Studies on the Constituents of the Bark of *Dalbergia hupeana*[1)]

Shoji YAHARA,[a] Seiko EMURA,[a] Huiming FENG[b] and Toshihiro NOHARA*,[a]

Faculty of Pharmaceutical Sciences, Kumamoto University,[a] 5–1 Oe-honmachi, Kumamoto 862, Japan and Nanjing Forestry University,[b] Nanjing, China. *Received January 5, 1989*

Two new triterpenoid glycosides, 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosiduronic acids (2 and 3) of 3β,22β-dihydroxyolean-12-en-29-oic acid and 3β,21β,22β-trihydroxyolean-12-en-29-oic acid, along with a known glycoside, kaikasaponin III (1), were isolated from the bark of *Dalbergia hupeana* HANCE. Their structures were determined by chemical and spectral methods.

Keywords *Dalbergia hupeana*; Leguminosae; triterpenoid glycoside; kaikasaponin III; glucuronide; 3β,22β-dihydroxyolean-12-en-29-oic acid; 3β,21β,22β-trihydroxyolean-12-en-29-oic acid

In the course of our systematic studies on the constituents effective for antihypercholesterolemia, we found the occurrence of a variety of novel bi-isoflavonoids in the heart wood of *Dalbergia odorifera* T. CHEN.[2)] In conection with this study, we have now investigated the constituents of another plant of the same genus, *Dalbergia hupeana* HANCE. (Leguminosae), which is widely distributed in China and has been used as a Chinese folk medicine, for example, as an antiscabietic. In this paper, we wish to describe the isolation and structure elucidation of two triterpenoidal glycosides.

The methanolic extract of the dried bark of *D. hupeana* was partitioned between EtOAc and water. The EtOAc extract was subjected to a combination of silica gel and Sephadex LH-20 column chromatographies and four known flavonoids were obtained. These flavonoids were identified as (+)-leiocarpin,[3)] (−)-leiocin,[3)] apigenin and isorhamnetin by comparison of their physical and spectral data with the reported values. On the other hand, evaporation of the aqueous layer provided a residue, from which, by a combination of MCI gel CHP 20P, Bondapak C_{18} and silica gel column chromatographies, two new triterpenoidal glycosides (**2** and **3**) were obtained together with a known saponin (**1**).

Compound **1**, pale gray fine needles, $[\alpha]_D$ −2.0°, showed an M−H ion peak at *m/z* 925 in the negative fast atom bombardment mass spectrum (FAB-MS). Acid hydrolysis of **1** provided a sapogenol identical with sophoradiol (**4**) along with the sugar components, glucuronic acid, galactose and rhamnose. The electron impact (EI)-MS of the peracetylated methyl ester derivative (**5**) of **1** exhibited fragment ions at *m/z* 273 (terminal peracetylated methylpentose cation) and 561 (terminal peracetylated methylpentosyl-hexose cation) originating from the sugar moiety, and fragment ions at *m/z* 466 (aglycone molecule–H_2O), 276 (D/E ring) and 190 (A/B ring) derived *via* the characteristic retro Diels–Alder type fragmentation at the C-ring on the aglycone moiety in the EI-MS.[4)] The carbon-13 nuclear magnetic resonance (^{13}C-NMR) (Table I) spectral data for **1** showed forty-eight carbon signals, which were superimposable on those of kaikasaponin III.[5)] Furthermore, signals due to the anomeric protons of glucuronic acid and galactose appeared at δ 4.45 (d, *J*= 7 Hz) and 4.62 (d, *J*=8 Hz), which were correlated with the respective H-2 signals at δ 4.04 (dd, *J*=7.9 Hz) and 3.83 (dd, *J*=8, 10 Hz) in the ^{1}H–^{1}H two dimensional correlated spectroscopy (^{1}H–^{1}H COSY) spectrum of **5**. The results indicated that the structure of the sugar part of **1** could be represented as α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosiduronic acid. Compound **1** was therfore concluded to be identical with kaikasaponin III.

Compound **2**, $[\alpha]_D$ −13.4°, showed a molecular peak due to $(M-H)^-$ at *m/z* 955 in the negative FAB-MS. Acid hydrolysis of **2** gave an aglycone and glucuronic acid, galactose and rhamnose for sugar. The aglycone, on treatment with diazomethane, gave the corresponding methyl ester (**6**), $[\alpha]_D$ +43.3°, which showed the molecular ion peak at *m/z* 486 and prominent fragment ion peaks at *m/z* 278 (D/E ring) and 207 (A/B ring) in the EI-MS, indicating the presence of one methoxycarbonyl group in the D/E ring in comparison with those of **4**. A comparative study of the ^{1}H-NMR spectra of **6** and **4** led to the following signal assignments: δ: 0.99, 1.07, 1.09, 1.23, 1.26, 1.26 and 1.69 (7 × *tert*-Me), 3.48 (1H, dd, *J*=5, 10 Hz, H-3α), 3.91 (1H, dd, *J*=2, 6 Hz, H-22α), 5.41 (1H, t, *J*=3 Hz, H-12) and 3.67 (3H, s, COOMe). The ^{13}C-NMR signals due to the sugar moiety (eighteen carbons) and carbons on the A—D rings of the aglycone part in **2** exhibited a good coincidence with those of **1**. The remaining signals at δ 42.6, 43.9, 38.9, 76.3, 20.3, 186.2 and 18.4 could be reasonably assigned to C-19—C-22 and C-28—C-30, respectively, on the E ring of the aglycone, by comparison with those of kudzusapogenol B methyl ester (**7**)[6)] possessing a 29-COOMe group, suggesting the existence of one methoxycarbonyl group at C-29. Therefore, the structure of **2** was elucidated as 3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyluronic acid 3β,22β-dihydroxyolean-12-en-29-oic acid.

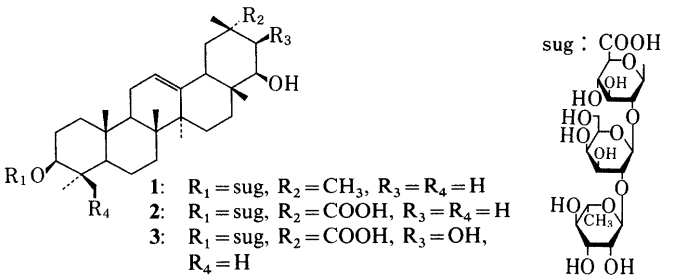
Compound **3**, giving an ion peak of $(M-H)^-$ at *m/z* 971 in the negative FAB-MS, showed signals due to the sugar moiety, which were superimposable on those of **1** and **2** in the ^{13}C-NMR spectrum. The EI-MS of the peracetylated methyl ester derivative (**8**) of **3** displayed fragment ion peaks at *m/z* 273 and 561 derived from the sugar residue, and peaks at *m/z* 568 (aglycone part–H_2O), 378 (D/E ring) and 190 (A/B ring) produced from the aglycone part. Thus, the aglycone of **3** was shown to possess a carboxyl group on the D/E ring. A comparative investigation of the ^{13}C-NMR spectral data of **3** with those of **7** allowed the assignment of carbon signals as given in Table I. The spectral data of **3** were shown to be almost identical with those of **7** except for the signals due to C-2 and C-3 (glycosylation shifts[7)]), C-4, C-23 and C-24 (shifts due to deoxygenation of the hy-

TABLE I. ^{13}C-NMR Assignments of **1**, **2**, **3**, **6**, Sophoradiol (**4**) and Kudzusapogenol B Methyl Ester (**7**) (in Pyridine-d_5 + D_2O)

	4	1	7	6	2	3
C-1	39.2	38.6	38.9	39.2	38.6	38.3
C-2	26.2	26.1	28.4	28.8	26.2	26.0
C-3	78.1	90.1	80.1	78.1	90.9	90.8
C-4	39.4	39.4	43.2	39.4	39.7	39.3
C-5	55.9	55.5	56.3	55.8	56.0	55.3
C-6	18.9	18.1	19.1	18.8	18.4	17.9
C-7	33.3	32.8	33.1	33.2	33.4	32.4
C-8	40.1	39.6	40.3	40.1	39.7	39.7
C-9	48.1	47.6	48.0	48.1	47.8	47.2
C-10	37.3	36.4	37.0	37.3	36.7	36.2
C-11	23.9	23.5	24.2	23.9	23.6	23.3
C-12	122.5	122.8	123.8	123.0	122.5	122.2
C-13	144.9	144.4	143.6	144.1	144.7	144.1
C-14	42.5	42.1	42.0	42.4	42.6	41.5
C-15	26.5	25.9	26.5	26.4	26.0	25.8
C-16	28.7	28.3	27.4	28.5	28.3	27.8
C-17	38.0	37.6	38.9	37.9	37.9	38.3
C-18	45.4	45.1	42.7	44.3	45.9	43.1
C-19	46.9	46.4	42.4	41.1	42.6	41.5
C-20	30.9	30.5	49.9	42.7	43.9	47.7
C-21	42.5	41.8	70.5	37.3	38.9	71.3
C-22	75.6	75.6	79.1	75.0	76.3	78.5
C-23	28.8	28.3	23.5	28.2	28.2	27.8
C-24	15.9	15.3	64.5	15.9	15.6	15.1
C-25	16.6	16.4	16.2	16.6	16.6	16.1
C-26	17.3	16.8	16.9	17.2	17.2	16.6
C-27	25.8	25.3	26.5	25.7	26.3	26.2
C-28	28.8	27.9	22.1	21.0	20.3	21.5
C-29	33.3	32.8	178.7	—[a]	186.2	185.8
C-30	21.2	20.7	16.6	18.8	18.4	17.9
COOMe			52.0	51.8		
glcUA						
1		104.5			104.8	104.4
2		78.2			78.3	77.5
3		75.6			76.3	76.0
4		73.8			73.7	73.1
5		76.0			76.5	76.1
6		176.5			175.9	175.9
gal						
1		102.1			102.3	101.8
2		78.0			78.3	77.7
3		75.2			75.5	74.9
4		70.1			70.4	70.0
5		76.0			76.5	76.7
6		61.9			62.4	62.2
rha						
1		101.2			101.6	101.1
2		71.8			71.9	71.3
3		71.8			71.9	71.3
4		73.3			73.5	73.1
5		68.8			69.2	68.9
6		18.3			18.4	17.9

a) Hidden by noise.

droxymethyl group at C-24) and C-29 (shift due to desmethylation). The results unambiguously demonstrated the structure of the aglycone part of **3** to be 3β,21β,22β-trihydroxyolean-12-en-29-oic acid. The ^{1}H-NMR spectrum of **8** showed seven singlet methyl signals between δ 0.82—1.43, ten acetyl signals between δ 1.95—2.15, two methoxycarbonyl signals at δ 3.66 and 3.75, and two doublet signals with J=3 Hz at δ 5.01 and 5.59 assignable to H-22 and H-21, respectively, both being geminal to the acetoxyl group. Moreover, signals between δ 3.80—5.35 due to the sugar moiety of **8** were identical with those of **5**. Consequently, the structure of **3** could be represented as



1: R_1=sug, R_2=CH_3, R_3=R_4=H
2: R_1=sug, R_2=COOH, R_3=R_4=H
3: R_1=sug, R_2=COOH, R_3=OH, R_4=H
4: R_1=R_3=R_4=H, R_2=CH_3
6: R_1=R_3=R_4=H, R_2=COOMe
7: R_1=H, R_2=COOMe, R_3=R_4=OH

Chart 1

shown in the formula.

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-360 digital polarimeter (cell length: 0.5 dm). MS were recorded with JEOL MS-01SG, DX-300 and DX-303HF spectrometers. ^{1}H-(400 MHz) and ^{13}C-(100 MHz) NMR spectra were taken with a JEOL GX-400 spectrometer. Gas liquid chromatography (GLC) was run on a Shimadzu gas chromatograph, model GC-3BF. Column chromatography was carried out with MCI gel CHP 20P (75—100 μm, Mitsubishi Chem. Ind. Co., Ltd.), Bondapak C_{18} (Waters Associates), Sephadex LH-20 (25—100 μm, Pharmacia Fine Chemicals) and Kieselgel 60 (70—230 mesh, Merck). TLC was conducted on precoated Kieselgel 60 F_{254} plates (0.2 mm, Merck) and spots were located by ultraviolet illumination and by the use of 10% H_2SO_4 sprays.

Extraction and Isolation The dried bark of *Dalbergia hupeana* HANCE. (2 kg) was extracted twice with MeOH (8 l each, with heating under reflux for 5 h). The MeOH extract was partitioned into EtOAc–water. Removal of the solvent from each phase under reduced pressure gave the EtOAc (42 g) and aqueous (57 g) extracts. Column chromatography of the EtOAc extract over silica gel ($CHCl_3$: MeOH = 100 : 1 → 10 : 1) furnished three fractions and the fraction containing flavonoids was purified by silica gel (hexane : EtOAc = 50 : 1 and benzene : EtOAc = 100 : 1) and Sephadex LH-20 (benzene : MeOH = 10 : 1) column chromatographies to afford (+)-leiocarpin (10 mg), (−)-leiocin (170 mg), apigenin (5 mg) and isorhamnetin (37 mg). Separation of the aqueous extract by MCI gel CHP 20P column chromatography (H_2O : MeOH = 1 : 0 → 4 : 1 → 3 : 2 → 2 : 3 → 1 : 4 → 0 : 1) furnished a crude saponin fraction (4.61 g, 80% MeOH eluate fraction), which was subsequently purified by silica gel ($CHCl_3$: MeOH : H_2O = 7 : 4 : 0.5) and Bondapak C_{18} (H_2O : MeOH = 3 : 1 → 1 : 1) column chromatographies to give **1** (150 mg), **2** (34 mg) and **3** (14 mg).

(+)-Leiocarpin An amorphous powder, $[\alpha]_D^{25}$ +136.1° (c=0.56, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.41, 1.42 (each 3H, s, Me-14, Me-15), 3.46 (1H, ddd, J=4, 7, 11 Hz, H-3), 3.65 (1H, t, J=11 Hz, H-2), 4.26 (1H, dd, J=4, 11 Hz, H-2), 5.45 (1H, d, J=7 Hz, H-4), 5.57 (1H, d, J=10 Hz, H-12), 5.89, 5.92 (each 1H, s, –O–CH_2–O–), 6.43 (1H, s, H-3′), 6.52 (1H, d, J=9 Hz, H-6), 6.63 (1H, d, J=10 Hz, H-11), 6.72 (1H, s, H-6′), 7.23 (1H, d, J=9 Hz, H-5).

(−)-Leiocin An amorphous powder, $[\alpha]_D^{25}$ −17.1° (c=0.58, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.41, 1.42 (each 3H, s, Me-14, Me-15), 2.83 (1H, dd, J=6, 16 Hz, H-4), 2.90 (1H, dd, J=11, 16 Hz, H-4), 3.49 (1H, m, H-3), 3.97 (1H, t, J=10 Hz, H-2), 4.34 (1H, dd, J=2, 10 Hz, H-2), 5.55 (1H, d, J=10 Hz, H-12), 5.85, 5.96 (each 1H, s, –O–CH_2–O–), 6.35 (1H, s, H-3′), 6.36 (1H, d, J=8 Hz, H-6), 6.58 (1H, s, H-6′), 6.63 (1H, d, J=10 Hz, H-11), 6.80 (1H, d, J=8 Hz, H-5).

Compound 1 (Kaikasaponin III) Pale gray fine needles, mp > 300 °C, $[\alpha]_D^{18}$ −2.0° (c=0.55, pyridine–H_2O, 1 : 1). ^{1}H-NMR (pyridine-d_5) δ: 0.85, 1.00, 1.03, 1.18, 1.24, 1.30, 1.31, 1.33 (each 3H, s, 8 × Me), 1.72 (3H, d, J=6 Hz, rha Me-6), 3.16 (1H, m, H-3), 5.34 (1H, br s, H-12), 6.22 (1H, s, rha H-1), glc UA and gal H-1: hidden by H_2O signal. ^{13}C-NMR: Table I.

Acid Hydrolysis of 1 A solution of **1** (5 mg) in 1 N HCl–H_2O (1 ml) was heated at 70 °C for 5 h, then it was poured into water and extracted with ether. Removal of the solvent furnished the ether extract, which was purified by silica gel (benzene : EtOAc = 5 : 1) column chromatography to give the aglycone (**4**), which was identified as sophoradiol by comparison with an authentic sample (thin layer chromatography (TLC) and ^{1}H-

NMR). Removal of the solvent from the water layer under an N_2 atmosphere gave a sugar mixture. The components were identified by TLC ($CHCl_3$: MeOH : acetone : H_2O = 3 : 3 : 3 : 1); *Rf* 0.56 (rhamnose), *Rf* 0.35 (galactose), *Rf* 0.12 (glucuronic acid), and GLC (2% OV-17 on Chromosorb W (60—80 mesh), N_2 flow rate 1 kg/cm^2, 3 mm × 1 m glass column, column temperature 150 °C); t_R 6.6 min, 8.8 min (tetramethylsilane (TMS)–rhamnose), t_R 21.2 min, 25.0 min (TMS–galactose).

Peracetylated Methyl Ester (5) of 1 A solution of **1** (5 mg) in Ac_2O–pyridine (1 : 1, 0.5 ml) was allowed to stand at room temperature for 16 h. The reaction mixture was evaporated by blowing N_2 over it to give a residue, which was treated with ethereal diazomethane. The reaction mixture was left to stand at room temperature overnight. The reaction mixture was evaporated *in vacuo* and the residue was purified by silica gel (hexane : EtOAc = 2 : 1) column chromatography to give the acetylated methyl ester (**5**, 1 mg). **5**: EI-MS *m/z*: 561, 466, 407, 276, 273, 216, 207, 190. ^{1}H-NMR ($CDCl_3$) δ: 0.82, 0.87, 0.89, 0.96, 0.97, 1.00, 1.07, 1.14 (each 3H, s, 8 × Me), 1.21 (3H, d, J = 6 Hz, rha Me-6), 1.99, 2.00, 2.01, 2.03, 2.06, 2.09, 2.10, 2.14, 2.15 (each 3H, s, 9 × Ac), 3.09 (1H, dd, J = 5, 11 Hz, H-3), 3.75 (3H, s, glc UA 6-COOMe), 3.85 (1H, dd, J = 7, 10 Hz, gal H-2), 3.86 (1H, m, gal H-5), 4.04 (1H, dd, J = 7, 9 Hz, glc UA H-2), 4.06 (1H, d, J = 9 Hz, glc UA H-5), 4.10 (3H, m, gal H_2-6, rha H-5), 4.45 (1H, d, J = 7 Hz, glc UA H-1), 4.62 (1H, d, J = 8 Hz, gal H-1), 4.64 (1H, t, J = 4 Hz, H-22), 4.92 (1H, dd, J = 3, 10 Hz, gal H-3), 4.99 (1H, s, rha H-1), 5.07 (1H, d, J = 3 Hz, rha H-2), 5.11 (2H, t, J = 10 Hz, rha H-4, glc UA H-3), 5.19 (1H, dd, J = 3, 10 Hz, rha H-3), 5.21 (1H, t, J = 10 Hz, glc UA H-4), 5.24 (1H, br s, H-12), 5.34 (1H, d, J = 3 Hz, gal H-4).

Compound 2 A pale yellow powder, $[\alpha]_D^{18}$ −13.4° (*c* = 0.92, pyridine–H_2O, 1 : 1). Neg. FAB-MS *m/z*: 955.489 (Calcd for $C_{48}H_{76}O_{19}-H$; 955.490), 977, 999. ^{1}H-NMR(pyridine-d_5–D_2O) δ: 0.86, 0.92, 1.20, 1.23, 1.26, 1.35, 1.74 (each 3H, s, 7 × Me), 1.79 (3H, d, J = 6 Hz, rha Me-6), 3.32 (1H, br dd, J = 3, 8 Hz, H-3), 5.28 (1H, br s, H-12), 5.48 (1H, d, J = 8 Hz, glc UA H-1), 5.97 (1H, s, rha H-1), gal H-1 : hidden by H_2O signal.

Acid Hydrolysis of 2 A solution of **2** (5 mg) in 1 N HCl–H_2O (1 ml) was treated as described for **1** to give the aglycone moiety and glucuronic acid, galactose and rhamnose as sugars. The aglycone moiety was treated with excess ethereal diazomethane and the reaction mixture was allowed to stand overnight. The product obtained after removal of the solvent was purified by silica gel column chromatography (benzene : EtOAc = 5 : 1) to give the methyl ester of the aglycone (**6**, 1 mg). **6**: a colorless powder, $[\alpha]_D^{19}$ +43.3° (*c* = 0.12, $CHCl_3$). EI-MS *m/z*: 486[M]$^+$, 468, 427, 409, 391, 278, 260, 219, 207, 190. ^{1}H-NMR (pyridine-d_5) δ: 0.99, 1.07, 1.09, 1.23, 1.26, 1.26, 1.69 (each s, total 7 × Me), 3.48 (1H, dd, J = 5, 10 Hz, H-3), 3.67 (3H, s, COOMe), 3.91 (1H, dd, J = 2,6 Hz, H-22), 5.41 (1H, t, J = 3 Hz, H-12). ^{13}C-NMR (pyridine-d_5–D_2O): Table I.

Compound 3 A pale yellow powder, $[\alpha]_D^{20}$ −0.6° (*c* = 1.01, 50% MeOH). Neg. FAB-MS *m/z*: 971.484 (Calcd for $C_{48}H_{76}O_{20}-H$; 971.485), 993, 1015. ^{1}H-NMR (pyridine-d_5–D_2O) δ: 0.82, 0.86, 1.18, 1.22, 1.29, 1.30, 1.89 (each 3H, s, 7 × Me), 1.78 (3H, d, J = 6 Hz, rha Me-6), 3.24 (1H, br d, J = 8 Hz, H-3), 5.23 (1H, br s, H-12), 5.40 (1H, d, J = 7 Hz, glc UA H-1), 5.97 (1H, s, rha H-1), gal H-1: hidden by H_2O signal.

Acid Hydrolysis of 3 A solution of **3** (2 mg) in 1 N HCl–H_2O (1 ml) was treated as described for **1** to give glucuronic acid, galactose and rhamnose.

Peracetylated Methyl Ester (8) of 3 A solution of **3** (3 mg) in Ac_2O–pyridine (1 : 1, 0.5 ml) was treated in the same way as described for **1** to give the acetylated methyl ester (**8**, 1 mg). **8**: EI-MS *m/z*: 568 (aglycone molecule –H_2O), 561, 509, 449, 389, 378, 318, 273, 258, 199, 190. ^{1}H-NMR ($CDCl_3$) δ: 0.82, 0.87, 0.94, 0.96, 1.07, 1.14, 1.43 (each 3H, s, 7 × Me), 1.21 (3H, d, J = 6 Hz, rha Me-6), 1.95, 1.99 × 2, 2.02, 2.06, 2.08, 2.09, 2.11, 2.15 × 2 (each s, total 10 × Ac), 3.08 (1H, dd, J = 5, 11 Hz, H-3), 3.66 (3H, s, C-29 COOMe), 3.75 (3H, s, glc UA 6-COOMe), 3.82 (1H, dd, J = 7, 10 Hz, gal H-2), 3.85 (1H, m, gal H-5), 4.04 (1H, dd, J = 7, 9 Hz, glc UA H-2), 4.07 (1H, d, J = 9 Hz, glc UA H-5), 4.10 (3H, m, gal H_2-6, rha H-5), 4.45 (1H, d, J = 8 Hz, glc UA H-1), 4.62 (1H, d, J = 8 Hz, gal H-1), 4.92 (1H, dd, J = 3, 10 Hz, gal H-3), 4.99 (1H, s, rha H-1), 5.01 (1H, d, J = 3 Hz, H-22), 5.07 (1H, d, J = 3 Hz, rha H-2), 5.11 (2H, t, J = 9 Hz, rha H-4, glc UA H-3), 5.18 (1H, dd, J = 3, 10 Hz, rha H-3), 5.21 (1H, t, J = 9 Hz, glc UA H-4), 5.31 (1H, brs, H-12), 5.35 (1H, d, J = 3 Hz, gal H-4), 5.59 (1H, d, J = 3 Hz, H-21).

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