Halogenated Sesquiterpenes from the Marine Red Alga *Laurencia saitoi* (Rhodomelaceae)

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Four new halogenated sesquiterpenes, 10-bromo-3-chloro-2,7-epoxychamigr-9-en-8α-ol (**1**), 2,10β-dibromochamigra-2,7-dien-9α-ol (**2**), (9*S*)-2-bromo-3-chloro-6,9-epoxybisabola-7(14),10-diene (**3**), and (9*R*)-2-bromo-3-chloro-6,9-epoxybisabola-7(14),10-diene (**4**), were characterized from the marine red alga *Laurencia saitoi*. In addition, two known halosesquiterpenes, 2,10-dibromo-3-chlorochamigr-7-en-9α-ol (**5**) and isolaurenisol (**6**), were also isolated and identified. Their structures were established on the basis of extensive analysis of spectroscopic data.

Introduction. – The marine red algal species of the genus *Laurencia* (order Ceramiales, family Rhodomelaceae) have been extensively investigated and were found to be rich sources of halogenated sesquiterpenes, diterpenes, triterpenes, and nonterpenoid C_{15}-acetogenins [1]. However, only one article describing chemical constituents of *L. saitoi* has been published, revealing the presence of halogenated and nonhalogenated diterpenes of parguerane, isoparguerane, and deoxyparguerane types [2].

In our continuing investigations on the chemical constituents of Chinese marine red algal species of the Rhodomelaceae family [3–12], we examined the chemical constituents of *L. saitoi* that was collected off the coast of northern Shandong Province, P. R. China. These efforts resulted in the isolation and identification of four new halogenated sesquiterpenes including 10-bromo-3-chloro-2,7-epoxychamigr-9-en-8α-ol (**1**), 2,10β-dibromochamigra-2,7-dien-9α-ol (**2**), (9*S*)-2-bromo-3-chloro-6,9-epoxybisabola-7(14),10-diene (**3**), and (9*R*)-2-bromo-3-chloro-6,9-epoxybisabola-7(14),10-diene (**4**). Additionally, two known sesquiterpenes, 2,10-dibromo-3-chlorochamigr-7-en-9α-ol (**5**) [13] and isolaurenisol (**6**) [14], were also identified. This article describes the isolation and structure determination of compounds **1**–**6**.

Results and Discussion. – The AcOEt-soluble fraction derived from the crude extract of dried and powdered *L. saitoi* was purified by a combination of silica gel and *Sephadex LH-20* column chromatography as well as by preparative TLC to yield compounds **1**–**6** (*Fig. 1*).

Compound **1** was obtained as colorless crystals. The EI-MS spectrum exhibited a characteristic molecular-ion cluster at *m*/*z* 352/350/348 (1:4:3; M^+), indicating the presence of one Br- and one Cl-atom in **1**. The molecular formula was determined as

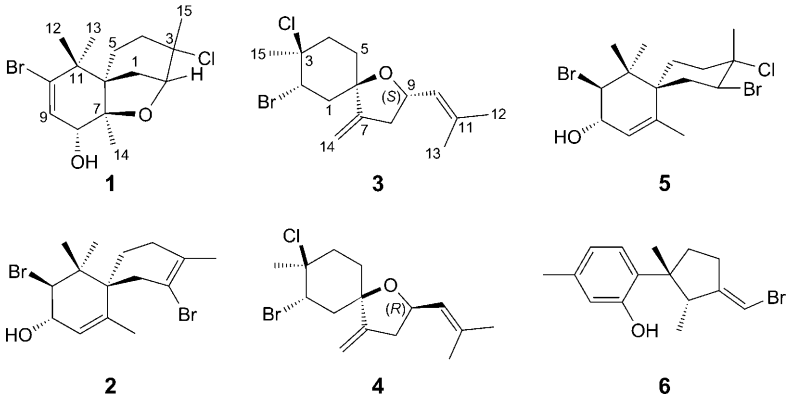

Fig. 1. *Compounds isolated from* L. saitoi

$C_{15}H_{22}BrClO_2$ on the basis of the HR-ESI-MS signal at *m/z* 373.0366 ($[M+Na]^+$, $C_{15}H_{22}{}^{81}Br^{35}ClNaO_2^+$), suggesting four degrees of unsaturation. The ^{1}H-NMR spectrum (*Table 1*) displayed four Me *singlet*s at δ(H) 1.61 (Me(15)), 1.33 (Me(14)), 1.18 (Me(12)), and 1.09 (Me(13)), two O-bearing CH groups with a broad *doublet* at δ(H) 4.34 (br. *d*, $J=7.4$, H–C(2)) and a *doublet* of *doublet*s at δ(H) 4.78 (*dd*, $J=4.7$, 1.8, H–C(8)), one olefinic *doublet* at δ(H) 5.98 (*d*, $J=1.8$, H–C(9)), and one OH *doublet* at δ(H) 3.41 (*d*, $J=4.7$, HO–C(8)). The ^{13}C-NMR (DEPT) spectrum (*Table 2*) exhibited the presence of 15 C-atoms including four Me, three CH_2, and three CH groups, and five quaternary C-atoms. Compound **1** was deduced to possess a chamigrane skeleton by analysis of its ^{1}H- and ^{13}C-NMR data. The ^{1}H,^{1}H-COSY correlations indicated the presence of three spin systems including $-CH_2-CH-$ (C(1) to C(2)), $-CH_2-CH_2-$ (C(4) to C(5)), and $-CHOH-CH=$ (C(8) to C(9)). In the HMBC spectrum, the observed correlations (*Fig. 2*) from Me(15) to C(2), C(3), and C(4), from Me(14) to C(6), C(7), and C(8), from Me(12) to C(6), C(10), C(11), and C(13), from Me(13) to C(6), C(10), C(11), and C(12), and from CH_2(5) to C(1), C(6), and C(7) established the connections of the above three spin systems. The epoxy linkage between C(2) and C(7) was established by the observed HMBC correlation from H–C(2) to C(7). The above spectral evidence established the constitutional formula for **1** (*Fig. 1*).

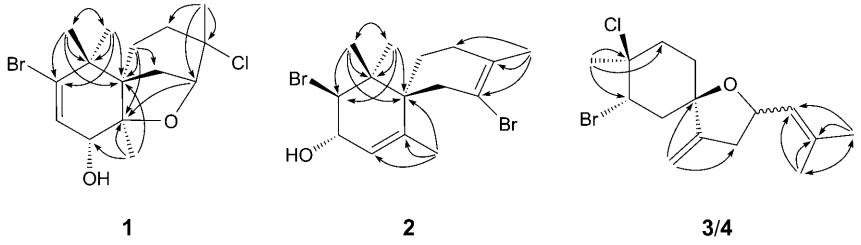

Fig. 2. *Selected HMBC for* **1**–**4**

Table 1. *^{1}H-NMR Data of* **1**–**4**. At 500 MHz, in $CDCl_3$. Assignments were corroborated by ^{1}H,^{1}H-COSY, HSQC, and HMBC experiments.

	1	**2**	**3/4**
CH_2(1)	1.72 (*d*, *J* = 12.3), 2.28 (*ddd*, *J* = 12.3, 7.4, 3.9)	2.32 (br. *d*, *J* = 18.0), 2.71 (br. *d*, *J* = 18.0)	2.08 (*dd*, *J* = 13.4, 13.1)/ 1.92 (*dd*, *J* = 13.4, 12.7), 2.28–2.32 (*m*)/2.36–2.40 (*m*)
H–C(2)	4.34 (br. *d*, *J* = 7.4)		4.69 (*dd*, *J* = 13.1, 5.0)/ 4.68 (*dd*, *J* = 12.7, 4.6)
CH_2(4)	1.93 (br. *dd*, *J* = 13.4, 6.1), 2.60 (*ddd*, *J* = 13.4, 13.4, 6.5)	2.13–2.17 (*m*)	2.20–2.24 (*m*), 2.48–2.52 (*m*)
CH_2(5)	1.57 (*ddd*, *J* = 13.4, 13.4, 6.1), 1.70–1.74 (*m*)	1.68–1.72 (*m*), 1.88–1.92 (*m*)	1.68–1.72 (*m*)/1.49–1.53 (*m*), 1.68–1.72 (*m*)/1.78–1.82 (*m*)
H–C(8) or CH_2(8)	4.78 (*dd*, *J* = 4.7, 1.8)	5.46 (br. *s*)	2.32–2.36 (*m*), 2.64 (br. *d*, *J* = 15.3)
H–C(9)	5.98 (*d*, *J* = 1.8)	4.27–4.31 (*m*)	4.58–4.63 (*m*)/4.52–4.57 (*m*)
H–C(10)		4.47 (*d*, *J* = 8.8)	5.22 (br. *d*, *J* = 8.3)/ 5.19 (br. *d*, *J* = 8.2)
Me(12)	1.18 (*s*)	0.98 (*s*)	1.72 (*s*)/1.70 (*s*)
Me(13)	1.09 (*s*)	1.13 (*s*)	1.76 (*s*)/1.75 (*s*)
Me(14) or CH_2(14)	1.33 (*s*)	1.74 (br. *s*)	4.79 (br. *s*), 4.97 (br. *s*)
Me(15)	1.61 (*s*)	1.81 (br. *s*)	1.74 (*s*)
OH	3.41 (*d*, *J* = 4.7)	2.31 (*d*, *J* = 3.6)	

Table 2. *^{13}C-NMR Data of* **1**–**4**. At 125 MHz, in $CDCl_3$. Assignments were corroborated by ^{1}H,^{1}H-COSY, HSQC, and HMBC experiments.

	1	**2**	**3/4**
CH_2(1)	33.1 (*t*)	40.6 (*t*)	47.23/44.64 (*t*)
H–C(2) or C(2)	84.6 (*d*)	119.0 (*s*)	60.33/60.20 (*d*)
C(3)	73.1 (*s*)	132.7 (*s*)	71.08 (*s*)
CH_2(4)	38.0 (*t*)	31.1 (*t*)	38.96/38.84 (*t*)
CH_2(5)	30.5 (*t*)	30.8 (*t*)	35.60/32.86 (*t*)
C(6)	49.9 (*s*)	47.7 (*s*)	83.12 (*s*)
C(7)	87.1 (*s*)	143.0 (*s*)	154.33 (*s*)
H–C(8) or CH_2(8)	71.3 (*d*)	123.8 (*d*)	39.59/39.54 (*t*)
H–C(9)	132.8 (*d*)	73.4 (*d*)	72.99/72.87 (*d*)
C(10) or H–C(10)	134.9 (*s*)	72.0 (*d*)	125.11 (*d*)
C(11)	45.3 (*s*)	44.3 (*s*)	137.16/136.99 (*s*)
Me(12)	22.8 (*q*)	17.7 (*q*)	18.41/18.34 (*q*)
Me(13)	28.6 (*q*)	25.2 (*q*)	25.84 (*q*)
Me(14) or CH_2(14)	22.5 (*q*)	22.8 (*q*)	104.72/104.66 (*t*)
Me(15)	27.0 (*q*)	22.9 (*q*)	23.49/23.43 (*q*)

The relative configuration of **1** was determined by a NOESY experiment. The observed NOESY correlation between Me(14) and CH_2(5) indicated their *cis*-orientation, while the correlation between H–C(2) and H–C(8) also indicated their *cis*-orientation. The observed NOESY correlation between Me(15) and Me(12)

indicated their *cis*-orientation. In contrast, no NOESY correlation was observed between H–C(2) and Me(14), indicating the *trans*-orientation for them. The above spectral evidence established the relative configuration and resulted in the assignment of the structure of **1** to be 10-bromo-3-chloro-2,7-epoxychamigr-9-en-8α-ol.

Compound **2** was obtained as a colorless oil. The EI-MS spectrum exhibited a characteristic molecular-ion cluster at *m/z* 380/378/376 (1:2:1; M^+), indicating the presence of two Br-atoms in **2**. The HR-FAB-MS signal at *m/z* 377.0133 ($[M+H]^+$, $C_{15}H_{23}{}^{79}Br_2O^+$) established its molecular formula to be $C_{15}H_{22}Br_2O$, suggesting four degrees of unsaturation. The ^{1}H-NMR spectrum (*Table 1*) revealed the presence of four Me *singlet*s at δ(H) 1.81 (Me(15)), 1.74 (Me(14)), 1.13 (Me(13)), and 0.98 (Me(12)), one O-bearing CH group *multiplet* at δ(H) 4.27–4.31 (H–C(9)), one O-/halogen-bearing CH group *doublet* at δ(H) 4.47 (*d*, $J=8.8$, H–C(10)), one broad *singlet* assignable to an olefinic H-atom at δ(H) 5.46 (br. *s*, H–C(8)), and one OH *doublet* at δ(H) 2.31 (*d*, $J=3.6$, HO–C(9)). The ^{13}C-NMR (DEPT) spectrum (*Table 2*) revealed the presence of four Me, three CH_2, three CH, and five quaternary C-atoms. Detailed examination of the NMR spectral data and comparison with those reported for 2,10-dibromo-3-chlorochamigr-7-en-9α-ol (**5**) [13] revealed that the structures of these two compounds are very similar. However, in the ^{13}C-NMR spectrum, the halogen-bearing CH and quaternary C-atom signals at δ(C) 62.4 for C(2) and 70.6 for C(3) in **5** were replaced by two significantly downfield shifted olefinic quaternary C-atom signals at δ(C) 119.0 for C(2) and 132.7 for C(3) in **2**. This observation was strongly supported by the fact that the halogen-bearing CH signal appearing at δ(H) 4.90 for H–C(2) in **5** was absent in the ^{1}H-NMR spectrum of **2**. The above NMR and MS data suggested that **2** was a derivative of **5**, arising by the loss of HCl [15][16]. The ^{1}H,^{1}H-COSY correlations from H–C(9) to H–C(8), H–C(10), and HO–C(9) confirmed the presence of a spin system =CH(8)–CH(9)OH–CH(10)–. In the HMBC spectrum, the observed correlations (*Fig. 2*) from Me(12) to C(6), C(10), C(11), and C(13), from Me(13) to C(6), C(10), C(11), and C(12), from Me(14) to C(6), C(7), and C(8), and from Me(15) to C(2), C(3), and C(4), further supported the proposed structure for **2** (*Fig. 1*).

The relative configuration of **2** was assigned by analysis of the coupling constant and by NMR data comparison with those of **5**. The H–C(9) and H–C(10) was assigned to be *trans* according to their large coupling constant ($J=8.8$). The relative configuration at C(6) was assigned to be the same as for **5** by detailed NMR data comparison (δ(C) 47.7 for **2** and δ(C) 47.9 for **5**) [13]. The above spectral evidence established the structure of **2** to be 2,10β-dibromochamigra-2,7-dien-9α-ol.

Compounds **3** and **4** were obtained as a colorless oily mixture in a 1:1 ratio. They displayed one spot on TLC and attempts to separate them by column chromatography or by preparative TLC failed with various solvent systems. By detailed NMR spectral data analyses, the structures of **3** and **4** were determined to be C(9) epimers of 2-bromo-3-chloro-6,9-epoxybisabola-7(14),10-diene [17]. The EI-MS showed a characteristic molecular-ion cluster at *m/z* 336/334/332 (1:4:3; M^+), suggesting the presence of one Br- and one Cl-atom in the molecules. The molecular formula was deduced to be $C_{15}H_{22}BrClO$ by a HR-ESI-MS signal at *m/z* 355.0451 ($[M+Na]^+$, $C_{15}H_{22}{}^{79}Br^{35}ClNaO^+$), indicating four degrees of unsaturation. The ^{1}H-NMR spectrum (*Table 1*) of the mixture of **3** and **4** revealed the presence of three Me *singlet*s at δ(H)

1.76 (and 1.75, Me(13)), 1.74 (Me(15)), and 1.72 (and 1.70, Me(12)), two O-/halogen-bearing CH groups with one *doublet* of *doublet*s at δ(H) 4.69 (and 4.68, H−C(2)) and one *multiplet* at δ(H) 4.58–4.63 (and 4.52–4.57, H−C(9)), one broad *doublet* assignable to an olefinic H-atom at δ(H) 5.22 (and 5.19, H−C(10)), and a pair of broad *singlet*s characteristic for terminal olefinic H-atoms at δ(H) 4.79 and 4.97 (CH_2(14)). The ^{13}C-NMR (DEPT) spectrum (*Table 2*) of the mixture of **3** and **4** revealed the presence of three Me, five CH_2, three CH, and four quaternary C-atoms. A detailed MS and NMR data comparison with those reported for (9*S* (or 9*R*))-2-chloro-3-bromo-6,9-epoxy-7(14),10-bisaboladiene, which were derived from the metabolite of *L. scoparia* [17], revealed that **3** and **4** differed from it mainly at C(2) and C(3). The Cl-bearing CH group signal at δ(C) 67.5 (and 67.4) for C(2) and the signal for a Br-bearing quaternary C-atom at δ(C) 68.17 (and 68.15) for C(3) in (9*S* (or 9*R*))-2-chloro-3-bromo-6,9-epoxybisabola-7(14),10-diene were replaced by the Br-bearing CH group signal at δ(C) 60.33 (and 60.20) for C(2) and the signal for a Cl-bearing quaternary C-atom at δ(C) 71.08 for C(3) in **3**/**4**. However, the ^{13}C-NMR data of C(2) and C(3) in **3**/**4** were respectively similar to those in 2,10-dibromo-3-chloro-β-chamigrene (with C(2) at δ(C) 60.3 and C(3) at δ(C) 70.7) indicating that C(2) and C(3) in **3**/**4** are bound to a Br- and a Cl-atom, respectively [18]. The ^{1}H,^{1}H-COSY correlations from CH_2(1) to H−C(2), from CH_2(4) to CH_2(5), and from H−C(9) to CH_2(8) and H−C(10), as well as the observed HMBC correlations (*Fig. 2*) from Me(12) to C(10), C(11), and C(13), from Me(13) to C(10), C(11), and C(12), from CH_2(14) to C(6) and C(8), and from Me(15) to C(2), C(3), and C(4), further confirmed the constitutional formula of **3**/**4**.

The relative configuration of **3**/**4** was determined by analysis of NMR data and comparison with literature reports [17][18]. The chemical shifts for H−C(2) at δ(H) 4.69 (*dd*, J = 13.1, 5.0; and 4.68 (*dd*, J = 12.7, 4.6)) and for C(2) at δ(C) 60.33 (and 60.20) as well as the C(3) signal observed at δ(C) 71.08 in **3**/**4** were identical with related signals observed in 2,10-dibromo-3-chloro-β-chamigrene, suggesting the relative configurations at C(2) and C(3) were the same as those for 2,10-dibromo-3-chloro-β-chamigrene [18]. The relative configuration at C(6) and C(9) were assigned to be the same as for (9*S* (or 9*R*))-2-chloro-3-bromo-6,9-epoxybisabola-7(14),10-diene by their identical NMR data [17]. The above spectral evidence established the structures of **3**/**4** to be (9*S* (or 9*R*))-2-bromo-3-chloro-6,9-epoxybisabola-7(14),10-diene.

Halogenated sesquiterpenes including chamigrane, bisabolane, laurane, snyderane, and brasilane classes were reported to be the main metabolites from the genus *Laurencia*, and chamigrane-type sesquiterpenes along with some unique rearranged derivatives occurred prevalently [1]. However, the sesquiterpenes with 2,7-epoxychamigrane skeleton such as **1** were less reported. To the best of our knowledge, up to date only two compounds of 2,7-epoxychamigrane class [19][20] were reported from the *Laurencia* species. The isolation of chamigrene derivatives **1** and **2** and bisabolene derivatives **3** and **4** was a new addition to the molecular diversity of sesquiterpenes from the genus *Laurencia*.

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Experimental Part

General. Column chromatography (CC): commercial silica gel (SiO_2; 200–300 mesh; *Qingdao Haiyang Chemical Group Co.*) and *Sephadex LH-20* (*Sigma*). TLC: precoated silica gel plates (*GF-254*; *Qingdao Haiyang Chemical Group Co.*). M.p.: *SGW X-4* micro-melting-point apparatus; uncorrected. Optical rotation: *Atago-Polax-L* polarimeter. NMR Spectra: *Bruker-Avance-500* spectrometer; at 500 (^{1}H) and 125 MHz (^{13}C); δ in ppm, J in Hz. Low- and high-resolution MS: *VG Autospec 3000* spectrometer; in *m/z* (rel. %).

Algal Material. The marine red alga *Laurencia saitoi* PERESTENKO was collected off the coast of Rongcheng of P. R. China in August 2006, and was identified by Dr. *L.-P. Ding* at the Institute of Oceanology, Chinese Academy of Sciences. A voucher specimen (HZ0608) has been deposited with the Key Laboratory of Experimental Marine Biology of the Institute of Oceanology, Chinese Academy of Sciences.

Extraction and Isolation. The dried and powdered alga *L. saitoi* (200 g) was extracted with $CHCl_3$/MeOH 1:1. After solvent removal, the residue was further extracted with 95% aq. EtOH. The concentrated extracts were combined and partitioned between H_2O and AcOEt. The AcOEt-soluble fraction was chromatographed by CC (SiO_2; petroleum ether (PE)/AcOEt, gradient): *Fractions I–VI*. *Fr. II* (eluted with PE/AcOEt 30:1) was further purified by CC (1. *Sephadex LH-20*; $CHCl_3$/MeOH 2:1; 2. SiO_2; PE/AcOEt 15:1) and prep. TLC (PE/AcOEt 5:1) to afford **2** (2.9 mg), **3**/**4** (5.2 mg, 1:1), and **6** (5.9 mg). *Fr. III* (eluted with PE/AcOEt 10:1) was also purified by CC (1. *Sephadex LH-20*; $CHCl_3$/MeOH 2:1; 2. SiO_2; PE/AcOEt 10:1) to obtain **5** (17.4 mg). *Fr. IV* (eluted with PE/AcOEt 5:1) was also separated by CC (1. SiO_2, PE/AcOEt 3:1; 2. *Sephadex LH-20*; $CHCl_3$/MeOH 1:1) and prep. TLC ($CHCl_3$/AcOEt, 5:1) to yield **1** (8.5 mg).

10-Bromo-3-chloro-2,7-epoxychamigr-9-en-8α-ol (= *(5a*R,*9*R,*9a*R*)-7-Bromo-3-chloro-2,3,4,5,9,9a-hexahydro-3,6,6,9a-tetramethyl-6*H*-2,5a-methano-1-benzoxepin-9-ol*; **1**). Colorless crystals. M.p. 204–206°. $[\alpha]_D^{21} = -58.5$ ($c = 0.13$, $CHCl_3$). ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. EI-MS: 352 (1), 350 (4), 348 (3, M^+), 321 (14), 319 (33), 317 (22), 269 (33), 172 (78), 157 (45), 137 (87), 121 (100). HR-ESI-MS: 373.0366 ($[M+Na]^+$, $C_{15}H_{22}{}^{81}Br^{35}ClNaO_2^+$; calc. 373.0369).

2,10β-Dibromochamigra-2,7-dien-9α-ol (= *(3*S,*4*S*)-4,8-Dibromo-1,5,5,9-tetramethylspiro[5.5]undeca-1,8-dien-3-ol*; **2**). Colorless oil. $[\alpha]_D^{21} = +3.1$ ($c = 0.13$, $CHCl_3$). ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. EI-MS: 380 (1), 378 (2), 376 (1, M^+), 363 (5), 361 (10), 359 (5), 282 (13), 281 (19), 280 (21), 279 (23), 278 (10), 199 (47), 187 (42), 157 (41), 133 (100), 119 (61). HR-FAB-MS: 377.0133 ($[M+H]^+$, $C_{15}H_{23}{}^{79}Br_2O^+$; calc. 377.0116).

*(9*S *(or 9*R*))-2-Bromo-3-chloro-6,9-epoxybisabola-7(14),10-diene* (= *(5*R,*7*S,*8*S*)-7-Bromo-8-chloro-8-methyl-4-methylidene-2-(2-methylprop-1-en-1-yl)-1-oxaspiro[4.5]decane*; **3**/**4**). Colorless oil. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. EI-MS: 336 (2), 334 (8), 332 (6, M^+), 319 (1), 299 (2), 297 (1), 278 (4), 253 (50), 217 (34), 197 (21), 169 (19), 133 (42), 85 (100). HR-ESI-MS: 355.0451 ($[M+Na]^+$, $C_{15}H_{22}{}^{79}Br^{35}ClNaO^+$; calc. 355.0440).

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