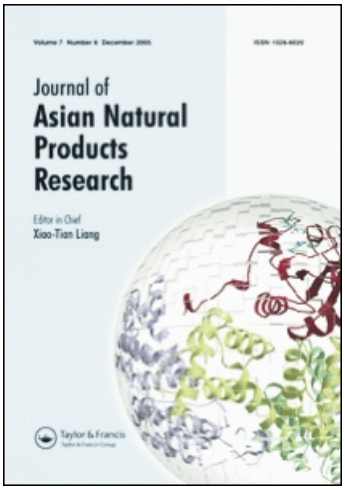

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Hui Yang[ab]; Bei Jiang[a]; Ai-Jun Hou[a]; Zhong-Wen Lin[a]; Han-Dong Sun
[a] Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, China [b] Chemistry Department, College of Life Science and Chemistry, Yunnan University, Kunming, China

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COLEBROSIDE A, A NEW DIGLUCOSIDE OF FATTY ACID ESTER OF GLYCERIN FROM *CLERODENDRUM COLEBROOKIANUM*

HUI YANG[a,b], BEI JIANG[a], AI-JUN HOU[a], ZHONG-WEN LIN[a] and HAN-DONG SUN[a,*]

[a]*Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, China;* [b]*Chemistry Department, College of Life Science and Chemistry, Yunnan University, Kunming 650091, China*

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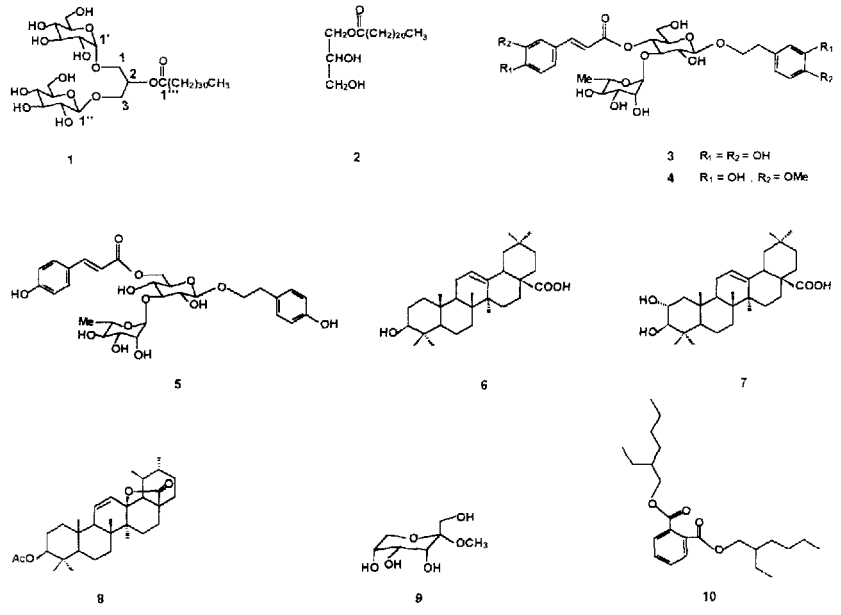
Colebroside A (**1**), a new diglucoside of fatty acid ester of glycerin, was isolated from the aerial parts of *Clerodendrum colebrookianum* Walp., along with nine known compounds (**2**–**10**). Their structures were elucidated by spectroscopic and chemical methods. Compounds **2**, **3**, **4**, **5**, **7**, **8**, **9** and **10** have been obtained from this plant for the first time.

Keywords: *Clerodendrum colebrookianum* Walp.; Verbenaceae; Diglucoside of fatty acid ester of glycerin; Colebroside A (**1**)

INTRODUCTION

Clerodendrum colebrookianum Walp. (Verbenaceae), is distributed widely in the South and Southeast Asia. In China, it mainly grows in the moist and waste place of the western and southern regions of Yunnan province up to an altitude of 280–2100 m [1]. In Chinese folk medicine terminology, *C. colebrookianum* Walp. has the functions of "expelling toxin by cooling, cooling blood to induce diuresis and purging heat" [2]. It has been used as a remedy for hypertension in India [3]. The chemical investigation of this

* Corresponding author. Tel.: 86-871-5150660. Fax: 86-871-5216343.
E-mail: hdsun@mail.kib.ac.cn.



SCHEME 1

plant has been reported [3–8]. In order to search for the biologically active constituents from this plant, we reinvestigated this medicinal plant.

In this paper, we wish to report the isolation and structural elucidation of a new compound, named colebroside A (**1**), as well as nine known compounds, including glyceryl-1-docosoicate (**2**), acteoside (**3**) [9], martinoside (**4**) [10], osmanthuside B_6 (**5**) [11], oleanolic acid (**6**) [12], maslinic acid (**7**) [13], 3β-acetoxyurs-11-en-28, 13-olide (**8**) [14], 2-O-methylalluloside (**9**) [15], and bis (2-ethylhexyl) phthalate (**10**) [16] (Scheme 1).

RESULTS AND DISCUSSION

Colebroside A (**1**) displayed strong IR bands at 3417(br.) and 1740 cm^{-1}, which suggested the presence of hydroxyl and carboxyl groups. The FABMS showed a molecular ion peak at m/z 879 $[M+1]^+$, which agreed with a molecular formula $C_{47}H_{90}O_{14}$, this conclusion was supported by its HRFABMS ($[M+1]^+$ 879.6363, calcd. 879.6409), ^{13}C NMR and DEPT spectral data (Table I). The ^1H and ^{13}C NMR spectra of **1** exhibited that it had no double bond and carbonyl group except for a carboxyl group. Thus, **1** contained two rings besides the carboxyl group based on a calculation of unsaturation degrees ($n = 3$). Moreover, the ^1H NMR spectrum showed

TABLE I ^{13}C NMR spectral data of **1** in C_5D_5N (100.6 Hz, δ in ppm from TMS)

C	1	C	1
1	68.1 t	**3″**	75.1 d
2	71.7 d	**4″**	70.6 d
3	68.1 t	**5″**	74.6 d
α-Glc		**6″**	63.5 t
1′	101.3 d	Acyl moiety	
2′	71.0 d	**1‴**	173.5 s
3′	72.2 d	**2‴**	34.4 t
4′	69.9 d	**3‴**	32.3 t
5′	72.9 d	**4‴–29‴**	29.7 t
6′	62.6 t	**30‴**	25.4 t
β-Glc		**31‴**	20.9 t
1″	105.5 d	**32‴**	14.4 q
2″	71.1 d		

TABLE II Some principal results from HMQC, ^{1}H–^{1}H COSY and HMBC correlations of **1**

Proton	*HMQC* (^{13}C)	*COSY* (^1H)	*HMBC* (^{13}C)
1a	1	1b, 2	
1b	1	1a, 2	1′
2	2	1a, 1b, 3a, 3b	(1), (3), 1‴
3a	3	2, 3b	1″
3b	3	2, 3a	
1′	1′	2′	1
1″	1″	2″	3

Two-bond correlations were shown in brackets.

the signals of one primary methyl group (δ 0.84, H-32‴), two methylenes bearing oxygen (δ 4.03, H-1a and 3a; δ 4.76, H-1b and 3b), one oxymethine (δ 5.66, H-2) and two anomeric protons (δ 5.52, H-1′ and δ 4.75, H-1″). The ^{13}C NMR spectrum revealed one carboxyl group (δ 173.5, C–1‴) and two D-glucopyranosyl groups (δ 101.3, 71.0, 72.2, 69.9, 72.9, 62.6 and δ 105.5, 71.1, 75.1, 70.6, 74.6, 63.5) [15], whose glycosidic linkages were shown to be α and β by the coupling constants ($J = 3.4$ and 7.4 Hz) of the anomeric proton signals, respectively. Furthermore, exhaustive acidic hydrolysis of **1** gave glucose identified by TLC comparing with authentic sample. This fact also indicated the presence of the glucopyranosyl group. All ^{1}H and ^{13}C NMR signals of **1** were assigned by HMQC, HMBC and ^{1}H–^{1}H COSY spectra as shown in Table I and in Experimental section, which suggested **1** to be a diglucoside of lacceroic acid ester of glycerin. The connectivities of the glucosyl units, lacceroyl group and glycerin were determined by the HMBC spectrum (Table II). Consequently, the structure of **1** was established as 1-O-(α-D-glucopyranosyl)-3-O-(β-D-glucopyranosyl)-glyceryl-2-lacceroicate.

The structures of the nine known compounds were characterized by direct comparison of their NMR, IR, UV and MS spectra with those reported previously. Compounds **2**, **3**, **4**, **5**, **7**, **8**, **9** and **10** were isolated from *C. colebrookianum* for the first time.

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were measured on a XRC-1 micro melting point apparatus and uncorrected. Optical rotations were taken on JASCO-20C digital polarimeter. IR spectra were recorded with Bio-Rad FTS-35 spectrometer. UV spectra were obtained on a UV 210A spectrometer. MS spectra were measured on a VG Auto Spec-3000 spectrometer. NMR spectra were run on Bruker AM-400 and DRX-500 spectrometers. Separation and purification were performed by column chromatography on silica gel (200–300 and 300–400 mesh) and reversed-phases materials (RP-18 and MCI gel CHP-20).

Plant Material

Plant material was collected in September 1996 from Xishuangbanna, Yunnan province, People's Republic of China and identified by Prof. Li Xi-wen. A voucher specimen (96-09-18) was deposited in the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, People's Republic of China.

Extraction and Isolation

The air-dried and powdered aerial parts (6.0 kg) of *C. colebrookianum* were extracted with 95% EtOH (3 × 20 l) under reflux and then concentrated *in vacuo* to give crude extract (619.0 g). The extract was suspended in H_2O and then successively partitioned with petroleum-ether (60–90°C), EtOAc and n-BuOH to afford petroleum-ether, EtOAc and n-BuOH residues 272.0, 98.0 and 206.4 g, respectively. The petroleum-ether residue was subjected to column chromatography over silica gel eluting with petroleum-ether/chloroform (1 : 0, 9 : 1, 3 : 1 and 0 : 1), chloroform/acetone (9 : 1, 3 : 1 and 0 : 1) to give fractions I–VII. Fractions III (20.0 g) and IV (8.0 g) were chromatographed on silica gel column developed with petroleum-ether/chloroform to afford compounds **6** (86 mg) and **8** (24 mg), respectively. Fractions V

(17.5 g), VI (8.0 g) and VII (20.0 g) were subjected to column chromatography and medium pressure column on silica gel with petroleum-ether/acetone, chloroform/acetone and chloroform/methanol as eluent repeatedly and finally yielded compounds **1** (595 mg), **2** (10 mg), **7** (21 mg) and **10** (117 mg).

After repeated silica gel and reversed phase silica gel (RP-18) as well as MCI gel CHP-20 (eluent: $CHCl_3$/MeOH, $CHCl_3$/MeOH/H_2O and MeOH/H_2O) column chromatography, compounds **3** (15.6 g), **4** (2.4 g), **5** (173 mg) and **9** (23 mg) were obtained from the EtOAc residue.

Exhaustive Acidic Hydrolysis

Compound **1** was hydrolyzed at 100°C for 1 h on TLC plates in a chamber filled with conc. HCl and the products were separated with solvent system [n-BuOH–EtOH–H_2O (4 : 1 : 5)], glucose was identified by comparison with authentic samples.

Colebroside A (**1**) $C_{47}H_{90}O_{14}$, colorless wax, $[\alpha]_D^{20.2}$ +71.17 (c 0.139, MeOH); IR (KBr) ν_{max} 3417(br.), 2927, 2856, 1740, 1643, 1465, 1151, 1074, 918 cm^{-1}; ^1H NMR (C_5D_5N, 400 MHz) δ 4.03 (each 1H, m, H-1a and 3a), 4.76 (each 1H, m, H-1b and 3b), 5.66 (1H, m, H-2), 5.52 (1H, d, $J = 3.4$ Hz, H-1′), 4.03–4.76 (6H, m, H-2′–6′), 4.75 (1H, d, $J = 7.4$ Hz, H-1″), 4.03–4.76 (6H, m, H-2″–6″), 2.35 (2H, t, $J = 7.2$ Hz, H-2‴), 1.06–2.07 (58H, m, H-3‴–31‴), 0.84 (3H, t, $J = 6.2$ Hz, H-32‴); positive ion FABMS *m/z* 879 $[M + 1]^+$ (3), 397 (10), 325 (6), 283 (13), 255 (100), 221 (12), 171 (28), 119(43).

Glyceryl-1-docosoicate (**2**) $C_{25}H_{50}O_4$, colorless wax, IR (KBr) ν_{max} 3309 (br.), 2959, 2919, 2851, 1731, 1471, 1394, 1288, 1198, 1180, 1124, 991 cm^{-1}; ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 65.2 (t, C-1), 70.34 (d, C-2), 63.40 (t, C-3), 174.2 (s, C-1′), 34.16 (t, C-2′), 31.69 (t, C-3′), 29.30 (t, C-4′–19′), 24.91 (t, C-20′), 22.63 (t, C-21′), 14.00 (q, C-22′); ^1H NMR ($CDCl_3$, 400 MHz) δ 4.12 (1H, dd, $J = 11.6$, 6.1 Hz, H-1a), 4.18 (1H, dd, $J = 11.6$, 4.5 Hz, H-1b), 3.91 (1H, m, H-2), 3.57 (1H, dd, $J = 11.5$, 5.8 Hz, H-3a), 3.68 (1H, dd, $J = 11.5$, 3.9 Hz, H-3b), 2.33 (2H, t, $J = 7.5$ Hz, H-2′), 1.23–1.60 (38H, m, H-3′–21′), 0.85 (3H, t, $J = 7.0$ Hz, H-22′); positive ion FABMS *m/z* 415 $[M + 1]^+$ (5), 391 (100), 359 (25), 331 (68), 313 (20), 279 (36), 239 (34), 167 (15), 149 (88), 113 (20).

Acteoside (**3**) $C_{29}H_{36}O_{15}$, amorphous white powder, $[\alpha]_D^{21.6}$ −79.31 (c 0.58, MeOH), UV (EtOH) λ_{max} 203.5, 220, 245, 286, 296, 332.5 nm; IR (KBr) ν_{max} 3400(br.), 2925, 1685, 1590, 1510, 1435, 1360, 1270, 1150, 1110, 1040, 805 cm^{-1}; negative ion FABMS *m/z* 623 $[M - 1]^-$ (100); Its ^1H and ^{13}C NMR spectral data, see Tables III and IV.

TABLE III The ^{1}H NMR spectral data of compound **3**, **4** and **5** in CD_3OD (400 MHz, δ in ppm from TMS and J in Hz)

Proton	**3**	**4**	**5**
Aglycone			
2	6.69 (1H, d, J = 2.0)	6.73 (1H, d, J = 2.1)	6.76 (1H, d, J = 8.2)
3			7.06 (1H, d, J = 8.0)
5	6.67 (1H, d, J = 8.0)	6.79 (1H, d, J = 8.1)	7.06 (1H, d, J = 8.0)
6	6.55 (1H, dd, J = 8.0, 2.0)	6.67 (1H, dd, J = 8.1, 2.1)	6.76 (1H, d, J = 8.2)
α_a	3.71 (1H, dd, J = 16.4, 8.0)	3.72 (1H, dd, J = 16.3, 8.0)	3.26–4.38 (1H, m)
α_b	4.03 (1H, dd, J = 16.4, 8.0)	4.05 (1H, dd, J = 16.3, 8.0)	3.26–4.38 (2H, m)
β	2.78 (2H, t, J = 8.0)	2.08 (2H, t, J = 7.4)	2.93 (2H, t, J = 7.3)
OMe		3.79 (3H, s)	
Acyl moiety			
2	7.06 (1H, d, J = 2.0)	7.19 (1H, d, J = 1.6)	6.94 (1H, d, J = 7.8)
3			7.31 (1H, d, J = 7.7)
5	6.78 (1H, d, J = 8.0)	6.81 (1H, d, J = 8.2)	7.31 (1H, d, J = 7.7)
6	6.94 (1H, dd, J = 8.0, 2.0)	7.07 (1H, dd, J = 8.2, 1.6)	6.94 (1H, d, J = 7.8)
β	6.27 (1H, d, J = 15.8)	6.34 (1H, d, J = 15.9)	6.26 (1H, d, J = 15.8)
γ	7.59 (1H, d, J = 15.8)	7.65 (1H, d, J = 15.9)	7.58 (1H, d, J = 15.8)
OMe			
Glucosyl group			
1	4.36 (1H, d, J = 7.8)	4.37 (1H, d, J = 8.0)	4.36 (1H, d, J = 7.8)
2–5	3.28–3.94 (4H, m)	3.28–3.93 (4H, m)	3.26–4.38 (4H, m)
$\mathbf{6_a}$			4.33 (1H, dd, J = 12.2)
$\mathbf{6_b}$			4.68 (1H, dd, J = 12.2)
Rhamnosyl group			
1	5.19 (1H br.s)	5.19 (1H, d, J = 1.3)	5.18 (1H, s)
2–5	3.28–3.94 (4H, m)	3.28–3.93 (4H, m)	3.26–4.38 (4H, m)
6	1.09 (3H, d, J = 6.0)	1.09 (3H, d, J = 6.2)	1.07 (3H, d, J = 6.4)

TABLE IV The ^{13}C NMR spectral data of compounds **3**, **4** and **5** in CD_3OD (100.6 MHz, δ in ppm from TMS)

Carbon	**3**	**4**	**5**
Aglycone			
1	131.5 s	133.0 s	127.7 s
2	116.3 d	113.1 d	116.2 d
3	145.9 s	147.5 s	130.0 d
4	144.5 s	147.4 s	146.8 s
5	117.1 d	117.1 d	130.0 d
6	121.3 d	121.2 d	116.2 d
α	72.1 t	72.1 t	72.1 t
β	36.4 t	36.5 t	37.2 t
OMe		56.6 q	
Acyl moiety			
1	127.6 s	127.7 s	127.2 s
2	114.7 d	112.0 d	129.7 d
3	147.9 s	149.4 s	116.5 d
4	149.6 s	150.8 s	149.7 s
5	116.5 d	116.6 d	116.5 d
6	123.2 d	124.3 d	129.7 d
α	168.3 s	168.3 s	168.3 s
β	115.3 d	115.2 d	114.8 d
γ	146.6 d	147.8 d	147.2 d
OMe		56.6 q	
Glucosyl group			
1	104.0 d	104.2 d	104.2 d
2	75.8 d	76.0 d	76.1 d
3	81.6 d	81.5 d	81.6 d
4	70.5 d	70.7 d	70.7 d
5	76.0 d	76.2 d	76.1 d
6	62.3 t	62.4 t	64.7 t
Rhamnosyl group			
1	102.9 d	102.9 d	102.9 d
2	70.3 d	70.4 d	70.4 d
3	73.7 d	73.8 d	73.8 d
4	72.2 d	72.3 d	72.3 d
5	72.0 d	72.0 d	70.7 d
6	18.4 q	18.4 q	18.4 q

Martinoside (**4**) $C_{31}H_{40}O_{15}$, amorphous white powder, $[\alpha]_D^{21.6}$ −67.52 (c 0.411, MeOH), UV (EtOH) λ_{max} 220, 229, 285, 299, 328 nm; IR (KBr) ν_{max} 3395 (br.), 2920, 1690, 1620, 1585, 1505, 1430, 1275, 1150, 1025, 805 cm^{-1}; negative ion FABMS *m/z* 651 $[M-1]^-$ (100); Its ^{1}H and ^{13}C NMR spectral data, see Tables III and IV.

Osmanthuside B$_6$ (**5**) $C_{29}H_{36}O_{13}$, amorphous white powder, $[\alpha]_D^{21.6}$ −48.84 (c 0.510, MeOH), UV (EtOH) λ_{max} 220, 245, 286, 332 nm; IR (KBr) ν_{max} 3450(br.), 2926, 1680, 1598, 1505, 1435, 1362, 1272, 1150, 1042, 809 cm^{-1}; negative ion FABMS *m/z* 591 $[M-1]^-$ (100); Its ^{1}H and ^{13}C NMR spectral data, see Tables III and IV.

3β-acetoxyurs-11-en-28,13-olide (**8**) $C_{32}H_{48}O_4$, colorless needles, m.p.: 230–232°C, $[\alpha]_D$ +47.91 (c 0.454, $CHCl_3$), IR (KBr) ν_{max} 2993, 2960, 2922, 2853, 1769, 1728, 1469, 1392, 1364, 1246, 1225, 1143, 1136, 1026, 993 cm^{-1}; ^1H NMR (C_5D_5N, 400 MHz) δ 4.50 (1H, dd, $J = 10.9$, 5.6 Hz, H-3α), 5.47 (1H, dd, $J = 10.3$, 3.6 Hz, H-11), 6.02 (1H, d, $J = 10.3$ Hz, H-12), 0.85 (each 3H, s, H-23 and 24), 0.94 (3H, s, H-25), 1.06 (3H, s, H-26), 1.21 (3H, s, H-27), 1.01 (3H, d, $J = 5.8$ Hz, H-29), 0.90 (3H, d, $J = 6.1$ Hz, H-30), 2.02 (3H, s, acetoxy H-2′); ^{13}C NMR (C_5D_5N, 100.6 MHz) δ 37.97 (t, C-1), 23.57 (t, C-2), 80.61 (d, C-3), 37.36 (s, C-4), 54.91 (d, C-5), 17.49 (t, C-6), 31.11 (t, C-7), 40.57 (s, C-8), 53.15 (d, C-9), 36.64 (s, C-10), 135.63 (d, C-11), 127.07 (d, C-12), 87.47 (s, C-13), 41.35 (s, C-14), 26.72 (t, C-15), 23.17 (t, C-16), 43.85 (s, C-17), 57.04 (d, C-18), 49.65 (d, C-19), 50.57 (d, C-20), 29.66 (t, C-21), 31.42 (t, C-22), 27.73 (q, C-23), 17.22 (q, C-24), 16.19 (q, C-25), 18.79 (q, C-26), 18.24 (q, C-27), 179.16 (s, C-28), 17.98 (q, C-29), 18.9 (q, C-30), 170.8 (s, acetoxy C-1′), 21.29 (q, acetoxy C-2′); EIMS (70 eV) *m/z* 496 $[M]^+$ (31), 468 $[M - CO]^+$ (16), 452 $[M - COO]^+$ (86), 438 (10), 332 (3), 300 (13), 277 (61), 263 (84), 248 (20), 217 (38), 204 (74), 189 (83).

Bis (2-ethylhexyl) phthalate (**10**) $C_{24}H_{38}O_4$, colorless oil, UV ($CHCl_3$) λ_{max} 203, 225, 270, 278 nm; IR ν_{max} 2961, 2932, 2862, 1730, 1600, 1581, 1464, 1382, 1275, 1124, 1074, 1040, 959 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.65 (each 1H, dd, $J = 5.6$, 2.2 Hz, H-3 and 6), 7.45 (each 1H, m, H-4 and 5), 4.17 (each 2H, dd, $J = 11.1$, 5.2 Hz, H-1′ and 1″), 1.64 (each 1H, m, H-2′ and 2″), 1.38 (each 2H, m, H-3′ and 3″), 1.28 (each 2H, m, H-4′, 4″, 5′, 5″, 7′ and 7″), 0.86 (each 3H, m, H-6′, 6″, 8′ and 8″); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 132.3 (s, C-1 and 2), 130.7 (d, C-3 and 6), 128.6 (d, C-4 and 5), 167.5 (s, C-α′ and α″), 67.91 (t, C-1′ and 1″), 38.61 (d, C-2′ and 2″), 23.62 (t, C-3′ and 3″), 22.80 (t, C-4′ and 4″), 28.77 (t, C-5′ and 5″), 13.83 (q, C-6′ and 6″), 30.23 (t, C-7′ and 7″), 10.77 (q, C-8′ and 8″); positive ion FABMS *m/z* 391 $[M + 1]^+$ (56), 279 (11), 261 (5), 167 (29), 149 (100), 113 (33), 71 (37).

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