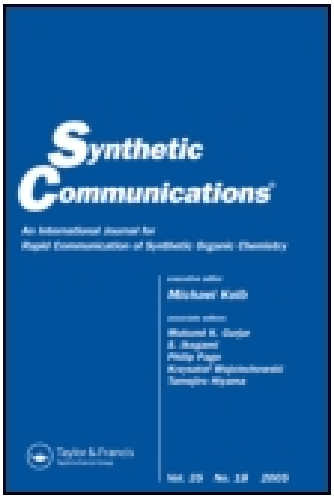

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Radical Cyclization Route to the Stereoselective Synthesis of (+)-*trans*-Cognac Lactone and (+)-*trans*-Aerangis Lactone

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Abstract: Stereoselective total synthesis of two chiral lactones, (+)-*trans*-cognac lactone (**1b**) and (+)-*trans*-aerangis lactone (**2c**), has been achieved from the same intermediate using a radical-based cyclization route.

Keywords: aerangis lactone, chiral lactones, cognac lactone, natural products

INTRODUCTION

The γ-lactones (five-membered) and δ-lactones (six-membered) functionalized at the ring carbons are useful as building blocks in natural product syntheses and are used in the perfume industry. Examples in this family are (−)-*cis* and (+)-*trans* cognac lactones **1a** and **1b**, and *cis* and *trans* aerangis lactones **2a, 2b, 2c**, and **2d**. The *cis* and *trans* cognac lactones were isolated from different types of wood, and they were identified as key flavors of aged alcoholic beverages such as whisky, brandy, wine, and cognac.[1–3] These two diastereomeric lactones have the same (*S*)-configuration at C-(4) and different configurations at C-(5). Aerangis lactones **2a**–**2d**[4] are natural fragrant molecules identified from the *Aerangis* species

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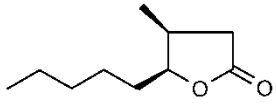
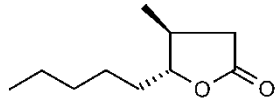
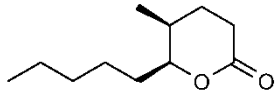
(native to Kenya and Tanzania). In 1995, Bartschat et al.[4b] obtained samples of four stereo isomers of aerangis lactone by chiral high-performance liquid chromatography.



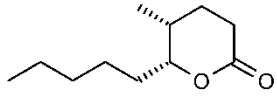
(-)-*cis*-cognac lactone
(4*S*, 5*S*)-1a



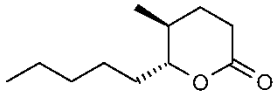
(+)-*trans*-cognac lactone
(4*S*, 5*R*)-1b



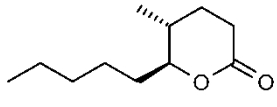
(-)-*cis*-aerangis lactone
(4*S*, 5*S*)-2a



(+)-*cis*-aerangis lactone
(4*R*, 5*R*)-2b



(+)-*trans*-aerangis lactone
(4*S*, 5*R*)-2c



(-)-*trans*-aerangis lactone
(4*R*, 5*S*)-2d

A variety of syntheses of racemic and enantiomerically pure cognac lactones in both diastereomeric forms is reported in the literature.[5] (±)-*cis*-Aerangis lactone was first obtained as a 1:1 mixture with the *trans*-diastereomer **2c** by hydrogenation of dihydrojasmone and subsequent Baeyer–Villiger oxidation.[6] The *cis* and *trans* isomers were found to show a very pleasant odor, reminiscent both of the smell of tuberose and gardenia and of the fragrance of caramel, condensed milk, and coconut.[6] As a consequence, the synthesis of disubstituted γ- and δ-lactones **1** and **2** has drawn much attention. As a part of our program on the synthesis of naturally occurring bio-active lactones,[7] we herein report a radical cyclization route for the synthesis of (+)-*trans*-cognac lactone (**1b**) and (+)-*trans*-aerangis lactone (**2c**).

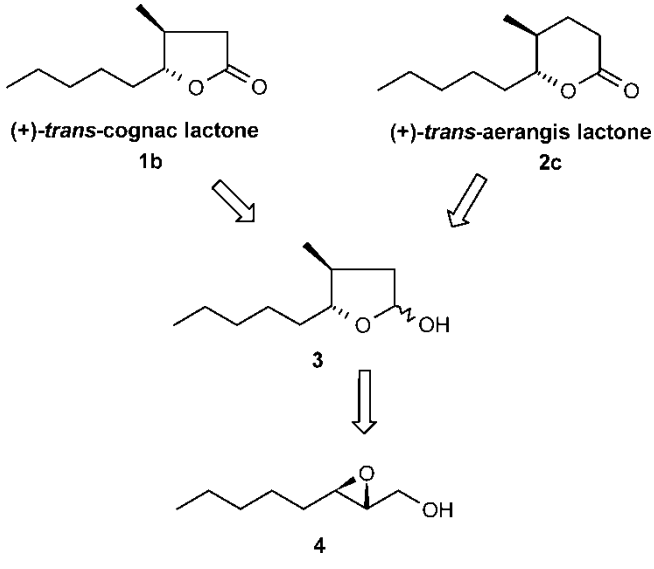
RESULTS AND DISCUSSION

Even though the radical-based five-membered lactone synthesis was reported from our group,[8] this is the first report of a synthesis of a six-membered lactone using the same strategy. While targeting synthesis of the six-membered lactone, (+)-*trans*-aerangis lactone **2c**, we could get a five-membered lactone, (+)-*trans*-cognac lactone **1b**, from the key intermediate

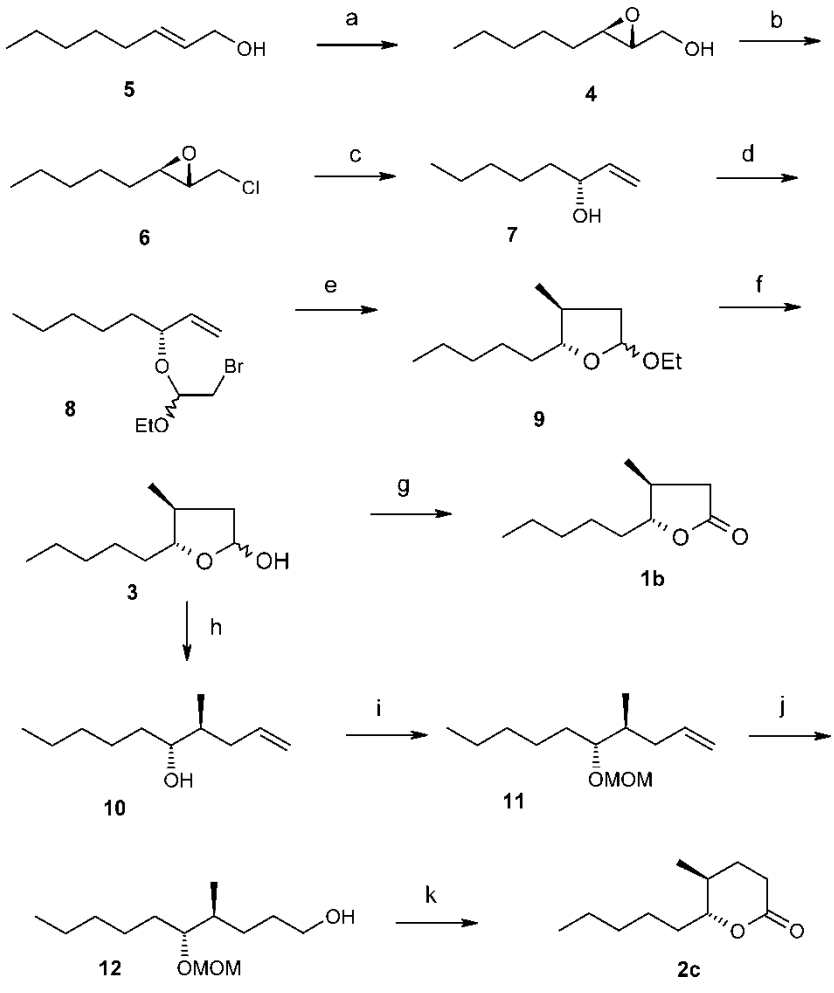
3. The intermediate **3** can be prepared from a chiral epoxy alcohol **4** as given in Scheme 1.

The synthesis of the two lactones **1b** and **2c** began with the readily available *E*-allyl alcohol **5** (Scheme 2). The alcohol **5** was subjected to Sharpless epoxidation conditions using (−) diethyl-D(-)-tartarate (DET), $Ti(OiPr_4)$, and cumenehydroperoxide in dichloromethane (DCM) at −24°C to afford 2,3-epoxy alcohol **4** in 78% yield. The epoxy alcohol **4** was converted to the corresponding 2,3-epoxy-1-chloride **6** by treatment with triphenylphosphine (TPP) in refluxing CCl_4 for 4 h. Reductive opening of **6** was achieved with Na in ether to furnish the desired terminal alkenic alcohol **7** in 70% yield. Treatment of **7** with N-bromosuccinamide and ethyl vinyl ether in DCM afforded the bromoacetal **8**.[9] The key step of the synthesis was the radical cyclization, which could be achieved by treatment of bromoacetal **8** with tri-*n*-butylstannane (Bu_3SnH), N,N′-azoisobutyronitrile (AIBN) catalyst (as a radical initiator), in refluxing benzene[10] for 4 h to give the cyclic ethyl acetal **9**. The cyclic acetal **9** was hydrolyzed using 60% AcOH under refluxing conditions to give a key intermediate lactol **3**, which on oxidation with pyridiniumchlorochromate (PCC) in DCM afforded the target molecule **1b** in 92% yield. The stereochemistry of the lactone **1b** was established to be *trans* by NMR spectral analysis, which showed a methyl resonance at 1.01 (d, $J = 5.9$ Hz) and H-5 at 3.82–3.94 (m, 1H), and also comparing the natural product spectral and optical rotation data.[5i]

The synthesis of *trans*-aerangis lactone was achieved from the key intermediate lactol **3** by manipulating the following reactions (Scheme 2).



Scheme 1. Retro synthetic analysis.



Scheme 2. Reagents and conditions: (a) (−)-DET, $Ti(OiPr)_4$, cumenehydroperoxide, DCM, −24°C, 78% (b) TPP, CCl_4, reflux, 70%, (c) Na, ether, 0°C−r.t., 70%, (d) NBS, ethyl vinyl ether, DCM, 0°C−r.t., (e) $(n\text{-}Bu)_3SnH$, benzene, reflux, (f) 60% AcOH, reflux, 68% (for three steps), (g) PCC, DCM, 92%, (h) *t*-BuOK, CH_3PPh_3I, 0°C−r.t., 53%, (i) MOMCl, iPr_2NEt, DCM, 0°C−r.t., 81%, (j) (i) $BH_3 \cdot THF$, (ii) NaOH, H_2O_2, 0°C−r.t., 88%, (k) (i) IBX, DCM−DMSO, 0°C−r.t., (ii) $NaClO_2$, NaH_2PO_4, DMSO, (iii) PTSA, MeOH 68% (for three steps).

Thus, chain elongation by one carbon atom was achieved via one-carbon Wittig olefination reaction with methyltriphenylphosphonium iodide in the presence of *t*-BuOK to afford the homologated compound **10** in 53% yield. The secondary hydroxyl group in compound **10** was protected as its methoxymethyl (MOM) ether by treatment with MOMCl, in the presence of Hunig's

base in DCM. Hydroboration of **11** using a $BH_3 \cdot THF$ complex (1 M solution) afforded a primary hydroxy compound **12** in 88% yield. The alcohol **12** was subjected to oxidation using iodoxybenzoic (IBX) in DCM–dimethylsulphoxide (DMSO) to afford the aldehyde; without isolation it was further oxidized to the corresponding acid using $NaClO_2$ and NaH_2PO_4 in DMSO. Acid was also used directly for the next step without further purification. Thus, acid on treatment with para-toluenesulphonic acid (PTSA) in MeOH produced the target molecule **2c** by deprotection of MOM group followed by in situ cyclization. Its spectral data and specific rotation were in complete agreement with those reported for the natural product.[5i]

In summary, we have described an elegant radical-based strategy for the synthesis of disubstituted five-and six-membered lactones, (+)-*trans*-cognac lactone (**1b**) and (+)-*trans*-aerangis lactone (**2c**), from the same key intermediate.

EXPERIMENTAL

All solvents were distilled before use. Dry solvents were prepared according to the standard procedures. All reactions were carried out under an N_2 atmosphere and monitored by thin-layer chromatography (TLC) on silica gel (60–120 mesh, Merck). NMR spectra were recorded on Bruker (300-MHz ^1H; 75-MHz ^{13}C) and Varian (200-MHz ^1H; 50-MHz ^{13}C) NMR spectrometers using $CDCl_3$ as solvent. Electrospray ionisation technique (ESI)-mass spectra were recorded with LC-MSD-Trap-SL (Agilent technologies). IR spectra were recorded with Fourier transform infrared spectroscopic technique (FTIR) (Thermo Nicolet Nexus 670 spectrometer). Optical rotations were measured with Jasco DIP-370 polarimeter at 20°C.

((*2S,3S*)-3-Pentyloxiran-2-yl) Methanol (4)

DCM (25 ml) was added to a powdered and activated molecular sieve (4 Å, 1.5 g), and the suspension was cooled to −24°C. D-(-)-DET (3.8 g, 18 mmol) and $Ti(OiPr)_4$ (5.3 g, 18 mmol) were added subsequently while stirring, and the resultant mixture was stirred for 30 min. To this stirred solution, allyl alcohol **5** (12 g, 93 mmol) was added and stirred for 30 min more. Then Cumene hydroperoxide (16.6 ml, 112 mmol) was added, and the reaction mixture was stirred for 3 h. After monitoring by TLC, the reaction mixture warmed to 0°C and quenched with water and sat. NaOH + NaCl solution, stirred for 30 min, and filtered through celite, and the filtrate was concentrated and eluted on a silica-gel column using hexane–ethyl acetate (70:30) to afford epoxy alcohol **4** (10.5 g, 78%) as a viscous liquid; IR (neat) = 3428, 2960, 2852, 1040 cm^{-1}; ^1H NMR

($CDCl_3$, 300 MHz) $\delta = 0.91$ (t, $J = 6.7$ Hz, 3H), 1.29–1.60 (m, 8H), 2.83–2.94 (m, 2H), 3.53–3.62 (m, 1H), 3.82–3.91 (m, 1H).

(*2R,3S*)-2-(Chloromethyl)-3-pentyloxirane (6)

Epoxy alcohol **4** (6 g, 41.6 mmol) was taken in a round-bottomed flask, and TPP (16.8 g, 62 mmol), $NaHCO_3$ (3.5 g, 41.6 mmol), and dry CCl_4 (10 ml) were added and refluxed for 4 h. After monitoring by TLC, the solvent was removed under vacuum, and the crude compound was purified using silica-gel column chromatography to afford the corresponding chloro compound **6** (4.7 g, 70%); ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 0.94$ (t, $J = 6.7$ Hz, 3H), 1.29–1.63 (m, 8H), 2.79–2.85 (dt, $J = 6.0$, 2.2 Hz, 1H), 2.92–2.98 (dt, $J = 5.2$, 2.2 Hz, 1H), 3.37–3.44 (dd, $J = 6.0$, 5.2 Hz, 1H) 3.59–3.66 (dd, $J = 6.0$, 5.2 Hz, 1H).

(*3R*)-1-Octen-3-ol (7)

Small shiny pieces of sodium metal (2.2 g, 96 mmol) were suspended in ether (10 ml), and a solution of chloro compound 6 (3.9 g, 24 mmol) in ether (10 ml) was added at 0°C slowly dropwise. After stirring for 2–3 h, the turbid liquid was decanted carefully into a conical flask (Na pieces should not come), washed with water, and extracted into ether. The organic layer was separated, dried over sodium sulphate, concentrated, and eluted on a silica-gel column to afford the neat olefin **7** (2.2 g, 70%) as a colorless oil; $[\alpha]_D^{25}$ −4.5 ($c = 0.5$, $CHCl_3$); IR (neat) = 3445, 2927, 2859, 1709 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 0.90$ (t, $J = 6.7$ Hz, 3H), 1.24–1.54 (m, 8H), 4.01–4.12 (m, 1H), 5.04–5.09 (dt, $J = 9.8$, 1.5 Hz, 1H), 5.16–5.21 (dt, $J = 17.3$, 1.5 Hz, 1H), 5.77–5.90 (m, 1H); EIMS: 127 ($M^+ - 1$).

(*4S,5R*)-4-Methyl-5-pentyltetrahydro-2-furanol (3)

A mixture of enol **7** (2.2 g, 17.8 mmol) and N-bromosuccinimide (NBS) (3.05 g, 17.8 mmol) in DCM was stirred at 0°C, ethyl vinyl ether (2.8 ml, 35.6 mmol) was added dropwise, and the reaction mixture was stirred for 4 h at rt. After monitoring by TLC, the solvent was removed under vacuum (the product formed was found to be unstable, so it was used directly). To the bromo acetal, tri-*n*-butyl tin hydride (5 ml, 18.75 mmol) was added over 30 min followed by AIBN (catalytic), and the mixture was refluxed in dry benzene for 2 h. Then the benzene was removed under vacuum. To the residue, 60% acetic acid was added, and the reaction mixture was again refluxed for 2–4 h. Then the mixture was quenched with sodium bicarbonate solution and extracted into ethyl acetate, concentrated, and purified with

silica-gel column chromatography to afford an inseparable anomeric mixture of two lactols **3** (2 g, 68%); ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 0.90$ (t, $J = 6.7$ Hz, 6H), 1.05 (dd, $J = 6.6$, 6.4 Hz, 6H), 1.25–1.65 (m, 18H), 1.70–1.81 (m, 1H), 1.99–2.16 (m, 2H), 2.27–2.37 (m, 1H), 3.22 (br s, 1H), 3.39–3.47 (m, 2H), 3.62–3.69 (m, 1H), 5.37 (dd, $J = 2.2$, 2.4 Hz, 1H), 5.45 (m, 1H).

(*4S,5R*)-4-Methyl-5-pentyltetrahydro-2-furanone (Cognac Lactone) (1)

PCC (0.67 g, 3.48 mmol) and celite were added to the lactol **3** (0.5 g, 2.9 mmol) in DCM (1 ml) and stirred at rt for 2–3 h. The solvent was removed under vacuum, and the mixture was directly eluted on silica gel to afford the target molecule cognac lactone (**1**) (0.45 g, 91.8%); $[\alpha]_D^{25} = +71.5$ ($c = 0.5$, $CHCl_3$); IR (neat) = 2932, 2865, 1777 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 0.90$ (t, $J = 6.7$ Hz, 3H), 1.01 (d, $J = 5.9$ Hz, 3H), 1.17–1.62 (m, 8H), 2.02–2.20 (m, 2H), 2.46–2.60 (m, 1H), 3.82–3.94 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 177.68$, 85.07, 36.00, 32.10, 30.96, 28.60, 24.21, 20.08,19.4, 14.12; EIMS: 169 ($M^+ - 1$).

(*4S,5R*)-4-Methyl-1-decen-5-ol (10)

Wittig salt (1.4 g, 3.5 mmol) was taken in a round-bottomed flask, and THF (2 ml) was added, followed by *t*-BuOK (0.325 g, 3 mmol), at 0°C. After 20 min, a solution of compound **3** (0.2 g, 1.2 mmol) in THF (1 ml) was added. The mixture was stirred at rt for 2 h, and after monitoring by TLC, was quenched with water and extracted into ethyl acetate. The organic layer was dried over sodium sulphate and concentrated to get the crude compound, which was eluted on a silica-gel column to afford the compound **10** (0.1 g, 52.6%); IR (neat) = 3444, 2956, 2925, 2856, 1611 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 0.86$–0.97 (m, 6H), 1.19–1.67 (m, 10H), 1.84–2.04 (m, 1H), 2.12–2.36 (m, 1H), 3.34–3.49 (m, 1H), 4.95–5.11 (m, 2H), 5.66–5.91 (m, 1H); EIMS: 169 ($M^+ - 1$).

(*4S,5R*)-5-(Methoxymethoxy)-4-methyl-1-decan (11)

To a solution of compound **10** (0.5 g, 2.94 mmol) in DCM (2 ml), Hunig's base (2.0 ml, 11.7 mmol) was added at 0°C and stirred for 10 min. Then MOMCl (0.35 ml, 4.4 mmol) was added and stirred at rt. After 1 h by checking the TLC, the reaction mixture was quenched with sodium bicarbonate and taken up into ethyl acetate. The organic layer was dried over sodium sulphate, and the solvent was removed under vacuum. Residue was subjected to a silica-gel column to get the corresponding MOM ether **11**

(0.5 g, 80.6%); IR (neat) = 3074, 2929, 1640, 1041 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) $\delta = 0.86–0.97$ (m, 6H), 1.22–1.45 (m, 8H), 1.71–1.91 (m, 2H), 2.10–2.28 (m, 1H), 3.35 (s, 3H), 3.36–3.39 (m, 1H), 4.59 (s, 2H), 4.94–5.03 (m, 2H), 5.66–5.81 (m, 1H); LCMS: 215 ($M^+ + 1$).

(*4S,5R*)-5-(Methoxymethoxy)-4-methyl-1-decan-1-ol (12)

To the borane tetrahydrofuran complex (1 M, 1.8 ml, 1.8 mmol) in THF (1 ml), the MOM ether **11** (0.4 g, 1.8 mmol) in THF (1 ml) was slowly added at 0°C dropwise. The reaction mixture was left overnight, basified with sodium hydroxide (3 N, 1 ml), and oxidized with 30% hydrogen peroxide (1 ml) in cold conditions. The mixture was taken up into ethyl acetate; the organic layer was dried over sodium sulphate and concentrated under vacuum. The residue was eluted on a silica-gel column to afford the hydroxy compound **12** (0.38 g, 88%); $[\alpha]_D^{25} = +11.8$ ($c = 0.5$, $CHCl_3$); IR (neat) = 3427, 2931, 1041 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) $\delta = 0.86–0.97$ (m, 6H), 1.10–1.17 (m, 13H), 3.36–3.40 (m, 4H), 3.60 (t, $J = 6.0$ Hz, 2H), 4.59 (s, 2H); EIMS: 231 ($M^+ - 1$).

(*5S,6R*)-5-Methyl-6-pentyltetahydro-2*H*-2-pyranone (Aerangis Lactone) (2)

The alcohol **12** (0.3 g, 1.28 mmol) in DCM (1 ml), DMSO (0.3 ml), and IBX (0.45 g, 1.54 mmol) were added at 0°C and stirred for 3 h. The reaction mixture was quenched with sodium bicarbonate and taken up into DCM, and the solvent was removed under the vacuum. The resultant crude compound was further oxidized as its corresponding acid by treating with $NaClO_2$ (0.11 g, 1.28 mmol) and $NaH_2PO_4 \cdot 2H_2O$ (0.2 g, 1.28 mmol) in DMSO (1 ml). The acid, upon treatment with PTSA in methanol, resulted in deprotection of MOM group and in situ cyclization, resulting in the target molecule aerangis lactone **2** (0.16 g, 68%); $[\alpha]_D^{25} = +41.05$ ($c = 0.5$, $CHCl_3$); IR (neat) = 2922, 2857, 1737, 1080 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) $\delta = 0.86–0.97$ (m, 6H), 1.19–1.47 (m, 8H), 1.55–1.76 (m, 2H), 1.92–2.07 (m, 1H), 2.23–2.34 (m, 2H), 4.04–4.14 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 171.92$, 76.21, 34.50, 32.63, 31.04, 29.98, 28.76, 26.04, 20.01, 18.63, 14.02; LCMS: 182 ($M^+ - 2$).

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