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Conversion of Grayanotoxin III to Grayanotoxin V, Rhodojaponin III and Rhodojaponin IV

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Treatment of grayanotoxin (G) III with CH_3CHO in the presence of anhydrous $CuSO_4$ afforded a diethylidene compound (**2**). Oxidation of **2** (CrO_3) and subsequent ozonolysis and hydrolysis (KOH–MeOH) gave G–V (**4**) in 34% overall yield. Direct ozonolysis of **2** produced rhodojaponin (R) IV (**8**) in 68% yield. Δ^2-Diethylidene compound (**10**) was oxidized to **11**, which on ozonolysis-hydrolysis furnished R–III (**12**) in 9.2% overall yield.

Keywords——*Leucothoe grayana* Max.; *Rhododendron japonicum* Suringer; grayanotoxin V; rhodojaponin III; rhodojaponin IV; ozonolysis; conversion of grayanotoxin III; selective masking and demasking of grayanoids

From the leaves of *Leucothoe grayana* Max. (Ericaceae), seventeen A-nor-B-homokauranoids, grayanotoxin I—XVII have been hitherto isolated.[2]

On the other hand, from the flowers of *Rhododendron japonicum* Suringer, seven toxic diterpenoids with the same skeleton, rhodojaponin I—VII have been isolated.[3] These grayanoids are generally highly oxygenated, bearing several hydroxyl or acetoxyl groups extending over the A, B, C and D rings, as exemplified by grayanotoxin III (G-III) (**1**). More highly oxygenated grayanoids contain a carbonyl group [grayanotoxin V (G-V) (**4**)] or an epoxide group [rhodojaponin III (R-III) (**12**)]. Structures of most of the grayanoids have been determined by correlating them chemically with the basic grayanoids, grayanotoxin I and grayanotoxin II.[4] However, interconversion among the grayanoids is not always simple, since they are acid sensitive, and selective masking and demasking reactions at a particular position are often difficult.

In the present paper, we should like to describe a selective method for masking and demasking of oxygen functions of grayanoids under mild conditions and conversion of G-III to G-V, R-III and rhodojaponin IV (R-IV) by means of the new procedure.

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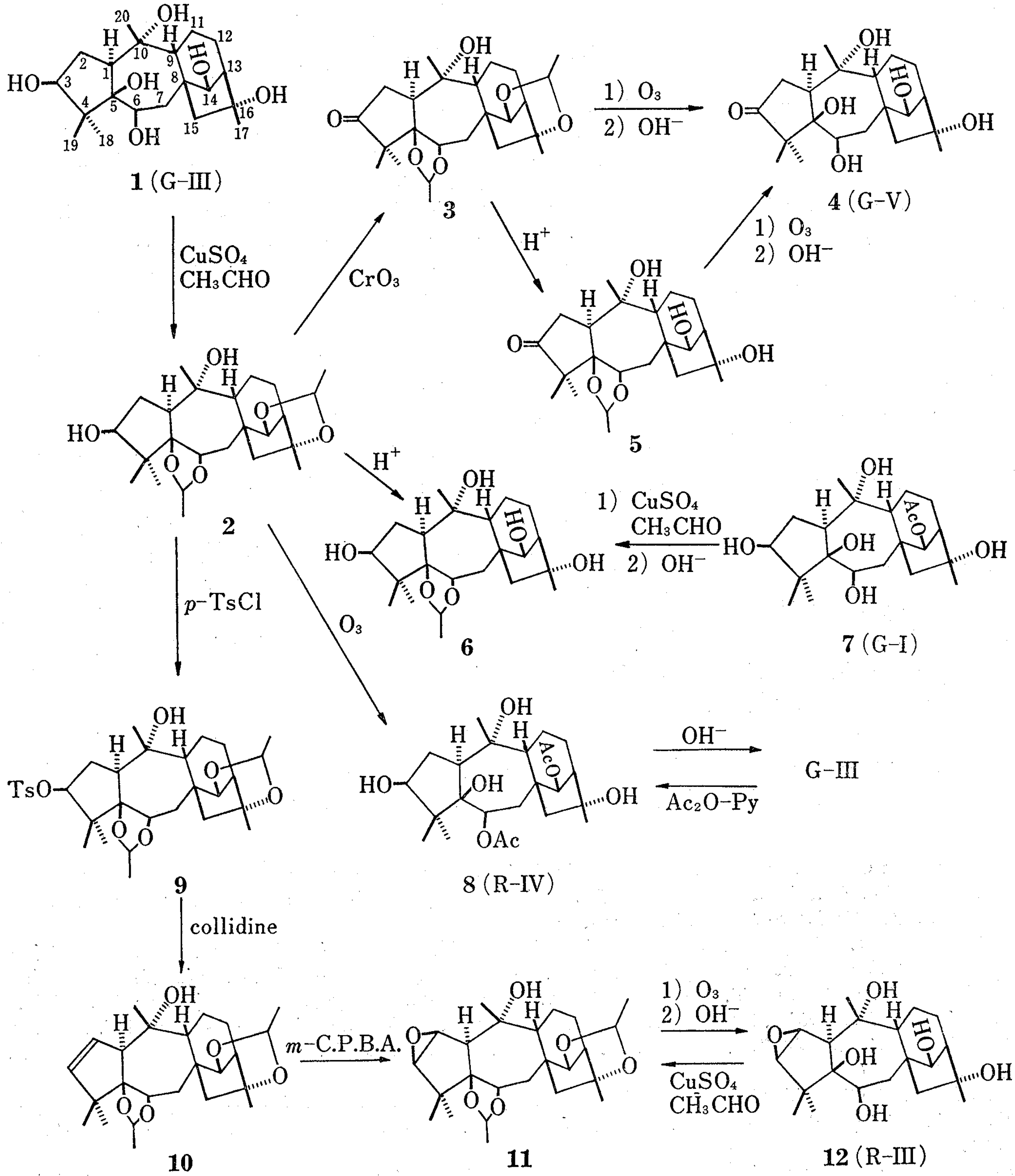
By the use of anhydrous $CuSO_4$ in acetaldehyde, G-III afforded at room temperature smoothly 5,6: 14,16-O-diethylidene G-III (**2**) in 82% yield, δ ($CDCl_3$) 4.23 (C-6H), 4.48 (s, C-14H). The compound **2** was next oxidized with CrO_3-pyridine to give 3-dehydro-diethylidene derivative **3**. The infrared (IR) spectrum of **3** in nujol indicated a tertiary O-H stretching band at 3513 cm^{-1} and a five membered C=O band at 1733 cm^{-1}. Hydrolysis of the 3-dehydro-diethylidene derivative **3** with dil. HCl at room temperature split preferentially the masking group at C-14 and C-16 to give 3-keto-5,6-monoethylidene derivative (**5**). The structure **5** was inferred by nuclear magnetic resonance (NMR) signals at δ ($CDCl_3$) 4.20 (C-6H) and 4.40 (C-14). However, since the removal of the second ethylidene group by acid accompanied side reactions such as elimination of the tertiary hydroxy groups, we next attempted the ozo-



m-C.P.B.A. = m-$ClC_6H_4CO_3H$

Chart 1

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5) P. Deslongchamps and C. Morau, *Can. J. Chem.*, **49**, 2465 (1971).

nolysis of **3** and **5** in accordance with the procedure proposed by P. Deslongchamps.[5] The 3-dehydro-diethylidene derivative (**3**) and 3-dehydro-monoethylidene derivative (**5**) were reacted with ozone to give the already known 6,14-diacetate and 6-monoacetate as oily products respectively. These products gave **4** by hydrolysis with 5% KOH–MeOH. Melting points, IR spectrum and NMR data of **4** were identical with those of natural G-V.

Similarly, hydrolysis of diethylidene G-III (**2**) with dil. methanolic HCl at room temperature afforded selectively 5,6-monoethylidene G-III (**6**), δ ($CDCl_3$) 4.15 (C-3H), 4.79 (C-6H). The IR spectrum and other physical data of **6** were identical with those of the compound derived from G-1. However, removal of the second ethylidene group under acidic conditions was also difficult in this case. On the contrary ozonolysis of diethylidene G-III (**2**) afforded smoothly diacetate (**8**), mp 221—227°, in 68% yield. The IR and NMR spectra indicated the presence of two acetoxy groups, 1733 and 1240 cm^{-1}, δ (C_5D_5N) 2.01 and 2.30 (each 3H, singlet), which were allocated at C-6 and C-14 on the basis of the characteristic splitting pattern of C-6 and C-14 protons at δ 5.19 and 6.10.

Diacetate (**8**) was identified with an authentic sample of R-IV by the use of thin-layer chromatography (TLC), IR and NMR spectroscopy.

On the other hand, monotosylate (**9**), obtained from **2**, was refluxed with collidine to give Δ^2-3-deoxy-diethylidene G-III (**10**) in 76% yield, δ (C_5D_5N) 5.54 and 6.15 (each 1H, d.d, $J_{1,2}=3.0$ Hz, $J_{2,3}=6.0$ Hz and $J_{3,1}=2.0$ Hz), which, on epoxidation with *m*-chloroperbenzoic acid afforded stereoselectively 2,3-epoxy-3-deoxy-diethylidene G-III (**11**). Ozonolysis and subsequent hydrolysis of **11** in the same way as mentioned above furnished **12** in an overall yield of 9.2% from G-III. The product was identical with an authentic sample of R-III in TLC, IR and NMR spectra.

Experimental

All melting points are uncorrected. The NMR spectra were obtained on a Hitachi R-22 spectrometer in $CDCl_3$ or C_5D_5N containing tetramethylsilane (TMS) as internal standard. Chemical shifts are reported as parts per million on the δ scale (s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet). The IR spectra were measured on a Shimadzu IR-400 spectrophotometer.

5,6: 14,16-O-Diethylidene G-III (**2**)——To a solution of 1 g of **1** in 30 ml acetaldehyde, 2 g of anhydrous cupric sulfate was added and the solution was stirred for 1 hr at room temperature. The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was crystallized from ether–*n*-hexane (1: 1) to give 840 mg of **2** as colorless prisms, mp 180—181°, IR ν_{max}^{Nujol}: 3480 and 3470 (OH), 1139, 1082 and 1000 cm^{-1}, NMR $\delta_{ppm}^{CDCl_3}$: 0.85, 1.07, 1.33 and 1.42 (each 3H, s), 1.30, 1.35 (each 3H, d, $J=5.0$ Hz, $\rangle$CH–C$\underline{H}_3$), 3.62 (1H, br.s, C–3H), 4.23 (1H, br.s, C-6H), 4.48 (1H, s, C–14H), 4.98 and 5.12 (each 1H, q, $J=5.0$ Hz, $\rangle$C$\underline{H}$–CH_3). *Anal.* Calcd. for $C_{24}H_{38}O_6$: C, 68.22; H, 9.07. Found: C, 68.37; H, 9.04.

5,6: 14,16-O-Diethylidene-3-dehydro G-III (**3**)——To a mixture of pyridine (10 ml) and CrO_3 (500 mg), 500 mg of **2** dissolved in 5 ml pyridine was added and allowed to stand overnight. The mixture was poured into ice water and the resultant solution was shaken 3 times with EtOAc. The combined EtOAc layers were washed with water, dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to give crystals. Recrystallization from ether–*n*-hexane gave 250 mg of **3** as colorless prisms, mp 251—252°, IR ν_{max}^{Nujol}: 3513 (OH), 1733 (C=O), 1095—1140 cm^{-1}, NMR $\delta_{ppm}^{CDCl_3}$: 0.93, 1.00, 1.25 and 1.34 (each 3H, s), 1.24 and 1.30 (each 3H, d, $J=4.8$ Hz, $\rangle$CH–C$\underline{H}_3$), 4.26—4.30 (1H, m, C–6H), 4.48 (1H, s, C–14H), 4.90 and 5.13 (each 1H, q, $J=4.8$ Hz, $\rangle$C$\underline{H}$–CH_3), MS *m/e*: 420 (M^+). *Anal.* Calcd. for $C_{24}H_{36}O_6$: C, 68.54; H, 8.63. Found: C, 68.58; H, 8.62.

3-Dehydro G-III (**=G–V**) (**4**)——Air containing ozone was passed through an ice cooled solution of 50 mg of **3** in 10 ml of EtOAc–AcOH (1: 1). After the absorption of ozone had ceased, the solution was treated with 3 ml of water and allowed to stand overnight. The solvent was removed *in vacuo*, and the residue containing diacetyl G–V was tried to crystallize from several solvents without success. After the reaction mixture was treated with 5% KOH–MeOH for 4 hr at 50°, the solution was evaporated under reduced pressure and the residue was extracted with EtOAc. The combined EtOAc layers were washed with water, dried over Na_2SO_4, and evaporated *in vacuo* to give crystals. Recrystallization from EtOAc gave 30 mg of **4** as colorless needles, mp 253—256°, IR ν_{max}^{Nujol}: 3550—3250 (OH), 1730 (C=O) cm^{-1}, NMR $\delta_{ppm}^{C_5D_5N}$: 1.16, 1.47, 1.53 and 1.73 (each 3H, s), 4.68 (1H, m, C–6H) and 5.07 (1H, s, C–14H). The IR spectrum and NMR data of **4** were identical with those of natural G–V.

5,6-O-Ethylidene-3-dehydro G-III (**5**)——To a solution of 100 mg of **3** in 10 ml of MeOH, 0.1 ml of conc. HCl was added and the mixture was allowed to stand at room temperature for 1 hr. The solution was neutralized with 10% Na_2CO_3, concentrated *in vacuo* and extracted 3 times with EtOAc. The combined EtOAc layers were washed with water, dried over Na_2SO_4 and evaporated *in vacuo* to give crystals. Recrystallization from EtOAc gave 70 mg of **5** as colorless needles, mp 232—238°, IR $\nu_{\max}^{\mathrm{Nujol}}$: 3460 (OH), 3330 (OH), 1734 (C=O) cm^{-1}, NMR $\delta_{\mathrm{ppm}}^{\mathrm{CDCl_3}}$: 0.98, 1.06 (each 3H, s), 1.40 (6H, s), 1.34 (3H, d, J=5.0 Hz, >CH–C$\underline{\mathrm{H}}_3$), 4.20 (1H, br. s, C–6H), 4.40 (1H, br. s, C–14H) and 4.48 (1H, q, J=5.0 Hz, >C$\underline{\mathrm{H}}$–CH_3). *Anal.* Calcd. for $C_{22}H_{34}O_6$: C, 66.98; H, 8.69. Found: C, 66.50; H, 8.68.

5,6-O-Ethylidene G-III (**6**)——To a solution of 100 mg of **2** in 10 ml of MeOH, 0.1 ml of conc. HCl was added and the resultant solution was allowed to stand at room temperature for 2 hr. The mixture was treated by the same method as above. Recrystallization from EtOAc–*n*-hexane gave 50 mg of **6** as amorphous solid, IR $\nu_{\max}^{\mathrm{KBr}}$: 3600—3200 (OH), 1138, 1100, 1060 and 1020 cm^{-1}. The IR spectrum of **6** was identical with that of the derivative from G-I.

5,6-O-Ethylidene G-III 3,14-Diacetate——To a solution of 100 mg of **6** in 1 ml of pyridine, 1 ml of Ac_2O was added and allowed to stand at room temperature overnight. The mixture was poured into ice water and extracted 3 times with EtOAc. The combined EtOAc layers were washed with water, dried over Na_2SO_4 and evaporated *in vacuo* to give crystals. Recrystallization from EtOAc–*n*-hexane gave 90 mg of 5,6-O-ethylidene G-III 3,14-diacetate, mp 152—155°, IR $\nu_{\max}^{\mathrm{KBr}}$: 3600—3250 (OH), 1720 (C=O) and 1245 (C–O–) cm^{-1}, NMR $\delta_{\mathrm{ppm}}^{\mathrm{CDCl_3}}$: 0.93 and 0.95 (each 3H, s), 1.37 (6H, s), 1.35 (3H, d, J=5.0 Hz, >CH–C$\underline{\mathrm{H}}_3$), 2.40 (6H, s, OAc×2), 4.15 (1H, m, C–3H), 4.79 (1H, m, C–6H), 4.93 (1H, q, J=5.0 Hz, >C$\underline{\mathrm{H}}$–CH_3) and 5.83 (1H, s, C–14H).

G-III 6,14-Diacetate (=R-IV) (**8**)——Air containing ozone was passed through an ice cooled solution of 200 mg of **2** in 10 ml of EtOAc–AcOH (1:1). After the absorption of ozone had ceased, the solution was treated with 3 ml of water and left overnight. The mixture was neutralized with 10% $NaHCO_3$, concentrated *in vacuo* and extracted 3 times with EtOAc. The combined EtOAc layers were washed with water, dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to give crystals. Recrystallization from EtOAc–*n*-hexane gave 150 mg of **8** as colorless needles, mp 221—227°, IR $\nu_{\max}^{\mathrm{Nujol}}$: 3578, 3342 (OH), 1733 (C=O) and 1240 (C–O–) cm^{-1}, NMR $\delta_{\mathrm{ppm}}^{\mathrm{C_5D_5N}}$: 0.96 and 1.70 (each 3H, s), 1.43 (6H, s), 2.01 and 2.30 (each 3H, s, –OAc×2), 3.80 (1H, m, C–3H), 5.19 (1H, m, C–6H) and 6.10 (1H, s, C–14H). *Anal.* Calcd. for $C_{24}H_{38}O_8 \cdot 1/2H_2O$: C, 62.18; H, 8.48. Found: C, 62.20; H, 8.72.

The IR spectrum and NMR data of **8** were identical with those of natural R–IV. Hydrolysis of **8** with 5% KOH gave G–III. **8** was identical with G–III 6,14-diacetate which were obtained from G–III on partial acetylation with Ac_2O-pyridine.

3-O-Tosyl-5,6:14,16-O-diethylidene G-III (**9**)——To a solution of 1 g of **2** in 10 ml of pyridine, 1.1 g of *p*-toluenesulfonyl chloride was added and the solution was allowed to stand at 0° for 5 day. The mixture was poured into ice water and the resultant precipitate was washed with water, dissolved in EtOAc, and the organic layer was dried over anhydrous Na_2SO_4, and evaporated *in vacuo* to give crystals. Recrystallization from EtOAc–*n*-hexane gave 950 mg of **9** as colorless needles, mp 162—165°, IR $\nu_{\max}^{\mathrm{Nujol}}$: 3480 (OH), 1598 and 1180—1085 cm^{-1}, NMR $\delta_{\mathrm{ppm}}^{\mathrm{CDCl_3}}$: 0.86 and 0.96 (each 3H, s), 1.33 (6H, s), 2.45 (3H, s, arom. –Me), 1.28 and 1.40 (each 3H, d, J=5.0 Hz, >CH–C$\underline{\mathrm{H}}_3$), 4.13 (1H, m, C–3H), 4.42 (2H, m, C–6H, C–14H), 5.00 and 5.40 (each 1H, q, J=5.0 Hz, >C$\underline{\mathrm{H}}$–CH_3), 7.34 and 7.82 (each 2H, d, J=8.2 Hz, arom. protons). *Anal.* Calcd. for $C_{31}H_{44}O_8S$: C, 64.56; H, 7.69. Found: C, 64.87; H, 7.80.

5,6:14,16-O-Diethylidene-Δ^2-3-deoxy G-III (10)——A solution of 300 mg of **9** in 30 ml of collidine was refluxed for 4 hr. After cooling it was poured into dilute H_2SO_4 and extracted with EtOAc. The combined EtOAc layers were washed with water, dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to give crystalline material. Recrystallization from EtOAc–*n*-hexane gave 160 mg of **10** as colorless needles, mp 179—182°, IR $\nu_{\max}^{\mathrm{KBr}}$: 3520 (OH), 1160—1085 cm^{-1}, NMR $\delta_{\mathrm{ppm}}^{\mathrm{C_5D_5N}}$: 0.80, 1.08, 1.36 and 1.65 (each 3H, s), 1.38 and 1.40 (each 3H, d, J=5.0 Hz, >CH–C$\underline{\mathrm{H}}_3$), 4.38 (1H, m, C–6H), 5.54 (1H, d.d, $J_{2,1}$=3.0 Hz, $J_{2,3}$=6.0 Hz, C–2H), 6.15 (1H, d.d, $J_{3,1}$=2.0 Hz, $J_{3,2}$=6.0 Hz, C–3H), 5.11 (1H, s, C–14 H), 5.00 and 5.40 (each 1H, q, J=5.0 Hz, >C$\underline{\mathrm{H}}$–CH_3). *Anal.* Calcd. for $C_{24}H_{36}O_5$: C, 71.25; H, 8.97. Found: C, 71.43; H, 9.19.

2,3-Epoxy-3-deoxy-5,6:14,16-O-diethylidene G-III (**11**)——To a solution of 110 mg of **10** in 10 ml of EtOAc, a mixture of 86 mg of *m*-chloroperbenzoic acid and 2 ml of methylene chloride was added and the whole was allowed to stand overnight at room temperature. After the mixture was treated with 10% aq. Na_2S (10 ml), the organic layer was washed with 5% $NaHCO_3$ and water, dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to give crystalline material. Recrystallization from $CHCl_3$–*n*-hexane gave 60 mg of **11** as colorless needles, mp 209—210°, IR $\nu_{\max}^{\mathrm{KBr}}$: 3520 (OH), 1080—1140 cm^{-1}, NMR $\delta_{\mathrm{ppm}}^{\mathrm{CDCl_3}}$: 0.88, 1.18, 1.30 and 1.53 (each 3H, s), 1.27 and 1.34 (each 3H, d, J=5.0 Hz, >CH–C$\underline{\mathrm{H}}_3$), 3.05 and 3.58 (each 1H, d, J=4.0 Hz, C–2H, C–3H), 4.25 (1H, m, C–6H), 4.53 (1H, s, C–14H), 4.86 and 5.12 (each 1H, q, J=5.0 Hz, >CH–C$\underline{\mathrm{H}}_3$). *Anal.* Calcd. for $C_{24}H_{36}O_6$: C, 68.54; H, 8.63. Found: C, 68.35; H, 8.97.

2,3-Epoxy-3-deoxy G-III (=R-III) (**12**)——Air containing ozone was passed through an ice cooled solution of 50 mg of **11** in 4 ml of AcOH–EtOAc (1:1). After the ozonization, the solution was treated with 3 ml of water and left overnight. The mixture was neutralized with 10% $NaHCO_3$, concentrated *in vacuo* and extracted 3 times with EtOAc. The usual working up of the extract gave an amorphous material. To a solution of the product in 2 ml of MeOH, 400 mg of anion exchange resin (IRA 400) was added and the mixture was refluxed for 1 hr. The resin was filtered off and the filtrate was evaporated under reduced pressure to give a crystalline solid. Recrystallization from EtOAc gave 20 mg of **12** as colorless needles, mp 285—287°, IR $\nu_{\max}^{\mathrm{KBr}}$: 3200—3600 (OH), 855 cm^{-1}, NMR $\delta_{\mathrm{ppm}}^{\mathrm{C_5D_5N}}$: 1.21, 1.47, 1.53 and 1.84 (each 3H, s), 3.18 and 4.15 (each 1H, d, J=3.0 Hz, C–2H, C–3H), 4.42 (1H, m, C–6H) and 4.83 (1H, s, C–14H). *Anal.* Calcd. for $C_{20}H_{32}O_6$: C, 65.19; H, 8.75. Found: C, 64.49; H, 9.00.

The IR spectrum and NMR data of **12** were identical with those of natural R-III.

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Chemische Untersuchungen der Inhaltsstoffe von *Pteris vittata* L.[1]

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Aus den oberirdischen Teilen von *Pteris vittata* L. wurden zwei neue Lignanglykoside, d.h., *cis*-Dihydro-dehydro-diconiferylalkohol-9-O-β-D-Glukosid (I) und Lariciresinol-9-O-β-D-Glukosid (III) isoliert und identifiziert.

Keywords——*Pteris vittata*; Pteridaceae; lignans; glucosides; dihydro-dehydro-diconiferylalcohol; lariciresinol; DCCC; NMR; chemotaxonomy

In Fortsetzung der chemischen und chemotaxonomischen Untersuchungen der Gattung *Pteris* und der verwandten Gattungen wurde *Pteris vittata* L. (jap. Name: Moejimashida, Fundort: Okinoerabu/Kagoshima-Präfektur, Sammelzeit: August, 1975) auf die Inhaltsstoffe untersucht und aus den oberirdischen Teilen zwei neue Lignan-Glykoside isoliert.

Glykosid A (I) wurde als amorphes Pulver vom $[\alpha]_D^{22}$ −23.6° (c=0.98, MeOH) erhalten. Enzymatische Hydrolyse ergab D-Glukose und ein amorphes Aglykon (II), $C_{20}H_{24}O_6$ (M^+ 360.1596) vom $[\alpha]_D^{22}$ −8.5° (c=0.96, Aceton). Die spektroskopischen Daten des Aglykons (II) sind nur mit der Struktur eines Dihydro-dehydro-diconiferylalkohols vereinbar. *rac*-Dehydro-diconiferylalkohol ist als Modellverbindung[3] bei der Lignin-Biosynthese bekannt.

Für die optisch aktiven Dihydro-dehydro-diconiferylalkoholen sind zwei Stereoisomeren beschrieben, d.h., eins ist derjenige vom Schmp. 102—103° und $[\alpha]_D^{20}$ +5.4° (c=2.0, Aceton), der Weinges und Mitarbb.[4] durch Hydrierung des natürlichen Dehydro-diconiferylalkohols erhielten und ein anderer derjenige vom $[\alpha]_D^{18}$ −4.9° (c=0.91, absol. Aceton), der Takemoto und Mitarbb.[5] durch alkalische Hydrolyse des natürlichen Diferulasäureester des Dihydro-dehydro-diconiferylalkohols erhielten. II erwies sich als identisch mit dem letzteren Isomeren durch Vergleich von Infrarot (IR)- und Kernmagnetische Resonanz (NMR-) Spektra.

Im NMR-Spektrum des Aglykon-Acetats (II′) erscheinen die Signale von Protonen der Acetoxy-tragenden Methylengruppen bei 4.07 (2H am C(9′), t, J= 7 Hz) und 4.31 (2H am C(9),

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