of 170 h. Reaction was promoted by the addition of *cyclo*hexane.

The products of the photoreactions possibly result from an initial attack on the substrate by a methyl radical arising from the direct decomposition of the tetra-acetate[7]. Analysis of gas evolved during the photo-oxidation of *cyclo*hexyl acetate showed a methane/carbon dioxide ratio close to 1. The recovered hydrocarbon from the photoreaction of *cyclo*hexane included a small proportion of methyl *cyclo*hexane.

On the other hand, the mechanism of the thermal reaction is less obvious but must involve an association of paraffin, oxidant and ester. Work on this aspect is continuing.

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Isolation of Ammonium Thiophosphite by means of Preparative Ion-exchange Chromatography

ALTHOUGH the existence of thio-derivatives of lower phosphorus anions has been accepted for some time, only one claim has been made of their isolation—by Lemoine[1,2] in 1881 and 1884. It now seems unlikely that his method of slow crystallization from a phosphorus sulphide hydrolysis mixture yielded single products, especially since he had no means of checking the purity.

A preliminary investigation showed that all of P_4S_3, P_4S_5, P_4S_7, and P_4S_{10} gave thiophosphorus species, in addition to simple phosphorus oxyanions when submitted to hydrolysis by solutions of sodium hydroxide or sulphide. Further investigation with anion-exchange columns coupled to a Technicon autoanalyser[3] established that one unidentified species was eluted just before monothiophosphate (PO_3S^{3-}) at *p*H 11·4 (see Fig. 1).

A linear gradient of increasing chloride concentration was used and comparison of the retention times of phosphite (HPO_3^{2-}) and phosphate (PO_4^{3-}) led to the prediction that this unknown anion was monothiophosphite (HPO_2S^{2-}).

Samples of this species were separated from the other phosphorus compounds by heavily overloading a large column (50 cm long, 3 cm diameter) of anion-exchange resin 'De-Acidite *FF*' and eluting with a constant strength of ammonium chloride buffered to *p*H 10 with ammonia. The resultant solution was evaporated down to a few millilitres at room temperature (20° C) under low vacuum and then adsorbed on to cellulose. Washing with a mixed solvent (42·5 isopropanol : 42·5 2-butanone : 15 conc. ammonia) removed the chloride, and the pure phosphorus salt was stripped off with ammoniated water. A white microcrystalline salt was precipitated from this solution with excess alcohol and the purity of the precipitated salt was checked using both thin-layer and anion-exchange chromatography.

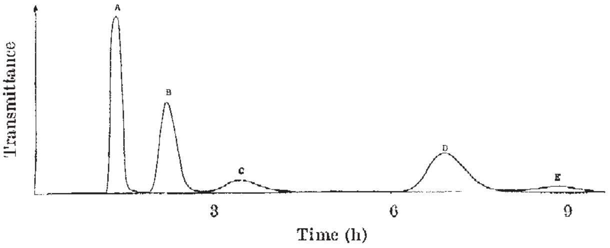


Fig. 1. Elution pattern of products formed after refluxing of P_4S_5 with excess 1 N sodium hydroxide for several minutes. *A*, Hypophosphite; *B*, phosphite; *C*, phosphate; *D*, unknown (monothiophosphite); *E*, monothiophosphate

The salt proved to be unstable towards water vapour, losing hydrogen sulphide in acid solution with the consequent formation of ammonium phosphite. Concentrated nitric acid and bromine water both react powerfully with the salt; a yellow solid is produced—presumably elemental sulphur. Its strong reducing properties are illustrated when silver nitrate is changed into the metal and a nickel spatula into black nickel sulphide.

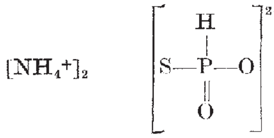
A precursory examination of the infra-red spectrum reveals a sharp peak at 2,350 cm⁻¹ which corresponds to the characteristic P—H stretching frequency. Weaker absorptions at 1,005 cm⁻¹ and 415 cm⁻¹ may be tentatively assigned to P—H deformation and P—S stretching vibrations respectively. A strong absorption due to the ammonium ion was seen at 1,415 cm⁻¹.

Analysis of the compound showed the phosphorus : sulphur : nitrogen ratio to be 1·00 : 1·01 : 2·03. For the empirical formula $(NH_4)_2HPO_2S$:

	P	S	N	H
Calculated	23·4	24·3	21·2	6·87
Found	22·7	23·8	20·8	7·01

The elution position under anion-exchange was sufficient evidence that there was one phosphorus atom per molecule. Moreover, the anhydrous nature was indicated when the salt decomposed on heating without melting, and no water was detected in the decomposition products.

From the foregoing evidence the salt appears to be anhydrous diammonium monothiophosphite and its structure probably resembles that of trisodium monothiophosphate[4], that is:



$$[NH_4^+]_2 \left[\begin{array}{c} H \\ | \\ S—P—O \\ \| \\ O \end{array}\right]^{2-}$$

Further investigations are in progress.

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Synthesis of Alkyl-β-D-xylopyranosides in the Presence of Mercuric Salts

SYNTHESIS of alkyl-β-D-glycosides has been achieved mainly through the reaction of poly-*O*-acetylglycosylhalides with alcohols in the presence of a heavy metal (Koenigs-Knorr).

Except with simple alcohols, the most common procedure has been to dissolve the *O*-acetylglycosylbromide in an inert dry solvent, after adding a drying agent and silver oxide (dry and freshly prepared) and then adding an excess of the appropriate alcohol.

In recent years, mercuric salts have frequently been used. While there seems to be a general tendency for the reaction to proceed with Walden inversion, either anomer may be produced, depending largely on the aglycon concentration. Although the time of reaction is much shorter and a commercially available catalyst is used, mercuric

Table 1. ACETYLATED β-D-XYLOPYRANOSIDES

	M.p. (° C) cryst. solvent	$(\alpha)^{20}_D$	Yield	Analytical value C	H	CH_3CO
Ethyl	106–108	−61° 5	48	51·4	6·6	42·5*
$C_{13}H_{20}O_8$	Ethanol	*c*, 4		51·3	6·7	42·3†
Propyl	108–109	−60° 6	40	52·8	6·9	40·5
$C_{14}H_{22}O_8$	Ethanol–water	*c*, 4		52·7	6·9	40·0
Isopropyl	122–124	−62° 5	35	52·8	6·9	40·5
$C_{14}H_{22}O_8$	Ethanol–water	*c*, 4		52·8	6·8	40·2
n-Butyl	100–101	−58° 0	41	54·2	7·2	38·5
$C_{15}H_{21}O_8$	Ethanol–water	*c*, 4		54·1	7·0	38·5
tert-Butyl	130–132	−44° 8	60	54·2	7·2	38·5
	Ethanol–water	*c*, 2		54·1	7·1	38·0
n-Amyl	54–55	−58° 7	60	55·5	7·5	37·0
$C_{16}H_{26}O_8$	Ethanol–water	*c*, 2		55·2	7·6	36·8
n-Hexyl	59–60	−56° 8	40	56·6	7·8	35·5
$C_{17}H_{23}O_8$	Methanol–water	*c*, 2		56·4	7·9	35·6
n-Heptyl	55–56	−55° 0	30	57·8	8·0	34·2
$C_{18}H_{30}O_8$	Methanol–water	*c*, 2		57·6	8·1	34·3
n-Octyl	52–53	−53° 4	30	58·7	8·3	33·0
$C_{19}H_{32}O_8$	Ethanol–water	*C*, 2		58·4	8·3	33·1

* Calculated.
† Found.

Table 2. β-D-XYLOPYRANOSIDES

	M.p. (° C) cryst. solvent	$(\alpha)^{20}_D$	Yield	Analytical value C	H
Ethyl	95–96	−37° 0	75	47·1	7·9*
$C_7H_{14}O_5$	Acetone	Water; *c*, 2		47·2	7·9†
Propyl	92–93	−58° 6	80	50·0	8·3
$C_8H_{16}O_5$	Acetone	Methanol; *c*, 2		50·1	8·4
Isopropyl	115–116	−66° 0	80	50·0	8·3
	Methylethylketone	Methanol; *c*, 4		49·9	8·4
n-Butyl	89–90	−54° 0	87	52·5	8·7
$C_9H_{18}O_5$	Acetone	Methanol; *c*, 4		52·5	8·7
tert-Butyl	122–123	−28° 5	80	52·5	8·7
	Acetone	Methanol; *c*, 2		52·3	8·8
n-Amyl	88–89	−54° 5	81	54·5	9·1
$C_{10}H_{20}O_5$	Acetone	Methanol; *c*, 2		54·5	9·1
n-Hexyl	88–89	−50° 9	78	56·4	9·4
$C_{11}H_{22}O_5$	Acetone	Methanol; *c*, 2		56·4	9·3
n-Heptyl	84–85	−48° 4	82	58·1	9·7
$C_{12}H_{21}O_5$	Acetone	Methanol; *c*, 2		57·9	9·6
n-Octyl	91–92	−45° 1	80	59·5	9·9
$C_{13}H_{26}O_5$	Acetone	Methanol; *c*, 2		59·6	9·9

* Calculated.
† Found.

salts apparently are not widely used, and this is especially so for higher alcohols.

In the present work we prepared the tri-*O*-acetyl-alkyl-β-D-xylosides by condensation of tri-*O*-acetyl-α-D-xylopyranosylbromide with the appropriate alcohol (up to *n*-octanol) and used mercuric acetate as a catalyst. In each case the β-anomer was formed in good yield. Thus, even with higher alcohols, the more simple reaction with mercuric salts can be used.

The alkyl-β-D-xylosides were prepared by catalytic deacetylation of the corresponding acetates.

*Preparation of the alkyl-tri-O-acetyl-*β-D*-xylosides.* The tri-*O*-acetyl-α-D-xylopyranosylbromide was prepared by the method of Barczai-Martos and Körösy[1]. In the condensation reaction all the apparatus and reagents had to be thoroughly dry. The presence of water would have resulted in the production of a considerable amount of by-products, chiefly 2,3,4-tri-*O*-acetyl-D-xylose and a xylobiosacetate, tentatively identified as β-D-xylopyranosyl-β-D-xylopyranoside-hexa-acetate.

Acetyl groups were determined by the method of Kunz[2]. Mercuric acetate (16 g, 0·05 mol.), absolute chloroform (200 ml.), 'Sikkon' (18 g) and the appropriate alcohol (1–1·5 mol., except for heptanol and octanol, where 0·2 mol. was used) were stirred for 15 min at room temperature. During stirring, acetobromoxylose (33·9 g; 0·1 mol.) was added and the mixture refluxed on a water bath for 15 min. After cooling, the solution was filtered, thoroughly washed with water, dried, using sodium sulphate, and evaporated *in vacuo*. The resulting syrups were crystallized from the appropriate solvent.

The amyl-, hexyl-, heptyl- and octyl-xylosideacetates were purified by dissolving the final syrups in petroleum ether (b.p. 60°–80°), filtering of an insoluble residue (tri-acetylxylose and xylobioseacetate) and evaporating the filtrate *in vacuo*. The residue was dissolved in 95 per cent ethanol and kept at 4°. The products crystallized very slowly when water was added drop by drop over a period of several days.

Table 1 shows the alkyl-tri-*O*-acetyl-β-D-xylosides which were prepared in this way (all rotations were determined for chloroform solutions).

*Preparation of alkyl-*β-D*-xylopyranosides.* The xylosides were prepared by catalytic deacetylation with sodium-methoxide as described by Thompson and Wolfrom[3]. Table 2 shows the β-D-xylopyranosides which were prepared.

We thank Prof. L. Massart for his advice in this work.

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Partial Specific Volumes of Solubilized Collagens and their Derived Gelatins

DETERMINATION of molecular weight by the method of sedimentation diffusion[1] necessarily involves the measurement of solute partial specific volume, $\bar{v}$. Owing to the highly viscous nature of solutions of soluble collagen, the determination of $\bar{v}$ for such materials is not easy. Previous investigators[2,3] have adopted a value of 0·70 ml/g for $\bar{v}$ of collagen; this is the value obtained for the much less viscous parent gelatin that is formed when collagen is denatured. It is thus implicitly assumed that there is no change in $\bar{v}$ on denaturation and we considered that this matter required experimental investigation. Accordingly, the normal pycnometric procedure for obtaining $\bar{v}$ has been utilized and found satisfactory for very dilute collagen solutions, despite the high viscosity. In 0·15 M citrate buffer, *p*H 3·67, at 20° C, typical values are:

calfskin acid soluble collagen, $\bar{v} = 0{\cdot}645 \pm 0{\cdot}010$ ml./g
calfskin soluble encollagen, $\bar{v} = 0{\cdot}625 \pm 0{\cdot}010$ ml./g
ossein soluble encollagen, $\bar{v} = 0{\cdot}650 \pm 0{\cdot}010$ ml./g

After thermal denaturation, the parent gelatin of acid soluble calfskin collagen gave $\bar{v} = 0{\cdot}695 \pm 0{\cdot}005$ ml./g at 40° C. This is in good agreement with the values previously obtained[2,3] for denatured ichthyocol and with the estimates computed from the amino-acid composition of gelatin[4,5] and the specific volumes of the component amino-acid residues[6].

The present results clearly demonstrate a significant change in $\bar{v}$ on denaturation of collagen, and the lower value in the undenatured state indicates not only a compact structure but also that strong intramolecular compressions must exist. At least a partial release of such compressions accompanies denaturation.

In the presence of 1 M sodium salicylate, a chemical denaturant, $\bar{v}$ for the calfskin parent gelatin is $0{\cdot}755 \pm 0{\cdot}010$ ml./g, a value much higher than that obtained by thermal denaturation. It is suggested that this result may reflect the release of highly compressed water from the protein by the binding of salicylate ions, though other mechanisms are not excluded. Rice *et al.*[7] have recently reported a small difference in $\bar{v}$ for calfskin collagen, according to whether the solvent is citrate or phosphate buffer. It would seem, therefore, that additional careful investigations of the variation of $\bar{v}$ with environment are required both for the highly compact collagen and for gelatin.

The introduction of the appropriate, new collagen values into the usual expression for molecular weight in terms of sedimentation and diffusion coefficients yields values some 17 per cent lower than previously obtained, in agreement with the indications of osmotic pressure work. By argu-