Bitter Diterpenoids from *Rabdosia shikokiana* (Makino) Hara

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Three new bitter diterpenoids, shikokianoic acid, shikokianal acetate, and 16,17-epoxyshikokianal acetate, have been isolated from the leaves of *Rabdosia shikokiana* (Makino) Hara. Their structures were established on the basis of spectral and chemical evidence.

In the previous paper,[1] we reported the structures of three *ent*-kaurenoids, rabdosianin A, B, and C, isolated from *Rabdosia shikokiana* (Makino) Hara. Our continuing search for bitter principles in this plant has now led to the isolation of three new diterpenoids, designated as shikokianoic acid, shikokianal, and 16,17-epoxyshikokianal, the last two as their acetates. The present paper deals with the structural elucidation of these new compounds.

Shikokianoic acid (**1**), $C_{24}H_{32}O_9$, mp 134—135 °C, $[\alpha]_D^{20}$ +3° (*c* 0.35, $CHCl_3$), was isolated as colorless flakes in 0.005% yield from the ether extract of the dried leaves by extensive column chromatography. It showed IR absorptions indicative of hydroxyl (3620, 3520) and carboxyl (3200—2500, and 1702 cm^{-1}) groups, and formed a triacetate (**2**), $C_{26}H_{34}O_{10}$, mp 144—145 °C, on acetylation with pyridine–acetic anhydride and a methyl ester (**3**), $C_{25}H_{34}O_9$, mp 224—226 °C, by treatment with diazomethane. The 400 MHz ^1H NMR spectrum showed signals due to two tertiary methyl groups at δ 1.00 and 1.22, two acetyl groups at δ 2.02 and 2.22, one methine proton on an oxygenated carbon atom at δ 3.94 (ddd, J=11.3, 9.2, and 8.4 Hz), one oxygenated methyl group at δ 4.62 and 5.00 (each d, J=12.7 Hz), two methine protons attached to carbon atoms bearing an acetoxyl group at δ 5.13 (dd, J=8.1 and 8.1 Hz) and 5.54 (dd, J=2.7 and 2.5 Hz), and one terminal methylene group at δ 5.00 (dd, J=2.5 and 0.8 Hz) and 5.21 (dd, J=2.7 and 0.8 Hz). In addition, extensive ^1H NMDR studies, summarized in Table 1, revealed the presence of the partial structures (**A**) and (**B**), the latter showing the following long-range couplings: $J_{H_{13},H_{17a}}=J_{H_{13},H_{17b}}=0.8$ Hz, $J_{H_{15},H_{17a}}=2.5$ Hz, and

Table 1. ^1H NMR spectra at 400 MHz of shikokianoic acid (**1**), shikokianal acetate (**8**), and 16,17-epoxyshikokianal acetate (**10**)[a]

	1	**8**	**10**
H_1	5.13 (dd, 8.1, 8.1)	4.73 (dd, 11.0, 4.3)	4.74 (dd, 11.0, 5.0)
$H_{2\alpha}$	*ca.* 1.90 (m)	1.88 (m)	*ca.* 1.85 (m)
$H_{2\beta}$	*ca.* 1.90 (m)	1.91 (m)	*ca.* 1.95 (m)
$H_{3\alpha}$	1.59 (m)	*ca.* 1.55 (m)	*ca.* 1.53 (m)
$H_{3\beta}$	1.52 (m)	1.49 (m)	*ca.* 1.53 (m)
H_5	3.67 (s)	3.19 (d, 2.7)	3.15 (d, 2.4)
H_6		9.99 (d, 2.7)	9.94 (d, 2.4)
H_9	2.49 (d, 11.3)	2.99 (d, 10.8)	3.05 (d, 10.3)
H_{11}	3.94 (ddd, 11.3, 9.2, 8.4)	4.95 (ddd, 10.8, 7.9, 7.9)	5.01 (ddd, 10.3, 10.3, 8.4)
$H_{12\alpha}$	2.63 (ddd, 12.9, 8.4, 8.4)	2.82 (ddd, 12.7, 8.7, 7.9)	2.58 (dd, 14.3, 10.3)
$H_{12\beta}$	1.34 (dd, 12.9, 9.2)	1.27 (ddd, 12.7, 7.9, 1.3)	1.34 (dd, 14.3, 8.4)
H_{13}	2.77 (dddd, 8.4, 5.4, 0.8, 0.8)	1.75 (dddd, 8.7, 4.9, 1.7, 1.4)	2.58 (m)
$H_{14\alpha}$	1.61 (d, 12.9)	1.60 (d, 11.9)	1.73 (d, 13.0)
$H_{14\beta}$	2.17 (dd, 12.9, 5.4)	2.28 (ddd, 11.9, 4.9, 1.3)	2.58 (m)
H_{15}	5.54 (dd, 2.7, 2.5)	5.60 (dd, 3.0, 2.7)	5.28 (s)
H_{17a}	5.00 (dd, 2.5, 0.8)	5.01 (dd, 2.7, 1.7)	2.77 (d, 4.6)
H_{17b}	5.21 (dd, 2.7, 0.8)	5.18 (dd, 3.0, 1.4)	2.93 (d, 4.6)
H_{20a}	4.62 (d, 12.7)	4.82 (d, 12.8)	4.70 (d, 12.7)
H_{20b}	5.00 (d, 12.7)	5.01 (d, 12.8)	4.86 (d, 12.7)
Me_{18}	1.00 (s)	1.09 (s)	1.06 (s)
Me_{19}	1.22 (s)	1.12 (s)	1.15 (s)
OAc	2.02, 2.22	2.01, 2.08, 2.30	2.03, 2.10, 2.29

a) The spectra were determined at 25 °C in $CDCl_3$ solutions with TMS as an internal standard. Multiplicity and J values (in Hz) are in parentheses.

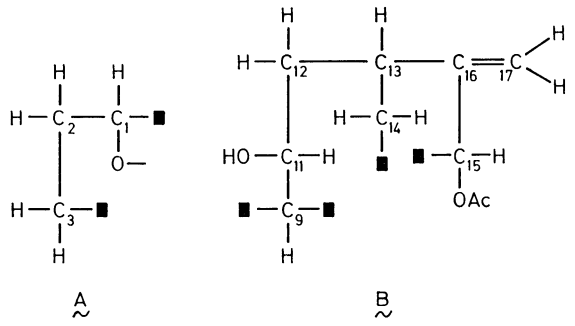
Table 2. ^{13}C chemical shifts of shikokianoic acid (**1**), shikokianal acetate (**8**), and 16,17-epoxyshikokianal acetate (**10**)[a]

Carbon	1	8	10
1	75.7	75.5	75.4
2	24.2	24.3	24.2
3	39.5	40.0	40.2
4	34.3	35.0	34.8
5	57.6	61.8	61.9
6	173.9[b]	202.7	203.1
7	173.4[b]	172.3	172.1
8	51.2	51.3	52.3
9	44.3	40.9	40.6
10	42.5	43.8	43.4
11	65.7	68.2	68.0
12	44.3	40.4	40.6
13	35.6	35.4	35.8
14	31.0	32.3	32.8
15	82.2	82.2	81.9
16	153.6	152.7	70.5
17	111.3	111.3	48.8
18	23.6	24.1	24.0
19	33.6	33.7	33.7
20	66.9	66.3	66.1
$\underline{C}OCH_3$	170.5	169.9	169.9
	170.3	169.7	169.7
		168.8	169.0
$CO\underline{C}H_3$	21.4	21.3(×2)	21.5
	20.9	20.8	21.4
			20.6

a) The spectra were measured at 100.61 MHz in $CDCl_3$ solutions and the shifts are given in ppm (δ) relative to the internal TMS. Assignments were made by off-resonance and selective proton-noise decoupling techniques. b) These assignments may be interchanged.

$J_{H_{15},H_{17b}}$=2.7 Hz. The ^{13}C NMR data (Table 2) showed the presence of one lactonic and one carboxylic carbon atoms (δ 173.4 and 173.9) along with four methylene groups, three methine groups, three oxygen-bearing methine groups, and three quaternary carbon atoms.

The spectral data and the analogy with the congeners isolated from *Rabdosia* species[1,2] suggested a B-seco-*ent*-kaurene type structure for shikokianoic acid, in which the partial structure (**A**) would form the A-ring and (**B**) the C- and D-rings. In the ^1H NMR spectrum of **3**, the chemical shifts of 18- and 19-methyl signals (δ 0.91 and 1.19) and the splitting pattern of the signal due to the methine proton on an oxygenated carbon atom in A-ring (dd, J=9.1 and 6.7 Hz) revealed that the location of the oxy linkage in A-ring is $C_{1\alpha}$ in analogy with isodonal (**4**).[2a,3] The β-configuration of the secondary hydroxyl group at C_{11} in **1** was evident from the coupling pattern and the large J values of H_{11} signal (ddd, $J_{H_9,H_{11}}$=11.3 Hz, $J_{H_{11},H_{12\alpha}}$=8.4 Hz, and $J_{H_{11},H_{12\beta}}$=9.2 Hz). The corresponding signal of shikodonin (**5**),[2b] in which the hydroxyl group at C_{11} is α-oriented, appeared as a doublet of doublets ($J_{H_9,H_{11}}$=6.0 Hz and $J_{H_{11},H_{12\alpha}}$=15.0 Hz).

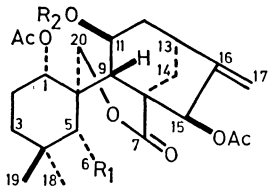


A B

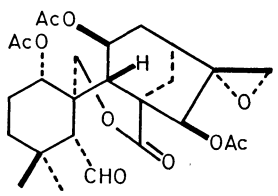
The treatment of **2** with diazomethane gave a methyl ester (**6**), $C_{27}H_{36}O_{10}$, mp 216—218 °C. The catalytic hydrogenation of **6** yielded a dihydro compound (**7**), $C_{27}H_{38}O_{10}$, mp 245—248 °C, as the major product. It is well known that the hydrogenation of the C_{16} double bond in such a skeleton occurs from the less hindered α-side and, hence, the newly introduced secondary methyl group must be β-oriented.[4] The ^1H NMR spectrum of **7** showed a signal of H_{15} as a doublet at δ 5.08 (J=10.5 Hz), the large J value of which defined the configuration of the acetoxyl group at C_{15} as β.[4] Of the positions of the carboxyl group in **1**, C_6 and C_7, possible from biogenetic considerations, the latter is rejected by the IR spectrum of **1** which did not show the presence of a γ-lactone but of a δ-lactone (1738 cm^{-1}). If the carboxyl group was settled on C_7 position, a γ-lactone should be formed at C_6–C_1 or C_6–C_{20}.

The position of closure of the lactone ring remained to be assigned and this was done by the scrutiny of ^1H NMR data and the study of the nuclear Overhauser effect (NOE). The preceding discussion limited this to C_7–C_1 and C_7–C_{20}. The signals of H_1 and H_5 in **2** were shifted upfield, as compared with those of **1**, and the degree of the shift of both signals was identical [δ(**2**)−δ(**1**)=−0.47 ppm]. This fact suggested that the hydroxyl group in **1** is situated at equal distances from both H_1 and H_5. In addition, irradiation at the resonance of H_{11} under NOE condition did not lead to a significant change in signal intensity of H_5, while irradiation at the resonance of H_1 produced a clear and reproducible enhancement of the intensity of H_{11} (11%) and H_5 (4%) signals. This fact revealed that H_{11} is disposed across H_1 from H_5. These observations, combined with the examination of the model, can be satisfied only by the closure of the lactone ring at C_7–C_{20}. From the evidence outlined above, we proposed the structure **1** for shikokianoic acid.

Shikokianal acetate (**8**), $C_{26}H_{34}O_9$, mp 192—194 °C, $[\alpha]_D^{20}$ +89° (*c* 0.26, $CHCl_3$), was isolated in 0.021% as white needles by the acetylation of a crude fraction and exhibited spectral data quite similar to those of **1**, except for the following observations. The IR spectrum did not show the presence of the hydroxyl and carboxyl groups present in **1** and, instead, showed the presence of a formyl group at 2740 and 1718 cm^{-1}. The ^1H NMR spectrum contained the signals of three acetoxyl groups, one more than those of **1**, and a grouping –CH–CHO [δ 3.19 and 9.99 (each d, J=



1 R_1 = COOH, R_2 = H
2 R_1 = COOH, R_2 = Ac
3 R_1 = COOMe, R_2 = H
6 R_1 = COOMe, R_2 = Ac
8 R_1 = CHO, R_2 = Ac



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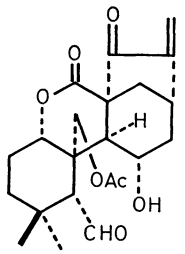

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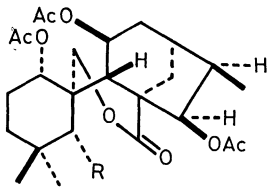
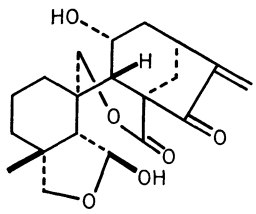


7 R = COOMe
9 R = CHO



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2.7 Hz)], the latter suggesting the location of the formyl group at C_6.[2a] These facts and the pertinent ^{13}C NMR data (Table 2) suggest that **8** has a structure close to that of **1**, in which the carboxyl and hydroxyl groups in **1** are displaced by the formyl and acetoxyl groups, respectively. This was confirmed by the chemical correlation of **8** with **1**. The catalytic hydrogenation of **8** gave a dihydro compound (**9**), $C_{26}H_{36}O_9$, mp 210—212 °C. The oxidation of **9** with Jones' reagent, followed by methylation with diazomethane, yielded a methyl ester (**7**), which was found to be identical with the compound derived from **1** as described above. Consequently, shikokianal acetate must be represented by structure **8**.

16,17-Epoxyshikokianal acetate (**10**), $C_{26}H_{34}O_{10}$, mp 205—206.5 °C, $[\alpha]_D^{20}$ +66° (*c* 0.32, $CHCl_3$), was isolated in 0.002% yield as colorless flakes by the acetylation of a crude fraction near shikokianal, the natural precursor of **8**. The spectral data suggested that the relationship of **8** to **10** was that of a olefin to the corresponding epoxide. In particular, the ^1H NMR spectrum of **10** contained signals due to a methylene group in an epoxide ring at δ 2.77 and 2.93 (each d, J=4.6 Hz) and lacked signals of an exocyclic methylene group, while the ^{13}C NMR spectrum contained two signals attributable to an epoxide moiety at δ 70.5 (s) and 48.8 (t). The structure of **10** was confirmed by its correlation with **8**. Thus, the treatment of **8** with *m*-chloroperbenzoic acid gave an epoxide, which was identical with **10** in all respects. This conversion also determines the configuration at C_{16} in **10**. Since the epoxidation of C_{16} double bond in such a compound is assumed to occur on the less hindered side of the molecule, the introduced oxygen atom must be α-oriented. Therefore, structure **10** is assigned to 16,17-epoxyshikokianal acetate. **10** is the first compound of *Rabdosia* diterpenoids which has an epoxide functionality at C_{16}–C_{17}.

Experimental

For general experimental details see Ref. 1.

Isolation. The ether extract (210 g)[1] of the dried leaves of *Rabdosia shikokiana* (Makino) Hara was subjected to chromatography over silicic acid (1.50 kg) eluting with $CHCl_3$–MeOH mixtures, with MeOH increasing from 0 to 10%. Elution with 5% MeOH in $CHCl_3$ gave a fraction (26.7 g) which was rechromatographed over silicic acid (900 g), using 50% ethyl acetate in petroleum ether, to yield a mixture of shikokianal and 16,17-epoxyshikokianal (7.10 g), and a fraction of shikokianoic acid (**1**) (718 mg). The former mixture was treated with acetic anhydride (30 ml) and pyridine (30 ml) at room temperature for 4 d and then worked up in the usual way. The resulting precipitates (3.10 g) were chromatographed over silicic acid (100 g), with ether as eluent, to give shikokianal acetate (**8**) (1.15 g) and 16,17-epoxyshikokianal acetate (**10**) (285 mg).

Shikokianoic Acid (1). The crude fraction was recrystallized from petroleum ether–ethyl acetate to give colorless flakes (262 mg), mp 134—135 °C, $[\alpha]_D^{20}$ +3° (*c* 0.35, $CHCl_3$); IR (nujol) 3620, 3520, 3200—2500, 1740, 1702, 1620, 1240, and 898 cm^{-1}; ^1H NMR (see Table 1); ^{13}C NMR (see Table 2); MS *m/e* 464 (M^+), 446 (M^+-H_2O), 422, 404 (M^+—AcOH), 386 (M^+-H_2O–AcOH), 362, and 344 (M^+—2AcOH). Found: C, 59.53; H, 6.99%. Calcd for $C_{24}H_{32}O_9\cdot H_2O$: C, 59.74; H, 7.10%.

Shikokianal Acetate (8). The crude material was recrystallized from EtOH to yield white needles (970 mg), mp 192—194 °C, $[\alpha]_D^{20}$ +89° (*c* 0.26, $CHCl_3$); IR (Nujol) 2740, 1760, 1740, 1718, 1660, 1240, and 915 cm^{-1}; ^1H NMR (see Table 1); ^{13}C NMR (see Table 2); MS *m/e* 490 (M^+), 448, 430 (M^+—AcOH), 388, 374, 370 (M^+—2AcOH), 360, 346, 328, 310 (M^+—3AcOH), and 300. Found: C, 63.33; H, 6.94%. Calcd for $C_{26}H_{34}O_9$: C, 63.66; H, 6.99%.

16,17-Epoxyshikokianal Acetate (10). The crude substance was recrystallized from ether-CH_2Cl_2 to afford colorless flakes (186 mg), mp 205—206.5 °C, $[\alpha]_D^{20}$ +66° (*c* 0.32, $CHCl_3$); IR (Nujol) 2755, 1745, 1730, 1720, 1230, and 908 cm^{-1}; ^1H NMR (see Table 1); ^{13}C NMR (see Table 2). Found: C, 61.46; H, 6.68%. Calcd for $C_{26}H_{34}O_{10}$: C, 61.65; H, 6.77%.

Acetylation of 1. A solution of **1** (30 mg) in acetic anhydride (1 ml) and pyridine (1 ml) was allowed to stand at room temperature for 2 d and then worked up in the usual way to give white precipitates (27 mg) which were subsequently recrystallized from ether–petroleum ether to yield a triacetate (**2**) as colorless needles (20 mg), mp 144—145 °C; IR (Nujol) 3200—2500, 1750, 1720, and 1220 cm^{-1}; ^1H NMR δ 1.03 and 1.16 (3H each, s, 18- and 19-Me), 2.04, 2.11, and 2.24 (3H each, s, 3Ac), 2.74 (1H, d, J=11.6 Hz, H_9), 3.20 (1H, s, H_5), 4.66 (1H, dd, J=11.0 and 4.3 Hz, H_1), 4.88 (1H, ddd, J=11.6, 8.5, and 8.5 Hz, H_{11}), 4.90 and 4.94 (1H each, d, J=12.8 Hz, H_{20}), 5.00 (1H, dd, J=2.4 and 1.2 Hz, H_{17a}), 5.21 (1H, dd, J=2.8 and 1.2 Hz, H_{17b}), and 5.58 (1H, dd, J=2.8 and 2.4 Hz, H_{15}). Found: C, 59.84; H, 6.81%. Calcd for $C_{26}H_{34}O_{10}\cdot 3/4H_2O$: C, 60.05; H, 6.88%.

Methylation of ***1***. A solution of **1** (60 mg) in ether (3 ml) was treated with ethereal diazomethane solution in the usual manner and the residue was recrystallized from ether–petroleum ether to give a methyl ester (**3**) as colorless plates (42 mg), mp 224—226 °C; IR ($CHCl_3$) 3580, 1735, 1220, and 902 cm^{-1}; ^1H NMR δ 0.91 and 1.19 (3H each, s, 18- and 19-Me), 2.02 and 2.27 (3H each, s, 2Ac), 2.22 (1H, dd, J=11.6 and 1.2 Hz, H_9), 3.72 (3H, s, OMe), 3.73 (1H, s, H_5), 3.84 (1H, ddd, J=11.6, 9.5, and 7.9 Hz, H_{11}), 4.69 (1H, dd, J=12.8 and 1.2 Hz, H_{20a}), 4.96 (1H, br s, H_{17a}), 4.98 (1H, d, J=12.8 Hz, H_{20b}), 5.14 (1H, dd, J=2.8 and 1.2 Hz, H_{17b}), 5.16 (1H, dd, J=9.1 and 6.7 Hz, H_1), and 5.54 (1H, dd, J=2.8 and 2.4 Hz, H_{15}). Found: C, 62.82; H, 7.19%. Calcd for $C_{25}H_{34}O_9$: C, 62.75; H, 7.16%.

Methylation of ***2***. A solution of **2** (35 mg) in ether (2 ml) was treated with ethereal diazomethane solution as described above and the product was recrystallized from ether–petroleum ether to yield a methyl ester (**6**) as colorless plates (34 mg), mp 216—218 °C; IR (Nujol) 1755, 1725, 1220, and 910 cm^{-1}. Found: C, 62.37; H, 6.82%. Calcd for $C_{27}H_{36}O_{10}$: C, 62.29; H, 6.97%.

Hydrogenation of ***6***. A mixture of **6** (34 mg) and 10% Pd–C (30 mg) in EtOH (3 ml) was stirred under a hydrogen atmosphere at room temperature for 12 h. The catalyst was removed by filtration and the filtrate was evaporated. The residue was recrystallized from ether–petroleum ether to give a dihydro compound (**7**) as white needles (26 mg), mp 245—248 °C; IR (Nujol) 1745, 1730, and 1225 cm^{-1}; ^1H NMR δ 0.83 (3H, d, J=7.6 Hz, 17-Me), 0.93 and 1.15 (3H each, s, 18- and 19-Me), 2.02, 2.13 ,and 2.25 (3H each, s, 3Ac), 2.60 (1H, d, J=11.9 Hz, H_9), 2.69 (1H, ddq, J= 10.5, 7.6, and 7.3 Hz, H_{16}), 3.19 (1H, s, H_5), 3.75 (3H, s, OMe), 4.64 (1H, dd, J=10.8 and 4.3 Hz, H_1), 4.82 (1H, ddd, J=11.9, 8.9, and 7.8 Hz, H_{11}), 4.93 and 5.01 (1H each, d, J=13.0 Hz, H_{20}), and 5.08 (1H, d, J=10.5 Hz, H_{15}). Found: C, 62.06; H, 7.40%. Calcd for $C_{27}H_{38}O_{10}$: C, 62.05; H, 7.33%.

Hydrogenation of ***8***. A mixture of **8** (52 mg) and 10% Pd–C (50 mg) in EtOH (5 ml) was treated under a hydrogen atmosphere as described above and the residue was recrystallized from EtOH to afford a dihydro compound (**9**) as colorless plates (35 mg), mp 210—212 °C; IR (Nujol) 1755, 1740, 1725, 1715, and 1225 cm^{-1}; ^1H NMR δ 0.83 (3H, d, J=7.5 Hz, 17-Me), 1.07 and 1.09 (3H each, s, 18- and 19-Me), 1.95, 2.07, and 2.21 (3H each, s, 3Ac), 5.07 (1H, d, J=10.2 Hz, H_{15}), and 9.93 (1H, d, J=2.2 Hz, H_6). Found: C, 63.32; H, 7.26%. Calcd for $C_{26}H_{36}O_9$: C, 63.40; H, 7.37%.

Conversion of ***9*** *into* ***7***. To a solution of **9** (30 mg) in acetone (2 ml) were added two drops of Jones' reagent with ice cooling. The mixture was stirred for 5 h at 0 °C, then worked up by dilution with water (20 ml), and extracted with ethyl acetate. The organic layer was washed with water, dried over Na_2SO_4, and evaporated to dryness. The amorphous residue was dissolved in ether (3 ml) and treated with ethereal diazomethane solution as described above. The product was recrystallized from ether–petroleum ether to give a methyl ester (18 mg) which was identified by mixed mp, IR, and ^1H NMR comparison with **7**.

Epoxidation of ***8***. A mixture of **8** (100 mg) and *m*-$ClC_6H_4CO_3H$ (40 mg) in dichloromethane (3 ml) was stirred at room temperature for 42 h under nitrogen atmosphere. The reaction mixture was worked up in the usual way and the product was chromatographed over silicic acid (8 g) with ether as eluent to yield an epoxide (46 mg) which was found to be identical with **10** in all respects.

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