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怒茶素——怒江山茶的一个新黄酮甙

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摘要: 用葡聚糖凝胶和树脂层析技术从云南省昆明地区产怒江山茶 (*Camellia saluenensis* Stapf ex Bean) 的鲜叶中分离到 11 个酚类化合物, 其中 10 个分别鉴定为已知的槲皮素类黄酮化合物及原花色素类化合物。另 1 个为新的黄酮甙, 经光谱与化学方法测定, 其化学结构为槲皮素 -3-O-β-D-木吡喃糖基(1→2)-α-L-鼠李吡喃糖基(1→6)-β-D-葡萄吡喃糖甙, 命名为怒茶素。

关键词: 山茶科; 怒江山茶; 酚类化合物; 黄酮甙; 怒茶素
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Saluenin, a New Flavonol Glycoside from *Camellia saluenensis*

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Abstract: By means of column chromatography of sephadex and macroporous resin, a new flavonol glycoside, saluenin, was isolated from the fresh leaves of *Camellia saluenensis* together with ten known phenolic compounds. The structure of saluenin was identified as quercetin 3-O-β-D-xylopyranoeyl(1→2)-α-L-rhamnopyranosyl(1→6)-β-D-glucopyranoside by spectral data and chemical methods.

Key words: Theaceae; *Camellia saluenensis*; Phenoloids; Flavonoid glycoside; Saluenin

Camellia saluenensis Stapf ex Bean is an endemic species to Yunnan Province of China. This plant is well known as a field ornamental because of its big and beautiful flowers. In the folk medicine, the leaves are always used as antipyretic and diuretic by minority people. As a part of our phytochemical and chemotaxonomic studies on Theaceae (Zhang *et al*, 1995), this paper deals with the isolation and structure elucidation of phenolic constituents of the leaves of *C. saluenensis*.

Results and Discussion

The acetone extract of fresh leaves of *C. saluenensis* was repeatedly chromatographed on Diaion Gel, Sephadex LH-20, MCI Gel CHP 20P and TSK Gel columns to yield eleven compounds (**1**~**11**) Among them, **2**~**11** are known phenolic compounds and were identified as quercetin (**2**), quercetin 3-O-β-glucopyranoside(**3**), quercetin 3-O-β-galactopyranoside(**4**), quercetin 3-O-α-L

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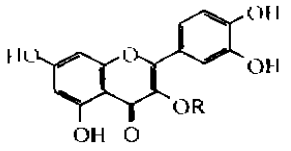
– rhamnopyranoside(**5**), quercetin 3 – O – α – L – arabinofuranoside(**6**), rutin(**7**) (Markham *et al*, 1978), (–) – epicatechin (**8**), procyanidin B – 2(**9**), procyanidin C – 1(**10**) (Zhang *et al*, 1994) and 3' – O – galloylprocyanidin B – 2(**11**)(Nonaka *et al*, 1983), respectively, by their physical and spectral data. Compound **1** is a new natural product.

Compound **1** was obtained as green – yellow powder. Negative FAB mass spectrum give a quasi molecular ion peak at m/z 741[M($C_{32}H_{38}O_{20}$) – H]$^-$ and fragment ions at 609[741 – pentose]$^-$ and 463[609 – deoxyl hexose]$^-$. The flavonoid skeleton of compound 1 was indicated by the proton signal of C – 5 hydroxyl group at δ 12.57 (1H, s) in ^{1}H NMR spectrum and the carbonyl signal at δ 177.71 in ^{13}C NMR spectrum. The presence of three carbon signals at δ 99.02(C – 6), 94.36(C – 8) and 133.61(C – 3), two proton singals of A – ring at δ 6.35(1H, s, H – 6) and 6.17(1H, s, H – 8), as well as proton signals of 3,4 – substituted B – ring at δ 7.53(1H, s), δ 7.51(1H, d, J = 8.4Hz) and δ 6.62(1H, d, J = 8.4Hz), suggested that the aglycone moiety was found to be coincident with those of quercetin (2). Acidic hydrolysis of compound 1 gave 2 and 7. Three anomeric carbon signals of sugar moiety appeared at δ 105.53, δ 101.63 and δ 101.28 while three anomeric protons at δ 5.29 (1H, d, J = 7.2Hz), δ 4.26(1H, s) and δ 4.21(1H, d, J = 7.2Hz). Compared with 7, compound 1 showed a set of additional signals corresponding to a β – D – xylopyranosyl unit in the ^{13}C NMR spectrum. It was also observed that the glycosylation shift effect in a downfield shift (10.76 ppm) at the C – 2 position of α – L – rhamnopyranosyl unit. It indicated that the interglycosyl linkage of terminal β – D – xylopyranosyl unit should be located on the C – 2 position of α – L – rhamnopyranosyl unit. All these were proved by HMBC experiment. The anomeric proton(δ 5.29) of β – D – glucopyranosyl unit correlated with C – 3(δ 133.61) of the alycone, the anomeric proton(δ 4.26) of α – L – rhamnopyranosyl unit correlated with C – 6(δ 67.87) of β – D – glucopyranosy unit and the anomeric proton(δ 4.21, d, J = 7.2Hz, 1H) of β – D – xylopyranosyl unit correlated with C – 2 (δ 81.28) of α – L – rhamnopyranosyl unit. From the above evidences, the structure of compound 1 was elucidated as quercetin 3 – O – β – D – xylopyranosyl (1→2) – α – L – rhamnopyranosyl(1→6) – β – D – glucopyranoside, given the trivial name as saluenin.

It is noticed that phenolic constituents of fresh leaves of *C. saluenensis* could be divided into two types, flavonoids and procyanidins. The content of quercetin (2) and its derivatives is higher than that of procyanidins. It will be a significant chemical marker for the chemotaxonomy of this genus.

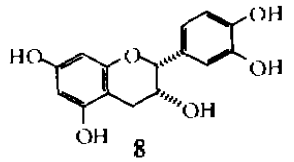
Experimental

General Mps were determined on a Kofler hot stage apparatus and corrected by authentic sample of caffeine (237 ℃). Optical rotations were measured with SP – EA – 300 apparatus. UV and IR spectra were recorded on Shimadzu UV – 210A and IR – 450 spectrophotometers, in MeOH and KBr pellets, respectively. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM – 400 NMR spectrometer and HMBC NMR spectra on a Bruker AM – 500 NMR spectrometer in DMSO – d_6 and CD_3OD using TMS as internal standards. FAB and EI mass spectra were obtained on a VG Autospec mass spectrometer. CC was carried out on Diaion Gel, Sephadex LH – 20, MCI Gel CHP 20P and TSK Gel. TLC was



R

1 — Glc(6-1)Rha(2-1)Xyl
2 — H
3 — Glc
4 — Gal
5 — Rha
6 — Ara(f)
7 — Glc(6-1)Rha



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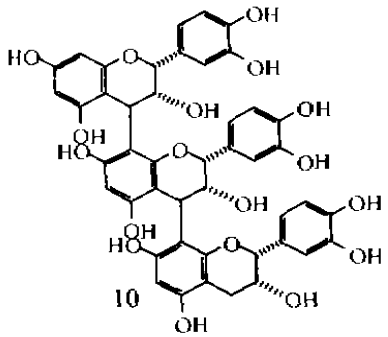

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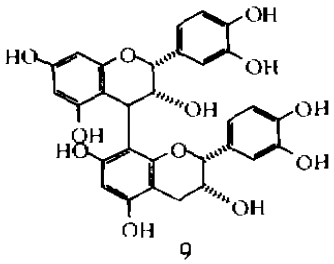

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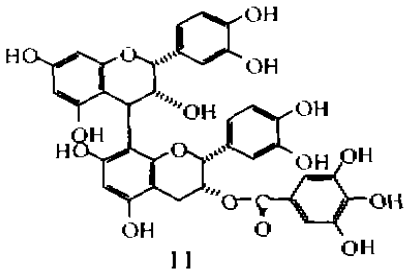

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conducted on precoated silica gel plates. Spots were detected by spraying with $FeCl_3$ and H_2SO_4.

Extraction and isolation

Plants material (*Camellia saluenensis* Stapf ex Bean) was collected in Novenmber 1996 in Kunming, Yunnan Province and identified by Prof. L. F. Xia, who is a *Camellia* expert at the Kunming Botanical Garden of the institute. The fresh leaves (1.6 kg) were extracted with 80% acetone at room temperature. The acetone extraction was concentrated under reduced pressure and diluted with water. The aqueous solution was subjected to a column contain Diaion gel and eluted successively with H_2O and MeOH, respectively. The MeOH fractions were combined, evaporated and then the residue was chromatographed over Sephadex LH – 20 and eluted with ethanol. Fractions 1 ~ 7 were obtained.

Fraction 1 was chromatographed on Sephadex LH – 20 column with 60% MeOH to give compound 1 (80mg).

Fraction 2 was condensed to small volume to obtain a crystal. After recrystalization, compound 8 (70mg) was obtained.

Fraction 3 was chromatographed over Sephadex LH – 20 column with 60% MeOH to afford a crystal, compound 3 (500mg). The mother liquor was chromatographed by TSK gel column with 50% MeOH to afford compound 4 (200mg).

Fraction 4 was subjected to repeatedly chromatograph on Sephadex LH – 20 column and TSK gel column eluted with 50% ~ 60% MeOH to afford compound 9(200mg), 10(100mg) and 11(80mg).

Fraction 5 was chromatographed on the column of MCI Gel CHP 20P and TSK Gel eluted with 50% MeOH to afford compound 6 (15mg).

Fraction 6 was over a column chromatography of Sephadex LH-20 eluted with 60% MeOH to afford compound 5 (100mg) and 7 (60mg).

Fraction 7 was filtered and compound 2 (500mg) was obtained.

Saluenin (1). Green yellow powder. Negative FAB-MS, m/z(%): 741[M($C_{32}H_{38}O_{20}$)-H]$^-$(100), 609[M-Xyl-H]$^-$(5), 463[609-Rha]$^-$(8). $[\alpha]_D^{25.5}$ +63.99°(MeOH, c 0.0029). IRν_{max} cm^{-1}: 3392, 2924, 2364, 1657, 1608, 1508, 1449, 1361, 1304, 1204, 1171, 1044, 996. UVλ_{max}(nm)(MeOH): 206.5, 257.2, 261.0, 288.0, 358.5. ^{13}C and ^1H NMR see Table 1 and 2.

Acid hydrolysis of saluenin (1) Compound 1 (30mg) was heated in 10 mL 1 mol/L HCl at 60 ℃ for 15 min, the hydrolyzed solution was chromatographed over sephadex LH-20 eluted with water and 50% MeOH and compound 2 (8mg) and 7 (7mg) were obtained.

Quercetin (2). pale yellow powder. Negative FAB-MS, m/z(%): 301[M($C_{15}H_{10}O_7$)-H]$^-$(100%). IR ν_{max} cm^{-1}:3324, 1665, 1611, 1562, 1522, 1452, 1407, 1382, 1319, 1261, 1214, 1199, 1170, 1132, 1092, 1014, 941. UVλ_{max}nm(MeOH):207.5, 284, 370.5. ^{13}C and ^1H NMR see Table 1 and 2.

Table 1 ^{13}C NMR data of compounds 1~7(in DMSO-d_6)

carbon	1			2	3	4	5	6	7	
2	157.04			146.79	156.68	156.22	156.42	156.31	156.48	
3	133.61			135.65	133.70	133.49	134.25	133.35	133.27	
4	177.71			175.78	177.74	177.41	177.72	177 65	177.28	
5	161.54			160.67	161.46	161.14	161.27	161.17	161.13	
6	99.02			98.13	99.06	98.58	98.90	96.68	98.57	
7	164.47			163.62	164.38	164.04	164.16	164.37	163.97	
8	94.36			93.30	93.94	93.40	93.81	93.54	93.46	
9	156.86			156.10	156.68	156.22	157.25	156.84	156.33	
10	104.31			102.97	104.31	103.86	104.20	103.86	103.9	
1'	121.65			121.92	121.50	121.06	120.74	120.93	121.48	
2'	116.20			115.03	115.57	115.11	115.43	115.50	115.13	
3'	145.02			145.00	145.03	144.71	145.17	145.05	144.64	
4'	148.71			147.64	148.70	148.35	148.40	148.45	148.29	
5'	115.50			115.55	116.51	115.59	115.66	115.50	116.20	
6'	121.55			119.94	121.93	121.85	121.08	121.63	121.13	
sugar	Glc	Rha	Xyl		Glc	Gal	Rha	Ara	Glc	Rha
1	101.63	101.28	105.53		101.35	101.69	101.82	107.84	101.16	101.00
2	74.12	81.28	74.37		74.41	71.16	70.38	82.06	74.01	70.52
3	76.36	69.77	76.75		76.75	73.17	70.53	76.98	76.55	69.97
4	70.14	71.05	70.58		70.19	67.85	71.25	85.20	70.28	71.83
5	76.98	68.19	65.79		77.57	75.73	70.02	60.69	75.85	68.10
6	67.87	17.84			61.24	60.06	17.43		66.90	17.57

Quercetin 3 – O – β – glucopyranoside(3). Negative FAB – MS, m/z(%): 463[M($C_{21}H_{20}O_{12}$) – H]$^-$ (100%). IRν_{max} cm^{-1}: 3368, 1659, 1607, 1565, 1499, 1446, 1363, 1305, 1274, 1200, 1170, 1114, 1081, 1062, 1013, 998, 936. UVλ_{max} nm(MeOH): 207.5, 257, 356.5. ^{13}C and ^{1}H NMR see Table 1 and 2.

Quercetin 3 – O – β – galactopyranoside(4). Negative FAB – MS, m/z(%): 463[M ($C_{21}H_{20}O_{12}$) – H]$^-$ (100%). IR ν_{max} cm^{-1}: 3318, 1658, 1608, 1565, 1503, 1453, 1367, 1260, 1209, 1174, 1126, 1091, 1051, 1021, 998, 941, 867, 816. UVλ_{max} nm(MeOH): 206, 256.5, 297, 360.5. ^{13}C and ^{1}H NMR see Table 1 and 2.

Quercetin 3 – O – β – L – rhamnopyranoside(5). Negative FAB – MS, m/z(%): 447[M ($C_{21}H_{20}O_{11}$) – H]$^-$ (100%). IR ν_{max} cm^{-1}: 3289, 1658, 1605, 1574, 1501, 1455, 1381, 1360, 1303, 1272, 1250, 1202, 1169, 1110, 1070, 1006, 998, 964, 918, 882. UVλ_{max} nm(MeOH): 206.5, 255, 351. ^{13}C and ^{1}H NMR see Table 1 and 2.

Table 2 ^{1}H NMR data of compounds 1 ~ 7(in DMSO – d_6)

proton	1	2	3	4	5	6	7
6	6.35, s	6.40, d, J = 1.6Hz	6.41,d, J = 1.9Hz	6.52, s	6.38 s	6.39,d, J = 1.2Hz	6.52,d, J = 2.0Hz
8	6.17, s	6.17,d, J = 1.6Hz	6.18,d, J = 1.5Hz	6.19,d, J = 2.0Hz	6.19,s	6.19,d J = 1.2Hz	6.18,d, J = 2.0Hz
2'	7.53, s	7.66,d, J = 1.2Hz		7.51,d, J = 2.4Hz	7.28, s	7.46,d, J = 1.6Hz	7.52, s
5'	6.62,d J = 8.4Hz	6.67,d, J = 8.4Hz		6.80,d, J = 8.8Hz	6.84,d, J = 8.0Hz	6.84,d, J = 8.4Hz	6.83,d, J = 8.4Hz
6'	7.51,d, J = 8.4Hz	7.53,dd, J = 8.8,1.2Hz		7.66,dd J = 8.4,2.0Hz	7.23,d, J = 8.0Hz	7.54,dd, J = 8.4,1.6Hz	7.53,dd, J = 8.6,2.0Hz
C5 – OH	12.57, s	12.49, s	12.60, s	12.62, s	12.64, s	12.62, s	12.62, s
Anomeric H							
Glc	5.29,d, J = 7.2Hz		5.41,d, J = 7.4Hz				5.34,d, J = 8.0Hz
Rha	4.26,s				5.23,s		4.36,s
Xyl	4.21,d, J = 7.2Hz						
Gal				5.34,d, J = 8.0Hz			
Ara						5.51,s	

Quercetin 3 – O – α – L – arabinofuranosid(6). Negative FAB – MS, m/z(%): 433[M ($C_{20}H_{18}O_{11}$) – H]$^-$ (100%). IR ν_{max} cm^{-1}: 3352, 1658, 1603, 1563, 1495, 1456, 1360, 1295, 1235, 1202, 1061, 1014, 938, 878, 802. UVλ_{max} nm(MeOH): 207, 256, 356. ^{13}C and ^{1}H NMR see Table 1 and 2.

Rutin(7) Negative FAB – MS, m/z(%): 609[M($C_{27}H_{30}O_{16}$) – H]$^-$ (100%). IRν_{max} cm^{-1}:

3422, 1656, 1604, 1506, 1456, 1363, 1297, 1204, 1169, 1122, 1090, 1064, 1015, 880, 809. UVλ_{max}nm (MeOH): 206, 256.5, 288, 356. ^{13}C and ^{1}H NMR see Table 1 and 2.

(−) − **Epicatechin** (**8**). White amorphous powder. Negative FAB − MS, m/z(%): 289[M ($C_{15}H_{14}O_6$) − H]$^-$ (100%). $[\alpha]_D^{17}$ + 75° (c 0.3800, MeOH). IRν_{max} cm^{-1}: 3392, 1608, 1510, 1440, 1365, 1285, 1202, 1160, 1110, 1060, 810. UVλ_{max}nm(MeOH): 208, 225, 280.5, 284. ^{1}H NMR(CD_3OD): δ4.80(1H, s, H − 2), 4.16(1H, m, H − 3), 2.79(1H, dd, J = 16.6, 4.6Hz, H − 4A), 2.64(1H, dd, J = 16.7, 3.5Hz, H − 4B), 5.87(1H, d, J = 2.2Hz, H − 6), 5.98(1H, d, J = 2.2Hz, H − 8), 6.98(1H, 1H, d, J = 1.4Hz, H − 2'), 6.77(2H, m, H − 5', 6'). ^{13}C NMR (CD3OD): δ79.1(C − 2), 66.6(C − 3), 28.5(C − 4), 157.1(C − 5), 96.2(C − 6), 157.2 (C − 7), 95.4(C − 8), 156.7(C − 9), 99.6(C − 10), 131.1(C − 1'), 115.5(C − 2'), 145.0(C − 3'), 145.1(C − 4'), 115.1(C − 5'), 119.1(C − 6').

Procyanidin B − 2 (**9**). White amorphous powder. Negative FAB − MS. m/z(%): 577[M ($C_{30}H_{26}O_{12}$) − H]$^-$ (100). $[\alpha]_D^{17}$ + 47.11° (c 0.0033. MeOH). IRν_{max} cm^{-1}: 3392, 1612, 1522, 1446, 1360, 1285, 1202, 1155, 1110, 1063, 823. UVλ_{max}nm (MeOH): 207, 281. ^{13}C NMR (CD_3OD): ring − A and C: δ76.3(C − 2), 78.7(C − 2'), 72.4(C − 3), 65.8(C − 3'), 36.3(C − 4), 28.8(C − 4'), 157.3, 156.9, 155.1(C − 5, 5', 7, 7', 9, 9'), 95.9, 95.4(C − 6, 6', 8, 8'), 96.9(C − 10), 100.1(C − 10'); ring − B: 131.8(C − 1), 115.6(C − 2), 144.9(C − 3), 144.7(C − 4), 115.5(C − 5), 119.0(C − 6), 131.3(C − 1'), 115.0(C − 2'), 144.5(C − 3'). 144.7(C − 4'), 114.7(C − 5'), 106.8(C − 6').

Procyanidin C − 1 (**10**). Brown powder. Negative FAB − MS, m/z(%): 865[M ($C_{45}H_{38}O_{18}$)$^-$H] − (100). $[\alpha]_D^{17}$ + 70.66° (c 0.0111, MeOH). IRν_{max} cm^{-1}: 3341, 1604, 1521, 1444. 1360, 1284, 1201. 1148, 1099. 1059. 995, 972, 855. UVλ_{max} nm (MeOH): 209.5, 280.5. ^{13}C NMR (CD_3OD): ring − A and C: δ79.72 (C − 2), 77.11(C − 2', 2"), 66.97(C − 3), 73.39, 72.84(C − 3', 3"), 29.69(C − 4), 37.43(C − 4', 4"), 154.43, 156.46. 156.86, 157.26, 157.80. 158.34(C − 5, 5', 5", 7, 7', 7", 9, 9', 9"). 96.66, 96.31(C − 6, 6', 6", 8, 8', 8"), 97.54, 100.76(C − 10, 10', 10"); ring − B: 132.67, 132.09(C − 1, 1', 1"). 115.16 (C − 2, 2', 2"), 115.34, 116.08(C − 5, 5', 5"). 145.43, 145.54. 145.67, 145.76, 145.91(C − 3, 3', 3", 4, 4', 4"). 119.19, 107.64(C − 6. 6', 6").

Procyanidin B − 2 3' − O − gallate (**11**). Off − white powder. Negative FAB − MS, m/z(%): 729 [M($C_{37}H_{30}O_{16}$) − H]$^-$ (100). $[\alpha]_D^{17}$ − 38.37° (c 0.0043, MeOH). IRν_{max} cm^{-1}: 3368, 1692, 1611, 1522, 1450, 1360, 1284, 1231, 1150, 1097, 1062, 1032, 872. UVλ_{max}nm (MeOH): 207. 280. ^{13}C NMR (CD_3OD): ring − A and C: δ75.04(C − 2), 79.92(C − 2'), 76.14(C − 3), 67.14 (C − 3'), 34.77(C − 4), 29.43(C − 4'), 157.54, 157.31, 156.51, 156.12(C − 5, 5', 7, 7', 9, 9'), 96.45(C − 6), 96.11(C − 6'). 97.24(C − 8), 107.25(C − 8'), 102.67(C − 10), 100.77(C − 10'); ring B: 131.93, 131.82(C − 1.1'), 116.00, 115.84, 115.20(C − 2. 2', 5, 5'), 145.76, 145.65, 145.39, 145.20(C − 3, 3', 4, 4'), 119.52, 119.79(C − 6, 6'); Galloyl group: 121.61(C − 1), 110.40(C − 2, 6), 146.07(C − 3, 5), 139.58(C − 4), 167.20(COO).

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《中国种子植物》数据库光盘出版

在国家自然科学基金委员会的支持下，《中国种子植物》数据库（中文光盘版）已于1999年7月30日前正式出版（作者：吴征镒、丁托娅）。

本光盘是一个数据库系统；它包括中国境内分布的全部种子植物各级分类单位的名称、分布地点、生境、海拔等项信息；所载信息，如：植物的中文名称、拉丁学名和异名以及它们的分布区域均作了缜密的考证；全部数据在计算机上标准化，按照植物学的规律建成数据库，并编制了此数据库的专用应用系统。在Windows9X操作系统的支持下，可以根据使用者的要求对这些信息从两个方向进行查询和再加工（如：1. 正向；向使用者提供某一分类单位的名称、分布、生境、海拔、经纬度等信息；2. 逆向；根据使用者指定的地点、生境或海拔等关键字、总结、归纳该关键字确定的范围内所分布的各级分类单位等项信息。）。本光盘已经脱离了人们对“书”的原有认识和概念；真正实现了资料信息化；它使植物学工作者彻底摆脱了一本本翻资料、一张张的做卡片的繁重手工劳动；使用者只需用鼠标轻轻一点，即可获得所需的植物信息。

本光盘对资源利用、环境保护、林业、农业、科研、教学以及国民经济发展决策等部门有重要的指导和参考应用价值。

欲购本数据库或需技术支持的用户，请直接与中国科学院昆明植物研究所联系。

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