A comparison of the incorporation ratios showed that the ^{35}S of cysteine(^{35}S) was most efficient as the origin of the thioglucoside moiety in sinigrin. The activity of thioglucose(^{35}S) administered was transferred to the thioglucoside moiety of sinigrin, but the incorporation ratio was unexpectedly low. It should be doubtful to assume that thioglucose would directly be incorporated into sinigrin. However it is plausible that the SH group of cysteine would be a source of sulphur of the thioglucoside moiety in sinigrin.

Experimental

Synthesis of Labelled Compounds and Measurement of Radioactivity——DL-Methionine(^{35}S), DL-cysteine-(^{35}S) hydrochloride and sodium sulphate(^{35}S) were obtained from commercial sources.

Sodium thioglucoside(^{35}S) was synthesized by a method of Horton.[9] Acetobromoglucose (560 mg) in EtOH (1 ml) was added to a solution of potassium ethylxanthate(^{35}S) (220 mg) in EtOH (1.5 ml). The mixture was heated on a boilling water bath for 5 min. After water (15 ml) was added to the mixture, oily substance was separated and solidified by scratching it with a glass rod. Water was removed by decantation.

The residual solid was washed with a small amount of water and dried in a desiccator. The recrystallization from petr. ether and EtOH afforded tetra-O-acetyl-β-D-glucopyranosyl ethylxanthate(^{35}S) (150 mg). The xanthate (100 mg) was hydrolyzed with abs.MeOH (1 ml) containing Na (9 mg) at $-15°$ for 10 min. The mixture was neutralized with 10% AcOH using phenolphthalein as an indicator. Ether (15 ml) was added to it and an oily substance was separated. The precipitates was acetylated with acetic anhydride in pyridine on standing overnight in icebox. The acetate was recrystallized from EtOH. Tetra-O-acetyl-S-acetyl-1-thio-β-D-glucopyranose(^{35}S) (30 mg) was obtained. mp 119° (lit. 121°). *Anal.* Calcd. for $C_{16}H_{22}O_{10}S$: C, 47.39; H, 5.34. Found: C, 47.29; H, 5.42. The acetate was hydrolyzed with abs.MeOH containing Na. and the oily sodium thioglucoside(^{35}S) was separated by the addition of ether to the mixture neutralized with 10% AcOH, which was administered into the plants as an aqueous solution.

Radioactivity was measured with Tri-Carb liquid scintillation spectrometer, series 314 EX (Packard Instrument Company, Inc.) by an ordinary method.

Administration of Labelled Compound into the Plants and Isolation of Sinigrin and Allyl thiourea——Labelled compounds were administered to horseradish leaves as described in the previous paper.[8] Sinigrin was isolated by the method reported previously[4] and converted into allyl isothiocyanate with myrosinase which was separated from yellow mustard seeds. Allyl isothiocyanate was isolated as allyl thiourea which was prepared by addition of an ammonia solution to it.

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9) D. Horton, "Method in Carbohydrate Chemistry", 2, edited by R. L. Whistler and M. L. Wolfrom, Academic Press, Inc., New York, 1963, p. 433.

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Syntheses of 2,3-Di-O-benzyl-*α*-L-*arabino*-pentodialdo-1,4-furanoside and Its *β*-Anomer

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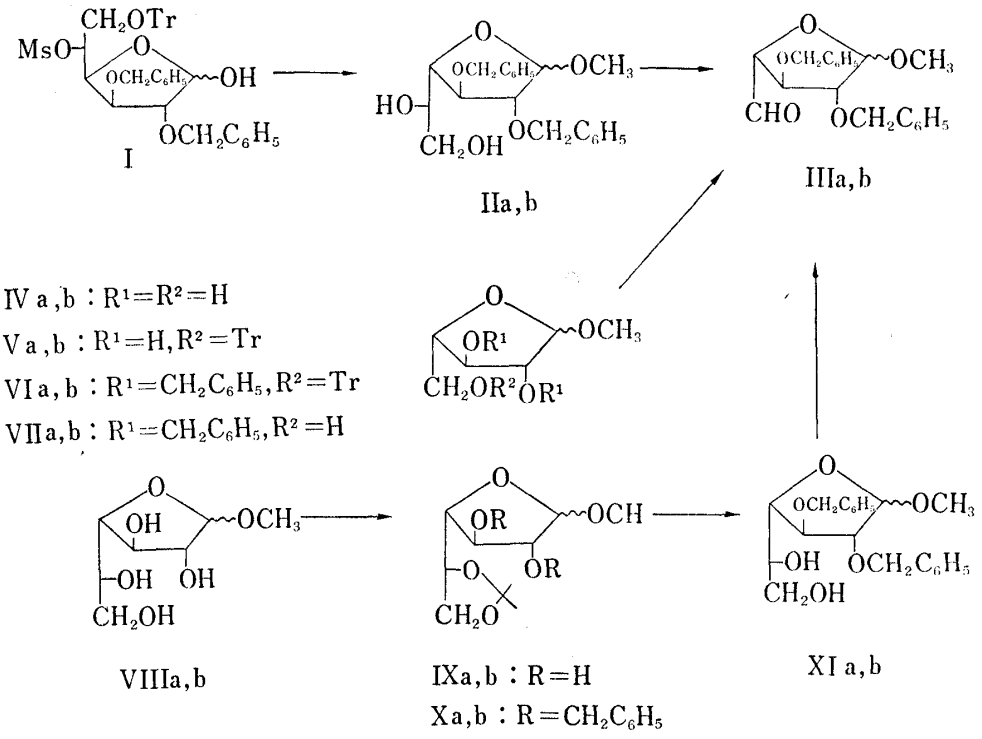
In a previous paper,[2] it was reported that treatment of 2,3-di-O-benzyl-5-O-mesyl-6-O-trityl-D-glucofuranose (I) with sodium methoxide under an oxide ring migration afforded

1) Location: *Hiromachi, Shinagawa-ku, Tokyo.*
2) T. Iwashige and H. Saeki, *Chem. Pharm. Bull.* (Tokyo), **15**, 132 (1967); H. Saeki, T. Iwashige, and E. Ohki, *ibid.*, **16**, 1040 (1968).

methyl 2,3-di-O-benzyl-α-L-altrofuranoside (IIa) and its β-anomer (IIb). The structures of these products were confirmed by oxidation to the corresponding 2,3-di-O-benzyl-L-*arabino*-pentodialdo-1,4-furanosides (IIIa and IIIb). The present paper concerns with syntheses of these dialdofuranosides by an unequivocal route from L-arabinose or D-galactose.

Methyl α-L-arabinofuranoside (IVa) and its β-anomer[3] (IVb) were tritylated in pyridine to the corresponding methyl 5-O-trityl-L-arabinofuranosides; α-anomer[4] (Va), mp 112—113°, $[\alpha]_D^{26}$ −89.1°, and β-anomer (Vb), mp 122—123°, $[\alpha]_D^{27}$ +50.9°. Benzylation[5] of Va and Vb in dimethyl sulfoxide yielded the corresponding methyl 2,3-di-O-benzyl-5-O-trityl-L-arabinofuranosides; α-anomer (VIa), mp 80—81°, $[\alpha]_D^{27}$ −41.2°, and β-anomer (VIb), syrup, $[\alpha]_D^{27.5}$ +31.3°. Treatment of VIa and VIb with 80% aqueous acetic acid gave syrupy methyl 2,3-di-O-benzyl-L-arabinofuranosides; α-anomer (VIIa), $[\alpha]_D^{27}$ −88.4°, and β-anomer (VIIb), $[\alpha]_D^{24.5}$ +43.0°. Oxidation of VIIa and VIIb with dicyclohexylcarbodiimide and phosphoric acid in dimethyl sulfoxide[6] afforded the corresponding methyl 2,3-di-O-benzyl-L-*arabino*-pentodialdo-1,4-furanosides which were characterized as semicarbazones; semicarbazone of the α-anomer (IIIa), mp 121—124°, $[\alpha]_D^{20}$ −46.4°, and semicarbazone of the β-anomer (IIIb), mp 154—156°, $[\alpha]_D^{20}$ +20.1°.

For an alternate route for preparation of IIIa and IIIb, methyl α-D-galactofuranoside (VIIIa) and its β-anomer[3] (VIIIb) were treated[7] with phosphorus pentoxide in acetone and gave methyl 5,6-O-isopropylidene-D-galactofuranosides; α-anomer (IXa), mp 84—85°, $[\alpha]_D^{20}$ +84.3°, and β-anomer (IXb), syrup, $[\alpha]_D^{20}$ −82.1°. Benzylation of IXa and IXb in dimethyl sulfoxide[5] yielded the corresponding methyl 5,6-O-isopropylidene-2,3-di-O-benzyl-D-galactofuranosides; α-anomer (Xa), mp 61.5—62°, $[\alpha]_D^{20}$ +35.3°, and β-anomer (Xb), syrup, $[\alpha]_D^{20}$ −61.9°. Treatment of Xa and Xb with 70% aqueous acetic acid at 50° afforded methyl



3) I. Augestad and E. Berner, *Acta Chem. Scand.*, **8**, 251 (1954).
4) H.G. Fletcher, Jr., *et al.* (C.P.J. Glaudemans and H.G. Fletcher, Jr., *J. Am. Chem. Soc.*, **87**, 4636 (1965)) reported the antipode of Va, methyl 5-O-trityl-α-D-arabinofuranoside, mp 112—113°, $[\alpha]_D^{20}$ +62.4° (AcOEt).
5) T. Iwashige and H. Saeki, *Chem. Pharm. Bull.* (Tokyo), **15**, 1803 (1967).
6) K.E. Pfitzner and J.G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3028 (1963); *ibid.*, **87**, 5661, 5670 (1965).
7) M.L. Wolfrom, F. Shafizadeh, R.K. Armstrong, and T.M. Shen Han, *J. Am. Chem. Soc.*, **81**, 3716 (1958).

2,3-di-O-benzyl-D-galactofuranosides; α-anomer (XIa), mp 83—85°, $[\alpha]_D^{20}$ +33.9°, and β-anomer (XIb), mp 89—91°, $[\alpha]_D^{20}$ −79.4°. XIa and XIb were oxidized with lead tetraacetate in benzene to give the same anticipated 2,3-di-O-benzyl-L-*arabino*-pentodialdo-1,4-furanosides (IIIa and IIIb), which were also characterized as their semicarbazones, as described before. These derivatives were identified with the corresponding samples obtained from I as already described in the preceding paper.[2]

Experimental[8]

Methyl 5-O-Trityl-α (and β)-L-arabinofuranoside (Va and Vb)——To a solution of 10 g of methyl α-L-arabinofuranoside[3] (IVa) in 150 ml of pyridine was added 25.6 g of trityl chloride and the mixture was allowed to stand at room temperature for 4 days. The reaction mixture was poured into H_2O and extracted with $CHCl_3$. The extract was washed with H_2O, dried over anhyd. $MgSO_4$, and was concentrated *in vacuo*. The concentrate was diluted with toluene and evaporated again *in vacuo* to remove pyridine. The syrup obtained by repeating this procedure was chromatographed on 300 g of silica gel. After removal of triphenylcarbinol eluted with benzene, elution with AcOEt–benzene (3:7 v/v) gave crystals of Va. Recrystallization from cyclohexane–AcOEt afforded the α-anomer (Va) as plates, mp 112—113°, $[\alpha]_D^{26}$ −89.1° (c=3.1, $CHCl_3$), $[\alpha]_D^{27}$ −66.7° (c=3.1, AcOEt). *Anal.* Calcd. for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45. Found: C, 74.06; H, 6.37.

Similar treatment of IVb[3] yielded the β-anomer as needles of mp 122—123°, $[\alpha]_D^{27}$ +50.9° (c=3.0, $CHCl_3$). *Anal.* Found: C, 73.83; H, 6.48.

Methyl 2,3-Di-O-benzyl-α (and β)-L-arabinofuranoside (VIIa and VIIb)—— A solution of 10 g of methyl 2,3-di-O-benzyl-5-O-trityl-α-L-arabinofuranoside[9] (VIa) in a mixture of 450 ml of AcOH and 120 ml of H_2O was warmed on a boiling water bath for 40—50 min. The cooled mixture was diluted with 250 ml of H_2O and allowed to stand in an ice-box. The resulting precipitate (triphenylcarbinol) was filtered off and the filtrate was evaporated *in vacuo* at below 45° to give a syrup which was chromatographed on 150 g of silica gel. The fractions eluted with AcOEt–benzene (1:9 v/v) afforded 5.0 g (85% yield) of VIIa as a syrup of $[\alpha]_D^{27}$ −88.4° (c=3.8, $CHCl_3$). *Anal.* Calcd. for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.47; H, 7.10.

The β-anomer[9] (VIb) was detritylated with AcOH as described for VIIa, and gave VIIb, a syrup, $[\alpha]_D^{25}$ +43.0° (c=2.6, $CHCl_3$), in 63% yield. *Anal.* Found: C, 69.48; H, 7.07.

In both cases, a mixture of some acetylated substances was also obtained as a by-product.

Methyl 5,6-O-Isopropylidene-α (and β)-D-galactofuranoside (IXa and IXb)——A solution of 17.5 g of methyl α-D-galactofuranoside (VIIIa)[3] in 300 ml of Me_2CO was added dropwise into 500 ml of abs. Me_2CO containing 34 g of P_2O_5 with stirring, and, after further addition of 170 ml of Me_2CO, the mixture was stirred for 15 min. The solution obtained by decantation from the solid was neutralized with Na_2CO_3, filtered, and evaporated *in vacuo*. The residue was dissolved in $CHCl_3$ and, after filtration, the solution was evaporated *in vacuo*, giving 18.9 g (92% yield) of IXa as a syrup, which crystallized on standing. The analytical sample of IXa, mp 84—85°, $[\alpha]_D^{20}$ +84.3° (c=5.3, $CHCl_3$), was obtained by recrystallization from benzene. *Anal.* Calcd. for $C_{10}H_{18}O_6$: C, 51.28; H, 7.69. Found: C, 50.87; H. 7.63.

Similar treatment of VIIIb[3] afforded the β-anomer (IXb) as a syrup, $[\alpha]_D^{20}$ −82.1° (c=8.7, $CHCl_3$). *Anal.* Found: C, 51.08; H, 7.70.

Methyl 2,3-Di-O-benzyl-5,6-O-isopropylidene-α(and β)-D-galactofuranoside (Xa and Xb)——A solution of 17.9 g of IXa in 75 ml of dimethyl sulfoxide was added dropwise into a solution of 17.4 g of KOH in 75 ml of dimethyl sulfoxide with stirring, and, after the mixture was stirred for 30 min, 27.3 g of benzyl chloride was dropped into the mixture and the mixture was stirred for further 2 hr. The resulting mixture was poured into ice-water, saturated with NaCl, and extracted with three 300 ml portions of ether. The combined extract was washed with H_2O, dried over anhyd. Na_2SO_4, and evaporated. The residue (30 g) was chromatographed on 600 g of silica gel. Elution with AcOEt–benzene (1:9 v/v) afforded 20.5 g (65% yield) of Xa as crystals which were recrystallized from hexane to needles of mp 61.5—62°, $[\alpha]_D^{20}$ +35.3° (c=4.3, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{26}O_6$: C, 69.54; H, 7.30. Found: C, 69.35· H, 7.16.

Similar treatment of IXb yielded Xb as a syrup of $[\alpha]_D^{20}$ −61.9° (c=5.9, $CHCl_3$) in the same yield. *Anal.* Found: C, 69.28; H, 7.33.

Methyl 2,3-Di-O-benzyl-α(and β)-D-galactofuranoside (XIa and XIb)——A solution of 10.5 g of Xa in 100 ml of 70% aqueous AcOH was allowed to stand overnight at room temperature. The resulting mixture was evaporated under a reduced pressure at below 45° to a syrup which was tritulated with benzene to give 8.2 g of XIa as crystals. Recrystallization from ether containing a small amount of benzene gave needles

8) Melting points are not corrected.
9) See the experimental section of a previous paper.[5]

of mp 83—85°, $[\alpha]_D^{20}$ +33.9° (c=4.0, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{36}O_6$: C, 67.36; H, 7.00. Found: C, 67.22; H, 6.98.

Similar treatment of Xb afforded XIb as needles of mp 89—91°, $[\alpha]_D^{20}$ −79.4° (c=5.2, $CHCl_3$), in the same yield. *Anal.* Found: C, 67.22; H, 6.98.

Methyl 2,3-Di-O-benzyl-α(and β)-L-*arabino*-pentodialdo-1,4-furanoside (IIIa and IIIb)——(i) To a solution of 6.27 g of VIIa and 18.7 g of dicyclohexylcarbodiimide in 91 ml of dimethyl sulfoxide was added 9.1 ml of 1M H_3PO_4 solution in dimethyl sulfoxide, and the mixture was allowed to stand at room temperature for 20 hr. The reaction mixture was diluted with cold water and, after standing for a few minutes, extracted with ether. The H_2O layer was also extracted several times with ether. The combined extracts were washed with H_2O, dried over anhyd. Na_2SO_4, evaporated *in vacuo* to give a thick syrup which was chromatographed on 180 g of silica gel. The fraction eluted with benzene–AcOEt (97:3 v/v) afforded 4.9 g (79%) of IIIa as a syrup which formed a semicarbazone of mp 124°, $[\alpha]_D^{20}$ −46.6° (c=1.1, $CHCl_3$). Similar treatment of VIIb afforded the β-anomer (IIIb) in 83% yield. IIIb formed a semicarbazone of mp 154—156°, $[\alpha]_D^{20}$ +20.1° (c=2.1, $CHCl_3$), and a 2,4-dinitrophenylhydrazone of mp 122—123°. (ii) To a solution of 1 g of XIa dissolved in 15 ml of dry benzene, 1.58 g of $Pb(OAc)_4$ was added in small portions with stirring. After standing at 50—55° for 15 min, excess of the reagent was decomposed by the addition of a small amount of ethylene glycol, and the mixture was evaporated *in vacuo*, giving the same IIIa which was analogously characterized as a semicarbazone of mp 124°. Similar oxidation of XIb yielded the same IIIb, and yields in both cases were almost quantitative.

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Isolation of A_1-Barrigenol from *Camellia Sasanqua*

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In a previous paper,[2] we have reported the isolation of eight sapogenols from the seeds of *Camellia Sasanqua* Thunb., camelliagenin A,[3] B,[3] C,[3] D, E, barringtogenol C,[4] theasapogenol A[5] and another unknown sapogenol, and assigned the structures for camelliagenins D and E.[6] We now wish to report the identity of the eighth sapogenol with A_1-barrigenol.[8,9]

Silica gel chromatography of the crude sapogenol mixture, followed by a repeated recrystallization, afforded a compound I, $C_{30}H_{50}O_5$, mp 271—274°. Acetylation of I with acetic anhydride in pyridine yielded a tetraacetate II, $C_{38}H_{58}O_9$, mp 190—193°, ν^{KBr} 1738 cm^{-1}. NMR spectrum of II in deuterochloroform exhibited seven singlets due to tertiary methyl groups at 0.85, 0.87, 0.93, 0.96, 1.00, 1.00, 1.53 ppm together with signals at 3.70 (1H, d,

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5) I. Yoshioka, T. Nishimura, A. Matsuda, and I. Kitagawa, *Tetrahedron Letters*, **1966**, 5979.
6) Yoshioka, *et al.* have independently proposed the same structure as for camelliagenin E for their theasapogenol E.[7] Recent direct comparison established their identity, hence the name theasapogenol E should be used because of its priority. We thank Professor Yoshioka, Osaka University, for the comparison.
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