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NEW SESQUITERPENE ARYL ESTERS FROM *ARMILLARIA MELLEA*

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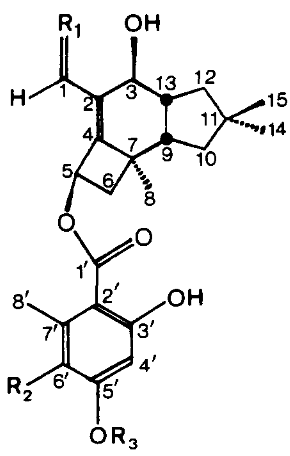
ABSTRACT.—Investigation of the mycelial extract of *Armillaria mellea* led to the isolation of two new sesquiterpene aryl esters, armillyl everninate (**3**) and arnamiol (**4**). Their structures were deduced from spectral data, methanolysis, and synthesis of the resulting aryl esters.

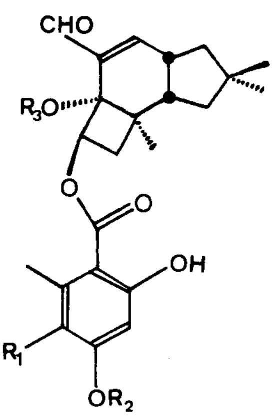
The pathogenic basidiomycete *Armillaria mellea* (Vahl: Fr) Kummer has proved a rich source of sesquiterpenoid aryl esters with a protoilludane skeleton. Armillyl orsellinate (**1**), the major component (1) of the mycelial extract, was identified by an X-ray analysis of its oxidation product (**2**). The absolute configuration of **1** was established (2) by a cd study of **2**. The orsellinates, melleolide (**5**), methyl melleolide (**6**), and the hydroxy-orsellinate judeol (**9**), were subsequently isolated (3, 4); the structures of **5** and **6** were established by X-ray crystallography. Two analogues of melleolide (**5**), armillarin (**7**) and armillaridin (**8**), were isolated (5) and identified on the basis of an X-ray analysis of **7**. We now report the isolation of two new sesquiterpenoid aryl esters for which the names armillyl everninate and arnamiol are proposed.

The mycelial extract of *A. mellea* was partitioned between $CHCl_3$-MeOH-H_2O (13:7:4) and the $CHCl_3$ layer fractionated by Sephadex LH-20. Silica gel chromatography of the nonpolar fractions yielded a mixture of two compounds. Chromatography of this mixture afforded armillyl everninate (**3**) and arnamiol (**4**).

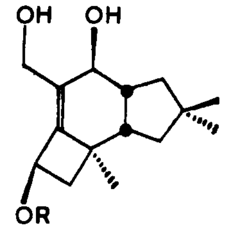
Armillyl everninate (**3**) mp 86-87°, had a molecular formula $C_{24}H_{32}O_6$, which was supported by its fab mass spectrum (glycerol, DMF) with $|MH|^+$ at *m/z* 417. The eims failed to give a parent molecular ion but displayed $|M\text{-}H_2O|^+$ at *m/z* 398. The base peak at *m/z* 165 suggested an aromatic ester moiety 14 amu higher than that for armillyl or-



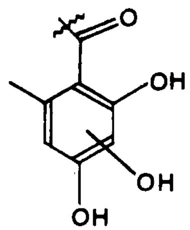
	R_1	R_2	R_3
1	H,OH	H	H
2	O	H	H
3	H,OH	H	CH_3
4	H,OH	Cl	CH_3



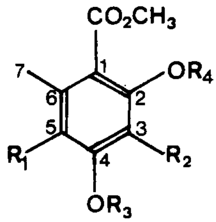
	R_1	R_2	R_3
5	H	H	H
6	H	H	CH_3
7	H	CH_3	H
8	Cl	CH_3	H



9 R=



10 R=H



	R_1	R_2	R_3	R_4
11	H	H	CH_3	H
12	H	H	H	H
13	H	Cl	H	H
14	Cl	H	H	H
15	Cl	H	CH_3	H
16	Cl	H	H	CH_3
17	Cl	H	$CH(CH_3)_2$	H

sellinate (**1**), (base peak at *m/z* 151, $[Ar(OH)_2MeCO]^+$). The 270 MHz ^{1}H-nmr spectrum closely resembled that of **1** (Table 1) but had a methoxyl instead of hydroxyl absorption. Extensive decoupling experiments and the ^{13}C spectrum (Table 2) confirmed the armillyl (*O*-methyl-orsellinate) structure. The presence of an intramolecularly hydrogen bonded signal at 11.68 ppm indicated methylation at the 5′ oxygen.

Methanolysis of **3** yielded, after separation on Sephadex LH-20, the unstable noncrystalline triol armillol (1) (**10**) and methyl everninate (**11**), mp 64-66°. The methyl ester obtained by degradation was identical to synthetic methyl everninate (**11**), mp 65-66°, prepared by standard methods (6). A discrepancy exists in recent literature values for the melting point of methyl everninate (**11**) 66-67° (7), 147-148° (8). The former is correct.

TABLE 1. ^{1}H-nmr Spectra[a] of Armillyl Orsellinate (**1**), Armillyl Everninate (**3**), and Arnamiol (**4**)

H	(**1**)[b](1)	(**3**)[c]	(**4**)[c]
H-1	4.18, 4.38 dd (13.0)	4.30, 4.38 dd (13.0)	4.31, 4.38 dd (12.1)
H-3	4.23 dd (9.0, 2.0)	4.21 dd (8.8, 2.9)	4.22 dd (8.2, 2.6)
H-5	5.98 ddd (7.0, 7.6, 2.0)	5.9 ddd (6.6, 8.5, 2.9)	6.01 ddd (7.3, 7.3, 2.6)
H-6α . . .	1.99 dd (7.6, 11.5)	1.96 dd (6.6, 11.7)	1.98 dd (7.3, 11.7)
H-6β . . .	2.70 dd (7.0, 11.5)	2.62 dd (8.5, 11.7)	2.64 dd (7.3, 11.7)
H9, 13 . . .	2.4-2.55m	2.3-2.5m	2.3-2.5m
H-10α . . .	1.07, 1.3, 1.4 and 1.8 4 × dd	1.18 dd (11.7, 2.0)	1.18 dd (11.7, 2.1)
H-10β . . .		1.83 dd (11.7, 5.9)	1.82 dd (11.7, 6.1)
H-12α . . .		1.32 dd (12.5, 9.5)	1.36 dd (13.0, 10.2)
H-12β . . .		1.45 dd (12.5, 7.3)	1.43 dd (13.0, 7.3)
CH_3-8 . . .	1.13 s	1.11 s	1.10 s
CH_3-14 . .	1.07 s	1.07 s	1.07 s
CH_3-15 . .	0.98 s	0.98 s	0.98 s
H-4′	6.14 d (2.2)	6.28 d (2.2)	—
H-6′	6.22 d (2.2)	6.33 d (2.2)	6.41 s
CH_3-8′ . . .	2.47 s	2.53 s	2.65 s
OCH_3 . . .	—	3.80 s	3.90 s

[a]Shifts in ppm and coupling constants as (Hz).
[b]$CDCl_3$ solution at 400 MHz.
[c]$CDCl_3$ solution at 270 MHz.

TABLE 2 ^{13}C-nmr Spectra of Armillyl Orsellinate (**1**), Armillyl Everninate (**3**), and Arnamiol (**4**)

C atom	(**1**)[a] (1)	(**3**)[b]	(**4**)[b]
1	58.6 t	58.8 t	59.0 t
2	131.8 s	142.5 s	142.5 s
3	74.4 d	74.4 d	74.6 d
4	127.8 s	133.2 s	133.8 s
5	69.8 d	69.9 d	70.8 d
6	40.7 t	40.7 t	40.9 t
7	39.8 t	39.9 s	40.1 s
8	21.0 q	20.9 q	21.2 q
9	47.0 d	47.2 d	47.4 d
10	46.2 t	46.4 t	46.6 t
11	38.6 s	38.6 s	39.0 s
12	46.1 t	46.0 t	46.2 t
13	49.5 d	49.8 d	50.1 d
14	29.4 q	29.3 q	29.5 q
15	28.8 q	26.8 q	27.0 q
1′	170.2 s	170.7 s	170.4 s
2′	104.2 s	104.7 s	106.3 s
3′	160.9 s	163.8 s	159.7 s
4′	100.8 d	98.6 d	98.5 d
5′	164.4 s	165.4 s	163.0 s
6′	111.5 d	111.0 d	115.7 s
7′	143.2 s	142.9 s	139.7 s
8′	24.2 q	24.2 q	19.8 q
OCH_3	—	55.1 q	56.3 q

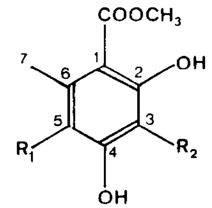
[a]$CDCl_3$ solution at 100.61 MHz.
[b]$CDCl_3$ solution at 67.8 Mhz.

Methylation of armillyl orsellinate (**1**) with CH_2N_2 yielded a compound identical in all respects to **3**. The structure of the natural product was therefore confirmed as armillyl everniate (**3**).

Arnamiol (**4**), mp 132-134°, had a molecular formula $C_{24}H_{31}ClO_6$, which was supported by its negative ion fab mass spectrum (glycerol, DMF) with $[M-H]^-$ at *m/z* 449 (^{35}Cl) and 451 (^{37}Cl). The eims did not show a parent molecular ion [$[M-H_2O]^+$ at *m/z* 432], a feature of the eims of **1** and **3**. The base peak at *m/z* 199, with a peak at 201 (35%), suggested a chlorinated everninate ester fragment. The 270 MHz ^{1}H-nmr spectrum (Table 1) indicated another armillyl orsellinate (**1**) derivative. The presence of only one aromatic hydrogen (δ 6.41 ppm) and a methoxyl (δ 3.90 ppm) confirmed the chloroeverninate ester. Decoupling experiments and the ^{13}C-nmr spectrum (Table 2) were compatible with an armillyl chloroeverninate structure. The position of the chlorine atom was assigned by examination of the ^{13}C spectra of methyl orsellinate (**12**), methyl 3-chloroorsellinate (**13**), and methyl 5-chloroorsellinate (**14**) (Table 3). Reported procedures were employed in the preparation of esters **12** (9), **13** (10), and **14** (8). The unsubstituted aryl carbon and the aryl methyl signals in the chloroorsellinates are easily distinguished. The relevant shifts in the ^{13}C-nmr spectrum of the natural product at 98.5 (d) and 19.8 (q) ppm are clearly associated with the 5-chloro isomer. The proposed structure **4** for arnamiol was proved by degradation and synthesis of the aryl ester degradation product.

Methanolysis of arnamiol (**4**) yielded armillol (**10**) and methyl 5-chloroeverninate (**15**), mp 146-148°, identical to synthetic methyl 5-chloroeverninate (**15**) prepared by standard methods (8). The alternative isomer methyl 5-chloroisoeverninate (**16**), mp 132-133°, was prepared via the isopropyl ether (**17**) followed by methylation and deprotection (11).

TABLE 3. ^{13}C nmr[a] of (**12**), (**13**), and (**14**)



	1	2	3	4	5	6	7	C=O	OCH_3
(**12**) $R_1=R_2=H$	105.8 s	160.3 s	101.4 d	165.4 s	111.4 d	144.1 s	24.4 q	172.2 s	52.0 q
(**13**) $R_1=H, R_2=Cl$	106.1 s	155.7 s	105.5 s	160.1 s	110.6 d	141.7 s	24.2 q	172.1 s	52.3 q
(**14**) $R_1=Cl, R_2=H$	107.1 s	156.0 s	102.0 d	162.9 s	113.9 s	139.5 s	19.9 q	171.4 s	52.3 q

[a]$CDCl_3$ solution at 67.8 MHz.

Unlike armillyl orsellinate (**1**) which exhibits activity against gram-positive bacteria, compounds **3** and **4** were found to be inactive. The activity of the corresponding derivatives **7** and **8** of the active melleolide (**5**) was not reported (5).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on a Kofler melting point apparatus and are uncorrected. The uv spectra were measured on a Perkin-Elmer spectrometer model 124. The ir spectra were recorded on a Perkin-Elmer spectrometer model 283B. Electron-impact mass spectra (ei) were taken on VG 70-70 spectrometer, and fab mass spectra (glycerol-DMF) were recorded on a Kratos MS-80 instrument. The 60 MHz ^1H-nmr spectra were recorded on a Perkin-Elmer R12. 270 MHz ^1H nmr and 67.8 MHz ^{13}C nmr were recorded on a JEOL GX-270. Merck kieselgel 60 (70-230 mesh) and Woelm TSC 04526 were used for column chromatography.

CULTURE CONDITIONS.—*A. mellea* (Vahl: Fr) Kummer (CPS 111.29) was initiated on malt agar for 21 days. Roux flasks (40 × 1 liter) each containing Difco potato-dextrose broth (250 ml) were innoculated with *A. mellea* and incubated at 25° for 35 days.

ISOLATION OF ARMILLYL EVERNINATE (**3**) AND ARNAMIOL (**4**).—The mycelium was extracted with MeOH. The methanolic extract was evaporated and partitioned between $CHCl_3$-MeOH-H_2O (13:7:4). The aqueous layer was reextracted with $CHCl_3$-MeOH-H_2O (13:7:4, lower layer) and the combined $CHCl_3$ layers evaporated to give a brown syrup (1.8 g).

Chromatography on Sephadex LH-20 (100 g, MeOH) yielded six fractions (1-6). Fraction 5 (750 mg) was rechromatographed on silica gel (19 g) [eluent: $CHCl_3$-MeOH-H_2O (300:16:1)] to give a non-polar fraction (193 mg) which was combined with fraction 4 (262 mg). The combined fractions were chromatographed on silica gel (47 g) [eluent: $CHCl_3$-MeOH (99:1)], yielding a mixture of two compounds (168 mg). These were separated on silica gel (20 g) [eluent: n-hexane-EtOAc-MeOH (40:15:1)] to yield armilyl everninate (**3**) (61 mg) and arnamiol (**4**) (81 mg).

ARMILLYL EVERNINATE (**3**).—Recrystallization from n-hexane-EtOAc gave needles mp 86-87°; $[\alpha]^{25}D$ −66° (c=0.79 MeOH); ir (KBr) 3360, 1640 cm^{-1}; uv (MeOH) λ max (log ε) 211 (4.33), 261(4.04), 298(3.78) nm; fabms $[MH]^+$ 417; eims *m/z* (%) 398(2), 380(1), 234(6), 217(28), 201(6), 182(35), 173(5), 165(100); ^1H and ^{13}C nmr, see Tables 1 and 2. *Anal.* Found: C, 69.29; H, 7.96. $C_{24}H_{32}O_6$ requires: C, 69.17; H, 7.74%.

ARNAMIOL (**4**).—Recrystallization from n-hexane-EtOAc gave needles mp 132-134°; $[\alpha]^{25}D$ −91° (c=0.73 MeOH); ir (KBr) ν max 3360, 1640 cm^{-1}; uv (MeOH) λ max (log ε) 217(4.36), 259(4.16), 298(3.93) nm; fabms $[M-H]^-$ 449; eims *m/z* (%) 432(2), 388(1), 234(8), 217(28), 216(68), 201(33), 199(100), 187(10), 172(25); ^1H and ^{13}C nmr, listed in Tables 1 and 2. *Anal.* Found: C, 63.91; H, 6.77; Cl, 8.19. $C_{24}H_{31}ClO_4$ requires: C, 63.92; H, 6.93; Cl, 7.86%.

METHANOLYSIS OF ARMILLYL EVERNINATE (**3**).—A solution of armillyl everninate (**3**) (30 mg) in MeOH (1 ml) and methanolic KOH (0.1M, 0.5 ml) was stirred at room temperature for 24 h. The solution was diluted with H_2O (3 ml), acidified with dilute HCl, and extracted with EtOAc (3 × 2 ml). The organic layer was washed with NaCl (saturated, 1 ml) and dried ($MgSO_4$). Evaporation yielded a residue which was separated on Sephadex LH-20 (30 g, MeOH). Early fractions gave methyl everninate (**11**) (14 mg) which recrystallized from n-hexane-Et_2O as rods mp 64-66° lit (7) mp 66-67°; ir (KBr) ν max 1648 cm^{-1}; uv (MeOH) λ max (log ϵ) 215(4.30), 260(4.13), 298(3.68) nm; ms *m/z* (%) 196(77), 164(100), 136(40), 121(12), 93(10); ^1H nmr ($CDCl_3$, 270 MHz) δ 2.49(3H, s, CH_3-7), 3.79(3H, s, OCH_3), 3.92(3H, s, CO_2CH_3), 6.28(1H, d, J=2.6 Hz, H-3), 6.33(1H, d, J=2.6 Hz, H-5), 11.78(1H, s, 2-OH); ^{13}C nmr ($CDCl_3$, 67.8 MHz) 172.2(C=O), 105.2(C-1), 163.9(C-2), 98.7(C-3), 165.6(C-4), 111.2(C-5), 143.1(C-6), 24.3(C-7), 51.8(ester OCH_3), 55.8(ether OCH_3). *Anal.* Found: C, 61.58; H, 6.08. Calcd. for $C_{10}H_{12}O_4$: C, 61.23; H, 6.31%.

Later fractions yielded armillol (**10**) (15 mg) an unstable solid; ^1H nmr ($CDCl_3$, 270 MHz, 0°) δ 0.96(3H, s, CH_3-15), 0.97(3H, s, CH_3-14), 1.08(3H, s, CH_3-8), 1.11(1H, dd, J=10.4, 2.1 Hz, H-10β), 1.34(2H, 2×dd, J=16.0, 8.6, 2.0 Hz, H-12), 1.76(2H, m, H-10β, H-6α), 2.25(1H, dd, J=11.4, 7.0 Hz, H-6β), 2.39(2H, m, H-9, H-13), 4.04(1H, dd, J=6.9, 2.2 Hz, H-3), 4.4(2H, dd, J=12.0 Hz, H-1), 4.9(1H, ddd, J=7.0, 7.6, 2.2 Hz, H-5); ^{13}C nmr ($CDCl_3$, 67.8 MHz) 147.7(C-2), 131.2(C-4), 74.2(C-3), 68.7(C-5), 59.1(C-1), 50.1(C-13), 48.7(C-12), 47.0(C-9), 46.1(C-10), 41.1(C-6), 39.7(C-7), 36.9 (C-11), 29.6(C-14), 27.1(C-15), 21.5(C-8).

METHYLATION OF ARMILLYL ORSELLINATE (**1**).—Freshly distilled ethereal CH_2N_2 was added to a solution of armillyl orsellinate (**1**) (20 mg) in Et_2O (2 ml). Evaporation and chromatography of the residue on silica gel (6 g) [eluent: n-hexane-EtOAc-MeOH (40:15:1)] yielded the product (18 mg), which had the same mp, $[\alpha]^{25}D$, ir, uv, ms, ^1H nmr, and ^{13}C nmr as the natural product **3**.

METHANOLYSIS OF ARNAMIOL (**4**).—A solution of arnamiol (**4**) (20 mg) in MeOH (1 ml) and methanolic KOH (0.1M, 0.5 ml) was stirred at room temperature for 42 h. After addition of H_2O (3 ml) and neutralization with dilute HCl, the solution was extracted with EtOAc (3×2 ml). The organic layer was washed with NaCl (saturated, 1 ml), dried ($MgSO_4$) and evaporated to yield a residue which was separated on Sephadex LH-20 (30 g, MeOH). Early fractions gave armillol (**10**) (10 mg), an unstable solid, with the same ^1H and ^{13}C nmr as above. Later fractions yielded methyl 5-chloro-2-hydroxy-4-methoxy-6-methylbenzoate (**15**) (10 mg) which recrystallized from Et_2O as needles mp 146-148°, lit. (12) mp 148°; ir (KBr) ν max 1640 cm^{-1}, uv (MeOH) λ max (log ϵ) 215(4.38), 253(3.94), 305(3.56) nm; ms *m/z* (%) 230, 232(47, 16); 198, 200(100, 53); 184(4); 170, 172(14, 7); 155(17). ^1H nmr ($CDCl_3$, 270 MHz) δ 2.63(3H, s, CH_3-7), 3.90(3H, s, OCH_3), 3.95(3H, s, CO_2CH_3), 6.43(1H, s, H-3), 11.56(1H, 2-OH); ^{13}C nmr ($CDCl_3$, 67.8 MHz) 171.7(C=O), 106.4(C-1), 159.6(C-2), 98.5(C-3), 163.0(C-4), 115.6(C-5), 139.7(C-6), 19.7(C-7), 52.3(ether OCH_3), 56.3 (ester OCH_3). *Anal.* Found: C, 52.06; H, 4.85; Cl, 15.18. Calcd. for $C_{10}H_{11}ClO_4$: C, 52.06; H, 4.77; Cl, 15.40%.

METHYL 5-CHLORO-2-HYDROXY-4-ISOPROPOXY-6-METHYLBENZOATE (**17**).—A solution of methyl 5-chloro-2,4-dihydroxy-6-methylbenzoate (**14**) (0.4 g), 2-bromo-propane (0.25 g) and K_2CO_3 (0.26 g) in DMF (10 ml) was stirred at 80° for 24 h. After cooling and addition of H_2O (10 ml), the solution was acidified with dilute HCl and extracted with Et_2O (2×10 ml). The organic layer was dried ($MgSO_4$) and evaporated to yield a residue which was chromatographed on silica gel (35 g) [eluent: CH_2Cl_2-EtOH (99:1)] to give **17** (0.2 g) which recrystallized from n-hexane Et_2O as cubes mp 68-70°, ir (KBr) ν max 1653 cm^{-1}; uv (MeOH) λ max (log ϵ) 215(4.41), 262(4.01), 307(3.64) nm; ms *m/z* (%) 258, 260(31, 10), 226(4); 216, 218(22, 7); 184, 186(100, 41); 156(19). ^1H nmr ($CDCl_3$, 60 MHz) δ 1.32 (6H, d, J=6 Hz, isopropyl $(CH_3)_2$), 2.55(3H, s, CH_3-7), 3.90(3H, s, CO_2CH_3), 4.56(1H, septet, J=6 Hz, isopropyl CH), 6.4(1H, s, H-3), 11.48(1H, s, 2-OH). *Anal.* Found: C, 55.29; H, 5.78; Cl, 13.37. $C_{12}H_{15}ClO_4$ requires: C, 55.71; H, 5.80; Cl, 13.73%.

METHYL 5-CHLORO-4-HYDROXY-2-METHOXY-6-METHYLBENZOATE (**16**).—Methyl 5-chloro-2-hydroxy-4-isopropoxy-6-methylbenzoate (**17**) (110 mg), (Me_2SO_4 (55 mg) and K_2CO_3 (60 mg) in Me_2CO (5 ml) was refluxed for 5 h. After addition of aqueous NaOH (5%, 20 ml), the solution was extracted with Et_2O (2×10 ml). The organic layer was dried ($MgSO_4$), evaporated, dissolved in dry CH_2Cl_2 (5 ml), and stirred at 0° under dry N_2. Next, $TiCl_4$ (0.2 ml) was added and the solution stirred at room temperature overnight. Then, H_2O (10 ml) was added and the solution extracted with Et_2O (3×5 ml). The Et_2O layer was extracted with NaOH (10%, 2×5 ml). The alkaline extract was acidified (dilute HCl) and extracted with Et_2O (3×5 ml). The organic layer was dried ($MgSO_4$) and evaporated to dryness to give **16** (67 mg) which recrystallized from n-hexane/Et_2O as needles mp 132-133°; ir (KBr) 3300, 1697 cm^{-1}; uv (MeOH) λ max (log ϵ) 207(4.38), 242(3.64), 287(3.48) nm; ms *m/z* (%) 230, 232(61,20); 215(3); 199, 201(100, 32); 184(7); 156(12). ^1H nmr ($CDCl_3$, 270 MHz) δ 2.30(3H, s, CH_3-7), 3.78(3H, s, OCH_3), 3.90(3H, s, CO_2CH_3), 5.90(1H, bs, 4-OH), 6.49(1H, s, H-3); ^{13}C nmr ($CDCl_3$, 67.8 MHz) 168.1(C=O), 117.5(C-1), 153.1(C-2), 97.3(C-3), 156.2(C-4), 112.3(C-5), 134.8(C-6), 17.5(C-7), 52.4(ether OCH_3), 56.1(ester OCH_3). *Anal.* Found: C, 52.10; H, 4.88; Cl, 15.50. $C_{10}H_{11}ClO_4$ requires: C, 52.06; H, 4.77; Cl, 15.40%.

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