In the future, we expect to examine the effect on BUN concentration of 6′-o-galloyl paeniflorin and procyanidin B-1, which can be isolated from Fr. 2-1 (EtOAc ext.), but only in very small amounts.

Furthermore, we are examining the relationship between the structure and the activity of various tannins, and the mode of action of the BUN-decreasing activity.

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Chemical and Biochemical Studies on Carbohydrate Esters. X.[1] Plant Growth Inhibition by Pure Anomers of Synthetic 1-O-Lauroyl-D-glucopyranose[2]

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Anomerically pure, synthetic 1-O-lauroyl-α- and -β-D-glucopyranoses exhibited strong plant growth inhibiting activity in the Avena coleoptile straight growth test at a final concentration of 500/3 ppm. The growth inhibition ratios obtained with α- and β-anomers were 94.2% and 81.6%, respectively. Under the same conditions, 2-O- and 4-O-lauroyl-D-glucopyranoses and the mono-, di-, and poly-substituted products obtained by selective lauroylation of maltose were all found to be ineffective. In view of these results, the presence of a lauroyl function, either axial or equatorial, at the C-1 position of a monosaccharide unit appears to be important for this biological activity.

Keywords——plant growth inhibiting effect; Avena coleoptile straight growth test; 1-O-lauroyl-α-D-glucopyranose; 1-O-lauroyl-β-D-glucopyranose; 2-O-lauroyl-D-glucopyranose; 4-O-lauroyl-D-glucopyranose; maltose esters of lauric acid

In our previous study,[4] a variety of fatty acid esters of D-glucose, sucrose, and trehalose were examined for their plant growth regulating abilities. It was found that mixtures containing the α- and β-anomers of 1-O-lauroyl-D-glucopyranose in different ratios could produce strong plant growth inhibition, when their abscisic acid (ABA)-like activities were evaluated in Nitsch's Avena coleoptile straight growth assay.[5] Under similar test conditions, lauric acid in the free form, 1-O-acyl-D-glucopyranosyl esters of caprylic, myristic, and stearic acids, 3-O- and 6-O-lauroyl-D-glucopyranose, and sucrose- and trehalose-monoesters of lauric acid were all found to be ineffective. These results suggested that the chain-length and location of the acyl function and also the monomeric nature of the carbohydrate unit are critical for the ABA-like effect of 1-O-lauroyl-glucose, although the stereochemistry at the anomeric center appeared to be unimportant. In an attempt to obtain more conclusive evidence, the same test as employed before has now been conducted with the following samples: anomerically pure 1-O-lauroyl-α- and -β-D-glucopyranoses, 2-O- and 4-O-lauroyl-D-glucopyranose, and maltose-mono-, -di-, and -polyesters of lauric acid. These preparations were obtained by the procedures described in our preceding papers.[1,6]

Materials and Methods

Test Samples——1-O-Lauroyl-α-D-glucopyranose (mp 74—76°),[6a] 1-O-lauroyl-β-D-glucopyranose (mp 104—107°),[6b] 2-O-lauroyl-D-glucopyranose (mp 132—134°),[6b] and 4-O-lauroyl-D-glucopyranose (mp 117—119°)[6b] were prepared by the cited methods. The maltose-mono-, -di-, and -poly laurates were obtained in the manner employed previously[1]: an equimolar mixture of anhydrous maltose and lauroyl chloride in pyridine was heated at 95—100° for 15 hr, and the resulting crude product was fractionated by column chromatography on silica gel with $CHCl_3$–MeOH (9: 1).

Test Method——The Avena coleoptile straight growth test was carried out in the presence of 3-indolylacetic acid (IAA). The general procedure was identical with that used in our previous work.[4] Oat seeds (*Avena sativa* L., cv. Victory) were grown for 3.5 days at 25° in darkness. The test sample was dissolved or suspended in water containing one drop of Tween 20. The following solutions were added successively to a test tube: 1 ml each of 10 mM KH_2PO_4–Na_2HPO_4 buffer solution (pH 5.2), test solution (or suspension) containing 500 ppm of the sample, and an aqueous solution of IAA (3 ppm). A section 6 mm in length was cut from the coleoptile about 2—3 mm below the tip, and 15 sections per tube were floated. After growth for 18 hr at 25° in the dark, the section length was measured, and the growth inhibition ratio was calculated based on the following equation: Growth inhibition ratio (%) $= 100 - (\Delta T/\Delta C \times 100)$, where ΔT is the average final length (mm) of the treated group minus the initial length (6 mm), and ΔC is the corresponding value for the control (buffer solution containing 1 ppm IAA).

Results and Discussion

The ABA-like activities of the samples tested are shown in Table I. Both the α- and β-anomers of 1-O-lauroyl-D-glucopyranose markedly inhibited the plant growth as expected from our previous experimental data obtained with the anomeric mixtures[4]: the α-anomer appeared to be more effective, though only slightly, than the β-anomer. The results confirm that the biological activity of 1-O-lauroylglucose is not affected significantly by the stereochemistry at the C-1 position of the carbohydrate unit, and also exclude the possibility that the growth inhibition caused by the anomeric mixtures might be due to a synergistic action.

TABLE I. ABA-like Activity of 1-O-Lauroylglucose and Related Preparations

Test sample	Growth inhibition ratio (%)
1-O-Lauroyl-α-D-glucopyranose	94.2
1-O-Lauroyl-β-D-glucopyranose	81.6
2-O-Lauroyl-D-glucopyranose	6.3
4-O-Lauroyl-D-glucopyranose	−1.3
Maltose monolaurate	4.6
Maltose dilaurate	−0.2
Maltose polylaurate	0.3

Other samples were all found to be ineffective. Since 2-O- and 4-O-lauroyl-D-glucopyranose failed to produce growth inhibition, it is now clear, taking the known inactivity of 3-O- and 6-O-lauroylglucose into account,[4] that all positional isomers of 1-O-lauroylglucose are devoid of ABA-like ability. Thus, it was concluded that the presence of the lauroyl function attached to the 1-OH group, either axial or equatorial, of the D-glucose unit is critical for this biological effect. In view of this conclusion, the previously observed inactivity of the sucrose- and the trehalose-monoester of lauric acid[4] was considered to be attributable to inappropriate locations of the acyl function introduced: sucrose and trehalose are non-reducing disaccharides and hence they lack free anomeric-OH groups to be acylated. This view was, however, ruled out by the observation that maltose-laurate preparations, which, as reported preliminarily, contained 1-substituted components,[1] also proved to be completely inactive. The inactivity of the sucrose-, trehalose, and maltose-esters of lauric acid may be accounted for by the dimeric nature of their carbohydrate units. In other words, monomeric nature of the carbohydrate residue has now been demonstrated to be another important factor in the ABA-like activity of 1-O-lauroylglucose.

So far, little is known about fatty acid esters of carbohydrates with plant hormonal effects. However, two interesting papers have been published during the course of this work. Grove *et al.*[7] reported that an active principle of "brassin" was a steroidal compound termed brassinolide. As cited in our preceding paper,[4] the active components contained in "brassin," which was first isolated from *Brassica napus* (rape) pollen in 1970 and shown to possess a novel plant growth promoting effect, were tentatively identified as the 1-glucosyl esters of fatty acids by Mandava *et al.*, though this conclusion was questioned by Milborrow *et al.* In 1979, Tanaka *et al.*[8] showed that synthetic 1-O-palmitoyl-, 1-O-oleoyl-, and 3-O-linolenoyl-D-glucopyranoses failed to exert "brassin"-type activity, but found that the last compound had a promoting effect on the germination of pollen and the growth of pollen tubes.

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Chemical and Biochemical Studies on Carbohydrate Esters. XI.[1] Antitumor Effects of Fatty Acid Monoesters of D-Glucose[2]

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1-O-, 3-O-, and 6-O-acyl-D-glucopyranoses carrying capryloyl, lauroyl, myristoyl, palmitoyl, and stearoyl functions were tested for their *in vivo* and *in vitro* antitumor