confirmed that 4-NOQO was formed by oxidation of 4-HAQO with oxygen in basic solution. But it would be probably unable to isolate 4-NOQO as a species stable enough for application to biological tests.

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On the Structure of Glycoside G and K of Bei-Wujiapi

As we reported in the previous papers,[1,2] *n*-BuOH soluble fraction of MeOH extracts of Chinese crude drug, Bei-Wujiapi (cortex of *Periploca sepium* BGE. (Asclepiadaceae)), was revealed to contain many glycosidic substances (A—N) by TLC.[3]

The mixture of glycosides was repeatedly purified by column chromatography affording three crystalline glycosides, tentatively named glycoside G (0.02% from dried material), glycoside H_1 (0.07%) and glycoside K (0.005%).

Glycoside G (I), $C_{36}H_{56}O_{13}$, mp 232—233°, colorless needles from AcOEt saturated with H_2O, $[\alpha]_D^{19}$ +30.2° (c=0.99, EtOH), infrared (IR) ν_{max}^{KBr} cm^{-1}: 3400, 1750, was acetylated with acetic anhydride and pyridine to give a tetraacetate, $C_{44}H_{64}O_{17}$, mp 198°, colorless needles from EtOH–*n*-hexane, $[\alpha]_D^{19}$ +17.8° (c=0.34, EtOH). IR ν_{max}^{KBr} cm^{-1}: 3500, 1750 (broad), 1235. Acid hydrolysis of I with both Kiliani mixture[4] and 0.05N H_2SO_4, yielded periplogenin,[5] D-cymarose, D-glucose, and periplobiose.[6] Enzymatic hydrolysis of I with taka-diastase-A gave D-glucose and product-GE (II), $C_{30}H_{46}O_8$, mp 146°/208° (double melting point), colorless needles from dil. EtOH, $[\alpha]_D^{19}$ +26.41° (c=0.92, 95% EtOH), IR ν_{max}^{KBr} cm^{-1}: 3400, 1750 which was identified as periplocymarin[5b] (III) by the mixed fusion and the comparison of TLC and IR spectrum with the authentic sample which was given us by Prof. T. Reichstein. The direct comparison of I with periplocin[6] (IV) has not yet done, but above mentioned characters of I suggest that I must be identical with periplocin. The physical constants of I, II and III, IV are comparatively summarized in Table I.

The second crystalline glycoside-K (V), $C_{40}H_{66}O_{16}$, mp 240—241°, colorless needles from MeOH–AcOEt saturated with H_2O, $[\alpha]_D^{20}$ −27.58° (c=1.16, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400, was methylated by Hakomori's method[7] to yield nona-O-methyl glycoside K (VI), $C_{49}H_{84}O_{16}$,

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4) H. Kiliani, *Chem. Ber.*, **63**, 2866 (1930).
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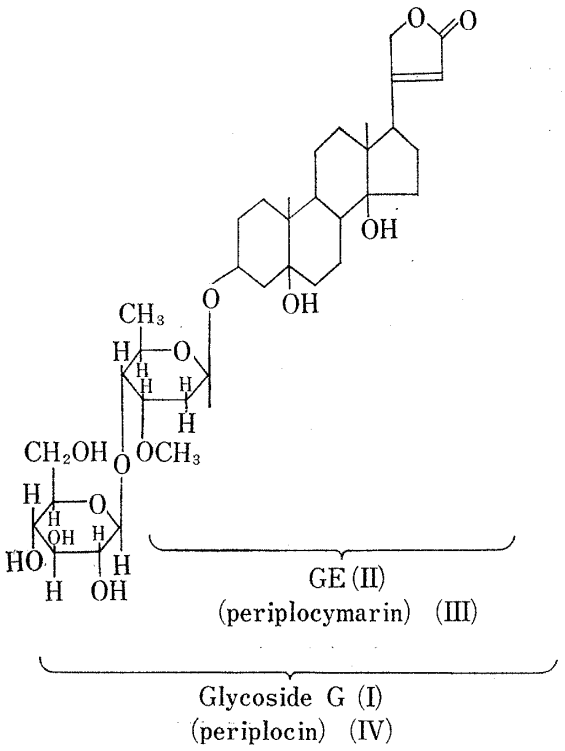
TABLE I



Compound	Formula	mp (°C)	$[\alpha]_D$
Glycoside G (I)	$C_{36}H_{56}O_{13}$	232—233	+30.2
Periplocin (IV)	$C_{36}H_{56}O_{13}$	224	+23.0
Glycoside G acetate	$C_{44}H_{64}O_{17}$	198	+17.8
Periplocin tetraacetate	$C_{44}H_{64}O_{17}$	195	+20.0
GE (II)	$C_{30}H_{46}O_8$	146/208	+26.4
Periplocymarin (III)	$C_{30}H_{46}O_8$	139/207	+29.0

Glucose	NMR anomer H δ=5.14 (d) J=7 cps	β
	$[M]_{D.G}-[M]_{D.GE}$ +69° methyl-α-D-glucopyranoside $[M]_D$: +307° methyl-β-D-glucopyranoside $[M]_D$: −63°	β
Cymarose	NMR anomer H δ=4.88 (q) J_1=3, J_2=9 cps	β
	$[M]_{D.GE}-[M]_{D.genin}$ +36° methyl-α-D-cymaropyranoside $[M]_D$: +370° methyl-β-D-cymaropyranoside $[M]_D$: +40°	β

mp 161—162°, colorless needles from *n*-hexane. $[\alpha]_D^{20}$ −31.34° (c=1.34, EtOH). IR ν_{max}^{KBr}: OH (nil) nuclear magnetic resonance (NMR) $\delta_{TMS}^{CDCl_3}$: 0.66, 3H (s), 1.00, 3H (s), 1.25, 3H (d), 1.34, 3H (d), 3.48—3.64, 3H×10 (s), 4.18, 1H (d), 4.38, 1H (d), 4.67, 1H (d), 5.40, 1H (q).

Hydrolysis of VI with 2N H_2SO_4 gave Δ^5-pregnene-3β,20α-diol monomethylether (VII), $C_{22}H_{36}O_2$, mp 132—133°, colorless needles from *n*-hexane, $[\alpha]_D^{20}$ −50.4° (c=1.04, 95% EtOH), 4-O-methyl-D-digitalose, 2,3,4-tri-O-methyl-D-glucose and 2,3,4,6-tetra-O-methyl-D-glucose. The identification of each O-methyl sugars were carried out by gas liquid chromatography (GLC), paper partition chromatography (PPC) and thin-layer chromatography (TLC). On oxidation with Jones' reagent,[8] VII gave 3β-methoxy-Δ^5-pregnen-20-one,[9] $C_{22}H_{34}O_2$, mp 124°, IR ν_{max}^{KBr} cm^{-1}: 1700. NMR $\delta_{TMS}^{CDCl_3}$: 0.65, 3H (s), 1.00, 3H (s), 2.11, 3H (s), 3.34, 3H (s), which was proved to be identical with the authentic sample by mixed fusion, TLC, IR spectra and nuclear magnetic resonance (NMR) spectra, leading to the formulation of VII as 3β-methoxy-Δ^5-pregnen-20α-ol.[10]

Enzymatic hydrolysis of glycoside K with takadiastase-A, gave D-glucose and glycosidic product-KE (VIII). Per-O-methyl-KE (IX). IR ν_{max}^{KBr}: OH (nil). NMR $\delta_{TMS}^{CDCl_3}$: 0.68, 3H (s), 1.00, 3H (s), 1.28, 3H×2 (d), 3.34—3.61, 3H×7 (s), 4.21, 1H (d), 4.68, 1H (d), 5.38, 1H (q), which was obtained from (VIII) by Hakomori's method, was degradated with dry methanol–HCl and then 2N HCl. The products were identified as 3β-methoxy-Δ^5-pregnen-20α-ol, 4-O-methyl-D-digitalose and 2,3,4,6-tetra-O-methyl-D-glucose by GLC, PPC and TLC.

From these experimental data, NMR spectra and comparison of $[M]_D$ of each products, the structure of V was established to be Δ^5-pregnene-3β,20α-diol(20)-β-D-glucopyranosyl-($1_{glu}\rightarrow 6_{glu}$)-$\beta$-D-glucopyranosyl($1_{glu}\rightarrow 2_{dig}$)-$\beta$-D-digitalopyranoside.

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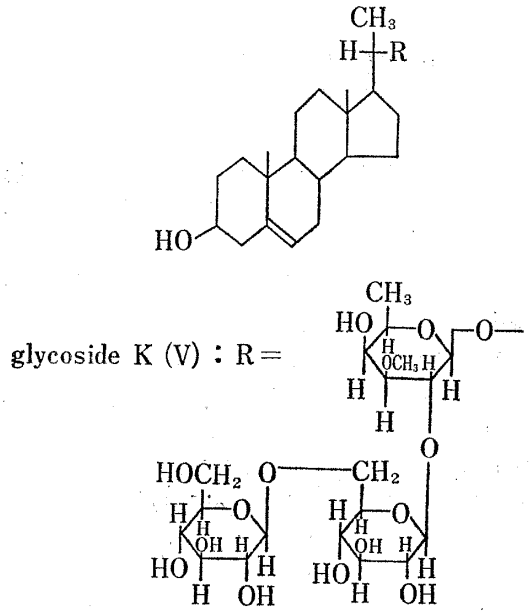
Table II



Glucose→glucose	NMR anomer H δ=4.38 J=8 cps	β
	$[M]_{D.K}-[M]_{D.KE}$ −35°	β
	methyl-α-D-glucopyranoside $[M]_D$ +307°	
	methyl-β-D-glucopyranoside $[M]_D$ −63°	
Glucose→digitalose	NMR anomer H δ=4.18 J=9 cps	β
Digitalose→genin	NMR anomer H δ=4.67 J=8 cps	β

It should be noted that glycoside-K (V) is the first example of the pregnane type glycoside whose sugar moiety links to the hydroxyl group other than C-3 of the aglycone.

The structural study of glycoside H_1 and the pharmacological investigation of these glycosides are now being in progress.

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