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A New α-Glucan from the Lichen *Parmelia caperata* (L.) Ach.

The water-soluble polysaccharide preparation obtained from *Parmelia caperata* (L.) Ach. ("Kiumenokigoke" in Japanese) was found in our previous screening test[1-3] to be highly effective against the implanted sarcoma-180 in mice Our subsequent studies have revealed that partially O-acetylated pustulan (a linear β-(1→6)-linked glucan) is the active principle of *Gyrophora esculenta* Miyoshi and some other related lichens.[3-8] More recently it has also been shown that *Cetraria richardsonii* Hook. contains lichenin (a (1→3)- and (1→4)-linked linear β-glucan) and isolichenin (a (1→3)- and (1→4)-linked linear α-glucan), and the former glucan showed much higher effect than the latter.[9] Although the polysaccharide constituents of *P. caperata* had not been reported, our preliminary examination suggested the presence of an unknown α-glucan(s) in the crude polysaccharide fraction (PC-1) prepared by adding ethanol to the aqueous extracts.[2] The fraction PC-1 appeared to be homogeneous as shown in the sedimentation pattern. However, it gave two well separated spots by zone-electrophoresis in borate buffer. By repetition of the freeze and thawing procedure, the fraction PC-1 could be readily separated into a major, cold water-insoluble polysaccharide fraction, named PC-3, and a minor, cold water-soluble fraction, designated PC-2 (respective yields, 3% and 0.6%). Both the fractions were obtained in electrophoretically homogeneous state, and the major one corresponded to the faster moving spot. Present communication describes the study on the structure of PC-3. It was a homo-glucan and showed a tendency to be precipitated with $Ba(OH)_2$ solution, but not with the Fehling solution. The glucan gave a positive plain ORD curve ($[\alpha]_D = +201°$, (2N-NaOH)) and showed characteristic absorptions at 925, 845, and 780 cm^{-1} in its infrared (IR) spectrum (KBr) indicating that α-D configuration is predominant in the molecule.

Isolichenin[10-12] and everniin[13] are the only α-glucans so far reported from lichens. Hitherto, the structure of the former glucan has been studied extensively, while that of the latter is still obscure. PC-3 could be distinguished from isolichenin by the negative colouration with iodine, by the sparing solubility in cold water, and by the different IR absorption pattern, in spite of the close ismilarity with isolichenin in their ultracentrifugal and electrophoretical behaviours. Gas liquid chromatography of the methanolysis products of PC-3 methyl ether prepared by using the Hakomori's method and the Kuhn procedure revealed the liberation of approximately equal amounts of methyl 2,3,6-tri-O-methyl- and methyl 2,4,6-tri-O-methyl-

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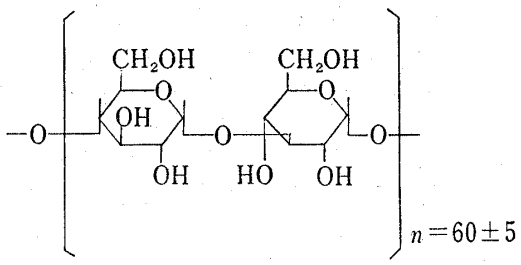
D-glucopyranoside, together with a small amount of methyl 2,3,4,6-tetra-O-methy-D-glucopyranoside. On periodate oxidation, it consumed 0.502 moles of the reagent per anhydroglucose unit. Above results indicated that the glucan is linear and contained α-(1→3)- and α-(1→4)-linkages in the same proportion. When analyzed the di- and tri-saccharides resulted from acetolysis of PC-3 by paper chromatography and electrophoresis, nigerose, maltose, 4-O-α-nigerosyl D-glucose, and 3-O-α-maltosyl D-glucose were detected; neither maltotriose nor nigerotriose could be observed. By the Smith degradation procedure it afforded α-glucosyl erythritol and glycolic aldehyde, which were identified by paper, thin-layer, and gas liquid chromatographic methods. Since no oligosaccharide alcohols were detectable, it is evident that blocks of adjacent (1→3)-linked glucose residues are absent in the molecule. These findings clearly indicated that the sequence of linkages in PC-3 is rather similar to that in nigeran, an intracellular polysaccharide of *Aspergillus niger*,[14,15] and evidently different from that in isolichenin where either single or pairs of α-(1→3)-linked glucose residues are flanked on each side by α-(1→4)-linked residues.[10] At present the name of isolichenin is restricted to the iodophilic polyglucose component occurred in *Cetraria islandica* (L.) Ach. and some other lichens.

The analogy of PC-3 to nigeran, however, is not complete in that the average chain length of the former determined by the end group assay and the methylation study was in the region of 100—130 glucose units, differing markedly from that of the latter ($\overline{DP}$, 300—350: *cf.*[12] isolichenin, $\overline{DP}$, 40—50), and also the fine structures should not be identical, since the presence of small proportion of (1→6)-bonds, besides the alternating sequence of (1→3)- and (1→4)-linkages, has been suggested in nigeran.



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On the basis of the results mentioned above, we now propose the structure (I) for the glucan PC-3. Therefore, it should be classified as a new type of α-glucan.

As has already been pointed out in our previous studies,[5-8] there must be some correlation between the taxonomical position of a lichen and its water-soluble polysaccharide constituents. Survey work on the distribution of this type of α-glucan is now under progress. The antitumour effect of PC-2 and PC-3 will be reported elsewhere.

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