C, 70.38; H, 8.78. IR cm^{-1} ($CHCl_3$): ν_{CO} 1752. NMR $\delta_{ppm}^{CDCl_3}$ 1.12, 1.18 (each 3H, singlet, $\geqslant C-CH_3 \times 2$), 1.38 (6H, singlet, $\geqslant C-CH_3 \times 2$), 1.40 (3H, singlet, $\geqslant C-CH_3$), 3.87 (2H, singlet, $\geqslant C-\underset{O}{\overset{H}{C}}-\underset{O}{\overset{H}{C}}-C\leqslant$), 4.92 (1H, broad singlet, $>C=C<^{H}_{H}$), 5.14 (1H, broad singlet, $>C=C<^{H}_{H}$).

This result proves that the epoxide group is situated on a cyclopentane ring.

Lyoniol-A seems to have the same carbon skeleton and a very similar stereostructure as grayanotoxin-I(X)[2] and rhodojaponin-II (XI)[3] because of a close relationship between the plant sources (toxic species of ericaceous family) and similar biological activity. Thus the structure of lyoniol-A should be represented by formula I. From the coupling constant of C_6–H and C_7–H and speculation about stereomodels we concluded that C_6–H, C_7–H are *trans* and, therefore the C_7-hydroxyl group must be α-configuration. The structures of VII and VIII supposed to be $\Delta^{10,20}$-ene-6,7-acetonide(vinyl protons) and $\Delta^{15,16}$-ene-6,7-acetonide-(allyl coupling of 17-methyl) respectively. Deacetyl derivative of I was thought to consume two moles of sodium periodate, but experiment resulted only one mole under a same condition as quinic acid consumed two moles of periodate. The grayanotoxin diketoderivative(XII)[4] consumes no periodate. Between this fact and resistance of lyoniol-A against sodium periodate there seems to be some relation ship. Further study is in progress.

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3) H. Hikino, K. Ito, T. Ohta, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **17**, 1078 (1969).
4) M. Yanai, H. Mishima, T. Kozima, H. Kakizawa, and K. Nakanishi, *Chem. Pharm. Bull.* (Tokyo), **17**, 2036 (1969).

[Chem. Pharm. Bull. 18(4) 856—858 (1970)]

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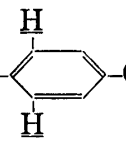
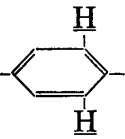
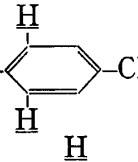
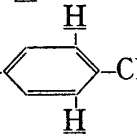
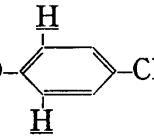
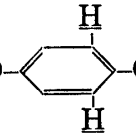
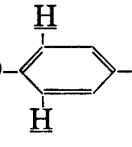
Structure of Innovanoside

A new glycoside, innovanoside, was isolated from the leaves of *Evodiopanax innovans* NAKAI (Araliaceae) as one of minor glycosidic constituents. The methanol extract of the leaves was concentrated, diluted with water, and the resinous precipitate was removed. The aqueous solution was extracted with ethyl acetate, the extract was dissolved in methanol–ethyl acetate and chromatographed on silica gel column. The eluate was rechromatographed on silica gel with chloroform–methanol mixture. From the main fraction yielded a white powder (innovanoside)(I), mp 122—128°, $[\alpha]_D^{15}$ −132° (c=1.1, methanol).[1] NMR $\delta_{ppm}^{d_6\text{-DMSO}}$: 2.34 (3H, singlet, $=\overset{|}{C}-C\underline{H}_3$), 4.3—5.6 (6H, broad, sugar hydrogen), 6.35 (1H, doublet, J=5.5

1) Melting points are uncorrected. Optical rotations were determined on a OR-10 spectrometer (Yanagimoto). NMR spectra were determined on a JNM-MH-60 spectrometer (Japan Electron Optics Lab. Tokyo Japan). Tetramethylsilane as internal standard.

cps, –O–CH=C<u>H</u>–CO–), 6.43 (1H, doublet, J=14.0 cps, ph–C=C–CO–), 6.85 (2H, doublet, J=8.5 cps, –O–  –CH=), 7.54 (2H, doublet, J=8.5 cps, –O–  –CH=), 7.62 (1H, doublet, J=14.0 cps, ph–C=C–), 7.96 (1H, doublet, J=5.5 cps, –O–C<u>H</u>=CH–CO–). *Anal.* Calcd. for $C_{21}H_{22}O_{10}\cdot 1\frac{1}{2}H_2O$: C, 54.66; H, 5.46. Found: C, 54.60; H, 5.48.

Innovanoside was dissolved in dilute potassium hydroxide solution, and then the solution was acidified after a few minutes with dilute sulfuric acid. Isoinnovanoside (II) was obtained as white precipitate, colorless prisms from dilute methanol, mp 222—227°, $[\alpha]_D^{15}$ −89° (c=2.5, methanol). NMR $\delta_{ppm}^{d_6\text{-DMSO}}$: 2.36 (3H, singlet, =C–C<u>H</u>$_3$), 4.2—5.8 (6H, broad, sugar hydrogen), 6.43 (1H, doublet, J=16.0 cps, ph–C=C–CO–), 6.48 (1H, doublet, J=5.5 cps, –O–CH=C<u>H</u>–CO–), 6.88 (2H, doublet, J=8.5 cps, –O–  –CH=), 7.55 (1H, doublet, J=16.0 cps, ph–C=C–), 7.57 (2H, doublet, J=8.5 cps, –O–  –CH=), 7.99 (1H, doublet, J=5.5 cps, –O–C<u>H</u>=CH–CO–), 9.94 (1H, broad singlet, ph–O<u>H</u>). *Anal.* Calcd. for $C_{21}H_{22}O_{10}\cdot\frac{1}{2}H_2O$: C, 56.86; H, 5.23. Found: C, 56.59; H, 5.03. II was methylated in ether with diazomethane to give monomethyl ether (III), colorless needles from ethyl acetate, mp 173—175°. NMR $\delta_{ppm}^{d_6\text{-DMSO+CDCl}_3}$: 2.44 (3H, singlet, =C–C<u>H</u>$_3$), 3.90 (3H, singlet, ph–O–C<u>H</u>$_3$), 4.5—5.8 (6H, broad, sugar hydrogen), 6.35 (1H, doublet, J=16.5 cps, ph–C=C–CO–), 6.43 (1H, doublet, J=5.5 cps, –O–CH=C<u>H</u>–CO–), 6.97 (2H, doublet, J=8.5 cps, –O–  –CH=), 7.52 (2H, doublet, J=8.5 cps, –O–  –CH=), 7.60 (1H, doublet, J=16.5 cps, ph–C=C–), 7.80 (1H, doublet, J=5.5 cps, –O–C<u>H</u>=CH–CO–). *Anal.* Calcd. for $C_{22}H_{24}O_{10}\cdot 1\frac{1}{2}\ H_2O$: C, 55.57; H, 5.72. Found: C, 55.30; H, 5.25. Hydrolysis of III with methanolic potassium hydroxide afforded maltol glucoside[2] and *trans-p*-methoxycinnamic acid. Innovanoside methyl ether (IV) was formed from I with diazomethane, colorless needles from ethyl acetate, mp 169—171°, $[\alpha]_D^{15}$ −63° (c=2.1, methanol). NMR $\delta_{ppm}^{d_6\text{-DMSO+CDCl}_3}$: 2.26 (3H, singlet, =C–C<u>H</u>$_3$), 3.75 (3H, singlet, ph–O–C<u>H</u>$_3$), 4.1—5.3 (5H, broad, sugar hydrogen), 5.85 (1H, doublet, J=12.0 cps, ph–C=C–CO–), 6.20 (1H, doublet, J=5.5 cps, –O–CH=C<u>H</u>–CO–), 6.76 (2H, doublet, J=8.5 cps, –O–  –CH=), 6.78

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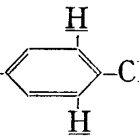
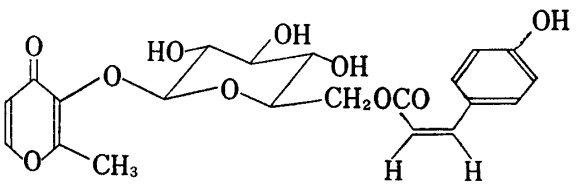
(1H, doublet, J=12.0 cps, ph–C(H)=C(H)–), 7.62 (2H, doublet, J=8.5 cps, –O–  –CH=), 7.74 (1H, doublet, J=5.5 cps, –O–CH=CH–CO–). *Anal.* Calcd. for $C_{22}H_{24}O_{10}\cdot 1/2H_2O$: C, 57.75; H, 5.51. Found: C, 57.69; H, 5.49. IV gave maltol glucoside and *cis-p*-methoxycinnamic acid by hydrolysis with potassium hydroxide. Thus innovanoside must be maltol glucoside *cis-p*-coumarate. The chemical shifts of olefinic protones of I and II suggest the stereostructure of these compounds.

Isoinnovanoside methyl ether (III) was synthesized to determine the position of attachment of the acid group as follows: maltol glucoside was treated with trimethylchlorosilane to yield tetrakistrimethylsilyl maltol glucoside, oil, bp 205—210° (3 mm Hg)(bath temperature), $[\alpha]_D^{28}$ −47°(c=1.0, chloroform). NMR $\delta_{ppm}^{CDCl_3}$: 0.06, 0.19, 0.23(36H, –Si(CH_3)$_3$×4), 2.37(3H, singlet, =C(–CH_3)–), 3.0—5.7 (7H, broad, sugar hydrogen), 6.37 (1H, doublet, J=5.5 cps, –O–CH=CH–CO–), 7.59 (1H, doublet, J=5.5 cps, –O–CH=CH–CO–). The per-silyl compound was stirred with potassium carbonate in methanol to liberate the 6-hydroxyl group,[3] and the reaction product was acylated by *p*-methoxycinnamoyl chloride in pyridine and then the remaining trimethylsilyl groups were removed with aqueous methanol. The product was purified by silica gel column and recrystallized from ethyl acetate: colorless needles, mp 173—175°, $[\alpha]_D^{15}$ −110° (c=1.5, methanol), which was identified with isoinnovanoside methyl ether by mixed melting point determination, infrared (IR) and nuclear magnetic resonance (NMR) spectra. Thus the structure of innovanoside must be maltol glucoside 6-*cis-p*-coumarate (I).



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