3,4-Dihydro-8-hydroxy-3-(*p*-hydroxyphenyl)isocarbostyryl (*dl*-11)——A mixture of *dl*-5 (0.50 g) and ethanol (10 ml) saturated with ammonia was heated at 100°C for 17 h in an autoclave. The residue obtained after concentration was mixed with dil.HCl and filtered. The crude product obtained was washed, dried and recrystallized from EtOH to give *dl*-11 as colorless needles of mp 202°C; yield, 0.32 g (64%). *Anal.* Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.48; H, 5.27; N, 4.95. IR ν_{max}^{KBr} cm^{-1}: 1652, 3070, 3170 (CONH). PMR (in acetone-d_6) δ: 3.13 (2H, d, $J=3$ Hz, CH_2), 4.83 (1H, t, $J=3$ Hz, –CHNH–), 6.6—7.4 (9H, m, aromatic-H, NH, and OH), 8.41 (1H, s, OH). MS *m/e*: 255 (M^+).

Antifungal Test——The antifungal activity was determined on agar plants by the two-fold dilution method. The experimental details were as reported in our previous paper.[6]

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Lactams. XVIII.[1] Oxidation of 1-Substituted 3-*tert*-Butylpiperidine with Mercuric Acetate–EDTA

Tozo Fujii,* Takashi Hiraga, and Masashi Ohba

Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan

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1-(3,4-Dimethoxyphenyl)-2-(3-*tert*-butylpiperidino)ethanol (**7**) was prepared from 3-*tert*-butylpyridine (**5**) through the quaternary salt **6**. The mercuric acetate–EDTA oxidation of **7** produced the 6-piperidone **10** and the 2-piperidone **13** in a ratio of 98: 2. The former piperidone was chemically correlated with the known 6-pyridone **8** through the lactam **9**, and **9** was converted into the benzoquinolizidine **11** by cyclization and reduction of the resulting iminium salt **12**.

Keywords——1,3-disubstituted piperidine; piperidone; benzoquinolizidine; quaternization; catalytic reduction; mercuric acetate–EDTA oxidation; *tert*-butyl group; steric effect; regioselectivity; stereoselectivity

One of the most important aspects of our recent chiral syntheses[2] of the Ipecac and *Alangium* alkaloids was the generation of the lactam carbonyl function at the 6-position of cincholoipon ethyl ester [(+)—**1**], a degradation product of the major *Cinchona* alkaloids,

by the mercuric acetate–ethylenediaminetetraacetic acid (EDTA) oxidation method.[3] In preliminary studies on this operation, we investigated the oxidation of 1,3-disubstituted piperidines (type **2**) with mercuric acetate–EDTA, and the effects of various 3-substituents on the position of oxidation in the heterocyclic ring have been catalogued[4] in terms of the ratios of the isomeric 6- (type **3**) and 2-piperidones (type **4**) formed. We have now extended our studies of the 3-substituent effect to cover the *tert*-butyl group, a highly branched, bulky hydrocarbon substituent. This work was facilitated by our recent discovery[5] of a new synthetic route to the required starting material 3-*tert*-butylpyridine (**5**) from α-*tert*-butylacrolein, which was found to produce base of prime quality.

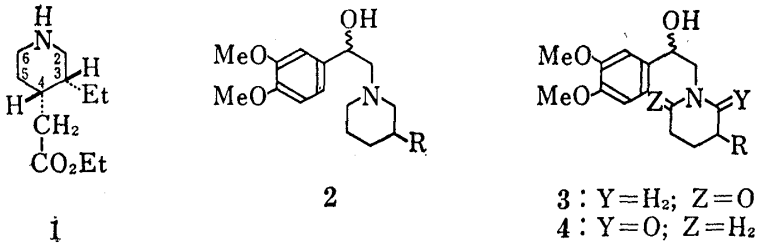

Chart 1

Quaternization of **5** with 3,4-dimethoxyphenacyl bromide[6] in benzene gave the salt **6** in 86% yield. Reduction of **6** with hydrogen and Adams catalyst followed by $NaBH_4$ afforded the piperidinoethanol **7** (99% yield), which was presumed to be a mixture of the two possible diastereomers. Since purification of **7** was difficult, it was directly oxidized with mercuric acetate–EDTA (boiling 1% aqueous AcOH, 1.5 h) according to the previously reported[4a] standard procedure, and two isomeric lactam alcohols **10** and **13** were obtained as diastereo-

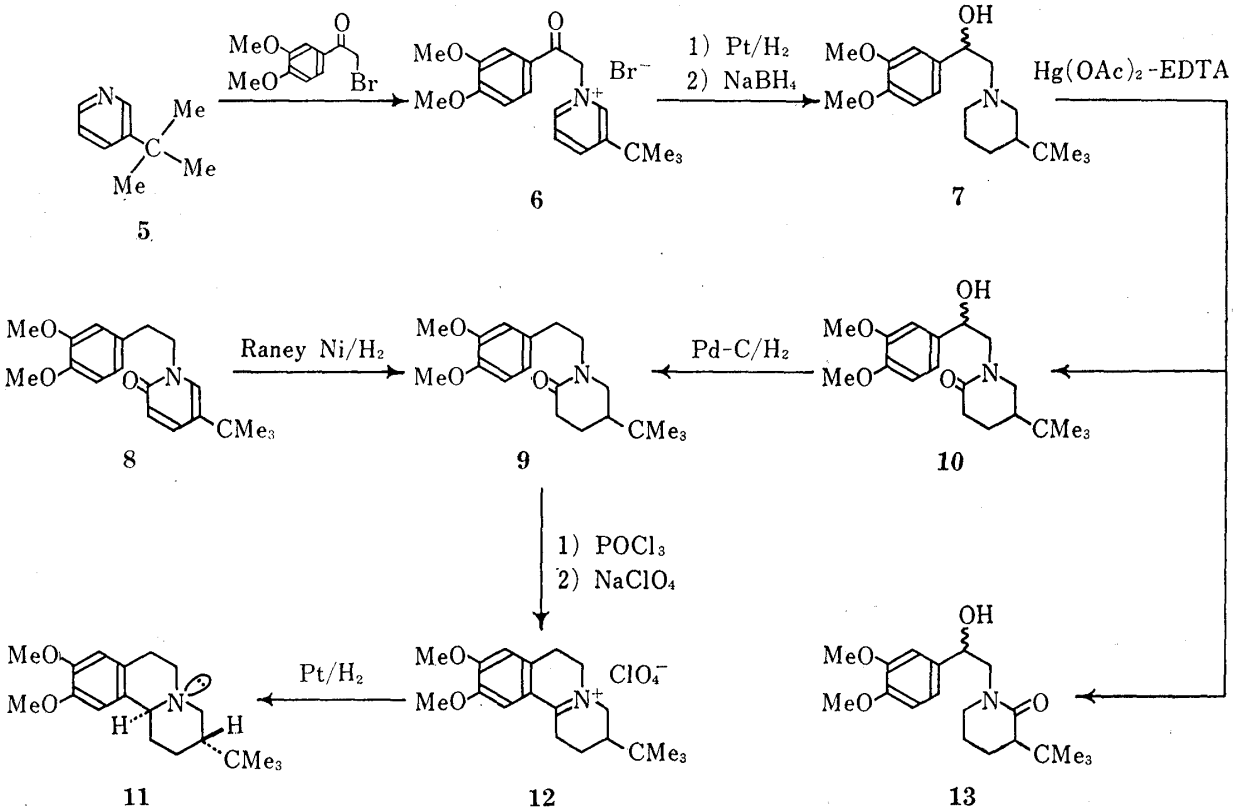

Chart 2

meric mixtures in a combined yield of 79%. The oxidation reaction was run in triplicate and chromatographic analysis of the products was carried out as reported previously;[4a] the isomer ratio of the piperidones was found to be **10**: **13**=98: 2.

The location of the lactam carbonyl group in **10** and **13** was assigned on the basis of the following evidence. On thin-layer chromatography (TLC) (Al_2O_3, AcOEt–hexane), **13** ran faster than **10**, and a similar difference in chromatographic mobility has been observed[4b] for the 2-piperidone **4** and the 6-piperidone **3** (R=Me, Et, *n*-Bu, iso-Pr, $PhCH_2$, or Ph). In the infrared (IR) spectrum in $CHCl_3$, **13** displayed the CO stretching vibration at 1607 cm^{-1}, and **10** at 1612 cm^{-1}. This is in agreement with our previous finding[4b] that 2-piperidones (type **4**: R=alkyl) show slightly lowered lactam ν_{CO} in comparison with the corresponding 6-piperidones (type **3**). In the nuclear magnetic resonance (NMR) spectrum in $CDCl_3$, the *tert*-butyl protons of **13** were less shielded than those of **10** by 0.2—0.3 ppm . The downfield shift observed reflects the deshielding effect of the lactam carbonyl group on the neighboring *tert*-butyl group in **13**. In the case of **10**, final identification as a 6-piperidone rested on its catalytic hydrogenolysis to the lactam **9**, which was identical with a sample prepared from the known 6-pyridone **8**[7] by catalytic reduction. On the other hand, the unavailability[7] of the isomeric 2-pyridone and the paucity of **13** did not permit the achievement of a parallel chemical correlation.

In our previous reports[4] dealing with the mercuric acetate–EDTA oxidation of 1,3-disubstituted piperidines (type **2**), we have already suggested that the 3-substituents (R in **2**) exert both steric and electronic effects to determine the regioselectivity in the lactam formation. The isomer ratio (**10**: **13**=98: 2) observed for the 3-*tert*-butyl group in the present study thus provides an additional and valuable example of the steric effect operating in such a reaction.

Finally, the lactam **9** was converted into the iminium salt **12** in 96% yield by cyclization with $POCl_3$ followed by treatment with $NaClO_4$. Catalytic hydrogenation of **12** afforded the benzoquinolizidine **11** (85% yield), which was shown to be isomer-free on TLC and NMR spectral analyses. The assignment of the *trans*-quinolizidine structure **11** with the equatorial *tert*-butyl group at the 3-position was based on Bohlmann's IR criterion[8] and a consideration of preferred conformation. Interestingly enough, this stereochemical result presents a contrast to our previous finding[9] that the stereoselectivity in a similar reduction of the methyl analog (**12**: Me for CMe_3) is not high.

Experimental

General Comments——All melting points were determined by using a Yamato MP-1 capillary melting point apparatus, and are corrected. Unless otherwise noted, the organic solutions obtained after extraction were dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. IR spectra were recorded on a JASCO IRA-2 spectrophotometer in Nujol mulls or in $CHCl_3$ solutions at 0.2 M concentration. NMR spectra were measured on a JEOL JNM-PMX-60 or JNM-FX-100 spectrometer at 24°C with Me_4Si as an internal standard (δ=0 ppm). See ref. 2*b* for other instrumentation and measurements. The following abbreviations are used: b=broad, d=doublet, d-d=doublet-of-doublets, m=multiplet, s=singlet. Microanalyses were performed by Mr. Y. Itatani and his associates at Kanazawa University.

1-(3,4-Dimethoxyphenacyl)-3-(1,1-dimethylethyl)pyridinium Bromide (6)——A mixture of 3-*tert*-butylpyridine (**5**)[5] (4.08 g, 30 mmol) and 3,4-dimethoxyphenacyl bromide[6] (8.57 g, 33 mmol) in dry benzene (75 ml) was stirred at room temp. for 48 h. The crystals that resulted were filtered off and washed with benzene (50 ml) to give a first crop. The filtrate and washings were combined, concentrated to a volume of 20 ml, and stirred at room temp. for 5 h to produce a second crop of crystals. Recrystallization of first and second crops of crystals from EtOH–ether (1: 1, v/v) yielded **6**·H_2O (10.64 g, 86%) as colorless needles, mp 100—108°C (dried over P_2O_5 at room temp. and 2 mmHg for 24 h); UV λ_{max}^{EtOH} 232.5 nm (ε 19900), 275 (16200), 311.5 (11100); IR ν_{max}^{Nujol} cm^{-1}: 3460, 3400 (H_2O), 1683 (CO); NMR ($CDCl_3$) δ: 1.43 (9H, s, Me_3C), 2.15 (s, H_2O), 3.82 and 3.83 (6H, s each, two MeO's), 6.82 (1H, d, J=8.8 Hz, $H_{(5')}$), 7.17 (2H, s, NCH_2CO), 7.47 (1H, d, J=1.6 Hz, $H_{(2')}$), 7.82 (1H, d-d, J=8.8 and 1.6 Hz, $H_{(6')}$), 7.85 (1H, d-d, J=7.6 and 5.6 Hz, $H_{(5)}$), 8.32 (1H, d, J=7.6 Hz, $H_{(4)}$), 9.12 (1H, d, J=5.6 Hz, $H_{(6)}$), 9.28 (1H, s, $H_{(2)}$). *Anal.* Calcd for $C_{19}H_{24}BrNO_3 \cdot H_2O$: C, 55.35; H, 6.36; N, 3.40. Found: C, 55.18; H, 6.23; N, 3.47.

1-(3,4-Dimethoxyphenyl)-2-[3-(1,1-dimethylethyl)piperidino]ethanol (7)——A mixture of **6** (10.64 g, 25.8 mmol) and EtOH (120 ml) was hydrogenated over Adams catalyst (300 mg) at 25°C and atmospheric

pressure. When *ca.* 3.2 mol eq of H_2 had been taken up during 15 h, the reaction was discontinued and the reaction mixture was filtered to remove the catalyst. The filtrate was neutralized with 2 N aq. NaOH (12.8 ml), and $NaBH_4$ (1.03 g, 27.2 mmol) was added in small portions. The resulting mixture was stirred at room temp. overnight and then concentrated *in vacuo*. The residue was partitioned between benzene and H_2O. The benzene extracts were dried (K_2CO_3) and concentrated to leave **7** (8.22 g, 99%) as a colorless, viscous oil, MS *m/e*: 321 (M^+); UV λ_{max}^{EtOH} 230 nm (ε 8900), 279 (3000); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH); NMR ($CDCl_3$) δ: 0.85 and 0.88 (9H, s each, diastereomeric Me_3C's), 1.0—3.6 (11H, unresolved m, two ring-CH_2's and -CH, three NCH_2's), 3.3—3.7 (1H, b, OH), 3.83 and 3.86 (6H, s each, two MeO's), 4.48—4.76 [1H, m, ArC<u>H</u>(OH)], 6.76—6.98 (3H, m, aromatic protons).

Mercuric Acetate-EDTA Oxidation of 7——The oxidation of **7** (10 mmol), presumed to be a diastereomeric mixture, was effected in triplicate and the product was worked up according to the previously reported[4a] standard procedure, giving the 6-piperidone **10** and the 2-piperidone **13** as diastereomeric mixtures in a combined yield of 79%. Separation of the two piperidones was accomplished by means of column chromatography using Al_2O_3 (300 g) and AcOEt–hexane (1: 2, v/v), and **13** was eluted faster than **10**. The average of the isomer ratios taken from three runs was **10**: **13** = 98: 2. The piperidones thus isolated were presumed to be diastereomeric mixtures but were characterized as follows.

1-[2-(3,4-Dimethoxyphenyl)-2-hydroxyethyl]-3-(1,1-dimethylethyl)-2-piperidone (13)——A slightly reddish, viscous oil, MS *m/e*: 335 (M^+); UV λ_{max}^{EtOH} 229.5 nm (ε 9900), 279 (3100); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3360 (OH), 1607 (lactam CO); NMR ($CDCl_3$) δ: 1.06 (9H, s, Me_3C), 1.3—2.0 (4H, m, $H_{(4)}$'s, $H_{(5)}$'s), 2.0—2.5 (1H, b, $H_{(3)}$), 2.6—3.3 (2H, b, $H_{(6)}$'s), 3.3—3.8 [2H, m, ArCH(OH)C<u>H</u>$_2$], 3.81 and 3.84 (6H, s each, two MeO's), 4.0—4.6 (1H, b, OH), 4.69—5.06 [1H, m, ArC<u>H</u>(OH)], 6.69—7.02 (3H, m, aromatic protons).

1-[2-(3,4-Dimethoxyphenyl)-2-hydroxyethyl]-5-(1,1-dimethylethyl)-2-piperidone (10)——Recrystallized from AcOEt as colorless needles, mp 134.5—138°C; MS *m/e*: 335 (M^+); UV λ_{max}^{EtOH} 230 nm (ε 9400), 279 (2900); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3340 (OH), 1612 (lactam CO); NMR ($CDCl_3$) δ: 0.77 and 0.83 (9H, s each, diastereomeric Me_3C's), 3.80 and 3.83 (6H, s each, two MeO's), 4.03 (1H, b, OH), 4.80—5.03 [1H, m, ArC<u>H</u>(OH)], 6.73—7.00 (3H, m, aromatic protons). *Anal.* Calcd for $C_{19}H_{29}NO_4$: C, 68.03; H, 8.71; N, 4.18. Found: C, 67.77; H, 8.84; N, 4.28.

1-(3,4-Dimethoxyphenethyl)-5-(1,1-dimethylethyl)-2-piperidone (9)——i) Hydrogenolysis of **10**: A mixture of the above diastereomeric mixture (336 mg, 1 mmol) of **10**, EtOH (20 ml), and 70% aq. $HClO_4$ (0.2 ml) was hydrogenated over 10% Pd-C (300 mg) at 3.3—3.4 atm and 29—30°C for 10 h. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was partitioned between benzene and H_2O. The benzene extracts were washed successively with sat. aq. $NaHCO_3$ and H_2O, dried, and concentrated to leave **9** (319 mg, 100%) as a slightly yellow solid. Recrystallization of the solid from hexane gave a pure sample as colorless needles, mp 76—79°C, which were identical (by mixture melting point test and comparison of IR spectra and TLC behavior) with a specimen obtained by method (ii).

ii) Hydrogenation of **8**: A solution of the pyridone **8**[7] (1.58 g, 5 mmol) in EtOH (30 ml) was hydrogenated over Raney Ni W-2 catalyst (5 ml) at ordinary pressure and 21°C for 9 h. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo*. The residue was dissolved in benzene (30 ml), and the benzene solution was washed successively with 5% aq. HCl, H_2O, 5% aq. NaOH, and H_2O, dried, and concentrated to leave a solid (1.42 g, 89%) of mp 75—79°C. On recrystallization from hexane, it furnished **9** as colorless needles, mp 76—79°C; MS *m/e*: 319 (M^+); UV λ_{max}^{EtOH} 230 nm (ε 9100), 281 (2900); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1624 (lactam CO); NMR ($CDCl_3$) δ: 0.82 (9H, s, Me_3C), 3.77 and 3.80 (6H, s each, two MeO's), 6.65 (3H, s, aromatic protons). *Anal.* Calcd for $C_{19}H_{28}NO_3$: C, 71.44; H, 9.15; N, 4.38. Found: C, 71.37; H, 9.28; N, 4.67.

3-(1,1-Dimethylethyl)-1,2,3,4,6,7-hexahydro-9,10-dimethoxybenzo[*a*]quinolizinium Perchlorate (12)——A stirred mixture of **9** (958 mg, 3 mmol), $POCl_3$ (6 ml), and dry benzene (12 ml) was refluxed for 3 h. Concentration of the mixture under vacuum left a yellowish-orange oil, which was washed with hexane and dissolved in H_2O (30 ml). The aqueous solution was washed with benzene and a solution of $NaClO_4$ (735 mg, 6 mmol) in H_2O (5 ml) was added. The crystals (1.16 g, 96%) that resulted were filtered off and recrystallized from 95% aq. EtOH to afford **12** as colorless prisms, mp 225—227°C (dec.); IR ν_{max}^{Nujol} cm^{-1}: 1662 (C=N$^+$); NMR ($CDCl_3$) δ: 0.97 (9H, s, Me_3C), 3.90 and 3.96 (6H, s each, two MeO's), 6.81 (1H, s, $H_{(8)}$), 7.19 (1H, s, $H_{(11)}$). *Anal.* Calcd for $C_{19}H_{28}ClNO_6$: C, 56.78; H, 7.02; N, 3.49. Found: C, 56.60; H, 7.05; N, 3.52.

(±)-3α-(1,1-Dimethylethyl)-1,3,4,6,7,11bα-hexahydro-9,10-dimethoxy-2*H*-benzo[*a*]quinolizine (11)——A solution of **12** (402 mg, 1 mmol) in 50% aq. EtOH (20 ml) was hydrogenated over Adams catalyst (50 mg) at atmospheric pressure and 18°C for 2 h. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo* to leave an oil, which was dissolved in H_2O (10 ml). The aqueous solution was made basic with 10% aq. NaOH and extracted with benzene. Drying (K_2CO_3) and concentration of the benzene extracts left a yellow oil, which was purified by column chromatography [Al_2O_3 (30 g), hexane–AcOEt (5: 1, v/v)] to provide **11** (258 mg, 85%) as a slightly yellowish solid. Recrystallization from hexane gave an analytical sample as colorless needles, mp 101.5—103°C; MS *m/e*: 303 (M^+); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2770 (*trans*-quinolizidine[8]); NMR ($CDCl_3$) δ: 0.91 (9H, s, Me_3C), 3.84 (6H, s, two MeO's), 6.57 (1H, s, $H_{(8)}$), 6.70 (1H, s, $H_{(11)}$). *Anal.* Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. Found: C, 74.97; H, 9.91; N, 4.81.

A similar hydrogenation of the crude iminium chloride (**12**: Cl^- for ClO_4^-), described above as **12**, in

H_2O produced **11** in 81% overall yield (from **9**).

The Hydrochloride of **11**: A small portion of **11** was dissolved in an excess of 10% (w/w) ethanolic HCl, and dry ether was added. The resulting precipitate was filtered off and recrystallized from acetone–EtOH (1: 1, v/v) to yield the hydrochloride as colorless scales, mp 249—251°C (dec.) (dried over P_2O_5 at 2 mmHg and room temp. for 20 h); IR ν_{max}^{Nujol} cm^{-1}: 2510 (NH^+), 1715 (Me_2CO contained); NMR (Me_2SO-d_6) δ: 0.92 (9H, s, Me_3C), 2.08 (2H, 1/3 Me_2CO), 3.75 (6H, s, two MeO's), 4.22 (1H, dull d-d, $H_{(11b)}$), 6.78 and 6.85 (1H each, s, aromatic protons), 10.8 (1H, b, NH^+). *Anal.* Calcd for $C_{19}H_{30}ClNO_2 \cdot 1/3CH_3COCH_3$: C, 66.86; H, 8.98; N, 3.90. Found: C, 66.85; H, 9.11; N, 3.97.

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Legume Saponins of *Gleditsia japonica* Miquel.[1] III. Further Desmonoterpenyl Glycosides of Echinocystic Acid

Takao Konoshima,* Yasuhiro Umegaki, and Tokunosuke Sawada

Kyoto College of Pharmacy, Nakauchi-cho 5, Misasagi, Yamashina-ku, Kyoto, 607, Japan

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Two triterpenoid saponins, gleditsia saponins E (GS-E) and G (GS-G), were isolated from legumes of *Gleditsia japonica* cv. 'Saponifera' (Leguminosae). These saponins contain monoterpene ester moieties. The desmonoterpenyl compounds, GS-E′ ($C_{69}H_{112}O_{34}$) and GS-G′ ($C_{64}H_{104}O_{30}$), were obtained from them by alkaline hydrolysis with K_2CO_3 and both were identified as echinocystic acid 3,28-O-bisdesmoside on the basis of physical data and degradation products.

Keywords——saponins; bisdesmoside; gleditsia saponin E; gleditsia saponin G; echinocystic acid; *Gleditsia japonica*; Leguminosae

In the preceding paper[1] we reported the isolation of the major saponin, gleditsia saponin C (GS-C), from the legume of *Gleditsia japonica* cv. 'Saponifera,' and the structure elucidation of the desmonoterpenyl compound GS-C′, which was obtained from GS-C by alkaline hydro-