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Studies on the Constituents of *Aeginetia indica* L. var. *gracilis* Nakai. Structures of Three Glycosides isolated from the Whole Plant

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Three glycosides named hydroxy-β-ionone glucoside (1), aeginetoside (2) and isoaucubin (3) were isolated from the *n*-butanol extract of *Aeginetia indica* L. var. *gracilis* Nakai. The structures of 1, 2 and 3 were elucidated by chemical and spectral studies.

Keywords——*Aeginetia indica* L. *var. gracilis* Nakai; Orobanchaceae; hydroxy-β-ionone glucoside; aeginetoside; isoaucubin; Wittig reaction; iridoid glucoside; ^{1}H NMR; ^{13}C NMR

Aeginetia indica L. var. *gracilis* Nakai (Orobanchaceae) (Japanese name, Nanbangiseru), a root parasite of eulalia or ginger, is widely distributed in Southeast Asia, India, the Philippines and Japan.[2)] Earlier investigations of this plant, dealing with the isolation and structure elucidation of aeginetic acid, aeginetolide and three polyene compounds were reported by Dighe.[3)] This paper deals with the isolation and structure elucidation of two new β-ionone type glycosides named hydroxy-β-ionone glucoside (**1**) and aeginetoside (**2**), and a new iridoid glycoside named isoaucubin (**3**) from the fresh whole plant. The fresh plant was first percolated with hot methanol. The concentrated methanol extract was dissolved in water and shaken with chloroform and then *n*-butanol. The *n*-butanolic layer,

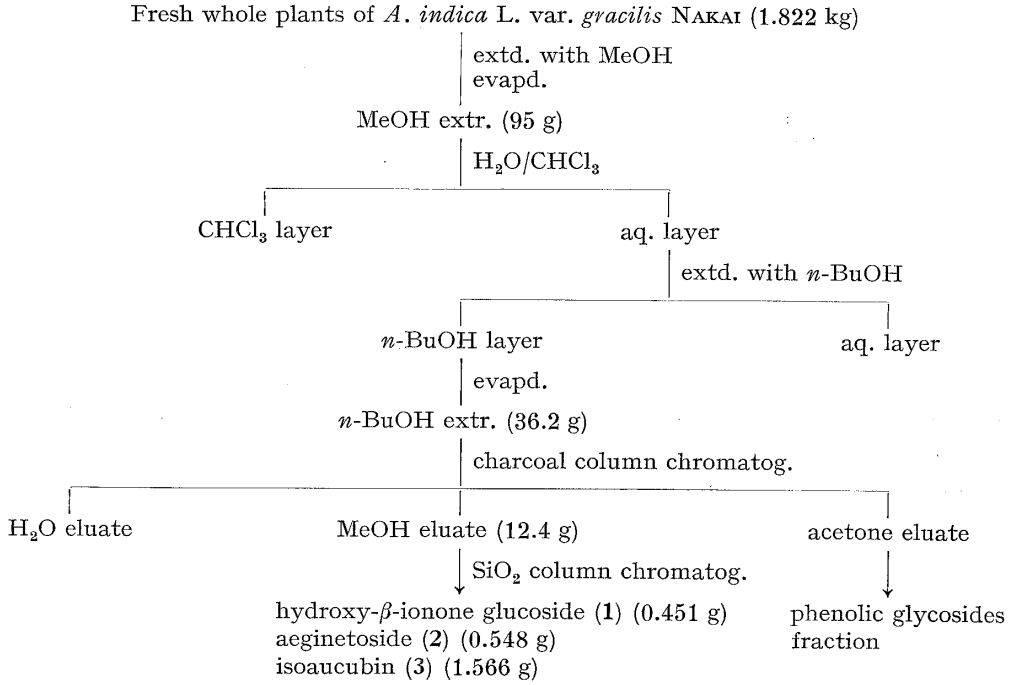


Chart 1. Isolation Procedure for the Glycosides

1) Location: *1421, Izumi, Komae-shi, Tokyo.*
2) J. Ohwi, "Flora of Japan," revised edition, Shibundo, Tokyo, 1965, p. 1217.
3) *a*) S.S. Dighe and A.B. Kulkarni, *Indian J. Chem.*, **11**, 404 (1973); *b*) *Idem, ibid.*, **11**, 413 (1973); *c*) S.S. Dighe, S.V. Manerikar and A.B. Kulkarni, *Indian J. Chem.*, **15B**, 546 (1977); *d*) *Idem, ibid.*, **15B**, 550 (1977).

after concentration, was purified by column chromatography on charcoal, developing with water, methanol and acetone, successively. The methanol eluate was rechromatographed on silica gel using a mixture of chloroform and methanol to furnish **1** (yield 0.025%), **2** (0.03 %) and **3** (0.086%). The acetone eluate gave two phenolic glycosides.

Hydroxy-β-ionone glucoside (**1**) was isolated as colorless needles, $C_{19}H_{32}O_8$, mp 214—215.5°, $[\alpha]_D$ −30.9° (c=0.42, EtOH). The ultraviolet (UV) spectrum of **1** showed an absorption maximum at 232 nm (log ε 4.04). It also gave absorption bands at 3500, 3300, 1680 and 1650 cm^{-1} in the infrared (IR) spectrum and positive Cotton effects at 212 nm ([θ]: +9400) and 316 nm ([θ]: +1000) and a negative one at 239 nm ([θ]: −14,100) in the circular dichroism (CD) spectrum, suggesting the presence of an α,β-unsaturated ketone and hydroxy groups.

On acetylation with acetic anhydride and pyridine at room temperature, **1** afforded a tetraacetate (**4**), $C_{27}H_{40}O_{12}$ [m/e: 556 (M^+)], mp 183—184°, $[\alpha]_D^{27}$ −75.9° (c=0.44, EtOH), IR (in KBr): 3510 (tertiary OH), 1770 (ester) cm^{-1}, UV (in EtOH): 230 nm (log ε 4.13). The proton nuclear magnetic resonance (^{1}H NMR) spectrum (in $CDCl_3$) of **4** showed three singlet methyl signals (δ 0.83, 1.12 and 1.20), one singlet methyl signal (δ 2.30) attributable to an α-methyl relative to a carbonyl group, and two olefinic protons (δ 6.19 and 7.32) with the coupling constant J=17 Hz (*trans* relationship). The carbon NMR (^{13}C NMR) spectrum of **4** showed the presence of a carbonyl carbon and two olefinic, three quaternary, three methylene and four methyl carbons outside the sugar moiety, as shown in Table I.[4]

Acid hydrolysis of **1** with 1 N HCl-dioxane afforded D-glucose and an aglycone (**5**), $C_{13}H_{22}O_3$, mp 107—108°, CD (in MeOH): $[\theta]_{212}$ +15300, $[\theta]_{242}$ −17500, $[\theta]_{320}$ +1100, which was identified as dihydroxy-β-ionone (**5**), previously isolated from the dried rhizoma of *Rehmania glutinosa* Liboscн. var. *purpurea* Makino (Scrophulariaceae)[5] (see "Experimental") by direct comparison (IR, mixed mp and CD). The structure of **5** isolated from *R. glutinosa* Liboscн. var. *purpurea* Makino had been elucidated as follows. The ^{1}H NMR spectrum of **5** showed the presence of three singlet methyls (δ 0.86, 1.13 and 1.23), an α-methyl (δ 2.30) relative to a carbonyl group, and trans olefinic protons [δ 6.19 and 7.32 (each d, J=17 Hz)]. The absorption bands at 3500 and 3450 cm^{-1} in the IR spectrum indicated the presence of hydroxyls. The mass spectrum of **5** showed peaks at m/e 226 (M^+), 208 (M^+-H_2O), 109 and 71 (M^+-155), suggested the presence of a 1,2-dihydroxy-2,6,6-trimethylcyclohexyl end-group, by comparison with hydroxylated carotenoids.[6]

On the basis of these physical data, **5** was presumed to be a dihydroxy-β-ionone derivative. Treatment of β-ionone with *m*-chloroperbenzoic acid (*m*-CPBA) followed by hydrolysis with 20% ethanolic sulfuric acid afforded (±)-1′,2′-dihydroxy-β-ionone (**5′**), $C_{13}H_{22}O_3$, colorless prisms, mp 111—112°, which was suggested to have a *trans* diol (*threo*-configuration).[7] The CD spectrum of **5′** showed no absorption in the region between 200—350 nm, indicating that **5′** is a racemate. Compound **5** and **5′** gave the same IR (in $CHCl_3$), mass, ^{1}H NMR and ^{13}C NMR spectra but different CD spectra, showing that the compounds have the same plane structure, and that **5** is optically active 1′,2′-*threo*-1′,2′-dihydroxy-β-ionone.

Next, catalytic hydrogenation of **4** over platinum oxide in acetic acid furnished **6** as colorless needles, $C_{27}H_{42}O_{11}$ [m/e: 542 (M^+)], mp 141—142.5°. The IR spectrum of **6** (in $CHCl_3$) showed no hydroxy band, indicating that glucose is linked to the C-2′ hydroxy group.

4) *a*) U. Vogeli, W. Eschnmoser, and C.H. Eugster, *Helv. Chim. Acta*, **58**, 2044 (1975); *b*) G. Englert, *Helv. Chim. Acta*, **58**, 2367 (1975).
5) The authors' unpublished data.
6) C.R. Enzell, G.W. Francis, and S. Liaaen-Jensen. *Acta Chem. Scand.*, **23**, 727 (1969).
7) *a*) P. Karrer and H. Sturzinger, *Helv. Chim. Acta*, **29**, 1829 (1946); *b*) W. Skorianetz and G. Ohloff, *Helv. Chim. Acta*, **56**, 2151 (1973); *c*) B.R. von Wartburg, H.R. Wolf, and O. Jeger, *Helv. Chim. Acta*, **56**, 1948 (1973); *d*) M. Akhtar, A.E. Fraruk, C.J. Harris, G.P. Moss, S.W. Russell, and B.C.L. Weedon, *J. Chem. Soc. Perkin I*, **1978**, 1511.

Table I. ^{13}C NMR Spectral Data for 2, 4, 5(5′) and 7 (δ, ppm from internal TMS at 20.0 MHz)

	2[a]	4[b]	5(5′)[b]	7[b]
C-1	59.4	d)	d)	61.3
2	129.5	198.8	198.6(198.9)	123.6
3	136.9	131.2	130.8(130.7)	138.6
4	134.1[c]	149.9	149.8(150.1)	132.6[c]
5	132.3[c]	—	—	131.9[c]
1′	80.1	78.8	79.6(79.6)	78.6
2′	83.7	83.1	74.9(74.9)	83.4
3′	32.3	32.4	36.3(36.3)[c]	32.3
4′	18.6	17.5	17.8(17.8)	17.6
5′	37.2	35.8	36.2(36.1)[c]	35.9
6′	39.6	38.6	38.5(38.5)	38.6
Sugar moiety				
1″	98.1	94.8	—	94.8
2″	75.4	71.5	—	71.3
3″	79.0	73.4	—	73.6
4″	71.8	68.7	—	68.8
5″	77.1	71.8	—	71.9
6″	63.1	62.3	—	62.5
Methyls	27.6	26.6	27.5(27.5)	26.4
	25.9	26.3	27.2(27.3)	24.5
	22.3	24.7	26.5(26.5)	21.0
	13.0	21.0	25.1(25.1)	12.8

The compounds **4** and **7** had additional signals arising from acetoxy groups at *ca.* 170 and 20 ppm.
a) Measured in CD_3OD.
b) Measured in $CDCl_3$.
c) These assignments may be reversed in each vertical column.
d) These carbons could not be distinguished from the other methyl signals

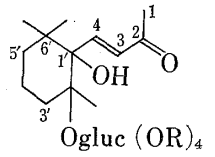
Furthermore, comparison of the ^{13}C NMR spectra of **4** with that of **5** indicated that the C-2′ signal is shifted downfield by 9.0 ppm, that the C-1′ and C-3′ signals are shifted upfield by 0.8 and 3.9 ppm, respectively, due to the glycosidation shifts,[8] while other carbons of both compounds appear at essentially the same positions (Table I). On the basis of the above results, the structure of **1** was elucidated as (—)-4-(1′,2′-*threo*-1′,2′-dihydroxy-2′-O-glucosyl-2′,6′,6′-trimethylcyclohexyl)-3-buten-2-one.

Aeginetoside (**2**) was obtained as colorless plates, $C_{21}H_{36}O_8$, mp 188—191°, $[\alpha]_D^{32}$ −61.2° (c=0.39, EtOH), UV λ_{max}^{EtOH} nm (log ε): 237 (4.15). Compound **2** showed no carbonyl band in the IR spectrum. The ^1H NMR spectrum of **2** (in acetone-d_6) showed four methyl signals [δ 0.82 (3H), 1.17 (6H) and 1.96 (3H)] and three olefinic protons [δ 5.52 (1H, m) and 6.32 (2H, s)]. On the other hand, the ^{13}C NMR spectrum of **2** showed four olefinic, four methyl, three quaternary and four methylene carbons as well as carbons of the sugar moiety. The chemical shift (δ 59.4) of one methylene carbon suggested the presence of a hydroxymethyl group and the carbon shifts of the sugar moiety suggested that **2** is a β-D-glucoside. Acetylation of **2** with acetic anhydride and pyridine afforded a pentaacetate (**7**), $C_{31}H_{46}O_{13}$ [m/e: 566 (M^+–AcOH)], mp 148—151°, $[\alpha]_D^{31}$ −64.7° (c=0.47, EtOH). The absorption band at 3530 cm^{-1} in the IR spectrum of **7** indicated the presence of a tertiary hydroxy group. The ^1H NMR spectrum of **7** showed the signals of three tertiary methyls [δ 0.80 (s), 1.03 (s) and 1.18 (s)], an olefinic methyl [δ 1.82 (br. s)], an olefinic hydroxymethyl group (δ 4.72, d, J=7 Hz), and three olefinic protons [δ 5.73 (1H, m) and 6.20 (2H, s)], indicating a conjugated olefinic system. These physical data show that **2** has a skeleton similar to that of **1** and has a

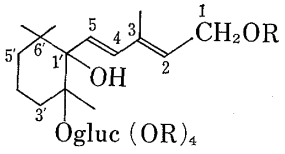
8) *a*) R. Kasai, M. Suzuo, J. Asakawa, and O. Tanaka, *Tetrahedron Lett.*, **1977**, 175; *b*) K. Tori, S. Seo, Y. Yoshimura, H. Arita, and Y. Tomita, *Tetrahedron Lett.*, **1977**, 179.

conjugated side chain $-CH=CH-C(CH_3)=CH-CH_2O-$ system. The ^{13}C NMR spectrum of **7** supports this view.

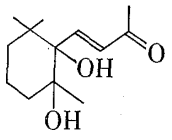
To confirm the structure of aeginetoside, **7** was prepared from **4** as described below. Treatment of **4** with carbethoxymethylenetriphenylphosphorane[9] at 150—180° (Wittig reaction[10]) afforded two isomeric esters **8**, $C_{31}H_{46}O_{13}$, mp 163—164°, $[\alpha]_D^{28}$ −90.6° (c=1.20, EtOH) and **9**, $C_{31}H_{46}O_{13}$, mp 140—142°, $[\alpha]_D^{29}$ −91.8° (c=0.59, EtOH). The ^1H NMR spectrum of **8** showed an olefinic methyl signal [δ 2.30 (br. s)], deshielded by the carbonyl group at C-1,[9] and two *trans* olefinic protons at δ 6.23 and 6.70 (each d, J=16 Hz). On the other hand, in the spectrum of **9**, an olefinic methyl overlapped with four acetyl signals at 1.98—2.08, and two olefinic protons were observed at 6.67 and 7.70 (each d, J=16 Hz), one of which was deshielded by the carbonyl group at C-1.[9] On the basis of these results, it is suggested that **8** and **9** possess a *trans-trans* and a *cis-trans* side chain, respectively.[11] Lithium aluminum hydride ($LiAlH_4$) reduction of **8** in tetrahydrofuran (THF), followed by acetylation with acetic anhydride and pyridine furnished a crystalline substance, which was identical with **7** by direct comparison (mixed mp and IR). Therefore, the structure of aeginetoside was established as **2**.



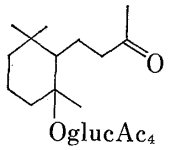
1 : R=H
4 : R=$COCH_3$



2 : R=H
7 : R=$COCH_3$



5(5′)



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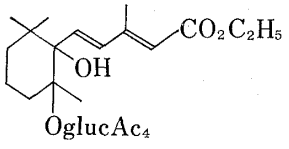

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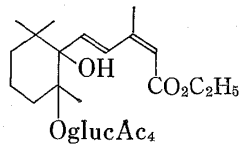

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Chart 2

Isoaucubin (**3**) was obtained as an amorphous powder giving a reddish-violet color on heating with mineral acid.[12] The ^1H NMR spectrum of **3** (in D_2O/DSS) showed a broad singlet at δ 4.15 (2H) assignable to an olefinic hydroxymethyl group and three olefinic protons at δ 5.08 (1H, d, J=6 Hz), 6.33 (1H, d, J=6 Hz) and 5.70 (1H, m) assignable to the C-4, C-3 and C-7 protons of aucubin-type iridoid glycosides, respectively. Acetylation of **3** with acetic anhydride and pyridine afforded a pentaacetate (**10**), $C_{25}H_{32}O_{14}$, mp 125°, $[\alpha]_D^{28}$ −46.3° (c=0.95, EtOH). IR (in KBr): 3520 cm^{-1} (tertiary OH). The ^1H NMR spectrum of **10** showed the presence of five acetoxyls (δ 2.01—2.14), a hydroxyl [δ 2.97 (1H, s, quenched with D_2O)] and the C-3 proton of an iridoid framework [δ 6.18 (1H, d, J=6 Hz)].

It is known that long-range coupling is generally observed between the protons at C-3 and C-5 (J<2 Hz) in the ^1H NMR spectra of aucubin-type iridoid glycosides.[13] However,

9) W.J. Considine, *J. Org. Chem.*, **27**, 647 (1962).
10) D.L. Roberts, R.A. Heckman, B.P. Hege, and S.A. Bellin, *J. Org. Chem.*, **33**, 3566 (1968).
11) M. Mousseron-Canet and M.A. Bartissol, *Bull. Soc. Chim. Fr.*, **1965**, 2440.
12) *a*) L.H. Briggs, B.F. Cain, P.W. LeQuesene, and J.N. Shoolery, *Tetrahedron Lett.*, **1963**, 69; *b*) J.M. Bobbit and K.P. Segebarth, "Cyclopentanoid Terpene Derivatives," ed. by W.I. Talor and A.R. Battersby, Marcel Dekker, Inc., New York, 1969. pp. 1—139.
13) *a*) M. Guiso, A. Agostini, and R. Marini-Bettolo, *Gazz. Chim. Ital.*, **104**, 403 (1974); *b*) A. Bianco, M. Guiso, C. Iavarone, and C. Trogolo, *Gazz. Chim. Ital.*, **105**, 175 (1975); *c*) *Idem, ibid.*, **106**, 725 (1976).

the signal at δ 6.18 (C-3 position) of **10** was split into a sharp doublet (J=6 Hz) only by coupling with the C-4 proton, indicating the absence of the proton at C-5 and the possible presence of a hydroxy group at that position. The presence of a quaternary carbon bearing an oxygen atom was supported by a signal at δ 72.0 (s) in the ^{13}C NMR spectrum of **10**.[14] Catalytic hydrogenation of **10** over palladium-charcoal in methanol afforded two crystalline substances, **11**, $C_{25}H_{36}O_{14}$, mp 125.5—126.5°, IR (in KBr): 3500 cm^{-1} (OH) and **12**, $C_{23}H_{34}O_{11}$, mp 83—84° $[\alpha]_D^{29}$ −39.7° (c=0.54, EtOH). Compound **12** showed no OH band in the IR spectrum, indicating that hydrogenolysis had taken place at C-5 and C-10.

On the other hand, catalytic hydrogenation of aucubin hexaacetate[15] by the same procedure afforded **13**, $C_{27}H_{38}O_{15}$[16] mp 156—157°, and **12**, $C_{23}H_{34}O_{11}$, mp 79.5—82°, $[\alpha]_D^{31}$ −47.3° (c=0.35, EtOH). The identity of the latter with **12** prepared from **10** was established by direct comparison (mixed mp and IR). Consequently, the structure of isoaucubin was established as **3**. Compound **3** seems to be the active compound involved in the color change to dark violet during immersion or drying of the plant.

The structures of the phenolic glycosides are under study in our laboratory.

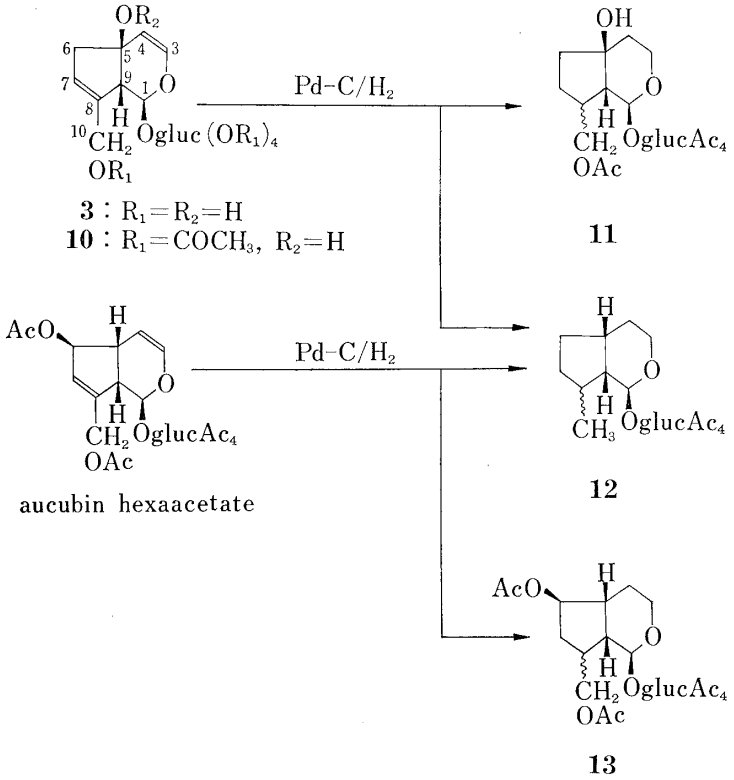

Chart 3

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus (a hot stage type) and are uncorrected. The UV spectra were recorded with a Hitachi 624 digital spectrophotometer and the IR spectra with a Hitachi EPI-G2 unit. The ^1H NMR spectra were recorded with a Varian model T-60 [with tetramethyl silane as an internal standard, or 3-trimethylsilyl-propanesulfonic acid sodium salt (DSS)

14) G. Schilling, W.D. Henkels, K. Kunstler, and K. Weinges, *Liebigs Ann. Chem.*, **1975**, 230.
15) Aucubin hexaacetate was prepared from aucubin isolated from *Vitex rotundifolia* L. *fil.* (Verbenaceae). The authors' unpublished data.
16) *a*) Y. Iwanami, Y. Hotta, T. Kubota, S. Fujise, T. Ishikawa, and H. Uda, *Nippon Kagaku Zasshi*, **76**, 77 (1965); *b*) H. Inouye and T. Yoshida, *Chem. Pharm. Bull.* (Tokyo), **19**, 1438 (1971).

in the case of D_2O]. The ^{13}C NMR spectra were recorded with a Varian model FT-80A. The mass spectra were measured with a Hitachi double-focusing mass spectrometer. The specific rotations were measured with a Jasco DIP-SL and the CD spectra with a Jasco J-20 spectrophotometer. The gas chromatograph used was a Hitachi model 073 with a hydrogen flame ionization detector. TLC plates were made with silica gel (Kieselgel F_{254}, Type 60, Merck), and silica gel (Kieselgel 70—325 mesh, Merck) was used for column chromatography.

Extraction——Fresh whole plants (1.822 kg) collected from the suburbs of Tokyo in September, 1976, were homogenized in MeOH and then extracted with MeOH under reflux 3 times. The combined extract was concentrated under reduced pressure to give a dark brown mass (95 g), which was dissolved in H_2O and extracted with $CHCl_3$ and then *n*-BuOH. The *n*-BuOH extract (36.2 g) was chromatographed on charcoal (150 g) developing with H_2O, MeOH and then acetone. The MeOH eluate (12.4 g) was chromatographed on silica gel (250 g), using $CHCl_3$–MeOH ($CHCl_3 \rightarrow 20\%$ MeOH in $CHCl_3$) to give a mixture of **1**, **2** and **3**; these compounds were separated by prep. TLC (plate, HF_{254}, Merck, developing solvent, $CHCl_3$: MeOH=3:1) to **1** (yield 0.451 g, 0.025%), **2** (0.548 g, 0.03%) and **3** (1.566 g, 0.086%).

Hydroxy-β-ionone Glucoside (1)——Colorless plates (from acetone), mp 214—215.5°. $[\alpha]_D^{23}$ −30.9° (c=0.42, EtOH). CD (c=0.058, MeOH) $[\theta]^{23}$ (nm): +9400 (212), −14100 (239), +1000 (316). UV λ_{max}^{EtOH} nm (log ε): 232 (4.04). IR ν_{max}^{KBr} cm^{-1}: 3500, 3300, 1680, 1650. *Anal.* Calcd. for $C_{19}H_{32}O_8$: C, 58.74; H, 8.30. Found: C, 58.71; H, 8.20.

Acetylation of 1, giving the Tetraacetate (4)——A solution of **1** (30 mg) in Ac_2O (1 ml) and pyridine (1 ml) was allowed to stand at room temperature overnight. The reaction mixture was poured into ice-water and the resulting precipitates were collected and crystallized from EtOH to give a tetraacetate (**4**) as colorless needles (24 mg). mp 183—184°. $[\alpha]_D^{27}$ −75.9° (c=0.44, EtOH). UV λ_{max}^{EtOH} nm (log ε): 230 (4.13). IR ν_{max}^{KBr} cm^{-1}: 3510, 1770, 1680, 1640. ^1H NMR (δ in $CDCl_3$): 0.83 (3H, s), 1.12 (3H, s), 1.20 (3H, s), 2.00—2.13 (12H, s, 4×OAc), 2.30 (3H, s), 4.11 (2H, m), 6.19 (1H, d, J=17 Hz), 7.32 (1H, d, J=17 Hz). The ^{13}C NMR spectral data are given in Table I. MS *m/e* (%): 556 (M^+, 1), 331 (55), 226 (10), 209 (32), 169 (100). *Anal.* Calcd. for $C_{27}H_{40}O_{12}$: C, 58.26; H, 7.24. Found: C, 58.42; H, 7.21.

Acid Hydrolysis of 1, giving 5 and Glucose——A solution of **1** (30 mg) in 1 N HCl (0.5 ml)-dioxane (0.5 ml) was heated at 70° for 1 hr and after cooling, the reaction mixture was passed through a Dowex 2×8 (2 ml) column and extracted with AcOEt. The AcOEt extract was washed with water, dried over Na_2SO_4 and concentrated to dryness. The residue was purified by prep. TLC (ether) to give **5** (1.4 mg). mp 107—108°. IR ν_{max}^{KBr} cm^{-1}: 3500, 3450, 1695, 1630. CD (c=0.0199, MeOH) $[\theta]^{23}$ (nm): +15300 (212), −17500 (242), +1100 (320). The aqueous layer was concentrated to dryness under reduced pressure. The residue was trimethylsilylated by the usual method. The presence of glucose was demonstrated by GLC. Conditions: column, 2% OV-17 on Uniport Q (80—100 mesh), 3 mm×2 m; column temperature, 220°. Glucose: t_R (min), 9.5 and 14.0.

Extraction of 5 from *Rehmania glutinosa* Libosch. var. *purpurea* Makino——The dry rhizoma of *R. glutinosa* Libosch. var. *purpurea* Makino (500 g) was extracted 3 times with ether under reflux. The ethereal extract (8 g), after concentration *in vacuo*, was chromatographed on silica gel (200 g) using benzene–ether (8:2) to give colorless prisms (from *n*-hexane–ether) (yield 50 mg). mp 105.5—106.5°. $[\alpha]_D^{30}$ −15.7° (c=0.28, EtOH). CD (c=0.0121, MeOH) $[\theta]^{23}$ (nm): +14900 (212), −17200 (242), +1400 (319). UV λ_{max}^{EtOH} nm (log ε): 235 (4.08). IR ν_{max}^{KBr} cm^{-1}: 3500, 3450, 1695, 1630. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3450, 1670, 1620. ^1H NMR (δ in $CDCl_3$): 0.82 (3H, s), 1.13 (3H, s), 1.23 (3H, s), 1.73 (2H, s, quenched with D_2O), 2.30 (3H, s), 6.33 (1H, d, J=16 Hz), 7.35 (1H, d, J=16 Hz). The ^{13}C NMR spectral data are given in Table I. MS *m/e* (%): 226 (M^+, 3), 208 (18), 109 (100), 99 (91), 71 (93). *Anal.* Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.84; H, 9.81. This compound was identical with **5** on direct comparison (mixed mp, IR and TLC).

Synthesis of 1′,2′-Dihydroxy-β-ionone (5′) from β-Ionone——A solution of β-ionone (580 mg) in dry benzene (5 ml) was treated with *m*-chloroperbenzoic acid (550 mg) in dry benzene (10 ml). After stirring for three days at room temperature, the reaction mixture was filtered and concentrated. Purification of the residue by prep. TLC ($CHCl_3$: MeOH=20:1) gave a colorless oil (620 mg). A solution of this colorless oil (51 mg) in 2 ml of 20% H_2SO_4–EtOH (1:3) was kept at room temperature for 17 hr. The reaction mixture was then poured into ice-water and extracted with ether. The ether extract was washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by prep. TLC (ether) to give colorless prisms (**5′**) (yield 18 mg). mp 111—112°. CD (c=0.045, MeOH): no absorption (200—350 nm). IR ν_{max}^{KBr} cm^{-1}: 3430, 1660, 1635. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3450, 1670, 1620. ^1H NMR (δ in $CDCl_3$): 0.80 (3H, s), 1.12 (3H, s), 1.22 (3H, s), 1.80, 1.93 (each 1H, s, quenched with D_2O), 2.30 (3H, s), 6.35 (1H, d, J=17 Hz), 7.37 (1H, d, J=17 Hz). The ^{13}C NMR spectral data are given in Table I. MS *m/e* (%): 226 (M^+, 3), 208 (13), 109 (100), 99 (74), 71 (81). *Anal.* Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.13; H, 9.78.

Catalytic Hydrogenation of 4, giving 6——PtO_2 (100 mg) was added to a solution of **4** (21 mg) in AcOH (5 ml) and the mixture was shaken in a hydrogen atmosphere at room temperature for 1 hr. After removing the catalyst by filtration, the solution was concentrated under reduced pressure to give a residue. Purification of this residue by prep. TLC (benzene: ether=1:1) gave colorless needles (**6**) (10 mg). mp 141—142.5°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750, 1370, 1230. MS *m/e* (%): 542 (M^+, 2), 331 (27), 195 (40), 169 (100), 125 (29). *Anal.* Calcd. for $C_{27}H_{42}O_{11}$: C, 59.76; H, 7.80. Found: C, 59.94; H, 7.79.

Aeginetoside (2)——Colorless plates from EtOH, mp 188—191°. $[\alpha]_D^{32}$ −61.2° (c=039,' EtOH). UV λ_{max}^{EtOH} nm (log ε): 237 (4.15). IR ν_{max}^{KBr} cm^{-1}: 3510, 3300, 1620. ^{1}H NMR (δ in acetone-d_6): 0.82 (3H, s), 1.17 (6H, s), 1.96 (3H, s), 5.52 (1H, m), 6.32 (2H, s). The ^{13}C NMR spectral data are given in Table I. *Anal.* Calcd. for $C_{21}H_{36}O_8 \cdot 1/2H_2O$: C, 59.27; H, 8.76. Found: C, 59.11; H, 8.49.

Acetylation of 2, giving the Pentaacetate (7)——A solution of **2** (65 mg) in Ac_2O (1 ml) and pyridine (1 ml) was allowed to stand at room temperature overnight. The reaction mixture was poured into ice-water and the resulting precipitates were collected and crystallized from EtOH to give a pentaacetate (7) as colorless needles (19 mg). mp 148—151°. $[\alpha]_D^{31}$ −64.7° (c=0.47, EtOH). UV λ_{max}^{EtOH} nm (log ε): 237 (4.58). IR ν_{max}^{KBr} cm^{-1}: 3530, 1755, 1740, 1620, 1230. MS *m/e* (%): 566 [(M$^+$−AcOH), 2], 331 (39), 169 (100), 109 (91). ^{1}H NMR (δ in $CDCl_3$): 0.80 (3H, s), 1.03 (3H, s), 1.18 (3H, s), 1.82 (3H, br. s), 2.02 (6H, s, 2×OAc), 2.04 (6H, s, 2×OAc), 2.06 (3H, s, OAc), 4.72 (2H, d, J=7 Hz), 5.73 (1H, m), 6.20 (2H, s). The ^{13}C NMR spectral data are given in Table I. *Anal.* Calcd. for $C_{31}H_{46}O_{13}$: C, 59.42; H, 7.40. Found: C, 59.62; H, 7.41.

Preparation of 8 and 9 from 4——Ethyl chloroacetate (1.23 g, 0.01 mol) was added to a solution of triphenylphosphine (2.63 g, 0.01 mol) in dry benzene (10 ml). The solution was refluxed for 2 hr and after cooling, the crude crystalline substance was washed with benzene then recrystallized from CCl_4–CH_2Cl_2 to give triphenylcarbethoxyphosphonium chloride (yield 985 mg), mp 82—83° (ref. mp 87—88°), which was dissolved in H_2O (20 ml). Phenolphthalein (1 drop) was added and the solution was made basic by the addition of 0.5 N NaOH to the end-point. The crude crystalline material was isolated by filtration, washed thoroughly with H_2O and recrystallized from benzene–pet. ether to give triphenylcarbethoxymethylenephosphorane as colorless prisms. mp 129.5—131° (ref. mp 123.5—125.5°) (yield 256 mg). A mixture of 4 (115 mg, 0.2 mmol) and triphenylcarbethoxymethylenephosphorane (90 mg, 0.3 mmol) was heated in an oil bath for 1.5 hr while the bath temperature was slowly increased from 150° to 180°. After cooling, the reaction mixture was purified by prep. TLC ($CHCl_3$: ether=5: 1) to furnish **8** (34 mg) and **9** (16 mg). **8**: colorless prisms from ether–*n*-hexane. mp 163—164°. $[\alpha]_D^{28}$ −90.6° (c=1.20, EtOH). UV λ_{max}^{EtOH} nm (log ε): 268 (4.39). IR ν_{max}^{KBr} cm^{-1}: 3550, 1760, 1736, 1698, 1605. ^{1}H NMR (δ in $CDCl_3$): 0.82 (3H, s), 1.07 (3H, s), 1.17 (3H, s), 1.28 (3H, t, J=7 Hz), 1.98—2.07 (12H, s, 4×OAc), 2.30 (3H, br. s), 4.18 (2H, q, J=7 Hz), 5.80 (1H, br. s), 6.23 (1H, d J=16 Hz), 6.70 (1H, d, J=16 Hz). *Anal.* Calcd. for $C_{31}H_{46}O_{13}$: C, 59.41; H, 7.40. Found: C, 59.56; H, 7.44. **9**: colorless needles from ether–*n*-hexane. mp 140—142°. $[\alpha]_D^{29}$ −91.8° (c= 0.59, EtOH). UV λ_{max}^{EtOH} nm (log ε): 269 (4.13). IR ν_{max}^{KBr} cm^{-1}: 3520, 1760, 1738, 1717, 1635, 1595. ^{1}H NMR (δ in $CDCl_3$): 0.83 (3H, s), 1.05 (3H, s), 1.17 (3H, s), 1.28 (3H, t, J=7 Hz), 1.98—2.08 (15H, s, 4×OAc and CH_3–C=), 4.13 (2H, q, J=7 Hz), 5.68 (1H, m), 6.67 (1H, d, J=16 Hz), 7.70 (1H, d, J=16 Hz). *Anal.* Calcd. for $C_{31}H_{46}O_{13}$: C, 59.41; H, 7.40. Found: C, 59.16; H, 7.20.

Treatment of 8 with $LiAlH_4$ followed by Acetylation, giving 7——A solution of **8** (17 mg) in dry tetrahydrofuran (THF) (0.5 ml) was treated with a suspension of $LiAlH_4$ (20 mg) in dry THF (0.5 ml) at room temperature. After stirring for 0.5 hr, the reaction mixture was treated with a small amount of H_2O to decompose excess $LiAlH_4$, filtered and concentrated. The residue was acetylated with Ac_2O (0.2 ml) and pyridine (0.5 ml) at room temperature overnight. The reaction mixture was treated with ice-water and extracted with AcOEt. The AcOEt extract was purified by prep. TLC (ether) to furnish colorless needles (3 mg). mp 148—150°. IR ν_{max}^{KBr} cm^{-1}: 3530, 1755, 1740, 1620, 1230. This compound was identical with 7 on direct comparison (mixed mp, IR and TLC).

Isoaucubin (3)——Amorphous powder. $[\alpha]_D^{24}$ −99.4° (c=1.63, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3350, 1650, 1230. ^{1}H NMR (δ in D_2O/DSS): 2.57 (2H, m), 3.08 (1H, m), 4.15 (2H, br. s, C_{10}–H), 5.08 (1H, d, J=6 Hz, C_4–H), 5.53 (1H, d, J=4 Hz, C_1–H), 5.70 (1H, m, C_7–H), 6.33 (1H, d, J=6 Hz, C_3–H).

Acetylation of 3, giving the Pentaacetate (10)——A solution of **3** (100 mg) in Ac_2O (1 ml) and pyridine (1 ml) was allowed to stand at room temperature overnight and then poured into ice-water. The precipitates were collected and recrystallized from ether–pet. ether to give a pentaacetate (**10**) as colorless needles (52 mg). mp 125°. $[\alpha]_D^{28}$ −46.3° (c=0.95, EtOH). IR ν_{max}^{KBr} cm^{-1}: 3520, 1760, 1650. ^{1}H NMR (δ in $CDCl_3$): 2.01—2.14 (15H, s, 5×OAc), 2.97 (1H, s, quenched with D_2O), 3.24 (1H, m), 3.76 (1H, m), 4.25 (2H, m), 4.60 (2H, m, C_{10}–H), 6.18 (1H, d, J=6 Hz, C_3–H). ^{13}C NMR (δ in $CDCl_3$): 92.3 (C-1), 138.9 (C-3), 111.4 (C-4), 72.0 (C-5), 45.3 (C-6), 129.4 (C-7), 135.2 (C-8), 54.9 (C-9), 61.7[a] (C-10), 96.0 (C-1′), 71.1 (C-2′), 72.9 (C-3′), 68.4 (C-4′), 72.1 (C-5′), 61.5[a] (C-6′). (a): These assignments may be reversed). *Anal.* Calcd. for $C_{25}H_{32}O_{14}$: C, 53.95; H, 5.80. Found: C, 53.77; H, 5.83.

Catalytic Hydrogenation of 10, giving 11 and 12——A solution of **10** (52 mg) in MeOH (10 ml) was treated with 10% Pd-C (90 mg) and the mixture was shaken in a hydrogen atmosphere at room temperature for 1 hr. After removing the catalyst by filtration, the solution was concentrated under reduced pressure and purified by prep. TLC (ether) to give **11** (8.2 mg) and **12** (12.2 mg). **11**: colorless prisms from ether. mp 125.5—126.5°. IR ν_{max}^{KBr} cm^{-1}: 3500, 1755. ^{1}H NMR (δ in $CDCl_3$): 2.00—2.10 (15H, s, 5×OAc), 2.77 (1H, s, quenched with D_2O). *Anal.* Calcd. for $C_{25}H_{36}O_{14}$: C, 53.56; H, 6.47. Found: C, 53.41; H, 6.45. **12**: colorless needles from *n*-hexane–cyclohexane. mp 83—84°. $[\alpha]_D^{29}$ −39.7° (c=0.54, EtOH). IR ν_{max}^{KBr} cm^{-1}: 1760, 1440, 1370. ^{1}H NMR (δ in $CDCl_3$): 0.99 (3H, d, J=6 Hz), 2.00—2.07 (12H, s, 4×OAc), 4.15 (2H, m). *Anal.* Calcd. for $C_{23}H_{34}O_{11}$: C, 56.78; H, 7.04. Found: C, 56.89; H, 7.08.

Catalytic Hydrogenation of Aucubin Hexaacetate——Aucubin hexaacetate (120 mg) was hydrogenated in the presence of prereduced 10% Pd-C (130 mg) in MeOH for 3 hr. After removing the catalyst by filtra-

tion, the solution was concentrated under reduced pressure to give a residue, which was purified by prep. TLC (ether) to furnish **12** (32.5 mg) and **13** (26.2 mg). **12**: colorless needles from *n*-hexane–$CHCl_3$. mp 79.5—82°. $[\alpha]_D^{31}$ −47.3° (c=0.35, EtOH). IR ν_{max}^{KBr} cm^{-1}: 1760, 1440, 1370. *Anal.* Calcd. for $C_{23}H_{34}O_{11}$: C, 56.78; H, 7.04. Found: C, 56.82; H, 7.05. This compound obtained here was identical with **12** prepared from **10** by direct comparison (mixed mp, IR and TLC). **13**: colorless needles from *n*-hexane–$CHCl_3$. mp 156—157°. *Anal.* Calcd. for $C_{27}H_{38}O_{15}$: C, 53.81; H, 6.36. Found: C, 53.81; H, 6.39.

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