oxazine (**17**) of mp 180—183°. Therefore, this suggested that these components of **16** were isomeric at the asymmetric center of the tetrahydropyranyl group. Steric configurations of these compounds (**12**—**17**) are designated as shown in Chart assuming that the predominant attack of osmium tetroxide[10] occurs at the unhindered site of the double bond of dihydro-1,2-oxazine (**11b**), followed by unequivocal displacement reactions of these substituents of the resulting *cis*-glycol (**12**). This was also supported by analysis of nuclear magnetic resonance spectra. Moreover, in the reductive displacement reaction of **15**, treatment of **15** with hydrazine hydrate and Raney Ni[11] or hydrogenation of **14** over Adams' catalyst, followed by addition of base, gave the same aziridine mixture (**16**), although the yield was lower.

These aziridine derivatives thus obtained were found to show no activity against leukemia L-1210.

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Studies on the Chemical Structures of the New Glucans isolated from *Gyrophora esculenta* Miyoshi and *Lasallia papulosa* (Ach.) Llano and Their Inhibiting Effect on Implanted Sarcoma 180 in Mice

Recently, we have reported[1] that the ethanol-precipitates prepared by adding ethanol to the aqueous extract of a lichen, *Gyrophora esculenta* Miyoshi, had remarkable inhibiting effect against subcutaneously implanted sarcoma 180 in mice. In this communication, we wish to describe the further study on the active principle of the lichen. The ethanol-precipitates were purified by freezing and thawing method to yield ultracentrifugally homogeneous white fibrous flakes, $[\alpha]_D^{19}$ −37.5° (c=0.5, 1 N NaOH). Yield, about 90%, based on ethanol-precipitates. On complete acid hydrolysis, it gave D-glucose as a sole product. (Total glucose content determined by the anthrone method was 98.4%). Its infrared spectrum had an absorption at 910 cm^{-1}. The inhibiting effect of the glucan was tested on solid sarcoma 180 under the same conditions as described in the previous paper.[1] The inhibition ratio was 99.1% and complete regression of the tumour occurred in 8 out of 10 mice. The active glucan liberated homo series of oligosaccharides by partial acid hydrolysis or by enzymolysis with a β-1,6-

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glucanohydrolase prepared from the culture filtrate of *Gibberella spp.* following the method of A. Shibata.[2] They were identified to be gentiobiose, gentiotriose, and gentiotetraose by comparison with the hydrolysates of the authentic sample[3] of pustulan,[5,6] a linear β-1,6-glucan isolated from *Umbilicaria pustulata* (L.) HOFFM. and *U. hirsuta* (SW.) ACH. The glucan was methylated according to the Hakomori's method,[7] and the methylated product, $[\alpha]_D^{18}$ $-15.4°$ ($c=0.26$, $CHCl_3$), was subjected to methanolysis to give methyl 2,3,4-tri-O-methyl-D-glucoside as a major product together with a trace amount of methyl 2,3,4,6-tetra-O-methyl-D-glucoside. The products were identified by gas chromatographic analysis. On the basis of above results, it has been revealed that the active glucan was closely related to pustulan[5,6] in the molecular structure. The similarity of both the glucans was further demonstrated by the findings that a mixed sample of them (1:1) gave a single peak in the sedimentation pattern, and their acetates showed approximately equal values of specific rotation (Acetate of the active glucan, $[\alpha]_D^{18}$ $+10.3°$ ($c=0.13$, $CHCl_3$); pustulan triacetate,[5] $[\alpha]_D$ $+9.1°$ ($c=0.3$, $CHCl_3$)). However, a significant difference was observed between their infrared spectra. The spectrum of the active glucan showed the absorption bands of ester at 1735 and 1250 cm^{-1}, while that of pustulan[4] had no absorptions around there. When treated with 2% sodium carbonate solution at room temperature for 20 min, the active glucan afforded a deacylated product, $[\alpha]_D^{16}$ $-37.4°$ ($c=0.5$, 1 N NaOH), whose infrared spectrum was superimposable with that of pustulan. As a conclusion, the active principle of this lichen has been proved to be a partially acylated β-1,6-glucan. This is the first example of acylated glucan from lichens. Two acidic polysaccharides, islandic acid[8-10] and luteic acid,[11-14] produced by *Penicillium* moulds, are known to be malonyl hemiesters of β-1,6-glucan, but it is evident that the active glucan, being neutral, is not identical with them. Further investigation is now under progress to elucidate the nature of the acyl grouping. It is of interest to note that deacylation of the active glucan resulted in less effect and peracetylation of it caused complete loss of the effect. (deacylated glucan, inhibition ratio, 85.5%, complete regression, 1/8; peracetate of the active glucan, inhibition ratio, 9.3%, complete regression, 0/10). Above results indicate that the presence of ester group gives some influence on the antitumour action.

The presence of the similar glucan has been found in *Lasallia papulosa* (ACH.) LLANO. The glucan, $[\alpha]_D^{21}$ $-38.8°$ ($c=0.32$, 2 N NaOH), IR ν_{max}^{KBr} cm^{-1}: 1735, 1250 (ester), 910 (β-linkage); acetate, $[\alpha]_D^{19}$ $+9.7°$ ($c=0.20$, $CHCl_3$), also showed remarkable effect on implanted sarcoma 180 (inhibition ratio, 98.4%, complete regression, 9/10). Owing to a lack of information concerning the nature of the acyl grouping, final conclusion of the identity between the glucans of *G. esculenta* and *L. papulosa* cannot presently be made.

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