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Studies on the Constituents of *Aloe saponaria* Haw. III.1) The Structures of Phenol Glucosides

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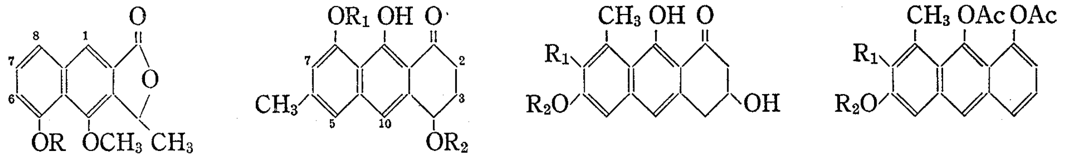
Phenolic glycosides of young subterranean stems of *Aloe saponaria* Haw. were examined to afford compound A—F.

On the basis of chemical and spectral evidences the structures of compound A(I), B(III), C(IV), D(V), E(VI) and F(VII) were determined to be 3-(1′-hydroxyethyl)-4-methoxy-5-hydroxy-2-naphthoic acid lactone 5-*O*-*β*-D-glucopyranoside (I), aloesaponol III 8-*O*-*β*-D-glucopyranoside (III), aloesaponol I 6-*O*-*β*-D-glucopyranoside (IV), aloesaponol II 6-*O*-D-glucopyranoside (V), aloenin (VI) and aloesin (VII), respectively.

Keywords——*Aloe saponaria* Haw.; Liliaceae; young subterranean stems; structures of phenol glucosides A, B, C, D, E and F; new naphthalene and tetrahydroanthracene derivatives

In the previous paper we described the structure elucidation of aloesaponol I—IV and the related anthraquinones from *Aloe saponaria* Haw.1,3) This paper deals with isolation and structure determination of phenol glucosides, 3-(1′-hydroxyethyl)-4-methoxy-5-hydroxy-2-naphthoic acid lactone (named isoeleutherol) 5-*O*-*β*-D-glucopyranoside (I), aloesaponol III 8-*O*-*β*-D-glucopyranoside (III), aloesaponol I 6-*O*-*β*-D-glucopyranoside (IV), aloesaponol II 6-*O*-D-glucopyranoside (V), aloenin and aloesin.



I : R=D-glc
Ia : R=D-glc(Ac)
II : R=H
IIa: R=Ac
IIb: $R=CH_3$

III : R_1=D-glc, $R_2=H$
IIIa: R_1=D-glc(Ac), $R_2=Ac$

IV: $R_1=COOCH_3$, R_2=D-glc
V : $R_1=H$, R_2=D-glc

IVa: $R_1=COOCH_3$, R_2=D-glc(Ac)
Va : $R_1=H$, R_2=D-glc(Ac)

Chart 1

The fresh chips of the plant were treated as described in the experimental section to yield phenol glucosides (A—F).

Compound A, mp 213—216°, $[\alpha]^{20}_{D}$ −37° (MeOH), $C_{20}H_{22}O_9 \cdot 2H_2O$ (I), indicating a blue fluorescence under ultraviolet (UV) light, gave a negative Gibbs' test. I revealed characteristic absorption bands (λ^{MeOH}_{max} nm: 247, 282, 300, 312, 352) due to naphthalene nucleus on UV and broad hydroxy absorption bands (λ^{KBr}_{max} cm^{-1}: 3370, 1760) on infrared (IR) spectra. Nuclear magnetic resonance (NMR) spectrum of I showed a doublet methyl proton signal at δ 1.75 ($J=6$), which coupled with a methine proton at δ 5.97 (q, $J=6$), a methoxy proton signal at δ 4.06 and an anomeric proton signal at δ 5.06 ($J=7$) besides the proton signals due to methines and a methylene of sugar moiety at the region of δ 3.2—4.0. Of aromatic proton signals two doublet protons ($J=6$) and a singlet proton signals appeared at δ 7.60, 7.90 and 8.28, respectively.

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1) Part II: A. Yagi, K. Makino, and I. Nishioka, *Chem. Pharm. Bull.* (Tokyo), **25**, 1764 (1977).
2) Location: *Maidashi, Higashi-ku, Fukuoka.*
3) A. Yagi, K. Makino, and I. Nishioka, *Chem. Pharm. Bull.* (Tokyo), **22**, 1159 (1974).

On acetylation with Ac_2O and pyridine I afforded tetraacetate (Ia), mp 98—101°, M^+ *m/e*: 574, showing no hydroxy absorption band on the IR spectrum. These spectral and chemical evidences led to the conclusion that I was mono glycoside of naphthalene derivatives.

On enzymic hydrolysis with hesperidinase[4] I gave a phenol aglycone II and D-glucose. The former showed a blue fluorescence under UV light and gave positive ferric hydroxamate and Gibbs' tests, while the latter was identified on paper chromatography (PPC). II, mp 162—164°, $C_{14}H_{12}O_4$, exhibited naphthalene absorption bands on the UV (λ_{max}^{MeOH} nm: 252, 308, 322, 348, 362) and a carbonyl absorption band on the IR spectra (ν_{max}^{KBr} cm^{-1}: 1750). Since II was stable to saponification, this compound was suggested to be a naphthalene derivative having a γ-lactone. These findings were supported by the mass spectral examination where fragment ion peak due to elimination of CH_3 and CO from parent ion appeared at *m/e* 201. The NMR spectrum of II showed a doublet proton signal at δ 1.73, which coupled with a methine proton (δ 5.84), a methoxy proton signal at δ 4.10, an ABC system with three aromatic proton signals at δ 7.06, 7.48, 7.52 (J=8; 2), a singlet aromatic proton signal at δ 8.20 and a hydroxy proton signal at δ 9.30.

On acetylation II afforded monoacetate (IIa), mp 130—131°, $C_{16}H_{14}O_5$. The NMR spectrum revealed a doublet methyl proton signal at δ 1.74, which coupled with a methine proton (δ 5.78), and a methoxy proton signal at δ 3.90. Of aromatic protons two protons at *ortho*- and *para* position of acetoxyl group appeared at δ 7.26 and 7.92. A proton at *meta* position of acetoxyl group and an aromatic proton appeared at δ 7.52 and 8.24, respectively. The assignment of an ABC system aromatic proton signal and a long range coupling between C_8–H (δ 7.92) and C_1–H (δ 8.24) were confirmed by spin decoupling experiments. These data suggested II to be an isomer of eleutherol isolated from *Eleutherine bulbosa* (Mill) Urb.[5]

On methylation with CH_2N_2 II gave monomethyl ether, mp 124°, $[\alpha]_D^{20}$ +35.6°, $C_{15}H_{14}O_4$ (IIb), indicating two methoxy proton signals at δ 3.94 and 4.05 on the NMR spectrum. The physical data of IIb are coinsided with those of methyleleutherol (mp 123°, $[\alpha]_D^{20}$ +37°),[5] and the structure of II was established to be 3-(1′-hydroxyethyl)-4-methoxy-5-hydroxy-2-naphthoic acid lactone, named isoeleutherol. Since I gave a negative Gibbs' test and showed an anomeric proton signal at δ 5.06 (d, J=7) on the NMR spectrum, I was demonstrated to be 5-*O*-β-D-glucopyranoside of II, and this conclusion was supported by the examination of the NMR spectrum of Ia in which four acetoxy methyl proton signals appeared at δ 2.00, 2.04, 2.06 and 2.12.

Compound B, mp 237—239° (decomp.), $[\alpha]_D^{22}$ −81.4° (MeOH), $C_{21}H_{24}O_9 \cdot 1/2H_2O$ (III), showed a characteristic yellow fluorescence under UV light and gave positive Gibbs' and $FeCl_3$ tests. III exhibited tetrahydroanthracene nucleus on the UV (λ_{max}^{MeOH} nm: 230, 260, 268, 294, 306, 320, 335, 390, 402; $\lambda_{max}^{MeOH-AlCl_3}$ nm: 234, 268, 276, 310, 324, 340, 430, 440), and broad hydroxyl and chelated carbonyl absorptions on the IR spectrum (ν_{max}^{KBr} cm^{-1}: 3420, 1630). The NMR spectrum indicated two methylene proton signals at δ 2.0—2.4 and 2.8—3.0, a methyl proton signal at δ 2.50, an anomeric proton signal at δ 5.02 (d, J=6), a multiplet methine proton signal at δ 5.04, doublet proton signals at δ 7.26 and 7.33 (J=2), a singlet proton signal at δ 7.37 and a hydrogen-bonded hydroxyl proton signal at δ 13.36 besides the proton signals due to methines and a methylene of sugar moiety at the region of δ 3.5—4.0. Therefore, III was presumed to be monoglycoside of tetrahydroanthracene derivatives.

On enzymic hydrolysis III afforded aloesaponol III which was identified by direct comparison (TLC, IR and mixed melting point) along with D-glucose.

The location of D-glucose in III was determined as follows. Appearance of a bathochromic shift on the UV spectrum caused by addition of $AlCl_3$, presence of a chelated carbonyl

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4) This enzyme was kindly supplied by Prof. Tanaka, Hiroshima University.

5) H. Schmid, Th. M. Meijer, and A. Ebnother, *Helv.*, 33, 595 (1950).

absorption band on the IR spectrum and a hydrogen-bonded hydroxyl proton signal on the NMR spectrum suggested the location of sugar moiety to be at C_4 or C_8–OH.

On acetylation with Ac_2O and pyridine III gave pentaacetate (IIIa), mp 189—192°, *m/e*: 630 (M^+), 570 (M^+–AcOH). On addition of $AlCl_3$ this compound indicated a bathochromic shift on the UV spectrum (λ_{max}^{MeOH} nm: 230, 257, 265, 294, 306, 320, 384, 400; $\lambda_{max}^{MeOH-AlCl_3}$ nm: 230, 266, 275, 296, 308, 325, 416, 438). On the NMR spectrum of IIIa a methine proton at C_4 appeared at δ 6.10 (t, $J=5$) along with a hydrogen-bonded phenol (C_9) and five acetyl methyl proton signals at δ 14.73 and 2.08—2.12, respectively.

Accordingly, the location of D-glucose residue in III has been established to be at C_8–OH and the structure of III was confirmed to be aloesaponol III 8-*O*-β-D-glucopyranoside.

Compound C, mp 224—227°, $[\alpha]_D^{20}$ −30° (MeOH), $C_{23}H_{26}O_{11}\cdot H_2O$ (IV), indicated a strong yellow fluorescence under UV light and a positive $FeCl_3$ test. IV gave broad glycosidal hydroxy, carbonyl and chelated carbonyl absorption bands on the IR spectrum (ν_{max}^{KBr} cm^{-1}: 3400, 1715, 1627). IV showed very similar UV absorption bands (λ_{max}^{MeOH} nm: 267, 276, 302, 313, 327, 377, 392; $\lambda_{max}^{MeOH-AlCl_3}$ nm: 276, 285, 318, 331, 415, 435) to those of aloesaponol I.3) The NMR spectrum revealed two singlets at δ 2.75 and 3.86, indicative of a methyl and a methoxycarbonyl proton signals, and two multiplet methylene proton signals at δ 2.9—3.2, a broad multiplet methine proton signal at δ 4.30 ($W/2=16$), an anomeric proton signal at δ 5.06 (d, $J=7$), two singlet aromatic proton signals at δ 7.06 and 7.28, and a hydrogen-bonded hydroxyl proton signal at δ 15.20 besides the proton signals due to methines and a methylene of sugar moiety at the region of δ 3.2—3.8.

Enzymic hydrolysis of IV afforded aloesaponol I which was identified by direct comparison (TLC and mixed melting point) along with D-glucose.

IV gave a positive $FeCl_3$ test and exhibited a bathochromic shift on the UV spectrum by addition of $AlCl_3$, a chelated carbonyl absorption band on the IR spectrum and a hydrogen-bonded hydroxyl proton signal on the NMR spectrum. Above evidences suggested the presence of a free phenol group at C_9 in IV. On acetylation with Ac_2O and pyridine IV afforded yellow fluorescent hexaacetate (IVa), mp 107—109°, *m/e*: 712 (M^+). The UV spectrum indicated very similar absorption bands to those of 1,6,9-triacetoxyl-7-carbomethoxyl-8-methylanthracene which was derived from acetylation of aloesaponol I.3) The NMR spectrum revealed six acetyl methyl proton signals at δ 2.03, 2.04, 2.07, 2.10 and 2.44, a methyl proton signal at δ 2.74 and a methoxycarbonyl proton signal at δ 3.92. Of aromatic proton signals an ABC system with proton signals due to C_2–H, C_3–H and C_4–H appeared at δ 7.82, 7.40 and 7.06, respectively, and two singlet proton signals of C_5–H and C_{10}–H at δ 7.32 and 8.18.

On the basis of these results it is reasonably concluded that D-glucose must be attached at C_6 and the structure of IV was established to be aloesaponol I 6-*O*-β-D-glucopyranoside.

Compound D, mp 210—215°, (V), revealed the same fluorescence and coloration to those of IV. V showed broad glycosidal hydroxy and chelated carbonyl absorption bands on the IR spectrum (ν_{max}^{KBr} cm^{-1}: 3300, 1605) and considerably similar absorption bands on the UV spectrum (λ_{max}^{MeOH} nm: 265, 273, 300, 310, 332, 380, 393; $\lambda_{max}^{MeOH-AlCl_3}$: 235, 274, 284, 306, 320, 333, 417, 440) to those of IV. On enzymic hydrolysis V afforded an aglycone, aloesaponol II, which was identified by direct comparison (TLC and mixed melting point) along with D-glucose.

On addition of $AlCl_3$ V indicated a bathochromic shift in the UV spectrum and a chelated carbonyl absorption band appeared on the IR spectrum. Therefore, V was assumed to be C_3 or C_6-*O*-glucoside of aloesaponol II.

On acetylation with Ac_2O and pyridine V gave white fluorescent hexaacetate (Va), mp 115—121°, *m/e*: 654 (M^+). By comparison of the UV (λ_{max}^{MeOH} nm: 252, 261, 310, 338, 358, 377, 397) and the IR (ν_{max}^{KBr} cm^{-1}: 1762, 1755, 1630) spectra with those of IVa, this compound (Va) was determined to be an anthracene homolog.

Thus, the structure of V was established to be aloesaponol II 6-*O*-D-glucopyranoside.[6]

Compound E, mp 129—131°, (VI), showed broad glycosidal hydroxy and carbonyl absorption bands on the IR spectrum ($\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400, 1680). Compound F, mp 143—145°, (VII), showed diagnostic absorption bands due to chromone ring on the UV spectrum ($\lambda_{\max}^{\mathrm{MeOH}}$ nm: 244, 252, 297) and broad glycosidal hydroxy, carbonyl and γ-pyrone absorption bands on the IR spectrum ($\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400, 1720, 1650). These spectral data suggested VI and VII to be aloenin[7] and aloesin,[8] respectively, which were isolated from *Aloe arborescens* MILL. var. *natalensis* BERGER. By direct comparison (UV, IR, TLC and mixed melting point) compound E and F were determined to be aloenin and aloesin, respectively.

Biogenetically, aglycones of the phenol glucosides could be well speculated by a cyclization process *via* polyketide composed of carbon 12, 14 and 16. And pharmacological studies on the phenolics isolated from this plant are in progress.

Experimental

Melting points were determined on a Yanagimoto melting point apparatus and uncorrected. IR spectra were obtained with KOKEN DS-301 and UV spectra were recorded with a Shimadzu SV-50A. NMR spectra were taken with a JEOL C-100H spectrometer. Chemical shifts were expressed in ppm from Me_4Si as internal reference and coupling constants (*J*) in Hz. Abbreviation used, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd=double doublet, br=broad, sug.=sugar. Mass spectra were determined on a JEOL-10 double forcus high resolution spectrometer. Optical rotation was measured on JASCO DIP-SL automatic polarimeter. TLC were performed on silica gel G (Merck) employing the following solvent systems. TLC-I: $CHCl_3$–MeOH–H_2O (7:3:1, lower layer), II: $CHCl_3$–MeOH–5% NH_4OH (4:2:1, lower layer), III: $CHCl_3$–EtOH–5% NH_4OH (3:4:2, lower layer) for glucosides and TLC IV: C_6H_6–acetone (5:1), V: hexane–ether (2:5), VI: EtOAc–$CHCl_3$ (1:1) for aglycones. PPC were performed on Toyo-roshi No. 50 employing the following solvent systems. PPC-I: BuOH–pyridine–H_2O (6:4:3, upper layer), II: BuOH–AcOH–H_2O (4:1:5, upper layer). As spraying reagents 1% Echtblausalz B(Merck)-KOH solution and 1% KOH–MeOH for phenolics, and aniline hydrogen phthalate for sugar were used. UV lamp (PUV-1B, Tokyo Kogaku Kikai) was used as a monitor.

Isolation of Phenol Glucosides——The fresh young chips (10 kg) of subterranean stems of this plant were successively extracted with MeOH (5 l) and EtOAc (5 l) four times, respectively. To the combined extracts (340 g) acetone (2 l) was added and the filtrate was concentrated to syrup. The syrup was treated with 90% MeOH and the MeOH extract (45 g) was partitioned between $CHCl_3$–C_6H_6 (2:1) and MeOH–H_2O (1:3). The upper layer was evaporated to dryness and the residue (20 g) was subjected to repeated silica gel chromatographies using $CHCl_3$–MeOH–H_2O (7:3:1, lower layer), $CHCl_3$–MeOH–H_2O (50:10:3, lower layer) and C_6H_6–acetone–H_2O (4:5:1) as solvents to give a mixture of compounds A—F. The mixture was subjected to gradient chromatography using the solvent composed of $CHCl_3$–75% MeOH to give compounds A, B, F and a mixture of compound C, D and E. Compound A and F were purified by preparative TLC by the use of solvent system TLC-II and -I, respectively, and compound B was purified by preparative TLC by the use of solvent system TLC-I followed by column chromatography (Sephadex LH-20). A mixture of compounds C, D and E was purified by preparative TLC by the use of solvent system TLC-I and -III. Yield: compound A (20 mg), B (2 mg), C (6 mg), D (1 mg), E (2 mg) and F (150 mg).

Compound A (I)——Recrystallization from acetone gave colorless needles of I, mp 213—216°, $[\alpha]_D^{20}$ −37° (c=0.5, MeOH), *Anal.* Calcd. for $C_{20}H_{22}O_9 \cdot 2H_2O$: C, 54.30; H, 5.92. Found: C, 53.92; H, 6.05; UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 247 (4.6), 282 (4.0), 300 (4.0), 312 (3.9), 352 (3.4); IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3370, 1760, 1590; NMR (d_6-acetone) δ: 1.75 (3H, d, J=6, CH_3), 4.06 (3H, s, CH_3O), 3.2—4.0 (sug. H), 5.06 (1H, d, J=7, anomeric H), 5.97 (1H, q, J=6, CH_3CH–), 7.60 (2H, d, J=6, C_6, C_7 or C_8–H), 7.90 (1H, d, J=6, C_6, C_7 or C_8–H), 8.28 (1H, s, C_1–H).

Tetraacetate (Ia)——I (12.5 mg) was acetylated with Ac_2O (1 ml) and pyridine (1 ml) at room temperature. After usual work up the product was chromatographed over silica gel using hexane–ether (1:1) as solvent to give colorless amorphous powder of Ia, mp 98—101° (7.4 mg). MS *m/e*: 574 (M^+), 331, 244; UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 256 (4.5), 279 (3.8), 296 (3.8), 310 (3.4), 354 (3.3); IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1765, 1593; NMR ($CDCl_3$) δ: 1.71 (3H, d, J=6, CH_3), 2.00 (3H, s, Ac), 2.04 (3H, s, Ac), 2.06 (3H, s, Ac), 2.12 (3H, s, Ac), 3.84 (3H, s, CH_3O), 4.30 (sug. H), 5.10—5.50 (sug. H), 5.77 (1H, q, J=6, CH_3CH–), 7.30 (1H, dd, J=8; 2, C_6 or C_8–H), 7.44 (1H, t, J=8, C_7–H), 7.73 (1H, dd, J=8; 2, C_6 or C_8–H), 8.15 (1H, s, C_1–H).

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[6] Y. Ida, T. Komori, T. Kawasaki, K. Yoshida, and K. Kato, *Yakugaku Zasshi*, **91**, 119 (1971).

[7] T. Suga, T. Hirata, and K. Tori, *Chemistry Letters*, **1974**, 715; K. Makino, A. Yagi, and I. Nishioka, *Chem. Pharm. Bull.* (Tokyo), **21**, 249 (1973).

[8] K. Makino, A. Yagi, and I. Nishioka, *Chem. Pharm. Bull.* (Tokyo), **7**, 1565 (1974).

Enzymic Hydrolysis of I——To a solution of I (1.1 mg) dissolved in H_2O (2 ml), hesperidinase (2 mg) was added and the reaction mixture was incubated for 15 minutes at 37°. The product was recrystallized from MeOH to give an aglycone (II) and D-glucose.

Aglycone (II)——Recrystallization from MeOH gave colorless needles of II, mp 162—164°, $[\alpha]_D^{20}$ +90° (c=0.85, $CHCl_3$), MS *m/e*: 244.077 (M^+, Calcd. for $C_{14}H_{12}O_4$, 244.074), 229 (M^+–CH_3), 201 (M^+–CH_3, –CO), 173 (M^+–CH_3, –CO, –CO), 158 (M^+–2×CH_3, –2×CO); UV λ_{max}^{MeOH} nm (log ε): 252 (4.9), 308 (3.9), 322 (3.9), 348 (3.9), 362 (3.9); IR ν_{max}^{KBr} cm^{-1}: 3300, 1750, 1590; NMR ($CDCl_3$) δ: 1.73 (3H, d, $J=6$, CH_3), 4.10 (3H, s, CH_3O), 5.84 (1H, q, $J=6$, CH_3CH–), 7.06 (1H, dd, $J=8$; 2, C_6 or C_8–H), 7.48 (1H, t, $J=8$, C_7–H), 7.52 (1H, dd, $J=8$; 2, C_6 or C_8–H), 8.20 (1H, s, C_1–H), 9.30 (1H, s, OH).

Monoacetate (IIa)——II (10 mg) was acetylated with Ac_2O (5 ml) and pyridine (1 ml) at room temperature. After usual work up the product was recrystallized from C_6H_6-acetone to give colorless needles of II-a (10 mg), mp 130—131°, MS *m/e*: 286.084 (M^+, Calcd. for $C_{16}H_{14}O_5$, 286.084; UV λ_{max}^{MeOH} nm (log ε): 242 (4.6), 245 (4.6), 280 (3.5), 292 (3.5), 304 (3.4), 332 (3.2), 346 (3.3); IR ν_{max}^{KBr} cm^{-1}: 1765, 1750, 1590; NMR ($CDCl_3$) δ: 1.74 (3H, d, $J=6$, CH_3), 2.44 (3H, s, Ac), 3.90 (3H, s, CH_3O), 5.78 (1H, q, $J=6$, CH_3CH–), 7.26 (1H, dd, $J=8$; 2, C_6–H), 7.52 (1H, t, $J=8$, C_7–H), 7.92 (1H, dd, $J=8$; 2, C_8–H), 8.24 (1H, s, C_1–H).

Monomethyl Ether (IIb)——II (15 mg) dissolved in MeOH (10 ml) was methylated with CH_2N_2 at room temperature. The product was recrystallized from ether to give colorless needles of IIb (15 mg), mp 124°, $[\alpha]_D^{20}$ +35.6° (c=0.77, $CHCl_3$); MS *m/e*: 258.088 (M^+, Calcd. for $C_{15}H_{14}O_4$, 258.089), 243 (M^+–CH_3), 251 (M^+–CH_3, –CO), 187; UV λ_{max}^{MeOH} nm (log ε): 250 (4.9), 305 (3.6), 315 (3.6), 358 (3.7); IR ν_{max}^{KBr} cm^{-1}: 1750, 1590; NMR ($CDCl_3$) δ: 1.79 (3H, d, $J=6$, CH_3), 3.94 (3H, s, CH_3O), 4.05 (3H, s, CH_3O), 5.79 (1H, q, $J=6$, CH_3CH–), 7.01 (1H, dd, $J=8$; 2, C_6 or C_8–H), 7.46 (1H, t, $J=8$, C_7–H), 7.60 (1H, dd, $J=8$; 2, C_6 or C_8–H), 8.16 (1H, s, C_1–H).

Compound B (III)——Recrystallization from acetone gave yellow needles of III, mp 237—239° (decomp.), $[\alpha]_D^{22}$ −81.4° (c=0.56, MeOH), *Anal.* Calcd. for $C_{21}H_{24}O_9 \cdot 1/2H_2O$: C, 58.74; H, 5.87. Found: C, 58.80; H, 5.38; UV λ_{max}^{MeOH} nm (log ε): 230 (4.2), 260 (4.2), 268 (4.3), 294 (3.4), 306 (3.4), 320 (3.2), 335 (3.1), 390 (3.5), 402 (3.5); $\lambda_{max}^{MeOH\text{-}AlCl_3}$ nm: 234, 268, 276, 310, 324, 340, 430, 440; IR ν_{max}^{KBr} cm^{-1}: 3420, 1630, 1620, 1582; NMR (d_6-acetone): δ: 2.0—2.4 (2H, m, C_3–H), 2.50 (3H, s, CH_3), 2.8—3.0 (2H, m, C_2–H), 3.5—4.0 (sug. H), 5.02 (1H, d, $J=6$, anomeric H), 5.04 (1H, m, C_4–H), 7.26 (1H, d, $J=2$, C_5 or C_7–H), 7.33 (1H, d, $J=2$, C_7 or C_5–H), 7.37 (1H, s, C_{10}–H), 13.36 (1H, s, OH).

Enzymic Hydrolysis of III——To a solution of III (3.3 mg) dissolved in H_2O (2 ml), hesperidinase (5 mg) was added and the reaction mixture was incubated for 30 minutes at 37°. The product was extracted with ether and the ether extract was recrystallized from hexane–ether (1: 1) to afford yellow aloesaponol III. D-Glucose in the H_2O layer was identified on PPC.

Pentaacetate (IIIa)——III (8 mg) was acetylated with Ac_2O (2 ml) and pyridine (2 ml) for 40 hr at room temperature. After the usual work up the product was chromatographed over silica gel using hexane–EtOAc (4: 1) as solvent to yield IIIa (4.5 mg). Recrystallization from ether gave pale yellow needles of IIIa, mp 189—192°, UV λ_{max}^{MeOH} nm (log ε): 230 (4.4), 257 (4.3), 265 (4.4), 294 (3.8), 306 (3.7), 320 (3.5), 384 (3.9), 400 (3.9); $\lambda_{max}^{MeOH\text{-}AlCl_3}$ nm: 230, 266, 275, 296, 308, 325, 416, 438; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1750, 1627, 1580; NMR ($CDCl_3$) δ: 2.08—2.12 (4×Ac, sug. and C_4–Ac), 2.2—2.4 (2H, m, C_3–H), 2.48 (3H, s, CH_3), 2.7—3.2 (2H, m, C_2–H), 3.8—5.6 (sug. H), 6.10 (1H, t, $J=5$, C_4–H), 7.00 (1H, d, $J=1.5$, C_5 or C_7–H), 7.09 (1H, s, C_{10}–H), 7.20 (1H, d, $J=1.5$, C_5 or C_7–H), 14.73 (1H, s, C_9–OH), MS *m/e*: 630 (M^+), 570 (M^+–AcOH), 331.

Compound C (IV)——Recrystallization from acetone gave pale yellow needles of IV, mp 224—227° (decomp.), $[\alpha]_D^{20}$ −30° (c=0.25, MeOH), *Anal.* Calcd. for $C_{23}H_{26}O_{11} \cdot H_2O$: C, 55.64; H, 5.69. Found: C, 55.29; H, 5.56; UV λ_{max}^{MeOH} nm (log ε): 267 (4.3), 276 (4.4), 302 (3.5), 313 (3.5), 327 (sh.), 377 (3.6), 392 (sh.); $\lambda_{max}^{MeOH\text{-}AlCl_3}$ nm: 276, 285, 318, 331, 415, 435; IR ν_{max}^{KBr} cm^{-1}: 3400, 1715, 1627, 1610, 1570; NMR (d_6-DMSO) δ: 2.75 (3H, s, CH_3), 2.9—3.2 (4H, m, C_2,C_4–H), 3.2—3.8 (sug. H), 3.86 (3H, s, $COOCH_3$), 4.30 (1H, m, $W/2=16$, C_3–H), 5.06 (1H, d, $J=7$, anomeric H), 7.06 (1H, s, C_5 or C_{10}–H), 7.28 (1H, s, C_5 or C_{10}–H), 15.20 (1H, s, OH).

Enzymic Hydrolysis of IV——IV (2.8 mg) was hydrolyzed with hesperidinase (5 mg) in the same way as described for the hydrolysis of I to give aloesaponol I as pale yellow needles (recrystallized from C_6H_6-acetone) along with D-glucose.

Hexaacetate (IVa)——IV (7 mg) was acetylated with Ac_2O (1 ml) and pyridine (1 ml) at room temperature. The product was chromatographed over silica gel by the use of C_6H_6–$CHCl_3$ (1: 1) as solvent to give pale yellow amorphous powder of IVa (5 mg), mp 107—109°, MS *m/e*: 712 (M^+), 670 (M^+—Ac), 628 (M^+—2×Ac), 382, 331; UV λ_{max}^{MeOH} nm (log ε): 254 (sh.), 263 (4.6), 302 (sh.), 359 (3.8), 379 (3.7), 400 (3.6); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1740, 1630; NMR ($CDCl_3$) δ: 2.03, 2.04, 2.07, 2.10 (12×H, s, each, 4×Ac), 2.44 (6H, s, 2×Ac), 2.74 (3H, s, C_5–H), 3.92 (3H, s, $COOCH_3$), 4.2—5.4 (sug. H), 7.06 (1H, dd, $J=7$; 2, C_4–H), 7.32 (1H, s, C_5–H), 7.40 (1H, t, $J=7$, C_3–H), 7.82 (1H, dd, $J=7$; 2, C_2–H), 8.18 (1H, s, C_{10}–H).

Compound D (V)——Recrystallization from acetone gave yellow needles of V, mp 210—215°; UV λ_{max}^{MeOH} nm (log ε): 265 (sh.), 273 (4.5), 300 (3.7), 310 (3.7), 322 (3.6), 380 (3.4), 393 (3.4); $\lambda_{max}^{MeOH\text{-}AlCl_3}$ nm: 235, 274, 284, 306, 320, 333, 417, 440; IR $\nu_{max}^{dioxane}$ cm^{-1}: 3300, 1605, 1590.

Enzymic Hydrolysis of V——V (1.5 mg) was treated with hesperidinase (5 mg) in the same way as described for III. The resulting aglycone was identified by direct comparison to be aloesaponol II and from the H_2O layer D-glucose was detected (on PPC).

Hexaacetate (Va)——V (4.4 mg) was acetylated with Ac_2O (2 ml) and pyridine (2 ml) at room temperature for 24 hr. The product was chromatographed over silica gel using hexane–ether (1:1) to give white amorphous powder of Va (2.7 mg), mp 115—121°, UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ε): 252 (sh.), 261 (4.9), 310 (3.7), 338 (3.6), 358 (3.6), 377 (3.5), 397 (3.4); IR $\nu_{\max}^{\text{CCl}_4}$ cm^{-1}: 1762, 1755, 1630, 1605; MS *m/e*: 654 (M^+), 612 (M^+-Ac), 570 ($M^+-2\times Ac$), 331, 324, 271, 229, 211, 187, 169.

Compound E (VI)——Recrystallization from acetone gave colorless needles of VI, mp 129—131°; UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ε): 303 (3.7); IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400, 1680, 1637, 1610, 1563.

Enzymic Hydrolysis of VI——VI (3 mg) was treated with hesperidinase (5 mg) as described for I. The product was recrystallized from ether to give colorless needles of the aglycone, mp 210—212°; UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ε): 252 (3.8), 288 (3.9), 310 (4.0); IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3370, 1675, 1630, 1605, 1565. The resulting D-glucose was also detected. The spectral data of VI and its aglycone were in good agreement with those of aloenin and its aglycone, respectively.

Compound F (VII)——Recrystallization from EtOAc gave pale yellow amorphous powder of VII, mp 143—145°; UV $\lambda_{\max}^{\text{MeOH}}$nm (log ε): 244 (4.1), 252 (4.1), 297 (3.9); IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400, 1720, 1650, 1600. The spectral data were in good agreement with those of aloesin.

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