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COUMARIN–HEMITERPENE ETHERS FROM *ARTEMISIA* SPECIES

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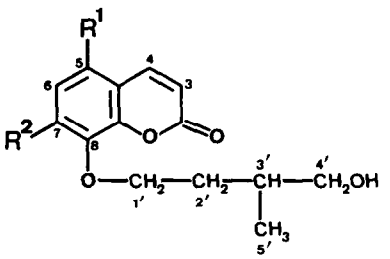
Key Word Index—*Artemisia lciniata*; *A. armeniaca*; *A. tanacetifolia*; Compositae; new coumarin–hemiterpene ethers.

Abstract—In addition to a known derivative, five new coumarin–hemiterpene ethers were isolated from the leaves of *Artemisia laciniata*, *A. armeniaca* and *A. tanacetifolia* and identified by ^{1}H NMR and, in part, by ^{13}C NMR spectroscopy. The coumarin patterns are characterized particularly by compounds with a hydroxylated and saturated isoprenoid unit attached to oxygen at the C-8 position and by 5,7,8-trioxygenated derivatives. The chemotaxonomic significance of the coumarin–terpenoid ethers within *Artemisia* is discussed.

INTRODUCTION

In connection with our current comparative investigations on secondary constituents of the genus *Artemisia* (Asteraceae–Anthemideae) it became apparent that the distribution of different types of coumarins represents a chemosystematic criterion which may contribute to a more natural infrageneric grouping. As already pointed out in preceding articles, the accumulation of coumarin–sesquiterpene ethers characterize *Artemisia pontica* L., *A. abrotanum* L. and some other species of the section *Abrotanum* Bess. [1–7], which may be regarded as closely related on the basis of morphological characters. Beyond that, a series of coumarin–hemiterpene ethers has been found to be typical for some other species of this section which are grouped together in the '*Heterophyllae*' [8].

From the three '*Heterophyllae*' species, *A. laciniata* Willd., *A. armeniaca* Lam. and *A. tanacetifolia* L., seven different coumarin–hemiterpene ethers have been isolated and identified. Five compounds have been proved to be new. Their structures were established by spectroscopic methods and are described in this paper.



	R^1	R^2
1	H	OCH_3
2	OH	OCH_3
3	OCH_3	OCH_3
4	$O-CH_2-CH=C(CH_3)-CH_3$	OCH_3

RESULTS AND DISCUSSION

The methanolic extract of the leaves of *A. laciniata*, *A. armeniaca* and *A. tanacetifolia* afforded the coumarins **1–5**, **7** and **8**. Compounds **1–4** and **8** are new and were designated as lacarol (**2**), methyllacarol (**3**), prenyllacarol (**4**), desoxylacarol (**1**) and artanin (**8**). The lacarol derivatives (**1–4**) are characterized by a hydroxylated and saturated isoprenoid unit attached to the C-8 position. Armin (**6**), a closely related derivative previously isolated from *A. armeniaca* [9], was not detected in this investigation. Apart from the isoprenoid units, the coumarin patterns of the three species are also characterized by the frequent occurrence of 5,7,8-trisubstituted derivatives (**2–4** and **8**), which otherwise have a rather limited distribution in the plant kingdom [10]. The structure elucidation of compounds **1–4** and **8** is mainly based on ^{1}H NMR data (in deuterochloroform and deuterobenzene), supported by further spectral evidence using ^{13}C NMR (**2** and **3**), UV, IR and mass spectrometry (see Table 1 and Experimental).

The pattern of the coumarin resonances in the ^{1}H NMR spectrum of **1** are typical of a 7,8-dialkoxy substituted coumarin: two AB systems at δ6.29/7.65 and 6.89/7.20 with an aromatic *ortho*-coupling of 9.5 and 9 Hz, respectively (compare ref. [11] for 7,8-dimethoxycoumarin). The coumarin proton resonances of **2–4** and **8** are typical for 5,7,8-trialkoxy substituted coumarins: one AB system for H-3/H-4 at *ca* δ6.2/8.0 and one singlet for H-6 at δ6.35 (compare ref. [11] for 5,7,8-trimethoxycoumarin). The UV data for **1–4** and **8** fully agree with the substitution pattern following from the ^{1}H NMR spectra.

The most interesting feature of the lacarols (**1–4**) is the presence of the isoprenoid unit

Table 1. ^{1}H NMR data for compounds **1**–**4** and **8** ($CDCl_3$ and C_6D_6, 250 MHz, δ)

		1		**2**		**3**		**4**		**8**	
Protons	No.	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
H	3	6.29	5.82 (*d*)	6.14	5.77 (*d*)	6.19	5.73 (*d*)	6.17	5.84 (*d*)	6.17	5.88 (*d*)
H	4	7.65	6.60 (*d*)	7.99	7.44 (*d*)	8.00	7.50 (*d*)	8.02	7.60 (*d*)	7.98	7.52 (*d*)
R^1	5	7.20	6.45 (*d*, H)	7.30	‡ (*br s*, OH)	3.96	3.13 (*s*, OMe)	§	§	3.95	3.12 (*s*, OMe)
H	6	6.89	6.22 (*d*)	6.31	5.40 (*s*)	6.35	5.73 (*s*)	6.36	5.94 (*s*)	6.35	5.77 (*s*)
R^2	7	3.95	3.23 (*s*, OMe)	3.83	3.22 (*s*, OMe)	3.93	3.29 (*s*, OMe)	3.94	3.32 (*s*, OMe)	3.92	3.32 (*s*, OMe)
OCH_2	1′	4.21	4.11 (*t*)	4.08	4.05 (*t*)	4.11	4.10 (*t*)	4.12	4.12 (*t*)	—	¶
CH_2*	2′	1.90	1.82 (*ddt*)	1.84	‡ (*ddt*)	1.85	1.85 (*ddt*)	‖	1.85 (*ddt*)	—	—
		1.78	1.61 (*ddt*)	1.75	‡ (*ddt*)	1.74	1.65 (*ddt*)	‖	1.72 (*ddt*)	—	—
CH	3′	2.17	2.14 (*m*)	2.18	2.19 (*m*)	2.16	2.20 (*m*)	2.16	2.21 (*m*)	—	—
CH_2* (OH†)	4′	3.68	3.53 (*dd*)	3.70	3.56 (*dd*)	3.68	3.60 (*dd*)	3.69	3.60 (*dd*)	—	—
		3.59	3.47 (*dd*)	3.61	3.51 (*dd*)	3.57	3.50 (*dd*)	3.57	3.51 (*dd*)	—	—
CH_3	5′	1.04	0.97 (*d*)	1.05	0.90 (*d*)	1.05	1.01 (*d*)	1.03	1.02 (*d*)	—	—

*Diastereotopic protons separated.

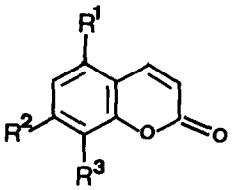
†The hydrolytic protons are usually very broad and not significant in diluted solutions; however, in a concentrated solution of **3** (8 mg very pure sample in 0.5 ml $CDCl_3$) the hydroxyl proton appeared as a *br t* (J = 6 Hz) at δ2.48 and the diastereomeric CH_2-4′ protons as two *br ddd* at the chemical shifts shown.

‡Very poor solubility in C_6D_6; weak signals cannot be assigned reliably.

§R^1 = $-OCH_2-CH=C(CH_3)_2$; data in $CDCl_3$: δ4.62 (2H, *d*, J = 7 Hz, OCH_2), 5.49 (1H, *br t*, J = 6 Hz, –CH=), 1.83 (3H, *br s*, Me), 1.78 (3H, *br s*, Me); the corresponding values in C_6D_6: δ4.19, 5.38, 1.62 and 1.45.

‖Obscured by the *br s* of the olefinic methyl groups; see fourth footnote.

¶The substituent at C-8 is $-OCH_2-CH=C(CH_3)_2$; data in $CDCl_3$: δ4.58 (2H, *d*, J = 7 Hz, OCH_2), 5.60 (1H, *br t*, J = 6 Hz, –CH=), 1.75 (3H, *br s*, Me); 1.70 (3H, *br s*, Me); the corresponding values in C_6D_6: δ4.73, 5.77, 1.61 and 1.55.



	R^1	R^2	R^3
5	H	$O-CH_2-CH=C(CH_3)-CH_3$	OCH_3
6	H	$O-CH_2-CH(CH_3)-CH_2-CH_2OH$	OH ref. [9]
7	H	OCH_3	$O-CH_2-CH=C(CH_3)-CH_3$
8	OCH_3	OCH_3	$O-CH_2-CH=C(CH_3)-CH_3$

$-OCH_2-CH_2-CH(CH_3)-CH_2OH$, not described previously for naturally occurring coumarins. The structure of this side chain was established unambiguously by ^1H NMR. There are two $-OCH_2-$ groups in the side chain, one shows up as a triplet of 2H and the other is represented by two diastereotopic protons with different chemical shifts (see Table 1). The latter must be associated with a $-CH_2OH$ group since, in very pure and not too diluted NMR samples, one observes a direct coupling of the two diastereomeric oxymethylene protons with the hydroxy proton (see Table 1, second footnote). The other $-OCH_2-$ is, therefore, directly linked to the coumarin moiety by an aromatic ether bond. The sequence of OCH_2-1′, CH_2-2′, CH-3′, CH_2OH-4′, CH_3-5′ follows immediately from a series of decoupling experiments. Irradiation at OCH_2-1′ affects only CH_2-2′, irradiation at CH_2-2′ affects CH_2-1′ and CH-3′, irradiation at CH-3′ shows clear effects for CH_2-2′, CH_2-4′ and CH_3-5′, etc. (for details see Experimental, compound **3**). It is interesting to note that some of the carbon–carbon single bonds in the side chain (C-2′–C-3′ and C-3′–C-4′) are obviously hindered in their free rotation since, for CH_2-2′ and OCH_2-4′, the corresponding diastereotopic methylene protons appear at significantly different chemical shifts. For OCH_2-1′ a sharp triplet of 2H indicates free rotation about the O–C-1′ and the C-1′–C-2′ bonds. Dimethylallyloxy side chains (present in **4**, **5**, **7** and **8**) are rather common in naturally occurring coumarins [10]. They are easily identified by the characteristic signals for OCH_2, the olefinic proton =CH– and the olefinic methyl groups.

One question still open is the assignment of the methoxy, hydroxy, dimethylallyloxy and 4-hydroxy-3-methylbutyloxy groups to the 5-, 7- and 8-positions of the coumarin moiety. The ^1H NMR spectra of compounds **1**–**4** and **8** in benzene-d_6 helped to solve this problem. It is well-known that methoxy resonances (or methyleneoxy resonances in the case of larger alkoxy side chains) suffer considerable aromatic solvent induced shifts (ASIS) to higher field if an *ortho* proton is next to the group in question; if no *ortho* proton is available the solvent molecules cannot arrange themselves close enough to produce significant solvent induced shifts [11]. In compound **1** this effect is large for the methoxy group [$\Delta\delta$ ($CDCl_3$–C_6D_6) 0.72] and very small for the $-OCH_2-$ group (δ0.10). As a consequence, the methoxy group has to be assigned to position C-7 of the coumarin, and $-OCH_2CH_2CH(CH_3)CH_2OH$ to position C-8 (compare Table 1). In the case of compound **2** the effect is small for $-OCH_2-$ and large ($\Delta\delta$0.61) for the methoxy group. The butoxy side chain is, therefore, positioned at C-8, and the methoxy group may be either positioned at C-5 (hydroxy group at C-7 or at C-7 (hydroxy group at C-5). However, the value of $\Delta\delta$ is, clearly, in favour of a 5-hydroxy-7-methoxy derivative: $\Delta\delta$0.61 agrees very well with a 7-methoxy group in 5,7,8-trisubstituted coumarin derivatives (e.g. $\Delta\delta$ 0.82 for 5-methoxy, 0.63 for 7-methoxy and 0.18 for 8-methoxy for 5,7,8-trimethoxycoumarin [11]); these values are consistent with all our data on related compounds within $\pm\delta$0.03; see the following discussion on compounds **3**, **4** and **8**. The 5-hydroxy-7-methoxy assignment for compound **2** is also supported by comparison of the ^{13}C NMR data for **2** and **3** (5,7-dimethoxy): the chemical shifts for the coumarin doublets, especially for C-6 and C-4 are different by $\Delta\delta$3.6 and 2.1, indicating a different substitution (hydroxy in **2** and methoxy in **3**) at C-5 rather than at C-7 (the resonances for the side chain carbons agree within δ0.3, see Experimental). The measurement of the nuclear Overhauser effect (NOE) is not suited to characterize a 5-methoxy or 7-methoxy group in 5,7,8-substituted coumarins. The relaxation of both 7-methoxy and 5-methoxy proceeds preferentially via H-6. This was proved by measurement of the differential NOE for compound **3**, where the irradiation of 5-methoxy as well as irradiation of 7-methoxy resulted in an enhancement of H-6 only; H-4 did not show any effect. This is explained by the steric hindrance caused by H-4, which does not allow a planar (or even close to planar) conformation of 5-methoxy with the methoxy group

orientated *syn* to H-4. Therefore, the favoured planar conformation of the arylic ether bond [12–14] forces 5-methoxy *syn* to H-6; as a consequence, for both methoxy groups, at either C-5 or C-7, only a NOE for H-6 is observable. The positions of the alkoxy group in compound **3** follow clearly from the deuterobenzene induced shifts: $\Delta\delta$ 0.64 for 7-methoxy; $\Delta\delta$ 0.83 for 5-methoxy; practically no effect is observed for $-OCH_2-$ (position C-8).

In compound **4** we have three different alkoxy groups. However, the solvent induced shifts allow a straightforward assignment. For the methoxy group a value of $\Delta\delta$0.62 indicates position C-7, a value of $\Delta\delta$0.00 for the methyleneoxy triplet $-OCH_2-CH_2-$ proves position C-8 for the 4-hydroxy-3-methylbutoxy group: the remaining dimethylallyloxy group is positioned at C-7 ($\Delta\delta$0.43 for the methyleneoxy doublet $-OCH_2-CH=$).

The two methoxy groups in **8** again show the characteristic aromatic solvent induced shifts for 5-methoxy ($\Delta\delta$0.83) and 7-methoxy ($\Delta\delta$0.60). The $-OCH_2-CH=C(CH_3)_2$ methyleneoxy doublet at C-8 has a value of $\Delta\delta$ −0.15, which may be due to the π–π interaction of the olefinic double bond with the aromatic solvent.

The mass spectra of compounds **1–4** and **8** agree with the proposed structures. The molecular ion peaks are very small in the electron impact mass spectra (see Experimental); the base peak is usually the product of elimination of the long side chain, representing the hydroxy derivative of the original ether [2]. There are almost no other fragments with a relative intensity above 10%. In the case of compound **4**, the field desorption technique had to be used to obtain a *m/z* value for the molecular ion. High resolution mass spectral data for **2** and **3** confirmed the corresponding molecular formulae (see Experimental).

The new coumarins, **1–4**, possess a chiral centre at C-3′. However, no optical activity could be detected by measurement of ORD or CD. In the case of compound **3** the optically active α-methoxy-α-trifluoromethylphenylacetic ester was prepared to prove the racemic nature of **3**. Indeed, the diastereomeric esters could be detected in the ^{1}H NMR spectrum in a ratio of 1:1. Usually the method of Dale *et al.* [15] is used for secondary alcohols with a chiral carbinol centre. In the case of **3** the chiral centre is a carbon atom next to a primary alcohol function. The effects are, therefore, very small but still detectable (250 MHz, benzene-d_6 solution) for the methoxy group of the reagent and even for the relatively remote 7-methoxy group of the coumarin moiety (see Experimental and compare ref. [16] for similar long range effects in related compounds).

EXPERIMENTAL

Plant material was grown from achenes received from various botanical gardens, as well as from a wild collection, and cultivated under field conditions in the Botanical Garden of the University of Vienna. [*A. tanacetifolia* (AR-963; Botanical Garden of Yakutsk, U.S.S.R.), *A. armeniaca* (AR-544; Botanical Garden Champex-Lac, France) and *A. lacmiata* (AR-932; Burgenland, eastern Austria).] Voucher specimens are deposited at the herbarium of the Institute of Botany, University of Vienna (WU).

Air-dried leaves (*A. tanacetifolia*, 29 g; *A. armeniaca*, 19 g; *A. lacmiata*, 61 g) were separately extracted with boiling MeOH for 45 min. The concd extracts were treated with hot H_2O to remove chlorophyll and partitioned between $CHCl_3$ and H_2O. The concd $CHCl_3$ fractions were separated by TLC on 1 mm thick layers of silica gel GF 254 using Et_2O–EtOAc (19:1) and EtOAc–EtOH (24:1) as solvents.

A. tanacetifolia afforded 3.8 mg **5**, 4.5 mg **7**, 3.2 mg artanin (**8**), and traces of desoxylacarol (**1**) and methyllacarol (**3**). *A. armeniaca* afforded 1.5 mg prenyllacarol (**4**), 3 mg desoxylacarol (**1**), 7 mg lacarol (**2**) and traces of methyllacarol (**3**). *A. laciniata* afforded 4 mg desoxylacarol (**1**), 14 mg methyllacarol (**3**) and traces of lacarol (**2**).

Desoxylacarol (**1**). 8-(4-Hydroxy-3-methylbutoxy)-7-methoxy-2*H*-1-benzopyran-2-one. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3532, 2972, 2923, 2853, 2279, 1740, 1604, 1500, 1440, 1379, 1347, 1290, 1263, 1118, 1074; UV $\lambda_{max}^{Et_2O}$ nm: 307, 257, 248, 219; MS (70 eV, 100°, *m/z*): 278 $[M]^+$ (1%) 192 [8-hydroxy-7-methoxycoumarin]$^+$ (100); ^{1}H NMR: see Table 1.

Lacarol (**2**). 5-Hydroxy-8-(4-hydroxy-3-methylbutoxy)-7-methoxy-2*H*-1-benzopyran-2-one. Colourless crystals from Et_2O; mp 112–113°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2973, 2929, 2860, 1439, 1379, 1347, 1290, 1117, 1073; UV $\lambda_{max}^{Et_2O}$ nm: 317, 263, 257, 218; MS (70 eV, 100°, *m/z*): 294 $[M]^+$ (0.4), 208 [5,8-dihydroxy-7-methoxycoumarin]$^+$ (100), 180 (19); high resolution MS: observed 294.110, $C_{15}H_{18}O_6$ requires 294.1104; ^{1}H NMR: see Table 1; differential NOE (in $CDCl_3$): irradiation at δ3.83: enhancement of the *s* at δ6.31; ^{13}C NMR [$CDCl_3 + CD_3OD$ (1:1), 250 MHz, δ]: 162.5 (*s*), 156.9 (*s*), 151.4 (*s*), 148.6 (*s*), 128.6 (*s*), (all other quarternary C resonances were too weak for detection), 140.7 (*d*, C-4), 110.0 (*d*, C-3), 95.4 (*d*, C-6), 33.2 (*d*, side chain CH), 72.8 (*t*, OCH_2), 67.8 (*t*, OCH_2), 34.0 (*t*, OCH_2-CH_2-CH), 56.3 (*q*, OMe), 17.1 (*q*, side chain Me); CD_3OD had to be added to increase the solubility of **2**.

Methyllacarol (**3**). 8-(4-Hydroxy-3-methylbutoxy)-5,7-dimethoxy-2*H*-1-benzopyran-2-one. Colourless crystals from Et_2O; mp 104–106°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3527, 2952, 1742, 1601, 1500, 1463, 1434, 1385, 1343, 1262, 1214, 1187, 1151, 1122, 1063; UV $\lambda_{max}^{Et_2O}$ nm: 321, 261, 255, 208; MS (70 eV, 100°, *m/z*): 308 $[M]^+$ (0.85%), 222 [8-hydroxy-5,7-dimethoxycoumarin]$^+$ (100), 207 (22); high resolution MS: observed 308.126, $C_{16}H_{20}O_6$ requires 308.1261; ^{1}H NMR: see Table 1; decoupling expts (in $CDCl_3$): irradiation of the *t* at δ4.11: the two *ddt* at δ1.85 and 1.74 are changed to two clear *dd* with J = 14 and 6 Hz, representing the AB part of an ABX system; irradiation at δ3.62 (average of δ3.68 and 3.57): the *m* at 2.16 becomes a somewhat simplified *m*; irradiation at δ2.48; the two *dd* at δ3.68 and 3.57 become sharper; irradiation at δ2.16: the two *dd* at δ3.68 and 3.57 become a simple AB system (two *d* with J_{gem} = 11 Hz), the *d* at δ1.05 becomes a *s*, and the two complex *ddt* at δ1.85 and 1.74 are simplified to two *br dt*; irradiation at δ1.80 (average of δ1.85 and 1.74): the *t* at δ4.11 changes to a sharp *s*, the *m* at δ2.16 shows some simplification and narrowing; irradiation at δ1.05: some narrowing of the *m* at δ2.16; differential NOE (in C_6D_6): irradiation at δ3.29: enhancement of the *s* at δ5.73; irradiation at δ3.13: enhancement of the *s* at δ5.73; ^{13}C NMR ($CDCl_3$, 250 MHz, δ): 160.9 (*s*), 156.4 (*s*), 152.4 (*s*), 104.3 (*s*), 98.1 (*s*) (the other quarternary C resonances were too weak for detection); 138.6 (*d*, C-4), 111.3 (*d*, C-3), 91.8 (*d*, C-6), 33.4 (side chain CH); 72.7 (*t*, OCH_2), 68.1 (*t*, OCH_2), 34.1 (*t*, OCH_2-CH_2-CH); 56.6 (*q*, OMe), 56.1 (*q*, OMe), 17.3 (*q*, side chain Me).

Prenyllacarol (**4**). 8-(4-Hydroxy-3-methylbutoxy)-7-methoxy-5-(3-methyl-2-butenyloxy)-2*H*-1-benzopyran-2-one. Colourless crystals from Et_2O; mp 89–92°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3516, 2972, 2927, 2862, 1736, 1599, 1496, 1455, 1379, 1348, 1260, 1151, 1118, 1074, 1058; UV $\lambda_{max}^{Et_2O}$ nm: 317, 260, 254, 221; MS (FD, *m/z*): 362 $[M]^+$ (100); ^{1}H NMR: see Table 1.

Artanin (**8**). 5,7-Dimethoxy-8-(3-methyl-2-butenyloxy)-2*H*-1-benzopyran-2-one. Colourless crystals from petrol; mp

108–111°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2935, 1741, 1601, 1500, 1463, 1433, 1378, 1341, 1289, 1259, 1212, 1186, 1148, 1120, 1056, 955; UV $\lambda_{max}^{Et_2O}$ nm: 315, 259, 255, 217; MS (70 eV, 100°, *m/z*): 290 $[M]^+$ (1.5), 222 [8-hydroxy-5,7-dimethoxycoumarin]$^+$ (100), 207 (18); ^{1}H NMR: see Table 1.

Diastereomeric esters of **3** *with Mosher reagent.* A soln of 5 mg **3** in 1 ml dry pyridine was treated over a period of 20 hr with 50 mg freshly prepared α-methoxy-α-trifluoromethylphenylacetic anhydride (prepared from the corresponding optically pure acid with $SOCl_2$). After proper work-up [15] the crude diastereomeric esters were subjected to ^{1}H NMR. The signal separation (high resolution, 250 MHz) proved to be better in C_6D_6: δ3.468 and 3.464 with an intensity ratio of 1:1 for the Ph–C(OMe) (CF_3)–CO–O resonances of the diastereomeric esters (reagent OMe), δ3.306 and 3.304 (ratio *ca* 1:1) for 7-OMe (coumarin moiety); 5-OMe at δ3.143 did not show any splitting. Further characteristic resonances: δ7.50 (1H, *d*, *J* = 9.5 Hz, H-3), 5.87 (1H, *d*, *J* = 9.5 Hz, H-2), 5.74 (1H, *s*, H-6), 4.23 (2H, *d*, *J* = 6 Hz, CH_2-4′), 3.96 (2H, t, *J* = 6 Hz, CH_2-1′).

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