

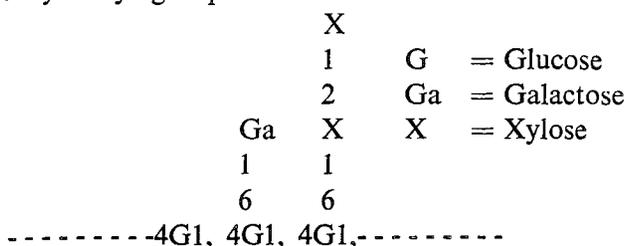
ACETYLATION OF TAMARIND SEED JELLOSE

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Received October 1, 1955

TAMARIND seed jellose is a polysaccharide* which is composed of galactose, xylose and glucose in the ratio of 1 : 2 : 3.^{1, 2} The repeating unit of the macromolecule has been recently shown to have the following structure, containing 16 free hydroxyl groups.³



The acetylation of the substance has been carried out under the same conditions as those adopted for starch,⁴ and the results are reported in this paper.

Jellose, like starch, undergoes progressive acetylation, depending upon the acetylating agent and the conditions of the experiment. If one hydroxyl in every one of the six saccharide rings of the hexasaccharide unit undergoes acetylation, a hexaacetate results corresponding to the monoacetyl derivative of starch. If two of the hydroxyls in every one of the six saccharide rings are acetylated, the product is a duodecaacetate corresponding to the diacetate of starch. If all the hydroxyls are acetylated, a hexadecaacetate forms, which corresponds to the triacetate of starch. Corresponding to these stages, the hexaacetyl, duodecaacetyl and hexadecaacetyl derivatives of jellose have

* In a recent note (*Curr. Sci.*, 1955, 24, 235) Savur has claimed to have isolated from tamarind kernel powder three distinct types of polysaccharide fractions, differing in their solubility and power of gelation. The author appears to suggest that the above fractions are different chemical entities. However, it is very likely that they may be the same polysaccharide existing in different degrees of polymerisation. The material used in the present investigation as also that employed for the earlier constitutional studies (Rao, P. S. and White, E. V., *J. Am. Chem. Soc.*, 1953, 75, 2617) was prepared and purified according to the procedure described earlier (Rao, P. S., Ghose, T. P. and Krishna, S., *J. Sci. and Ind. Res.*, 1946, 4, 705). It did not show any heterogeneity on repeated precipitations from dilute aqueous solutions by means of alcohol, the purified product having a specific rotation of 71.4° in 0.25 per cent. aqueous solution and a pentosan content of 30.5 per cent. (Rao, P. S. and Krishna, S., *Curr. Sci.*, 1946, 15, 133).

been obtained. It may, however, be noted that the reaction need not invariably take place in the stepwise manner indicated; in fact, as in the case of starch, intermediate acetyl derivatives are also formed.

It may be mentioned that the polysaccharide undergoes acetylation even with boiling glacial acetic acid in the presence of anhydrous sodium acetate (*cf.* starch⁵) and the extent of acetylation depends on the duration of the treatment.

The acetyl derivatives are as a class insoluble in water and, some, even in organic solvents. The solubility appears to depend not only on the extent of acetylation but also on the degree of depolymerisation that the molecule undergoes during the chemical treatment. The insoluble products can be rendered soluble in organic solvents by treatment with a hot mixture of sulphuric and glacial acetic acids. In appropriate solvents some of the acetyl derivatives yield fairly strong, flexible, glossy and transparent films which adhere to glass, wood and metal surfaces. From this point of view the product obtained by the action of boiling acetic acid is particularly good. Further, some of the acetates, on account of their wide melting-range, may be useful as thermoplastic resins.

EXPERIMENTAL

Action of glacial acetic acid.—Dry jellose (10 g.) was refluxed with 200 c.c. of glacial acetic acid and one gram of anhydrous sodium acetate for varying periods. After each treatment the mixture was poured on crushed ice and the resulting solid was filtered, boiled with small quantities of fresh water to remove any unreacted jellose, cooled, filtered, washed with alcohol and finally dried in vacuum. The properties of the different products are given in the following table:—

TABLE I

Length of treatment	Acetyl value	Properties
12 hours	12.39%	Insoluble in water and all the ordinary organic solvents.
24 hours	16.58%	Behaves similar to the previous case but swells in glacial acetic acid.
36 hours	19.98%	Soluble in alcohol, pyridine and dilute acetic acid but not in water, acetone and chloroform.

In the first two cases (boiling for 12 and 24 hours) the yields were not high, because the products were contaminated with considerable quantities of unreacted jellose. In the third case, however, the yield was 8 g. from 10 g. of the jellose. In this treatment the reaction product went into solution in the acetic acid and did not separate out on simple dilution, but only on saturation with sodium chloride. Its solutions on slow evaporation left fairly strong, pliable and transparent films. It softened at 270° and became dark at higher temperatures, but did not melt below 320°.

Jellose hexaacetate.—The jellose was initially gelatinized by treatment with formic acid. Dry jellose (10 g.) was gradually added to 100 c.c. of 90 per cent. formic acid with continuous stirring. The substance immediately swelled, forming a thick viscous solution. An analysis of the isolated product showed that the formic acid reacted with the jellose, converting the latter into the hexaformyl derivative $[(\alpha)_D^{25^\circ}]$ in formic acid solution ($c = 0.3\%$) = + 46.3°; softens at 260°, swells enormously on further heating but does not melt below 320°. Continuing the stirring, acetic anhydride (100 c.c.) was added dropwise. Since carbon monoxide was evolved as a result of the decomposition of formic acid, the operation was carried out in a fume chamber. During the reaction the temperature rose gradually and had to be controlled by means of crushed ice. When the addition of acetic anhydride was over, the reaction mixture was cooled and treated with ice-cold water. On vigorous stirring a faintly brownish solid separated. The yield was 12 g. It was insoluble in alcohol, acetone, chloroform, pyridine, etc., and was moderately soluble in formic acid, in which $[\alpha]_D^{25^\circ}$ was + 59.4° ($c = 1\%$). It softened at 230° and melted with decomposition at 280°. This corresponded to the hexaacetyl derivative of the jellose (Found:—COCH₃, 22.4; [C₃₄H₅₀O₂₈ (COCH₃)₆]_n requires—COCH₃, 22.2%).

In the above experiment smaller quantities of formic acid could be used for swelling the jellose but the difficulty was as regards the stirring. Even in 10 per cent. concentration, the jellose formed a thick dough with the acid. However, when the formic acid was sprayed on the jellose triturating in a mortar, the swelling was quite rapid and efficient. By this means the weight of formic acid necessary for swelling could be reduced to an amount equal to the weight of jellose.

Jellose duodecaacetate.—The experiment was carried out as in the previous case but with the difference that acetic anhydride containing 1 per cent. of concentrated sulphuric acid was used instead of acetic anhydride alone, and the product was duodecaacetate. The isolation and purification were done

as in the previous case (Found:—COCH₃, 36.0; [C₃₄H₄₄O₂₈(COCH₃)₁₂]_n requires—COCH₃, 36.4%). The yield was 12.5 g. from 10 g. of the jellose. It was soluble in acetone, acetic acid and pyridine and was insoluble in chloroform and alcohol. In pyridine solution (0.75%), [α]_D^{25°} was + 51.6°. Softening at 240°, it did not melt below 320°.

Jellose hexadecaacetate.—If in the above experiment the reaction mixture was heated at 95° C. for two hours with continuous stirring, the completely acetylated product was obtained. During the first hour the temperature was slowly raised to 95° and was subsequently maintained thereat for the rest of the period. On dilution with ice-cold water and stirring, the acetyl derivative separated out. The yield was 16.6 g. from 10 g. of the jellose. The product was soluble in acetic acid, acetone, chloroform and pyridine but not in alcohol, and exhibited a specific rotation of + 28.5° in pyridine solution (c = 0.5%). It softened at about 240°, assumed a dough-like structure at 280° and did not melt below 320°. It was largely the completely acetylated derivative (Found:—COCH₃, 44.3; [C₃₄H₄₀O₂₈(COCH₃)₁₆]_n requires—COCH₃, 43.4%).

Conversion of insoluble into soluble acetates.—The insoluble acetate (10 g.) was suspended in 100 c.c. of glacial acetic acid containing 1.5 per cent. of concentrated sulphuric acid, and the suspension was heated on an oil-bath. The temperature was slowly raised to 95° during the course of an hour and the heating was continued for another hour at the same temperature. The mixture was then diluted with ice-cold water, whereupon the “soluble” acetate separated (yield: 9.5 g.).

Experiments on the utilisation of the acetates.—Since the melting range of the acetates is fairly wide, covering nearly 60° from the softening point to the formation of the melt, the substances, it was felt, might be useful as thermoplastic materials. However, preliminary experiments on moulding of the esters at temperatures just a little above the softening points indicated that the casts were rather brittle, though the surface was glossy. Addition of plasticisers like camphor, phthalic anhydride and esters of phthalic acid in varying amounts improved the properties of the casts to different degrees. Phthalic anhydride and esters of phthalic acid (25 per cent. addition) gave the best results but even then the casts were not sufficiently strong and tough. In these experiments the duodeca ester gave much better results than the other acetates. The addition of cellulose acetate by about 25 per cent. improved the strength of the jellose acetate moulds (*cf.* starch esters⁴).

The films formed by the evaporation of the solutions of the hexadeca-acetate, though transparent and glossy, were very brittle. Addition of plasticisers did not improve the properties appreciably. On the other hand the films formed from the duodeca ester were strong and tough and plasticisers (the anhydride and the esters of phthalic acid), when added in about 25 per cent. further improved the properties. Being transparent, glossy and water-resistant, the films may find application in the preparation of water-proof covers. In this connection special mention may be made of the lower acetylated products obtained by the treatment of the jellose with boiling glacial acetic acid for 36 hours. Their films from pyridine solution were pliable, fairly strong and transparent.

When applied to wood in pyridine solution the coatings of plasticised acetates resembled varnishes. These coatings adhere to glass and metals as well, and on drying, particularly at higher temperatures, they become flexible and impermeable to moisture. A suitable concentration in these experiments was found to be 5 per cent.

SUMMARY

The hexa, duodeca and hexadeca acetyl derivatives of tamarind seed jellose have been prepared by treatment with acetic anhydride under different conditions. Boiling glacial acetic acid also effects partial acetylation.

Some of the acetyl derivatives in appropriate solvents give fairly strong, flexible, glossy and transparent films, which adhere to glass, metallic and also wooden surfaces. They may also be useful as thermoplastic resins on account of their wide melting range.

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