

and these are linked, therefore, through $C_{(1)}$ and either $C_{(2)}$ or $C_{(4)}$, if the possibility of the presence of furanose residues is discounted. The resistance to attack of the remaining 20 per cent can be explained only by the presence of 1:3-linkages.

Complete methylation and hydrolysis gave 2-methyl-, 2:3-dimethyl-, 2:4-dimethyl-, and 2:3:4-trimethyl-D-xylose, the proportion of the last compound agreeing with the presence of one non-reducing end-group for every 20-21 xylose residues. This separation was achieved by filter-paper chromatography; a more detailed analysis must await the use of the cellulose column. It is evident, however, that this marine xylan contains both 1:3- and 1:4-unions between the xylose units, and that even apart from this difference in its general structure, it differs from esparto xylan². The possibility that the substance examined is a mixture of two xylans built up with 1:3 and 1:4-linkages respectively appears to be discounted by the fact that careful fractionation of both the acetate and the methyl derivative failed to effect any separation. In a general way, therefore, this xylan appears to be analogous to lichenin³, which has been shown to contain D-glucopyranose units linked through the 1:3- and 1:4-positions in the proportion of about 1 in 3.

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¹ Barry and Dillon, *Nature*, **146**, 620 (1940).

² Chanda, Hirst, Jones and Percival, *J. Chem. Soc.*, 1289 (1950).

³ Meyer and Gürtler, *Helv. Chim. Acta*, **30**, 751 (1947). Boissonnas, *ibid.*, 1703 (1947).

As obtained by us, the xylan of *R. palmata* after purification contained 0.5 per cent of ash and had $[\alpha]_D - 99.3^\circ$ ($c = 1.44$ H₂O). Methylation followed by hydrolysis gave the same methyl xyloses as those obtained by the Edinburgh workers, and they were roughly estimated to be in the same proportion.

The xylan was partially oxidized by periodic acid, and the oxidized product gave with ammonia a white precipitate which, after purification, contained 2.7 per cent of nitrogen. This substance was assumed to be an aldehyde ammonia formed by the combination of two molecules of ammonia with each pair of aldehyde groups produced by the oxidation, and on this basis it was calculated that one xylose residue in seven was vulnerable to periodic acid. In view, however, of the much higher figure for α -glycol units found by Percival and Chanda, it must be assumed that only a small fraction of the total aldehyde groups combine with ammonia before precipitation arrests further action.

Titration of the formic acid produced by oxidation with potassium periodate¹ gave 1 mole of formic acid to 7 xylose residues, while determinations of the formaldehyde produced by periodate oxidation (at the reducing end of the chain)² gave 1 mole to 39-40 residues.

These results suggest that this xylan has a structure similar to that proposed by Chanda, Hirst, Jones and Percival³ for esparto xylan, namely, a chain of xylose anhydride units with one branch. The algal xylan, however, appears to contain only about 40 xylose units in the molecule as against 75 in the esparto product. The high proportion of formic acid

points to a linkage at the reducing end through $C_{(4)}$, which would yield 2 moles of formic acid, rather than through $C_{(3)}$, which would yield 1 mole only.

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¹ Halsall, Hirst and Jones, *J. Chem. Soc.*, 1427 (1947).

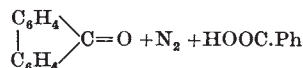
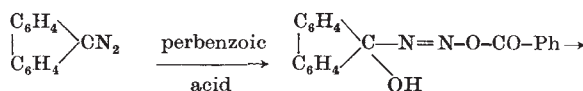
² Bell, *J. Chem. Soc.*, 992 (1948).

³ Chanda, Hirst, Jones and Percival, *J. Chem. Soc.*, 1289 (1950).

Action of Perbenzoic Acid on Diphenylene Diazomethane

WHEN an ice-cold benzene solution (12 c.c.) of perbenzoic acid (0.6 gm.) was added (during a period of 5 min.) to a benzene solution (12 c.c.) of diphenylene diazomethane (0.5 gm.) at 45°, a vigorous evolution of gas was observed. The temperature was kept at 45° for a further 10 min. and benzoic acid removed by extraction with sodium carbonate. The product was dried *in vacuo* and the residue recrystallized from dilute methyl alcohol yielding fluorenone (0.15 gm.).

This seems to be the first case where $>CN_2$ has been directly transformed to $>C=O$.

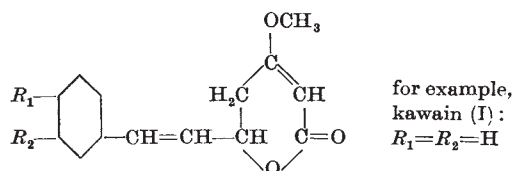


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Synthesis of Kawain

DURING 1914-33 Borsche¹ isolated several structurally related substances from kawa resin. He proposed the general formula:



Neither Borsche nor the other workers in this field have synthesized any of these substances.

It occurred to us that a relatively simple synthesis should be possible by a Reformatsky condensation between cinnamic aldehyde or its derivatives and ethyl- γ -bromo- β -methoxycrotonate. Under the conditions of the reactions the initial condensation