aminopyridine with ethyl 3-chloropropionate in lieu of the imidate I under the same conditions described above.

Several compounds of the type II were synthesized under similar reaction conditions to those as for the compound II (R=H). The results are listed in Table I and II. All of these compounds are novel in literature to date. It, however, was found that the substitution of a methyl group at 6-position on 2-aminopyridine hindered the production of the objective compound but afforded only a hydrochloride salt of 2-amino-6-methylpyridine. This exception seems to be due to a steric hindrance of a methyl group.5)

The study on the reaction of the imidate I with amino heterocycles of other types, which the structure are similar to that of 2-aminopyridine (for example, when 2-aminopyrimidine was used in lieu of 2-aminopyridine in this reaction, 3,4-dihydro-1*H*-2-oxo-pyrimido[1,2-*a*]-pyrimidin-5-ium chloride was obtained, see Table II.), is now being in progress.

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5) H.C. Brown, D. Gintis and H. Podall, *J. Am. Chem. Soc.*, **78**, 5376 (1956).

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A New Iridoid Glycoside from *Gardenia jasminoides*

Genipin-1-β-gentiobioside

The fruits of *Gardenia jasminoides* Ellis f. *grandiflora* (Lour.) Makino (Rubiaceae) are being used as an antiphlogistic under the name Shan-zhi-i (山梔子).

The occurrence of gardenoside and geniposide in this plant was already reported.1) We have now isolated a new iridoid glycoside from the methanol extracts of the fruits of the same plant and elucidated its structure as genipin-1-β-gentiobioside (I).

I, $C_{23}H_{34}O_{15}\cdot 1/2\ H_2O$, mp 193—195°, was obtained as a white powder2) from ethanol, $[\alpha]_{\mathrm{D}}\simeq 0^\circ$, $[\alpha]_{405}+33.5^\circ$ (c=1.0, MeOH), UV $\lambda_{\max}^{\mathrm{EtOH}}$: 238 mμ (log ε 4.11), IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}:1710, 1690, 1640, NMR $\delta_{\mathrm{DSS}}^{\mathrm{D_2O}}$: 2.50—3.00 (2H, m, H-5,9), 3.78 (3H, s, $-OCH_3$), 4.32 (2H, m, H–10), 5.33 (1H, d, J=7 cps, H–1), 5.95 (1H, m, H–7), 7.66 (1H, d, J=1.5 cps, H–3), 4.53 (1H, d, J=7 cps) and 4.88 (1H, d, J=7 cps) (anomeric protons of sugar moiety).

On acetylation with acetic anhydride and pyridine I gave octaacetate(II) $C_{39}H_{50}O_{23}$, mp 167—169° as colorless needles, $[\alpha]_{\mathrm{D}}\simeq 0^\circ$ (c=0.5, MeOH), IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1760, 1720, 1640, NMR $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$: 2.00—2.22 ($-COCH_3\times 8$), 3.75 (3H, s, $-OCH_3$), 4.77 (2H, s-like, H–10), 5.31 (1H, d, J=5.5 cps, H–1), 5.91 (1H, m, H–7), 7.46 (1H, s, H-3).

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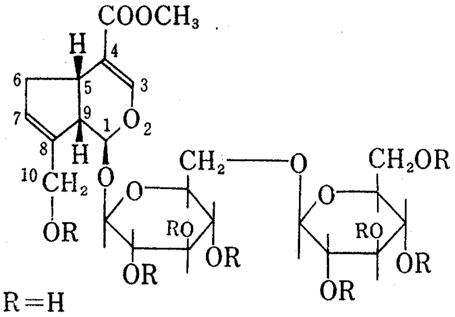
1) H. Inouye, S. Saito, H. Taguchi and T. Endo, *Tetrahedron Letters*, **1969**, 2347.
2) Carefull recrystallization from acetone gave fine needles mp 227—229°.

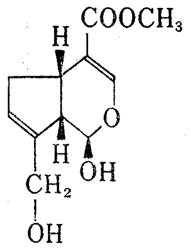
Enzymatic hydrolysis of I with β-glucosidase afforded D-glucose and genipin[1,3] (III), $C_{11}H_{14}O_5$, mp 119—121°, which was identified with the authentic sample by the mixed melting point and the comparison of IR spectra.

Catalytic hydrogenation of I over Pd-charcoal in methanol afforded a 10-deoxy-7,8-dihydro derivative (IV), which was converted to heptaacetate (V) $C_{37}H_{50}O_{21}$, mp 192—193°, $[\alpha]_D$ $-51°$ (c=0.5, MeOH). Enzymatic hydrolysis of IV with β-glucosidase followed by acetylation gave colorless plates mp 53—56°, $[\alpha]_D$ $-76°$ (c=0.5, EtOH), which was identified by the mixed melting point and the comparison of IR spectra with the authentic sample of VI, $C_{13}H_{18}O_5$, mp 58—59°, $[\alpha]_D$ $-71°$, obtained from bisdesoxydihydrodeacetylasperulosidic acid methyl ester (bisdesoxydihydromonotropein methyl ester)[1,4] by the same procedure.

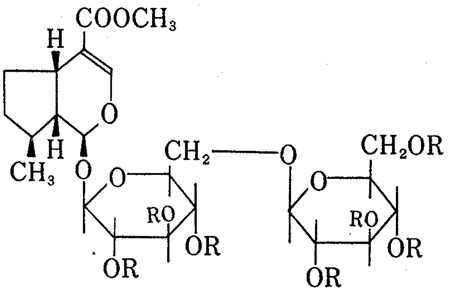
The sugar moiety was proved to be linked with C-1 OH of the aglycon and was proved to be a disaccharide, since eight acetyl signals were observed in the NMR spectrum of II.



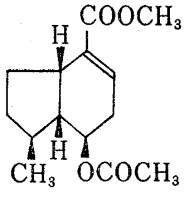
I : R=H
II : R=COCH₃
VII : R=CH₃



III



IV : R=H
V : R=COCH₃



VI

Methylation of I by Hakomori's method[5] gave permethyl glycoside (VII) as a colorless oil. IR ($CHCl_3$) no OH band, NMR $\delta^{CDCl_3}_{TMS}$: 3.37 (3H, s), 3.43 (3H, s), 3.51 (3H, s), 3.55 (9H, s), 3.61 (3H,s), 3.66 (3H,s), 3.76 (3H,s) ($-OCH_3 \times 9$), 5.23 (1H, d, J=6 cps, H-1), 5.86 (1H, m, H-7), 7.56 (1H, d, J=1.5 cps, H-3), 4.30 (1H,d, J=7 cps) and 4.70 (1H, d, J=7 cps) (anomeric protons of the sugar moiety). Methanolysis of VII with 5% methanolic hydrogen chloride gave methyl-2,3,4,6-tetra-O-methyl-D-glucopyranoside and methyl-2,3,4-tri-O-methyl-D-glucopyranoside, which were identified by gas liquid chromatography.

The NMR spectrum of I (in D_2O) showed two anomeric protons of the sugar moiety at δ 4.53 (d, J=7 cps) and 4.88 (d, J=7 cps) to prove tbe β-linkage between two glucose moieties and also that between the sugar moiety and aglycon.

The structure of I was thus established to be genipin-1-β-D-gentiobioside.

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3) C. Djerassi, T. Nakano, A.N. James, L.H. Zalkow, E.J. Eisenbraun and J.N. Shoolery, *J. Org. Chem.*, **26**, 1192 (1961).
4) H. Inouye, T. Arai and Y. Miyoshi, *Chem. Pharm. Bull.* (Tokyo), **12**, 888 (1964).
5) S. Hakomori, *J. Biochem.* (Tokyo), **55**, 205 (1964).