life of an amino column was found to be only 50 to 200 working days. As column packing and testing took only 2 or 3 hours, column deterioration was not considered to be a serious problem.

The preparative column was packed using Partisil 5μm silica by the same upward-downward-"slamming" procedure previously described. Stainless steel tubing 300mm x 7.8mm was used for the column and 5.5g of the packing material was slurried in a 3:1 chloroform:methanol mixture (70ml).

The eluting solvent used for the majority of the work was prepared by mixing acetonitrile (Hypersol grade ex BDH Limited) (900ml), with deionised water (100ml) and ammonia solution (0.5ml, sp.gr. 0.88), the solvent mixture being degassed with helium and the temperature allowed to rise to room temperature before use. If the mixtures under examination contained predominantly methyl ethers or urons, i.e. compounds with short elution times, then improved resolutions were obtained by weakening the eluting solvent to 19:1 acetonitrile to water. Other solvents and chemicals, except where stated, were general purpose laboratory reagents.

Preparation of Samples

Where possible pure reference materials (5-10mg) were dissolved in 10ml of the eluting solvent but when the sample had limited solubility in the eluting solvent, it was found to be advantageous to dissolve the material in water (1ml) and to dilute with acetonitrile (9ml). With resinous samples about 200mg were treated as above. With highly condensed samples neither of these techniques was too satisfactory because of the difficulty of dispersing the material in water and this type of sample was dissolved in dimethylformamide (1ml) and diluted with acetonitrile (9ml). The sample plus solvent, was shaken vigorously and allowed to stand and, if necessary, the sample solution was filtered through a 0.5µm filter before injection.

Reference Materials. Urea-Formaldehyde Compounds and Reaction Products

Monomethylolurea (MMU; I), dimethylolurea (DMU; II), methylenediurea (MDU; IV), monomethylolureamonomethylether (MMU. MME; XXIV), dimethylol-ureadimethylether (DMU.DME; XXV) and dimethylolureamonomethylether (DMU.MME; XXVI) were all synthesised by methods published earlier[3].

$CH_3OCH_2NHCONH_2$ — XXIV

$CH_3OCH_2NHCONHCH_2OCH_3$ — XXV

$CH_3OCH_2NHCONHCH_2OH$ — XXVI

The following reactions with varying molar ratios of urea and formaldehyde were carried out.

1. ALKALINE UREA-FORMALDEHYDE CONDENSATE, MOLAR RATIO 1:3

Disodium hydrogen phosphate (0.1g) was dissolved in 50% aqueous formaldehyde solution (1.8g), urea (0.6g) was added and the solution was

stirred and allowed to stand at room temperature for two hours. Samples for chromatography were taken at intervals.

The main product of this reaction was DMU (II) with smaller amounts of MMU (I), asymDMU (XXII) and TMU (III) (Fig.12; P.42)

2. ALKALINE MDU (IV):FORMALDEHYDE CONDENSATE, MOLAR RATIO 1:1

MDU (IV; 1.3g) was dissolved in water (5ml) at 40°C, disodium hydrogen phosphate (0.1g) was added and when dissolved, 50% aqueous formaldehyde solution (0.6g) was added. The mixture was allowed to stand at room temperature and samples were taken at intervals.

3. ALKALINE MDU (IV):FORMALDEHYDE CONDENSATE, MOLAR RATIO 1:1.5

This was prepared as above but 50% aqueous formaldehyde solution (0.9g) was used.

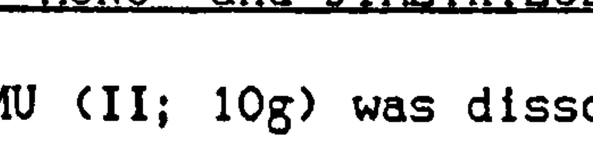
4. ALKALINE MDU (IV):FORMALDEHYDE CONDENSATE, MOLAR RATIO 1:2

This was prepared as above but 50% aqueous formaldehyde solution (1.3g) was used.

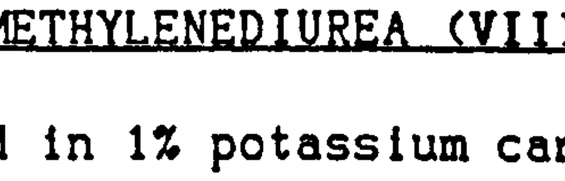
The reaction MDU (IV) with formaldehyde at pH 8 (reactions 2, 3 and 4) produced a mixture of methylol MDU compounds. At a molar ratio of 1:1, the main product was the primary monomethylol methylenediurea (MMMDU; V) with smaller amounts of the secondary monomethylolmethylenediurea (XXVII). At a higher molar ratio (1:2), the main reaction product was the primary dimethylolmethylenediurea (DMMDU; VI) with smaller amounts of the secondary dimethylol compounds, (XXVII, XXIX and XXX) and two other compounds, possibly the trimethylolmethylenediureas (XXXI and XXXII). (Fig.14; P.45). The intermediate molar ratio condensate (1:1.5) gave

mono- (V) and disubstituted (VI) compounds in approximately equal amounts.

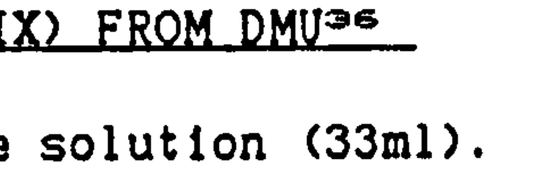
XXVII



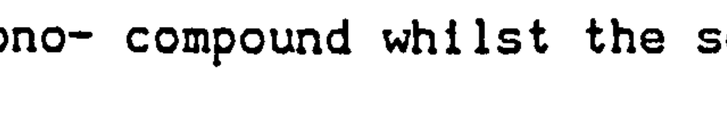
XXVIII



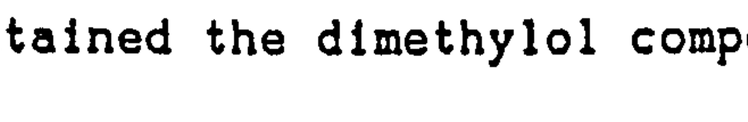
XXIX



XXX



XXXI



XXXII

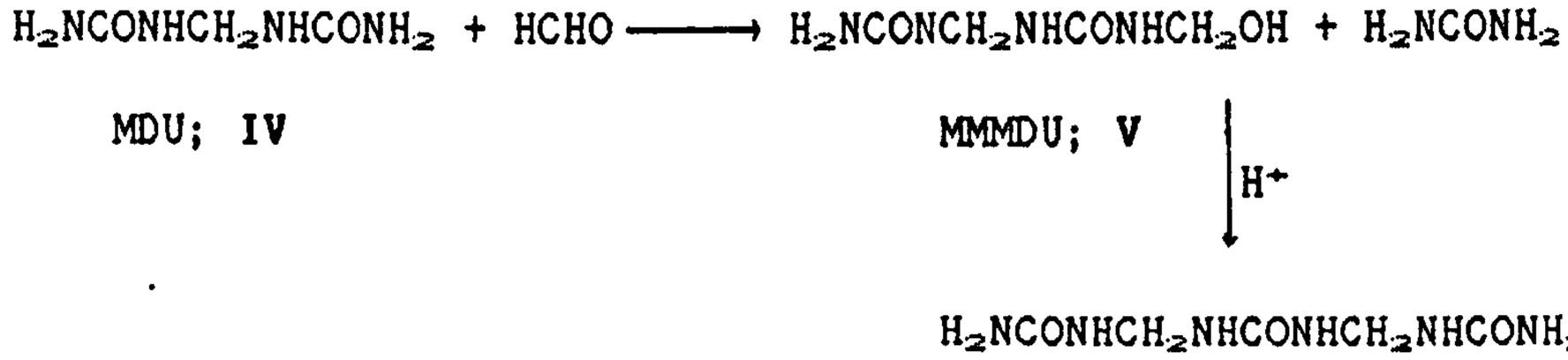
5. MONO- and DIMETHYLOLOXYMETHYLENEDIUREA (VIII AND IX) FROM DMU[36]

DMU (II; 10g) was dissolved in 1% potassium carbonate solution (33ml). After standing for three weeks at room temperature, the precipitate (1g) which had formed, was filtered off. The supernatant liquor and the solid material were both used as standards, the liquid being relatively rich in the mono- compound whilst the solid contained the dimethylol compound as the main product.

6. CRUDE DIMETHYLENETRIUREA (DMTU; XVIII)

MDU (IV: 6.6g, 0.05mol) was dissolved in water (100ml) at 60°C. Disodium hydrogen phosphate (0.2g) was added and when dissolved, 50% aqueous formaldehyde (3.0g, 0.05mol) was added. The reaction mixture was allowed to stand for one hour. The crude monomethylol MDU (V) was filtered off, washed with cold water and dissolved in the minimum amount of water at 60-70°C. Urea (30g, 0.5mol) and sodium dihydrogen phosphate (0.5g) were

added to the solution and after standing overnight the crude DMTU (XVIII) was filtered off and washed thoroughly with water.



7. DIMETHYLOLURON (DMuron; XII)

10M Sodium hydroxide (2ml) was added to 50% aqueous formaldehyde (72g, 1.2mol) followed by urea (12g, 0.2mol) and the solution heated to boiling for 1 minute. The pH was adjusted to 8 with 90% formic acid and about 40ml of water and formaldehyde removed by vacuum distillation at 40-50°C in a rotary evaporator. Three extractions with 100ml of a 1:1 mixture of chloroform and acetonitrile removed the dimethyloluron (XII) from the reaction mixture presumably as the dihemiformal (pure DMuron (XII) is only sparingly soluble in this solvent mixture and impurities such as DMU (II) and TMU (III) remain behind.) DMuron (XII) was separated from excess residual formaldehyde and water by chromatography on a semi-preparative Partisil 5μm silica column (300mm x 7.8mm) using 10% methanol in chloroform as the eluant. The structure was proved by infra-red, ^{1}H-nmr (Figs.5 and 6; P.34) and ^{13}C-nmr spectroscopy; ring C: 77.4ppm. chain C: 66.9ppm, carbonyl C: 152.3ppm, solvent DMSO-d_6. m.p. 91 - 92°C. C, H and N analysis gave C, 37.2%; H, 6.0%; N, 17.7%. ($C_5H_{10}N_2O_4$ requires C, 37.0%; H, 6.2%; N, 17.3%). DMuron (XII) in the solid state, has not previously been reported in the literature.

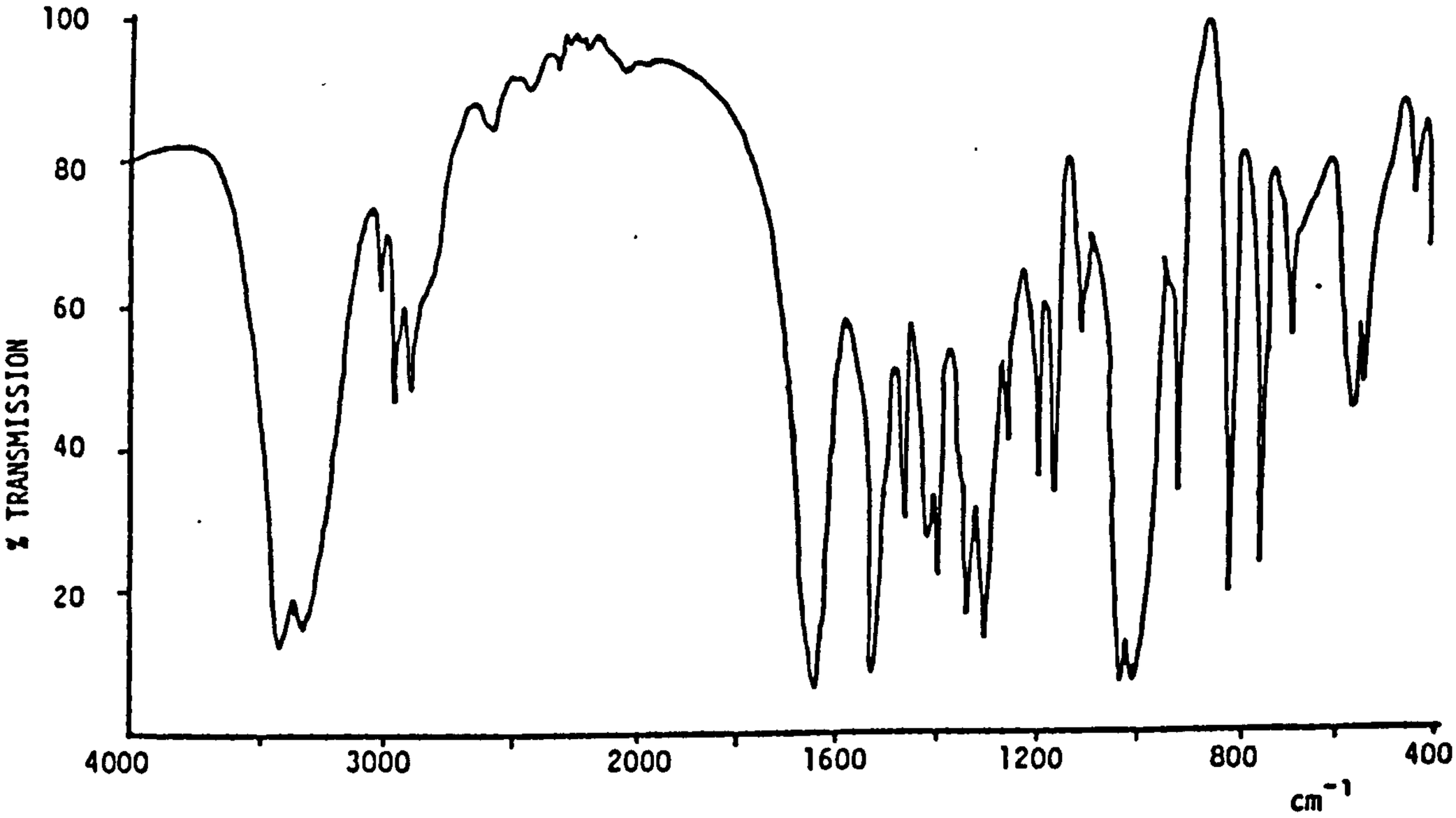


Fig.5. Infra-red spectrum of dimethyloluron (XII).

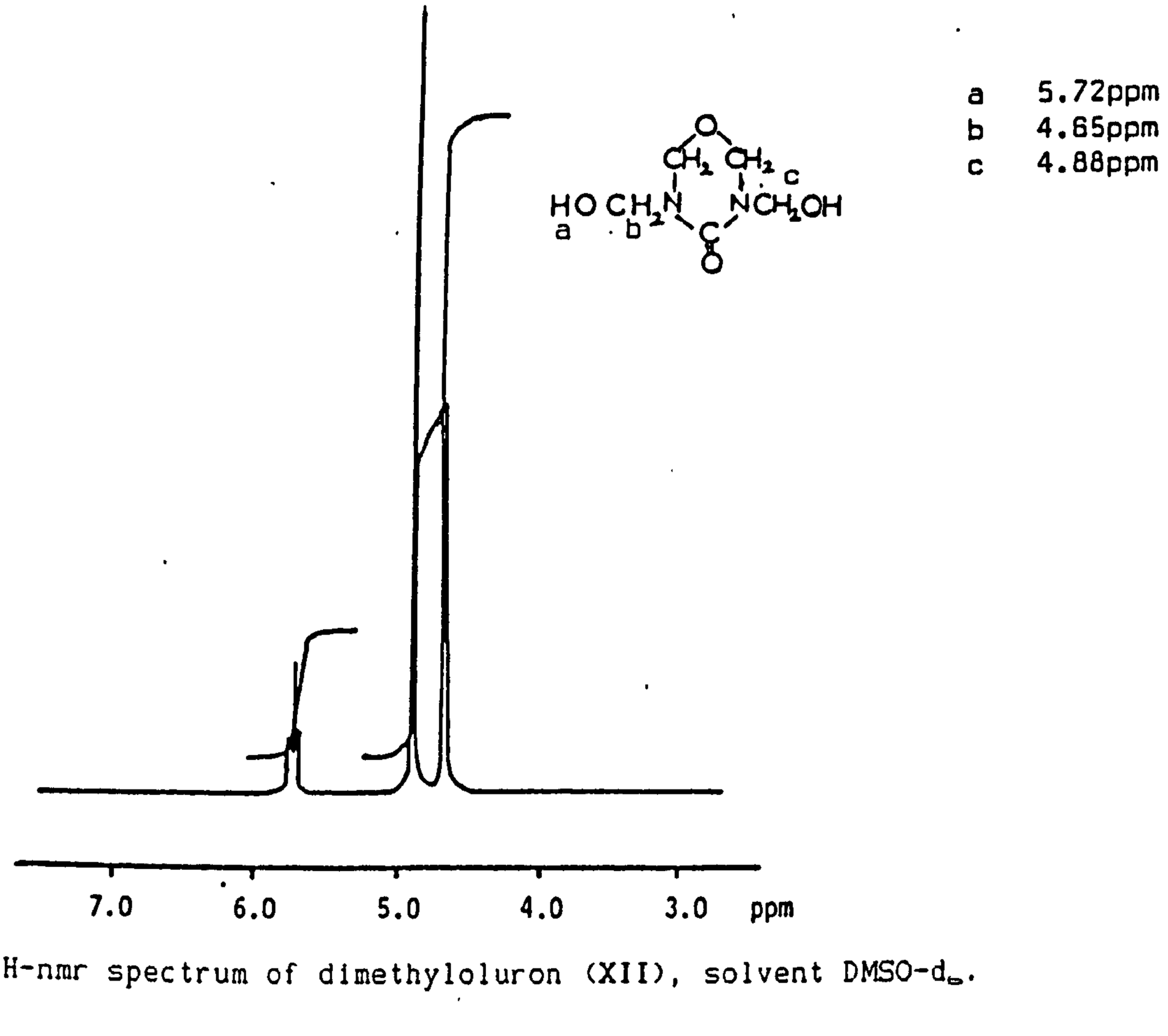


Fig.6. ^{1}H-nmr spectrum of dimethyloluron (XII), solvent DMSO-d_6.

8. URON (X) AND MONOMETHYLOLURON (MMuron; XI)

Pure dimethyloluron (XII; 0.04g, 0.00025mol), urea (0.03g, 0.0005mol) and sodium dihydrogen phosphate (0.005g) were dissolved in water (0.2ml). The solution was heated carefully at 100°C for 5 minutes, cooled and extracted with 3 x 1 ml portions of acetonitrile. The combined acetonitrile extracts were evaporated to dryness at room temperature using a jet of air. The urons were separated efficiently on a 250mm x 4.8mm amine column using 19:1 acetonitrile to water as the eluting solvent. Uron (X) itself was identified by infra-red, ^{1}H-nmr (Figs.7 and 8; P.36) and ^{13}C-nmr spectroscopy; ring C: 75.6 ppm (in $CDCl_3$). Insufficient sample was obtained for a C, H and N analysis. Monomethyloluron (XI) was strongly indicated by its chromatographic behaviour and its infra-red and ^{1}H-nmr spectra (Figs.9 and 10; P.37). Insufficient sample was obtained for a ^{13}C-nmr spectrum or for a C, H and N analysis. Monomethyloluron (XI) has not previously been reported in the literature.

4. RESULTS AND DISCUSSION

Evaluation of Chromatograms.

One of the major problems encountered in the chromatography of urea-formaldehyde compounds on an aminopropyl column was the slow but inevitable change of retention characteristics. For the most part, this rendered absolute retention times unreliable and it was found useful to adopt a procedure of multiple relative retention times. The two compounds used for reference in this study were urea and dimethylolurea (DMU; II) and using this technique, chromatograms were relatively easy to interpret. It is still considered good practice, however, to run

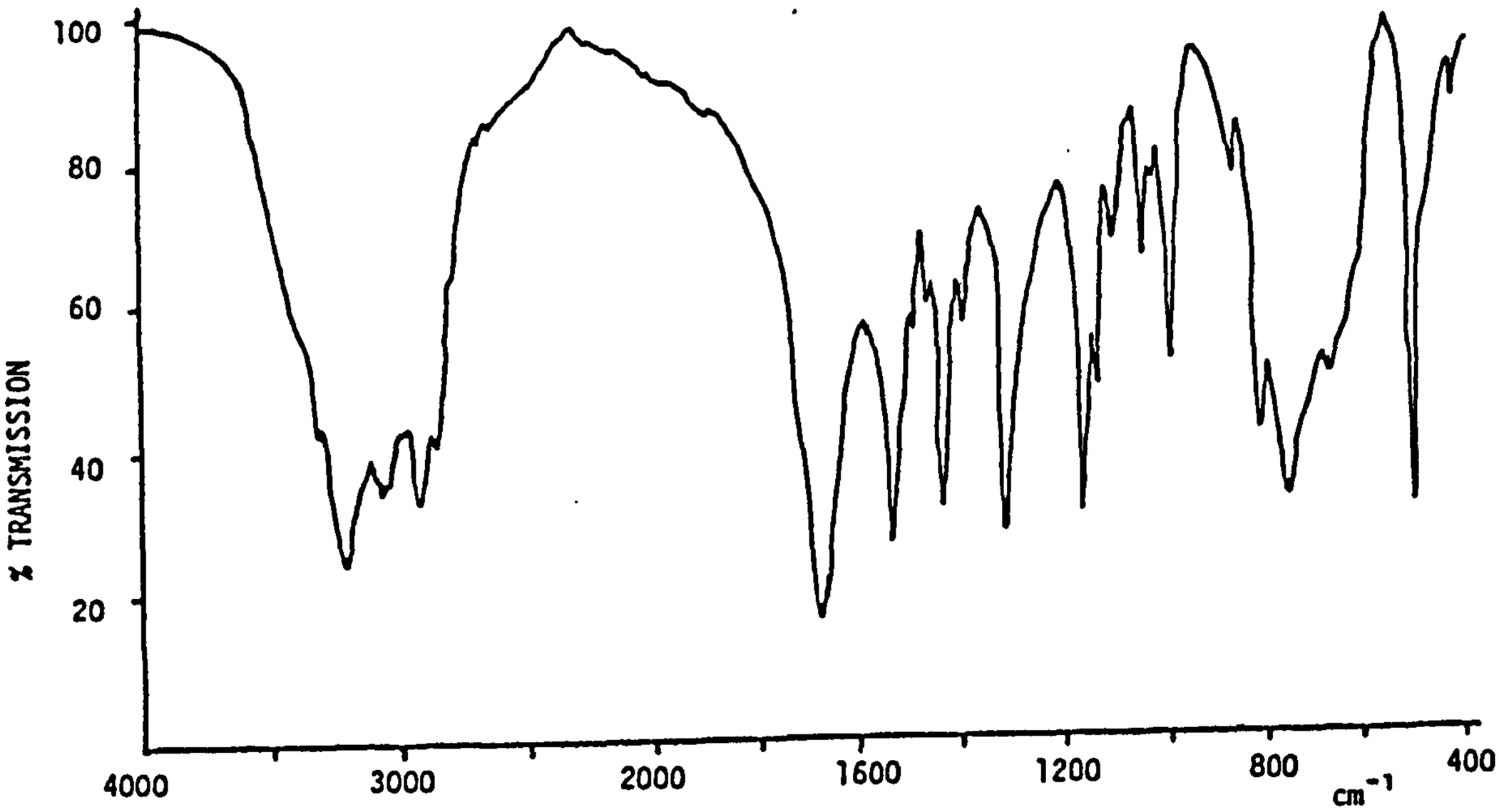


Fig.7. Infra-red spectrum of uron (X).

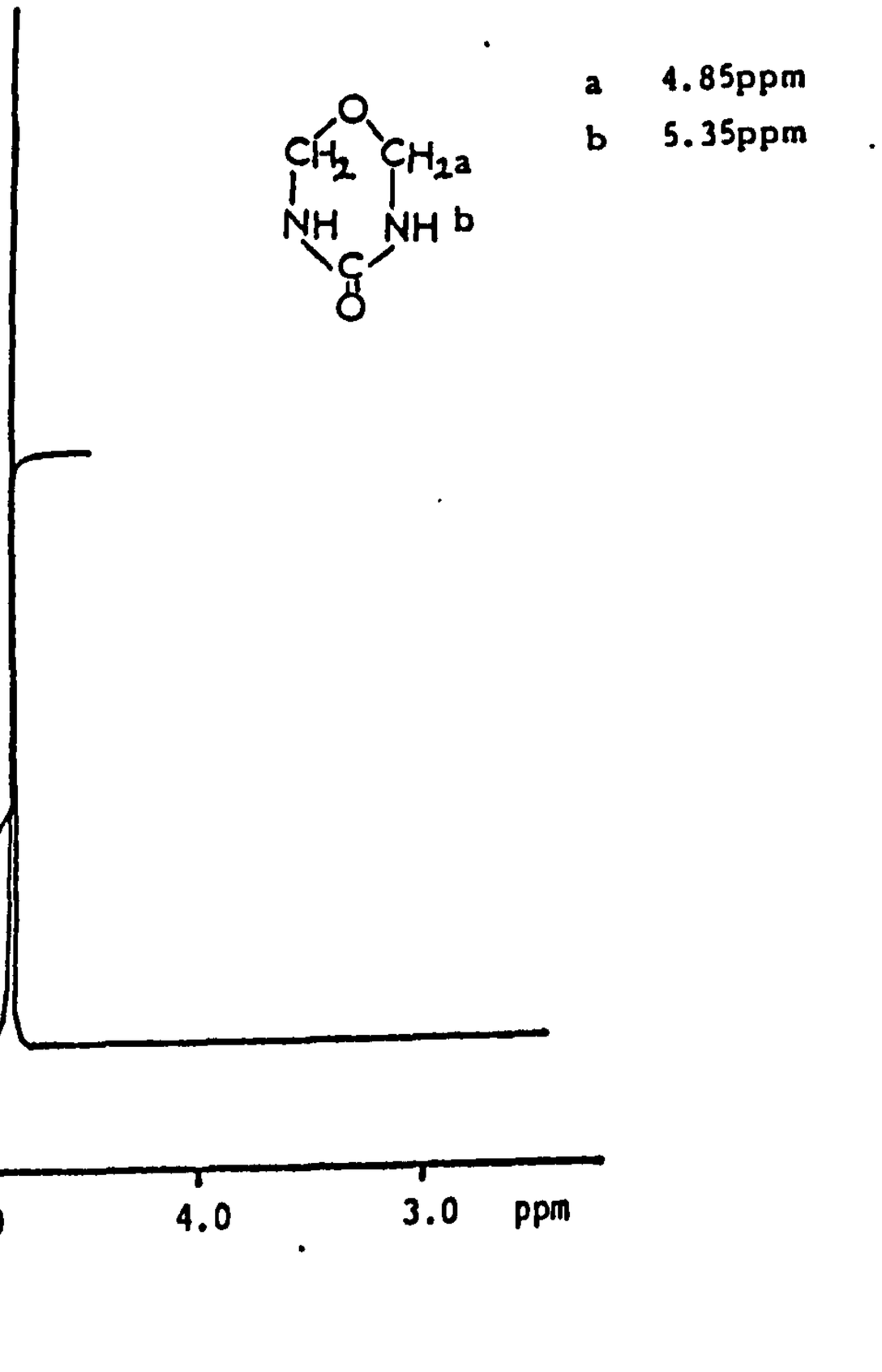


Fig.8. ^{1}H-nmr spectrum of uron (X).

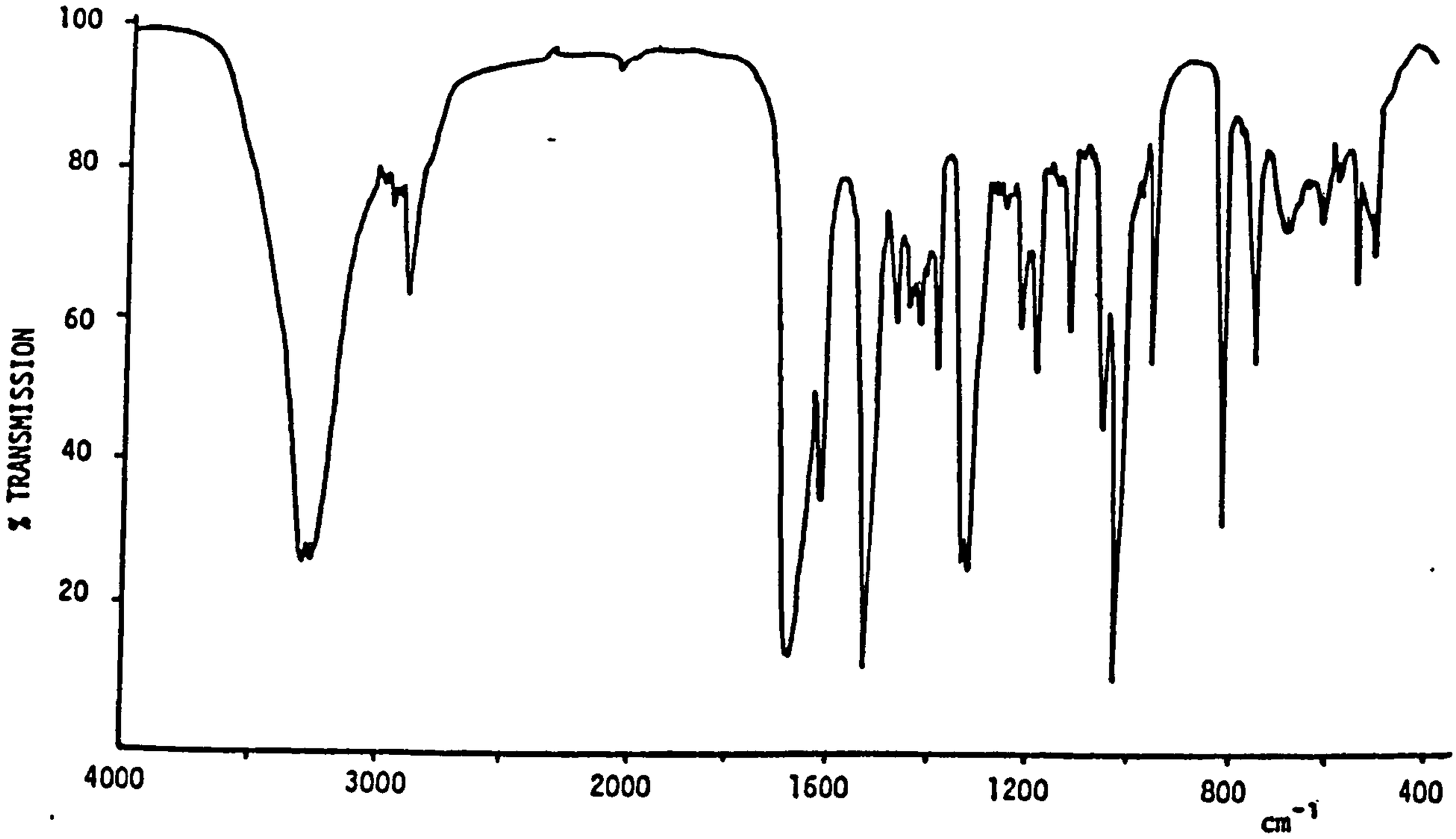


Fig.9. Infra-red spectrum of monomethyluron (XI).

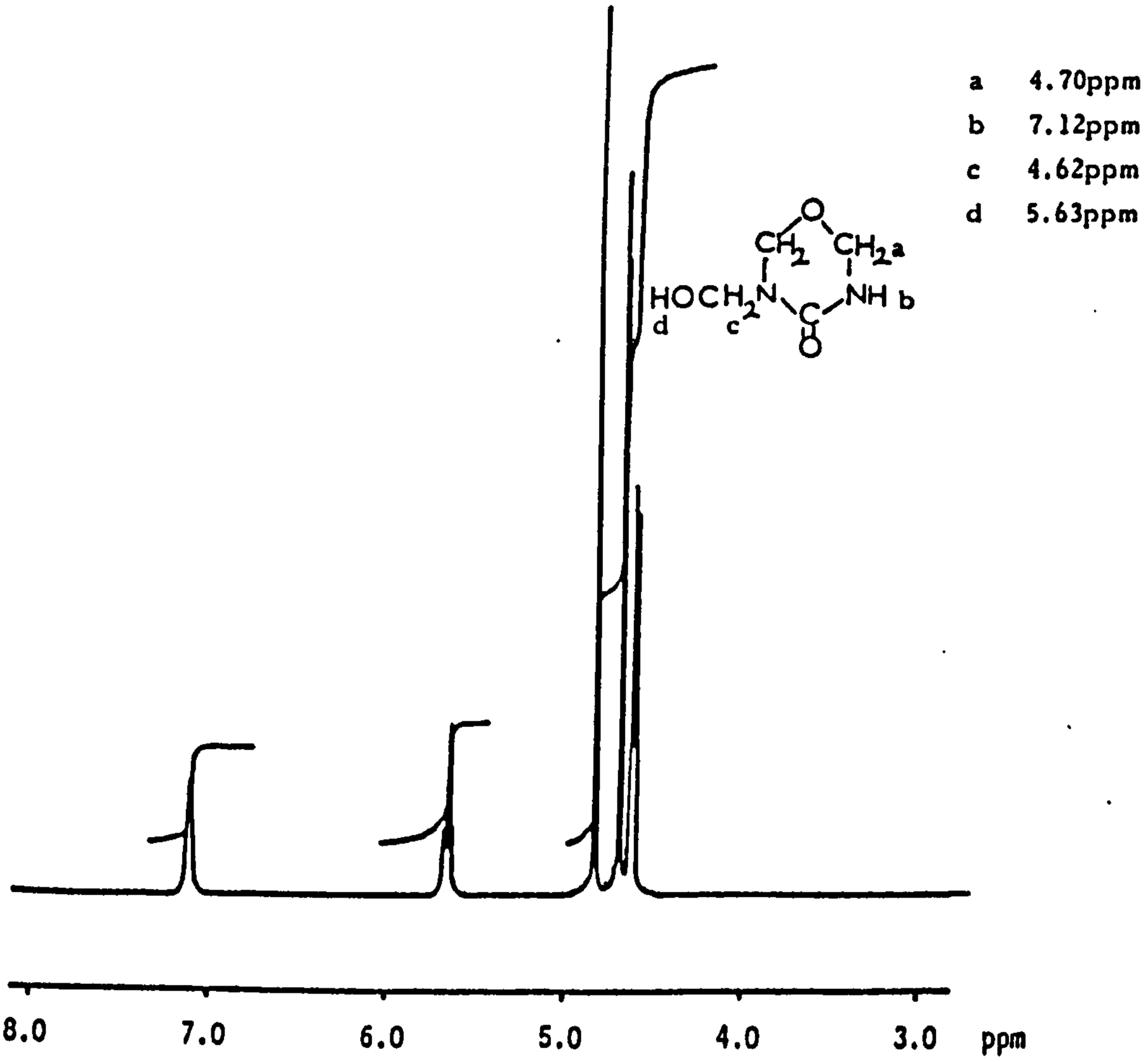


Fig.10. ^{1}H-nmr spectrum of monomethyloluron (XI).

standard solutions at regular intervals so that the state of the column is continually monitored.

The following are examples of solutions which can be used as standards:

1. Urea, MMU (I), DMU (II), MDU (IV) and glycerol (Fig.11; P.39),
2. DMuron (XII), MMuron (XI) and uron (X) (Reaction product 8; P.33),
3. MMMDU (V) and DMMDU (VI) (Reaction product 4; P.31),
4. MMOMDU (VII) and DMOMDU (IX) (Reaction product 5; P.32).

All reference compounds were prepared in eluting solvent and were stable for several months.

Table 2 (P.41) is a list, in increasing retention time, of the peaks observed in the chromatography of the various reference compounds and reaction mixtures. Also given are relative retention times a) to urea for early eluting compounds and b) to DMU (II) for late eluting compounds. The elution times of dimethylformamide (DMF), water, and formaldehyde are included in the Table. Glycerol eluted at a position in the chromatogram where no urea-formaldehyde compounds were observed, and was found to be suitable for use as an internal standard for the estimation of compounds such as urea, MMU (I), DMU (II), MDU (IV) and DMuron (XII) in urea-formaldehyde compositions.

Peak identification.

SIMPLE COMPOUNDS.

The chromatography of simple reference compounds and well characterised urea derivatives (vide supra) resulted in easy and unambiguous identification of about half the peaks encountered in conventional urea-formaldehyde reaction mixtures (Fig.11; P.39).

standard solutions at regular intervals so that the state of the column is continually monitored.

The following are examples of solutions which can be used as standards:

1. Urea, MMU (I), DMU (II), MDU (IV) and glycerol (Fig.11; P.39),
2. DMuron (XII), MMuron (XI) and uron (X) (Reaction product 8; P.33),
3. MMMDU (V) and DMMDU (VI) (Reaction product 4; P.31),
4. MMOMDU (VII) and DMOMDU (IX) (Reaction product 5; P.32).

All reference compounds were prepared in eluting solvent and were stable for several months.

Table 2 (P.41) is a list, in increasing retention time, of the peaks observed in the chromatography of the various reference compounds and reaction mixtures. Also given are relative retention times a) to urea for early eluting compounds and b) to DMU (II) for late eluting compounds. The elution times of dimethylformamide (DMF), water, and formaldehyde are included in the Table. Glycerol eluted at a position in the chromatogram where no urea-formaldehyde compounds were observed, and was found to be suitable for use as an internal standard for the estimation of compounds such as urea, MMU (I), DMU (II), MDU (IV) and DMuron (XII) in urea-formaldehyde compositions.

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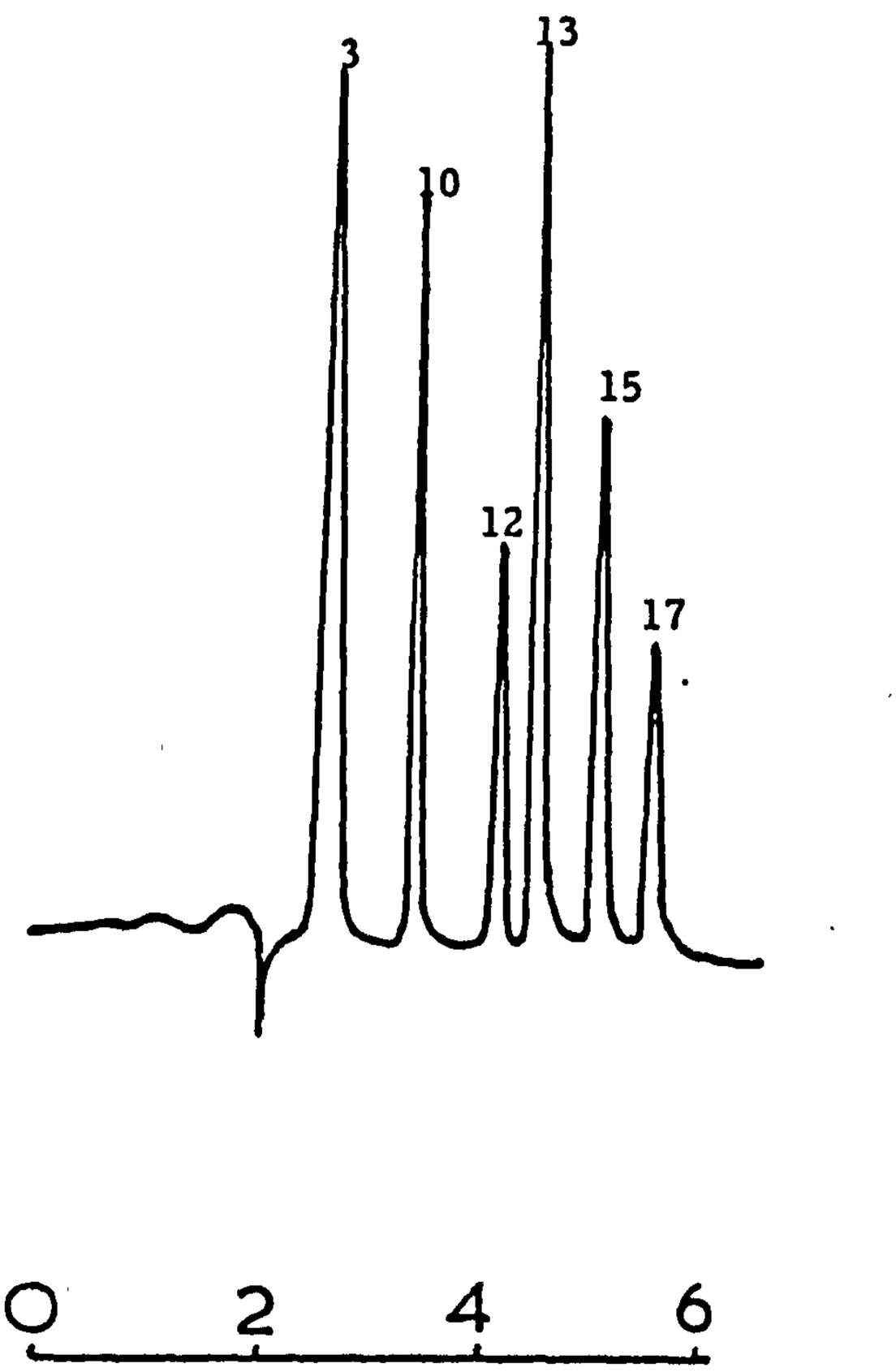


Fig.11. Chromatogram of test mixture; urea MMU (I), DMU (II), MDU (IV) and glycerol. For peak identification see Table 2 (P.41).

METHYLOLUREAS. (Reaction product 1; P.30)

Examination of Reaction Product 1 (P.30) enabled N,N-dimethylolurea (asymDMU; XXII) and trimethylolurea (TMU; III) to be tentatively identified (Fig.12; P.42). The compounds giving the peaks of interest were collected off the column and the solvent removed by careful evaporation at room temperature, using a jet of air. To ensure that the recovery procedure had not significantly affected the purity of the compounds, small amounts of the collected materials were rechromatographed. The infra-red and ^{1}H-nmr spectra, when compared with the literature[34] unambiguously confirmed the nature of the peaks.

It has been shown in a previous study[7] that with urea-formaldehyde compounds there can exist a simple relationship between the log of the retention time (t_r) and the degree of substitution. The concept was once again found to hold true (Fig.13; P.43) and in the case of the methylolureas a plot of k' against the number of methylol groups was a straight line. When log k' of asymDMU (XXII) and TMU (III) were plotted to lie on the same line with urea and MMU (II) then it could be readily seen that a second methylol substituent on a terminal nitrogen atom has only half the effect on the retention time as the first substituent (Fig.13; P.43).

METHYLOLMETHYLENEDIUREAS (Reaction products 2, 3 and 4; P.31)

The reaction between MDU (IV) and formaldehyde is complicated leading to 12 possible mono-, di- and trimethylol MDU's. Many of these derivatives are, however, unlikely and only about 7 peaks were actually observed. It was possible to obtain information on the nature of some of these peaks by reacting MDU (IV) and formaldehyde together at pH values slightly above 7 and with a low MDU (IV):formaldehyde ratio and a short reaction time the predominant product was monomethylolmethylenediurea (MMMDU; V).

	Compound	Code	Ident.*	Retention Time (min) absolute	Retention Time (min) relative to urea	Retention Time (min) relative to DMU
1	Dimethylformamide	-	-	2.16	-	-
2	Formaldehyde	-	-	2.25	-	-
3	Water	-	-	2.52	-	-
4	Dimethylolurea dimethylether	XXV	D	2.41	0.73	-
5	Monomethylourea monomethylether	XXIV	D	2.79	0.84	-
6	Uron	X	D	2.84	0.86	-
7	Monomethyloluron	XI	D	3.03	0.91	-
8	Dimethylourea monomethylether	XXVI	D	3.19	0.96	-
9	Dimethyloluron	XII	D	3.20	0.96	0.58
10	Urea	-	D	3.32	1	0.60
11	?	-	U	3.87	1.17	0.70
12	Monomethylolurea	I	D	4.12	1.24	0.75
13	Glycerol	-	D	4.45	1.34	0.80
14	N,N-dimethylolurea	XXII	D	4.87	1.47	0.88
15	Methylenediurea	IV	D	5.05	-	0.91
16	sec-Monomethylolmethylenediurea	XXVII	T	5.31	-	0.96
17	N,N'-dimethylolurea	II	D	5.33	-	1
18	Oxymethelenediurea	VII	T	5.60	-	1.01
19	Trimethylolurea	III	D	6.53	-	1.18
20	Monomethylolmethylenediurea	V	D	6.75	-	1.22
21	sec-dimethylolmethylenediurea	XXVIII or XXIX	T	7.35	-	1.33
22	Monomethyloloxymethelenediurea	VIII	P	7.7	-	1.39
23	?	-	U	8.6	-	1.57
24	Dimethylenetriurea	XVII	D	9.2	-	1.66
25	Dimethylolmethylenediurea	VI	P	9.85	-	1.78
26	Dimethyloloxymethylenediurea	IX	P	10.5	-	1.90
27	Trimethylolmethylenediureas	XXXI	T	11.2	-	2.03
28	Trimethylolmethylenediureas	XXXII	T	12.2	-	2.21

* Identification: D=definite, P=probable, T=tentative, U=unknown

Table 2. Peaks observed in urea-formaldehyde reaction products in order of increasing elution time.

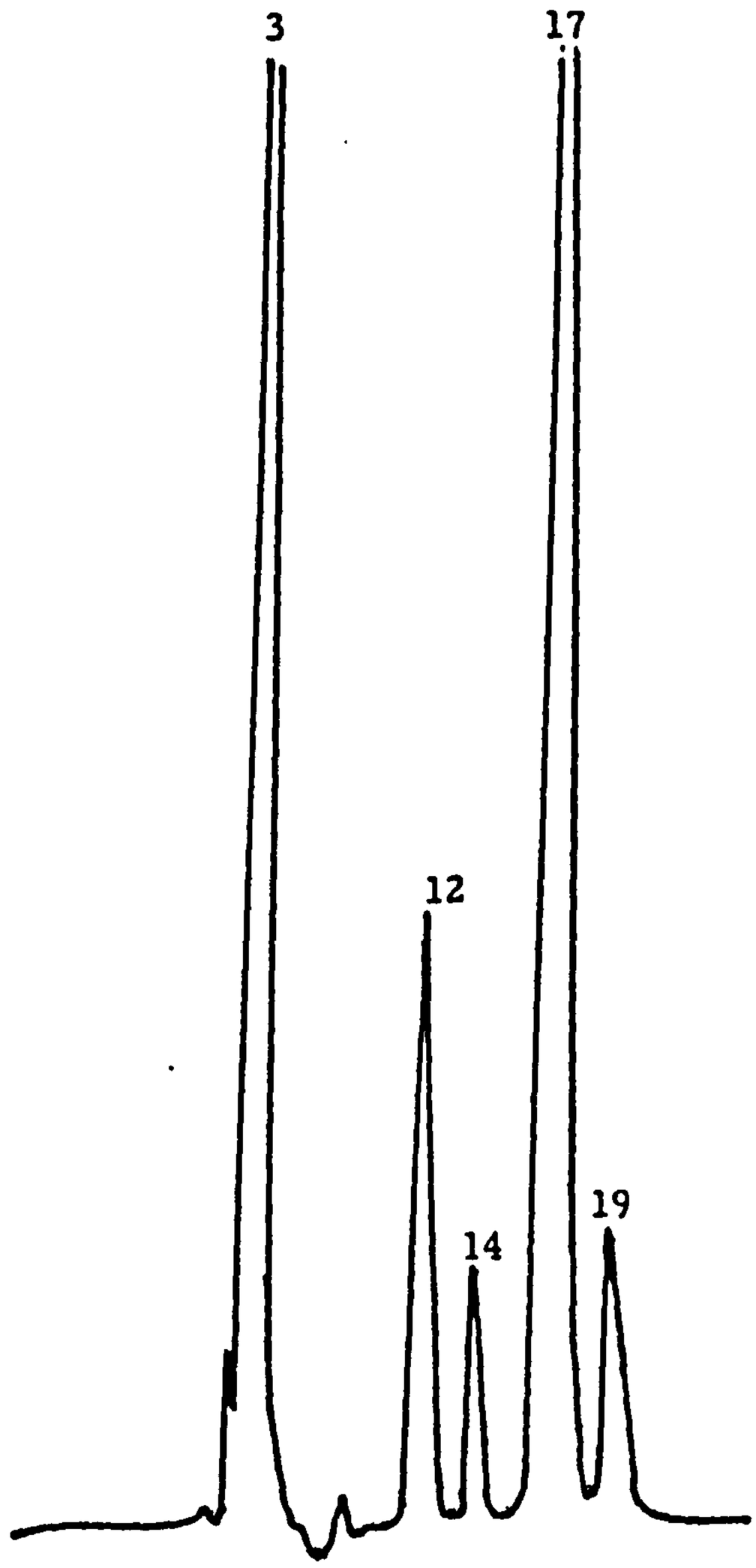


Fig. 12. Chromatogram of reaction product 1 showing asymDMU (XXII) and TMU (III). For peak identification see Table 2 (P.41).

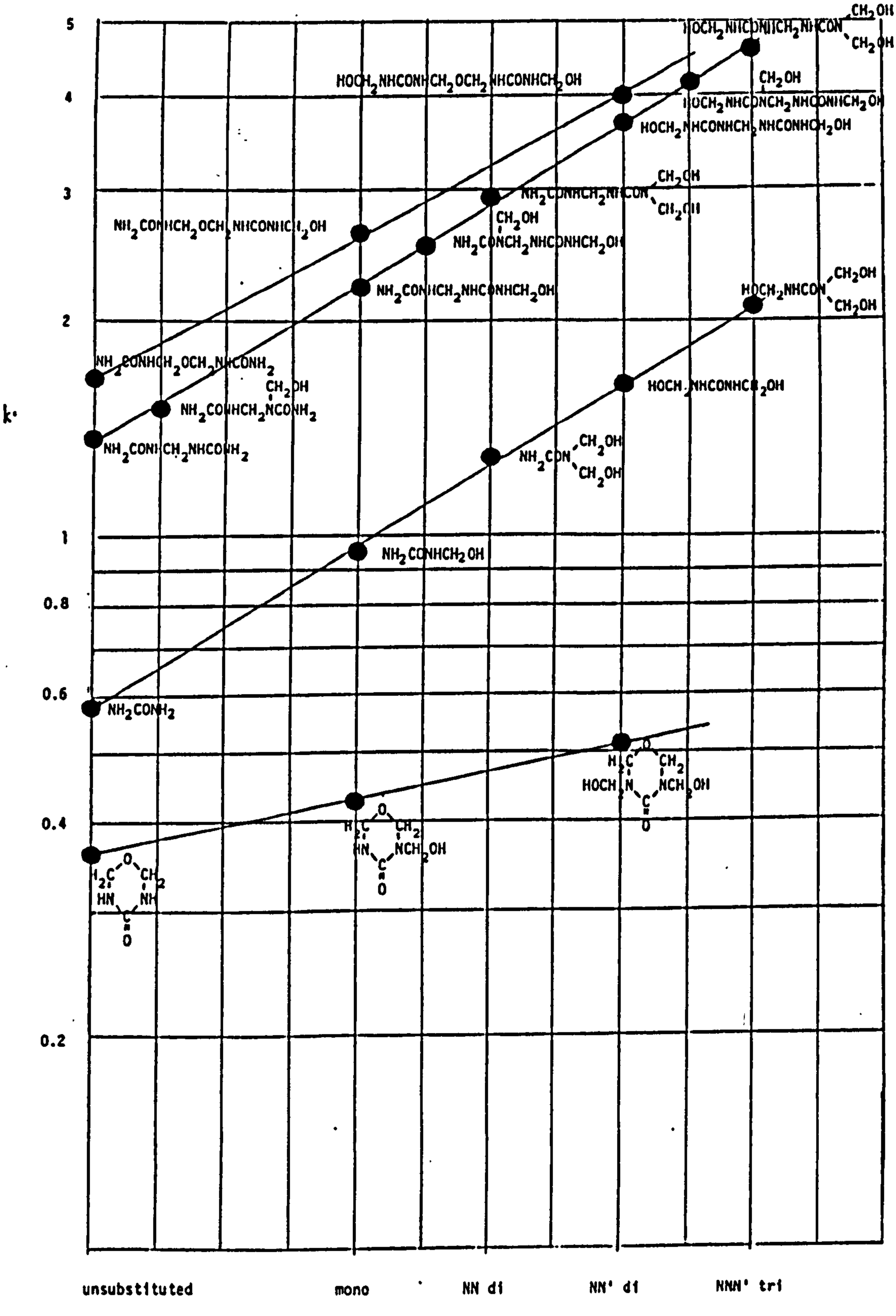


Fig.13. Effects of degree of substitution on retention times. k' is the capacity factor and equals $(t_r - t_o)/t_o$ where t_r is the retention time of the solute and t_o is the retention time of an unretained solute.

As the amount of formaldehyde and the reaction times are increased, di- and then trimethylol substitution is favoured. A typical chromotogram is shown in Fig.14 (P.45).

As with the urea series, MDU (IV) and its mono- and dimethylol derivatives (V and VI) follow the simple relationship between log k' and the degree of substitution. It can be seen (Fig.14; P.46) that two unidentified peaks (21 and 23) occur between MMMDU (V) and the symmetrical DMMDU (VI). Using the behaviour of the dimethylolureas (II and XXII) as a guide it seems likely that a second methylol substituent on the terminal nitrogen atom of MMMDU (V) will have only half the effect of the first on the retention time.

$$H_2NCONHCH_2NCONHCH_2OH + HCHO \longrightarrow H_2NCONHCH_2NCON(CH_2OH)CH_2OH$$

IV XXX

Plotting log k' of these two peaks on the MDU (IV) derivative line shows indeed that one of them behaves in accordance with a DMMDU structure having two methylol groups on a terminal nitrogen atom (XXX). Considering the position of the second peak which should correspond to one of the terminal nitrogen atom - chain nitrogen atom disubstituted structures,

$H_2NCONHCH_2N(CH_2OH)CONHCH_2OH$ (XXVIII) or $H_2NCON(CH_2OH)CH_2NHCONHCH_2OH$ (XXIX)

it would seem that a methylol substituent on a chain nitrogen atom will have half the effect of a second substituent on the terminal nitrogen

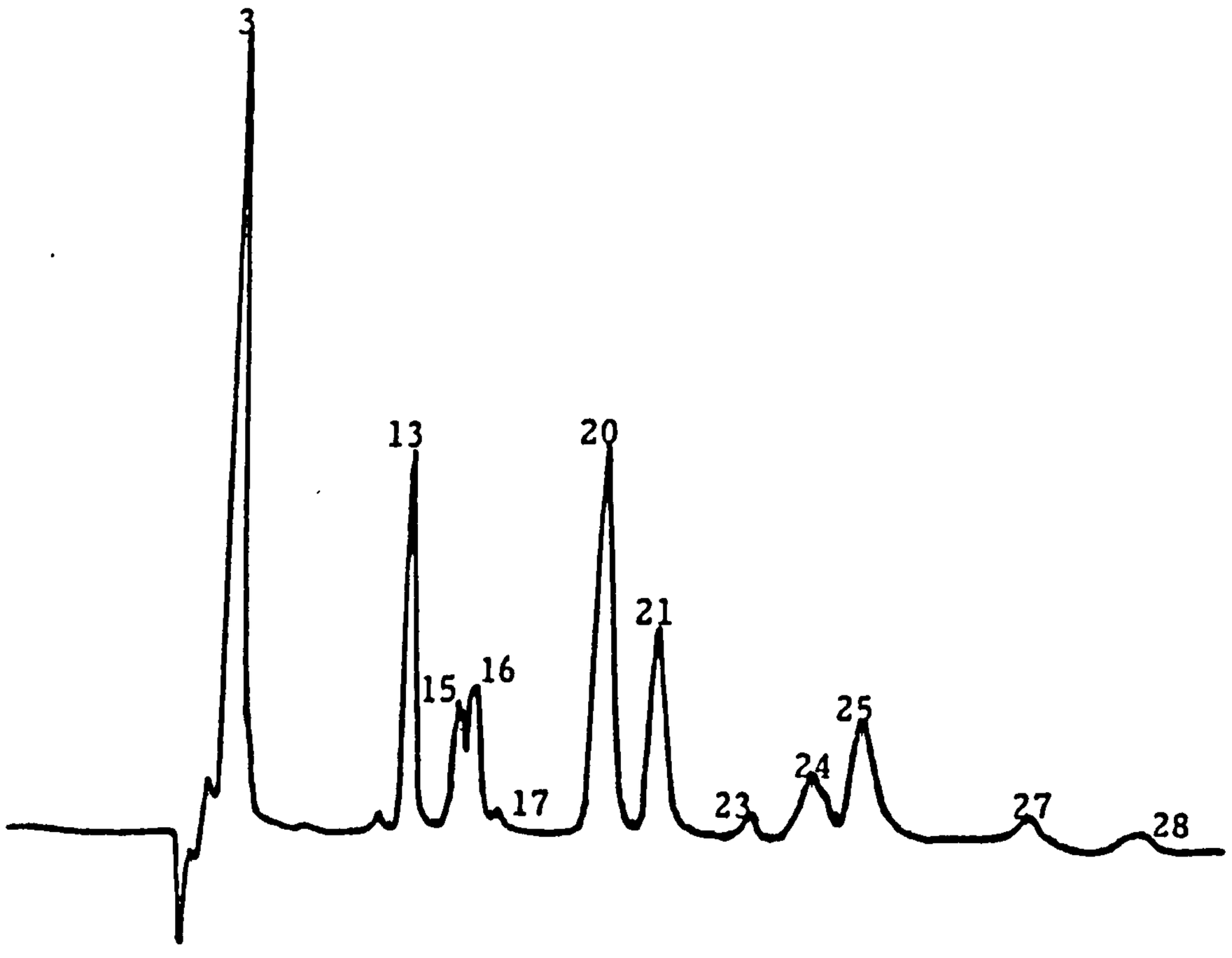


Fig.14. Chromatogram of MDU (IV) and formaldehyde reacted at pH for 8 h at 21°C. For peak identification see Table 2 (P.41).

atom and only one quarter the effect of the first substituent on a terminal nitrogen atom (see Fig.13; P.43). Two peaks occur at longer retention times which again appear to follow the structure/retention time relationship described above. In this way these compounds have been tentatively identified as having the two most probable trimethylol MDU structures (XXXI and XXXII), (see Table 2; P.41)

METHYLOLOXYMETHYLENEDIUREAS (Reaction product 5; P.32)

The insoluble material from reaction mixture 6 showed one major peak which was attributed to DMOMDU (IX)[35]. The chromatogram of the supernatant liquor showed another large peak at shorter retention time which was thought likely to be the mono- compound, MMOMDU (VIII), considering that it would be more soluble in water than the dimethylol compound. When log k' for these compounds was plotted against the substitution pattern, a line having virtually the same gradient as that of the urea and MDU derivatives was obtained and furthermore, there was a small peak to be seen at the elution time corresponding to zero substitution, which could tentatively be assigned to the parent compound, oxymethylenediurea (VII). Kumlin and Simonson[6] identified MMOMDU (VIII) and DMOMDU (IX) in the reaction mixture described by Zigeuner[35] and characterised them conclusively by spectroscopic means.

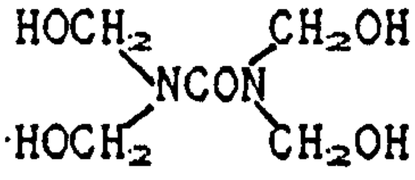
DIMETHYLENETRIUREA (Reaction product 6; P.32)

One major peak was observed in the chromatogram and as urea and formaldehyde under acid conditions form MDU (IV) in high yield, it could safely be assumed that this peak was due to DMTU (XIX)

URONS (Reaction products 7 and 8; P.33)

Chromatography of pure DMuron (XII) from reaction mixture 7 and uron (X) and MMuron (XI) from reaction mixture 8 identified the simple urons. A plot of log k' for these compounds against the substitution pattern again gave a straight line as for the other three series of compounds previously discussed.

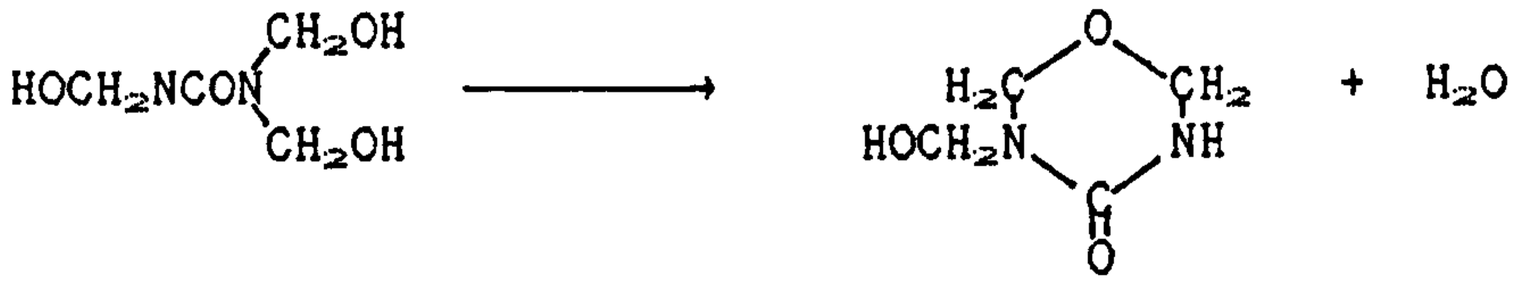
Thus 21 compounds formed in simple urea-formaldehyde reactions have been identified, the nature of only 2 or 3 small peaks being as yet unknown[51]. This study confirms the observations of Kottes Andrews[14] and Kumlin and Simonson[34] that there is no evidence for the occurrence of tetramethylolurea (XXXIII) among the reaction products.



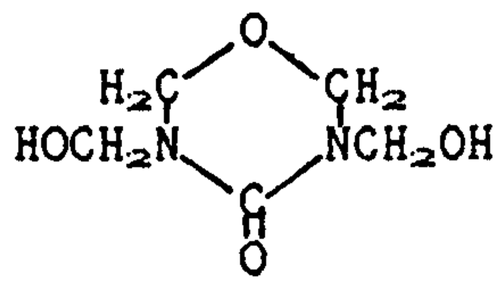
XXXIII

Considering the formation of uron structures in urea-formaldehyde reactions, the implications are that either trimethylolurea (III) is converted to MMuron (XI) (scheme I), which in the formaldehyde rich reaction mixture then rapidly forms DMuron (XII) or alternatively the DMuron (XII) precursor is tetramethylolurea (XXXIV) which is too unstable to be chromatographed. (scheme II).

scheme I

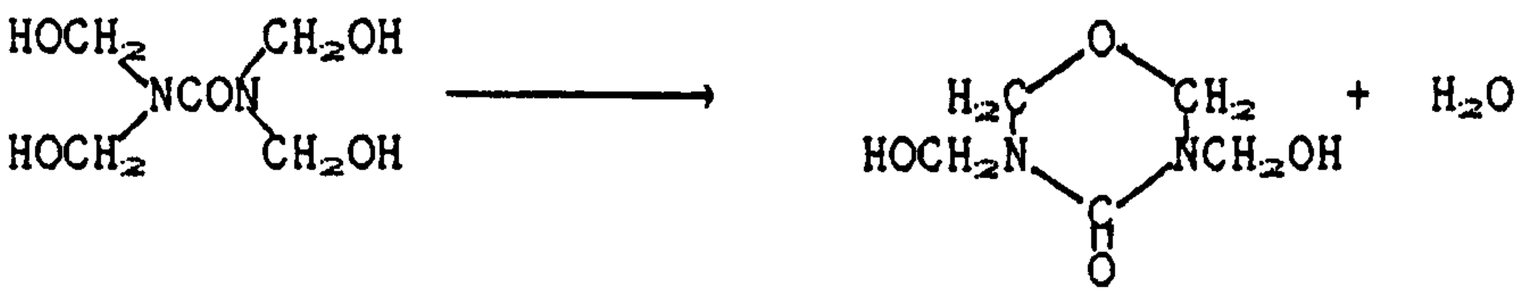


III XI



XII

scheme II



XXXIII XII

This technique has been used successfully for a year at Borden (U.K.) Limited to characterise urea- formaldehyde reaction products (Fig.15; P.49) and to estimate the more important compounds such as urea, MMU (I) and DMU (II). It has proved to be a very powerful method for investigating the significance of various manufacturing parameters and will contribute in the future to a deeper understanding of urea-formaldehyde chemistry.

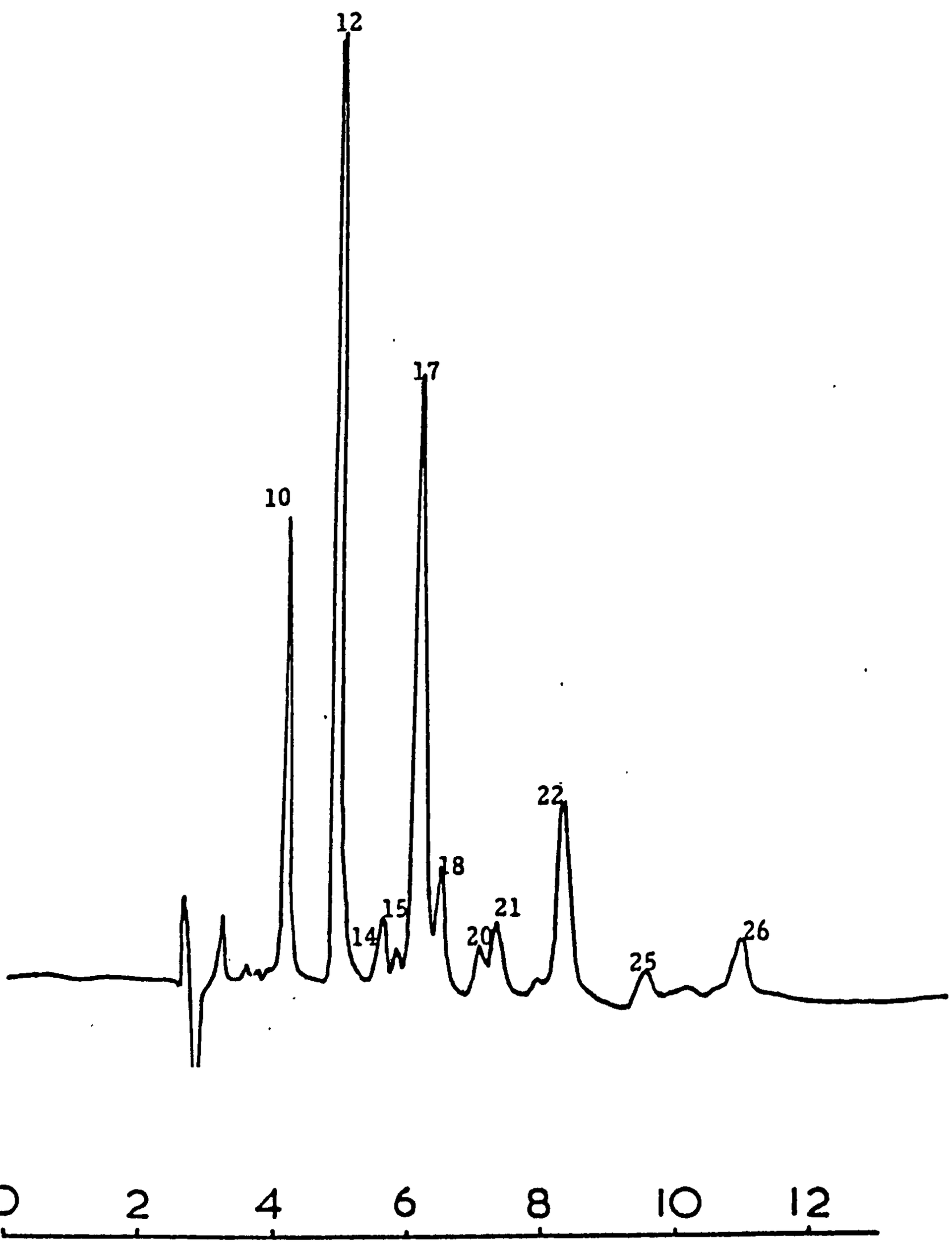


Fig.15. Chromatogram of urea-formaldehyde reaction product (U:F 1:1.4) reacted at 70°C for 2 h at pH 9. For peak identification see Table 2 (P.41).

III. APPLICATIONS OF CHROMATOGRAPHIC METHODS TO THE CHEMISTRY OF UREA-FORMALDEHYDE RESINS

A. Scope of the Investigation

The liquid chromatographic techniques which have been described in Part II of this thesis enabled the early stages of the reaction between urea and formaldehyde to be studied in detail. It seemed likely that if the course of the reaction between urea and formaldehyde under a particular set of reaction conditions was established as far as the formation of the small molecules was concerned, then many useful assumptions about subsequent reaction pathways could be postulated. For example if a set of reaction conditions initially produced methylene linked urea compounds to the virtual exclusion of ether containing compounds then the combination of the small molecules to form large molecules would be likely to proceed through methylene groups.

The first stages in the reaction of urea and formaldehyde under both alkaline and acidic conditions, lead to the formation of firstly mono- and secondly dimethylolurea (MMU; I and DMU; II). These compounds have been prepared by several workers[7,38,39] and have been studied in detail by De Jong and De Jonge[1,40,41] who determined the reaction rates, order of reaction and activation energy for the formation and hydrolysis of these simple products. The reactions were shown to be reversible and the composition of the equilibrium mixture to be independent of pH. De Jong and De Jonge have also studied the formation of trimethylolurea (TMU; III)[42] and Kumlin and Simonson[34] have isolated the trimethylol compound (TMU; III) and N,N-dimethylolurea (asymDMU; XXII) by liquid

chromatography and subsequently obtained ^{1}H-nmr spectra of both compounds.

The condensation of methylolureas and urea in acid solution to form methylene linkages has been studied by De Jong and De Jonge[43,44]. As with the formation of methylol compounds the reaction proved to be reversible and values for rate constants and activation energies were obtained. The same authors have also made efforts to investigate the initial reactions which lead to the formation of larger molecules[45,46].

Very few authors have attempted to investigate the formation of ether groups although Zigeuner and co-workers[36,47] reacted alkaline condensates of urea and formaldehyde with 2,4-dimethylolphenol and interpreted the results as an indication of the occurrence of linear ether structures. In more recent times, linear ethers have been detected by ^{13}C-nmr spectroscopy[48].

Cyclic ethers (urons) were first synthesised by Kadowaki[39] using strongly alkaline conditions and Beacham *et al.*[49] using very acid conditions. It was realised that when excessive amounts of formaldehyde were present then under conditions of extreme pH values, cyclic structures could be produced in commercial resins.

Classical analytical methods have been used for many years in an attempt to obtain an insight into the structure of urea-formaldehyde compositions. The total formaldehyde content of a resin can be determined relatively easily by hydrolysis with 50% aqueous phosphoric acid, distillation and estimation by forming the cyanohydrin compound

with potassium cyanide[50]. Formaldehyde present as methylol groups and linear ether groups can be routinely estimated by an iodine titration method developed by De Jong and De Jonge[40] but no classical method is available for obtaining information on the level of linear or cyclic ether groups in a urea-formaldehyde composition.

By far the most important advance in the detection and determination of structural units in urea-formaldehyde compositions has been made through nmr spectroscopy. ^{1}H-nmr has been of interest but ^{13}C studies have been much more useful in providing information on the bulk structures of urea-formaldehyde reaction products. Many studies have been made but probably the most comprehensive is the one by Slonin *et al.*[50].

The various parameters which can be altered during the condensation of urea and formaldehyde are as follows.

1) Relative molar ratio of formaldehyde to urea. The range of formaldehyde to urea currently in use for preparing urea-formaldehyde resins is from 1:1 to about 1:8.

2) The pH of the reaction. Generally this falls into four zones:-

   i. very acid

   ii. slightly acid

   iii. slightly-alkaline

   iv. very alkaline

In industry, resins are currently commercially made using all of these different pH conditions sometimes in isolation but more often two or more in sequence. There are several consequences of reacting at high or low pH values notably the formation of ammonia and carbon dioxide from urea and the disproportionation of

formaldehyde to form ethanol and formic acid at high pH values (the Cannizzaro reaction). Cyclic structures (urons and possibly triazinones) can be formed under conditions of extreme pH. Cyclic ether structures are thought to contain reacted formaldehyde in a non-hydrolysable form and thus the level of uron in a resin may be very significant when the formaldehyde liberating potential of a resin is considered.

3) Temperature and time of reaction. Obviously under one specific set of reaction conditions, low temperature and short reaction time could lead to quite different products when compared with more vigorous conditions.

4) The nature of the formaldehyde used. Formaldehyde may be stored as a strong aqueous solution stabilised against the production of paraformaldehyde by a relatively small amount of urea and when used in this form in place of normal formaldehyde the reactivity and to some extent the nature of the products are different. In addition urons and possibly triazinones may be formed on storage

Urea-formaldehyde resins are manufactured and sold for many different applications and as far as possible the properties of the resins are tailored to suit the requirements for each specific use. Properties which are important to the resin user are listed below.

1) Amount of formaldehyde evolved:

   a) during mixing with catalyst

   b) on curing with acid catalysts

   c) on curing by heating

   d) on time ageing after cure.

2) Water resistance of the crosslinked resin. Obviously structures

made with urea-formaldehyde resins which have to tolerate damp conditions or conditions of high humidity must be relatively stable to hydrolysis.

3) Tack. There are applications where urea-formaldehyde resins are used in which tack is of considerable importance eg chipboard manufacture. Resins prepared by different techniques and containing different structures behave differently in this respect.

4) Storage life. This is normally quite short, often only one month and structural changes affect this resin property quite markedly.

5) Stability of foamed resin. This is an important factor for firelighter resins and insulating materials.

6) Stability of the resin suspension in water.

7) Biogradability.

Properties 6) and 7) are important for materials used as nitrogen fertilizers.

8) The degree of ionic nature in a resin. This is important for resins which are used as "wet strength" resins for paper coating and these resins are often amine modified.

As discussed in the introduction, the new chromatographic techniques now available have been able to give an insight into the nature of urea-formaldehyde resins which before this time had not been possible.

B. The Initial Reactions of Urea and Formaldehyde in the pH Range 5.5 to 8.3 and Molar Ratio Range 1:1.5 to 1:2.5

1. INTRODUCTION

The majority of urea-formaldehyde resins are manufactured commercially using a urea to formaldehyde molar ratio between 1:1.5 and 1:2.5 and this process involves two stages. The first stage is an initial reaction at neutral or slightly alkaline pH which is believed to be a moderately fast, moderately exothermic addition of urea and formaldehyde leading to methylol compounds. It is generally accepted that it is not practical to carry out the initial addition reaction at pH values lower than 7 because then the reaction is so exothermic that it cannot easily be controlled and thus the normal pH limits for this first addition stage are 7 to 8.3. The second stage is a reaction which is believed to involve the condensation of the methylolureas to form methylene and possibly oxy-dimethylene linked polyureas and is carried out at a slightly acid pH range normally of 6.5 to 5.5. Manufacture is often terminated with the addition of a second charge of urea, which is primarily added to reduce the level of free formaldehyde and it is likely that methylolureas are formed almost instantaneously.

2. EXPERIMENTAL

The general procedure adopted was that described in II B3 (P.28).

Standardisation

Using solutions of urea, MMU (I), DMU (II) and DMuron (XII) from 1-10mg in 10ml of the chromatographic mobile phase and injecting 100µl by means of a fixed sample loop onto the amino column, a series of calibration

curves were produced (Fig.16; P.57) of peak areas against weight of standard. The solvent flow rate through the chromatographic column was set at 2ml min^{-1}, the attenuation of the refractive index detector was set at 16x and the attenuation of the Hitachi D2000 integrator was set at 6x.

Urea-formaldehyde Reaction

50% aqueous formaldehyde solution having a methanol content of <1%, (20g) was cooled to <30°C and adjusted to pH 7 with 5M sodium hydroxide solution. Disodium hydrogen phosphate (0.1g) was added and when in solution was followed by the calculated amount of urea. When homogeneous, the solution was adjusted to the pH of the experiment by the addition of 5M sodium hydroxide solution or 1.7M phosphoric acid solution using a pH meter and heated in a briskly boiling water bath. Samples (approximately 0.5g) were withdrawn at 60°C, at 95°C and then at ten minute intervals over a one hour period unless gelation occurred. Samples were stored at -5°C until analysed.

Preparation for Analysis.

As was discussed earlier (P.28), the characteristics of the amino column changed in a fashion which was apparently associated with the use to which it had been subjected. For this reason, when analysing complex samples of unknown composition, it was imperative that the position of certain key peaks was accurately known. To this end, solutions of these key compounds were chromatographed before each working day and were run until consistent values for the retention times were obtained.

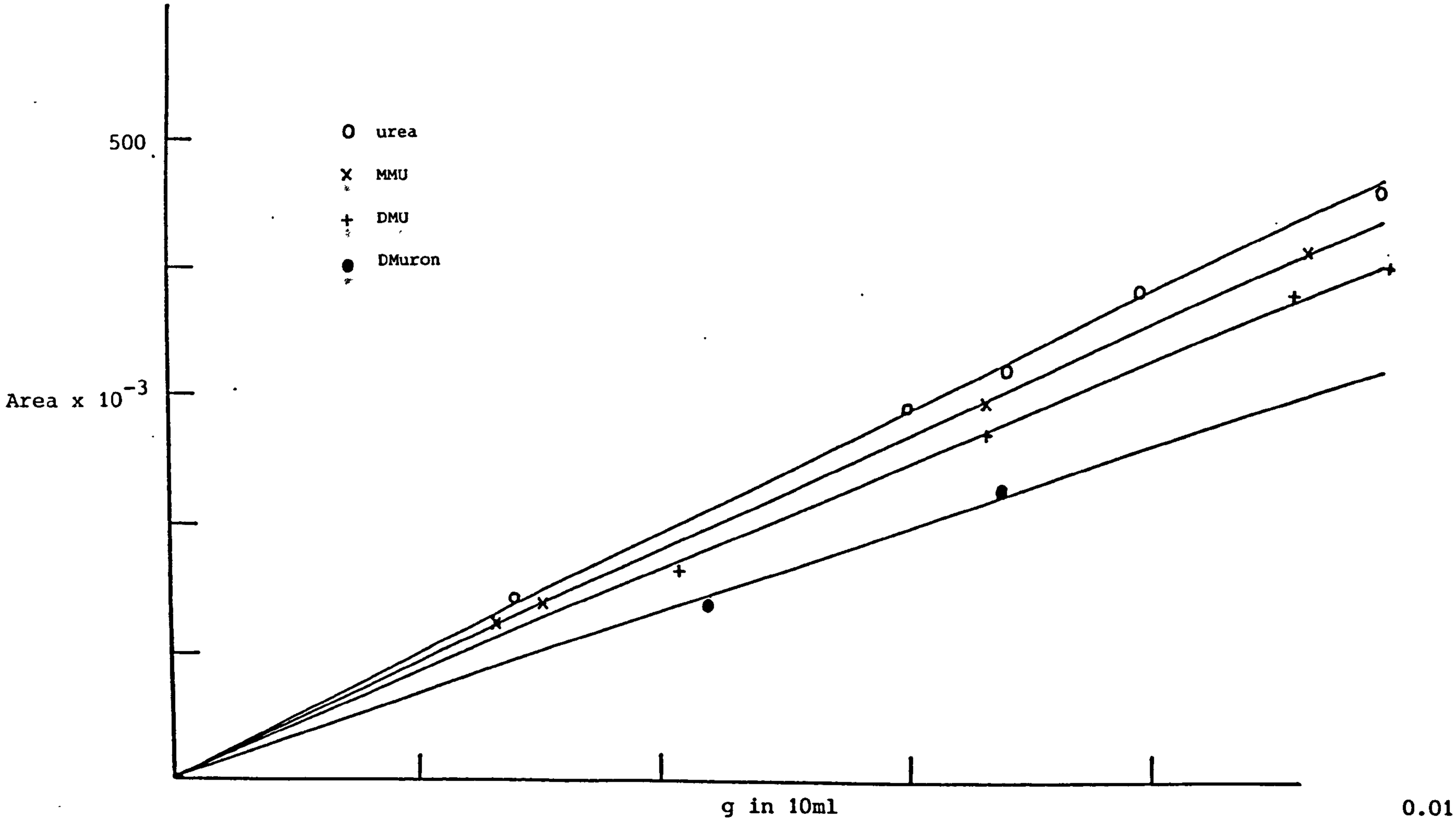


Fig.16. Calibration curves for urea, MMU (I), DMU (II) and DMuron (XII).

Depending on the samples being analysed one or more of the following solutions were used.

i. Urea, MMU (I), DMU (II)

ii. Methylolated MDU containing MDU (IV), MMMDU (V) and DMMDU (VI)

iii. Methylolated OMDU containing MMOMDU (VIII) and DMOMDU (IX)

iv. DMuron (XII), MMuron (XI), uron (X)

When the retention times had fallen to values which were approximately 60% or 70% of the original, the column was repacked and at frequent intervals standard solutions of urea, MMU (I) DMU (II) and DMuron (XII) were run to ensure that the calibration curves remained valid.

Sample Preparation.

The samples (approximately 50mg) were accurately weighed into 10ml vials. Water (0.5ml) was added and the resin dispersed/dissolved by stirring with a glass rod. Acetonitrile (9ml) was then added with vigorous stirring, the vial was closed, shaken vigorously and allowed to stand. If clear, the supernatant liquid was used directly but if turbid, it was filtered through a 0.5µm filter. The solution (100µl) was injected onto the column via a 100µl sample loop and peak areas were automatically recorded.

3. DISCUSSION AND RESULTS

When this study was conceived, it was intended to examine the full range of molar ratios and pH values if significant differences in the reaction patterns were observed at the high and low values of molar ratios and pH. With pH variation this was necessary but the reactions at high and low molar ratio values were similar and the consequences of reacting mixtures at intermediate values were quite predictable.

Consequently urea-formaldehyde reaction products with molar ratio values lying between 1:1.5 and 1:2.5 were not examined.

Six reactions were carried out under the following conditions.

Molar ratio 1:1.5 at pH values 5.5, 6.6 and 8.3

Molar ratio 1:2.5 at pH values 5.5, 6.6 and 8.3

Table 2 (P.41) shows that the chromatographic pairs of peaks due to N,N-dimethylolurea (asymDMU; XXII) and methylenediurea (MDU; IV), due to trimethylolurea and monomethylolmethylenediurea (TMU; III) and MMMDU; V), and due to urea and dimethyloluron (DM uron; XII) can, if the column is beginning to deteriorate, be poorly separated, whereas the other peaks , for the most part are still well resolved. By chance this uncertainty is either not of great importance or the nature of the peak can be deduced by other means. The first pair of compounds is present in urea-formaldehyde compositions at a relatively low level and circumstances which lead to the formation of significant levels of asymDMU (XXII) (during the addition stage where pH >6.6 and the molar ratio of urea:formaldehyde is <1:2) would not be expected to lead to the formation of MDU (IV), which is formed in acid solution where the molar ratio of urea:formaldehyde is ideally 2:1.

With the second pair of compounds TMU (III) and MMMDU (V), the shape of the peak (broad and tailing for TMU (III) (Fig.12; P.42)), the molar ratio and the state of the condensation can indicate the contribution each compound is making to the chromatographic peak.

Similarly with the third pair of compounds, urea and DMuron (XII), urons are likely only to be formed in reaction mixtures a) rich in formaldehyde

and b) after the initial addition reaction is complete (see below). These conditions are quite contrary to those favouring the presence of free urea.

Examination of the chromatograms shows that the study of the reaction between urea and formaldehyde can conveniently be considered in two distinct stages; firstly an addition reaction and secondly a condensation reaction

The Addition Reaction

Over the whole of both the pH range and the molar ratio range studied, the addition reaction followed the same course.

i. The formation of MMU (I) from urea and one molecule of formaldehyde.

ii. The formation of DMU (II) and asymDMU (XXII), from MMU (I) and one molecule of formaldehyde.

iii. The formation of TMU (III) from DMU (II) and asymDMU (XXII) and one molecule of formaldehyde.

The results are summarised in Table 3 (P.61).

The Condensation Reaction

The most important and most easily understood stage in the condensation process appeared to be the formation of methylolmethylenediureas and methyloloxymethylenediureas. The four compounds which were formed to the greatest extent were the monomethyol compounds MMMDU (V) and MMOMDU (VIII) where the methylol substitution is at a primary nitrogen and the disubstituted compounds DMMDU (VI) and DMOMDU (IX) which likewise have primary substitution.

Identity	Relative Retention Time(to DMU)	Molar Ratio 1:1.5									Molar Ratio 1:2.5												
		% @ 60°C			% @ 100°C			% after 20m @ 100°C			% after 1h @ 100°C			% @ 60°C			% @ 100°C			% after 20m @ 100°C			% after 1h @ 100°C		
		pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3
U	0.57	2.9	4.6	6.6	0.6	3.7	4.7	GE	1.5	4.2	GE	GE	1.3	1.1	T	2.0	1.0*0.7*0.3			0.4*1.1*	-		0.1*0.6*	-	
	0.59	-	-	-	-	-	-	L	-	-	L	L	-	-	-	-	-	-	-	0.2	0.3	-	0.1	0.2	-
?	0.66	-	-		0.1	-		LED	-	-	LED	LED	-	-	-	-	-	-	-	0.2	0.1	-	T	0.1	-
MMU	0.73	13.7	27.3	19.8	1.0	19.8	23.2		4.4	14.6			3.4	14.1	4.9	16.3	2.2	4.5	7.6	0.6	1.7	4.1	0.2	0.5	1.7
asym DMU	0.86	4.0	2.2	5.2	0.4	2.6	2.7		~0.4	~1.0			T	2.3	3.0	4.4	1.9	2.8	4.0	0.2	0.9	1.6	0.2	0.5	0.8
?	0.93	0.4	-	-	0.1	-	-			T			T	-	-	-	-	-	-	-	-	-	-	-	-
DMU	1	14.2	24.3	20.1	1.3	20.6	23.7		4.4	12.2			2.1	20.6	29.1	19.8	11.3	23.2	25.8	2.9	8.1	15.4	1.3	3.5	5.8
TMU	1.07	-	1.7	7.2	-	~2.0	3.3		-	T			-	~3.0	10.4	8.8	~6.0	16.5	16.7	~3	4.6	~6	-	2.0	~1

T = Trace

* There is probably a contribution from a second compound in these high urea figures.

Table 3. The addition reaction.

These compounds have been well characterised and their positions on the chromatogram are accurately known. The behaviour of the secondary substituted compounds is understood and small peaks can be observed which correspond to some of these compounds but as expected their formation is not favoured in the reaction cf. the relative amounts of asymDMU (XXII) to DMU (II) (Fig.12; P.42)

Figs.17-20 (Pp. 63, 64, 65, 66) show typical chromatograms illustrating the effects of varying the condensation conditions with respect to molar ratio, pH and temperature. Table 4 (P.67) shows the amounts of the most abundant condensation products being formed during the reaction under the varying conditions.

4. CONCLUSIONS

The Addition Reaction (Table 3; P.61) A summary of the salient features of this reaction are given below.

a) The lower the pH the faster the reaction proceeded.

b) asymDMU (XXII) was formed to the extent of about 10% of the symmetrical molecule (II) and disappeared more quickly than the latter.

c) There was no evidence for the formation of tetramethylolurea (XXXIII).

d) TMU (III) formed even at a urea to formaldehyde molar ratio of 1:1.5 at up to 35% of the DMU (II) level. It did, however, disappear much more quickly than the DMU (II), either by condensation reactions, or by dissociating to form DMU (II) and formaldehyde.

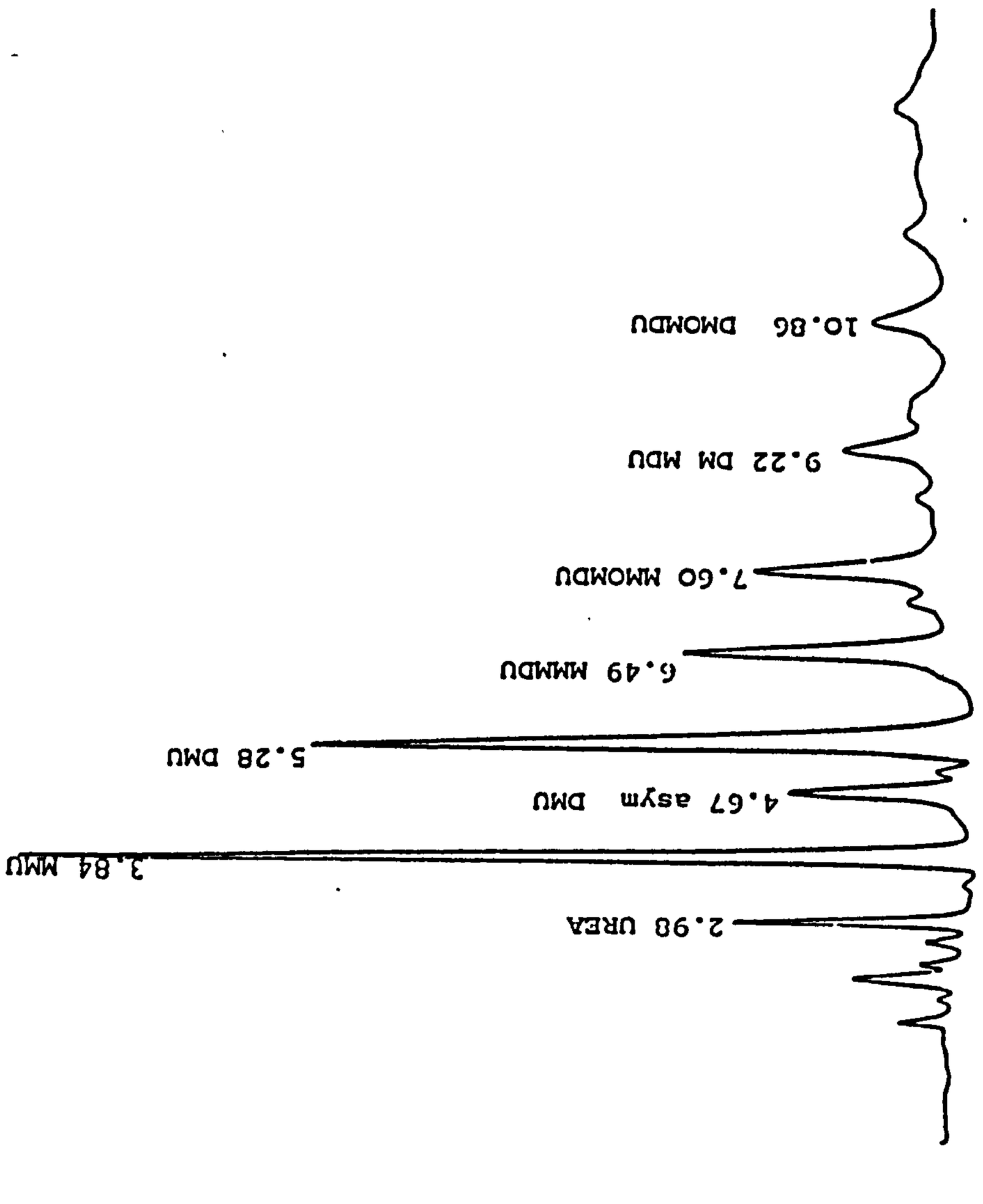

10.86 DMOMDU
9.22 DM MDU
7.60 MMOMDU
6.49 MMMDU
5.28 DMU
4.67 asym DMU
3.84 MMU
2.98 UREA
U:F 1:1.5, pH 5.5 heated to 60°C.

Fig. 17.

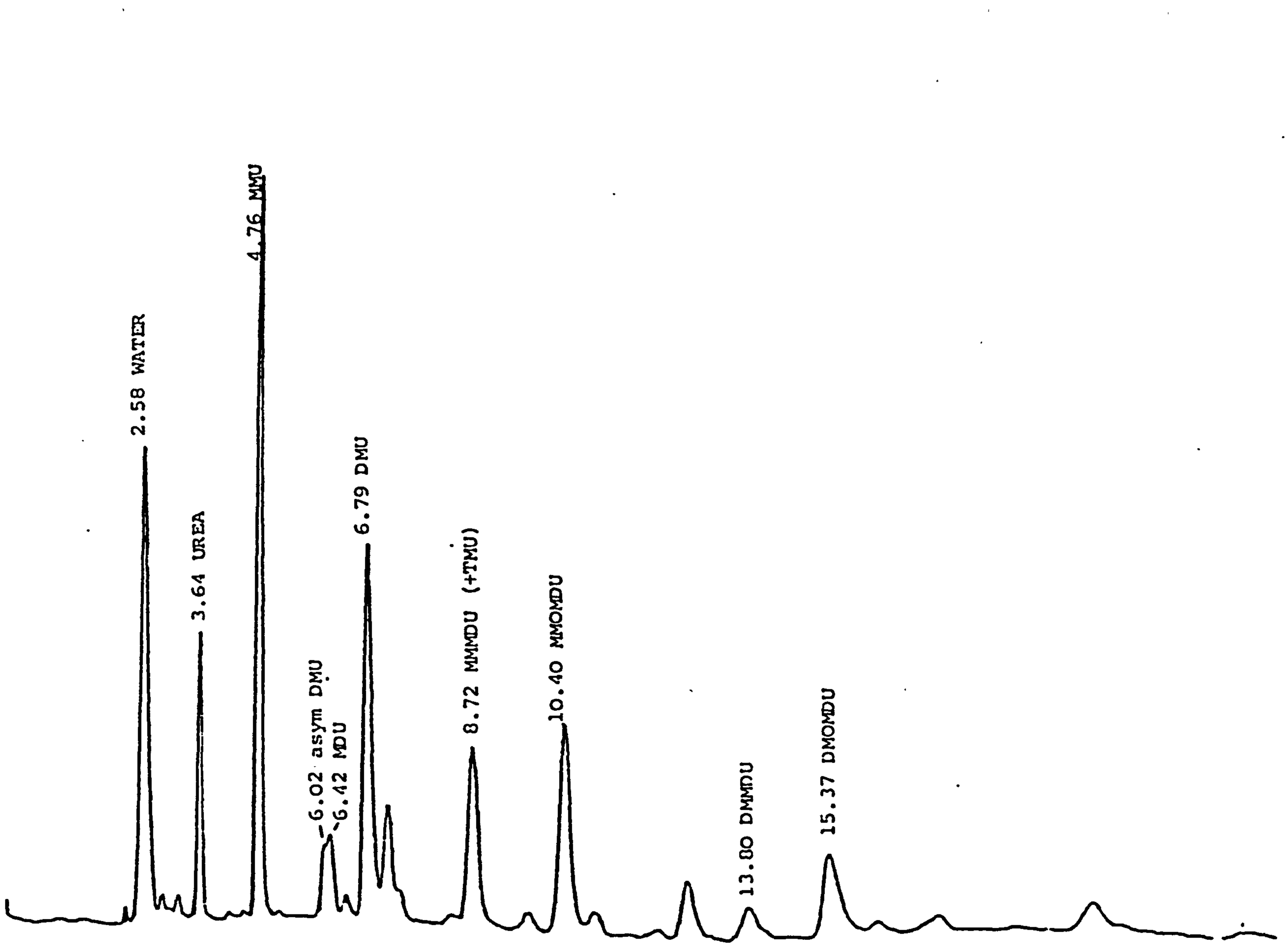


Fig. 18. Urea-formaldehyde reaction product; U:F 1:1.5, pH 8.3,40 min at 100°C.

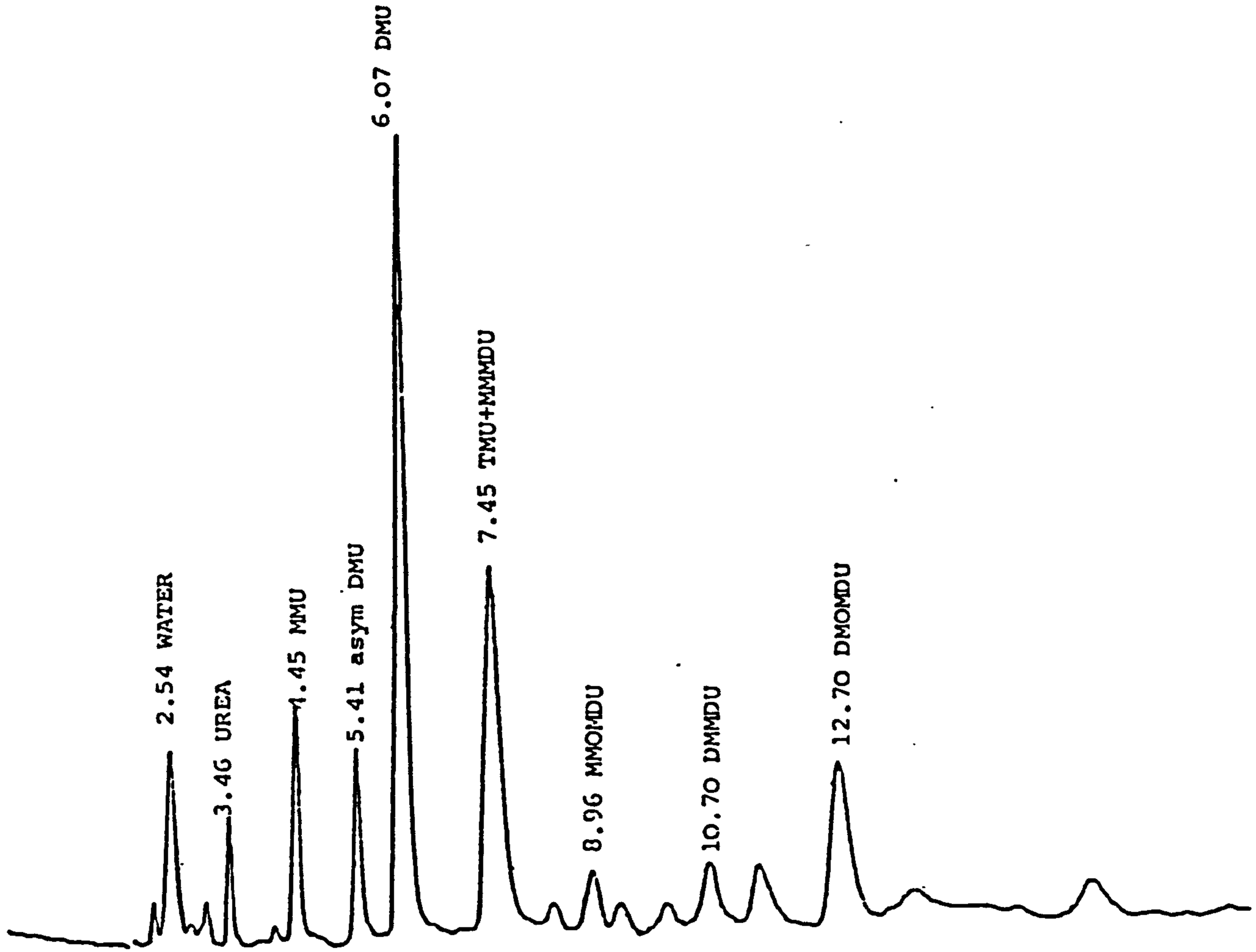


Fig.19. Urea-formaldehyde reaction product; U:F 1:2.5, pH 5.5, at reflux.

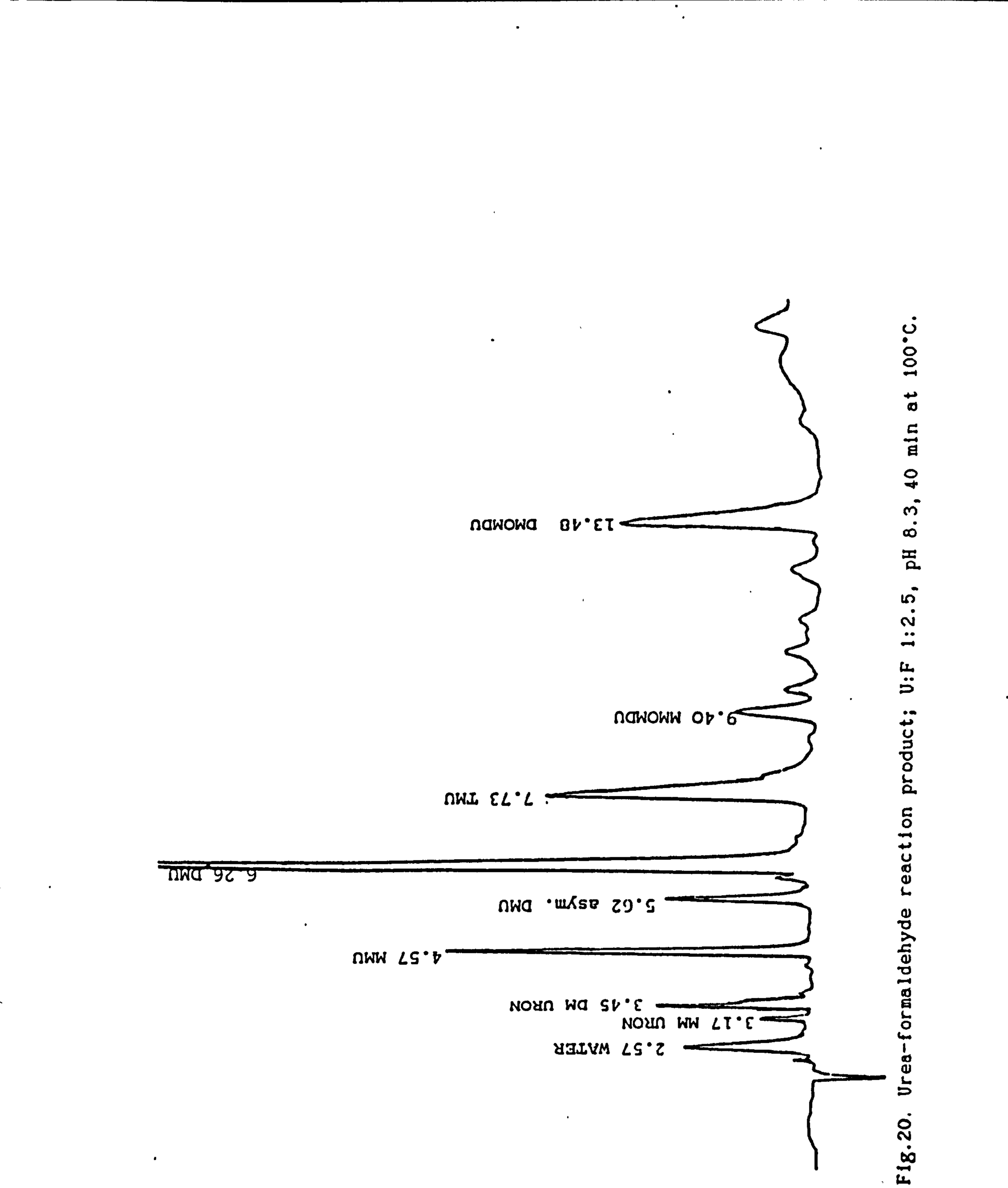


Fig. 18.20. Urea-formaldehyde reaction product; U:F 1:2.5, pH 8.3, 40 min at 100°C.

Identity	Relative Retention Time (tc DMU)	Molar Ratio 1:1.5									Molar Ratio 1:2.5								
		% @ 60°C			% @ 100°C			% after 20m @ 100°C			% after 1hr @ 100°C			% @ 60°C			% @ 100°C			% after 20m @ 100°C			% after 1hr @ 100°C		
		pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3	pH 5.5	pH 6.6	pH 8.3
MDU	0.90	~2	-	-	~0.2	-	-	GEL	~0.5	-	GEL			-	-	-	-	-	-	-	-	-	-	-	-
MMMDU	1.28	9.4	-	-	0.9	2.0	-		1.0	2.0			1.7	*	*	*	*	*	*	*	*	*	*	*	*
MM MDU	1.50	7.1	-	-	0.6	3.3	2.1	LED	1.5	5.3	LED		1.2	1.2	T	-	1.0	1.2	-	T	0.8	1.5	T	0.3	0.5
DMMDU	1.80	4.6	-	-	0.6	1.8	-	D	1.6	0.3	D		0.2	1.7	-	-	1.3	0.8	-	0.5	0.6	-	0.3	0.3	0.2
DMOMDU	2.20	3.0	-	-	0.6	2.7	2.1		1.6	4.1			0.7	2.4	1.4	-	4.2	5.0	1.0	0.4	3.7	5.3	T	1.3	2.4
Ratio $\frac{\text{Ether}}{\text{Methylene}}$ — ($\frac{\text{DMO:IDU}}{\text{DMMDU}}$)		0.7	-	-	1.0	1.5	1.0		1.0	1.3			-	1.4	-	-	3.2	6.2	>10	0.8	6.2	>20	-	4.3	12
% Soluble		63	61	59	7	57	61		20	50			20	52	50	61	36	56	55	10	37	39	5	12	18

T = Trace

* Interfering peaks present (mainly TMU)

Table 4. The condensation reaction.

At a molar ratio of 1:2.5 TMU (III), could be present at the same level as DMU (II) and although it again disappeared more quickly than the DMU (II), this effect was not so marked as at lower urea to formaldehyde ratios.

At a molar ratio of 1:1.5 due to condensation reactions being at a minimum, more TMU (III) was formed at pH 8.3 than at pH 6.6 or 5.5; at the high molar ratio of 1:2.5, much larger quantities of TMU (III) were formed, as would be expected.

The Condensation Reaction (Table 4; P.67) A summary of the salient features of this reaction are given below.

a) At both high and low molar ratios, the reaction between urea and formaldehyde proceeded faster, the lower the pH. This was shown by the relatively large amounts of methylene and oxymethylene linked compounds being formed at 60°C at pH 5.5 whilst at higher pH values, products of this nature were not observed in measurable amounts (except at a molar ratio of 1:2.5 and pH 6.6 when DMOMDU (IX) occurred at the 1.4% level).

b) At pH 5.5, once the temperature had reached 95°C, some of the methylene and oxymethylene compounds initially formed, reacted further to give larger molecules.

It was deduced that a useful method to obtain an indication of the degree of reaction was to total up the percentages of the compounds visible in the chromatogram i.e. the low molecular mass materials and as the reaction proceeded this total would become smaller. Values for "% Soluble" are given in Table 4 (P.67).

c) Urons did not seem to be produced in large quantities in any of the

reactions studied. However at a molar ratio of 1:2.5, the apparent urea concentration could be higher at pH 5.5 than at pH 6.6, which was contrary to expectation as the methylol urea levels were low. It was quite possible that a significant contribution to this peak was being made by dimethyloluron (XII) but not more than a maximum of 1.0% could be formed as a consideration of the size of the peak shows.

d) Probably the most important information to arise from this study was the relative amounts of methylene and oxymethylene compounds which were formed in the initial condensation stages. Peaks due to MMOMDU (VIII) were difficult to quantify especially when the molar ratio was 1:2.5, due to interference by large TMU (III) peaks. Therefore ratio studies were confined to the dimethylol derivatives.

In the pH range studied the formation of the linear ether tended to be the predominant reaction. At high pH the ratio of ether to methylene compound could be as high as 20:1 in favour of the ether and even at pH 5.5, as much ether could be formed as methylene compound.

The formation of methylene linked compounds and linear ethers is fundamentally different because the former reaction involves one molecule of formaldehyde in the link and the latter requires two. Thus if DMMDU (VI) is considered to be formed from MMU (I) and DMU (II), DMOMDU (IX) will be formed from two molecules of DMU (II).

$$\underset{\mathbf{I}}{H_2NCONHCH_2OH} + \underset{\mathbf{II}}{HOCH_2NHCONHCH_2OH} \longrightarrow \underset{\mathbf{VI}}{H_2NCONHCH_2NHCONHCH_2OH}$$

$$2 \times \underset{\mathbf{II}}{HOCH_2NHCONHCH_2OH} \longrightarrow \underset{\mathbf{IX}}{HOCH_2NHCONHCH_2OCH_2NHCONHCH_2OH}$$

It follows that reaction mixtures rich in formaldehyde and therefore DMU (II) will be more predisposed to form ether links than methylene links. In view of the two different mechanisms involved considerations of relative rates of formation of the two types of compound were probably not of much value.

Linear ethers are not favoured structures in commercial preparations for, under the curing conditions (low pH plus sometimes heat) linear ethers evolve formaldehyde. Also any residual ether groups remaining will, over a period of time, be converted to the methylene compound. Thus the knowledge that under normal conditions for making urea-formaldehyde condensates, linear ethers are produced to such a high degree is invaluable information to the synthetic chemist and may allow the design of more effective commercial formulations.

e) The reaction carried out between urea and formaldehyde at pH 5.5 with a molar ratio of 1:2.5 gave a product which was noticeably different from other reaction products obtained at this stage. The material obtained after heating for 15 minutes at 95°C was clear and totally water soluble although the chromatograms obtained during its formation were little different from those of other condensation products. It seemed likely that there was a reaction occurring which was not obviously apparent when only simple chromatograms were run on the samples. This unusual behaviour of urea-formaldehyde reaction mixtures was investigated and the results are given in the next section.

C. The Formation and Reactions of Ammonia in Urea-Formaldehyde Resins

1. INTRODUCTION

It is a well known fact[52] that urea solutions decompose on heating to form ammonia and carbon dioxide and the reaction has been reported to be catalysed by acid and base. It is therefore very possible that ammonia can be formed during the manufacture of urea-formaldehyde resins and although the quantities may not be significant at pH values near to neutral they may be substantial at higher or lower values.

Simple urea-formaldehyde reaction products are opalescent and have little or no water tolerance. In the previous section IIIB (P.70), however, mention was made of the fact that a urea-formaldehyde mixture of relatively high molar ratio (1:2.5, urea:formaldehyde) at pH 5.5 formed a condensate after 10 minutes at 95°C, which was clear and totally soluble in water. Further reaction caused an increase in relative molecular mass but the unusual solubility characteristics remained unaltered. It is obvious that a fundamentally different reaction was involved in the formation of this urea-formaldehyde condensate and it seems possible that this could be a consequence of the formation of ammonia (as NH_4^+) under the moderately acid conditions.

The first task, therefore, in this investigation was to determine the amount of ammonia formed in such reaction mixtures.

If ammonia is formed in quantity and it is judged likely that the novel state of the urea-formaldehyde condensate is a consequence of its presence in the system, then it is of paramount importance to determine

the way it modifies the simple urea-formaldehyde reaction. It seemed reasonable to expect that tetrahydro 1,3,5-triazin-4-one (XIII) would form easily from DMU (II) and ammonia, as the 4-substituted derivatives are well known, but attempts to synthesise this compound were unsucsessful, only hexamethylenetetramine (hexamine; XXIII) and urea being detectable. If however, ammonia or indeed hexamine was added to a urea-formaldehyde resin during the reaction, no hexamine could be detected after the condensation was complete. Consequently, the fate of ammonia when added to reacting urea and formaldehyde also required investigation. The formation of hexamine from ammonia and formaldehyde only goes to completion under neutral conditions and Plöchl[53] and Knüdsen[54] showed that aqueous solutions of ammonia when heated with formaldehyde under acid conditions formed salts of firstly mono-methylamine then dimethylamine and finally trimethylamine. Knüdsen[54] showed that two molecules of formaldehyde were involved with one molecule of ammonia to form methylamine, the first molecule of formaldehyde probably reacting to form methyleneimine $CH_2=NH$ and the second molecule then reducing this intermediate to methylamine, CH_3NH_2.

$$NH_3 + HCHO \longrightarrow CH_2=NH \qquad CH_2=NH + HCHO \longrightarrow CH_3NH_2$$

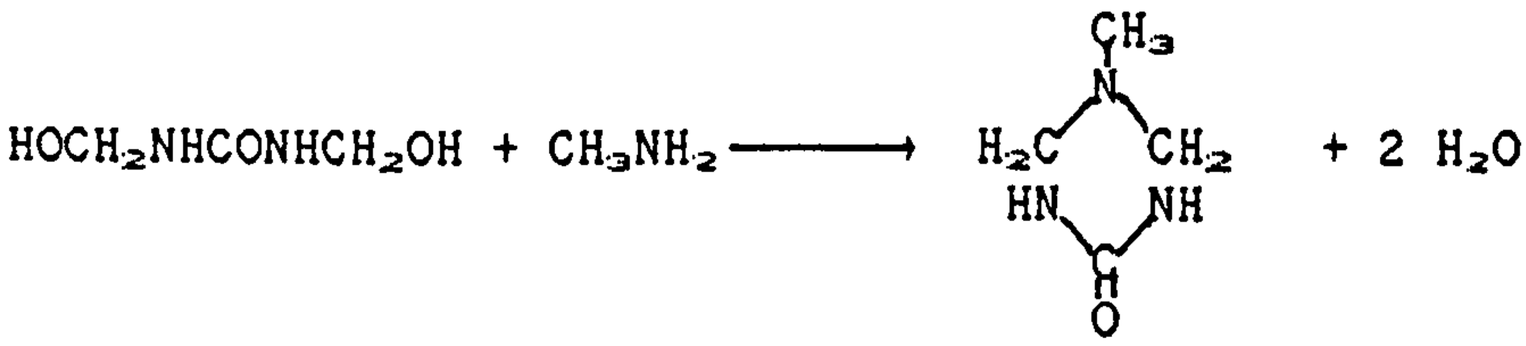
This process would be repeated in the further reactions to form dimethylamine and subsequently trimethylamine, although the course of this latter reaction is difficult to understand.

$$CH_3NH_2 + HCHO \longrightarrow CH_2=NCH_3$$

$$CH_2=NCH_3 + HCHO \longrightarrow (CH_3)_2NH$$

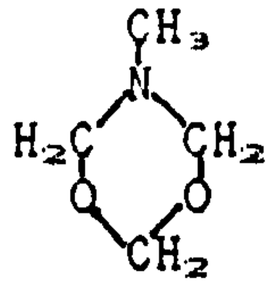
Knüdsen[54] showed that trimethylamine was not formed at temperatures less than 105°C.

It is now interesting to consider the likely fate of the methylamine as it is produced from the ammonia. As mentioned above, it could react further with formaldehyde to form dimethylamine, or it could combine with DMU (II) or TMU (III) to produce tetrahydro 5-methyl-1,3,5-triazin-4-one (methyltriazinone; MT; XXXIV).



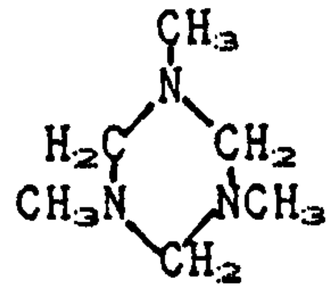
XXXIV

(The reactions of amines and methylol ureas to form triazinones have been studied extensively by Burke[57] and Paquin[58]).
Walker[55] in his monograph "Formaldehyde" mentions other reaction products of urea, formaldehyde and aliphatic amines such as: methylamine triformal (XXXV)



XXXV

and trimethyltrimethylenetriamine (XXXVI)



XXXVI

It seems however that the conditions necessary to form these latter two compounds are much more stringent than for triazinones[59].

2. EXPERIMENTAL AND RESULTS

Hydrolysis of Urea to Form Ammonia

A 10% urea solution in water was buffered with 1.3% of sodium dihydrogen phosphate and adjusted to the appropriate pH (3.5-7.5, as shown in Fig.21; P.75) with 1.7M phosphoric acid or 5M sodium hydroxide solution. The solution was heated to reflux and a sample removed after 10 minutes. The ammonia content was measured by means of a commercial ammonia ion selective electrode and the results are shown in Fig.21 (P.75).

It seems that the rate of hydrolysis of urea to form ammonia in the pH range 3 to 7 is directly proportional to the log of the hydrogen ion concentration. The amount of ammonia formed is quite large, for example 0.4% of the urea in a 10% solution at pH 5 when heated at 100°C for 10 minutes will be converted to ammonia.

The Formation of Amines

i. The Detection of Methylamine, Dimethylamine and Trimethylamine.

The method used was based on work carried out by Dubin[56] who used the reaction of 2,4-dinitrofluorobenzene with free amino groups to form dinitrobenzylamines which were subsequently assayed by UV spectroscopy.

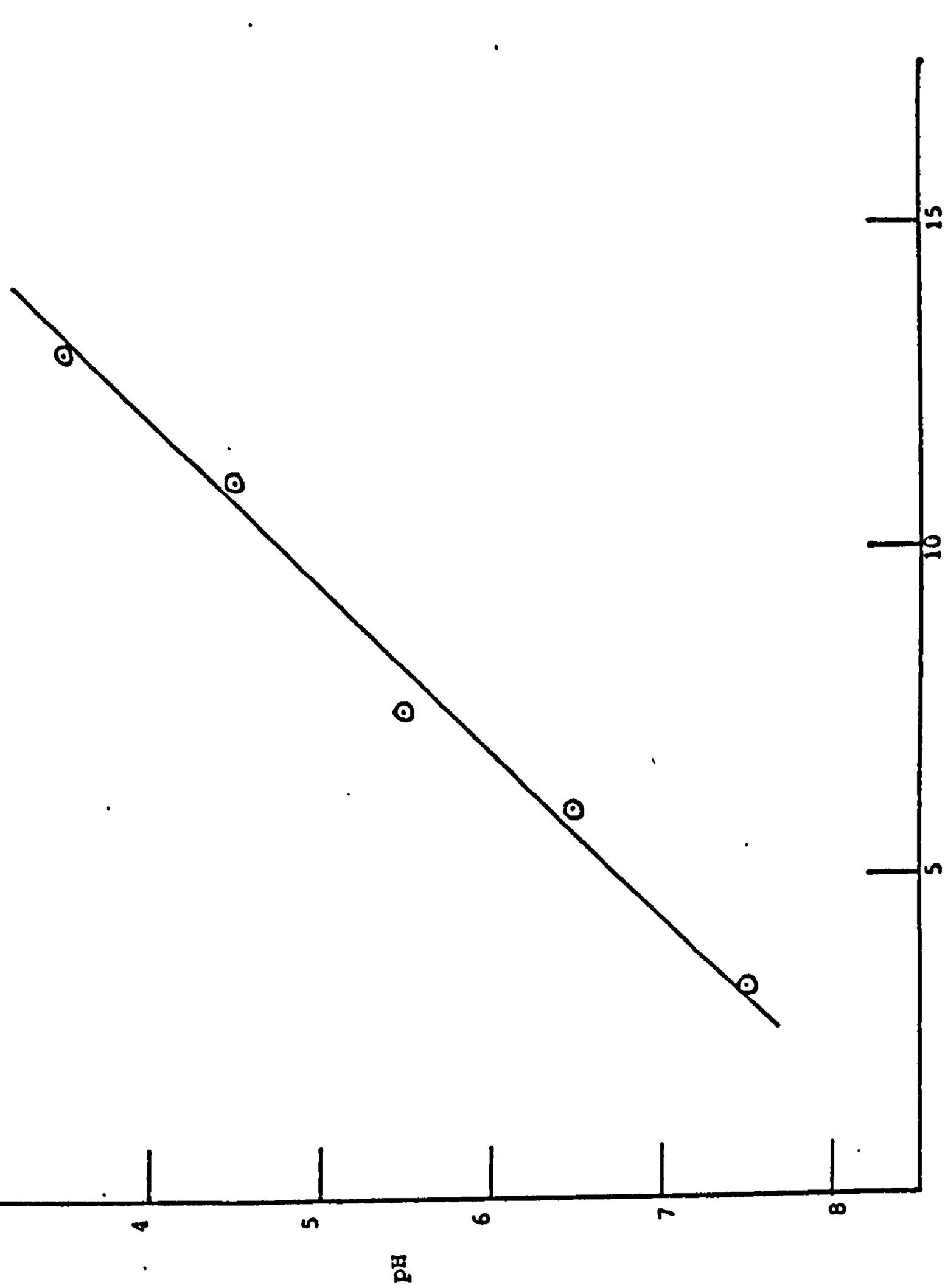


Fig.21. The formation of ammonia from urea at various pH values.

In this study, the derivatives were separated by liquid chromatography and detected by means of a UV detector.

A solution of 2,4-dinitrofluorobenzene in acetone, (0.65% v/v) was mixed with an aqueous solution of sodium borate, (2.5% w/v) in the ratio of 1:10, immediately before use. Two drops of aqueous amine solution (0.005%w/v), were mixed with two drops of the reagent and heated in an oven at 65°C for 15 minutes. The amine/reagent solution was allowed to evaporate and the derivative was dissolved in methanol (50µl) and diluted with the chromatographic mobile phase (4ml). The insoluble inorganic material was allowed to settle and the supernatant liquor used for chromatographic analysis.

The general chromatographic procedure used was that described in Section 11 B3 (P.28) but a UV detector set to absorb at 352nm was used. Chromatography on a reversed phase octadecylsilane (ODS) column was first investigated but a solvent system that gave suitable retention times for the mono- and diamine derivatives, failed to separate the peak due to the large excess of unreacted 2,4-dinitrofluorobenzene reagent from the diamine derivative peak. It was considered that conventional chromatography offered a better chance of success and using an eluant composed of heptane: chloroform (80:20), a good separation was obtained on a nitrile column (Spherisorb CN). No peak due to trimethylamine was observed under these conditions in accordance with the investigations of Knüdsen[54]. To determine whether ammonia or hexamine (XXIII) would interfere, solutions of these two materials were substituted for the amine solutions and the reaction with 2,4-dinitrofluorobenzene was

carried out. No derivative peaks were produced when these reactants were subjected to chromatography.

ii. The Ammonia-Formaldehyde Reaction.

Sodium dihydrogen phosphate (0.1g) was added to a solution of ammonium chloride (0.1g) in 2.5% w/v aqueous formaldehyde solution (100ml) and the pH was adjusted to 2.5 using 1.7M phosphoric acid. The solution was then heated on a vigorously boiling water bath.

Samples were taken as follows.

1) One drop on mixing.

2) One drop at reflux.

3) One drop after 10 minutes at 95°C.

4) One drop after 20 minutes at 95°C.

Sample 1 gave no peak for amine derivatives.

Sample 2 showed a methylamine derivative peak equivalent to a concentration of CH_3NH_2 of about 0.0005%.

Sample 3 again gave a methylamine derivative peak but the concentration had increased approximately ten fold, equivalent to about 0.005% methylamine. Also present was a dimethylamine derivative peak about half the size of the monomethylamine derivative peak (equivalent to about 0.002% dimethylamine). Sample 4 again showed about 0.005% monoamine derivative but the diamine peak was now equivalent to about 0.01% dimethylamine. Chromatograms showing the reaction procedure are illustrated in Fig.22 (P.78).

The Formation of Triazinones

i. The Preparation of Dimethylolmethyltriazinone (DMMT; XXXVII).

It has been shown[57] that urea (1mol), formaldehyde (2mol) and

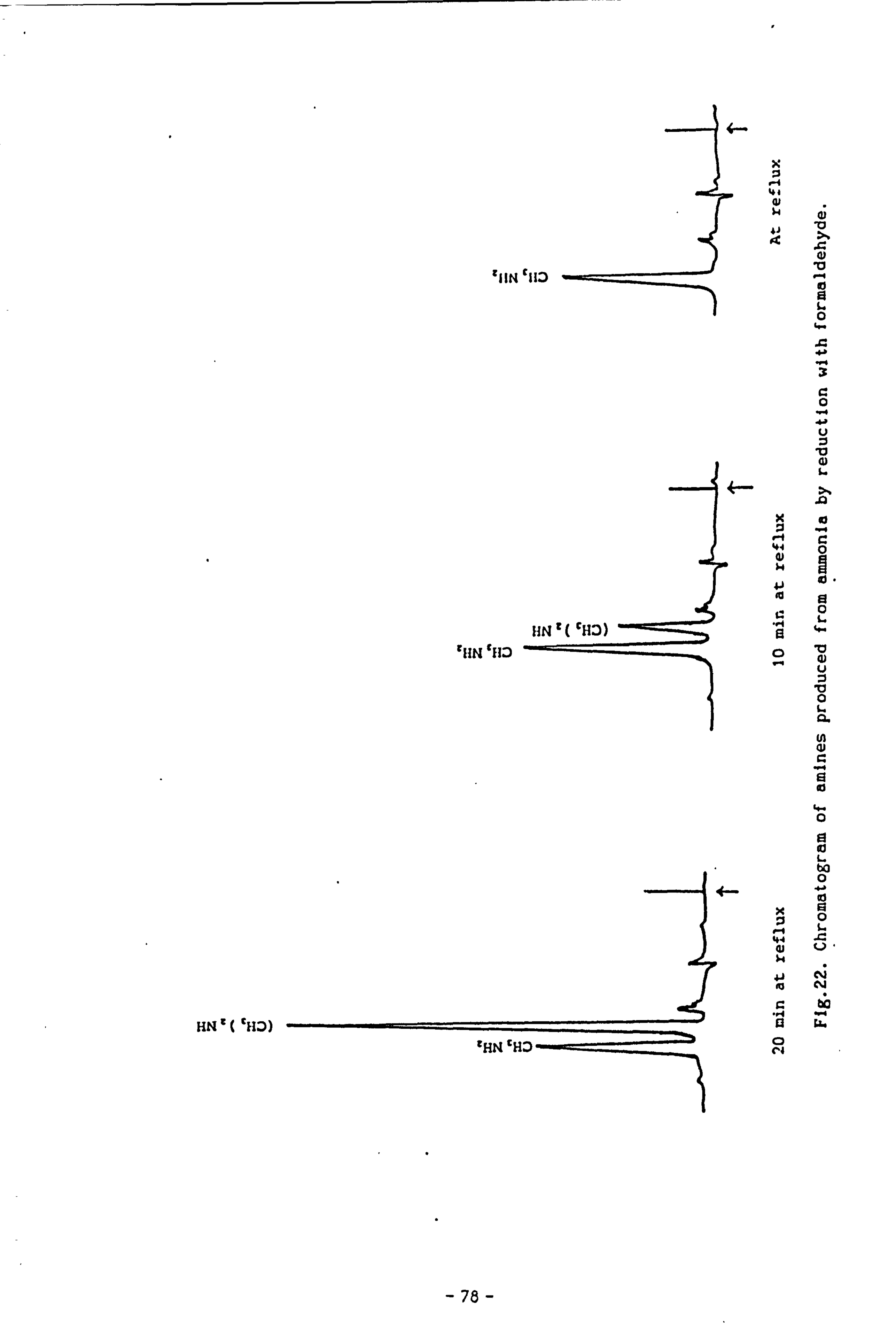
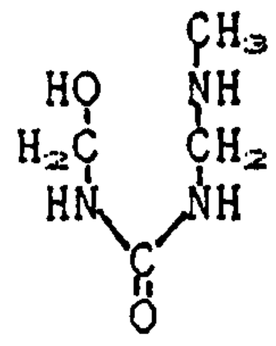


Fig.22. Chromatogram of amines produced from ammonia by reduction with formaldehyde.

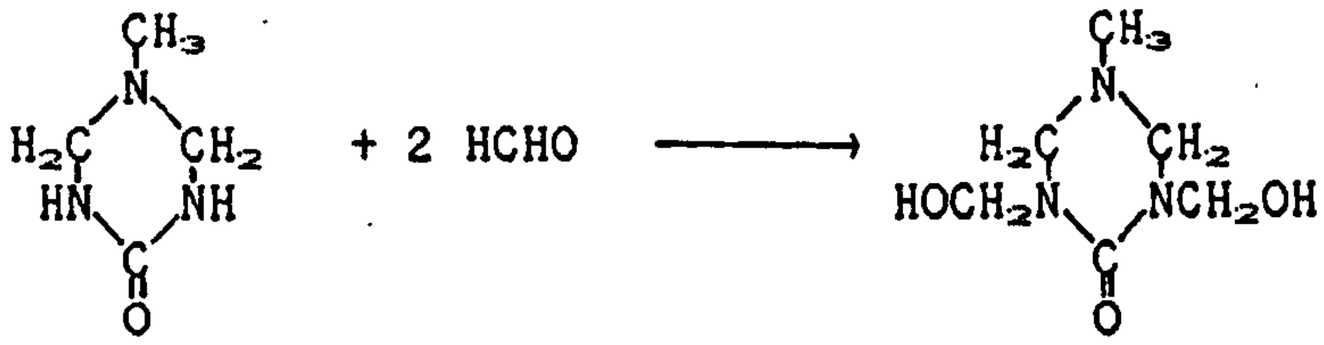
methylamine (1mol) when reacted together in any order will rapidly and easily form methyltriazinone (**XXXIV**).

Urea (30g; 0.5mol) was added to 50% aqueous formaldehyde solution (60g; 1mol) which had previously been neutralised and buffered with disodium hydrogen phosphate (0.5g). The reaction was allowed to proceed at 60°C for 2 hours to form DMU (II) in good yield. A 27% aqueous solution of methylamine (113g; 0.5mol) was added with cooling over a period of about 30 minutes.

Although the amine odour is minimal at this stage indicating that the methylamine had reacted, it seems that only an unstable intermediate is formed, possibly



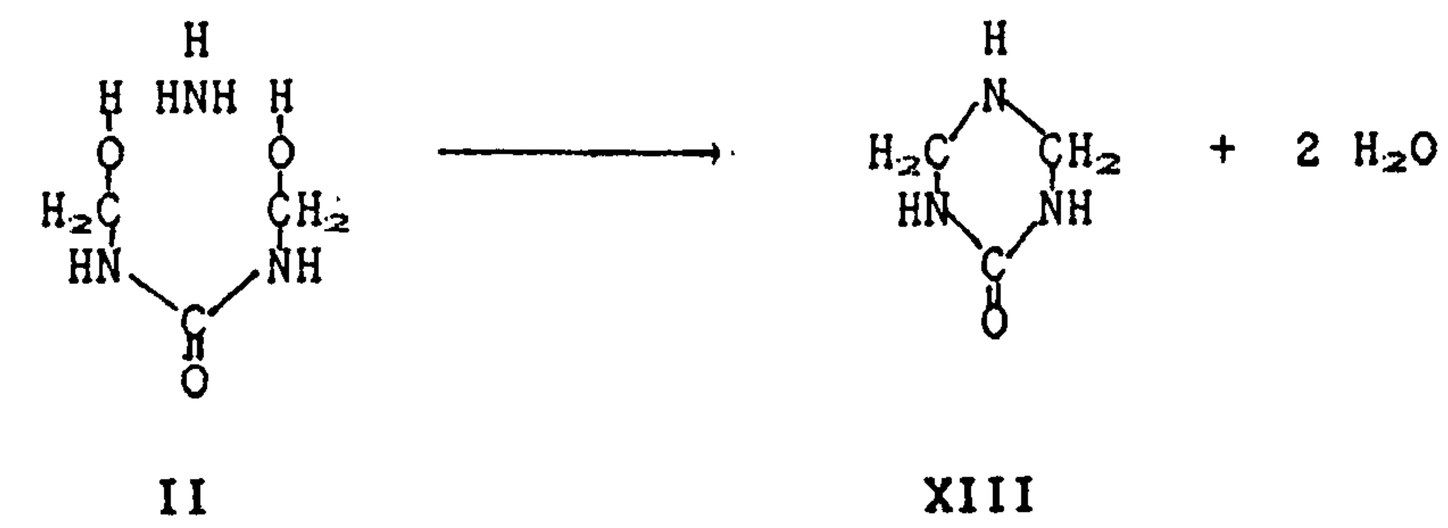
as it tended to decompose on recrystallisation. The compound was not, however, isolated and no evidence was obtained to support the suggested structure. The reaction mixture was refluxed for 2 hours to complete the formation of the cyclic compound and cooled to 0°C overnight. The crude methyltriazinone (**XXXIV**) was filtered off and recrystallised from ethanol, m.p. 195-198°C (lit.[57] m.p. 210°C). As the compound was only to be used as a synthesis intermediate, it was not considered necessary to introduce a purification stage. The structure was further verified by infra-red, and ^{13}C-nmr spectroscopic techniques. The methyl-triazinone (**XXXIV**) was then converted into the dimethylol compound according to the following scheme.



XXXIV XXXVII

50% aqueous formaldehyde solution (12g; 0.2mol) was neutralised using 5M sodium hydroxide solution, buffered with disodium hydrogen phosphate (0.5g) and methyltriazinone (XXXIV) (11.5g; 0.1mol) was added. The mixture was warmed to 50°C and water (about 30ml) was added to dissolve the methyltriazinone (XXXIV). After reacting for two hours at 60°C, the mixture was cooled to 0°C and kept thereat overnight. The resulting crude material was filtered off and recrystallised from ethanol to give dimethylolmethyltriazinone (XXXVII), m.p. 109°C. The structure was verified by infra-red and ^{13}C-nmr spectroscopic techniques.

Attempts to prepare the parent compound, tetrahydro 1,3,5-triazin-4-one (XIII) from DMU (II) (or urea and formaldehyde in a molar ratio of 1:2 and at pH 8.3) and ammonia or hexamine were unsuccessful.



II XIII

In one experiment urea (30g), 50% aqueous formaldehyde (60g) and disodium hydrogen phosphate (0.5g) were reacted together overnight. The

crude DMU (II) was broken up, 35% aqueous ammonia solution (25g) was added and the mixture heated gently to 70°C. Within five minutes, the odour of ammonia had disappeared and the mixture was allowed to cool. After twenty four hours, the mass was broken up and filtered to give 15g of a material which melting point, infra-red and ^{13}C-nmr spectroscopy showed to be DMU (II). The residue was a viscous liquid and not easy to crystallise. The experiment was repeated using twice the amount of ammonia (50g) and the mixture at the final stage was heated at 80°C for two hours. The reaction product was concentrated in a rotary evaporator at 45°C to give a viscous liquid. As the triazinone (XIII) should be more soluble in non-polar solvents than DMU (II) and possibly hexamine (XXIII), the reaction mixture was extracted in turn with chloroform, diethylether, ethyl acetate and ethanol. An infra-red spectroscopic examination of the small amount of material that was extracted, revealed that only traces of DMU (II), urea and hexamine (XXIII) were present. No evidence was obtained that any triazinone formation had occurred and a possible explanation is that hexamine (XXIII) is a very stable molecule and its formation from ammonia and the formaldehyde present in relatively unstable compounds, such as DMU (II) is the preferred reaction to the formation of the triazinone ring structure. It is possible, therefore, that in a mixture of ammonia and formaldehyde (or formaldehyde donor) only hexamine and the compound in excess, (ammonia or formaldehyde), can exist. A literature search for any reference to the parent triazinone (XIII) was not successful and it can only be concluded that so far this compound has not been prepared.

ii. The Reaction of Ammonia with Formaldehyde and Urea

50% w/v aqueous formaldehyde solution (40g; 0.66mol) was adjusted to pH

5.5 with 5M sodium hydroxide solution and sodium dihydrogen phosphate (0.4g) was added followed by urea (16g; 0.26mol), the temperature being maintained at 60°C for two hours to allow the formation of di- and trimethylolurea (II and (III). Hexamine (XXIII) (2g equivalent to 0.04 mol ammonia) was added to the solution, allowed to dissolve and the solution heated to reflux.

Samples were taken as follows.

1) On mixing.

2) After standing overnight at 25°C.

3) After 30 minutes at 60°C.

4) At reflux.

5) After 15 minutes at reflux.

Using the aminopropyl column and acetonitrile:methanol (4:1) as eluting solvent (formulated to separate DMMT (XXXVII), from MMU (I)), the samples were checked for a peak eluting at the same time as DMMT (XXXVII) (retention time about 3.19 minutes with a solvent flow of 1.5ml min^{-1}). After heating for 30 minutes at 60°C a small peak was observed which after 15 minutes at 100°C was equivalent to about 0.5% of the reaction mixture. "Spiking" (adding a small amount of standard) with DMMT (XXXVII) increased the size of the peak of interest, indicating that it was indeed likely that DMMT (XXXVII) had been formed.

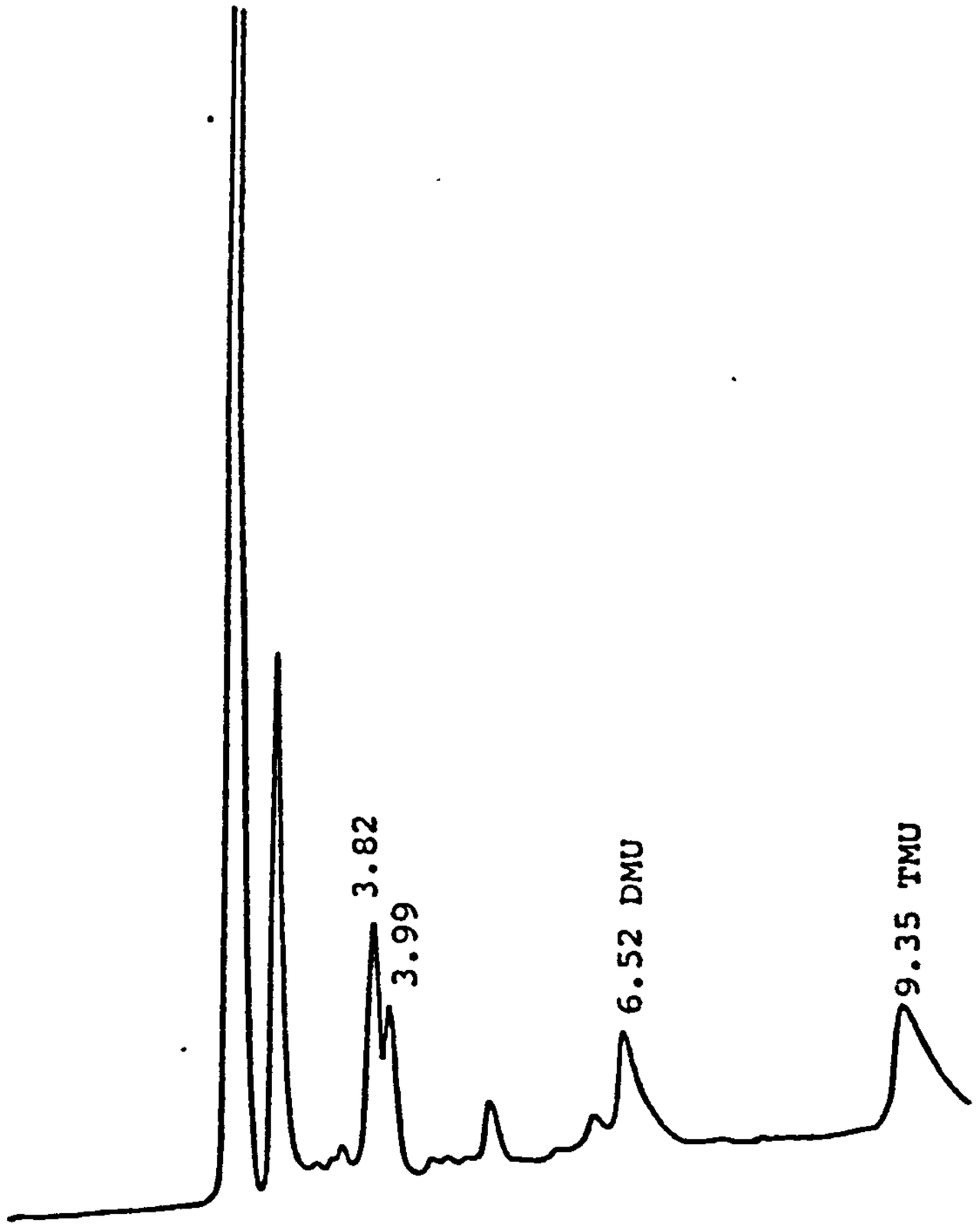
Judging by the solubility characteristics of DMuron (XII), DMMT (XXXVII) which has a similar structure, should be more soluble in relatively non-polar solvents e.g. chloroform and acetonitrile than its precursors, urea and DMU (II) and other linear water soluble components of the reaction mixture. In order, therefore, to attempt to concentrate the cyclic compound, if indeed it was present in the reaction mixture, 10g

of the mixture taken at the final stage of the reaction, was dried with anhydrous sodium sulphate (2g) and extracted with acetonitrile (3x20ml). The acetonitrile was removed at 40°C by blowing a jet of air over the liquid and final removal of solvent was carried out in a vacuum oven at 40°C to yield about 1g of acetonitrile soluble material. When chromatographed as before, a peak at 3.9 minutes was obtained which was much larger than the one detected in the unconcentrated sample (Fig.23a and Fig.23b; P.84). "Spiking" with DMMT (XXXVII) again increased the size of the peak of interest giving further evidence that methyltriazinones were present (Fig.23c; P.84).

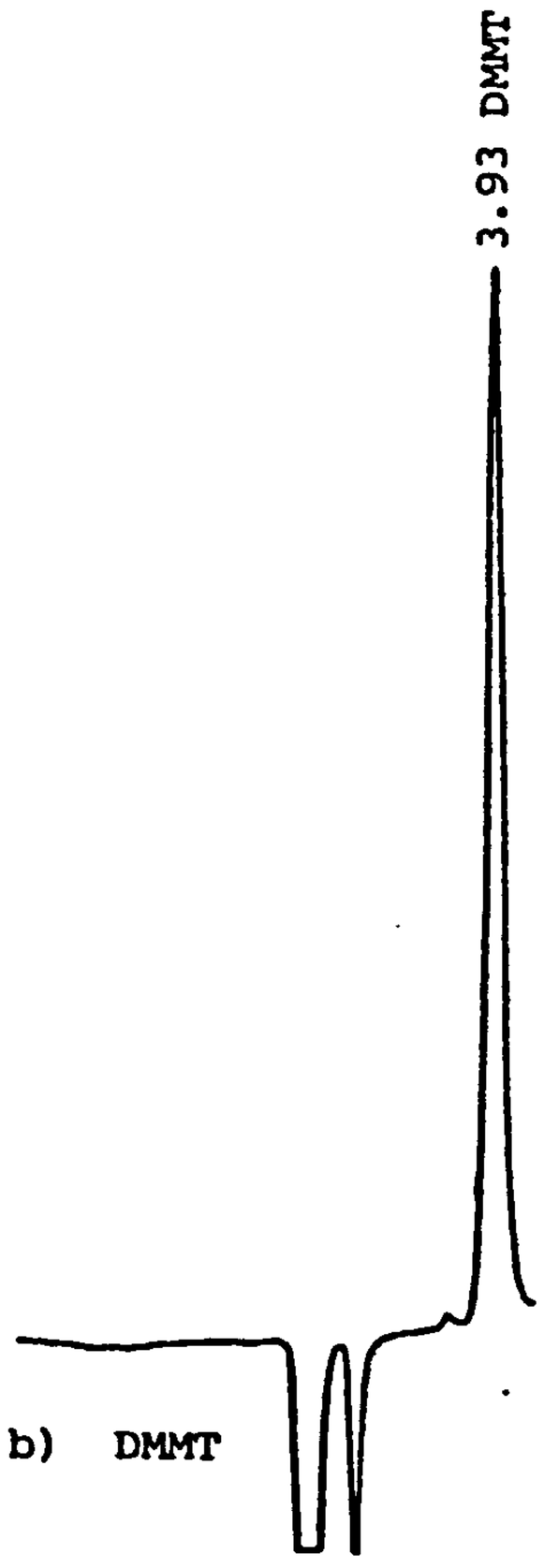
A ^{13}C-nmr spectrum of the reaction mixture giving the chromatogram illustrated in Fig.23b (P.84), showed the $\geq N-CH_3$ peak of the triazinone thus confirming the chromatographic evidence.

3. DISCUSSION AND CONCLUSIONS

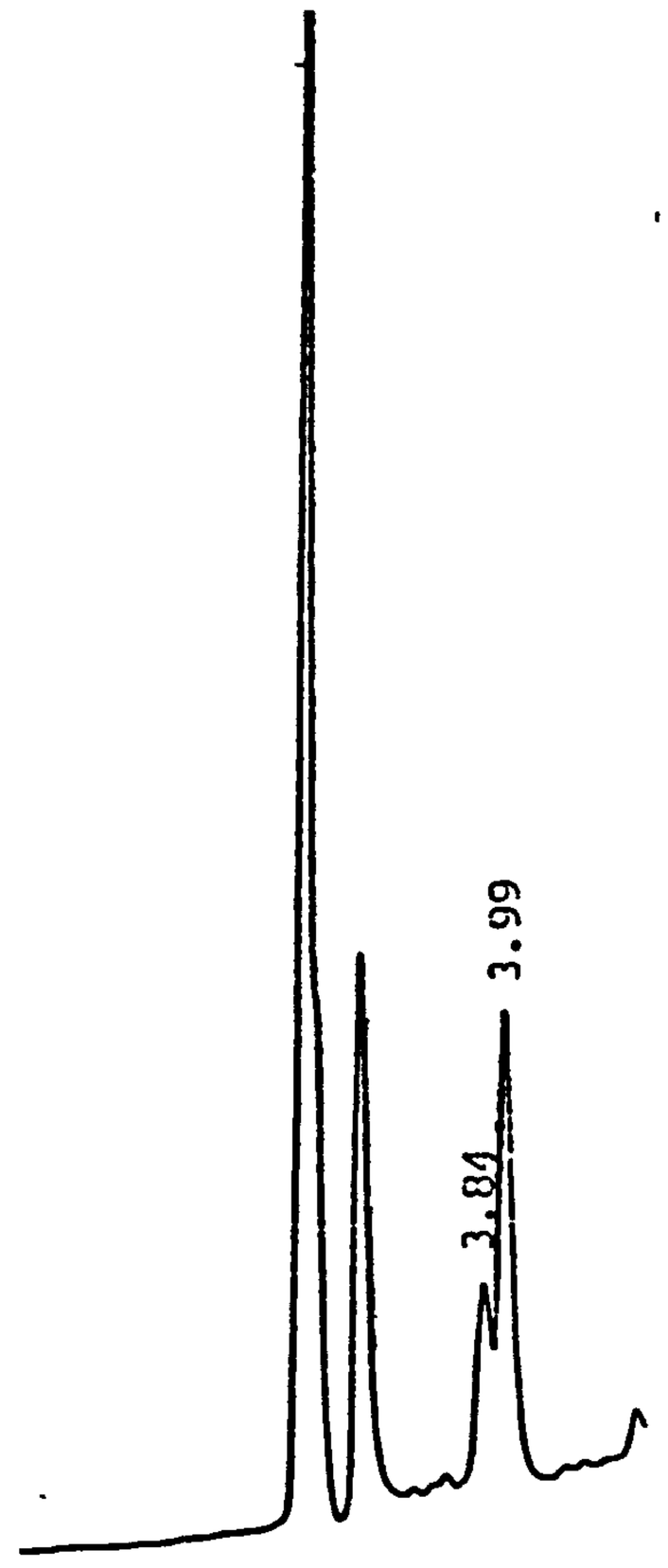
It has been shown that ammonia will be formed in considerable amounts when urea and formaldehyde are reacted together at moderately low pH values. As the ammonia is formed there is a rapid reaction involving two molecules of formaldehyde to produce methylamine. the fate of which seems fairly clear. If the molar ratio of fomaldehyde to urea is high enough (e.g. >2:1) to form DMU (II) and TMU (III) in substantial quantities, then the methylamine reacts with methylolated urea to form methyltriazinone moieties in the urea-formaldehyde network before further reduction of the amine can take place. These cyclic amines will confer the high water solubility on the resin which has previously been reported (P.70). Triazinone modified urea-formaldehyde resins fall into the area of textile treatment chemistry which has been covered in many



a) Acetonitrile soluble material



b) DMMT



c) Sample (a) plus DMMT

Fig.23. The reaction of ammonia with formaldehyde and urea.

patents and for this reason it is not proposed to extend this particular investigation further.

From this study, two facts have become highly significant in the chemistry of urea-formaldehyde resins.

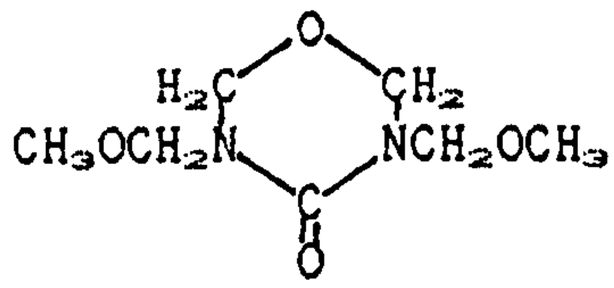
i. Ammonia added as a coreactant will rapidly be reduced to methylamine, using up in the process, two molecules of formaldehyde. If the original molar ratio of formaldehyde to urea is high (e.g. >2:1), then it is probable that the ammonia will become bound up in the resin as methyltriazinone residues, whereas if this ratio is low (e.g. <1.2:1), it is quite possible there will not be sufficient formaldehyde available to form triazinone structures and the methylamine could finally end up as di- or even trimethylamine, thus depleting the system of formaldehyde even further. Investigations into the reactions of ammonia in systems low in formaldehyde is envisaged as a separate study to be undertaken in the future.

ii. The production of one molecule of dimethylolmethyl 1,3,5-triazin-4-one (**XXXVII**) involves one and a half molecules of urea and six molecules of formaldehyde. If the formation of triazinones is considerable, then this disproportionate consumption of formaldehyde in the reaction mixture will have a marked effect on the molar ratio of formaldehyde to urea. However should ammonia (5% is a typical level) be added as coreactant in the urea-formaldehyde reaction, then the consumption of formaldehyde (relative to urea) in the formation of methylamine and finally methyltriazinone (**XXXIV**) will be much more dramatic, for in this instance six molecules of formaldehyde will be consumed for only one molecule of urea.

D. The Formation of Tetrahydro 1,3,5-oxadiazin-4-ones (Urons) in Urea-Formaldehyde Resins

1. INTRODUCTION

Kadowaki in 1936[39] synthesised the first compound containing the tetrahydro-1,3,5-oxadiazin-4-one structure, to which he gave the name uron. The compound produced was 3,5-di(methoxymethyl)tetrahydro 1,3,5-oxadiazin-4-one (dimethoxymethyluron; **XXXVIII**).



XXXVIII

Later Beachem et al[43], removed the methoxymethyl group from dimethoxymethyluron (**XXXVIII**) by acid hydrolysis and obtained the parent compound in low yield. Kadowaki carried out the cyclisation reaction at high pH while commercial procedures introduced in recent years[59] tend to favour uron production at low pH values. It seems that urea-formaldehyde reaction mixtures of high formaldehyde to urea molar ratio (>4:1) at high or low values of pH, will produce uron structures with relative ease, and concentrating the reaction mixture ie removal of water, may also be a major factor in driving the reaction forward. Up to the present time, the factors affecting the formation of urons and the properties of urons once formed have been little investigated.

This study is subdivided into four main sections:

i) the formation of urons in alkaline urea-formaldehyde systems,

ii) the formation of urons in acid urea-formaldehyde systems,

iii) the reactivity of simple urons,

iv) the formation of urons in urea-formaldehyde chains at high pH.

2. THE FORMATION OF URONS IN ALKALINE UREA-FORMALDEHYDE SYSTEMS

Scope of the Investigation

It is known that at pH values near to neutral, urons are not formed (*vide supra*). At high pH values the Cannizzaro reaction produces formic acid, as formate, (plus methanol) from the formaldehyde making it very difficult to maintain a stable pH and therefore quite impractical for commercial resin production and for this reason, the range chosen for detailed study was from pH 8 to pH 12. Below molar ratios of urea:formaldehyde of 1:2.5 (*vide supra*), significant amounts of urons are not formed whereas at a molar ratio of 1:6 the conversion of urea to urons is almost quantitative. Variations in the degree of uron formation, resulting from changes in synthesis parameters are likely to be evident in the molar ratio range of urea:formaldehyde from 1:2.5 to 1:4.5 and this range was therefore considered to be most useful for detailed investigation.

Reaction mixtures which would be expected to form small amounts of urons, i.e. at a pH one unit higher than neutral and only moderately high levels of formaldehyde, were subjected to a concentration step, to ascertain if the yield of urons could be increased.

Experimental

The general procedure adopted was that described in II B3 (P.28) and III B2 (P.55). To investigate the effect of concentrating a urea-formaldehyde reaction mixture, 50% aqueous formaldehyde solution (25g), was adjusted to pH 7 with 5M sodium hydroxide solution and disodium hydrogen phosphate (0.2g) was added. Urea (10g) was added (to give a urea:formaldehyde

molar ratio of 1:2.5) and when dissolved, the solution was finally adjusted to pH 8 using 5M sulphuric acid or 5M sodium hydroxide. The mixture was first allowed to react at 35°C overnight and then placed in a rotary evaporator where water (and some formaldehyde) was distilled off at 60°C. Samples were taken as follows.

i) Before concentration.

ii) After 11% of volatile material had been removed.

iii) After 18% of volatile material had been removed.

iv) After 23% of volatile material had been removed.

The procedure was repeated using 50% formaldehyde solution (45g) and urea (10g) to give a reaction mixture having a urea:formaldehyde molar ratio of 1:4.5.

Results

Table 5 (P.89) shows the amounts of uron formed under the various reaction conditions. Also shown are the totals of low molecular mass urea-formaldehyde compounds and the theoretical urea content, as urea itself, as DMU (II) and as DMuron (XII) so that an indication of the degree to which the reaction has proceeded can be obtained.
Fig.24 (P.90) is a typical chromatogram of a urea-formaldehyde reaction product where the formation of uron is substantial.

At molar ratios of urea:formaldehyde of 1:2.5 and 1:4.5 at pH 8, concentration of the reaction medium did not produce urons at levels exceeding 2% in any of the samples tested.

	Molar Ratio 1:2.5			Molar Ratio 1:3.5			Molar Ratio 1:4.5		
	pH 8	pH 10	pH 12	pH 8	pH 10	pH 12	pH 8	pH 10	pH 12
% Urea calculated									
(i) as urea		29			22			18	
(ii) as DMU (II)		57			44			36	
(iii) as DMuron (XII)		78			59			49	
% Low molecular mass UF compounds									
(i) on mixing	51	43	25	40	38	33	30	28	20
(ii) 10 min at 95 °C	39	34	3	30	25	28	25	25	34
% Uron (DMuron (XII) + MMuron XI) after									
(i) 10 min at 95 °C	0.5	10	<1	1	6	17	1	11	27
(ii) 20 min at 95 °C	1	13	<1	1	11	20	2	15	32

Table 5. The reaction of urea and formaldehyde at high pH values.

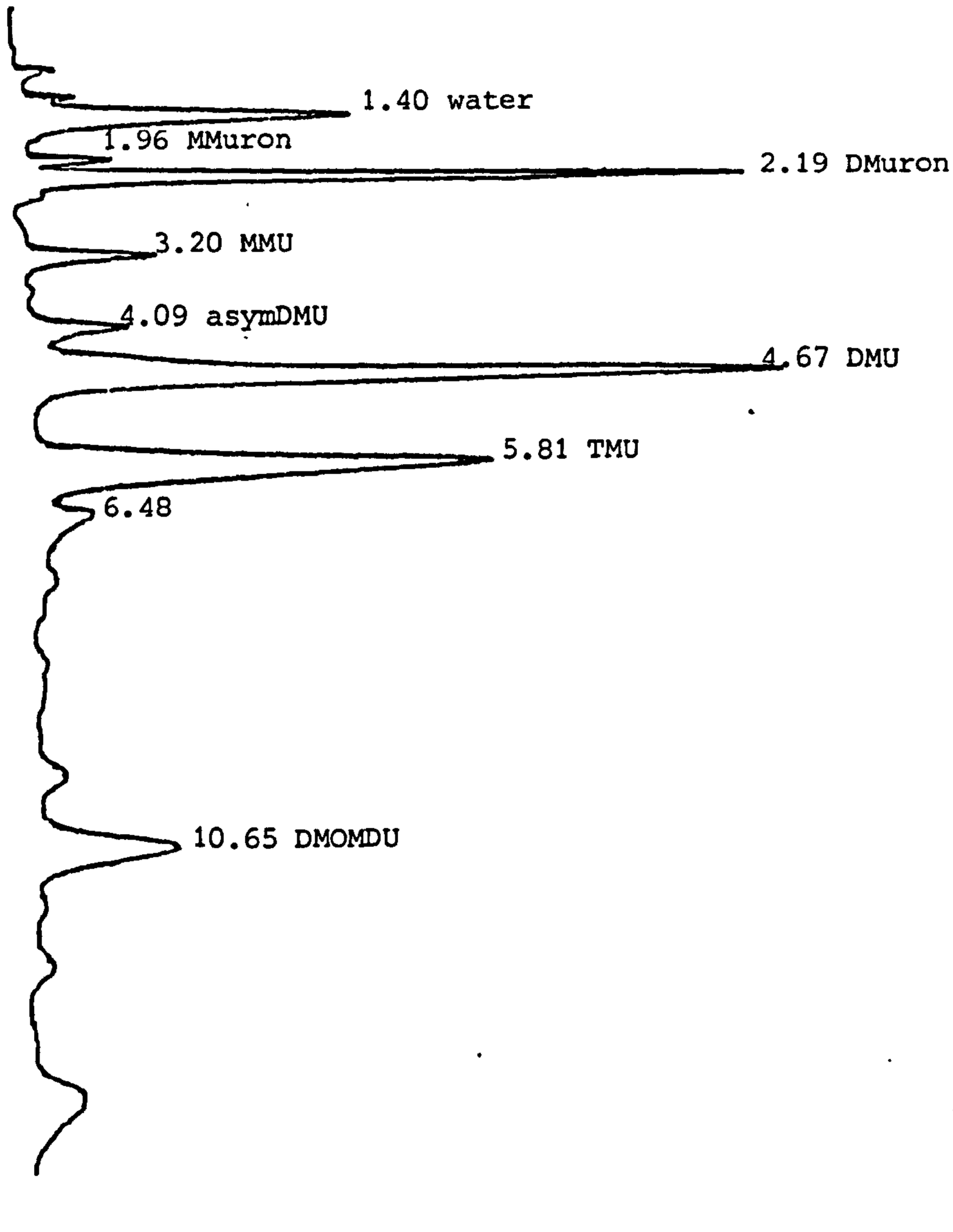


Fig.24. Chromatogram showing substantial uron formation.

Discussion and Conclusions

The following points about this series of experiments should be noted.

1. The quantitative results obtained at pH 12 are somewhat suspect since this high level of alkalinity is difficult to maintain due to formate ion formation produced by the Cannizzaro reaction.

$$2\ HCHO \xrightarrow{OH^-} HCOOH + CH_3OH$$

2. The levels of uron in Table 5 (P.89) are the sum of the mono- and dimethylolurons (XXI and XII).

Monomethyloluron (XI), however, was only produced in significant amounts in the reaction at pH 10 in the urea:formaldehyde 1:2.5 molar ratio reaction.

The following conclusions can be drawn.

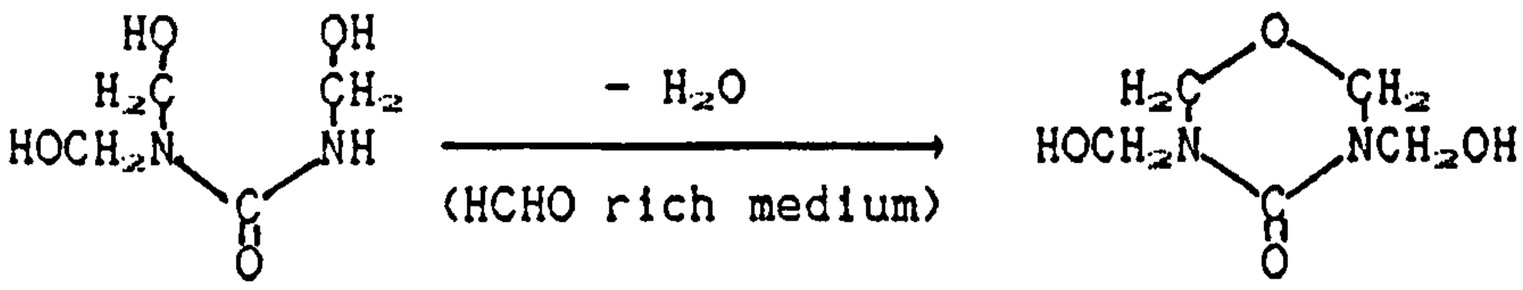
i. Very little uron is formed in any of the reaction mixtures during the initial reaction which, in this investigation (in batches of about 50g) raised the temperature of the reactants to about 60°C.

ii. The combination of high pH (10 and over) and a low urea:formaldehyde molar ratio of <1:3, was necessary for significant uron formation.
At pH 8 the formation of urons was very low and not affected by a concentration step, whereas at pH 10, the uron yield was high. To obtain maximum uron production as quickly as possible however, the pH should be 12 when approximately 70% of the urea is converted to DMuron (XII) in 20 minutes at 100°C.

iii. At pH 12 and with a urea:formaldehyde molar ratio of 1:2.5 there is a rapid reaction to form insoluble high molecular mass material.

iv . Highly alkaline mixtures of low urea:formaldehyde molar ratios e.g. pH 12 and molar ratio 1:4.5, showed another interesting property, namely that after the initial reaction had taken place and the temperature had risen to about 70°C, only about 60% of the reactants were present as low molecular mass compounds and the uron content was low, whereas on heating to 100°C for 10 minutes most of the high molecuar mass material was converted to low molecular mass dimethyloluron (XII).

v. In the original Kadowaki[33] synthesis of urons, a concentration stage was introduced. The reason for this step being included by Kadowaki in his preparation could be either to remove water prior to etherification with methanol to form the dimethoxymethyl compound (XXXVIII) or to encourage the formation of the uron ring by elimination of water as shown below.



III XII

Judging by the effect of concentration of mixtures having urea:formaldehyde molar ratios of 1:4.5 and 1:2.5 at pH 8, it appeared that removal of water from the reaction mixture played no part in the cyclisation step. The limited cyclisation that occurred during dehydration was likely to be a result of holding the reaction mixture at a slightly elevated temperature (about 40°C) for an extended time period.

3. THE FORMATION OF URONS IN ACID UREA-FORMALDEHYDE SYSTEMS

Introduction

Various Borden companies throughout the world produce resins for manufacturing chipboard which have low formaldehyde release characteristics and are called "LPC" resins. This acronym is said to stand for "low pH condensation". The general method of preparation is to charge all of the formaldehyde into the reaction vessel, to adjust the pH to a suitable value (<2.0), using a strong acid such as 50% sulphuric acid, to add a relatively small amount of the urea, (approximately 10% of the total) and then to react at about 70°C until the solution clears. This occurs quite quickly, and a further amount of urea (again about 10%) is then added. This sequence of events is continued until all of the urea has been added. The reaction mixture is checked after each urea addition to ensure that all the urea has dissolved and the reaction mixture is clear. The fact that the resin clears after reacting for a short time indicates that solubilising groups, small molecules or both are being formed in the resin. Investigations reported in section IIIC (P.71) have shown that triazinones can be formed in urea-formaldehyde reaction mixtures quite quickly if the molar ratio and pH are favourable but other evidence[59] suggests that the solubilising groups are urons.

The present investigation sets out to identify the course of the acid condensation and to discover some of the criteria involved. Because the manufacturing process for "LPC" resins involves the repeated addition of relatively small amounts of urea, only the reaction which occurs during the initial addition of urea, was investigated, using a typical urea:formaldehyde molar ratio of 1:8.

Experimental

The general procedure adopted was as described in II B3 (P.28) and III B2 (P.55). When a phosphoric acid-phosphate buffer system was used to control pH then the high concentration of ionic material in the analyte caused the acetonitrile:water eluting solvent to separate into an aqueous and a non-aqueous layer. It was found experimentally that this could be prevented by deionising with a small amount of mixed cationic and anionic exchange resins or better still to control the pH using 10% aqueous p-toluenesulphonic acid solution instead of phosphoric acid.

The first reaction mixture to be studied was urea:formaldehyde molar ratio of 1:8 at pH 2. During the reaction two new compounds were produced and to obtain pure samples of these from the chromatographic column (suitable for spectrographic analysis), it was necessary to weaken the eluting solvent to give greater separation of the peaks of interest. Several solvent systems and columns were tried in an attempt to improve the separation of the peaks from themselves and from dimethyloluron (XII). Finally, samples were collected from the aminopropyl column using acetonitrile:water (65:1) as the eluting solvent. When the separated peaks were re-examined by analytical chromatography it was found that they were still rather impure. A substantial improvement in the purity of the first compound (Peak 1, Fig.25; P.95) was made by extracting the main impurity, dimethyloluron (XII), with methanol thus giving a sample that was about 90% pure. The second compound (Peak 2, Fig.25; P.95) was about 70% pure.

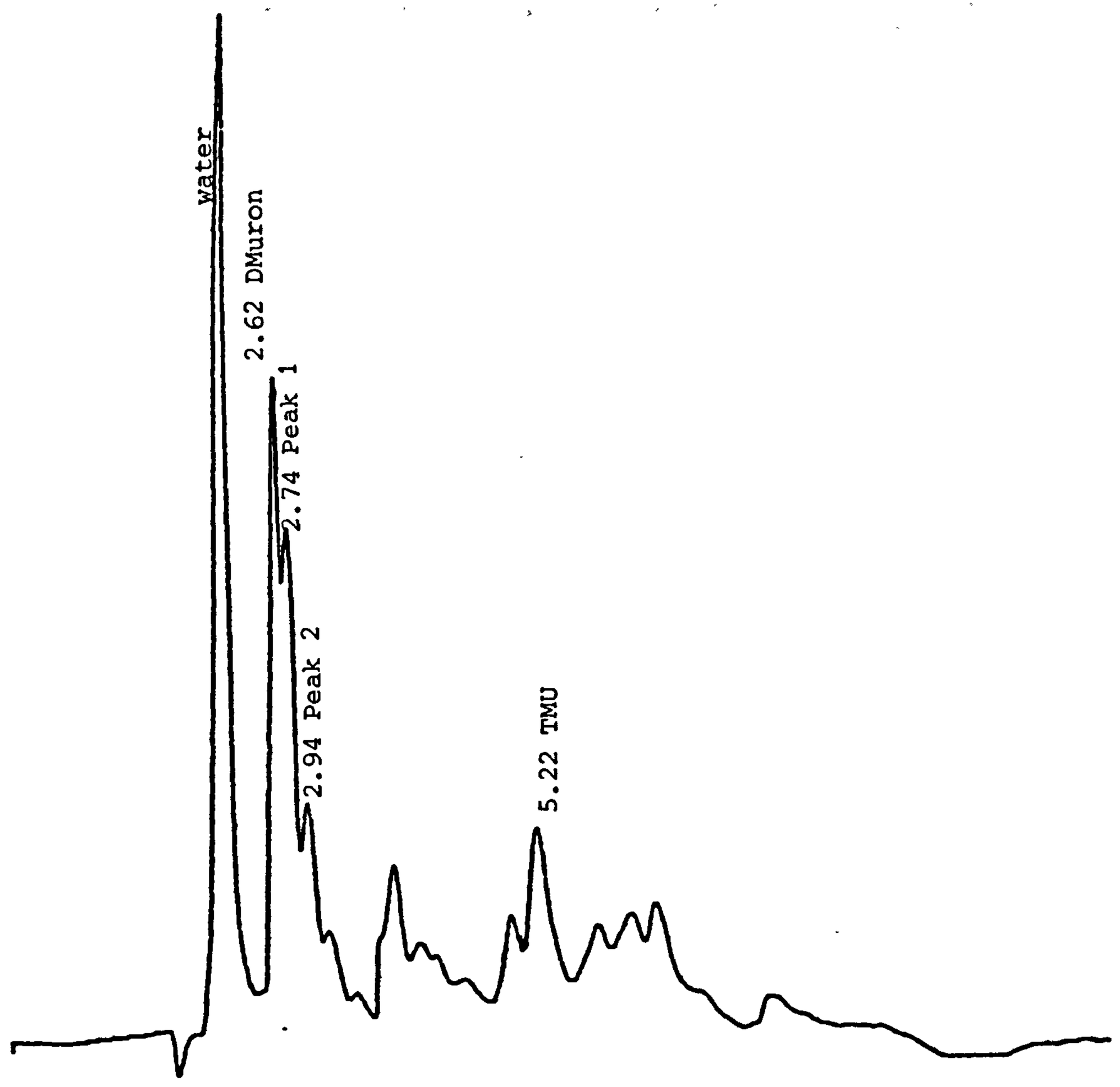
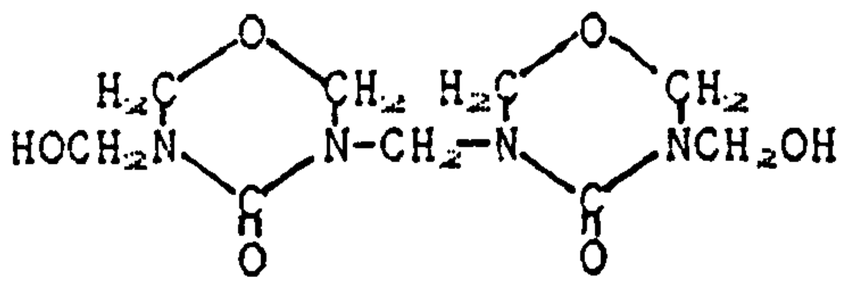


Fig.25. Chromatogram showing the formation of methylene urons.

Results

1. Identification of unknown materials.

The two so far unidentified compounds isolated by chromatography from the urea-formaldehyde reaction mixture, molar ratio 1:8 at pH 2 (Fig.25; P.95) were analysed by infra-red and ^{1}H-nmr spectroscopy (Figs.26-30; Pp.97-101). The infra-red spectra showed that both compounds had a large peak at 810cm^{-1} and since all urons so far examined have absorbed strongly at this frequency, this was good evidence that cyclic ether structures were present. The ^{1}H-nmr spectrum of Peak 1 (Fig.26; P.97) had three singlets in the 4.5 to 5.0ppm range, a doublet at 4.64ppm and a triplet at 5.75ppm. A decoupling experiment showed that the triplet, as expected, arose from hydroxyl protons in methylol groups and the doublet from the methylene protons in the methylol groups. The singlets arose from methylene groups in the uron ring and possibly from methylene groups linking uron structures. One of the singlets had only half the integral of the other two and could be considered to arise from a methylene group between two uron residues. The compound dimethylolmethylenediuron (DMmethylenediuron XXXIX) fitted the spectroscopic evidence so far.



XXXIX

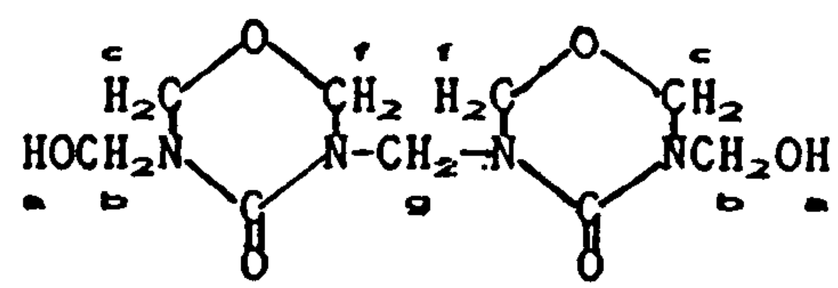


Fig.26. ^{1}H-nmr spectrum of dimethylomethylenediuron (XXXIX), solvent DMSO-d_6.

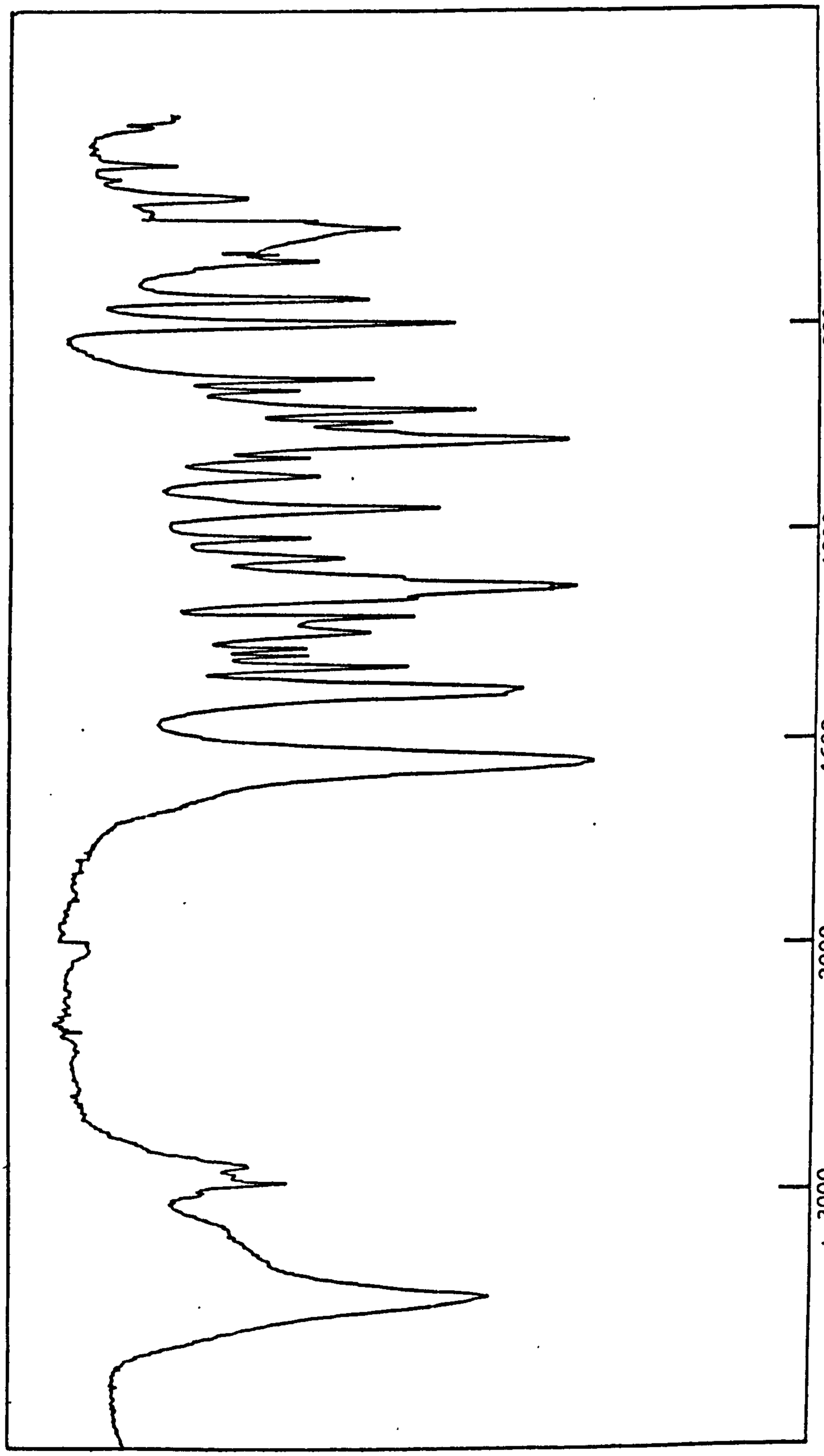


Fig.27. Infra-red spectrum of dimethylolmethylenediuron (XXXIX).

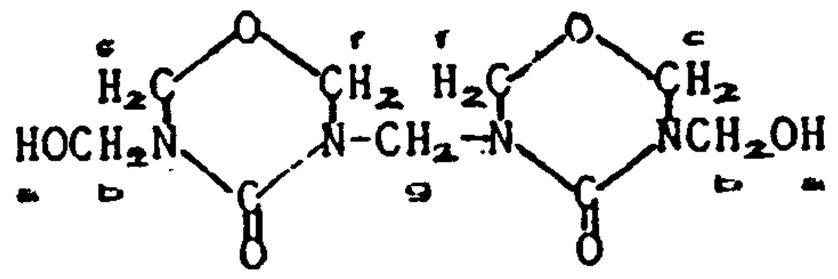


Fig.28. ^{13}C-nmr spectrum of dimethylolmethylenediuron (XXXIX).

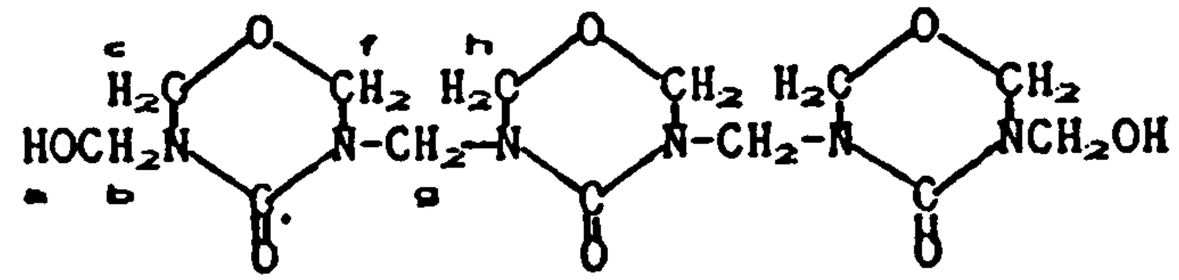


Fig.29. ^{1}H-nmr spectrum of dimethylodimethylenetriuron (XXXX), solvent CH_3OH-d_4

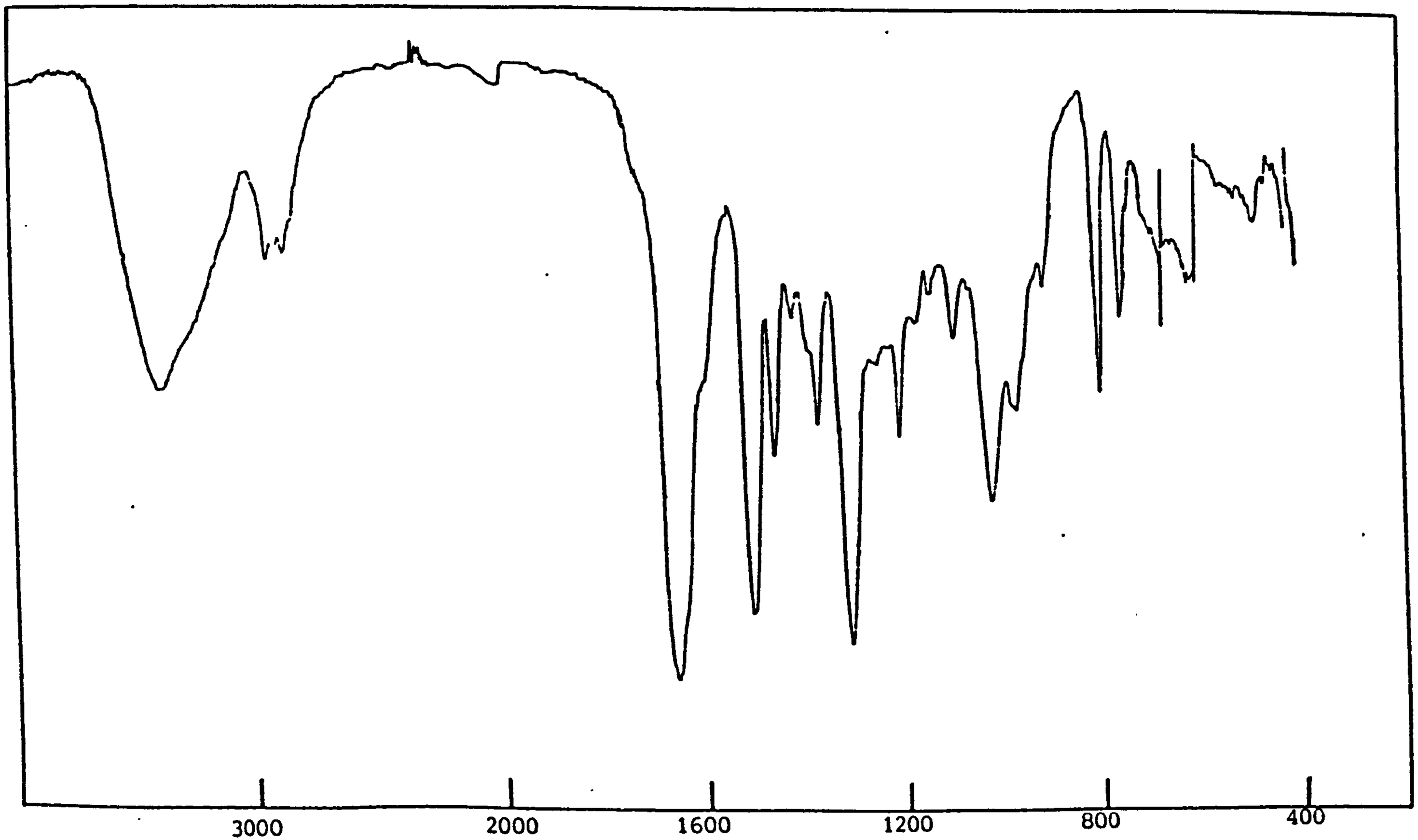
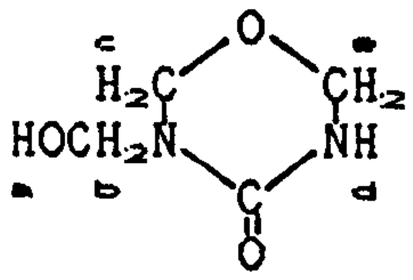
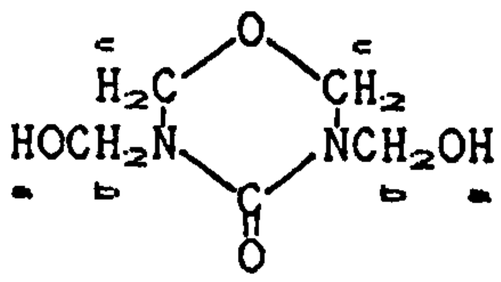
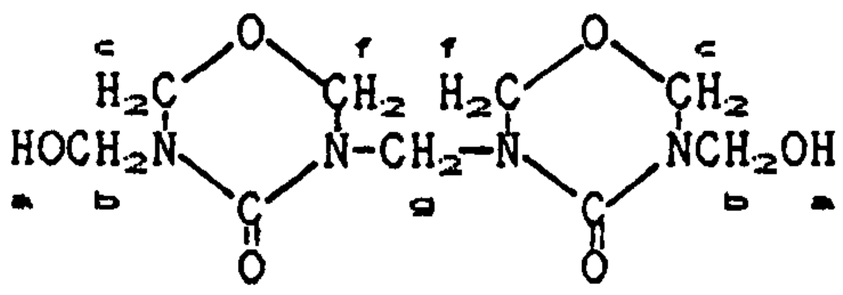


Fig.30. Infra-red spectrum of dimethylodimethylenetriuron (XXXX).

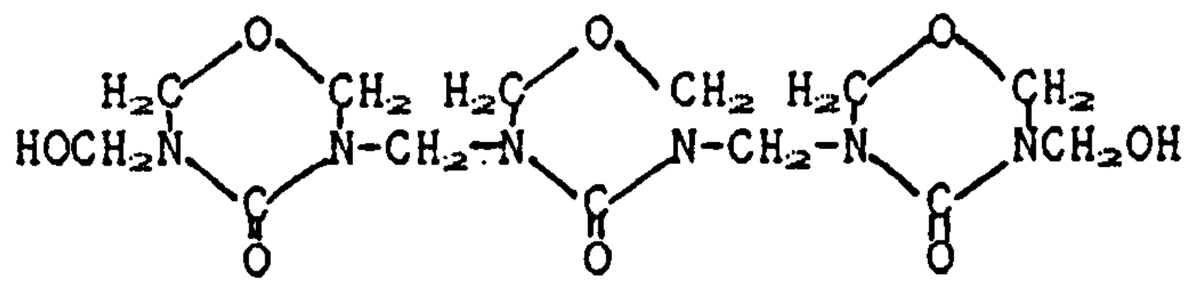
A detailed analysis of the ^{1}H- and ^{13}C-nmr spectral absorbances for substituted urons is given below,

Compound		^{1}H			^{13}C
	ppm	H	Integral	Splitting*	ppm
	5.63	a	1	T	-
	4.62	b	2	D	-
	4.87	c	2	S	-
	7.12	d	1	D	-
	4.70	e	2	S	-
	5.72	a	1	T	-
	4.65	b	2	D	66.9
	4.88	c	2	S	77.4
	-	d	-	-	-
	-	e	-	-	-
	5.75	a	1	T	-
	4.64	b	2	D?	66.9
	4.87	c	2	S	77.4
	-	d	-	-	-
	-	e	-	-	-
	4.94	f	2	S	78.6
	4.68	g	1	S?	53.3

* S=singlet, D=doublet, T=triplet

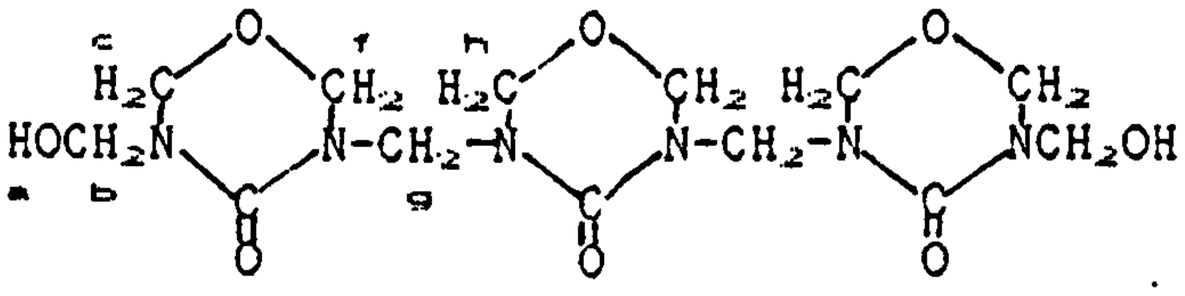
Comparison of the above data with the ^{1}H-nmr spectra of other uron compounds, namely dimethyloluron (XII; Fig.6; P.34) and monomethyloluron (XI; Fig.10; P.37), revealed exactly which methylene groups were associated with each singlet peak. Confirmation that the chromatographic peak was indeed due to dimethylolmethylenediuron (XXXIX) was obtained from a ^{13}C-nmr spectrum (Fig.28; P.99) which showed four methylene carbons. The small peaks in this spectrum are due to impurities. The spectrum, however, was easy to interpret. Two peaks at 66.9ppm and 77.4ppm corresponded exactly with the signals observed in DMuron (XII; P.33) attributable to carbon attached to hydrogen (c) in the ring and to carbon attached to hydrogen (b) in the methylol group. The low field signal at 53.3ppm was judged likely to arise from the methylene linkage carbon attached to hydrogen (g) and the final signal at 78.6ppm was attributed to the other ring carbon attached to hydrogen (f).

It was then suspected that Peak 2 could be the next member of the homologous series namely dimethyloldimethylenetriuron (XXXX)



XXXX

and the five singlets in the ^{1}H-nmr spectrum (Fig.29; P.100) were assumed likely to arise from the five different methylene groups in the above compound. A tentative assignment of the peaks using the knowledge gained from the detailed analysis of the ^{1}H-nmr spectrum of Peak 1 (Fig.26; P.97) was made as follows.



ppm	H	Integral	Split*
-	a	-	-
4.78	b	1	S
4.93	c	1	S
-	d	-	-
-	e	-	-
4.98	f	1	S
4.90	g	1	S
4.99	h	1	S

The hydroxyl hydrogen was not seen because the sample was run in CD_3OD. The lack of splitting in (b) is similarly explained. Insufficient material was available for a ^{13}C-nmr spectrum.

ii. The reaction at pH 2.

The condensation reaction at pH 2 was studied in some detail and the following results were obtained.

As the urea dissolved in the acid formalin, the temperature rose and at about 40°C, the reaction mixture became cloudy.

Chromatographic analysis showed that the sample contained

urea	0.4%
MMU (I)	1.5%
DMU (II)	1.1%
DMMDU (VI)	0.8%

plus several small peaks.

The total chromatographable material amounted to about 5% which was equivalent to only about 25% of the initial urea charge.

As the reaction proceeded the temperature rose to 85°C whereupon the mixture became clear. Liquid chromatographic analysis showed the low molecular mass fraction consisted of the following.

DMuron (XII)	2%
DMU (II)	0.4%
Unknown	2%

plus several small peaks.

Again only about 25% of the urea was in a form which gave peaks on the chromatogram. A third sample was taken when the temperature had risen to 95°C. Liquid chromatographic analysis showed the following.

DMuron (XII)	12%
Unknown	1.5%

plus 3 small peaks

The total chromatographable material was about 15% which corresponded to about 50% of the urea charge.

The final sample was taken after heating at 100°C for 10 minutes.

Liquid chromatograhic analysis showed the following.

DMuron (XII)	5%
DMmethylenediuron (XXXIX)	6%
DMdimethylenetriuron (XXXX)	4%

plus other small peaks

The total chromatographable material was about 18% which corresponded to some 60% of the initial urea charge.

iii. The effect of pH on condensation.

Formalin at pH values ranging from 1.25 to 3.5 was reacted with urea (molar ratio urea:formaldehyde, 1:8) and all of the reaction mixtures became cloudy at about 60°C. Heating was continued to 95°C in a boiling water bath and the reaction mixtures were observed for clarity and tested for the formation of urons by chromatography.

The results are given below in Table 6.

pH of formalin	pH after urea addition	pH after 5 min at 95°C	Observations after 5 min at 95°C
3.5	3.9	3.8	Cloudy, no uron formed
2.5	3.7	3.3	Cloudy, no uron formed
2.0	3.4	2.9	Cloudy, no uron formed
1.5	3.0	1.9	Clear after 4 min, uron +ve
1.25	2.9	1.9	Clear after 4 min, uron +ve

Table 6. The effect of pH on condensation.

iv. The influence of the quality of formaldehyde and urea on the reaction at low pH values.

Three samples of formalin of varying quality and two of urea were reacted together. The formalin pH was adjusted to 1.5 (see P.94) and the molar ratio of urea to formalin was 1:8.

The formalin samples used had the following properties.

Sample A. Fresh formalin with very low levels of impurities manufactured with a silver catalyst.

Sample B. Moderately old formalin containing an average level of impurities manufactured with a metal oxide catalyst.

Sample C. Sample A with added methanol and aged at 70°C for 2 days to produce methyl formate and other impurities.

Two urea samples were used.

Sample 1) commercial "prilled" (5mm spheres) urea, high in impurities.

Sample 2) analytical reagent grade from BDH Limited.

The results are given in Table 7.

Sample		pH after	pH after	Time to clear
Formalin	Urea	urea addition	reaction	at 95°C
A	1	3.0	1.9	4 minutes
B	1	2.6	2.1	3 minutes
C	1	2.9	1.9	4 minutes
A	2	2.9	2.0	4 minutes

Table 7. Influence of quality of reactants on reaction rate.

Discussion and Conclusions

i. Identification of unknown peaks.

Nmr and infra-red spectra (Figs.26-30; Pp.97-101) of two compounds, occurring in substantial amounts in the low pH condensation reaction, have been obtained. The spectra have lead to the identification of these materials as dimethylolmethylenediuron (XXXIX) and dimethyloldimethylene-triuron (XXXX). Both compounds were unknown before this research was carried out.

ii. The general reaction at low pH.

There is now no doubt that the water solubilising groups produced in this type of reaction are urons. In the reactions studied, the urea was added to the acid formaldehyde and a rapid reaction was observed. Most of the reaction products were of such a high molecular mass that they were out of the range of liquid chromatography and the small amount of chromato-graphable material consisted of methylolureas. The conclusions to be drawn from these observations are that a rapid addition reaction of the urea and formaldehyde took place producing methylolureas which then condensed rapidly together forming large molecules.

As the temperature was raised a small amount of dimethyloluron (XII) was formed accompanied by an even smaller amount of a material not previously observed in urea-formaldehyde reactions and not identified (Fig. 31; P.108). The peak at 5.18 minutes could be confused with trimethylolurea (III) but the shape is not consistent with this assumption (too symmetrical, cf. TMU (III) in Fig.12; P.42) and it is not likely that TMU (III) would occur in this sample when it was not present in the sample

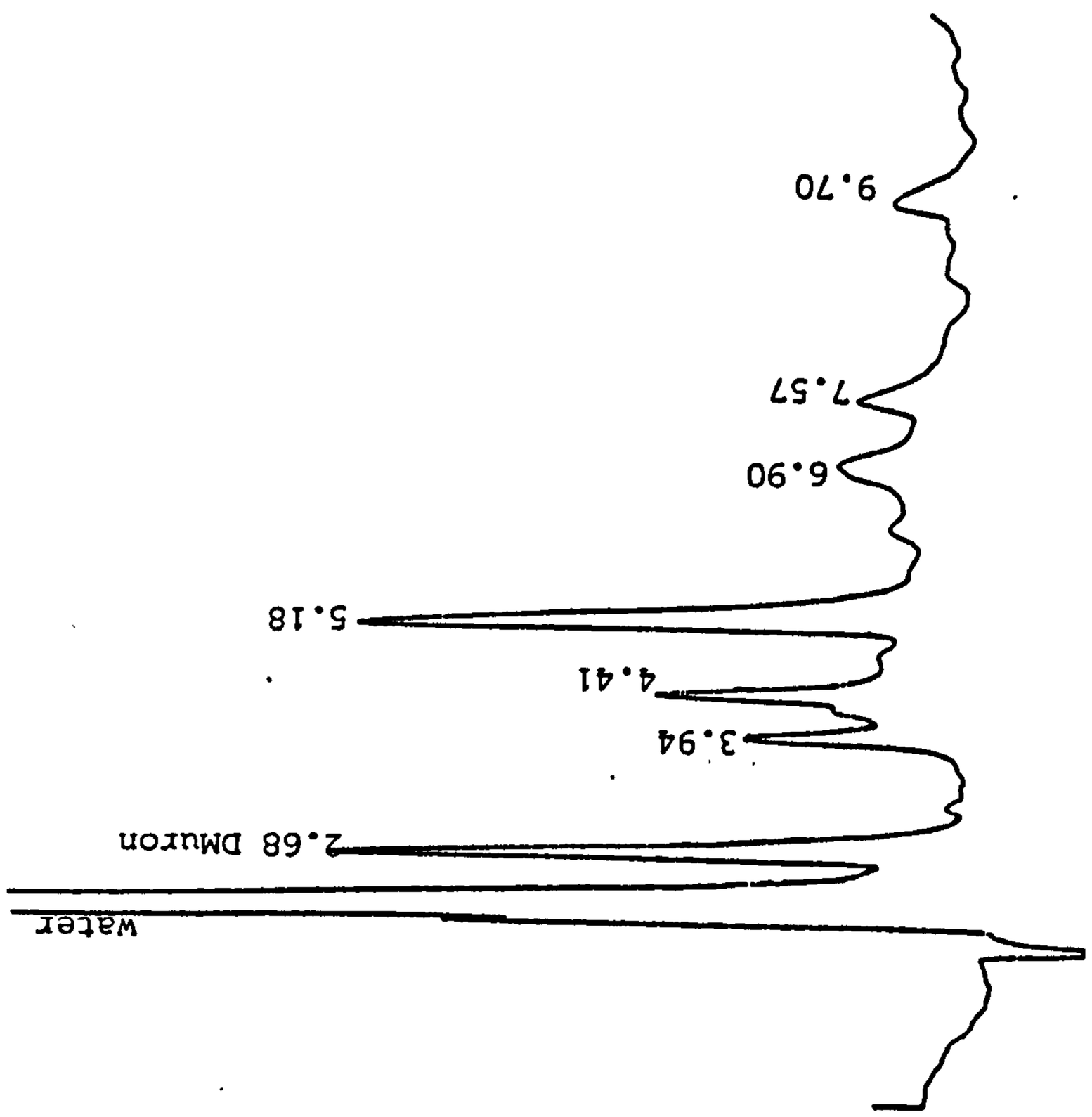
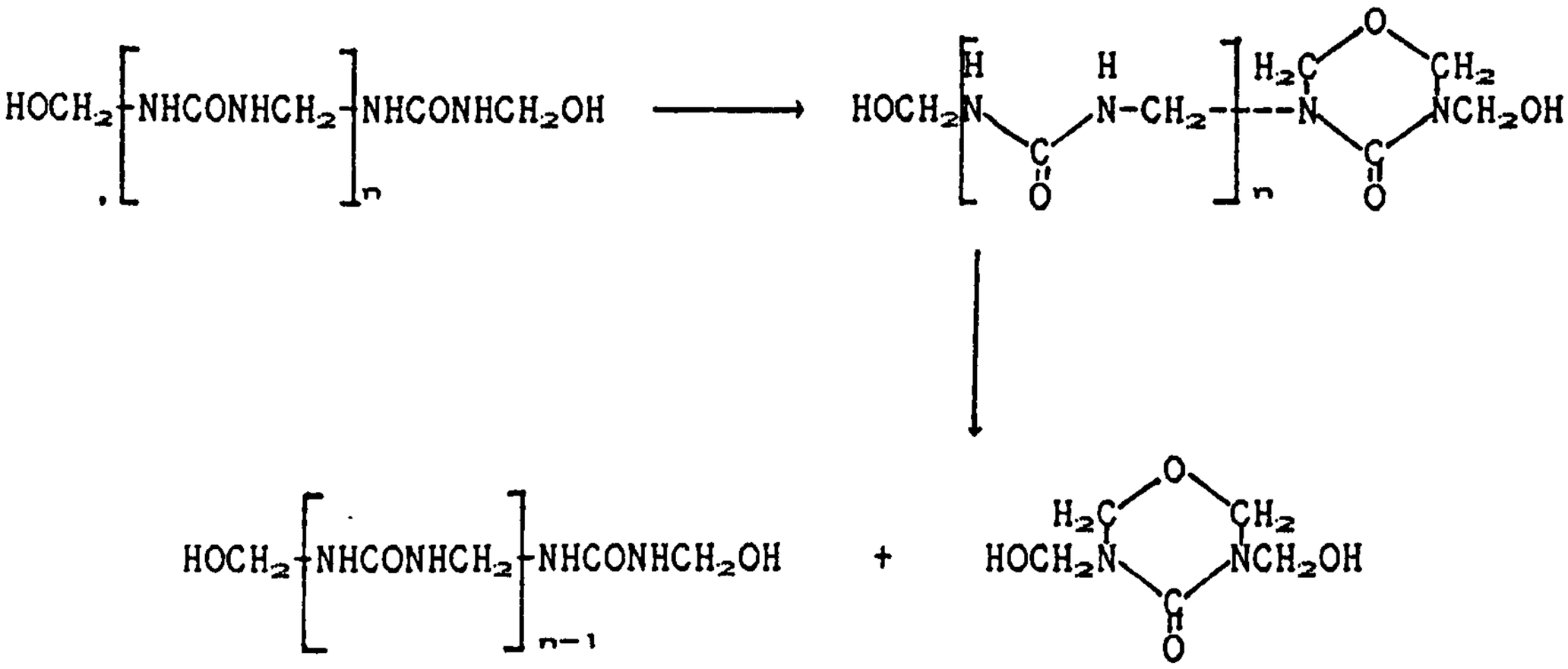


Fig.3.1. Urea-formaldehyde reaction product; U:F 1:8, pH 2, heated to 85°C

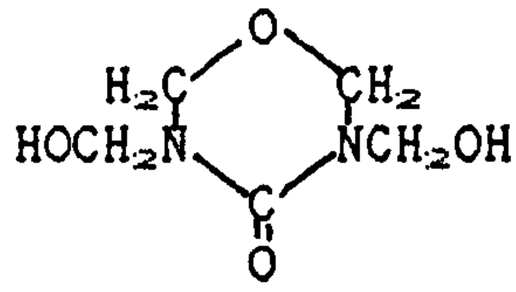
taken a short time before, i.e. when the material had been subjected to less condensation. It thus seems possible that this material is a methylolated uron-urea fragment indicating that the high molecular mass material originally present has reacted with the large excess of formaldehyde which has converted the urea residues into uron rings. It would seem that as this transformation takes place, the chains fracture giving segments of ever decreasing size.



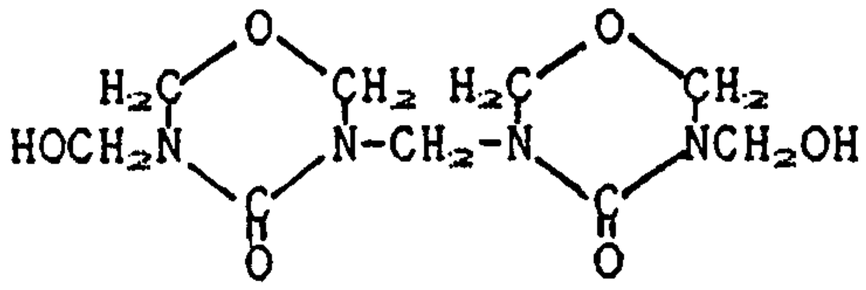
XII

On raising the temperature to 95°C, analysis showed that the amount of dimethyloluron (XII) was increasing dramatically and the low molecular mass material had increased to account for 50% of the original urea charge. Analysis of the final sample, taken after heating the reaction mixture to 100°C for 10 minutes, indicated that most of the original urea was in the form of small molecules and that the dimethyloluron level had dropped considerably forming dimethylolmethylenediuron (XXXIX) and dimethyloldimethylenetriuron (XXXX).

It was evident therefore that at low pH values, after the rapid hydrolysis of the urea-formaldehyde chains and simultaneous formation of uron structures, a relatively slow reaction occurred producing a methylolated poly(methyleneuron) oligomeric series of compounds.

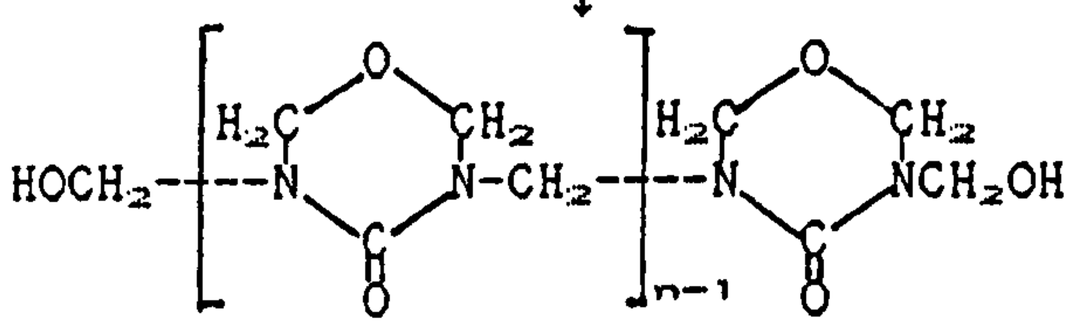
n 

XII



n/2

XXXIX



iii. The effect of pH on condensation.

Chromatography showed that clarification of a solution occurred at the same time as uron formation commenced and for some of this work, the clarification of a sample was used as a uron formation indicator. It seemed that a pH of 2.0 was very critical in the condensation of urea with formaldehyde to form urons. Above pH 2.0, uron formation was negligible, whereas below pH 2.0, uron formation occurred rapidly.

It was observed that the initial pH of the formaldehyde solution had a marked effect on the pH drop after the urea was added and had reacted for five minutes at 95°C. The degree of the pH fall was greater the lower the initial pH. For example a formalin solution at pH 2.5, rose to pH 3.7 on addition of the urea and then dropped to pH 3.3 on reaction whereas a solution at pH 1.5 rose to pH 3.0 when the urea was added and fell to pH 1.9 after the reaction had occurred.

An explanation for this behaviour cannot be offered at present and as this aspect of urea-formaldehyde chemistry can only be considered of fringe interest to this study a further investigation was not undertaken.

iv. The influence of the quality of both the formalin and the urea on the formation of urons.

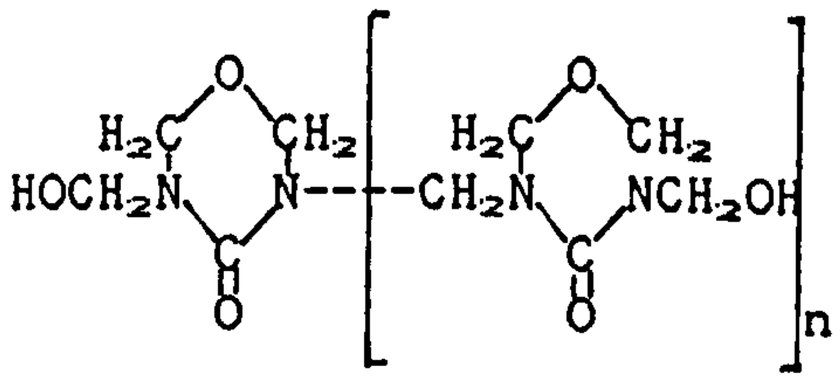
It seems that the levels of impurities in the urea and formaldehyde affected the pH to which the reacting compounds rose on mixing (Table 7; P.106). The pH after the reaction had proceeded for a short time at 95°C, however, seemed little different whether the level of impurities was high or low. This fact will make the manufacture and control of urea-formaldehyde resins at low values of pH easier than was at one time thought.

4. THE REACTIONS OF SIMPLE URONS

Introduction

It has now been clearly established (*vide supra*) that under conditions of extreme pH and a high molar ratio of formaldehyde to urea, dimethyloluron (DMuron; XII) can be formed in significant amounts and it is not difficult to control the reaction conditions so that almost a quantitative yield is produced from the urea (N.B. formaldehyde always has to be in considerable excess).

Almost nothing is known at present of the reactivity of the simple urons except that under low pH conditions in the presence of excess formaldehyde, DMuron (XII) will undergo self condensation reactions (see P.109) to form an oligomeric series of methyleneurons.



It is, however, of considerable importance to the resin chemist to ascertain whether the urons (typified by DMuron; XII) will react with urea compounds and if reaction does occur, then to determine the mechanisms operating and the products of the reactions.

Experimental and Results

Previously (II B3(7); P.33), small amounts of pure DMuron (XII) were obtained by chromatographically separating the compound of interest from a urea-formaldehyde reaction mixture but to carry out a study of the

reactions of DMuron (XII), it was necessary to obtain the compound in larger quantities.

i. Preparation of dimethyloluron (DMuron; XII)

The method of Kadowaki[39] which gives DMuron (XII) in good yield, but containing large quantities of formaldehyde and water is described earlier in the text (P.33) and by following this procedure, crude DMuron (XII) (about 30g) was obtained. It had been observed previously when preparing this compound, that in the presence of relatively small amounts of formaldehyde and water, it was impossible to induce it to crystallise out of solution. A programme of work was undertaken to attempt to remove the formaldehyde by chemical means from the crude DMuron (XII). The following investigations were made.

a. Removal of formaldehyde with alkaline hydrogen peroxide. The formaldehyde was easily converted into formate but the alkaline conditions produced a considerable amount of MMuron (XI) by destructive hydrolysis/oxidation of one of the methylol groups of the DMuron (XII). Some high molecular mass material was also produced further complicating the purification. For these reasons, it was considered unlikely that substantial amounts of DMuron (XII) would easily be obtained by this approach.

b. Removal of formaldehyde with sodium sulphite. Sodium sulphite did not dissolve in an acetonitrile solution of the crude DMuron (XII) and in the solid state would not react with the formaldehyde. An aqueous slurry of sodium sulphite only removed about 50% of the free formaldehyde over a period of two days.

A considerable amount of time was spent unsuccessfully attempting to remove the formaldehyde chemically and finally the following procedure was adopted to produce about 1g of DMuron (XII), purity about 85%.

The crude DMuron (XII) (30g), containing about 25% unreacted formaldehyde, was separated from high molecular mass compounds and most of the di- and trimethylolurea (II and III) by extracting several times with acetonitrile:chloroform (1:1) (200ml). The solvent was removed in a rotary evaporator giving about 20g of DMuron (XII) still containing most of the unreacted formaldehyde but now fairly pure with respect to other urea compounds. The extracted material was placed in large (1,000ml) beakers in films not exceeding 5mm in depth and jets of air were blown over the surfaces for up to 4 weeks to remove the excess formaldehyde. After this time the crude DMuron (XII) had acquired the consistency of a semi-solid and all of the fractions were bulked together and stored in a refrigerator for one to two weeks at 0°C. About 50ml of acetonitrile at 0°C was added and the DMuron (XII) was rapidly dispersed and filtered through a cooled sintered glass crucible. The solid DMuron (XII) was then recrystallised from acetonitrile (2g in 20ml) to give about 1g of material which was shown by chromatographic analysis to be about 85% pure, m.p. 82 - 86°C.

ii. Reaction of DMuron (XII) with urea.

a. Molar Ratio DMuron (XII):urea, 1:2 and pH 5.

DMuron (XII), (0.04g; 0.0025mol) and urea (0.03g; 0.005mol) were mixed with water (0.03ml) containing sodium dihydrogen phosphate (0.007g). The mixture was warmed gently and at about 40°C, a clear solution formed. At this point a sample was taken and further samples were taken as

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indicated in the results below. The samples were examined by the normal chromatographic method as detailed in III B2 (P.55).

	Retention time (min)	Identity	%
Sample 1 (on mixing at 40°C)	3.37	DMuron	27
(only two peaks were obtained)	3.48	urea	38
Sample 2 (at 95°C)	3.13	MMuron	8
	3.39	DMuron	20
	3.48	urea	36
	4.42	MMU	<1
	5.55	MDU	<1
	10.13	DMTU?	<1
Sample 3 (7min at 95°C)	3.01	uron	8
	3.12	MMuron	10
	3.39	DMuron	4
	4.01	uron compound?	1
	3.49	urea	15
	5.53	MDU	8
	10.13	DMTU?	4
Sample 4 (15min at 95°C)	3.00	uron	16
	3.12	MMuron	2
	3.39	DMuron	2
	4.02	uron compound?	2
	5.53	MDU	2
	6.73	?	1

Fig.32a and b (P.117) and Fig.33c and d (P.118) are chromatograms illustrating this experiment.

b. Molar ratio DMuron (XII): urea, 1:1 pH 8.3. The general conditions for the reaction were as described above (ii.a) but using disodium hydrogen phosphate (0.007g) to control the pH. Samples were examined chromatographically and the results were as follows.

Sample 1. (taken after 24h at room temperature)

No peaks other than the starting materials were visible.

Sample 2. (at 95°C)

The only peak visible other than starting materials was MMuron (XI).

Sample 3. (10min at 95°C)

There was no major reaction peak detectable and the main products were MMuron (XI) and MMU (I).

iii. Reaction of DMuron (XII) with DMU (II)

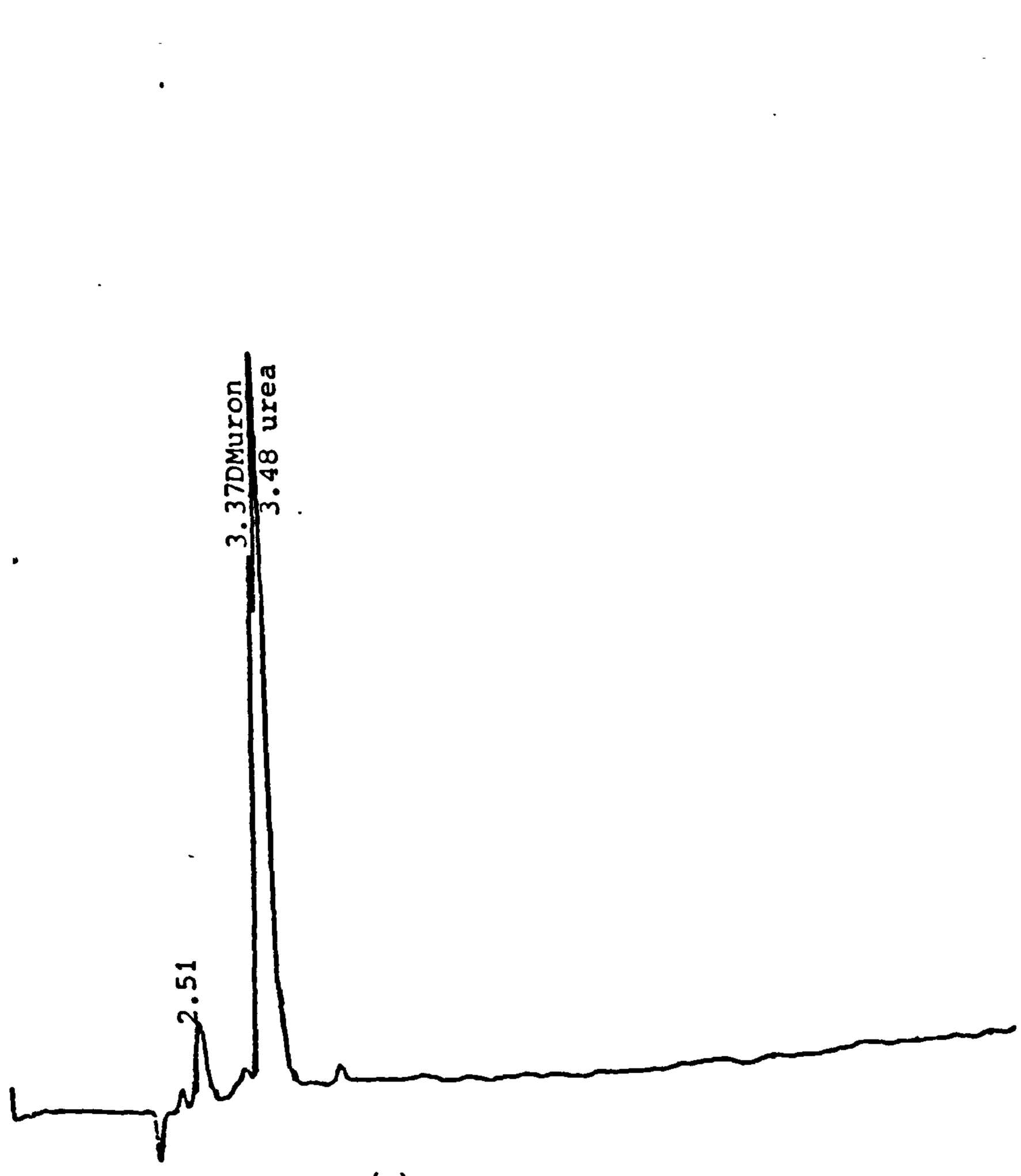
Molar ratio DMuron (XII):DMU (II), 1:1 and pH 8.3.

The reaction conditions were as described above (ii.b). No major reaction product peaks were observed. There were several peaks visible on the chromatogram which were too small to identify.

iv. Reaction of DMuron (XII) with DMU (II) and excess formaldehyde.

Molar ratio DMuron (XII):DMU (II):formaldehyde, 1:1:2 and pH 8.

The reaction conditions were as described above (ii.b). The results obtained were as follows.



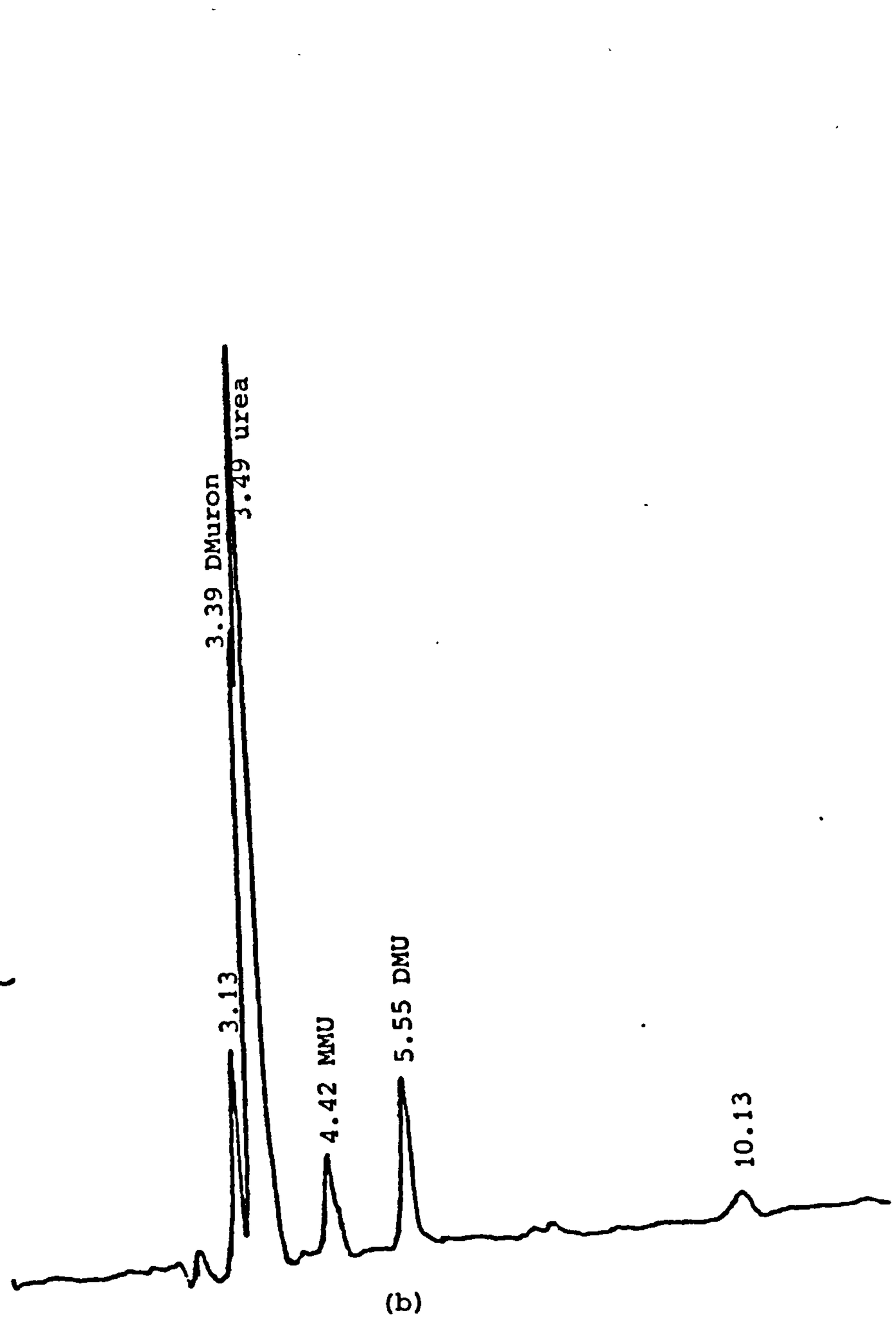


Fig.32. DMuron (XII) urea reaction, molar ratio 1:1, pH 5 (a) at 40°C; (b) at 95°C.

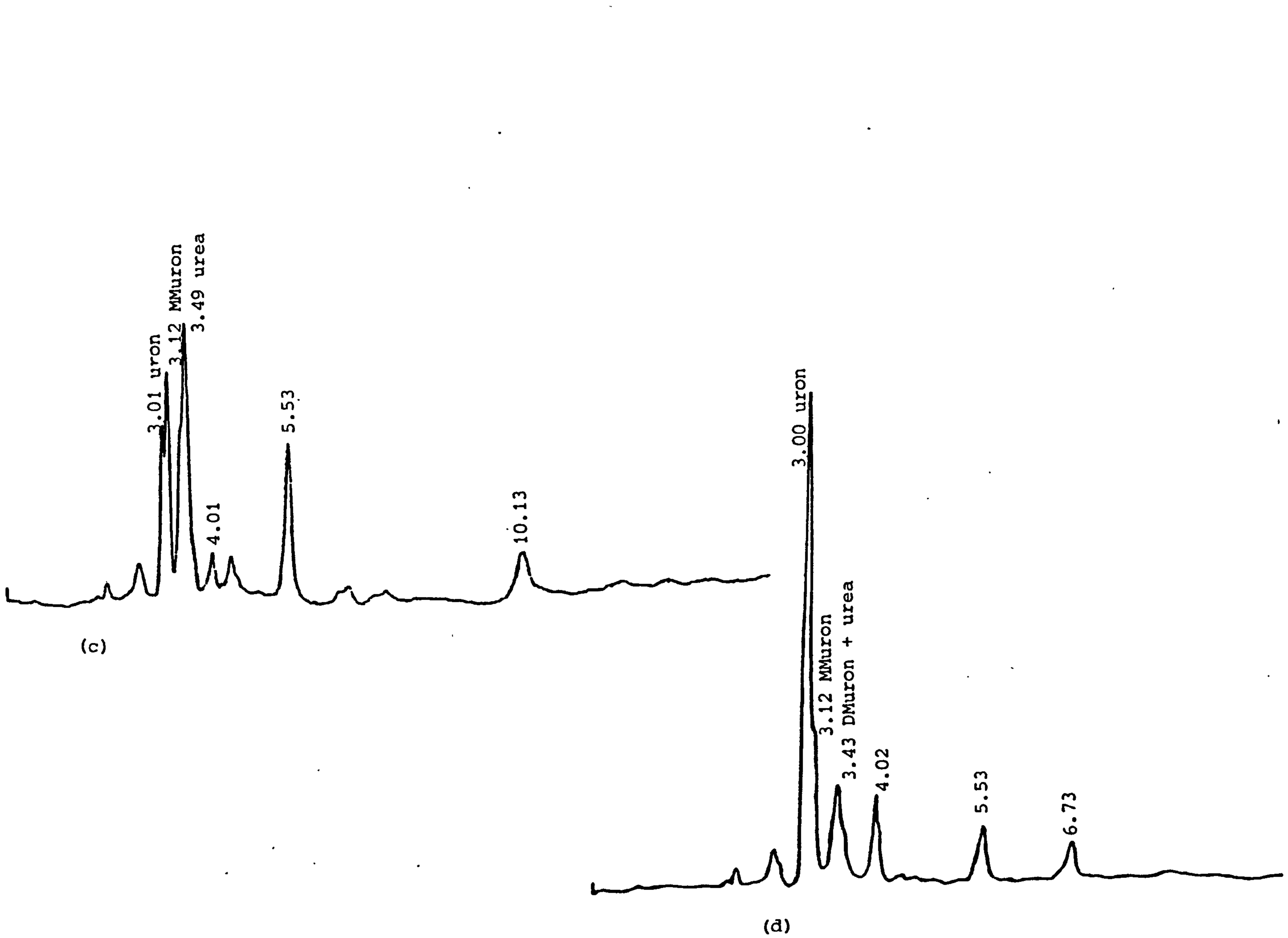


Fig.33. DMuron (XII) urea reaction, molar ratio 1:1, pH 5 (c) 7 min at 95°C. (d) 15 min at 95°C.

Sample 1. (10min at 95°C)

The DMuron (XII) concentration was almost unchanged; much DMU (II) had reacted and some TMU (III) had formed

Sample 2. (45min at 95°C).

The DMuron (XII) concentration was still high; all DMU (II) had reacted and no large unidentified peaks were observed.

Sample 3. (1h 15min at 95°C).

The chromatogram obtained was essentially the same as for Sample 2.

Discussion and Conclusions

1. Preparation of dimethyloluron (DMuron; XII).

A method has been developed for the purification of DMuron (XII) from the crude material. Chemical methods for removing the large excess of free formaldehyde were not successful but a method involving room temperature evaporation of unreacted formaldehyde was found satisfactory although extremely time consuming. The conditions however, were so mild that dehydroxymethylation of the DMuron (XII) did not take place to any great extent. The yield was very small <0.5% from the crude DMuron (XII) but it was considered likely that the level of impurities formed in the initial reaction, although relatively low, prevented to a large extent solidification of the DMuron (XII). It thus seems reasonable to suggest that one method of increasing the yield of DMuron (XII) would be to modify the method of synthesis to reduce the level of by-products produced in the formation of the formaldehyde rich DMuron (XII).

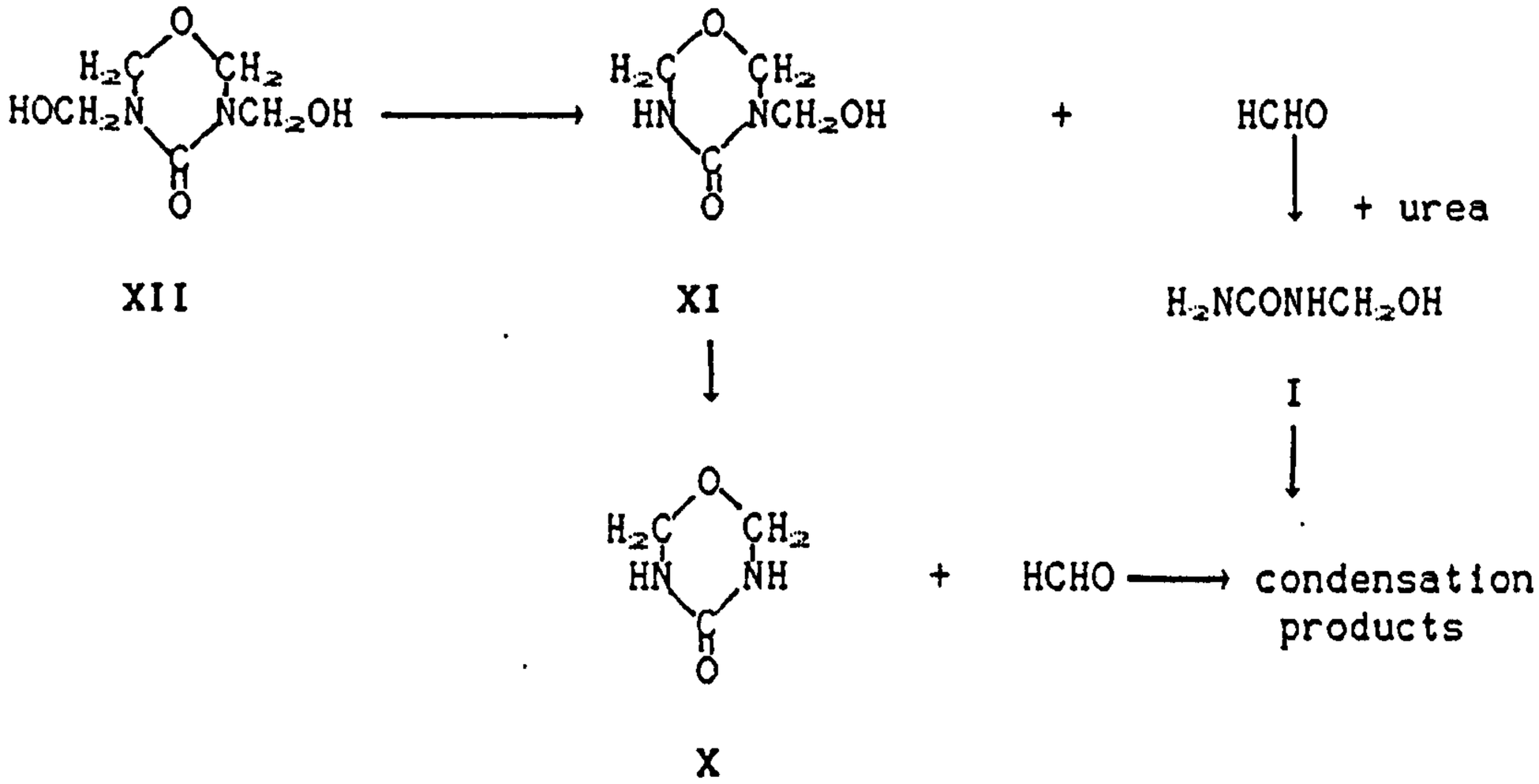
ii. Physical properties of DMuron (XII).

DMuron(XII) as the hemiformal i.e. in the presence of excess formaldehyde, is a viscous liquid. It was found to be miscible with acetonitrile in all proportions and to be very soluble in acetonitrile/ chloroform mixtures. On the other hand pure DMuron (XII) was found to be quite soluble (20 - 30%) in acetonitrile at room temperatures but at lower temperatures (0°C), its solubility was found to be much less (about 2%) which made crystallisation from acetonitrile solution possible if somewhat protracted, due to the tendency to form supersaturated solutions which produced solid DMuron (XII) only slowly. Efforts to recrystallise DMuron (XII) from more common solvents such as ethanol or ethyl acetate were unsuccessful

iii. The reactions of DMuron (XII) with urea.

It was considered likely that any reaction of the methylol group on the uron ring with urea or urea derivatives, would take place most easily under acid conditions (analogous to the reactions of DMU (II) at pH 5). It was obvious from the first experiment (P.114) that DMuron (XII) did not react easily with urea and no trace of a uron-urea reaction product was detected. Initially one molecule of formaldehyde was lost from the DMuron (XII) producing MMuron (XI). The formaldehyde reacted very quickly with the urea to form methylolureas which condensed together in a normal condensation scheme as shown in section III (P.60). Subsequently the second molecule of formaldehyde, combined as a methylol group, split off from the DMuron (XII) giving the parent uron compound, and the formaldehyde then reacted into the growing urea-formaldehyde molecules. The parent compound (uron; X) was observed to be relatively stable under these conditions and only slowly decomposed to give urea and formalde-

hyde. These reactions are illustrated in the scheme shown below and chromatograms obtained in this run are shown in Figs.32 and 33 (Pp.117 and 118) respectively.

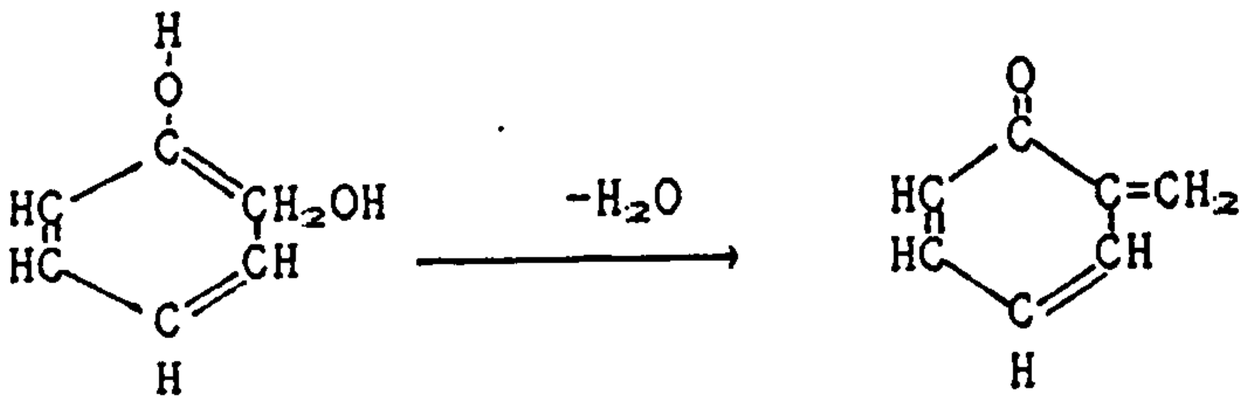


The reaction was repeated under alkaline conditions (pH 8.3) to see if by some unusual facet of urea-formaldehyde chemistry, a radically different reaction would occur at this higher pH. Once again the final products from the reaction were the parent uron compound (X) and high molecular mass urea-formaldehyde molecules. In an effort to prevent the dissociation of the DMuron (XII), two further experiments were performed,. the first using DMU (II) in place of urea and the second with an additional two molecules of formaldehyde. In both cases, no uron-urea compounds.were detected.

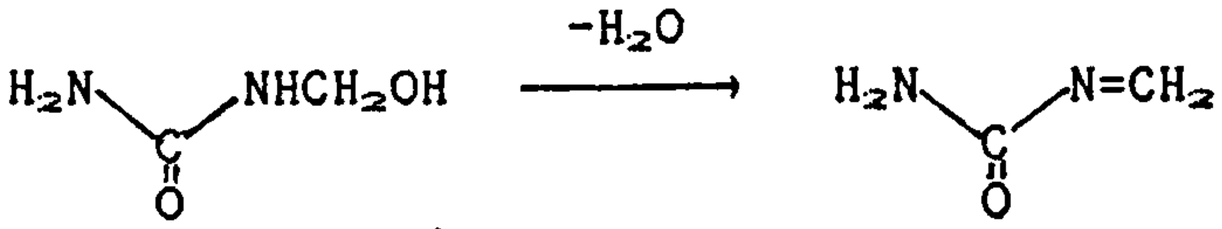
It was thus clearly demonstrated that the reaction of uron compounds with urea or methylolated urea compounds was, at best, only extremely slow under conditions of moderate pH and in the absence of a substantial excess of formaldehyde, hydrolysis of the DMuron (XII) occurred to a marked degree. This observation is of prime importance for chemists

involved in the preparation of commercial urea-formaldehyde compositions because it implies that the simple approach to the formation of uron modified urea-formaldehyde structures i.e. following the route described above, will not be successful. It seemed that the only simple route to uron-urea compounds was in the production of uron structures in large urea-formaldehyde molecules which had been synthesised in a separate reaction step. This aspect of the chemistry is described in section III D5 (P.123).

Urea-formaldehyde chemistry is in many respects similar to that of phenol with formaldehyde and the low level of reactivity of methylol-urons may be explained if the mechanism of urea-formaldehyde condensation is similar to the established mode of methylolphenol condensation. It has been clearly shown by Hultzsch[60], and supported by modern studies[61], that methylolphenols react through a quinone methide intermediate.



In a similar way, primary methylolureas could firstly form a methylene-imide as a reactive intermediate



Methylol groups attached to uron rings, however, cannot form an intermediate of this sort, and this could account for their greatly reduced reactivity.

5. THE FORMATION OF URON STRUCTURES IN UREA-FORMALDEHYDE CHAINS

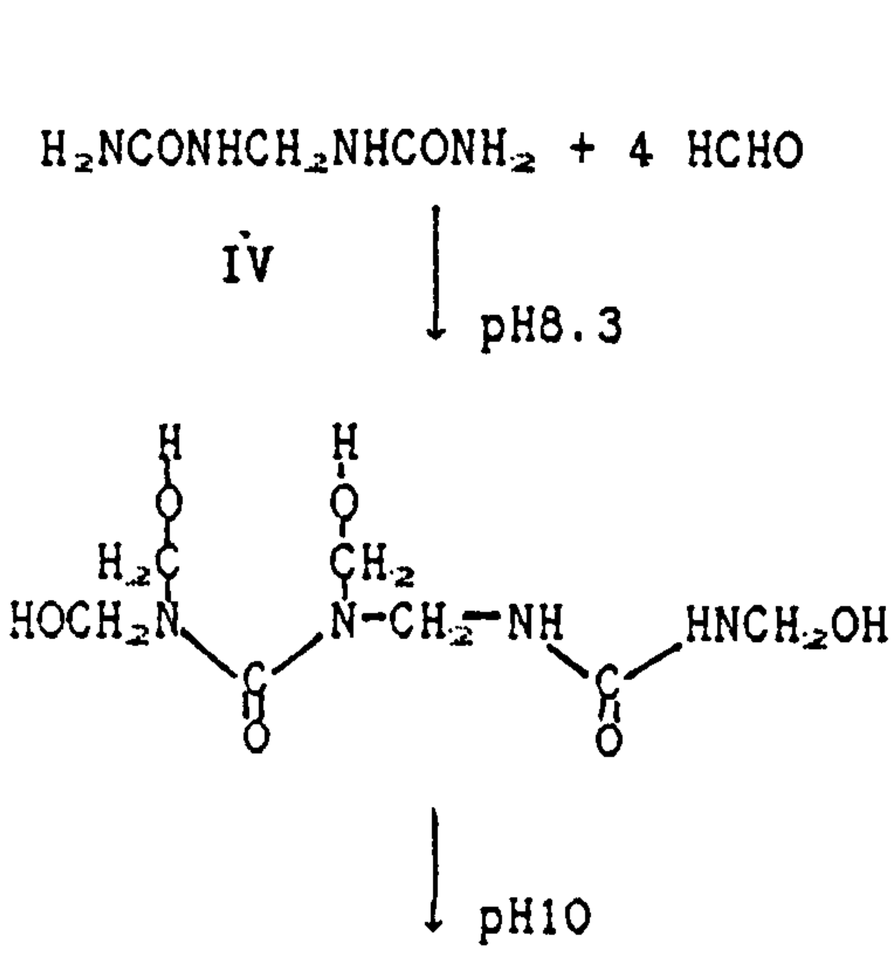
Introduction

It is highly desirable that the resin chemist in certain cases, should be able to introduce some uron structures into the urea-formaldehyde matrix, because the formaldehyde in the uron ring is stable to the relatively high temperature and low pH conditions, which can occur during the cure cycle. In addition the uron ring being difunctional and therefore unable to take part in crosslinking reactions, can act as a plasticiser in the urea-formaldehyde chain and confer unusual properties on the cured resin. As was shown in section III D4 (P.112), urons do not readily react with urea or urea derivatives such as DMU (II) and therefore an alternative approach to the formation of uron-urea compounds had to be adopted.

By reacting urea and formaldehyde (molar ratio 1:0.5) at pH 5, a series of linear urea-formaldehyde molecules are formed, typified by MDU (IV)[3], with predominantly methylene links between the urea groups. Increasing the pH to 8.3 and adding approximately a further four molar proportions of formaldehyde, leads to the replacement of a high percentage of amido hydrogen atoms by methylol groups, thus giving a mixture of methylolated methylenediurea compounds some of which should be suitable for the formation of uron rings at pH values of less than 2 or more than 10. However urea-formaldehyde polymers at pH values lower than 2 i.e. in one of the regions where urons normally form, in the absence of sufficent formaldehyde (normal conditions), rapidly produce insoluble, intractable, poly(methyleneurea) compounds corresponding to the cured state of the resin. As was demonstrated in section III D3 (P.93), a urea-formaldehyde

resin, prepared at pH 2 or less in the presence of large excess of formaldehyde, (consisting of urea-methylene-urea compounds), will first hydrolyse and then react further to give a good yield of DMuron (XII) which as previously mentioned, has been shown to be most unreactive towards urea and its methylol derivatives. At pH values of 10 and over, however, the urea-methylene-urea linkage is much more stable and it may be possible to readily form uron structures in the chain.

The method employed to detect this uronisation reaction, if indeed it occurred, was to use the most simple methylolated chain molecule MDU (IV), as the starting material. The following scheme shows the formation of a typical tetramethylolated methylenediurea from MDU (IV) and its conversion to the corresponding uron-urea compound (XXXXI).



XXXXI

Experimental

The chromatographic apparatus and procedure was as described in sections II B3 (P.28) and III B2 (P.55).

Methylenediurea (MDU; IV) (0.67g; 0.005mol) was reacted with 50% aqueous formaldehyde (1.2g; 0.02mol) (molar ratio MDU (IV): formaldehyde 1:4) in the presence of disodium hydrogen phosphate (0.2g) and water (0.5ml) at 90°C for one hour. A liquid chromatographic examination showed that the majority of the MDU (IV) had been converted into methylol derivatives after this time. The reaction mixture was then adjusted to pH 10 with 5M sodium hydroxide solution and was further heated at 95°C for two minutes. A sample was taken and examined by liquid chromatography.

Results and Discussion

Figs.34 (P.126) and 35 (P.127) are chromatograms illustrating the methylolation of MDU (IV) and the uronisation of the methylolated MDU respectively. Examination of the chromatogram of the methylolation step showed that the amount of MDU (IV) remaining after the reaction with formaldehyde was minimal and methylolated MDU compounds such as DMMDU (VI) and two TMMDU isomers (probably XXXI and XXXII) could be identified.

When the pH was raised to 10 and the reaction mixture was heated at 95°C for two minutes, three major peaks eluting early in the chromatogram, (peaks 1, 2 and 3. Fig.35; P.127) were observed, which could not be identified by comparison of their retention times with those of known compounds. Other peaks eluting later, were also quite different from the well known compounds described at length in section II B (P.41) and the peaks previously attributed to di-and the two trimethylol MDU compounds (VI, XXXI and XXXII) had completely disappeared.

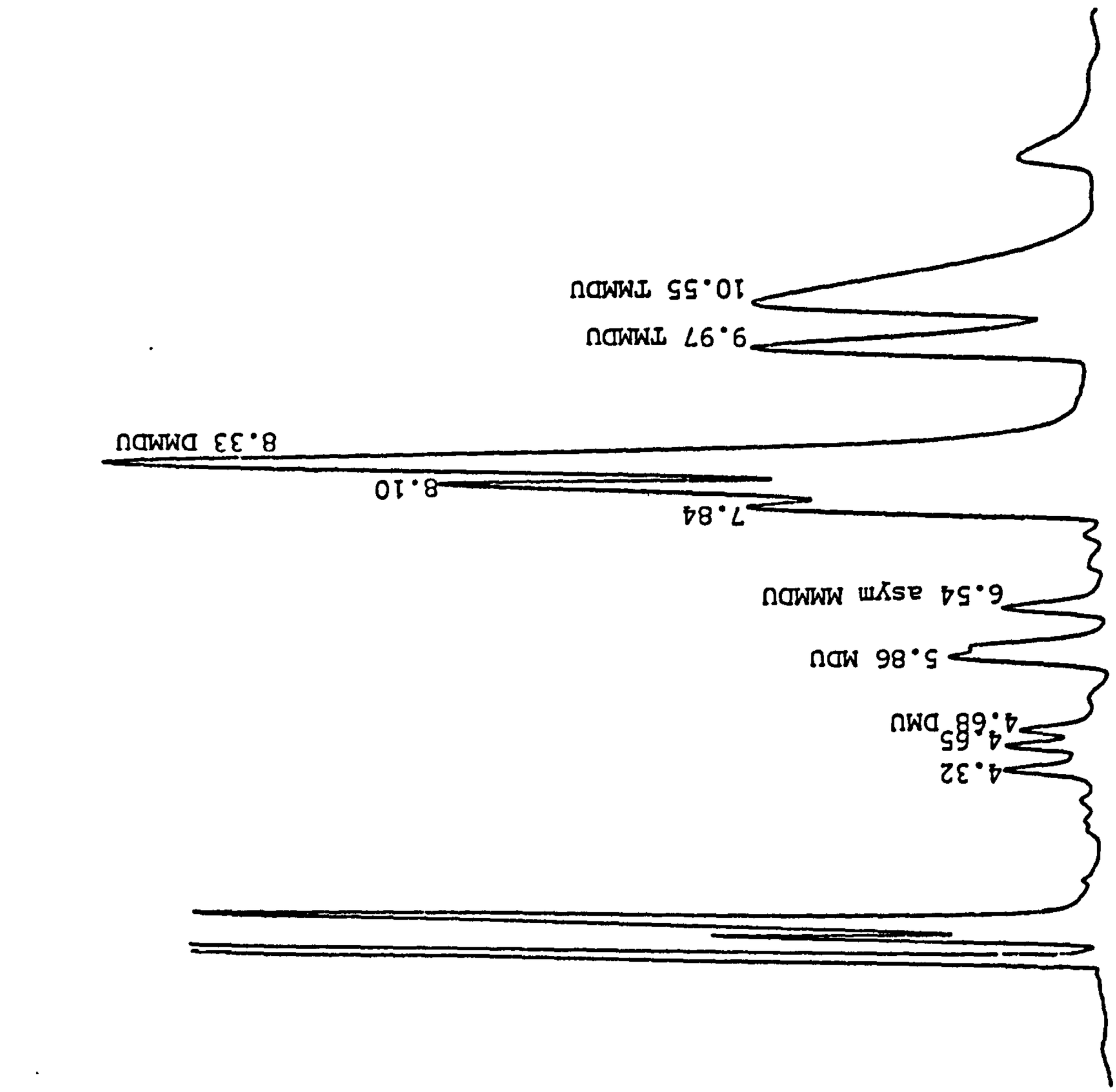


Fig.34. The methylolation of methylenediurea (IV).

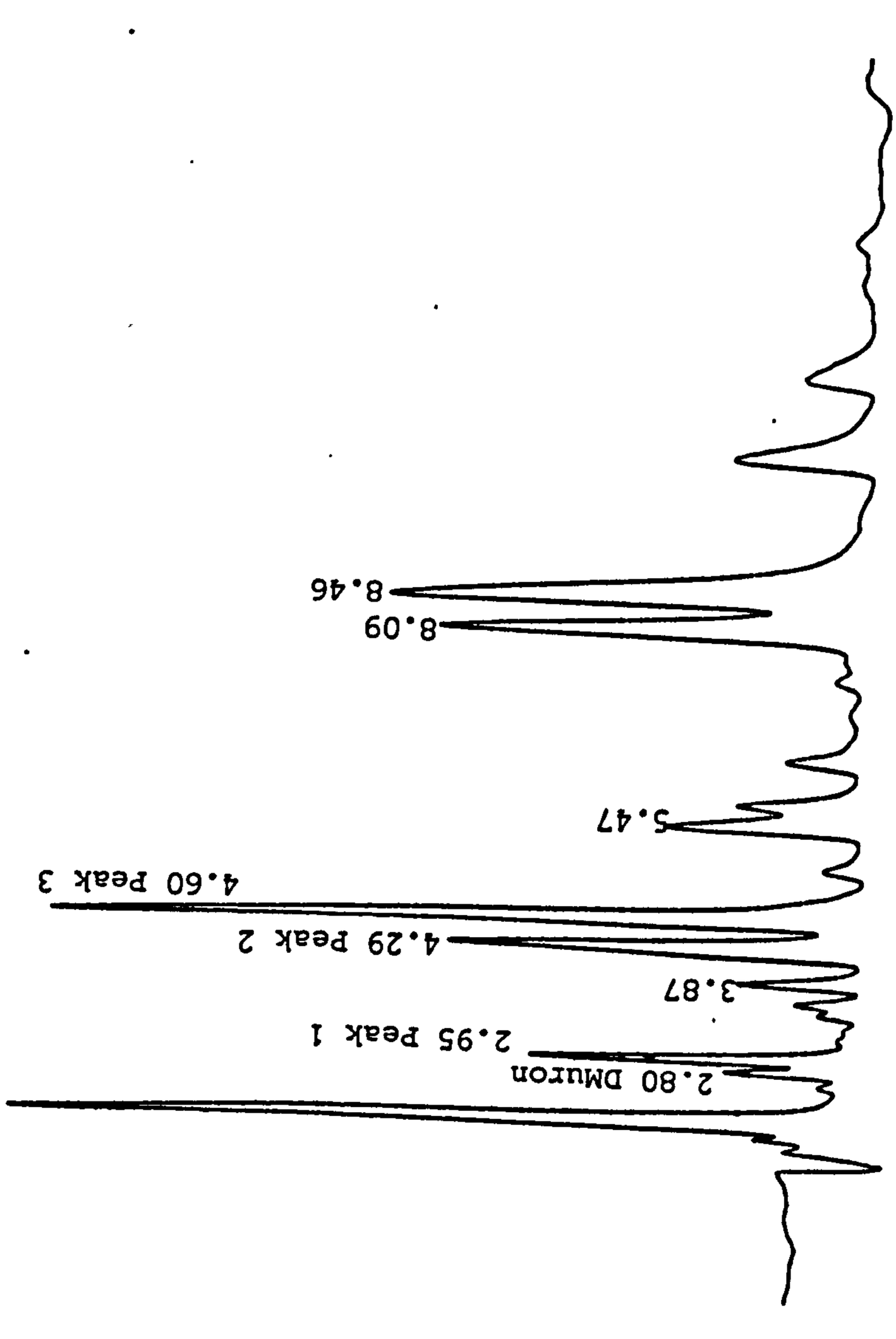
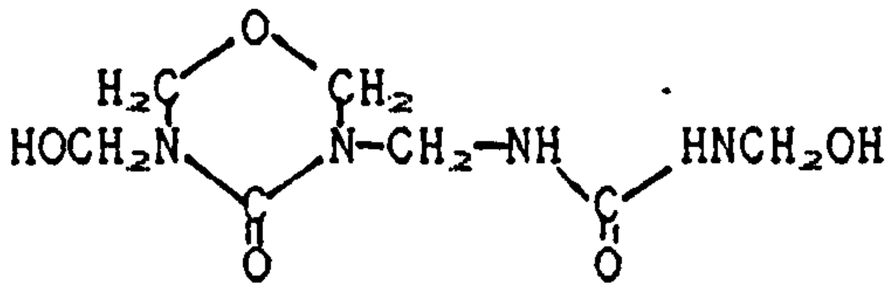


Fig.35. The uronisation of methylolated methylenediurea.

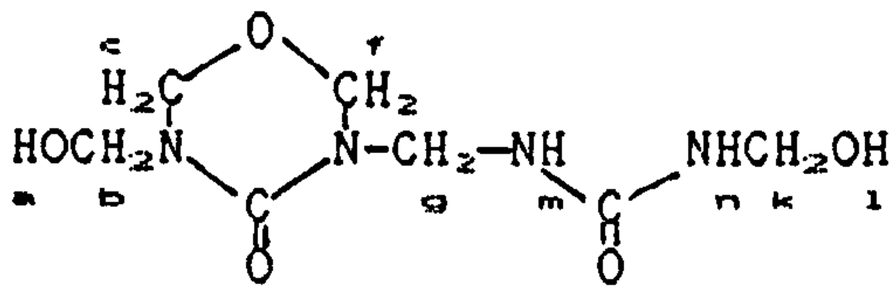
Using a preparative aminopropyl column 300mm x 7.8mm, packed in a similar fashion to the analytical column (see Section II B3; P.28) but employing a larger amount of the packing material (6g), small amounts of the compounds giving peaks 1, 2 and 3 (Fig.35; P.127) were obtained for subsequent spectroscopic analysis. Peaks 1 and 3 were present in sufficient quantities and were well separated from interfering compounds enabling infra-red, ^{1}H-nmr and ^{13}C-nmr spectra to be obtained. Peak 2 occurred at a lower level and (with preparative chromatography, as used on this occasion) was not well separated from a smaller peak eluting at a shorter retention time and peak 3 eluting immediately afterwards. Sufficient material, of purity about 70% (by liquid chromatography) was, however, collected to enable useful infra-red and ^{1}H-nmr spectra to be obtained.

The retention time relative to DMU (II) of peak 1 was 0.67 minutes and this figure was close to the value obtained (0.62 minutes) for DMmethylenediuron'(XXXIX) (see section III D3; P.96). The infra-red, ^{1}H-nmr and ^{13}C-nmr spectra confirmed that peak 1 was indeed due to DMmethylenediuron (XXXIX).

The infra-red, ^{1}H-nmr and ^{13}C-nmr spectra of peak 3, which appeared to be a new compound, are shown in Figs.36, 37 and 38 (Pp.130,131 and 132). The infra-red spectrum showed a peak at 810cm^{-1} which is typical of a uron ring and two peaks in the amide II region indicating the presence of two amide species probably in a combined uron-urea molecule. This was strongly supported by two carbonyl carbon peaks, observed in the ^{13}C-nmr spectrum, data for which are recorded in Table 8 (P.129) and which fit the following structure XXXXI.



XXXX1

Compound	Group	^1H ppm	Integral	Split	^{13}C ppm
$HOCH_2NHCONH_2$ l k m n	l	5.25	-	-	-
	k	4.41	-	-	63.5
	m	6.59	-	-	-
	n	5.62	-	-	-
	carbonyl	-	-	-	158.9
$H_2NCONHCH_2NHCONH_2$ p	p	4.19	-	-	45.5
	carbonyl	-	-	-	157.5
$H_2NCON(CH_2OH)_2$ r s	r	4.65	-	-	-
	s	5.50	-	-	-
	a	5.72	1	T	-
	b	4.64	2	D	66.9
	c	4.84	2	S	78.4
	f	4.88	2	S	77.2
	g	4.45	2	D	49.2
	m	6.66	1	T(unresolved)	-
	n	6.77	1	T	-
	k	4.45	2	DxD	63.5
	l	5.30	1	T	-
	uron carbonyl	-	-	-	152.8
	urea carbonyl	-	-	-	157.5

S=singlet, D=doublet, DxD=doublet of doublets, T=triplet

The letters (a-s) have been chosen to facilitate cross reference to P.102 which gives nmr data on urons.

Table 8. Nmr data of some reference compounds and compound XXXXI (peak 3)

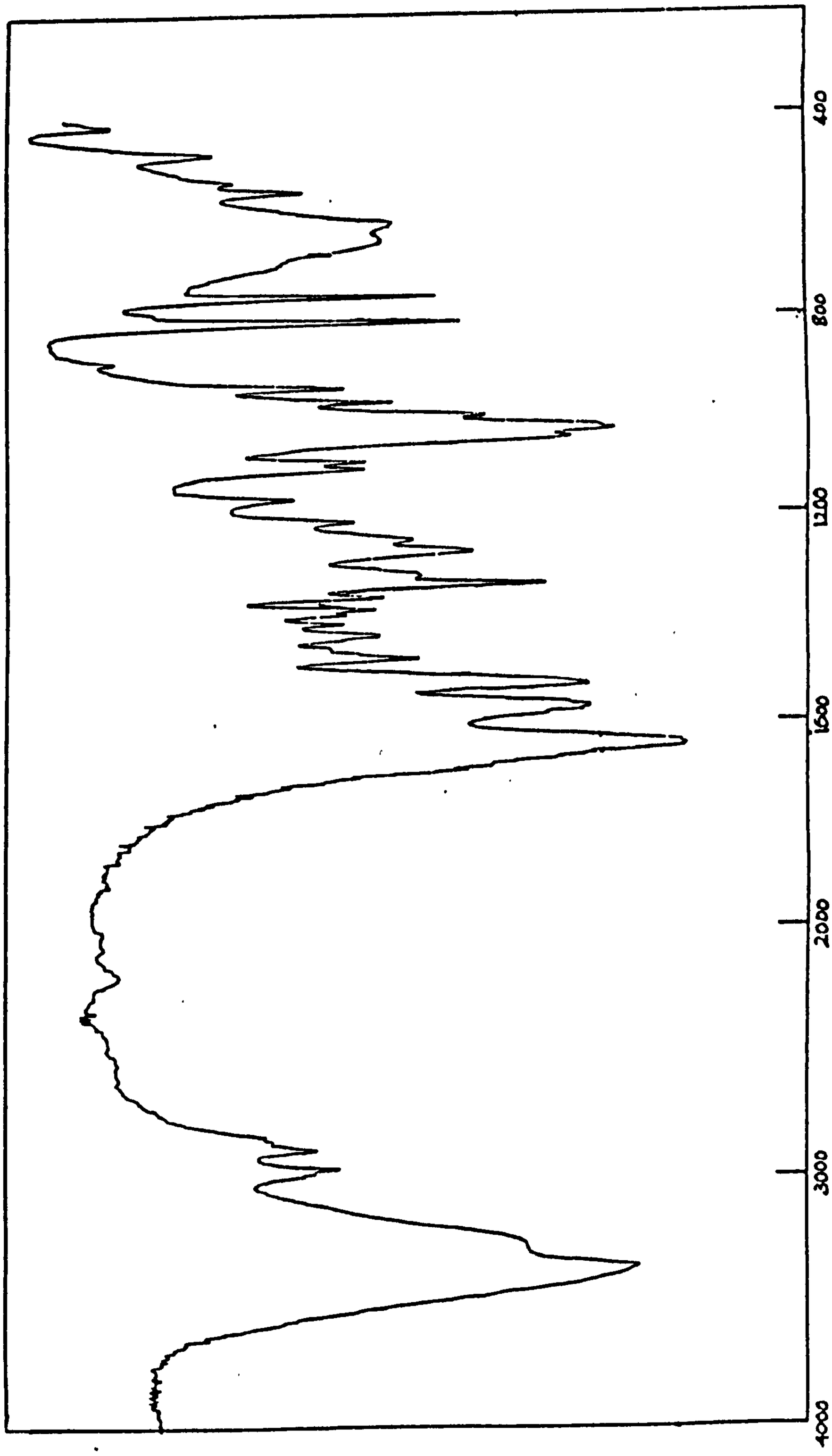


Fig.36. The infra red spectrum of compound XXXXI (Peak 3).

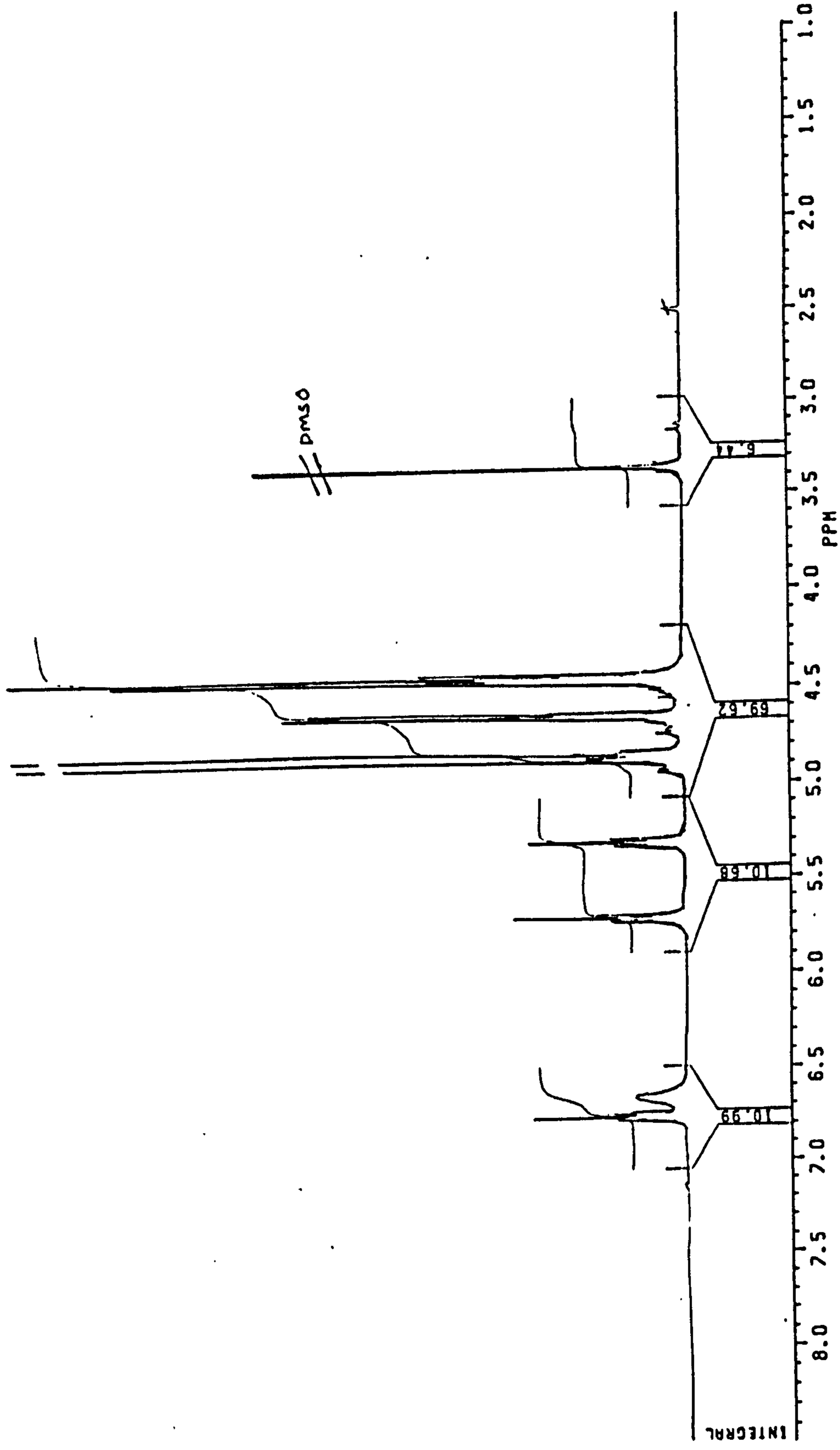


Fig.37. The ^{1}H-nmr spectrum of compound XXXI (Peak 3).

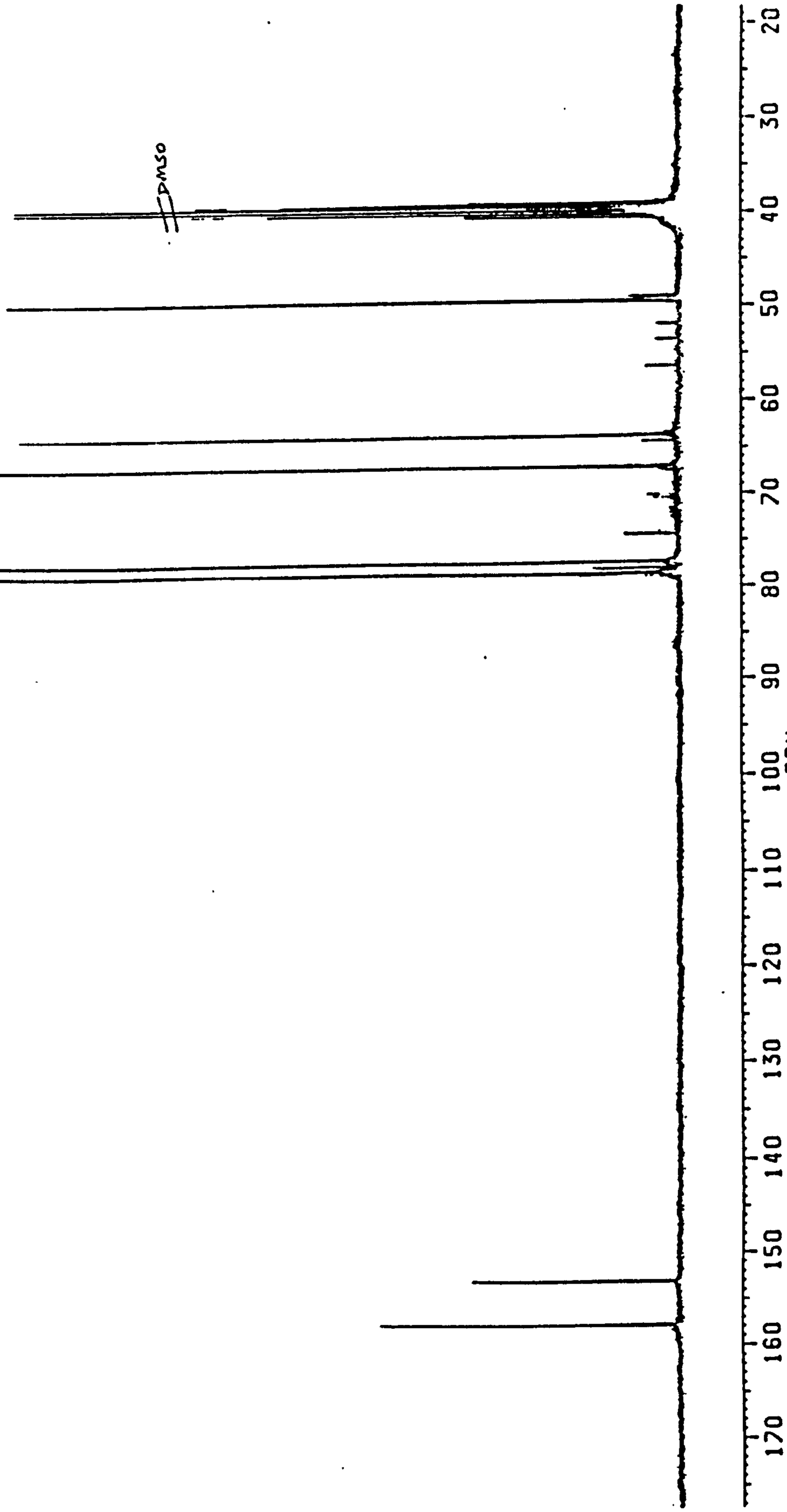


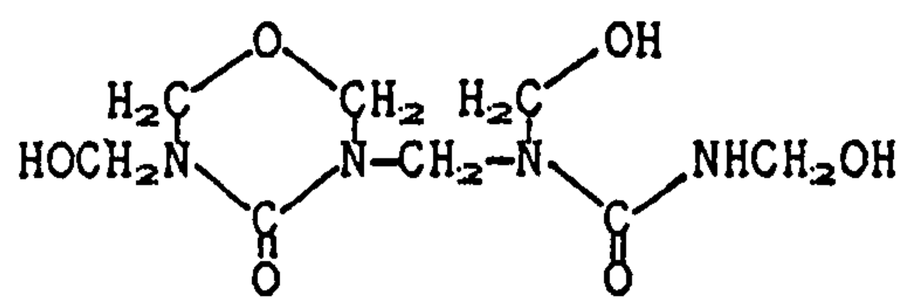
Fig.38. The ^{13}C-nmr spectrum of compound XXXXI (Peak 3).

Referring to the data on uron compounds given on P.102, it seemed likely that the ^{1}H-nmr absorbances at 5.72ppm and 4.64ppm in compound (XXXXI) arose from protons in a methylol group (the hydroxyl group (a) and the methylene group (b) respectively) attached to a uron ring. Further evidence for this assumption was obtained by irradiating at 5.72ppm causing decoupling of the 4.64ppm doublet which reverted to a singlet. The presence of a uron ring was confirmed by the two singlets at 4.84ppm and 4.88ppm which arose from the ring CH_2 protons (c and f). Interpretation of the urea function was more difficult due mainly to the complex peak cluster at about 4.45ppm. There were however, three more triplets in the spectrum with integrals showing one proton each and it seemed likely that two signals arose from single protons on nitrogen atoms and the other from a single proton in a hydroxyl group. Previously interpreted spectra (Table 8; P.129) showed that a hydroxyl proton in a primary methylol group in a linear urea derivative absorbed around 5.25ppm. This had an associated CH_2 proton absorption around 4.41ppm. Irradiating the peak at 5.30ppm showed that there was an associated absorption in the 4.45ppm cluster and that the 5.30ppm absorption arose from a proton in a methylol hydroxyl group (l). Irradiating at 6.77ppm and 6.66ppm both caused further variations to occur in the 4.45ppm cluster. It seemed likely therefore that this cluster arose from a doublet CH_2 proton (g) and a doublet of doublet CH_2 protons (k).

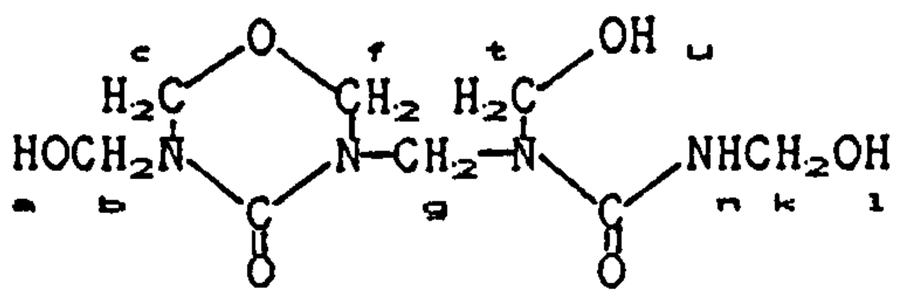
The ^{13}C-nmr spectrum had two carbonyl carbon peaks at 152.8ppm and 157.5ppm which were considered to arise from a uron carbonyl carbon and a urea carbonyl carbon respectively. There was an absorption at 49.2ppm which, by reference to the spectra of known compounds, could be interpreted as arising from a methylene carbon (g) linking the uron

structure to the urea structure. The peaks at 66.9ppm and 63.5ppm were considered likely to arise from the uron methylol CH_2 (b) and urea methylol CH_2 (k) carbon atoms respectively and the absorptions at 77.2ppm and 78.4ppm from the uron ring CH_2 carbon atoms (f and c respectively).

Peak 2 was more difficult to identify mainly because there was insufficient sample for a ^{13}C-nmr spectrum but the infra-red spectrum (Fig.39; P.135) with multiple -OH stretching at 3300cm^{-1} and a ring absorbtion at 810cm^{-1}, and the ^1H-nmr spectrum (Fig.40; P.136).supported a uron-urea structure **XXXXII** .



XXXXII



Group	ppm	Integral	Split
a	5.77	1	T
b	4.65	2	D
c	4.87	2	S
f	4.94	2	S
g	4.73	4	S ***
t	4.72		D
u	5.70	1	T
n	7.54	1	T***
k	4.51	2	DxD
l	5.35	1	T

The absorbances at 7.38, 7.14, 6.74, 6.66, 4.83 and 4.45ppm were considered to arise from impurities.

S=singlet, D=doublet, DxD=doublet of doublets, T=triplet, ***=unresolved

The letters (a to u) were chosen to allow simple cross reference to P.102 and Table 8 (P.129) which give nmr data of the reference compounds.

Table 9. ^1H-nmr data of compound **XXXXII** (peak 2).

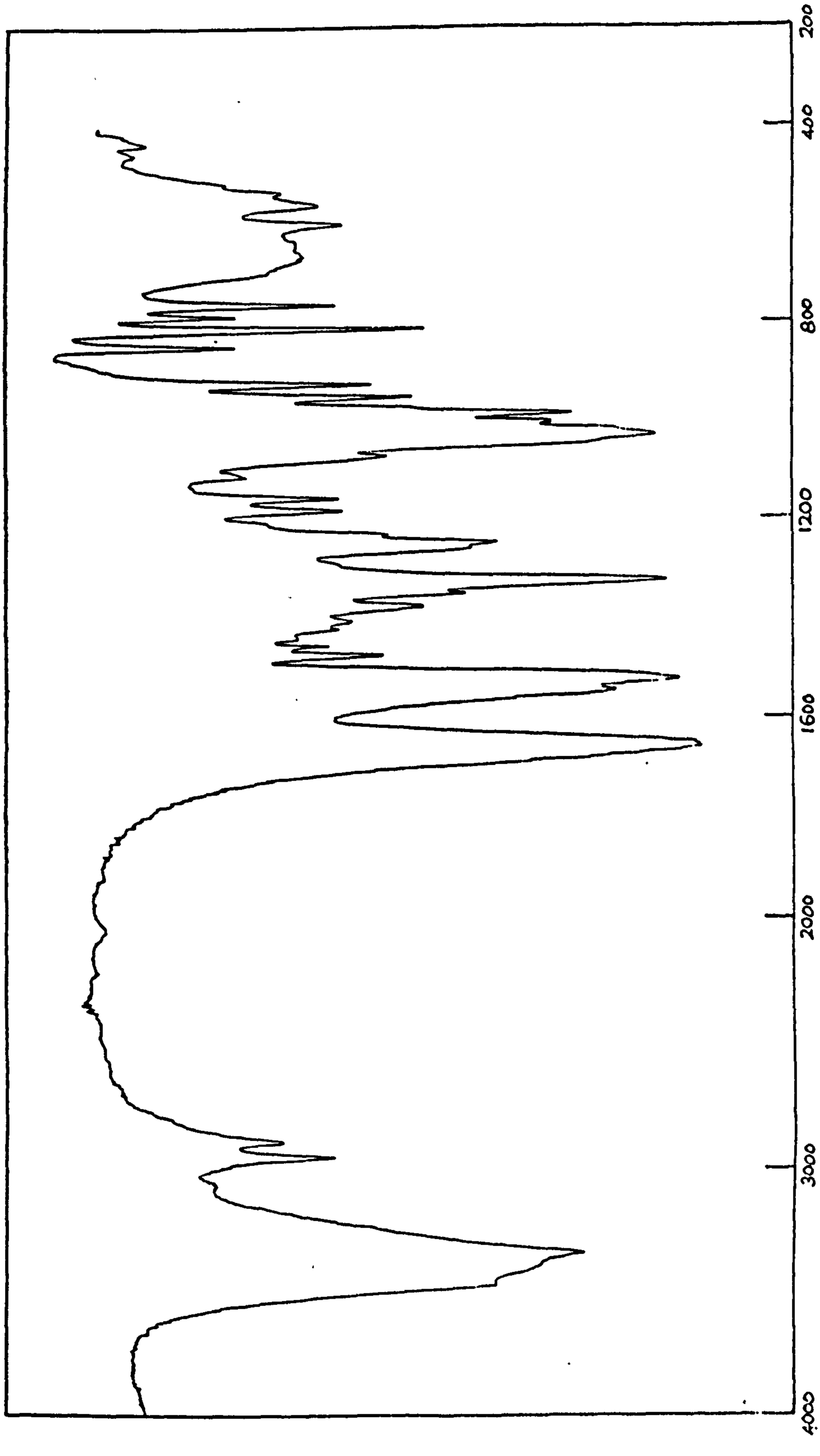


Fig.39. The infra-red spectrum of compound XXXII (Peak 2).

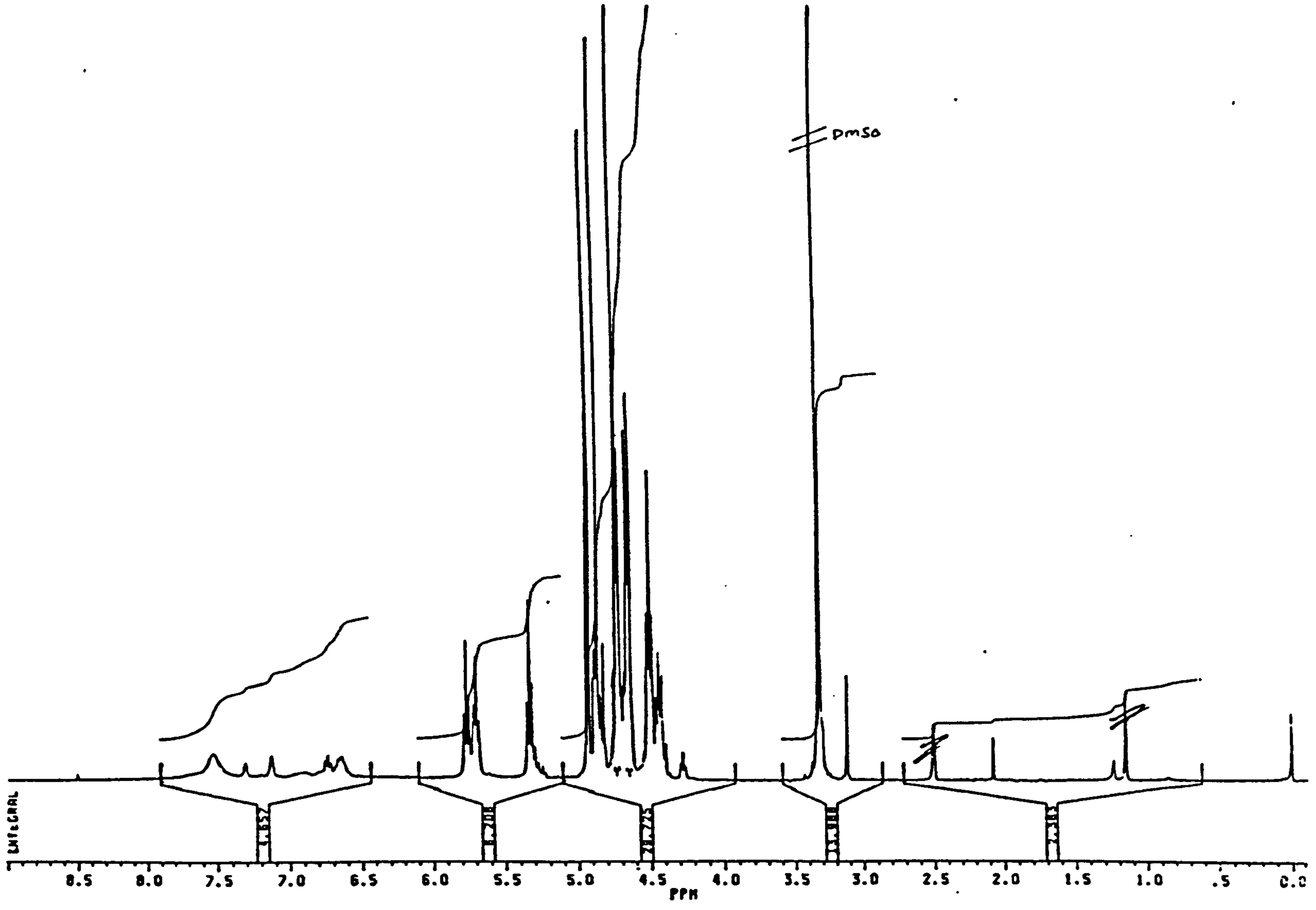


Fig.40. The ^{1}H-nmr spectrum of compound XXXXII (Peak 2).

From the nmr interpretation of compound **XXXXI** on P.133, the absorptions at 5.77ppm and 4.65ppm appeared to arise from the methylol group protons (hydroxyl (a) and methylene (b) respectively) attached to a uron ring and irradiating at 5.77ppm gave a singlet at 4.65ppm, as expected. The two singlets at 4.94ppm and 4.87ppm were assigned to the CH_2 protons in the uron ring (f and c). Three triplets (integral values of 1) were apparent in the spectrum and it was considered likely that peaks at 5.70ppm and 5.35ppm arose from hydroxyl group protons whilst the unresolved triplet at 7.54ppm arose from an >NH proton. Irradiating at 5.35ppm transformed the doublet of doublets at 4.51ppm into a simple doublet and these absorbances could therefore be attributed to the primary methylol protons (hydroxyl (l) and methylene (k) respectively) attached to the urea residue. Irradiating at 5.70ppm caused the doublet at 4.72ppm to become a singlet. These two signals were therefore attributed to protons in another methylol group, this time attached to a tertiary nitrogen atom (t). The only peak remaining was the singlet at 4.73ppm which was therefore assigned to the protons in the methylene group (g), linking the uron to urea residues. The absorption is at a higher field than the CH_2 protons in compound **XXXXI** (see Table 8; P.129) but a shift to higher field is not unexpected (compare the linking methylene group in DMmethylenediuron **XXXX** which absorbs at 4.68ppm; P.102) due to the two adjacent nitrogen atoms being tertiary.

Thus there seemed good justification for structure **XXXXII** and the knowledge acquired about this reaction from previous experiments would point to this type of structure. It seemed puzzling, however, that a compound having three methylol groups (XXXXII, peak 2) should elute before a similar compound possessing only two methylol groups (XXXXI,

peak 3). This is contrary to the well established chromatography of both uron and urea compounds. Doubt was thus cast on the spectroscopic evidence for this peak and to attempt to resolve the problem, the experiment was repeated, the chromatographic peak was trapped and infra-red and 'H-nmr spectra re-run, giving the same results as before. It is possible that unusual hydrogen bonding effects have caused this anomolous behaviour and this suggestion is supported by the shift of the NH absorption to high field compared to the >NH absorption in compound XXXXI.

Conclusions

The formation of uron structures in methylolated methyleneurea chains was easily achieved by simply raising the pH to ≥10 and heating to 95°C for two minutes. This procedure for synthesising combined urea-uron structures may well have most important implications for the urea resin industry and undoubtedly will add another dimension to urea-formaldehyde synthetic resin chemistry at Borden UK Limited. A simple infra-red spectrophotometric method for determining total uron content of urea-formaldehyde resins has been developed by adding known amounts of DMuron (XII) to a simple urea-formaldehyde resin and measuring the uron ring absorption at 810cm^{-1}.

Two new uron-urea compounds (XXXXI and XXXXII) have been isolated and well characterised. Their infra-red and 'H-nmr spectra have been recorded and one of the compounds was formed in large enough quantities to allow a ^{13}C-nmr spectrum to be obtained.

E. THE NATURE OF UREA-FORMALDEHYDE CONCENTRATE

1. INTRODUCTION

Urea-formaldehyde concentrate is the term used for a strong (55%) aqueous solution of formaldehyde to which approximately 0.2mol of urea has been added. The urea acts as a solution stabiliser allowing it to be stored at ambient temperatures without paraformaldehyde precipitation occurring. Experience has shown, however, that the effective formaldehyde concentration in the concentrate can, depending on age, fall somewhat short of the absolute level and it seemed likely that some of the formaldehyde could be present in a non-reactive form. A knowledge of the nature of the molecular species in which the formaldehyde exists, would therefore be of use to the research chemist working with formaldehyde and urea-formaldehyde resins.

2. EXPERIMENTAL

The sample of concentrate used in this investigation was obtained from Borden (España) SA and was approximately four weeks old when examined. The low molecular mass fraction of the sample was studied by the normal liquid partition chromatographic method as detailed in II B3 (P.28) and the higher molecular mass material by the size exclusion procedure given in Section II A2 (P.10).

3. RESULTS

1. Liquid partition chromatography.

A chromatogram of the urea-formaldehyde concentrate is shown in Fig.41

(P.141). Only four major peaks were visible and the identities and concentrations are given below.

Retention time (min)	Identity	%
2.2	water	-
2.86	DMuron	4.8
5.05	DMU	2.6
5.98	TMU	11.7

ii. Size exclusion chromatography.

A chromatogram of the urea-formaldehyde concentrate is shown in Fig.42 (P.142) and the results are given below.

Number average molecular mass,	Mn	175
Weight average molecular mass,	Mw	355
Z average molecular mass,	Mz	665
Dispersity		2.0

4. DISCUSSION and CONCLUSIONS

The value obtained for the weight average molecular mass, Mw, corresponded to the molecular mass of a fully methylolated oxymethylene-diurea. About 80% of the concentrate (excluding water) was accounted for by mono- and diurea compounds, the remaining 20%, consisting of urea-formaldehyde chains of up to about eight urea-formaldehyde units in length.

The formaldehyde content of urea-formaldehyde concentrate has been routinely estimated for many years by the sulphite and the peroxide methods[60,61]. Formaldehyde present as methylene linkages would not have been assayed by these techniques and as the % formaldehyde fell short of

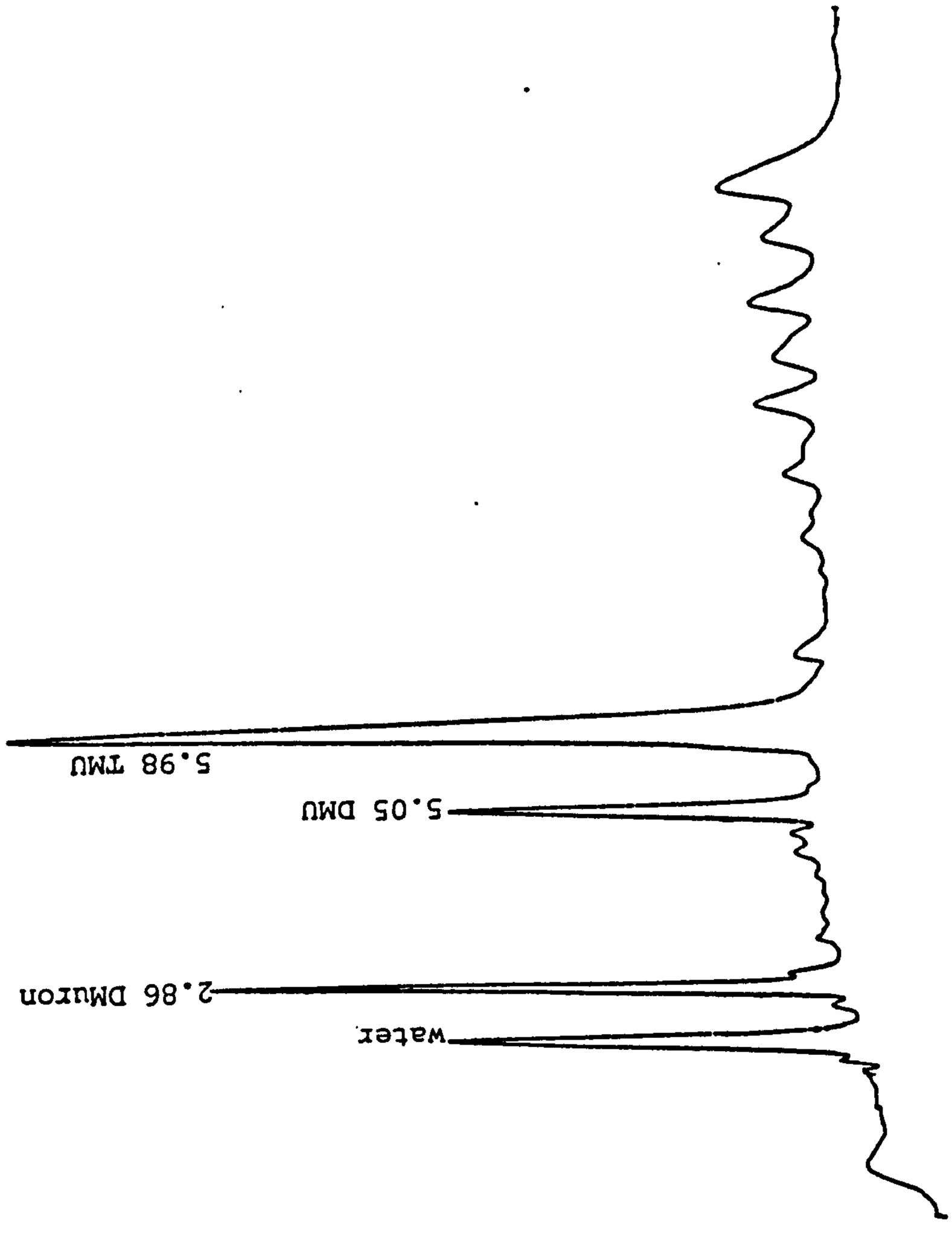


Fig.41. The liquid chromatogram of urea-formaldehyde concentrate.

NO-AVG 0.175759E3
WT-AVG 0.356734E3
Z-AVG 0.665317E3
VIS-AVG 0.356653E3

DISPERSITY 0.202967E1

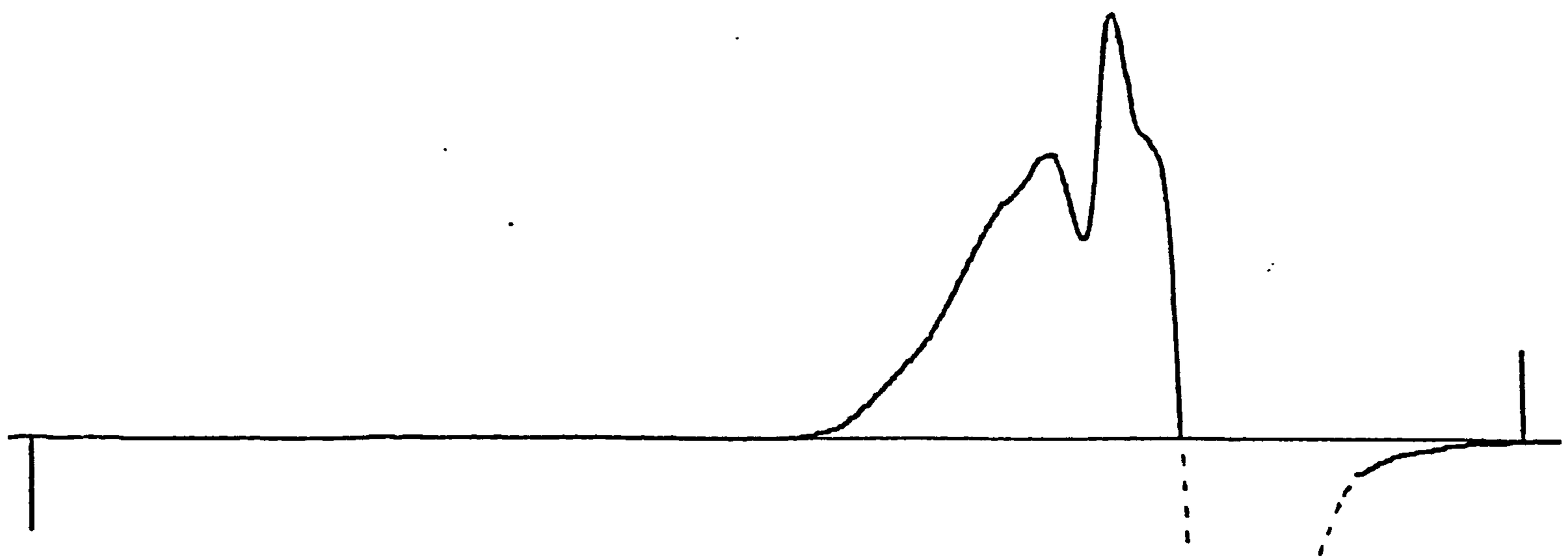


Fig.42. The SEC chromatogram of urea-formaldehyde concentrate.

the theoretical by only a few percent, it could be fairly assumed that methylene groups, if present, were only at a very low level and most of the formaldehyde in combination with urea and not in the form of methylol groups must have been present as linear ethers. In the sample of concentrate used, there was 3.6% of DMuron (XII) and this material as shown earlier (see III D4; P.120) is unreactive to urea, formaldehyde and combinations thereof. It seemed likely, therefore, that the presence of DMuron (XII) is the simple explanation of why urea-formaldehyde concentrate, especially when some weeks old, behaves as if a small fraction of the formaldehyde is unreactive.

Thus liquid chromatographic techniques have contributed considerably to the knowledge of the nature of urea-formaldehyde concentrate and will in the future enable the composition and thus reactivity, to be closely monitored.

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Size Exclusion Chromatography of Urea Formaldehyde Resins in Dimethylformamide Containing Lithium Chloride

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Synopsis

A rapid, reproducible method for investigating the molecular mass distribution of urea formaldehyde resins by size exclusion chromatography has been developed. By using concentrated lithium chloride solution to prepare the sample, materials of high viscosity and high molecular mass can be easily dissolved. Chromatography in dimethyl formamide containing lithium chloride eliminates hydrogen bonding and ensures that realistic values for molecular mass averages are obtained.

INTRODUCTION

During the past 15 years, a substantial effort has been made to study the molecular mass distribution of urea formaldehyde (UF) resins by size exclusion chromatography (SEC).[1-12] It seems, however, that a rapid, reproducible, and accurate procedure which will classify all UF resins including the most highly condensed types has yet to be reported.

Serious difficulties arise due to the poor solubility of high molecular mass material in any simple solvent or combination of solvents. Even the most effective solvent, i.e., dimethylsulfoxide will not dissolve completely a UF resin of high molecular mass.[10] Strong intermolecular hydrogen bonds form between the polar sites on the molecules, producing a supermolecular structure.

For many years it has been realized that strong aqueous solutions of lithium chloride will easily dissolve UF resins even when condensed to a high degree. Hope et al.[2] in an early article on the subject refer to this approach for sample preparation. It is clear that in some way lithium chloride eliminates the hydrogen bonds which are responsible for the association effect. The solutions obtained are clear, are of low viscosity, and can be infinitely diluted with solvents such as DMF and dimethylsulfoxide. The chemical nature of the resins is not altered, and the solute in solution remains unchanged for 24 h at room temperature.

It has been appreciated for some time that the addition of lithium halide to dimethylformamide (DMF) shows advantages over DMF alone when used as a solvent for the SEC of thermoplastic polymers. Cha[13] investigated the chromatography of polyacrylonitrile containing some sulfonate groups using lithium bromide in DMF as a solvent. He found that the salt caused an increase in the elution time of the polymer from the column and attributed this effect to charge neutralization and thus a reduction in the effective molecular size. However, Coppola et al.[14] working with uncharged

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polyacrylonitrile considered that the effect on the solute molecular size was too great to be explained by this effect. They suggested that the lithium salt prevented the molecules associating together and allowed the polymer to elute at its true position.

DMF containing lithium salts has been used by a variety of other workers as a solvent for the SEC of polymers. Kenyon and Mottus[15] studied a variety of thermoplastic polymers while Hann[16] worked with polyurethanes and Connors et al.[17] found that the addition of LiBr to DMF simplified the chromatograms of lignins. Cathodic electrodipping primers were examined successfully by Nömayr et al.[18] These workers also studied the effect of varying the strength of the lithium salt in the solvent establishing that concentrations in excess of 0.5% produced essentially the same chromatogram.

In this study, evidence has been obtained which indicates that there is a strong association between some of the lithium salt used in the preparation of the solution and the dissolved solute. This occurs to such a degree that the salt will pass with the urea derivative through the chromatographic column.

Calibration of the chromatographic columns for the analysis of UF resins has caused problems for previous workers; however, when polyethylene glycol and urea–formaldehyde standards are used in a solvent containing a lithium salt, a logical relationship is apparent.

EXPERIMENTAL

Equipment

The chromatography system consisted of: a Waters 6000A pump; Rheodyne 70–10 injection valve fitted with a 100-μL loop and Model 70-11 filler port; Polymer Laboratories PL GEL 10-μm columns, porosities 10^4, 500, and 50 Å, all 300 × 7.7 mm, housed in a Waters column oven; a Waters R-401 Differential Refractometer; a Waters Model 730 Data Module with GPC integration option.

Reagents

Anhydrous lithium chloride (GPR grade from BDH); dimethyl formamide (reagent grade from BDH).

Calibration Standards

Polyethylene glycols were from Polymer Laboratories (Calibration Kit PEG-10); Urea (AR grade from BDH); Monomethylol urea (MMU), dimethylol urea (DMU), and methylene diurea (MDU) were prepared as described elsewhere.[19] Crude trimethylene tetraurea containing some hexa- and octaurea compounds was prepared as detailed below.

Preparation of Trimethylene Tetraurea

Methylene diurea (22.5 g, 0.17 mol) was dissolved in 250 mL water warmed to about 45°C. Formaldehyde solution (l g of 50%, 0.017 mol) was added

followed by 1 drop of concentrated phosphoric acid. The solution was allowed to stand overnight, and the material which had precipitated out was filtered off and washed well with water. A chromatographic examination showed the material to be free from methylene diurea and to contain higher molecular mass oligomers (6 and 8 urea units), which could also be used for calibration.

Preparation of Samples

Many resin samples are only partially soluble in DMF unless a high initial concentration of lithium chloride is present. This causes the intermolecular hydrogen bonds to break, resulting in the resin dissolving completely. Once in solution the resin sample is infinitely dilutable with DMF. The salt concentration in the sample solution is adjusted to the same strength as that in the chromatographic solvent using one of two procedures. The first method, used with relatively low molecular mass resins, is to dissolve the sample (0.2 g) in molar lithium chloride solution in DMF (1 mL) and then dilute tenfold with DMF. The second method of sample preparation used with more difficult samples including semisolid materials is to add solid lithium chloride (0.04 g) to the sample (0.2 g) and mix vigorously with a small volume of DMF (up to 0.5 mL). After the sample has dissolved completely and sometimes warming to about 45°C may be necessary, DMF is added to give a final volume of 10 mL. To protect the columns, any extraneous particles which may be present are removed by passing the sample solution through a 0.5 μm filter.

Chromatographic Procedure

The SEC columns are thermostatted at 25 $\pm$ 1°C and equilibrated by passing the solvent (0.1*M* LiCl in DMF) at a flow rate of 1 mL min^{-1} until the retention times of a mixture of PEG standards is constant and identical with the retention times used in the calibration of the columns. If this cannot be achieved, the columns must be recalibrated.

With the sensitivity of the detector set to a suitable value (X16), 100 μL of sample solution is injected onto the columns via the sample loop.

Samples

Many samples of UF resins have been examined by this technique. Two typical resins illustrating the various aspects of the chromatography are considered in detail:

Resin A: A moderately condensed resin of high molar ratio (1:1.8) with no end urea addition.

Resin B: A moderately condensed resin with a very high initial molar ratio (1:2.0) but with a second urea addition to give a lower final molar ratio (1:1.4).

Both resins were tested when fresh and when considerably aged after storage at 21°C. These resins were further used to demonstrate the reproducibility of the method and to examine the effects of varying the salt concentration both in the sample solution and in the mobile phase.

RESULTS

Calibration Standards

Urea-formaldehyde condensation products and polyethylene glycols (PEG) of known molecular mass were chosen as calibration standards since the former can be directly related to the resins and the PEGs should behave similarly due to their polar nature. However, it was found that, although the plot of the PEG standards was linear over a large part of the range (see Fig. 1), there was poor resolution and nonlinearity at the low molecular mass end. Furthermore, the retention times of the urea derived standards did not correlate with the polymeric standards. Other polar materials such as sucrose, glucose, and water showed unexpectedly short retention times, i.e., they behaved in a similar manner to the urea compounds. Since SEC strictly separates by molecular size rather than molecular mass a possible explanation was that total solvation of the molecules was occurring at —OH and —NH groups. This would explain both the short retention times and the poor resolution as the difference between the effective masses would then be small.

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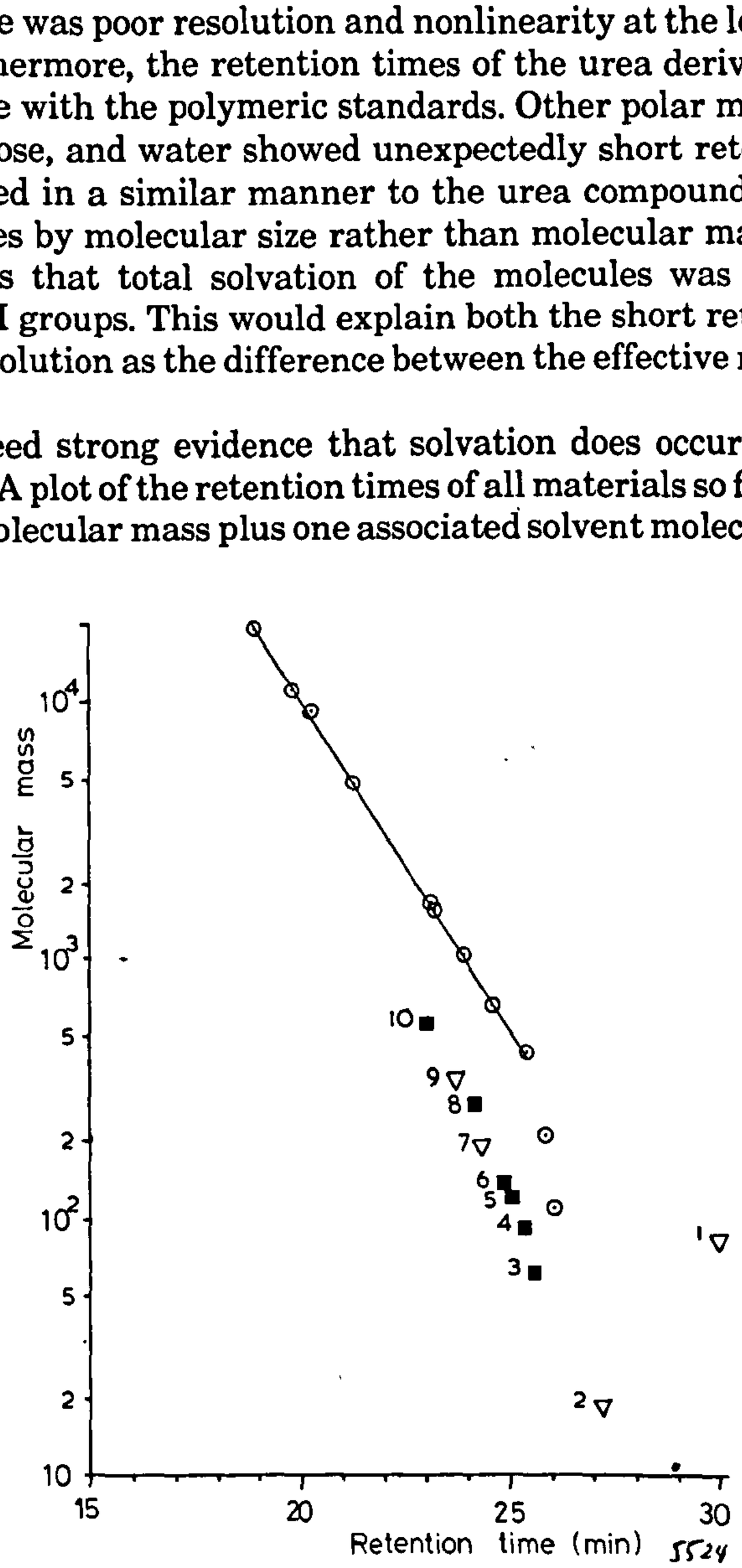

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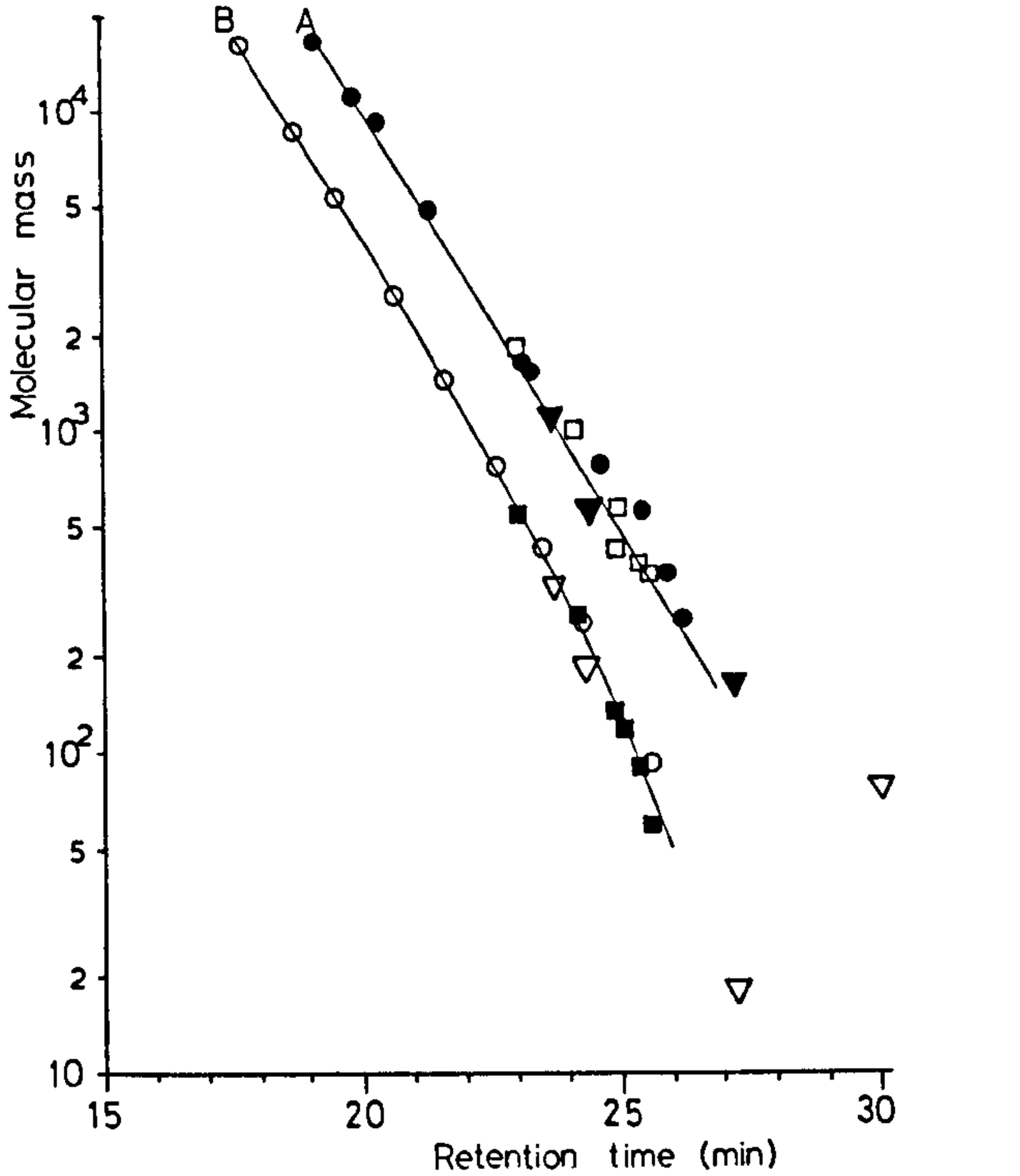

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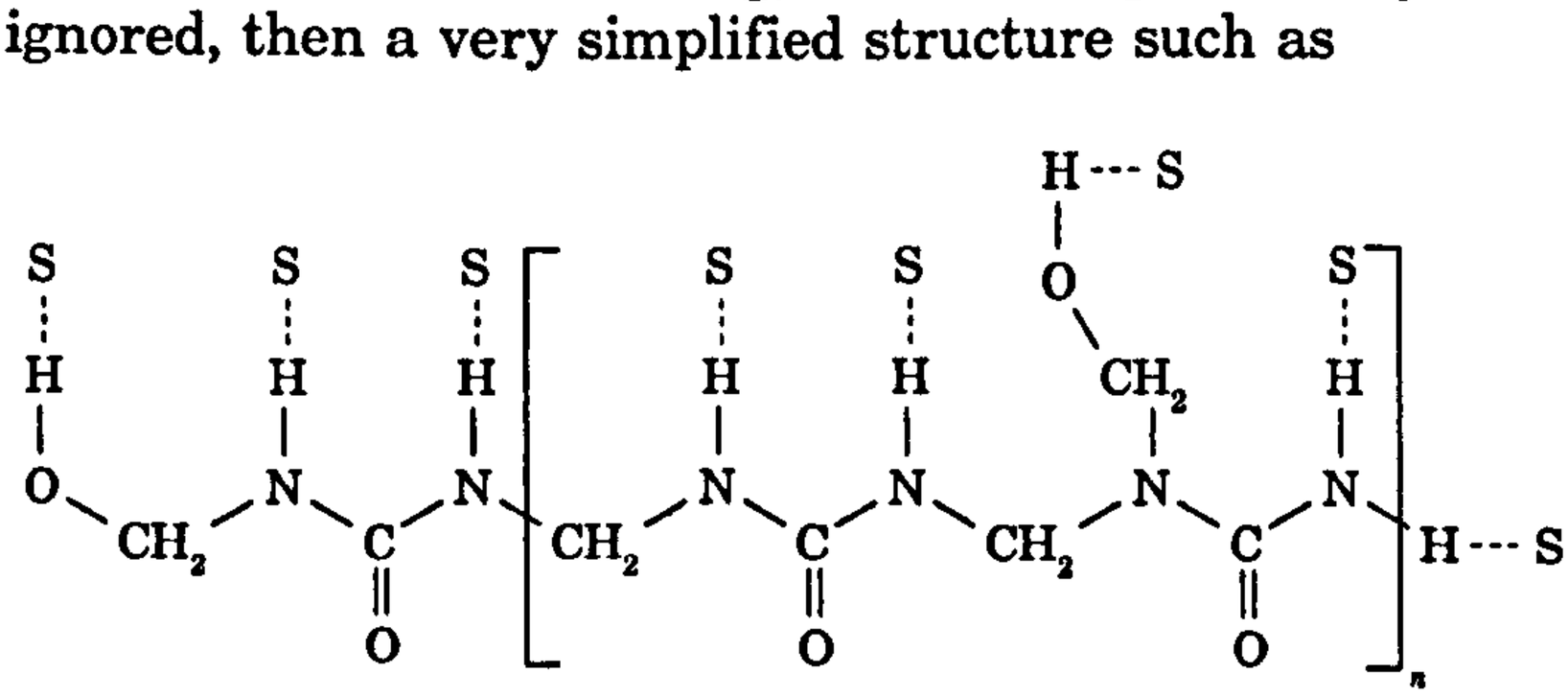

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can serve as a basis for calculating the contribution made by the solvent molecules to the molecular mass. Thus by assuming various values for n (the number of repeating units in the UF molecule) it is possible to replot the calibration curve [Fig. 2(A)] in terms of the unsolvated species. For example, taking a value for n of 30, the totally solvated molecule has an effective mass of 14,362. Using this mass, a retention time of 19.5 min is obtained from Figure 2(A). This retention time is then plotted against the corresponding mass of the unsolvated molecule (5310) to give a point on the new curve [Fig. 2(B)]. The calculated figures are in agreement with the experimentally determined points, and this calibration plot enables direct determination of the molecular mass averages of UF resins.

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Standard deviation for samples 1–5		±1.2	±16	±73	±0.07
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appears to be some very high molecular mass material which is excluded, and a somewhat variable pattern of peaks is produced, the position and intensity of which seem dependent on the method of sample preparation and the age of the solution. An example of this type of chromatogram is shown in Figure 3(a). Using LiCl in DMF as the eluting solvent for the analysis of about 50 UF samples, only one partially gelled sample showed any signs of exclusion.

Reproducibility

Five samples of resin were prepared for analysis using the methods described previously, four using lM LiCl and diluting, the fifth using solid LiCl. The molecular mass figures obtained are given in Table I. The results obtained on samples prepared using different procedures are included for comparison purposes. The samples were prepared at the same time and were run one after another. Once in solution, samples were found to be stable for up to 24 h. After 3 days some distinct changes were noticeable.

Resin Samples

Two resin samples A and B were studied for changes in molecular mass distribution on storage for a period of about 6 months. Chromatograms of

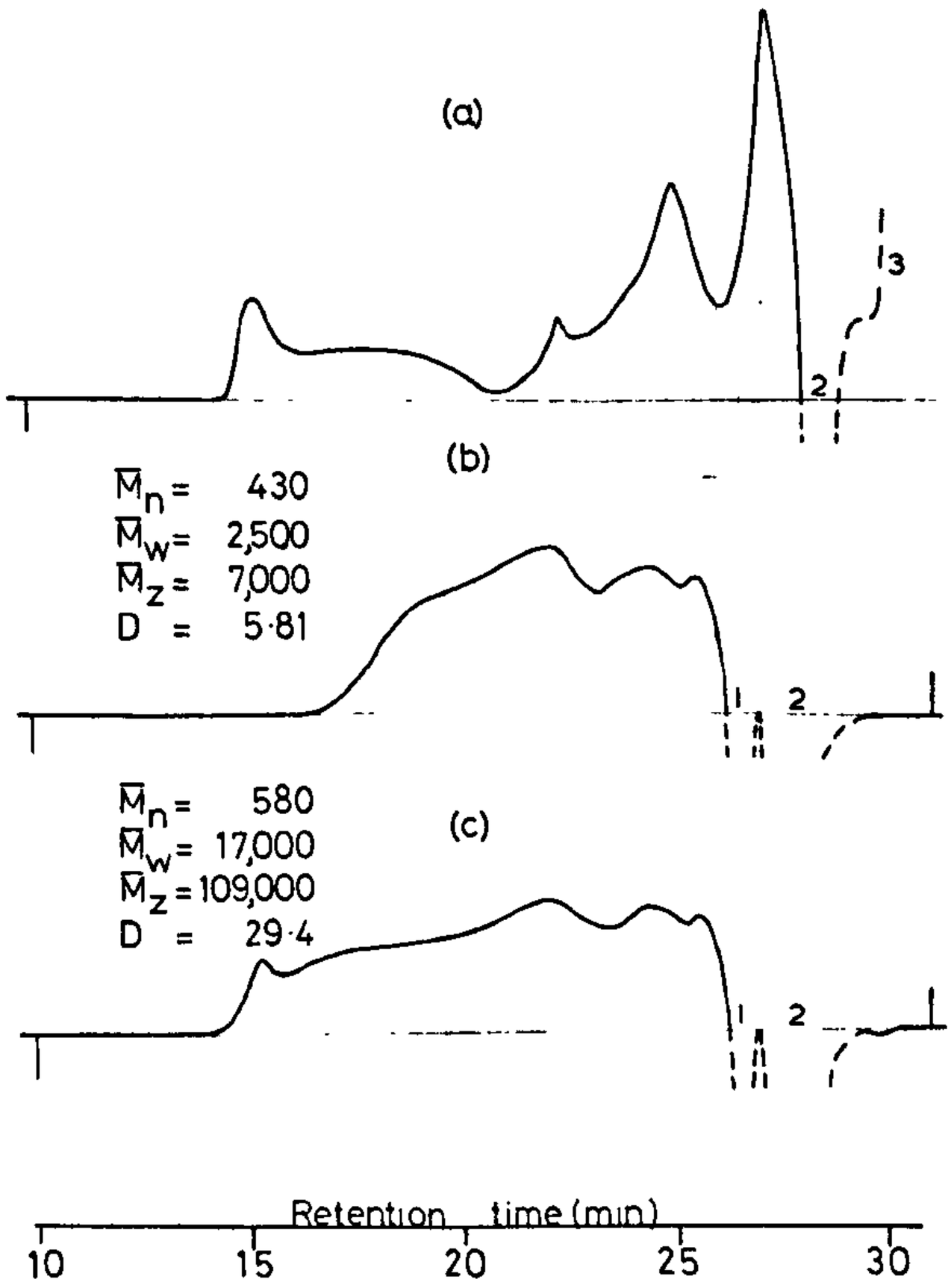

Fig. 3. Resin A: (a) fresh sample dissolved in DMSO/DMF (1/10) and run in a mobile phase of DMF alone; (b) fresh sample dissolved and run in 0.1*M* LiCl in DMF; (c) sample aged for about 6 months at 21°C dissolved and run in 0.1*M* LiCl in DMF. Peak identification: (1) lithium chloride; (2) water; (3) DMSO.

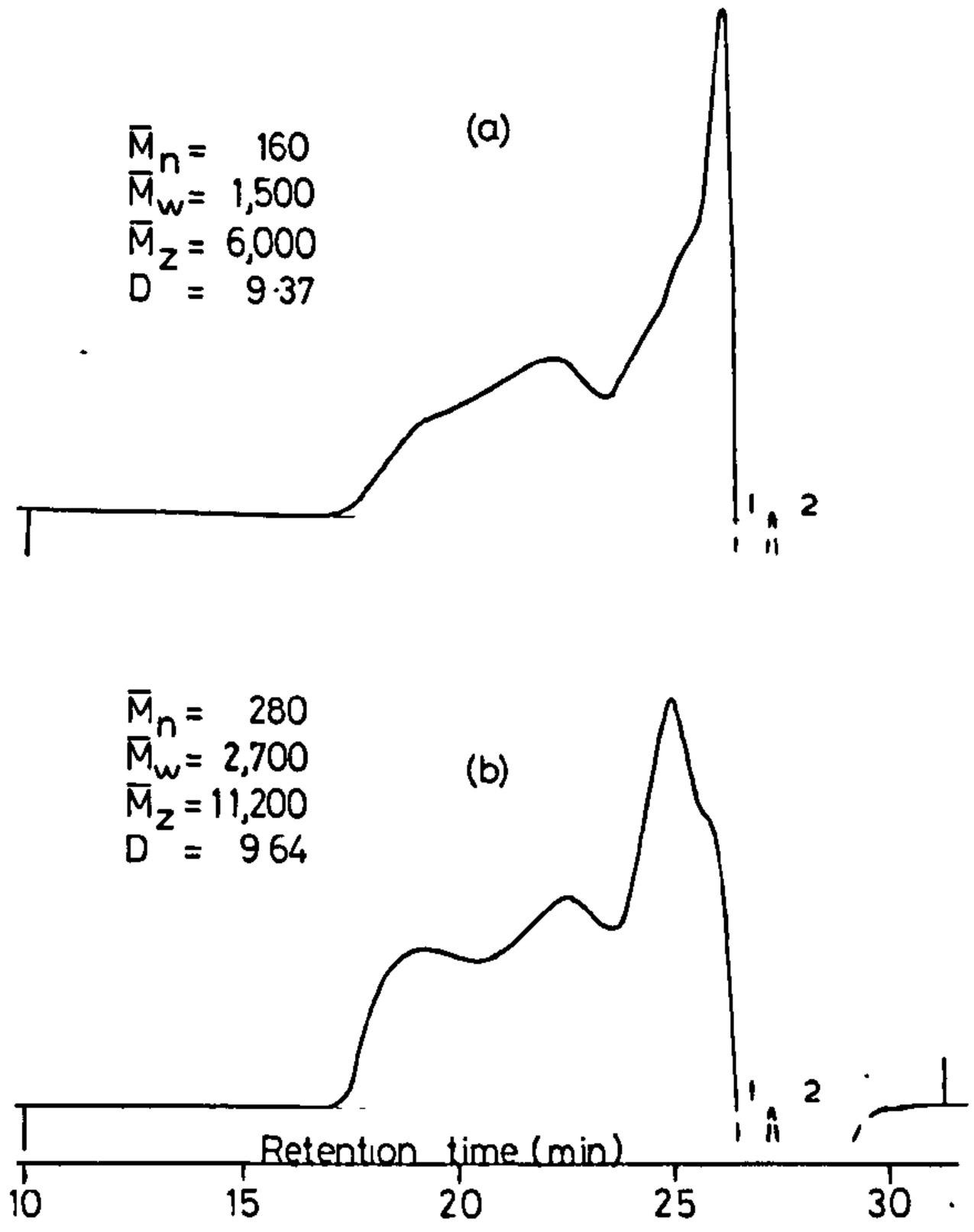

Fig. 4. Resin B: (a) fresh sample; (b) sample aged for about 6 months at 21°C. Both samples dissolved and run in 0.1*M* LiCl in DMF. Peak identification: (1) lithium chloride; (2) water.

fresh and old resins are shown in Figures 3(b), (c), and 4. It can be seen that resin A with no end urea addition shows a fairly even distribution when fresh, the low molecular mass end altering only slightly on aging while the medium to high molecular mass region becomes much more extended. Resin B containing the end urea shows a large low molecular mass peak when fresh which diminishes considerably on aging, producing a large increase in medium molecular mass materials while the high molecular mass end is relatively slow to change.

DISCUSSION

The objectives at the outset of this work were to develop a method of determining the molecular mass distribution of UF formulations which was rapid, reproducible, and applicable to all types of samples. Since the introduction of semirigid microparticulate crosslinked polystyrene gels, analysis times of 30 min or less have been commonplace. These columns therefore show a considerable advantage over the types previously used in this field, which were usually composed of large soft particles often based on a polysaccharide or a polyester.

The three-column set which was employed gives a separation time of about 30 min using a flow rate of 1 mL min^{-1} of DMF containing LiCl (0.1*M*). The columns were stored in this solvent when not in use and proved stable and reliable over a period of many months. There was no significant change in the calibration plot during this period.

The choice of the solvent has been crucial to the success of this investigation since it eliminates the hydrogen bonding in the solute and allows complete solvation of the molecules to occur. As a consequence, a rational calibration curve has been obtained leading to meaningful values for $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$, and polydispersity. In the absence of lithium salt the degree of molecular association is variable, rendering all results thus obtained virtually meaningless.

Obviously some assumptions have had to be made about the structure of the polymer chain, but this is invariably the case when calibrating SEC columns for molecular mass determinations. These assumptions are only likely to cause significant errors in samples having final molecular ratios above about 1:2 (U:F) and commercial materials of this type are fairly rare.

The action of the lithium salt in rendering UF polymers soluble is not completely understood. However, it has been shown experimentally that lithium salt is transported through the SEC column with the urea derivative and that each urea group is associated with one molecule of LiCl probably via the carbonyl oxygen.

The lithium salt not only confers solubility on the polymer but also provides a secondary beneficial effect in that there is an increased detector response to the urea compounds compared with that observed in DMF alone. Since a lithium ion is associated with each urea unit, this effect is shown over the whole molecular mass range. On the other hand, the high degree of solvation of the urea derivatives means that there is very little relative difference in the molecular size of the low molecular mass components, causing poor resolution of these materials. However, the complete separation of these materials is not necessary for the purposes of determining average molecular masses, and they are better separated, using other techniques such as high performance liquid chromatography.

The actual values obtained for the molecular mass averages of commercial samples have varied widely. Typical figures found for freshly prepared materials were: $\overline{M}_n$ between 140 and 500; $\overline{M}_w$ between 800 and 3000; $\overline{M}_z$ between 3000 and 25,000; polydispersity between 5 and 20. These values can increase substantially on storage at 21°C for 6 months (see Figs. 3 and 4).

It can be concluded that this approach to the SEC of UF compositions is a viable method of quality control. It is also a powerful procedure for investigating the formation of the urea–formaldehyde polymers and not least their aging characteristics. Although only urea–formaldehyde polymers have been investigated in this study, it is likely that this technique could be useful in the analysis of similar materials such as melamine formaldehyde resins.

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Size Exclusion Chromatography of Formaldehyde Resins in Dimethylformamide Containing Lithium Chloride

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Synopsis

A rapid, reproducible method for investigating the molecular mass distribution of urea formaldehyde resins by size exclusion chromatography has been developed. By using concentrated lithium chloride solution to prepare the sample, materials of high viscosity and high molecular mass can be easily dissolved. Chromatography in dimethyl formamide containing lithium chloride eliminates hydrogen bonding and ensures that realistic values for molecular mass averages are obtained.

INTRODUCTION

During the past 15 years, a substantial effort has been made to study the molecular mass distribution of urea formaldehyde (UF) resins by size exclusion chromatography (SEC).[1-12] It seems, however, that a rapid, reproducible, and accurate procedure which will classify all UF resins including the most highly condensed types has yet to be reported.

Serious difficulties arise due to the poor solubility of high molecular mass material in any simple solvent or combination of solvents. Even the most effective solvent, i.e., dimethylsulfoxide will not dissolve completely a UF resin of high molecular mass.[10] Strong intermolecular hydrogen bonds form between the polar sites on the molecules, producing a supermolecular structure.

For many years it has been realized that strong aqueous solutions of lithium chloride will easily dissolve UF resins even when condensed to a high degree. Hope et al.[2] in an early article on the subject refer to this approach for sample preparation. It is clear that in some way lithium chloride eliminates the hydrogen bonds which are responsible for the association effect. The solutions obtained are clear, are of low viscosity, and can be infinitely diluted with solvents such as DMF and dimethylsulfoxide. The chemical nature of the resins is not altered, and the solute in solution remains unchanged for 24 h at room temperature.

It has been appreciated for some time that the addition of lithium halide to dimethylformamide (DMF) shows advantages over DMF alone when used as a solvent for the SEC of thermoplastic polymers. Cha[13] investigated the chromatography of polyacrylonitrile containing some sulfonate groups using lithium bromide in DMF as a solvent. He found that the salt caused an increase in the elution time of the polymer from the column and attributed this effect to charge neutralization and thus a reduction in the effective molecular size. However, Coppola et al.[14] working with uncharged

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polyacrylonitrile considered that the effect on the solute molecular size was too great to be explained by this effect. They suggested that the lithium salt prevented the molecules associating together and allowed the polymer to elute at its true position.

DMF containing lithium salts has been used by a variety of other workers as a solvent for the SEC of polymers. Kenyon and Mottus[15] studied a variety of thermoplastic polymers while Hann[16] worked with polyurethanes and Connors et al.[17] found that the addition of LiBr to DMF simplified the chromatograms of lignins. Cathodic electrodipping primers were examined successfully by Nömayr et al.[18] These workers also studied the effect of varying the strength of the lithium salt in the solvent establishing that concentrations in excess of 0.5% produced essentially the same chromatogram.

In this study, evidence has been obtained which indicates that there is a strong association between some of the lithium salt used in the preparation of the solution and the dissolved solute. This occurs to such a degree that the salt will pass with the urea derivative through the chromatographic column.

Calibration of the chromatographic columns for the analysis of UF resins has caused problems for previous workers; however, when polyethylene glycol and urea–formaldehyde standards are used in a solvent containing a lithium salt, a logical relationship is apparent.

EXPERIMENTAL

Equipment

The chromatography system consisted of: a Waters 6000A pump; Rheodyne 70–10 injection valve fitted with a 100-μL loop and Model 70-11 filler port; Polymer Laboratories PL GEL 10-μm columns, porosities 10^4, 500, and 50 Å, all 300 × 7.7 mm, housed in a Waters column oven; a Waters R-401 Differential Refractometer; a Waters Model 730 Data Module with GPC integration option.

Reagents

Anhydrous lithium chloride (GPR grade from BDH); dimethyl formamide (reagent grade from BDH).

Calibration Standards

Polyethylene glycols were from Polymer Laboratories (Calibration Kit PEG-10); Urea (AR grade from BDH); Monomethylol urea (MMU), dimethylol urea (DMU), and methylene diurea (MDU) were prepared as described elsewhere.[19] Crude trimethylene tetraurea containing some hexa- and octaurea compounds was prepared as detailed below.

Preparation of Trimethylene Tetraurea

Methylene diurea (22.5 g, 0.17 mol) was dissolved in 250 mL water warmed to about 45°C. Formaldehyde solution (l g of 50%, 0.017 mol) was added

followed by 1 drop of concentrated phosphoric acid. The solution was allowed to stand overnight, and the material which had precipitated out was filtered off and washed well with water. A chromatographic examination showed the material to be free from methylene diurea and to contain higher molecular mass oligomers (6 and 8 urea units), which could also be used for calibration.

Preparation of Samples

Many resin samples are only partially soluble in DMF unless a high initial concentration of lithium chloride is present. This causes the intermolecular hydrogen bonds to break, resulting in the resin dissolving completely. Once in solution the resin sample is infinitely dilutable with DMF. The salt concentration in the sample solution is adjusted to the same strength as that in the chromatographic solvent using one of two procedures. The first method, used with relatively low molecular mass resins, is to dissolve the sample (0.2 g) in molar lithium chloride solution in DMF (1 mL) and then dilute tenfold with DMF. The second method of sample preparation used with more difficult samples including semisolid materials is to add solid lithium chloride (0.04 g) to the sample (0.2 g) and mix vigorously with a small volume of DMF (up to 0.5 mL). After the sample has dissolved completely and sometimes warming to about 45°C may be necessary, DMF is added to give a final volume of 10 mL. To protect the columns, any extraneous particles which may be present are removed by passing the sample solution through a 0.5 μm filter.

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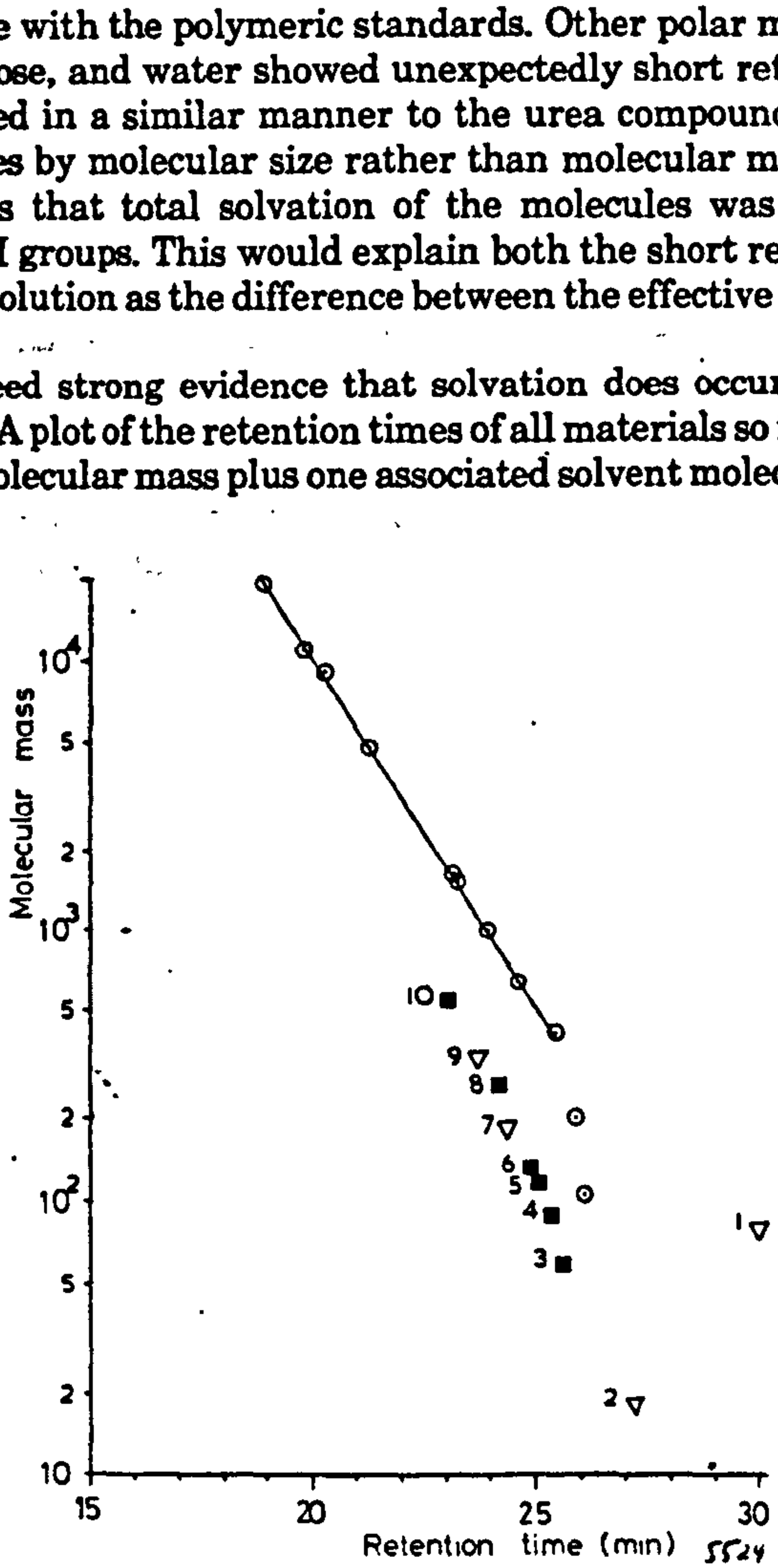

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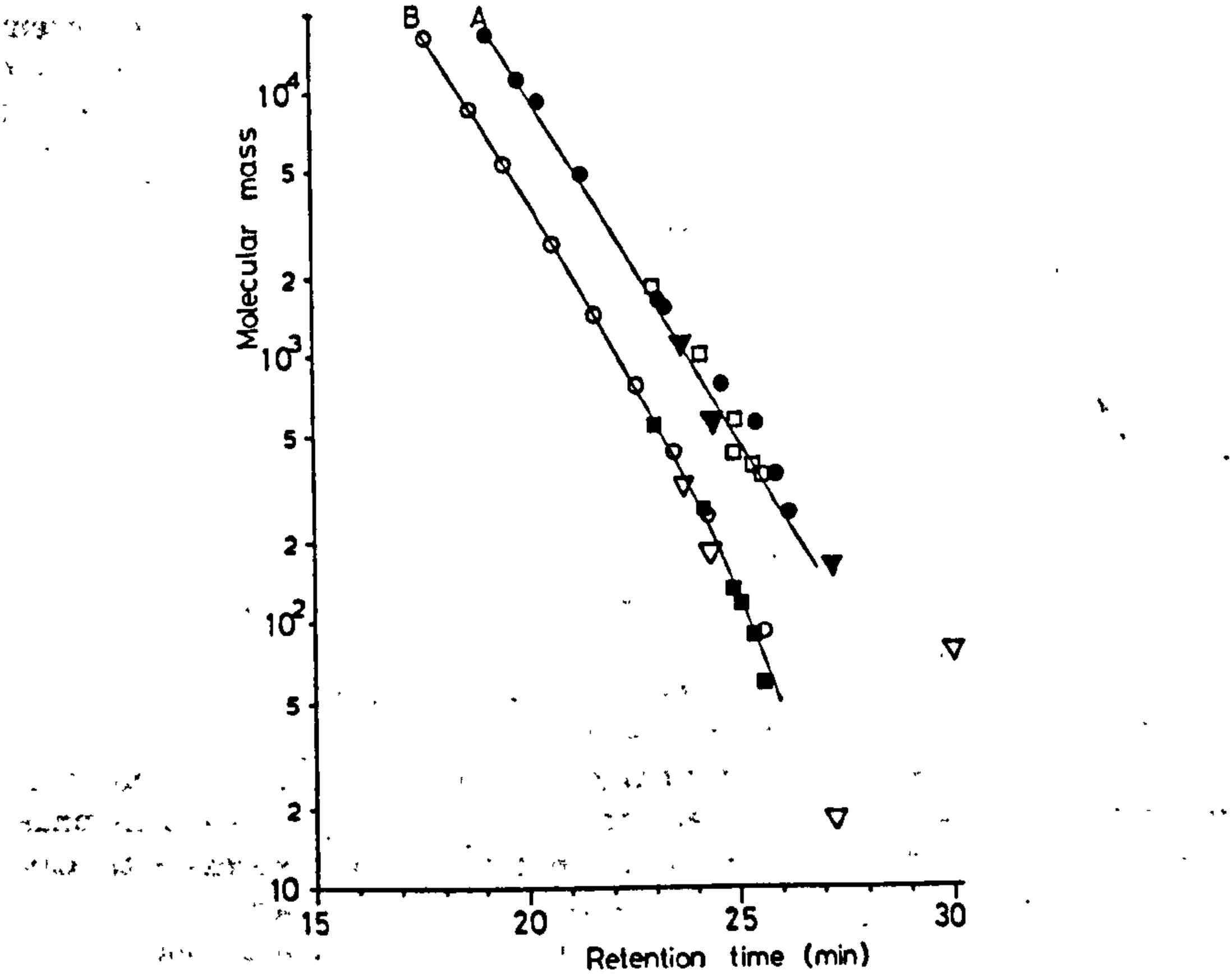

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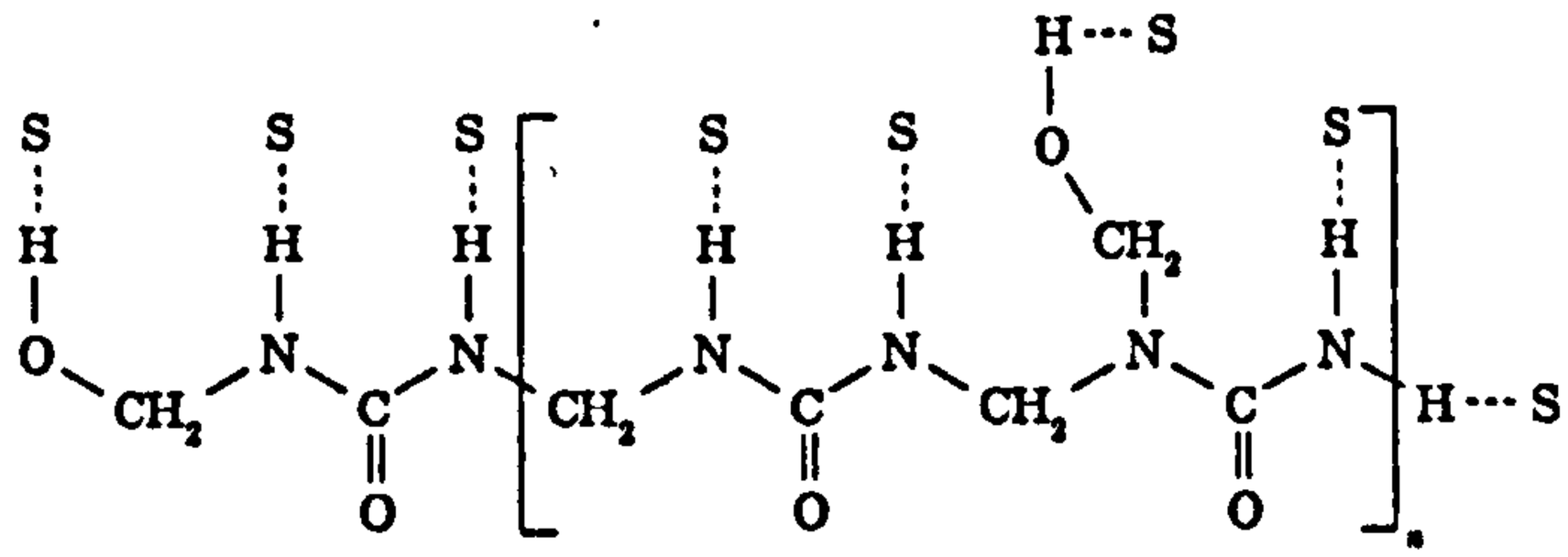

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Standard deviation for samples 1–5		±1.2	±16	±73	±0.07
Coefficient of variation for samples 1–5		0.83%	1.15%	1.31%	0.73%

appears to be some very high molecular mass material which is excluded, and a somewhat variable pattern of peaks is produced, the position and intensity of which seem dependent on the method of sample preparation and the age of the solution. An example of this type of chromatogram is shown in Figure 3(a). Using LiCl in DMF as the eluting solvent for the analysis of about 50 UF samples, only one partially gelled sample showed any signs of exclusion.

Reproducibility

Five samples of resin were prepared for analysis using the methods described previously, four using 1M LiCl and diluting, the fifth using solid LiCl. The molecular mass figures obtained are given in Table I. The results obtained on samples prepared using different procedures are included for comparison purposes. The samples were prepared at the same time and were run one after another. Once in solution, samples were found to be stable for up to 24 h. After 3 days some distinct changes were noticeable.

Resin Samples

Two resin samples A and B were studied for changes in molecular mass distribution on storage for a period of about 6 months. Chromatograms of

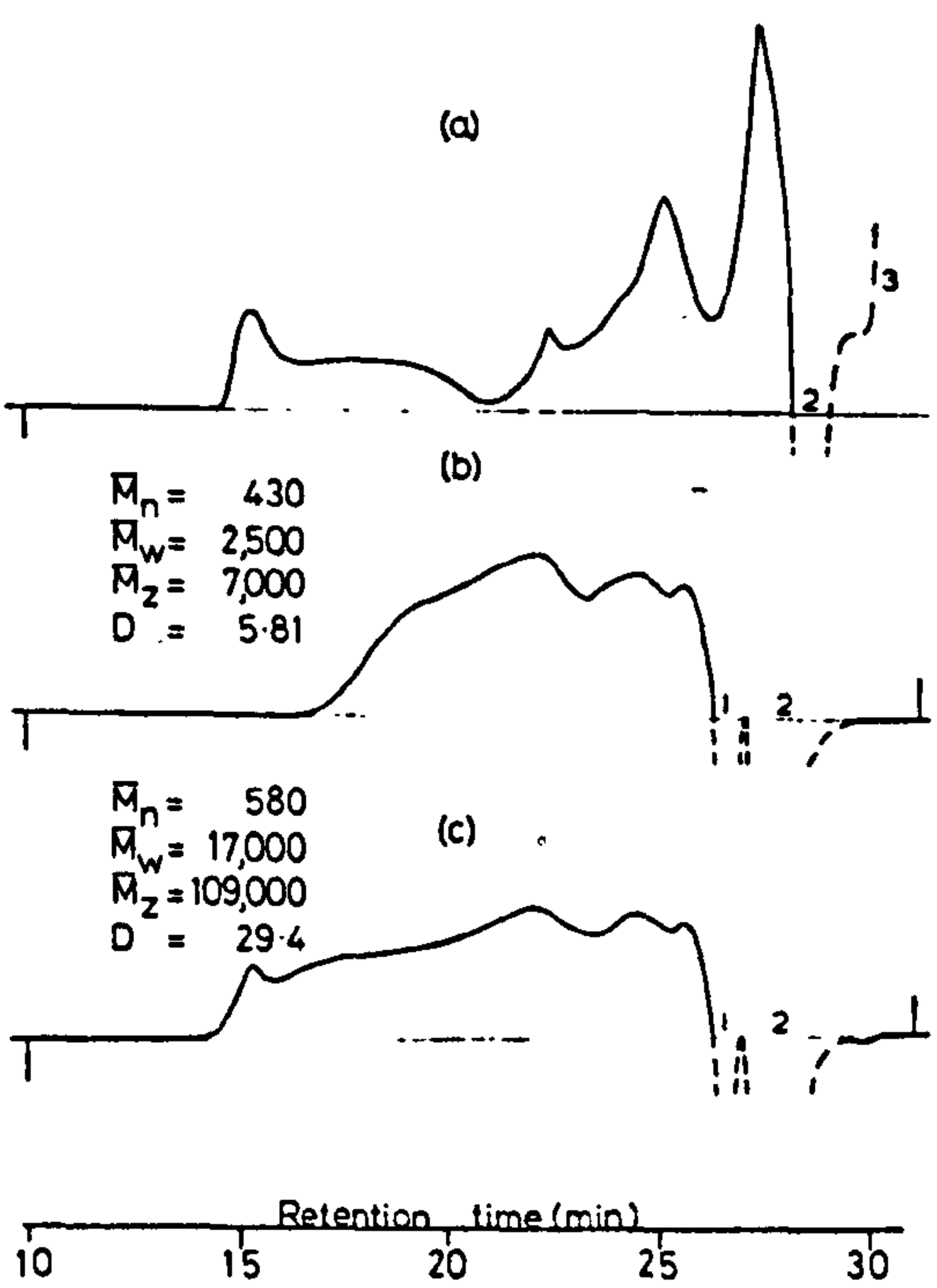

Fig. 3. Resin A: (a) fresh sample dissolved in DMSO/DMF (1/10) and run in a mobile phase of DMF alone; (b) fresh sample dissolved and run in 0.1*M* LiCl in DMF; (c) sample aged for about 6 months at 21°C dissolved and run in 0.1*M* LiCl in DMF. Peak identification: (1) lithium chloride; (2) water; (3) DMSO.

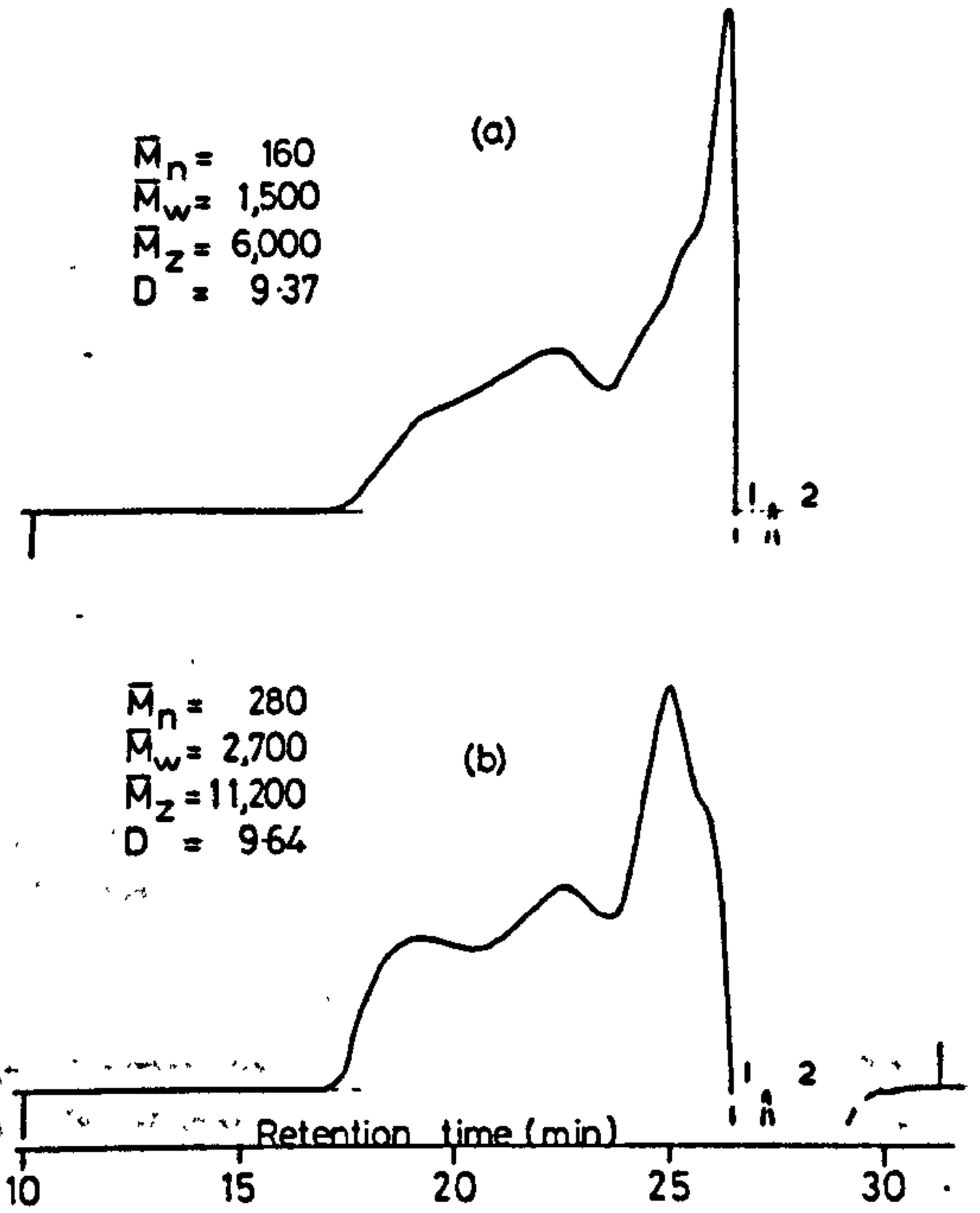

Fig. 4. Resin B: (a) fresh sample; (b) sample aged for about 6 months at 21°C. Both samples dissolved and run in 0.1*M* LiCl in DMF. Peak identification: (1) lithium chloride; (2) water.

fresh and old resins are shown in Figures 3(b), (c), and 4. It can be seen that resin A with no end urea addition shows a fairly even distribution when fresh, the low molecular mass end altering only slightly on aging while the medium to high molecular mass region becomes much more extended. Resin B containing the end urea shows a large low molecular mass peak when fresh which diminishes considerably on aging, producing a large increase in medium molecular mass materials while the high molecular mass end is relatively slow to change.

DISCUSSION

The objectives at the outset of this work were to develop a method of determining the molecular mass distribution of UF formulations which was rapid, reproducible, and applicable to all types of samples. Since the introduction of semirigid microparticulate crosslinked polystyrene gels, analysis times of 30 min or less have been commonplace. These columns therefore show a considerable advantage over the types previously used in this field, which were usually composed of large soft particles often based on a polysaccharide or a polyester.

The three-column set which was employed gives a separation time of about 30 min using a flow rate of 1 mL min^{-1} of DMF containing LiCl (0.1*M*). The columns were stored in this solvent when not in use and proved stable and reliable over a period of many months. There was no significant change in the calibration plot during this period.

The choice of the solvent has been crucial to the success of this investigation since it eliminates the hydrogen bonding in the solute and allows complete solvation of the molecules to occur. As a consequence, a rational calibration curve has been obtained leading to meaningful values for $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$ and polydispersity. In the absence of lithium salt the degree of molecular association is variable, rendering all results thus obtained virtually meaningless.

Obviously some assumptions have had to be made about the structure of the polymer chain, but this is invariably the case when calibrating SEC columns for molecular mass determinations. These assumptions are only likely to cause significant errors in samples having final molecular ratios above about 1:2 (U:F) and commercial materials of this type are fairly rare.

The action of the lithium salt in rendering UF polymers soluble is not completely understood. However, it has been shown experimentally that lithium salt is transported through the SEC column with the urea derivative and that each urea group is associated with one molecule of LiCl probably via the carbonyl oxygen.

The lithium salt not only confers solubility on the polymer but also provides a secondary beneficial effect in that there is an increased detector response to the urea compounds compared with that observed in DMF alone. Since a lithium ion is associated with each urea unit, this effect is shown over the whole molecular mass range. On the other hand, the high degree of solvation of the urea derivatives means that there is very little relative difference in the molecular size of the low molecular mass components, causing poor resolution of these materials. However, the complete separation of these materials is not necessary for the purposes of determining average molecular masses, and they are better separated, using other techniques such as high performance liquid chromatography.

The actual values obtained for the molecular mass averages of commercial samples have varied widely. Typical figures found for freshly prepared materials were: $\overline{M}_n$ between 140 and 500; $\overline{M}_w$ between 800 and 3000; $\overline{M}_z$ between 3000 and 25,000; polydispersity between 5 and 20. These values can increase substantially on storage at 21°C for 6 months (see Figs. 3 and 4).

It can be concluded that this approach to the SEC of UF compositions is a viable method of quality control. It is also a powerful procedure for investigating the formation of the urea–formaldehyde polymers and not least their aging characteristics. Although only urea–formaldehyde polymers have been investigated in this study, it is likely that this technique could be useful in the analysis of similar materials such as melamine formaldehyde resins.

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Liquid Chromatographic Procedure for the Separation and Characterisation of Simple Urea - Formaldehyde Reaction Products

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A procedure is described for separating about 20 simple, low relative molecular mass urea - formaldehyde reaction products by liquid chromatography on an aminopropyl column using aqueous acetonitrile as eluent. The technique is shown to have considerable advantages over previously published methods. The preparation and characterisation of some reference compounds, which so far have been little studied, are given in detail. The use of reaction mixtures of urea and formaldehyde for identifying peaks is described. Almost all of the peaks observed in commercial urea - formaldehyde formulations can now be identified by this technique.

Keywords: *Liquid chromatography; urea - formaldehyde resins separation; characterisation; urons*

Resins produced by the condensation of urea and formaldehyde occupy an important position in many branches of industry. Although numerous analytical investigations into the course of the urea - formaldehyde (UF) reaction and the nature of the finished resin have been undertaken, there are still aspects of its chemistry that are not understood. This is in part due to the complex series of reactions that occur between urea and formaldehyde, leading to the formation of methylol and methylene compounds and both linear and cyclic ethers (urons). Thus the number of compounds produced can be very large indeed. Difficulties also arise owing to both the instability of UF compounds and the very limited solubility of compounds having a relative molecular mass greater than about 200.

Reliable information on the average properties of UF reaction products has been obtained (notably by NMR measurements,[1] which show the over-all chemical composition and by size exclusion chromatography,[2] which gives the range of relative molecular masses) but separation and quantitation of individual components in the reaction mixture has proved more difficult. Thin-layer chromatography has been used to identify and quantify a small number of the low relative molecular mass compounds that are formed, but its range is limited and the experimental procedure is long and difficult to perform.[3,4]

Some efforts have been made to investigate urea - formaldehyde reaction products and other amide - formaldehyde compounds by liquid chromatography but a simple, rapid, efficient and universal method has not yet been reported. Kumlin and Simonson[5,6] studied UF condensates using a cation-exchange resin in the Li^+ form. The resin used was of large particle size and although a separation of about 10 compounds was achieved, the efficiency of the column was low and a full analysis run took some 120 min to complete.

Murray *et al.*[7] used a reversed-phase column to separate biuret, triuret and methylenediurea, which occur as impurities in fertiliser-grade urea, and Davidson[8] separated urea, methylenediurea and dimethylenetriurea in a similar fashion in UF fertiliser compositions. Beck *et al.*[9] used a cation-exchange resin in the Li^+ form to examine durable press finishes. Textile finishes were also studied by Kottes Andrews[10] using a reversed-phase column.

In this paper, the limitations of these liquid chromatographic procedures are discussed and a method is reported that will separate UF condensation products efficiently and quickly. Details are given for the preparation of reference materials and of the methods used for identifying the chromatographic peaks.

Preliminary Investigations

In order to separate the many compounds formed when urea and formaldehyde react together and to ensure that the analysis is complete in as short a time as possible, it was decided to investigate the potential of reversed-phase silica columns rather than the ion-exchange columns used by Kumlin and Simonson,[5] as these were reported to be inefficient and slow.

In the course of the investigation, several 5-μm reversed-phase packing materials from various manufacturers were examined, including Zorbax ODS, LiChrosorb ODS and Spherisorb ODS. A mixture of urea, monomethylolurea (MMU), dimethylolurea (DMU) and methylenediurea (MDU) was used as a simple test solution and it was found that the elution patterns were slightly but significantly different. With Zorbax and LiChrosorb, DMU and MDU were not separated and with Spherisorb the resolution of urea and MMU was inadequate. However, by coupling a Zorbax column to a Spherisorb column, complete resolution of the test mixture could just be achieved. Although the analysis time was long and the separation was barely adequate, this column configuration was used for several months to estimate low relative molecular mass compounds in UF compositions.

In order to attempt to improve the analysis, a column packed with Hypersil C_{22} Super was used in the hope that the longer carbon chains would retain the molecules of interest to a greater degree. The results were disappointing, showing little improvement when compared with the usual ODS packings.

The limitations of chromatographing UF compounds in the conventional reversed-phase mode are as follows. 1. Resolution of the simplest compounds is very difficult to achieve; with more complex mixtures considerable peak overlap occurs and the chromatography becomes meaningless. 2. Many compounds such as uron and its methylol derivatives elute at the solvent front even when using the weakest solvent and it does not seem likely that this difficulty can be overcome. The analysis time is about 25 min for a typical mixture.

It was thought that a better separation of the methylol compounds could be achieved by using a more polar column. Also, the increased interaction between the polar stationary phase and the UF compounds could give greater flexibility with the eluting solvent.

A column was packed with a hydroxy-terminated material (LiChrosorb Diol) and the test solution of urea, MMU, DMU and MDU was chromatographed using water as the eluting solvent. The elution pattern was markedly different to that

obtained with the hydrophobic ODS columns. The hydroxy compounds DMU and MMU eluted first, followed by urea and MDU. It was apparent that the –OH · · · NH– hydrogen bonding effect was more powerful than the –OH · · · OH– interaction and compounds were eluting according to their =NH content. This order of elution from the column was contrary to the ideal pattern and it was considered likely that the chromatography of UF mixtures would be complicated on such a column. The possibility of reversing this elution pattern by using an amine column seemed worth investigating.

An aminopropyl-terminated phase, Techsil NH_2 (5 μm), was examined and, using the aqueous solvent as before, all the test compounds eluted at the solvent front. However, an amino column has the characteristics of a "normal" phase and water is likely to be the strongest solvent available. Using methanol as a potentially weaker eluent, a partial separation was achieved and the elution pattern (parent compound, monomethylol compound and dimethylol compound) seemed most encouraging. Methanol was replaced by acetonitrile in the hope that the absence of solvent - solute hydrogen bonding would, firstly, accentuate differences between the zero, mono- and dimethylol compounds thus giving better separation of the test mixture and secondly, increase the elution time. This proved to be so, and after a final adjustment of the solvent strength by the addition of 10% water, an almost ideal system for separating the test mixture was obtained.

The flexibility of the system was demonstrated when less polar compounds such as uron and its methylol derivatives, hitherto eluting at the solvent front, were completely separated by reducing the solvent strength, *i.e.*, the water content.

Thus a system that seemed almost ideal for the chromatography of simple urea - formaldehyde compounds was developed. The column had high efficiency (8000 plates), the peak shape under normal conditions was good, the analysis time was short, being approximately 10 min for the test mixture of urea, MMU, DMU and MDU, and the elution pattern was favourable.

Experimental

Apparatus

The chromatographic equipment used consisted of a Waters 6000 A pump, a Rheodyne 70-10 injection valve fitted with a 100-μl loop and a Model 70-11 filler port, a Waters R401 differential refractometer and a Waters Model 730 Data Module. A 2-μm in-line filter was positioned between the injector and the column.

The analytical columns employed were made from 250 × 4.6 mm i.d. stainless-steel tubing with zero dead volume fittings. The columns were packed using the slurry technique developed by Kirkland.[11]

The initial upward displacement with methanol was followed by downward displacement and "slamming" to improve the stabilisation of the bed. The slurry used for packing the 5-μm aminopropyl-bonded silica to produce the columns used for the majority of this work was prepared by dispersing 3.5 g of Techsil NH_2 (5 μm) packing material in 70 ml of chloroform - methanol (3 + 1) by ultrasonic agitation. The aminopropyl-bonded silica columns usually have an adequate lifetime, but when used for the analysis of materials with a high proportion of free formaldehyde they can deteriorate quickly. This is possibly due to an irreversible amino - aldehyde interaction taking place and is seen by shortened retention times and a lack of resolution of methylenediurea (MDU) and asymmetric dimethylolurea (asym. DMU). In order to attempt to offset this problem, a small amount of ammonia (0.01 M) is added to the eluting solvent. Depending on the type of sample under investigation, the life of an amino column is between 50 and 200 working days. Column packing and testing take only 2–3 h and consequently column deterioration is not considered to be a serious problem.

One of the preparative columns was packed using Partisil 5-μm silica by the same upward - downward - "slamming" procedure previously described. Stainless-steel tubing, 300 × 7.8 mm i.d., was used for the column and 5.5 g of the packing material was slurried in 70 ml of chloroform - methanol (1 + 1). Octadecylsilane (ODS)-bonded silica (Partisil 10) was used in the other preparative column. Column packing was by the method already described after slurrying in propan-2-ol.

The eluting solvent used for most of the work was prepared by mixing 900 ml of acetonitrile of Hypersol grade (BDH Chemicals, Poole, UK) with 100 ml of de-ionised water and 0.5 ml of ammonia solution (sp. gr. 0.880). The solvent mixture was de-gassed with helium and the temperature allowed to rise to room temperature before use.

If the mixtures under examination contained predominantly methyl ethers or urons, *i.e.*, compounds with short elution times, then improved resolutions were obtained by weakening the eluting solvent to 2.5 or 5% water in acetonitrile.

Other solvent and chemicals, except where stated, were general-purpose laboratory reagents.

Preparation of Samples

Where possible, reference materials (5–10 mg) were dissolved directly in 10 ml of eluting solvent. If limited solubility was a problem, a solution in 1 ml of water was prepared, with gentle heating if necessary, and then diluted to 10 ml with acetonitrile.

With resinous samples, about 200 mg were taken and low-condensed materials that were totally soluble were dissolved directly in the eluting solvent. However, when the average molecular mass was large and a considerable proportion (up to 80% of the UF) was insoluble, the above techniques were unsatisfactory. The best approach was then to dissolve the sample in 1 ml of dimethylformamide and dilute to 10 ml with acetonitrile. The sample plus solvent was shaken vigorously and allowed to stand. If necessary, the sample solution was filtered through a 0.5 μm filter before injection.

Reference Compounds and Mixtures

Monomethylolurea (MMU), dimethylolurea (DMU), methylenediurea (MDU), monomethylolurea monomethyl ether (MMU.MME), dimethylolurea dimethyl ether (DMU.DME) and dimethylurea monomethyl ether (DMU.MME) were all synthesised by methods published earlier.[3] The following reaction products of urea and formaldehyde were prepared.

1. *Alkaline UF condensate, molar ratio* 1:3. Urea, 0.6 g; 50% aqueous formaldehyde solution, 1.8 g; disodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$), 0.2 g; water, 5 g. The buffer was dissolved in the formaldehyde solution and the urea added. The solution was stirred and allowed to stand at room temperature. Samples were taken at intervals.

2. *Alkaline MDU:F condensate, molar ratio* 1:1. MDU, 1.3 g; 50% aqueous formaldehyde solution, 0.6 g; disodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$), 0.1 g; water, 5 g. MDU was dissolved in the warmed water, Na_2HPO_4 was added and, when dissolved, the formaldehyde was added. The mixture was allowed to stand at room temperature and samples were taken at intervals.

3. *Alkaline MDU:F condensate, molar ratio* 1:1.5. This was prepared as for No. 2, but 0.9 g of 50% formaldehyde solution was used.

4. *Alkaline MDU:F condensate, molar ratio* 1:2. This was prepared as for No. 2 but 1.3 g of 50% formaldehyde solution were used.

5. *Dimethylene ether from DMU (Zigeuner and Pitter).*[12] DMU (10 g) was dissolved in 33 ml of 1% potassium carbonate solution. After 3 weeks, about 1 g of precipitate had formed. The supernatant liquor and the precipitated material were examined.

6. *Crude dimethylenetriurea (DMTU).* MDU (6.6 g, 0.05 M) was dissolved in 100 ml of water at 60 °C. Disodium hydrogen orthophosphate (0.2 g) was added and, when dissolved, 3 g (0.05 M) of 50% formaldehyde were added. The reaction mixture was allowed to stand for 1 h. The crude monomethylol MDU was filtered off, washed with cold water and dissolved in the minimum amount of water at 60–70 °C. Urea (30 g, 0.5 M) and 0.5 g of sodium dihydrogen orthophosphate were added and dissolved in the solution. After standing overnight, the crude DMTU was filtered off and washed thoroughly with water.

7. *Dimethylol uron (DM uron).* A 2 ml volume of 40% sodium hydroxide was added to 50% formaldehyde (72 g, 1.2 M). Urea (12 g, 0.2 M) was dissolved in this alkaline formaldehyde and the solution was heated to boiling for 1 min. The pH was adjusted to 8 with formic acid and about 40 ml of water and formaldehyde were removed by vacuum distillation at 40–50 °C in a rotary evaporator. Extraction with chloroform • acetonitrile (1 + 1) removed the dimethylol uron from the reaction mixture, presumably as the di(hemiformal) (pure dimethylol uron is only sparingly soluble in this solvent mixture). This extraction procedure gave a good separation of the dimethylol uron from impurities such as DMU and TMU.

DM uron was separated from the excess of residual formaldehyde and water by chromatography on a semi-preparative Partisil 5-μm silica column (300 × 7.8 mm i.d.) using 10% methanol in chloroform as the eluent. The structure was confirmed by infrared, ^{1}H NMR (Figs. 1 and 2) and ^{13}C NMR spectroscopy: ring C, 77.4 p.p.m.; chain C, 66.9 p.p.m.; carbonyl C, 152.3 p.p.m.; solvent, DMSO-d_6, m.p. 87–90 °C.

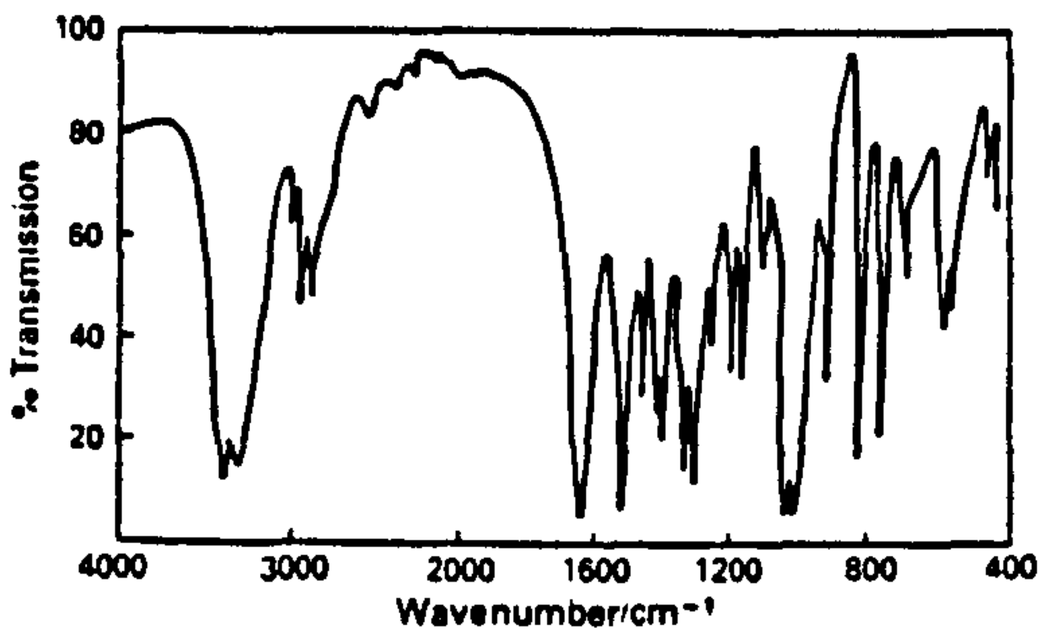


Fig. 1. Infrared spectrum of dimethylol uron

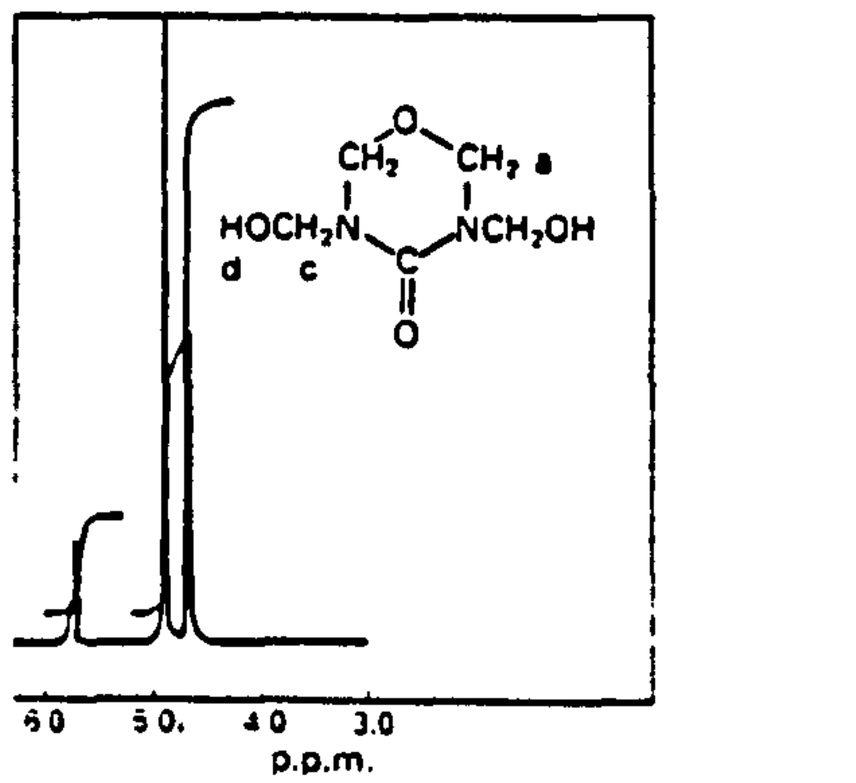


Fig. 2. ^{1}H NMR spectrum of dimethylol uron (solvent DMSO-d_6). a. 4.88; c. 4.65; and d. 5.72 p.p.m.

8. *Uron and monomethyloluron.* Pure dimethyl uron, 0.04 g (0.00025 M), urea, 0.03 g (0.0005 M) and sodium dihydrogen orthophosphate, 0.005 g, were dissolved in about 0.2 ml of water. The solution was heated carefully at 100 °C for 5 min, then cooled and extracted with 3 × 1 ml of acetonitrile. The combined acetonitrile extracts were evaporated to dryness at room temperature using a jet of air.

The urons were separated efficiently on a 250 × 4.8 mm i.d. amine column using 2.5% water in acetonitrile as the eluting solvent. Uron itself was identified by infrared, ^{1}H NMR (Figs. 3 and 4) and ^{13}C NMR spectroscopy: ring C, 75.6 p.p.m. (in $CDCl_3$). Monomethyl uron was indicated by its chromatographic behaviour and its infrared and proton NMR spectra (Figs. 5 and 6). Insufficient sample was obtained for a ^{13}C spectrum.

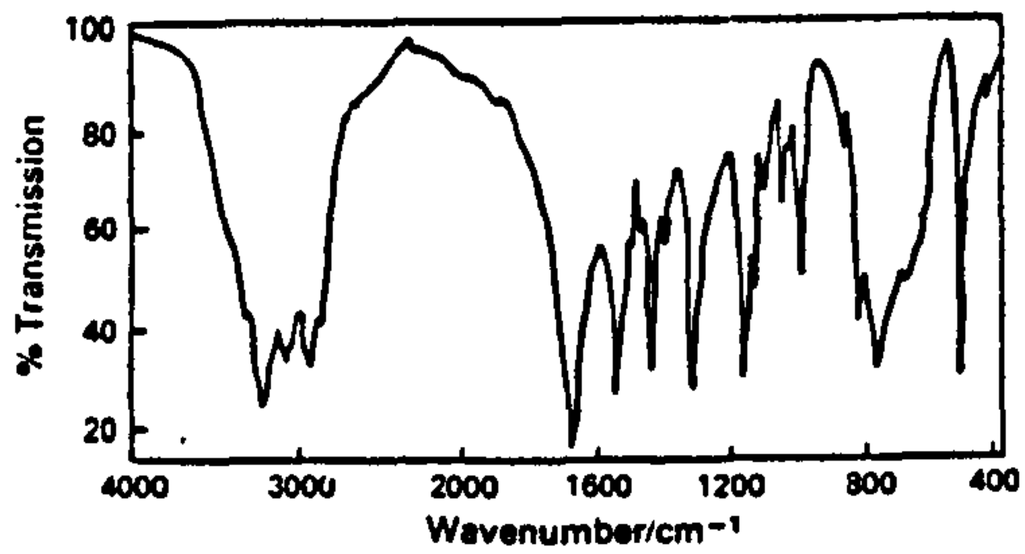


Fig. 3. Infrared spectrum of uron

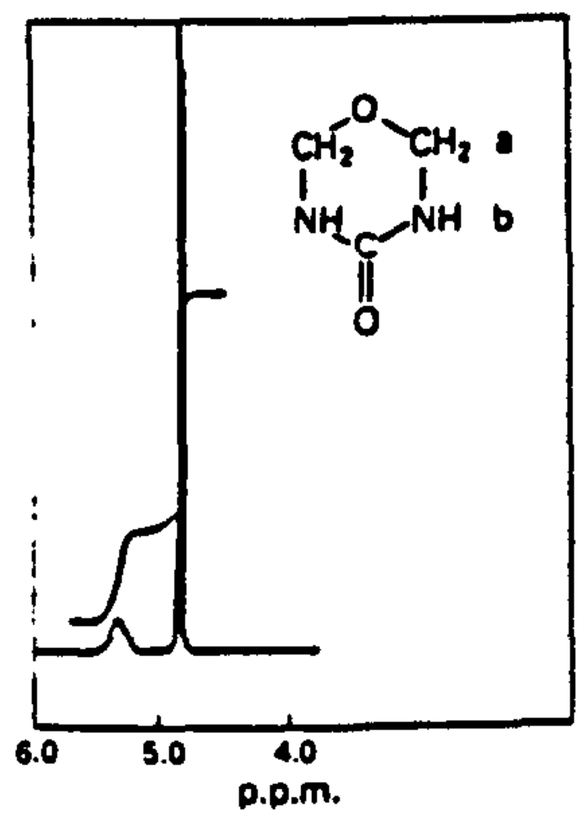


Fig. 4. ^{1}H NMR spectrum of uron (solvent $CDCl_3$). a. 4.85; and b. 5.35 p.p.m.

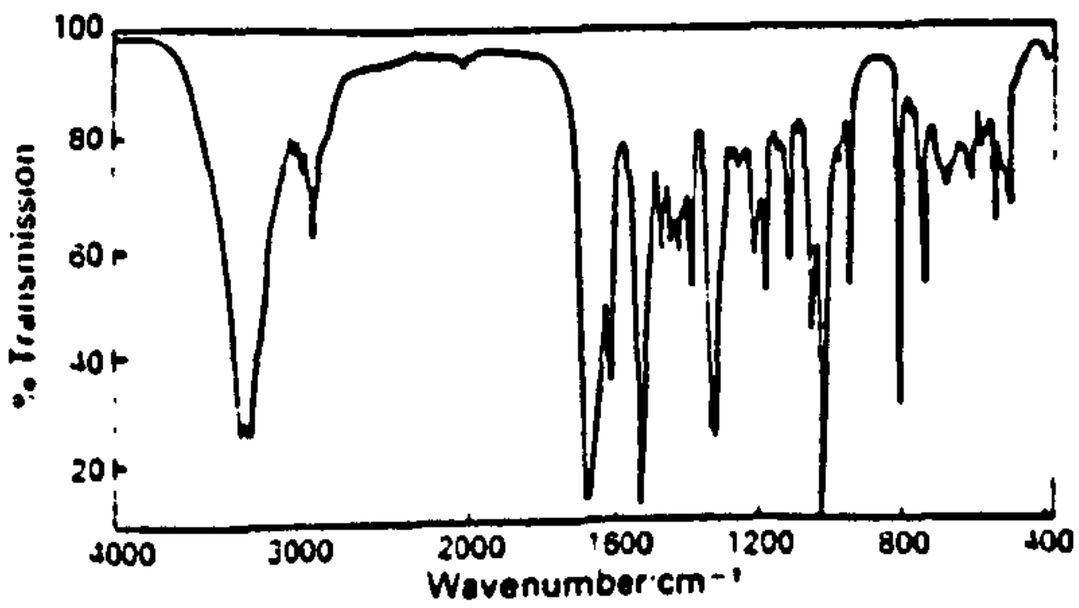


Fig. 5. Infrared spectrum of monomethylol uron

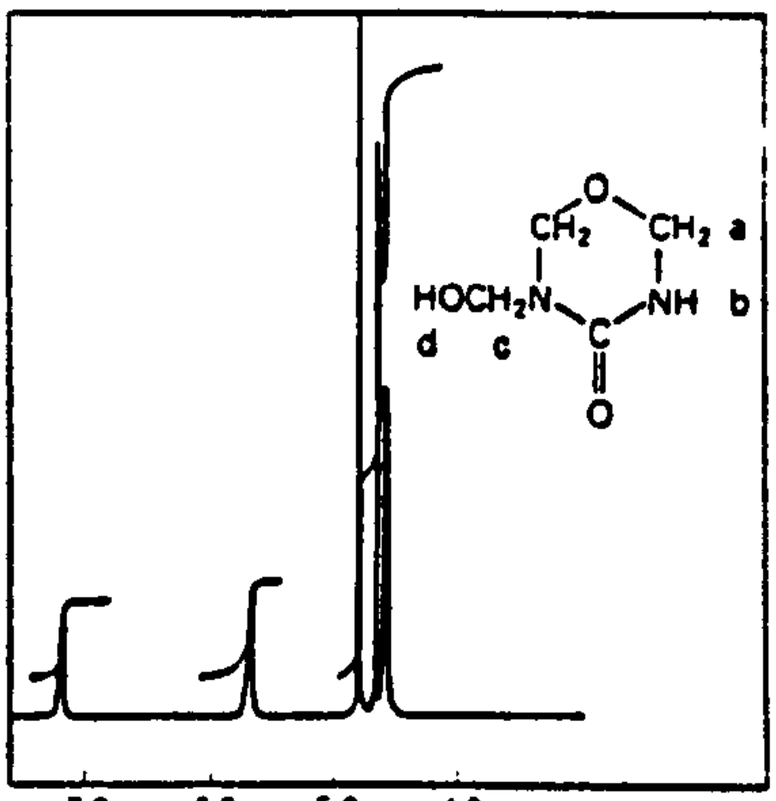


Fig. 6. ^1H NMR spectrum of monomethylol uron (solvent DMSO-d_6). a, 4.70; b, 7.12; c, 4.62; and d, 5.63 p.p.m.

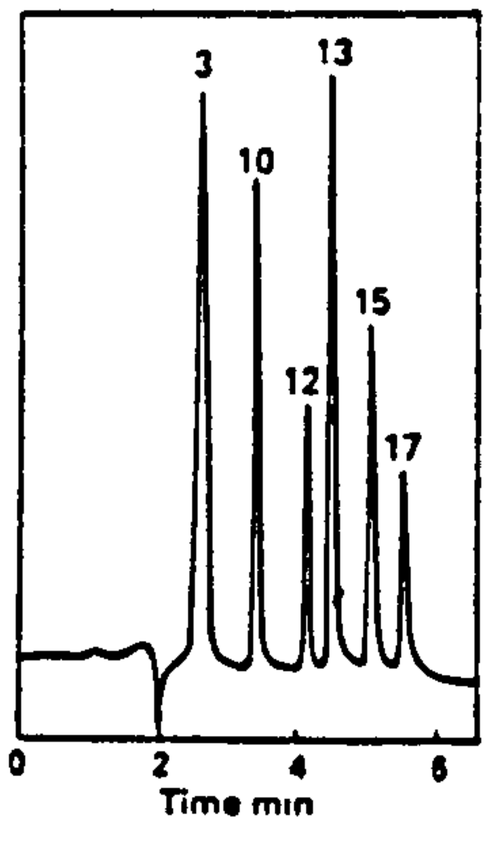


Fig. 7. Chromatogram of test mixture: urea, MMU, DMU, MDU and glycerol (for peak identification, see Table 1)

Results and Discussion

Evaluation

One of the major problems in the chromatography of urea - formaldehyde compounds on an aminopropyl column is the slow but inevitable change of retention characteristics. For the most part, this renders absolute retention times unreliable and it has been found to be useful to adopt a procedure of multiple relative retention times. The two compounds used for reference in this study were urea and DMU. Using this technique, the chromatograms are fairly easy to interpret. However, it is still considered to be good practice to run standard solutions at regular intervals so that the state of the column is continually monitored. The following are examples of solutions which can be used: urea, MMU, DMU, MDU and glycerol (Fig. 7); DM uron containing MM uron and uron itself if possible; methylolated MDU; and methylolated OMDU, all prepared in eluting solvent and stable for several months.

Table 1 is a list, in increasing retention time, of the peaks observed in the chromatography of the various reference compounds and reaction mixtures. The retention times given are typical of those obtained with a new column . Also given are retention times relative (a) to urea for early eluting compounds and (b) to DMU for late eluting compounds. The elution times of dimethylformamide (DMF), water and formaldehyde are included. Glycerol elutes in a chromatographic "window" and is suitable for use as an internal standard for the determination of compounds such as urea, MMU, DMU, etc., in UF compositions.

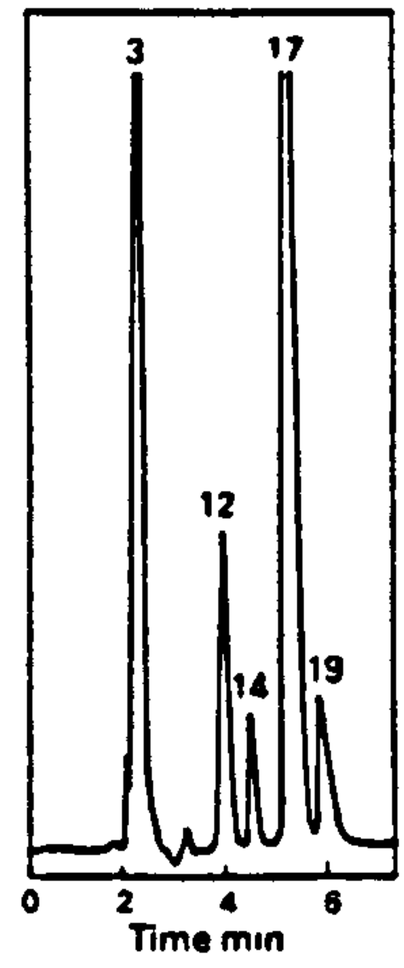


Fig. 8. Chromatogram of reaction product 1 showing N,N-DMU and TMU (for peak identification, see Table 1)

Peak Identification

Simple compounds

The chromatography of simple reference compounds and well characterised urea derivatives (see above) resulted in the easy and unambiguous identification of about half the peaks encountered in conventional urea - formaldehyde reaction mixtures.

Methylolureas

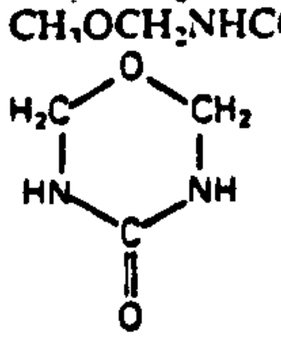
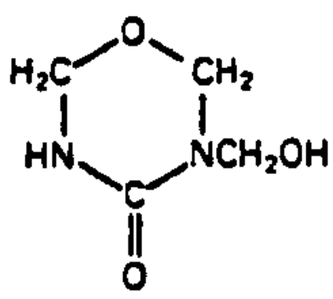
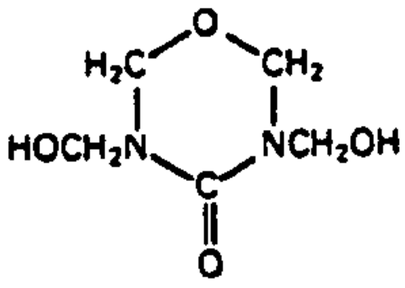
Examination of reaction product 1 enabled N,N-dimethylolurea (asym. DMU) and trimethylolurea (TMU) to be tentatively identified (Fig. 8). The peaks of interest were collected from the column and the solvent removed by careful evaporation at room temperature using a jet of air. To ensure that the recovery procedure had not significantly affected the purity of the compounds, small amounts of the collected materials were re-chromatographed. The infrared and proton NMR spectra unambiguously confirmed the nature of the peaks.

It has been shown in a previous study[3] that with urea - formaldehyde compounds there can exist a simple relationship between the logarithm of the retention time and the degree of substitution. This concept was again found to hold true (Fig. 9) and in this instance a plot of k' against the number of methylol groups is a straight line. [k' is the capacity factor, equal to $(t_r - t_m)/t_m$; t_r is the retention time of the compound and t_m is the retention time of an unretained solute]. When log k' of asym. DMU and TMU are plotted to lie on the same line it can be readily seen that a second methylol substituent on a terminal nitrogen has only half the effect on the retention time as the first substituent.

Methylolmethylenediureas

The reaction between MDU and formaldehyde is complicated, leading to 12 possible mono-, di- and trimethylol MDU's. However, many of these derivatives are unlikely and only about seven peaks are actually observed. It is possible to

Table 1. Peaks observed in urea - formaldehyde reaction products in order of increasing elution time

No.	Compound	Structure	Identification*	Retention time/min relative to Absolute	Urea	DMU
1	Dimethylformamide			2.16		
2	Formaldehyde	HCHO		2.25		
3	Water			2.52		
4	Dimethylolurea dimethyl ether	$CH_3OCH_2NHCONHCH_2OCH_3$	D	2.41	0.73	
5	Monomethylolurea monomethyl ether	$CH_3OCH_2NHCONH_2$	D	2.79	0.84	
6	Uron		D	2.84	0.86	
7	Monomethylol uron		D	3.03	0.91	
8	Dimethylolurea monomethyl ether	$CH_3OCH_2NHCONHCH_2OH$	D	3.19	0.96	
9	Dimethylol uron		D	3.20	0.96	0.58
10	Urea	H_2NCONH_2	D	3.32	1	0.60
11	Unknown		U	3.87	1.17	0.70
12	Monomethylolurea	$H_2NCONHCH_2OH$	D	4.12	1.24	0.75
13	Glycerol		D	4.45	1.34	0.80
14	*N.N*-Dimethylolurea	$H_2NCON(CH_2OH)_2$	D	4.87	1.47	0.88
15	Methylenediurea	$H_2NCONHCH_2NHCONH_2$	D	5.05		0.91
16	*sec*-Monomethylolmethylenediurea	$H_2NCONHCH_2N(CONH_2)CH_2OH$	T	5.31		0.96
17	*N.N'*-Dimethylolurea	$HOCH_2NHCONHCH_2OH$	D	5.53		1
18	Oxymethylenediurea	$H_2NCONHCH_2OCH_2NHCONH_2$	T	5.60		1.01
19	Trimethylolurea	$HOCH_2NHCON(CH_2OH)_2$	D	6.53		1.18
20	Monomethylolmethylenediurea	$HOCH_2NHCONHCH_2NHCONH_2$	P	6.75		1.22
21	Asym. dimethylolmethylenediurea	$HOCH_2NHCON(CH_2OH)CH_2NHCONH_2$ or $HOCH_2NHCONHCH_2N(CH_2OH)CONH_2$	T	7.35		1.33
22	Monomethyloloxymethylenediruea	$HOCH_2NHCONHCH_2OCH_2NHCONH_2$	P	7.7		1.39
23	Unknown		U	8.6		1.56
24	Dimethylenetriurea	$H_2NCONHCH_2NHCONHCH_2NHCONH_2$	D	9.2		1.66
25	Dimethylolmethylenediurea	$HOCH_2NHCONHCH_2NHCONHCH_2OH$	P	9.85		1.78
26	Dimethyloxymethylenediurea	$HOCH_2NHCONHCH_2OCH_2NHCONHCH_2OH$	P	10.5		1.90
27	Trimethylolmethylenediurea	$HOCH_2NHCONHCH_2NHCON(CH_2OH)_2$	T	11.2		2.03
28	Trimethylolmethylenediurea	$HOCH_2NHCONHCH_2(CH_2OH)CONCH_2OH$	T	12.2		2.21

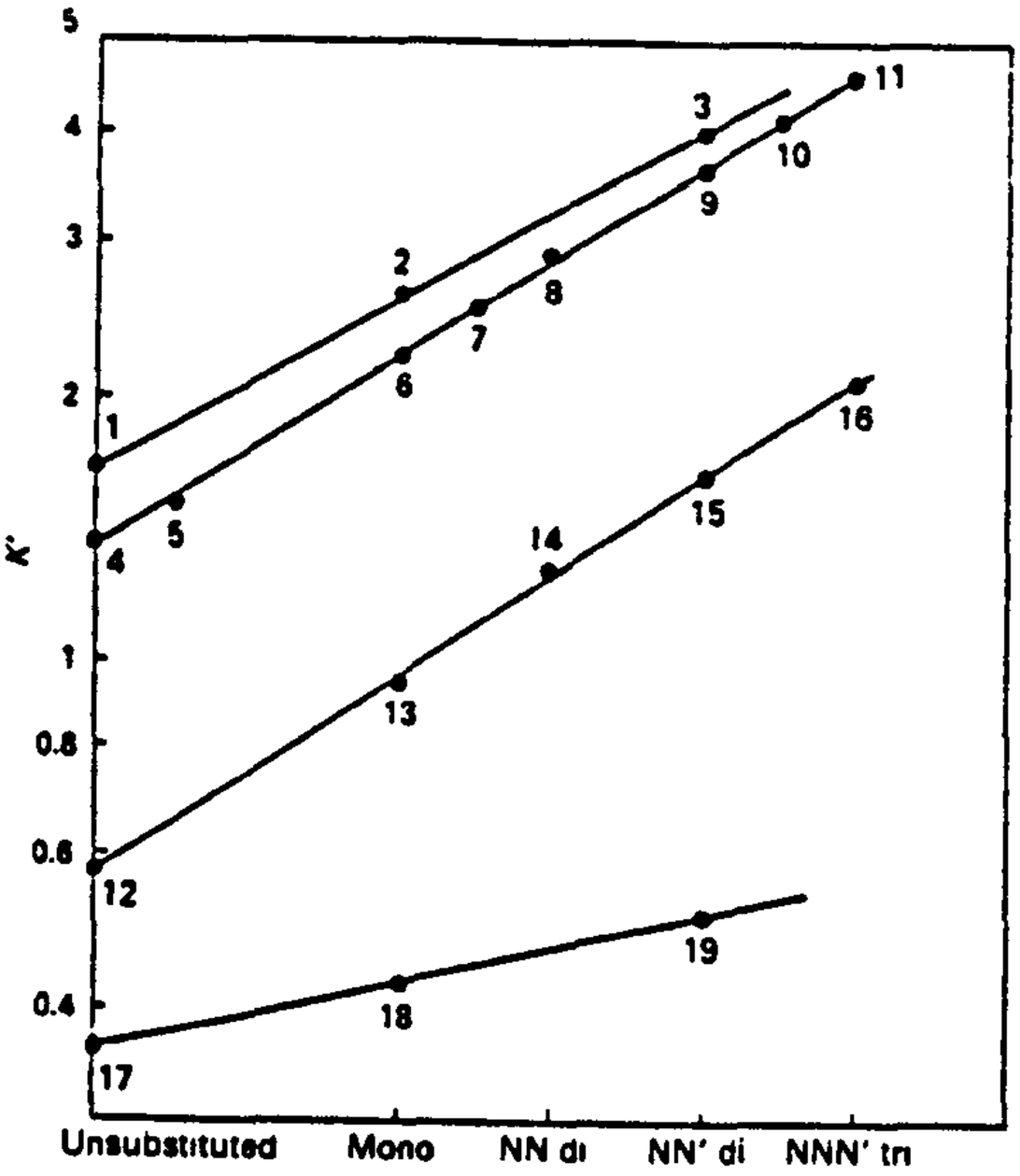
* D = definite. P = probable. T = tentative. U = unknown.

obtain information about the nature of some of these peaks by reacting MDU and formaldehyde together at slightly alkaline pH (reaction mixtures 2. 3 and 4). With a low MDU : F ratio and a short reaction time the predominant product is monomethylolmethylenediurea (MMMDU). As the amount of formaldehyde and the reaction times are increased. di- and then trimethylol substitution is favoured.

A typical chromatogram is shown in Fig. 10. As with the urea series. MDU and its mono- and dimethylol derivatives follow the simple relationship between log k' and the degree of substitution. It can be seen (Fig. 9) that two peaks occur between MMMDU and the symmetrical DMMDU. Using the behaviour of the dimethylolureas as a guide it seems likely that a second methylol substituent on the terminal nitrogen of MMMDU will have only half the effect of the first on the retention time. Plotting log k' of these two peaks on the MDU derivative line shows indeed that one peak behaves in accordance with the asym. DMMDU structure. $H_2NCONHCH_2NHCON(CH_2OH)_2$. Considering the position of the second peak. which should be one of the terminal nitrogen - chain nitrogen disubstituted structures ($H_2NCONHCH_2N(CH_2OH)CONHCH_2OH$ or $H_2NCON(CH_2OH)CH_2NHCONHCH_2OH$). it would seem that a methylol substituent on a chain nitrogen will have half the effect of a second substituent on the terminal nitrogen and only one quarter the effect of the first substituent on a terminal nitrogen (Fig. 9). Two peaks occur at longer retention times. which again appear to follow the structure - retention time relationship described above. In this way these compounds have been tentatively identified as having the two most probable trimethylol MDU structures (Table 1).

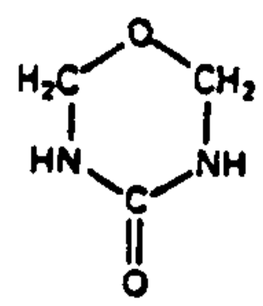
Methyloloxymethylenediureas

The insoluble material from reaction mixture 6 showed one major peak. which could safely be assumed to be DMOMDU.

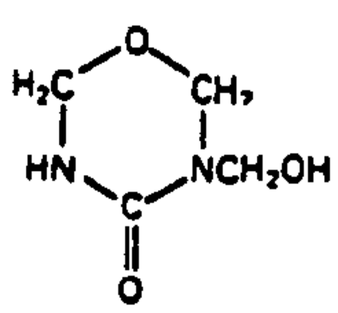


1 = $NH_2CONHCH_2OCH_2NHCONH_2$
2 = $NH_2CONHCH_2OCH_2NHCONHCH_2OH$
3 = $HOCH_2NHCONHCH_2OCH_2NHCONHCH_2OH$
4 = $NH_2CONHCH_2NHCONH_2$
5 = $NH_2CONHCH_2NCONH_2$ (with CH_2OH on the N)
6 = $NH_2CONHCH_2NHCONHCH_2OH$
7 = $NH_2CONCH_2NHCONHCH_2OH$ (with CH_2OH on the N)
8 = $NH_2CONHCH_2NHCON(CH_2OH)_2$
9 = $HOCH_2NHCONHCH_2NHCONHCH_2OH$
10 = $HOCH_2NHCONCH_2NHOONHCH_2OH$ (with CH_2OH on the N)
11 = $HOCH_2NHCONHCH_2NHCON(CH_2OH)_2$
12 = NH_2CONH_2
13 = $NH_2CONHCH_2OH$
14 = $NH_2CON(CH_2OH)_2$
15 = $HOCH_2NHCONHCH_2OH$
16 = $HOCH_2NHCON(CH_2OH)_2$

17 =



18 =



19 =

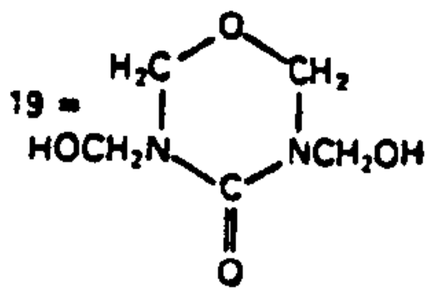


Fig. 9. Effect of degree of substitution on retention times. $k' = (t_r - t_m)/t_m$, where t_r is the retention time of the solute and t_m is the retention time of a non-retained solute

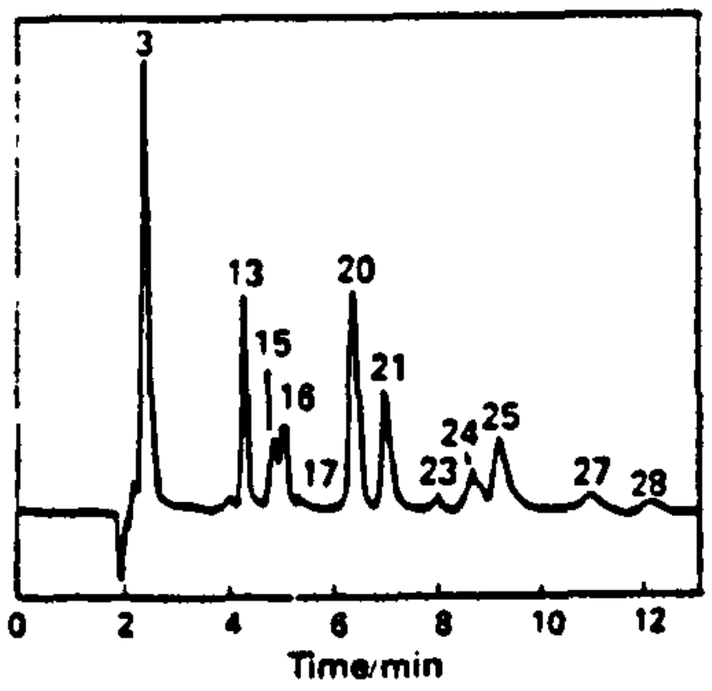


Fig. 10. Chromatogram of MDU and formaldehyde reacted at pH 8 for 8 h at ambient temperature (for peak identification, see Table 1)

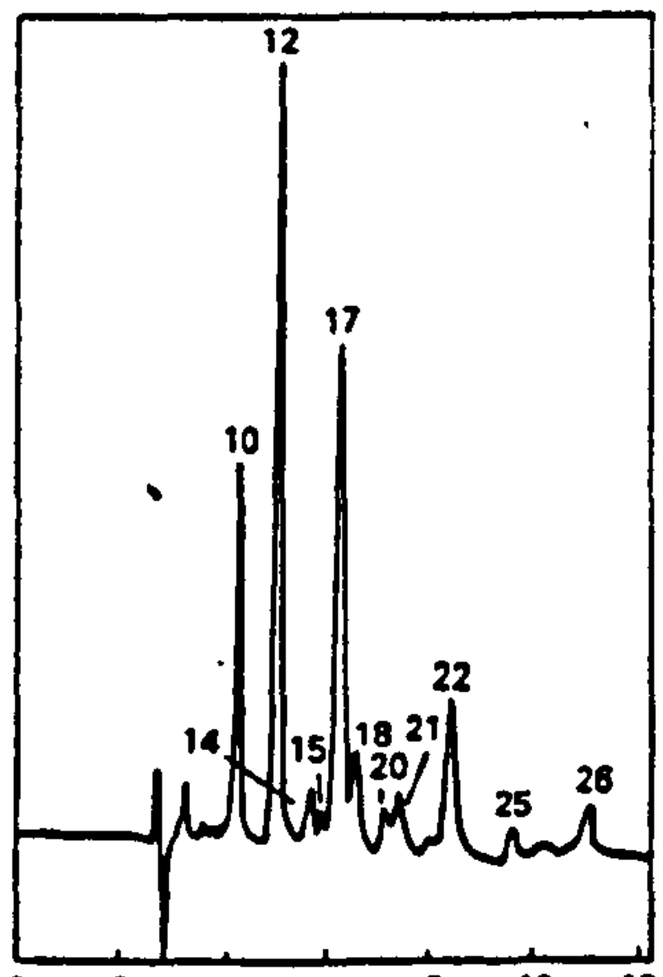


Fig. 11. Chromatogram of UF reaction product U:F 1:1.4 reacted at 70 °C for 2 h at pH 9 (for peak identification, see Table 1)

The chromatogram of the supernatant liquor showed another large peak at a shorter retention time, which is likely to be the mono compound. When log k' for these compounds is plotted against the substitution pattern, a line having virtually the same gradient as the urea and MDU derivative line is obtained. Further, there is a small peak at the elution time corresponding to zero substitution, which can be tentatively attributed to the parent compound, oxymethylenediurea. Kumlin and Simonson[6] identified MMOMDU and DMOMDU in the reaction mixture described by Zigeuner and Pitter[12] and characterised them conclusively by spectroscopic means.

Urons

Chromatography of pure dimethyl uron (DM uron) from reaction mixture 7 and uron and monomethyl uron (MM uron) from reaction mixture 8 identifed the simple urons. A plot of log k' for these compounds against the substitution pattern again gave a straight line as for the other three series of compounds previously discussed.

Thus about 20 compounds formed in simple urea - formaldehyde reactions have been identified, the nature of only two or three small peaks being as yet unknown.

This study confirms the observations of Kottes Andrews[10] and Kumlin and Simonson[13] that there is no evidence for the occurrence of tetramethylolurea. Considering the formation of the uron ring, the implications are that either the

trimethylolurea is converted into MM uron, which in the formaldehyde-rich reaction mixture is converted rapidly into DM uron, or, alternatively, tetramethylol uron is formed but is too unstable to be chromatographed.

This technique has been used successfully for a year to characterise UF reaction products (Fig. 11) and to determine the more important compounds such as urea, MMU and DMU. It has proved to be a very powerful method for investigating the significance of various manufacturing parameters and will contribute in the future to a deeper understanding of urea - formaldehyde chemistry.

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Liquid Chromatographic Procedure for the Separation and Characterisation of Simple Urea - Formaldehyde Reaction Products

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A procedure is described for separating about 20 simple, low relative molecular mass urea - formaldehyde reaction products by liquid chromatography on an aminopropyl column using aqueous acetonitrile as eluent. The technique is shown to have considerable advantages over previously published methods. The preparation and characterisation of some reference compounds, which so far have been little studied, are given in detail. The use of reaction mixtures of urea and formaldehyde for identifying peaks is described. Almost all of the peaks observed in commercial urea - formaldehyde formulations can now be identified by this technique.

Keywords: *Liquid chromatography; urea - formaldehyde resins separation; characterisation; urons*

Resins produced by the condensation of urea and formaldehyde occupy an important position in many branches of industry. Although numerous analytical investigations into the course of the urea - formaldehyde (UF) reaction and the nature of the finished resin have been undertaken, there are still aspects of its chemistry that are not understood. This is in part due to the complex series of reactions that occur between urea and formaldehyde, leading to the formation of methylol and methylene compounds and both linear and cyclic ethers (urons). Thus the number of compounds produced can be very large indeed. Difficulties also arise owing to both the instability of UF compounds and the very limited solubility of compounds having a relative molecular mass greater than about 200.

Reliable information on the average properties of UF reaction products has been obtained (notably by NMR measurements,[1] which show the over-all chemical composition and by size exclusion chromatography,[2] which gives the range of relative molecular masses) but separation and quantitation of individual components in the reaction mixture has proved more difficult. Thin-layer chromatography has been used to identify and quantify a small number of the low relative molecular mass compounds that are formed, but its range is limited and the experimental procedure is long and difficult to perform.[3,4]

Some efforts have been made to investigate urea - formaldehyde reaction products and other amide - formaldehyde compounds by liquid chromatography but a simple, rapid, efficient and universal method has not yet been reported. Kumlin and Simonson[5,6] studied UF condensates using a cation-exchange resin in the Li^+ form. The resin used was of large particle size and although a separation of about 10 compounds was achieved, the efficiency of the column was low and a full analysis run took some 120 min to complete.

Murray *et al.*[7] used a reversed-phase column to separate biuret, triuret and methylenediurea, which occur as impurities in fertiliser-grade urea, and Davidson[8] separated urea, methylenediurea and dimethylenetriurea in a similar fashion in UF fertiliser compositions. Beck *et al.*[9] used a cation-exchange resin in the Li^+ form to examine durable press finishes. Textile finishes were also studied by Kottes Andrews[10] using a reversed-phase column.

In this paper, the limitations of these liquid chromatographic procedures are discussed and a method is reported that will separate UF condensation products efficiently and quickly. Details are given for the preparation of reference materials and of the methods used for identifying the chromatographic peaks.

Preliminary Investigations

In order to separate the many compounds formed when urea and formaldehyde react together and to ensure that the analysis is complete in as short a time as possible, it was decided to investigate the potential of reversed-phase silica columns rather than the ion-exchange columns used by Kumlin and Simonson,[5] as these were reported to be inefficient and slow.

In the course of the investigation, several 5-μm reversed-phase packing materials from various manufacturers were examined, including Zorbax ODS, LiChrosorb ODS and Spherisorb ODS. A mixture of urea, monomethylolurea (MMU), dimethylolurea (DMU) and methylenediurea (MDU) was used as a simple test solution and it was found that the elution patterns were slightly but significantly different. With Zorbax and LiChrosorb, DMU and MDU were not separated and with Spherisorb the resolution of urea and MMU was inadequate. However, by coupling a Zorbax column to a Spherisorb column, complete resolution of the test mixture could just be achieved. Although the analysis time was long and the separation was barely adequate, this column configuration was used for several months to estimate low relative molecular mass compounds in UF compositions.

In order to attempt to improve the analysis, a column packed with Hypersil C_{22} Super was used in the hope that the longer carbon chains would retain the molecules of interest to a greater degree. The results were disappointing, showing little improvement when compared with the usual ODS packings.

The limitations of chromatographing UF compounds in the conventional reversed-phase mode are as follows. 1, Resolution of the simplest compounds is very difficult to achieve; with more complex mixtures considerable peak overlap occurs and the chromatography becomes meaningless. 2, Many compounds such as uron and its methylol derivatives elute at the solvent front even when using the weakest solvent and it does not seem likely that this difficulty can be overcome. The analysis time is about 25 min for a typical mixture.

It was thought that a better separation of the methylol compounds could be achieved by using a more polar column. Also, the increased interaction between the polar stationary phase and the UF compounds could give greater flexibility with the eluting solvent.

A column was packed with a hydroxy-terminated material (LiChrosorb Diol) and the test solution of urea, MMU, DMU and MDU was chromatographed using water as the eluting solvent. The elution pattern was markedly different to that

obtained with the hydrophobic ODS columns. The hydroxy compounds DMU and MMU eluted first, followed by urea and MDU. It was apparent that the –OH · · · NH– hydrogen bonding effect was more powerful than the –OH · · · OH– interaction and compounds were eluting according to their =NH content. This order of elution from the column was contrary to the ideal pattern and it was considered likely that the chromatography of UF mixtures would be complicated on such a column. The possibility of reversing this elution pattern by using an amine column seemed worth investigating.

An aminopropyl-terminated phase, Techsil NH_2 (5 μm), was examined and, using the aqueous solvent as before, all the test compounds eluted at the solvent front. However, an amino column has the characteristics of a "normal" phase and water is likely to be the strongest solvent available. Using methanol as a potentially weaker eluent, a partial separation was achieved and the elution pattern (parent compound, monomethylol compound and dimethylol compound) seemed most encouraging. Methanol was replaced by acetonitrile in the hope that the absence of solvent - solute hydrogen bonding would, firstly, accentuate differences between the zero, mono- and dimethylol compounds thus giving better separation of the test mixture and secondly, increase the elution time. This proved to be so, and after a final adjustment of the solvent strength by the addition of 10% water, an almost ideal system for separating the test mixture was obtained.

The flexibility of the system was demonstrated when less polar compounds such as uron and its methylol derivatives, hitherto eluting at the solvent front, were completely separated by reducing the solvent strength, *i.e.*, the water content.

Thus a system that seemed almost ideal for the chromatography of simple urea - formaldehyde compounds was developed. The column had high efficiency (8000 plates), the peak shape under normal conditions was good, the analysis time was short, being approximately 10 min for the test mixture of urea, MMU, DMU and MDU, and the elution pattern was favourable.

Experimental

Apparatus

The chromatographic equipment used consisted of a Waters 6000 A pump, a Rheodyne 70-10 injection valve fitted with a 100-μl loop and a Model 70-11 filler port, a Waters R401 differential refractometer and a Waters Model 730 Data Module. A 2-μm in-line filter was positioned between the injector and the column.

The analytical columns employed were made from 250 × 4.6 mm i.d. stainless-steel tubing with zero dead volume fittings. The columns were packed using the slurry technique developed by Kirkland.[11]

The initial upward displacement with methanol was followed by downward displacement and "slamming" to improve the stabilisation of the bed. The slurry used for packing the 5-μm aminopropyl-bonded silica to produce the columns used for the majority of this work was prepared by dispersing 3.5 g of Techsil NH_2 (5 μm) packing material in 70 ml of chloroform - methanol (3 + 1) by ultrasonic agitation. The aminopropyl-bonded silica columns usually have an adequate lifetime, but when used for the analysis of materials with a high proportion of free formaldehyde they can deteriorate quickly. This is possibly due to an irreversible amino - aldehyde interaction taking place and is seen by shortened retention times and a lack of resolution of methylenediurea (MDU) and asymmetric dimethylolurea (asym. DMU). In order to attempt to offset this problem, a small amount of ammonia (0.01 M) is added to the eluting solvent. Depending on the type of sample under investigation, the life of an amino column is between 50 and 200 working days. Column packing and testing take only 2–3 h and consequently column deterioration is not considered to be a serious problem.

One of the preparative columns was packed using Partisil 5-μm silica by the same upward - downward - "slamming" procedure previously described. Stainless-steel tubing, 300 × 7.8 mm i.d., was used for the column and 5.5 g of the packing material was slurried in 70 ml of chloroform - methanol (1 + 1). Octadecylsilane (ODS)-bonded silica (Partisil 10) was used in the other preparative column. Column packing was by the method already described after slurrying in propan-2-ol.

The eluting solvent used for most of the work was prepared by mixing 900 ml of acetonitrile of Hypersol grade (BDH Chemicals, Poole, UK) with 100 ml of de-ionised water and 0.5 ml of ammonia solution (sp. gr. 0.880). The solvent mixture was de-gassed with helium and the temperature allowed to rise to room temperature before use.

If the mixtures under examination contained predominantly methyl ethers or urons, *i.e.*, compounds with short elution times, then improved resolutions were obtained by weakening the eluting solvent to 2.5 or 5% water in acetonitrile.

Other solvent and chemicals, except where stated, were general-purpose laboratory reagents.

Preparation of Samples

Where possible, reference materials (5–10 mg) were dissolved directly in 10 ml of eluting solvent. If limited solubility was a problem, a solution in 1 ml of water was prepared, with gentle heating if necessary, and then diluted to 10 ml with acetonitrile.

With resinous samples, about 200 mg were taken and low-condensed materials that were totally soluble were dissolved directly in the eluting solvent. However, when the average molecular mass was large and a considerable proportion (up to 80% of the UF) was insoluble, the above techniques were unsatisfactory. The best approach was then to dissolve the sample in 1 ml of dimethylformamide and dilute to 10 ml with acetonitrile. The sample plus solvent was shaken vigorously and allowed to stand. If necessary, the sample solution was filtered through a 0.5 μm filter before injection.

Reference Compounds and Mixtures

Monomethylolurea (MMU), dimethylolurea (DMU), methylenediurea (MDU), monomethylolurea monomethyl ether (MMU.MME), dimethylolurea dimethyl ether (DMU.DME) and dimethylurea monomethyl ether (DMU.MME) were all synthesised by methods published earlier.[3] The following reaction products of urea and formaldehyde were prepared.

1. *Alkaline UF condensate, molar ratio* 1:3. Urea, 0.6 g; 50% aqueous formaldehyde solution, 1.8 g; disodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$), 0.2 g; water, 5 g. The buffer was dissolved in the formaldehyde solution and the urea added. The solution was stirred and allowed to stand at room temperature. Samples were taken at intervals.

2. *Alkaline MDU:F condensate, molar ratio* 1:1. MDU, 1.3 g; 50% aqueous formaldehyde solution, 0.6 g; disodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$), 0.1 g; water, 5 g. MDU was dissolved in the warmed water, Na_2HPO_4 was added and, when dissolved, the formaldehyde was added. The mixture was allowed to stand at room temperature and samples were taken at intervals.

3. *Alkaline MDU:F condensate, molar ratio* 1:1.5. This was prepared as for No. 2, but 0.9 g of 50% formaldehyde solution was used.

4. *Alkaline MDU:F condensate, molar ratio* 1:2. This was prepared as for No. 2 but 1.3 g of 50% formaldehyde solution were used.

5. *Dimethylene ether from DMU (Zigeuner and Pitter).*[12] DMU (10 g) was dissolved in 33 ml of 1% potassium carbonate solution. After 3 weeks, about 1 g of precipitate had formed. The supernatant liquor and the precipitated material were examined.

6. *Crude dimethylenetriurea (DMTU)*. MDU (6.6 g, 0.05 M) was dissolved in 100 ml of water at 60 °C. Disodium hydrogen orthophosphate (0.2 g) was added and, when dissolved, 3 g (0.05 M) of 50% formaldehyde were added. The reaction mixture was allowed to stand for 1 h. The crude monomethylol MDU was filtered off, washed with cold water and dissolved in the minimum amount of water at 60–70 °C. Urea (30 g, 0.5 M) and 0.5 g of sodium dihydrogen orthophosphate were added and dissolved in the solution. After standing overnight, the crude DMTU was filtered off and washed thoroughly with water.

7. *Dimethylol uron (DM uron)*. A 2 ml volume of 40% sodium hydroxide was added to 50% formaldehyde (72 g, 1.2 M). Urea (12 g, 0.2 M) was dissolved in this alkaline formaldehyde and the solution was heated to boiling for 1 min. The pH was adjusted to 8 with formic acid and about 40 ml of water and formaldehyde were removed by vacuum distillation at 40–50 °C in a rotary evaporator. Extraction with chloroform - acetonitrile (1 + 1) removed the dimethylol uron from the reaction mixture, presumably as the di(hemiformal) (pure dimethylol uron is only sparingly soluble in this solvent mixture). This extraction procedure gave a good separation of the dimethylol uron from impurities such as DMU and TMU.

DM uron was separated from the excess of residual formaldehyde and water by chromatography on a semi-preparative Partisil 5-μm silica column (300 × 7.8 mm i.d.) using 10% methanol in chloroform as the eluent. The structure was confirmed by infrared, ^{1}H NMR (Figs. 1 and 2) and ^{13}C NMR spectroscopy: ring C, 77.4 p.p.m.; chain C, 66.9 p.p.m.; carbonyl C, 152.3 p.p.m.; solvent, DMSO-d_6, m.p. 87–90 °C.

8. *Uron and monomethyloluron*. Pure dimethyl uron, 0.04 g (0.00025 M), urea, 0.03 g (0.0005 M) and sodium dihydrogen orthophosphate, 0.005 g, were dissolved in about 0.2 ml of water. The solution was heated carefully at 100 °C for 5 min, then cooled and extracted with 3 × 1 ml of acetonitrile. The combined acetonitrile extracts were evaporated to dryness at room temperature using a jet of air.

The urons were separated efficiently on a 250 × 4.8 mm i.d. amine column using 2.5% water in acetonitrile as the eluting solvent. Uron itself was identified by infrared, ^{1}H NMR (Figs. 3 and 4) and ^{13}C NMR spectroscopy: ring C, 75.6 p.p.m. (in $CDCl_3$). Monomethyl uron was indicated by its chromatographic behaviour and its infrared and proton NMR spectra (Figs. 5 and 6). Insufficient sample was obtained for a ^{13}C spectrum.

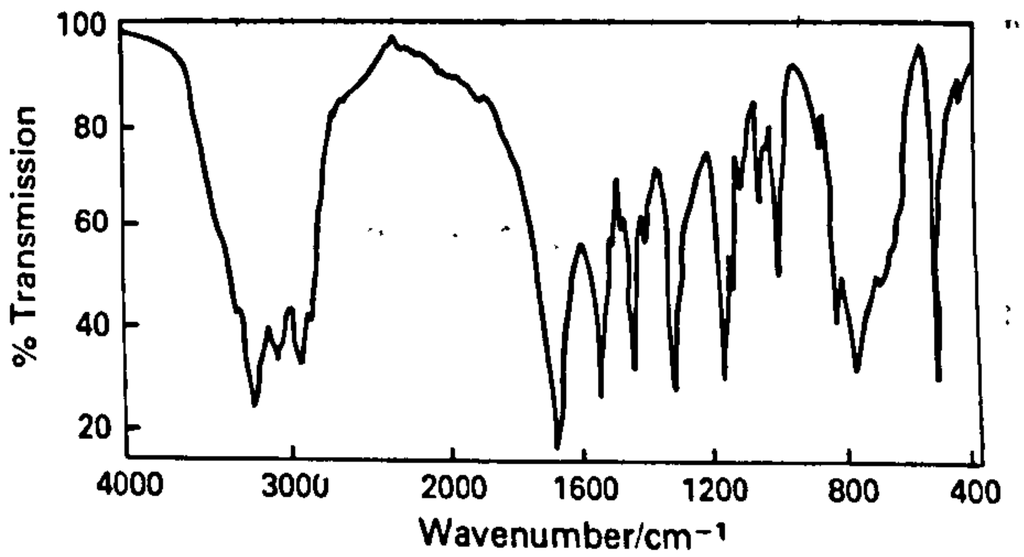


Fig. 3. Infrared spectrum of uron

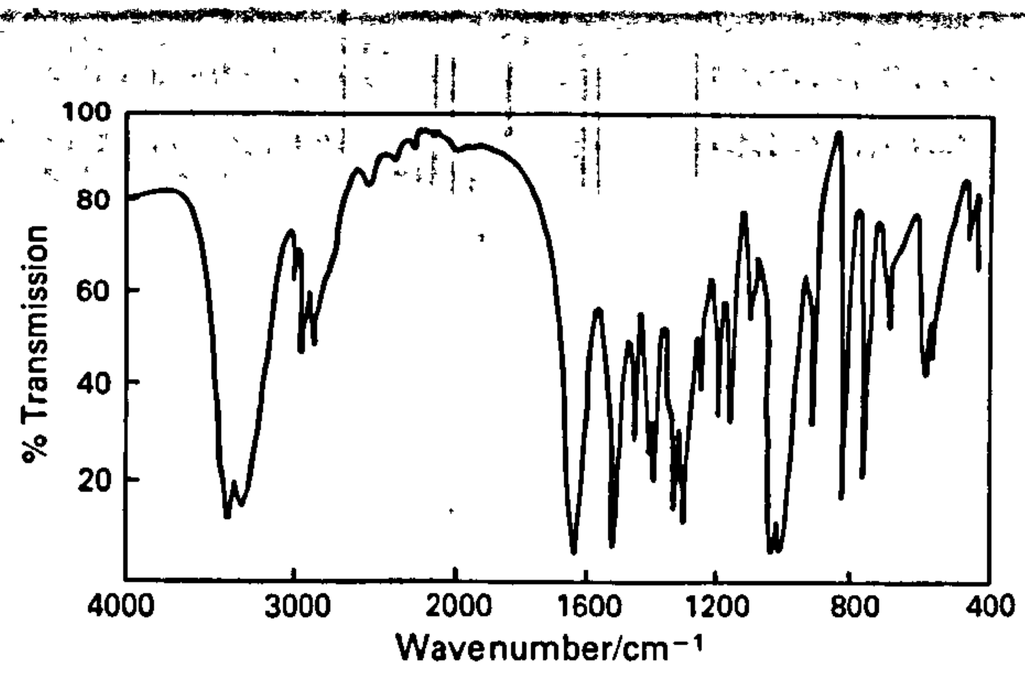


Fig. 1. Infrared spectrum of dimethylol uron

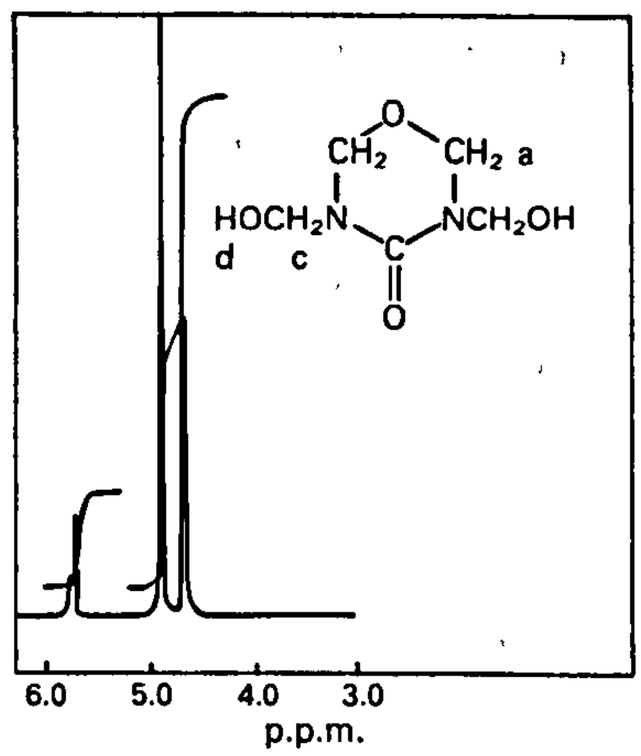


Fig. 2. ^{1}H NMR spectrum of dimethylol uron (solvent DMSO-d_6). a, 4.88; c, 4.65; and d, 5.72 p.p.m.

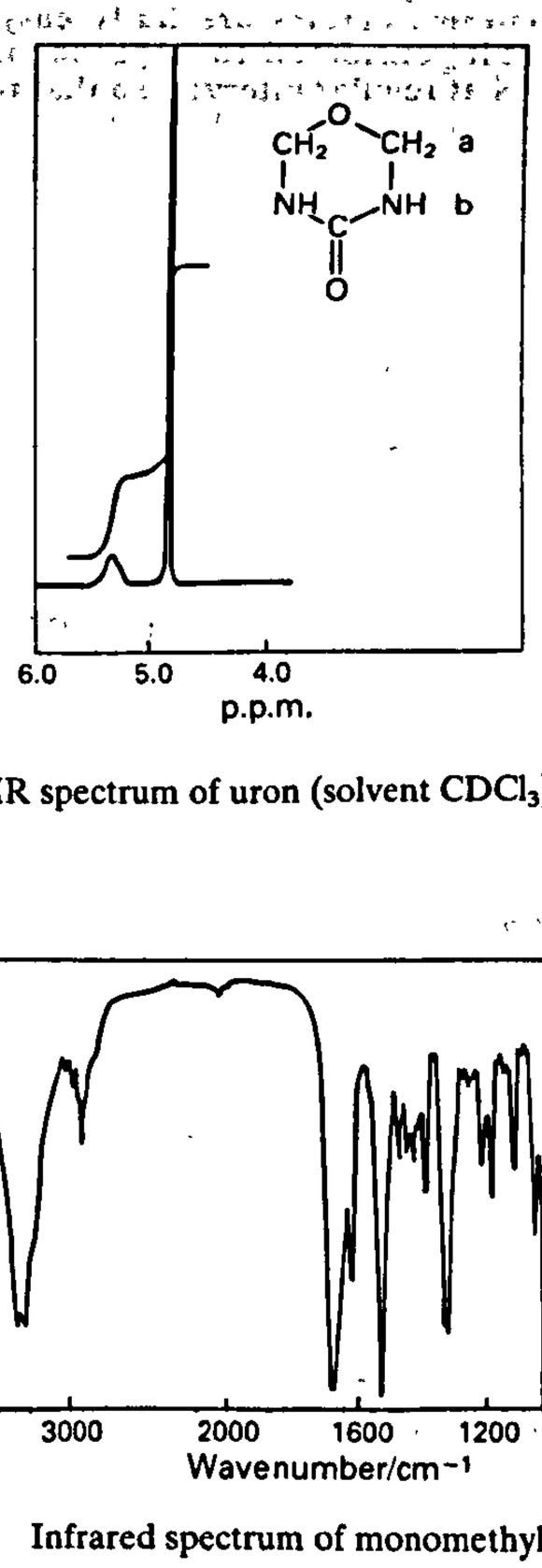


Fig. 4. ^{1}H NMR spectrum of uron (solvent $CDCl_3$). a, 4.85; and b, 5.35 p.p.m.

Fig. 5. Infrared spectrum of monomethylol uron

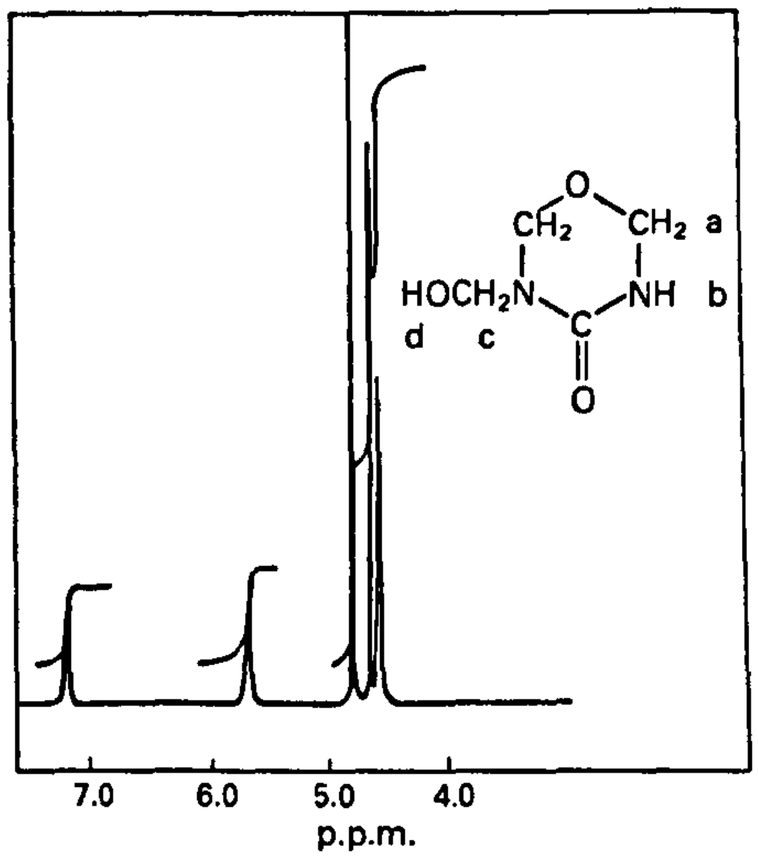


Fig. 6. ^{1}H NMR spectrum of monomethylol uron (solvent DMSO-d_6). a, 4.70; b, 7.12; c, 4.62; and d, 5.63 p.p.m.

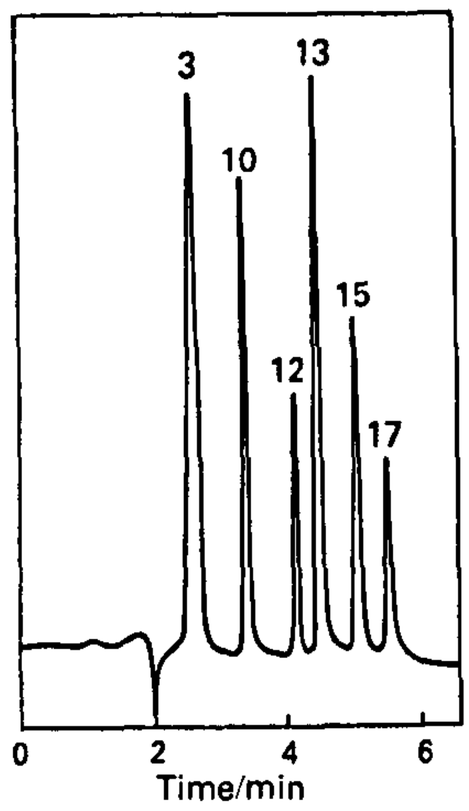


Fig. 7. Chromatogram of test mixture; urea, MMU, DMU, MDU and glycerol (for peak identification, see Table 1)

Results and Discussion

Evaluation

One of the major problems in the chromatography of urea - formaldehyde compounds on an aminopropyl column is the slow but inevitable change of retention characteristics. For the most part, this renders absolute retention times unreliable and it has been found to be useful to adopt a procedure of multiple relative retention times. The two compounds used for reference in this study were urea and DMU. Using this technique, the chromatograms are fairly easy to interpret. However, it is still considered to be good practice to run standard solutions at regular intervals so that the state of the column is continually monitored. The following are examples of solutions which can be used: urea, MMU, DMU, MDU and glycerol (Fig. 7); DM uron containing MM uron and uron itself if possible; methylolated MDU; and methylolated OMDU, all prepared in eluting solvent and stable for several months.

Table 1 is a list, in increasing retention time, of the peaks observed in the chromatography of the various reference compounds and reaction mixtures. The retention times given are typical of those obtained with a new column . Also given are retention times relative (a) to urea for early eluting compounds and (b) to DMU for late eluting compounds. The elution times of dimethylformamide (DMF), water and formaldehyde are included. Glycerol elutes in a chromatographic "window" and is suitable for use as an internal standard for the determination of compounds such as urea, MMU, DMU, etc., in UF compositions.

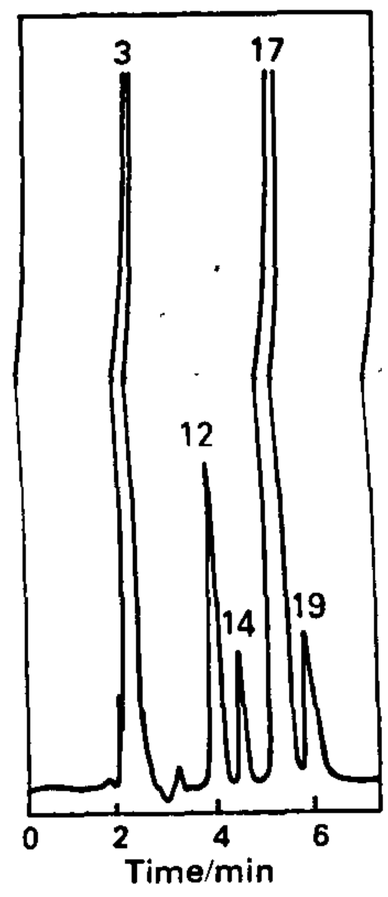


Fig. 8. Chromatogram of reaction product 1 showing *N,N*-DMU and TMU (for peak identification, see Table 1)

Peak Identification

Simple compounds

The chromatography of simple reference compounds and well characterised urea derivatives (see above) resulted in the easy and unambiguous identification of about half the peaks encountered in conventional urea - formaldehyde reaction mixtures.

Methylolureas

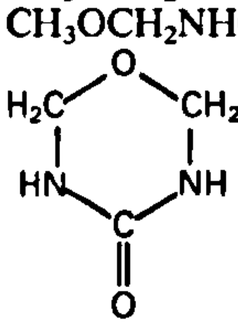
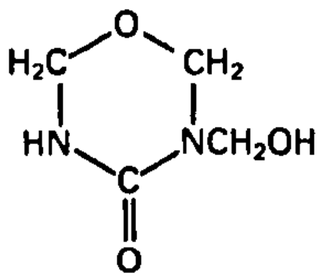
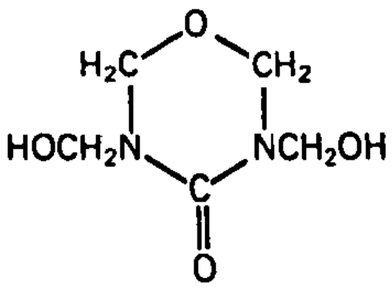
Examination of reaction product 1 enabled *N,N*-dimethylolurea (asym. DMU) and trimethylolurea (TMU) to be tentatively identified (Fig. 8). The peaks of interest were collected from the column and the solvent removed by careful evaporation at room temperature using a jet of air. To ensure that the recovery procedure had not significantly affected the purity of the compounds, small amounts of the collected materials were re-chromatographed. The infrared and proton NMR spectra unambiguously confirmed the nature of the peaks.

It has been shown in a previous study[3] that with urea - formaldehyde compounds there can exist a simple relationship between the logarithm of the retention time and the degree of substitution. This concept was again found to hold true (Fig. 9) and in this instance a plot of k' against the number of methylol groups is a straight line. [k' is the capacity factor, equal to $(t_r - t_o)/t_o$; t_r is the retention time of the compound and t_o is the retention time of an unretained solute]. When log k' of asym. DMU and TMU are plotted to lie on the same line it can be readily seen that a second methylol substituent on a terminal nitrogen has only half the effect on the retention time as the first substituent.

Methylolmethylenediureas

The reaction between MDU and formaldehyde is complicated, leading to 12 possible mono-, di- and trimethylol MDUs. However, many of these derivatives are unlikely and only about seven peaks are actually observed. It is possible to

Table 1. Peaks observed in urea - formaldehyde reaction products in order of increasing elution time

No.	Compound	Structure	Identification*	Retention time/min relative to Absolute	Urea	DMU
1	Dimethylformamide			2.16		
2	Formaldehyde	HCHO		2.25		
3	Water			2.52		
4	Dimethylolurea dimethyl ether	$CH_3OCH_2NHCONHCH_2OCH_3$	D	2.41	0.73	
5	Monomethylolurea monomethyl ether	$CH_3OCH_2NHCONH_2$	D	2.79	0.84	
6	Uron		D	2.84	0.86	
7	Monomethylol uron		D	3.03	0.91	
8	Dimethylolurea monomethyl ether	$CH_3OCH_2NHCONHCH_2OH$	D	3.19	0.96	
9	Dimethylol uron		D	3.20	0.96	0.58
10	Urea	H_2NCONH_2	D	3.32	1	0.60
11	Unknown		U	3.87	1.17	0.70
12	Monomethylolurea	$H_2NCONHCH_2OH$	D	4.12	1.24	0.75
13	Glycerol		D	4.45	1.34	0.80
14	*N,N*-Dimethylolurea	$H_2NCON(CH_2OH)_2$	D	4.87	1.47	0.88
15	Methylenediurea	$H_2NCONHCH_2NHCONH_2$	D	5.05		0.91
16	*sec*-Monomethylolmethylenediurea	$H_2NCONHCH_2N(CONH_2)CH_2OH$	T	5.31		0.96
17	*N,N'*-Dimethylolurea	$HOCH_2NHCONHCH_2OH$	D	5.53		1
18	Oxymethylenediurea	$H_2NCONHCH_2OCH_2NHCONH_2$	T	5.60		1.01
19	Trimethylolurea	$HOCH_2NHCON(CH_2OH)_2$	D	6.53		1.18
20	Monomethylolmethylenediurea	$HOCH_2NHCONHCH_2NHCONH_2$	P	6.75		1.22
21	Asym. dimethylolmethylenediurea	$HOCH_2NHCON(CH_2OH)CH_2NHCONH_2$ or $HOCH_2NHCONHCH_2N(CH_2OH)CONH_2$	T	7.35		1.33
22	Monomethyloloxymethylenediruea	$HOCH_2NHCONHCH_2OCH_2NHCONH_2$	P	7.7		1.39
23	Unknown		U	8.6		1.56
24	Dimethylenetriurea	$H_2NCONHCH_2NHCONHCH_2NHCONH_2$	D	9.2		1.66
25	Dimethylolmethylenediurea	$HOCH_2NHCONHCH_2NHCONHCH_2OH$	P	9.85		1.78
26	Dimethyloxymethylenediurea	$HOCH_2NHCONHCH_2OCH_2NHCONHCH_2OH$	P	10.5		1.90
27	Trimethylolmethylenediurea	$HOCH_2NHCONHCH_2NHCON(CH_2OH)_2$	T	11.2		2.03
28	Trimethylolmethylenediurea	$HOCH_2NHCONHCH_2(CH_2OH)CONCH_2OH$	T	12.2		2.21

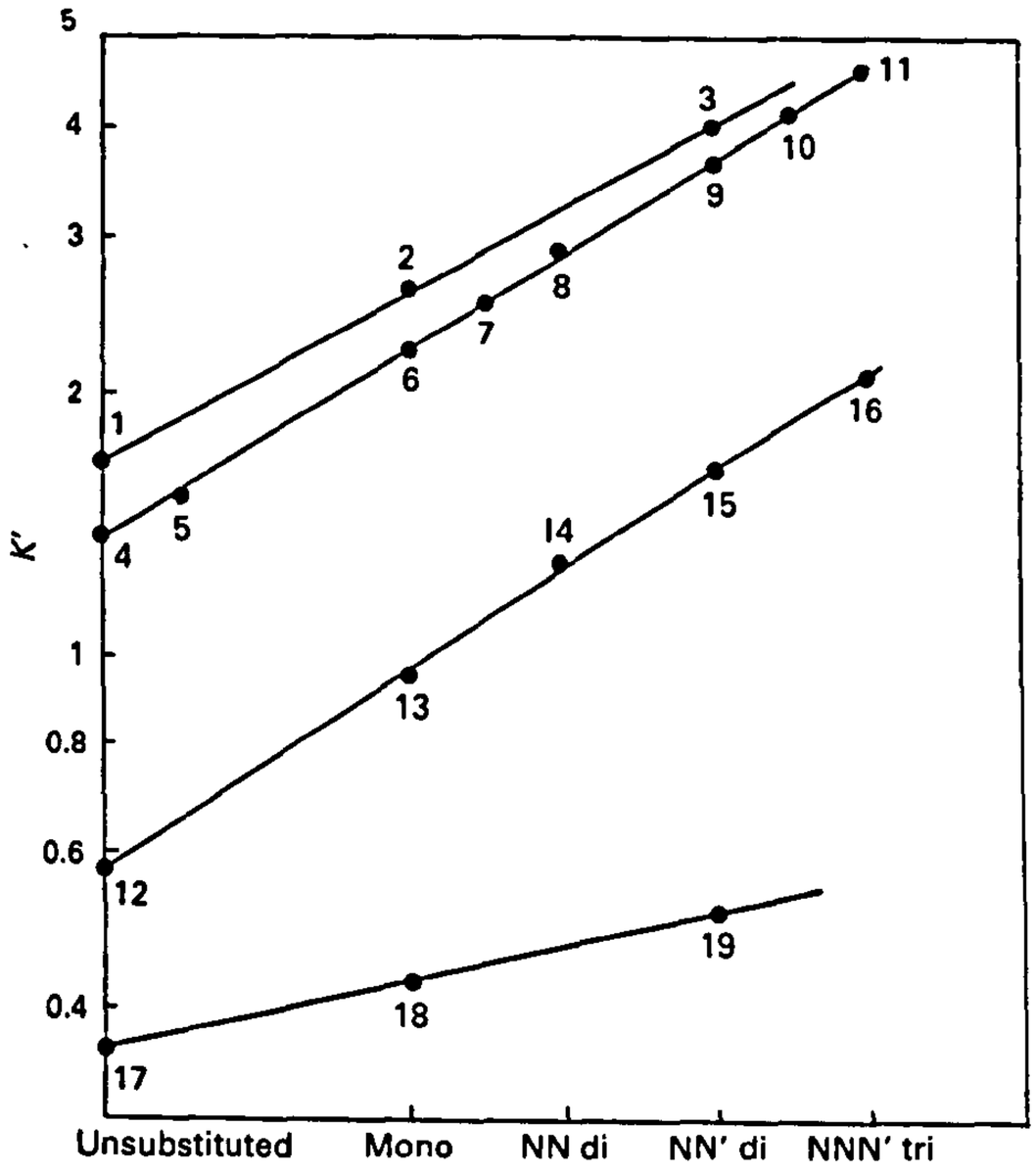
* D = definite, P = probable, T = tentative, U = unknown.

obtain information about the nature of some of these peaks by reacting MDU and formaldehyde together at slightly alkaline pH (reaction mixtures 2, 3 and 4). With a low MDU : F ratio and a short reaction time the predominant product is monomethylolmethylenediurea (MMMDU). As the amount of formaldehyde and the reaction times are increased, di- and then trimethylol substitution is favoured.

A typical chromatogram is shown in Fig. 10. As with the urea series, MDU and its mono- and dimethylol derivatives follow the simple relationship between log k' and the degree of substitution. It can be seen (Fig. 9) that two peaks occur between MMMDU and the symmetrical DMMDU. Using the behaviour of the dimethylolureas as a guide it seems likely that a second methylol substituent on the terminal nitrogen of MMMDU will have only half the effect of the first on the retention time. Plotting log k' of these two peaks on the MDU derivative line shows indeed that one peak behaves in accordance with the asym. DMMDU structure, $H_2NCONHCH_2NHCON(CH_2OH)_2$. Considering the position of the second peak, which should be one of the terminal nitrogen - chain nitrogen disubstituted structures ($H_2NCONHCH_2N(CH_2OH)CONHCH_2OH$ or $H_2NCON(CH_2OH)CH_2NHCONHCH_2OH$), it would seem that a methylol substituent on a chain nitrogen will have half the effect of a second substituent on the terminal nitrogen and only one quarter the effect of the first substituent on a terminal nitrogen (Fig. 9). Two peaks occur at longer retention times, which again appear to follow the structure - retention time relationship described above. In this way these compounds have been tentatively identified as having the two most probable trimethylol MDU structures (Table 1).

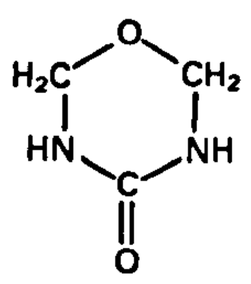
Methyloloxymethylenediureas

The insoluble material from reaction mixture 6 showed one major peak, which could safely be assumed to be DMOMDU.



1 = $NH_2CONHCH_2OCH_2NHCONH_2$
2 = $NH_2CONHCH_2OCH_2NHCONHCH_2OH$
3 = $HOCH_2NHCONHCH_2OCH_2NHCONHCH_2OH$
4 = $NH_2CONHCH_2NHCONH_2$
5 = $NH_2CONHCH_2NCONH_2$ (CH_2OH)
6 = $NH_2CONHCH_2NHCONHCH_2OH$
7 = $NH_2CONCH_2NHCONHCH_2OH$ (CH_2OH)
8 = $NH_2CONHCH_2NHCON(CH_2OH)_2$
9 = $HOCH_2NHCONHCH_2NHCONHCH_2OH$
10 = $HOCH_2NHCONCH_2NHOONHCH_2OH$ (CH_2OH)
11 = $HOCH_2NHCONHCH_2NHCON(CH_2OH)_2$
12 = NH_2CONH_2
13 = $NH_2CONHCH_2OH$
14 = $NH_2CON(CH_2OH)_2$
15 = $HOCH_2NHCONHCH_2OH$
16 = $HOCH_2NHCON(CH_2OH)_2$

17 =



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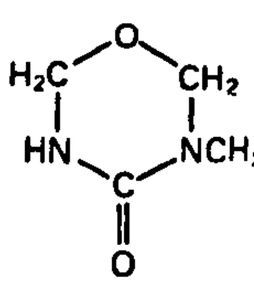

19 =

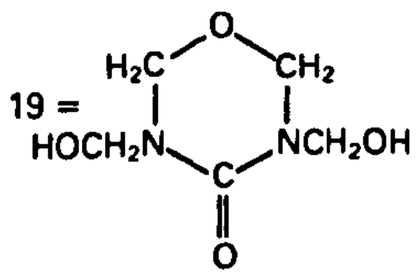

Fig. 9. Effect of degree of substitution on retention times. $k' = (t_r - t_o)/t_o$, where t_r is the retention time of the solute and t_o is the retention time of a non-retained solute

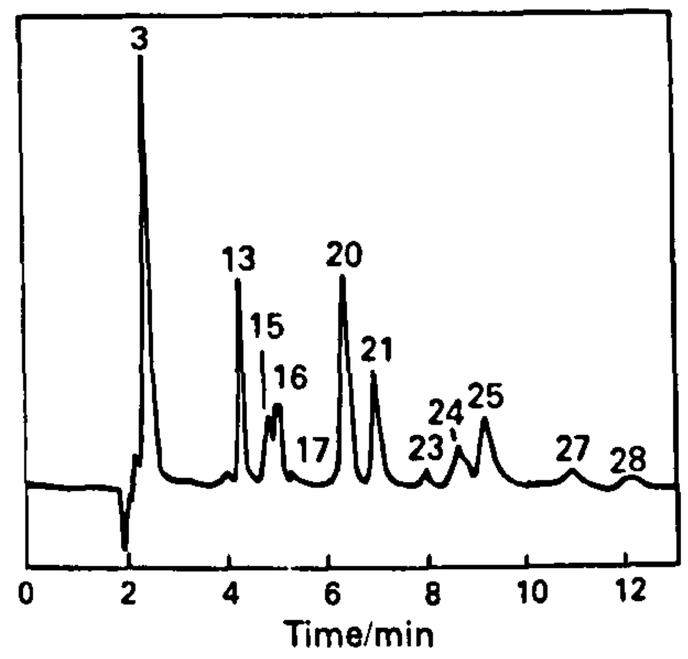

Fig. 10. Chromatogram of MDU and formaldehyde reacted at pH 8 for 8 h at ambient temperature (for peak identification, see Table 1)

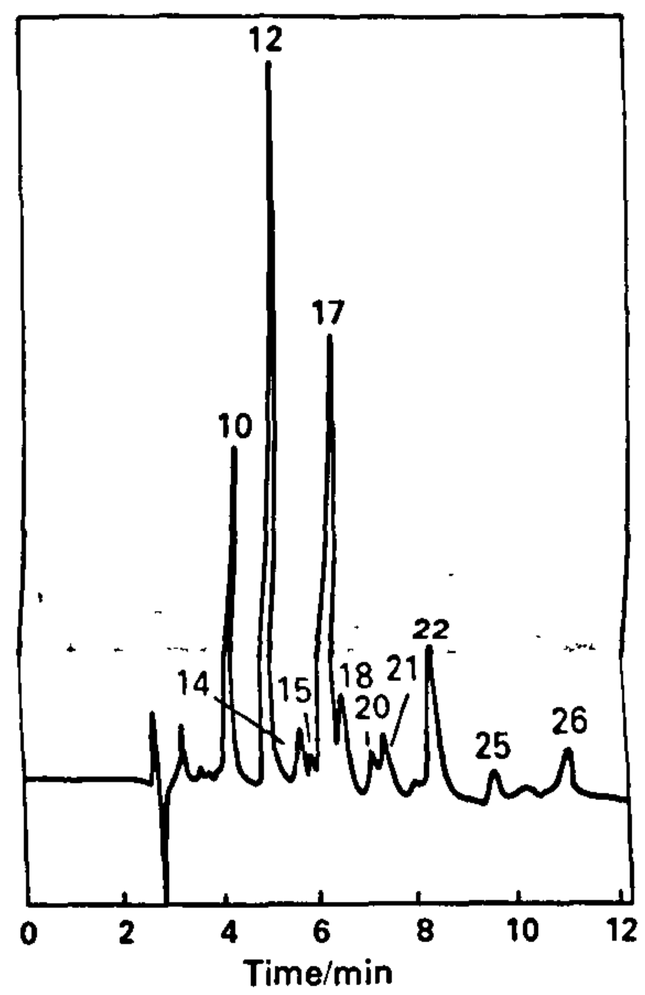

Fig. 11. Chromatogram of UF reaction product U : F 1 : 1.4 reacted at 70 °C for 2 h at pH 9 (for peak identification, see Table 1)

The chromatogram of the supernatant liquor showed another large peak at a shorter retention time, which is likely to be the mono compound. When log k' for these compounds is plotted against the substitution pattern, a line having virtually the same gradient as the urea and MDU derivative line is obtained. Further, there is a small peak at the elution time corresponding to zero substitution, which can be tentatively attributed to the parent compound, oxymethylenediurea. Kumlin and Simonson[6] identified MMOMDU and DMOMDU in the reaction mixture described by Zigeuner and Pitter[12] and characterised them conclusively by spectroscopic means.

Urons

Chromatography of pure dimethyl uron (DM uron) from reaction mixture 7 and uron and monomethyl uron (MM uron) from reaction mixture 8 identifed the simple urons. A plot of log k' for these compounds against the substitution pattern again gave a straight line as for the other three series of compounds previously discussed.

Thus about 20 compounds formed in simple urea - formaldehyde reactions have been identified, the nature of only two or three small peaks being as yet unknown.

This study confirms the observations of Kottes Andrews[10] and Kumlin and Simonson[13] that there is no evidence for the occurrence of tetramethylolurea. Considering the formation of the uron ring, the implications are that either the

trimethylolurea is converted into MM uron, which in the formaldehyde-rich reaction mixture is converted rapidly into DM uron, or, alternatively, tetramethylol uron is formed but is too unstable to be chromatographed.

This technique has been used successfully for a year to characterise UF reaction products (Fig. 11) and to determine the more important compounds such as urea, MMU and DMU. It has proved to be a very powerful method for investigating the significance of various manufacturing parameters and will contribute in the future to a deeper understanding of urea - formaldehyde chemistry.

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