

CXII.—*Studies in Polymerisation. Part I. 2:3:4-Trimethyl l-Arabanolactone.*

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IN view of the current tendency to regard cellulose, inulin, and possibly starch and other complex polysaccharides as polymerides of anhydrohexose units (Hess and Schultze, *Annalen*, 1926, **448**, 99; H. Pringsheim, *Ber.*, 1926, **59**, 3008; M. Bergmann, *Ber.*, 1926, **59**, 2079), the communication of definite experimental evidence of the molecular association of simple derivatives of the natural sugars is of special interest.

A conspicuous example of the ease of polymerisation of a unit of this nature is furnished by our recent studies of the behaviour of 2:3:4-trimethyl *l*-arabanolactone (I). This compound, which has hitherto been obtained only in the form of a syrup, is now shown to be crystalline in the pure state (needles, m. p. 45°), and to display a specific rotation +180° in water, as compared with the former value +145° (Pryde, Hirst, and Humphreys, *J.*, 1925, **127**, 355). The crystalline lactone is readily soluble in cold ether and in other organic solvents as well as in water. In the liquid condition, it is hygroscopic, absorbing water with great rapidity on exposure to the atmosphere; in the crystalline state, it displays this property only to a limited extent. Nevertheless, after 2 days' exposure, the crystals change to a liquid which is almost entirely the free mono-

basic acid. It is therefore evident that the monomeric form of the lactone, which contains a simple six-membered ring, is characterised by its high rotatory power, ready fusibility, high solubility, and by the ease with which it is hydrolysed in the presence of water vapour.

When the lactone is kept, however, for some time in an atmosphere containing traces of acetyl chloride vapour or of hydrogen chloride gas, it undergoes a remarkable change. The transformation product is a white powder which is insoluble in ether and sparingly soluble in benzene or other organic solvents. From solution in hot benzene, it separates as a white, colloidal precipitate which, on removal from the solvent, appears as a mass of microscopic, barrel-shaped crystals having a considerably higher melting point ($135\text{--}138^\circ$) than the original lactone (45°). This crystalline transformation product is stable during many weeks in moist air, and the specific rotation in benzene is only about one-fifth of that of the original lactone. The analytical figures indicated that the new product possessed the same or almost the same empirical formula as the simple lactone, whilst it was shown by titration that complete transformation to the sodium derivative of the simple acid occurred after heating for 20 minutes at 100° with a slight excess of *N*/10-sodium hydroxide. With the theoretical amount of alkali this period was not sufficient to effect complete disruption of the complex, thus indicating that the latter is possessed of far greater stability than the simple lactone towards hydrolytic agents.

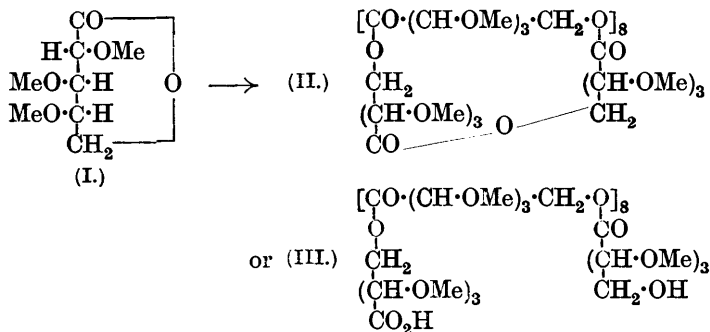
The foregoing evidence, particularly the behaviour towards solvents, pointed unmistakably to the identification of the compound as a polymeride of the trimethyl arabonolactone. This deduction was confirmed by determinations of molecular weight in boiling benzene, which yielded the figures 1900 ($c = 1.05$) and 2100 ($c = 2.25$). Moreover, it was found that the polymeride could be completely transformed to the simple crystalline lactone by heating to 175° in a vacuum, or by successive treatment with alkali and the equivalent of dilute mineral acid. Indeed, the regenerated lactone solidified even without preliminary distillation, yielding crystals, m. p. 45° , identical with the initial material. There can thus be little doubt that the polymerised product consists of a complex containing about ten associated molecules of the simple lactone $C_8H_{14}O_5$.

The important consideration arises whether the polymerisation occurs as a result of the union of the pre-formed, six-membered rings by the exercise of residual valencies, or whether structural change is responsible for the formation of a long chain or a large ring of carbon and oxygen atoms united only by principal valencies. At present there is no evidence to support the former view, whilst

the properties of the polymeride appear to favour the latter hypothesis. Thus the lower specific rotation of the polymerised compound suggests the elimination of the original six-membered ring and favours the probability of a chain formula in which the lower order of rotatory power may be expected. Again, the much enhanced stability of the polymeride towards moisture would seem to indicate a profound modification of the easily ruptured ring of the initial lactone. So remarkable a change in a simple monocyclic sugar derivative of this nature is unexpected, since earlier examples of such a change have usually been furnished mainly by dicyclic compounds, such as the glucosans. Evidence of the polymerisation of the γ -derivatives of sugars has been adduced, but this has usually been indeterminate in character. We incline to attribute to the new polymeride the formula (II), symbolising a chain of some 50 carbon atoms and 11 oxygen atoms, which may be closed, or which may have the two terminal groups as shown in (III). That a ring structure such as (II) would probably be strainless is conceivable from the work of Ruzicka and his co-workers (*Helv. Chim. Acta*, 1926, 9, 499).

Analysis fails to decide with certainty between these alternatives, although it may be remarked that the analytical figures correspond more closely with the closed-chain formula (II).

Some evidence of the partial hydrolysis of the polymeride is given by its behaviour in water, in which it is very sparingly soluble in the cold. The hot aqueous solution was feebly acid to litmus, and the acidity did not increase on boiling; and the cooled solution, which deposited only a negligible quantity of the substance, showed a small lævorotation. Evaporation to dryness gave the original polymeride, apparently pure, in the form of broken prisms, *m. p.* 136—139°. The change to lævorotation after boiling with water may be due to the transformation of the cyclic compound (II) to the open-chain compound (III).



The existence of a crystalline polymeride of this nature, and the simple means by which it can be formed or disrupted, provide a significant commentary on the formulæ which have recently been proposed for cellulose, representing this polysaccharide as polymerised anhydro-glucose, $C_6H_{10}O_5$. Although there remains the possibility that our complex substance may be a mixture of higher polymerides giving an average molecular weight only, yet the crystalline character of the product as revealed under the microscope appears to point to its homogeneity.

EXPERIMENTAL.

2 : 3 : 4-Trimethyl 1-Arabanolactone.—Crystalline trimethyl methyl-arabinoside (m. p. 44°) was hydrolysed by 3% hydrobromic acid, and the product oxidised at $65-70^\circ$ with bromine. The lactone, a viscid, colourless, hygroscopic liquid (n_D^{15} 1.4630), very readily soluble in ether and other organic solvents, solidified to a mass of silky, prismatic needles, m. p. 45° with previous softening. After being drained on porous tile in a vacuum, the product gave: C, 50.7; H, 7.3; OMe, 45.5 ($C_8H_{14}O_5$ requires C, 50.5; H, 7.4; OMe, 48.9%). The specific rotation in water ($c = 1.411$) was initially $[\alpha]_{5461}^{21} + 206.3^\circ$, $[\alpha]_{5780}^{21} + 183.5^\circ$, $[\alpha]_D^{21} + 179.5^\circ$; falling after about 4 hours to $[\alpha]_{5461}^{20} + 17^\circ$. The specific rotation in benzene ($c = 0.86$) was $[\alpha]_{5461}^{21} + 203.5^\circ$, the solution showing no mutarotation.

Polymeride of 2 : 3 : 4-Trimethyl 1-Arabanolactone.—When the syrupy (un-nucleated) lactone was left for some weeks in a closed vessel containing a trace of the vapour of acetyl chloride (and presumably also of hydrogen chloride), it was transformed to a solid, apparently amorphous mass. This was triturated with ether, and after filtration an insoluble, white powder was obtained. The ethereal solution, on evaporation, left a minute quantity of syrup, which was probably the unchanged lactone or an admixture of its lower polymerides. The same polymeride was obtained when the pure crystalline lactone was left during 3 days, along with a tube containing a little acetyl chloride, in a desiccator which was opened occasionally to admit moist air. In this case, the lactone was transformed to the polymeride without becoming liquid. The transformation was also produced (i) by direct treatment of the simple lactone with liquid acetyl chloride, and (ii) by leaving the crystalline lactone in an atmosphere containing hydrogen chloride gas. In the latter case, the change was accompanied by liquefaction, the product afterwards solidifying.

The solid polymeride was sparingly soluble in cold water and slightly more soluble in hot water. At 90° , this solution ($c = 0.39$) showed no appreciable rotation in a 2-dm. tube. On cooling, a

slight opalescence appeared, producing a sediment which was negligible in amount. The solution was slightly lævorotatory, very faintly acid to litmus, and did not reduce Fehling's solution. On evaporation to dryness, the polymeride was recovered quantitatively quite free from oil or other products.

The polymeride obtained by any of the methods already described could be purified from benzene-light petroleum and afterwards from benzene alone. From these solvents, the product separated in colloidal form and afterwards became micro-crystalline; m. p. 135—138°, sintering at about 130° [Found: C, 50.4; H, 7.5; OMe, 46.3; *M*, ebullioscopic in benzene, 1900 ($c = 1.05$), 2100 ($c = 2.25$). The decameric form (II), $(C_8H_{14}O_5)_{10}$, requires C, 50.5; H, 7.4; OMe, 48.9%; *M*, 1900. The open-chain formula (III), $(C_8H_{14}O_5)_{10} + H_2O$, requires C, 50.05; H, 7.4; OMe, 48.5%; *M*, 1918].

Depolymerisation.—The polymeride was quantitatively converted into the simple lactone, $C_8H_{14}O_5$, by heating in a bath at 175° under 0.03 mm. pressure. After the heating had been continued at this temperature for $\frac{1}{2}$ hour, the product distilled, leaving no residue, and completely solidified spontaneously without further purification. The monomeric lactone thus regenerated had m. p. 42° and was identical with the original lactone.

When the polymeride was dissolved in a 50% excess of *N*/10-caustic soda and heated at 100° during 20 minutes, it was completely transformed to sodium trimethyl *l*-arabonate (Found: equivalent of alkali, 8.45 c.c. Calc.: 8.2 c.c.). An amount of *N*/10-hydrochloric acid exactly equivalent to the alkali present was then added, the solution evaporated to dryness at 30° in a vacuum, and the residue extracted with a little cold ether; the syrupy lactone (m. p. 45°) was thus recovered, and this solidified at once on nucleation with the original preparation of 2 : 3 : 4-trimethyl arabonolactone, with which it was shown to be identical by a determination of the mixed melting-point. When the polymeride was dissolved in the exact equivalent of *N*/10-sodium hydroxide (calculated on a simple lactone formula), and the solution heated at 100° during 20 minutes, there remained a 6% excess of alkali, showing that depolymerisation was not quite complete. The specific rotation of the polymeride in benzene ($c = 0.6$) was $[\alpha]_{5461}^{21} + 39^\circ$, the solution not showing mutarotation.

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