Synthesis P. Ramesh Paper

Protecting-Group-Free Total Synthesis of 8-Methoxygoniodiol

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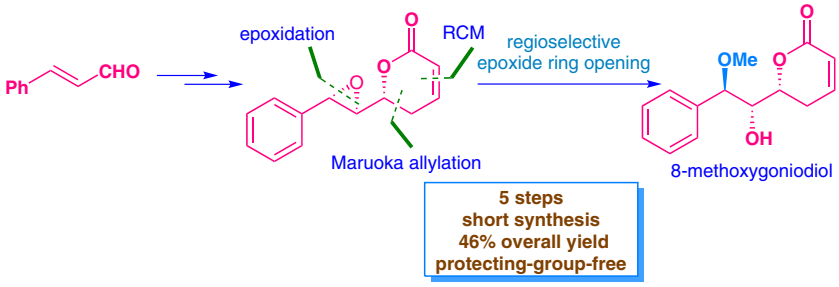


Received: 07.05.2016
Accepted after revision: 09.06.2016
Published online: 21.07.2016
DOI: 10.1055/s-0035-1561491; Art ID: ss-2016-z0324-op

Abstract A concise stereoselective total synthesis of the naturally occurring styryl lactone 8-methoxygoniodiol in five simple steps from readily available inexpensive *trans*-cinnamaldehyde is described. The efficient synthesis features a successful protecting-group-free strategy, with desirable step- and atom-economy. The synthetic strategy relies on a Maruoka asymmetric allylation, an epoxidation, a ring-closing metathesis, and a stereoselective epoxide ring opening as key steps.

Key words lactones, methoxygoniodiol, natural products, total synthesis, Maruoka allylation, ring-closing metathesis

Despite many tremendous strategic and methodological advances of recent decades,[1] the art and science of natural product total synthesis is still far from attaining maturity. The use of protecting groups in natural product synthesis has become routine, even on molecules of low complexity; however, the use of protecting groups adds at least two extra steps (protection and deprotection) to the synthetic sequence, leading to losses of material, increased costs for additional reagents and for waste disposal, and decreases in the step economy of the overall process.[2] Also, the atoms corresponding to the protecting group are not found in the final product, which is an unfavorable result in terms of atom economy.[3] Nobel laureate R. H. Grubbs stated that, '*The major challenges are the construction of molecules without using protecting-group chemistry and the ability to put molecules together in fast and efficient ways*'.[4] The total synthesis of natural products from readily available starting materials, without using any protecting groups, is a desirable but challenging research task, and several protecting-group-free total syntheses of complex natural products have recently been reported in the literature.[5]

The δ-lactone ring is a core structural motif in numerous bioactive natural products and synthetic drugs displaying a broad range of potent biological activities.[6] Because of their unique structure and broad spectrum of biological properties, such as antitumor, antibacterial, antifungal, insect-growth inhibition, and immunosuppressive properties, natural products containing an α,β-unsaturated δ-lactone moiety have attracted considerable attention from researchers.[7] Moreover, the unsaturated δ-lactone unit is responsible for biological activity as a result of its inherent ability to act as a Michael acceptor in the presence of functional groups.[8] A series of bioactive natural styryl lactones exhibiting antitumor activities have been isolated from various *Goniothalamus* species.[9] One such lactone is 8-methoxygoniodiol (**1**; Figure 1), isolated from the stems and leaves of *Goniothalamus amuyon*, a plant used in traditional medicine for the treatment of edema and rheumatism.[10,11] The compound exhibits cytotoxicity against various human tumor cell lines.[11] The relative and the absolute configuration of compound **1** has been assigned on the basis of an X-ray single-crystal analysis.

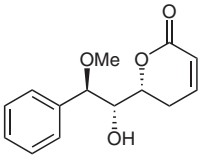
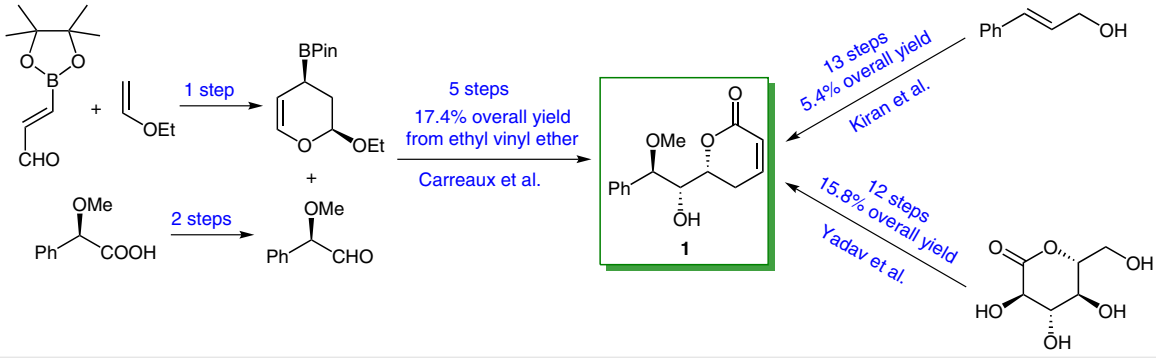


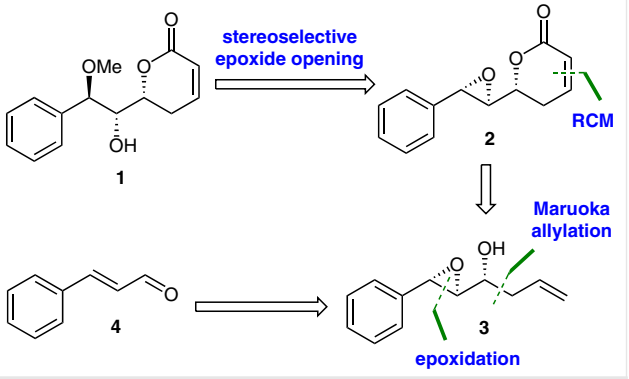
Figure 1 The structure of 8-methoxygoniodiol (**1**)

Numerous extensive synthetic efforts have been made toward the total synthesis of this class of natural products,[12] and there have been three reports on total syntheses of 8-methoxygoniodiol (**1**; Scheme 1). These syntheses were based on a common strategy that requires multistep operations involving the use of protecting-group manipula-



Scheme 1 Previous syntheses of 8-methoxygoniodiol (**1**)

tions and that affords low overall yields. Carreaux et al.[13] reported the first total synthesis of **1** by using a catalytic asymmetric hetero-Diels–Alder/allylboration sequence involving three partners, starting from ethyl vinyl ether and (*R*)-*O*-methylmandelic acid, with a 17.4% overall yield. Yadav and co-workers[14] employed δ-glucuronolactone as a chiral source for the synthesis of **1** in twelve steps and with an overall yield of 15.8%. Kiran et al.[15] recently reported the synthesis of 8-methoxygoniodiol (**1**) in 5.4% overall yield through an (*R*,*R*-salen)Co(OAc)-catalyzed hydrolytic kinetic resolution of *anti*-(2*SR*,3*RS*)-2-[methoxy(phenyl)methyl]oxirane, prepared from *trans*-cinnamyl alcohol.

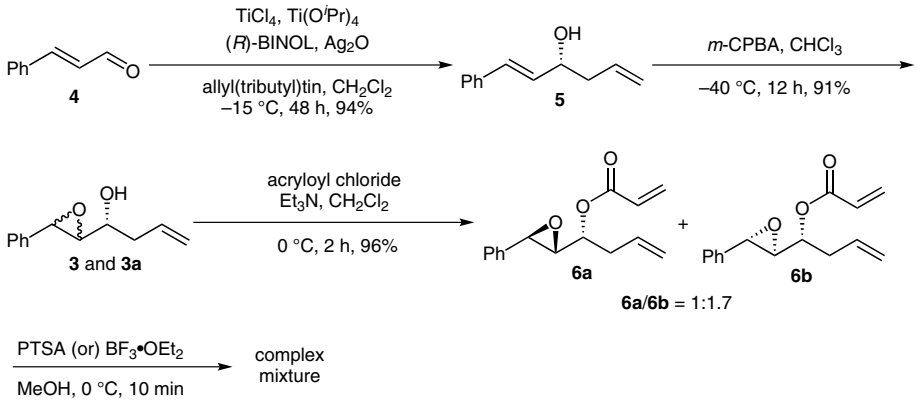


Scheme 2 Retrosynthesis of 8-methoxygoniodiol (**1**)

Here, we report a five-step synthesis of 8-methoxygoniodiol (**1**) by a short and efficient route, using a protecting-group-free strategy, from commercially available inexpensive *trans*-cinnamaldehyde.

Our retrosynthetic analysis toward 8-methoxygoniodiol (**1**) is shown in Scheme 2. We envisioned that **1** might be synthesized from goniothalamin oxide (**2**) by stereo- and regioselective cleavage of the epoxide ring with methanol as a nucleophile. Oxide **2** might be obtained by acrylation followed by ring-closing metathesis of alcohol **3**, which in turn might be prepared by sequential Maruoka asymmetric allylation and *syn*-epoxidation of *trans*-cinnamaldehyde.

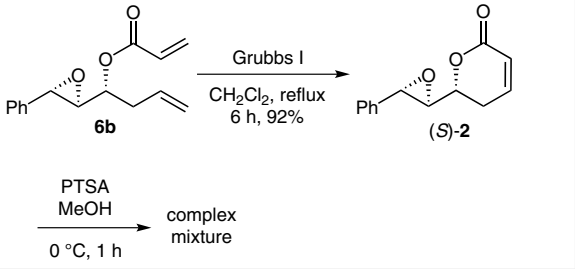
Our synthesis commenced with the preparation of the homoallylic alcohol **5**. The lactone stereogenic center in **1** was introduced by Maruoka asymmetric allylation[16] of readily available *trans*-cinnamaldehyde to give the enantiomerically enriched alcohol **5** in 94% isolated yield and >95% ee, as determined by chiral HPLC analysis. Next, we investigated the stereo- and chemoselective epoxidation of the internal double bond in alcohol **5** (Scheme 3). After a brief optimization of the reaction conditions, we found that *syn*-ep-



Scheme 3 Synthesis of epoxides **6** and attempts at cleavage of the epoxide ring

oxidation[17] of alcohol **5** with *m*-chloroperoxybenzoic acid in $CHCl_3$ at –40 °C generated a 1.7:1 inseparable mixture of epoxides **3** and **3a**, with the desired β-epoxide **3** as the major isomer. Attempts at Sharpless asymmetric epoxidation of **5** to obtain **3** as a single isomer failed in this case. Subsequently, treatment of the mixture of epoxy alcohols **3** and **3a** with acryloyl chloride in the presence of Et_3N in CH_2Cl_2 provided the corresponding acryloyl esters **6a** and **6b**. Having obtained the epoxy acrylate fragments **6** in three steps, we proceeded to the stereo- and regioselective epoxide opening with methanol under acidic condition. Unfortunately, treatment of **6b** with PTSA (or $BF_3{\cdot}OEt_2$) in MeOH at 0 °C gave a complex mixture of products containing none of the starting material.

Next, we focused our attention on the synthesis of (*S*)-goniothalamin oxide [(*S*)-**2**]. Diene **6b** was subjected to ring-closing olefin metathesis[18] by using the Grubbs I catalyst in refluxing CH_2Cl_2 to give the desired (*S*)-goniothalamin oxide [(*S*)-**2**] in 92% yield (Scheme 4).



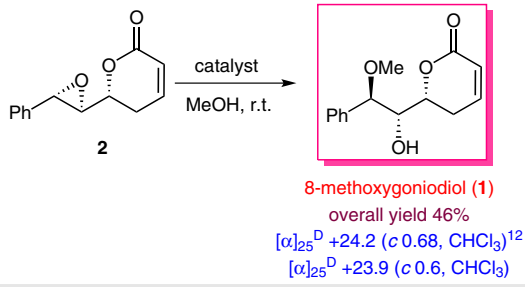
Scheme 4 Efforts toward epoxide ring opening of (*S*)-**2**

With the desired (*S*)-goniothalamin oxide [(*S*)-**2**] in hand, we turned our attention to the key step in the synthesis of the styryl lactone natural product **1**: the stereo- and regioselective epoxide ring opening of (*S*)-**2** with methanol as the nucleophile. Numerous methods have been reported in the literature for the stereo- and regioselective epoxide opening with various alcohols and phenols.[19] Initially, we carefully explored various conditions for acid-promoted epoxide ring opening of (*S*)-**2** in methanol (Table 1). When the reaction was carried out in the absence of a catalyst, no product was obtained and the starting material was recovered (Table 1, entry 8). The use of PTSA as catalyst in methanol led to complete conversion of the starting material into a complex mixture (entry 1). However, satisfactory results were obtained with most Lewis acid catalysts, and treatment of (*S*)-goniothalamin oxide (**2**) with one equivalent of various Lewis acids in MeOH at room temperature gave the desired product **1** in excellent yields. Pleasingly, 8-methoxygoniodiol (**1**) was obtained in high yield and with high regio- and stereoselectivity when $Eu(OTf)_3$ or $Sn(OTf)_2$ was used as the catalyst in methanol at room temperature (entries 3, 6, and 7 and Scheme 5).

Table 1 Screening of Catalysts for the Stereo- and Regioselective Epoxide Ring Opening of (*S*)-**2** with Methanol[a]

Entry	Catalyst	Time (h)	Yield	dr[b]
1	PTSA	1	–[c]	ND[d]
2	AgOTf	3	95	91:9
3	$Sn(OTf)_2$	5	92	94:6
4	$Sc(OTf)_3$	12	93	93:7
5	$In(OTf)_3$	5	91	92:8
6	$Eu(OTf)_3$	5	96	94:6
7[e]	$Eu(OTf)_3$	12	96	94:6
8	–	12	NR[f]	ND

[a] Unless otherwise specified, all reactions were performed on a 0.25 mmol scale of (S)-**2** with 1 equiv catalyst at r.t in MeOH (0.6 mL).
[b] Determined by ^1H NMR spectroscopy of the crude mixture.
[c] A complex mixture of products was obtained.
[d] Not determined.
[e] 10 mol% catalyst was used.
[f] No reaction.



Scheme 5 Stereoselective epoxide ring opening of (*S*)-**2**

The spectral data (^1H and ^{13}C NMR) of the synthetic product **1** were in complete agreement with those reported for the natural product.

In summary, we have developed a short and efficient stereoselective total synthesis of 8-methoxygoniodiol (**1**) in a protecting-group-free fashion with a high overall yield. The developed synthetic strategy is simple, extremely fast, and requires only five steps from commercially available *trans*-cinnamaldehyde. The concise and protecting-group-free nature of the overall synthetic design should permit the development and biological testing of structural analogues of **1** in the future.

Solvents were dried over standard drying agents and were freshly distilled before use. All moisture-sensitive reactions were carried out under N_2. Organic solutions were dried over anhydrous $MgSO_4$ and concentrated below 40 °C in vacuo. All column chromatographic separations were performed over silica gel (60–120 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV spectrometer with $CDCl_3$ as solvent at 300, 400, or 500 MHz (^1H) or at 75, 100, or 125 MHz (^{13}C), with TMS as internal standard. Optical rotations were measured with a JASCO DIP-370 digital polarimeter at 25 °C. Mass spectra were

recorded on a Bruker Micro-TOF-Q mass spectrometer with electrospray ionization. High-resolution mass spectra were recorded on an Agilent mass spectrometer using ESI-TOF.

(1*E*,3*R*)-1-Phenylhexa-1,5-dien-3-ol (5)

Ti(*i*-PrO)$_4$ (0.26 mL, 0.90 mmol) was added to a stirred solution of $TiCl_4$ (33 μL, 0.30 mmol) in CH_2Cl_2 (10 mL) at 0 °C under N_2. After 1 h, Ag_2O (140 mg, 0.60 mmol) was added at r.t., and the mixture was stirred in the dark for 5 h. (*R*)-1,1′-Binaphthalene-2,2′-diol (346 mg, 1.21 mmol) was added at r.t., and the mixture was stirred for a further 2 h. The solution containing the catalyst generated in situ was cooled to –15 °C and treated sequentially with *trans*-cinnamaldehyde (0.8 g, 6.06 mmol) and allyl(tributyl)tin (2.06 mL, 6.65 mmol). The resulting mixture was stirred for 48 h at –15 °C. The reaction was quenched with sat. aq $NaHCO_3$ (10 mL), and the mixture was extracted with Et_2O (3 × 10 mL). The organic layers were combined, dried ($MgSO_4$), concentrated under reduced pressure, and purified by flash column chromatography [silica gel, hexane–EtOAc (9:1)] to give a colorless liquid; yield: 1 g (94%, >95% ee).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.15 (m, 5 H), 6.57 (d, *J* = 16.0 Hz, 1 H), 6.19 (dd, *J* = 16.0, 6.2 Hz, 1 H), 5.90–5.76 (m, 1 H), 5.20–5.07 (m, 2 H), 4.36–4.27 (m, 1 H), 2.47–2.30 (m, 2 H), 1.64 (d, *J* = 3.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.5, 133.9, 131.4, 130.2, 128.5, 127.5, 126.4, 118.3, 71.6, 41.9.

ESI-MS: *m/z* = 175 $[M + H]^+$.

(1*R*)-1-[(2*R*,3*R*)-3-Phenyloxiran-2-yl]but-3-en-1-yl Acrylate (6a) and (1*R*)-1-[(2*S*,3*S*)-3-Phenyloxiran-2-yl]but-3-en-1-yl Acrylate (6b)

A solution of MCPBA (70%) (114 mg, 0.95 mmol) in $CHCl_3$ (3 mL) was added to a stirred solution of alcohol **5** (150 mg, 0.86 mmol) in $CHCl_3$ (5 mL) at –40 °C under N_2. After 12 h, the mixture was washed with 10% aq Na_2CO_3 (2 × 5 mL). The combined organic layers were dried ($MgSO_4$), concentrated under reduced pressure, and purified by flash column chromatography [silica gel, hexane–EtOAc (9:1)] to afford an inseparable mixture of epoxides **3** and **3a** as a colorless oil; yield: 149 mg (91%).

Et_3N (381 μL, 2.74 mmol) and acryloyl chloride (95 μL, 1.17 mmol) were added to a stirred solution of **3** and **3a** (149 mg, 0.78 mmol) in CH_2Cl_2 (5 mL) at 0 °C, and the mixture was stirred for 2 h. The reaction was quenched with H_2O (1 mL), and the product was extracted with CH_2Cl_2 (2 × 5 mL). The organic layer was dried ($MgSO_4$), evaporated under reduced pressure, and purified by column chromatography (silica gel, hexane) to afford acryl esters **6a** and **6b** in a 1:1.7 ratio as colorless oil; yield: 184 mg (96%).

6a

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.24 (m, 5 H), 6.43 (dd, *J* = 17.2, 1.3 Hz, 1 H), 6.12 (dd, *J* = 17.2, 10.3 Hz, 1 H), 5.90–5.80 (m, 2 H), 5.19–5.12 (m, 2 H), 4.99 (dt, *J* = 7.3, 5.1 Hz, 1 H), 3.94 (d, *J* = 1.9 Hz, 1 H), 3.07 (dd, *J* = 5.4, 1.9 Hz, 1 H), 2.63–2.57 (m, 1 H), 2.56–2.50 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 136.5, 132.4, 131.3, 128.4 (2 C), 128.2, 128.0, 125.5 (2 C), 118.5, 72.0, 61.8, 57.2, 35.7.

ESI-MS: *m/z* = 267 $[M + Na]^+$.

6b

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.24 (m, 5 H), 6.48 (dd, *J* = 17.3, 1.3 Hz, 1 H), 6.18 (dd, *J* = 17.3, 10.3 Hz, 1 H), 5.89 (dd, *J* = 10.3, 1.3 Hz, 1 H), 5.85–5.77 (m, 1 H), 5.17–5.11 (m, 2 H), 4.99 (q, *J* = 12.8, 6.7 Hz, 1 H), 3.79 (d, *J* = 1.9 Hz, 1 H), 3.18 (dd, *J* = 5.7, 1.9 Hz, 1 H), 2.59–2.49 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 136.2, 132.1, 131.4, 128.5 (2 C), 128.4, 128.1, 125.5 (2 C), 118.8, 72.9, 62.5, 56.5, 36.0.

ESI-MS: *m/z* = 267 $[M + Na]^+$.

(6*R*)-6-[(2*S*,3*S*)-3-Phenyloxiran-2-yl]-5,6-dihydro-2*H*-pyran-2-one [2; (*S*)-Goniothalamin Oxide]

Grubbs-I catalyst (33 mg, 0.04 mmol) was added to a solution of acrylate **6b** (100 mg, 0.41 mmol) in CH_2Cl_2 (7 mL) at r.t., and the mixture was stirred for 6 h at reflux. The mixture was then concentrated and the residue was purified by flash column chromatography [silica gel, hexane–EtOAc (7:3)] to give a white solid; yield: 81 mg (92%); $[\alpha]_D^{25}$ +96.9 (*c* 0.7, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 5 H), 6.93 (ddd, *J* = 9.7, 5.4, 2.8 Hz, 1 H), 6.07 (ddd, *J* = 9.7, 2.4, 1.0 Hz, 1 H), 4.68 (ddd, *J* = 10.6, 4.5, 3.6 Hz, 1 H), 4.08 (d, *J* = 1.8 Hz, 1 H), 3.24 (dd, *J* = 3.6, 2.1 Hz, 1 H), 2.69–2.63 (m, 1 H), 2.58–2.52 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.8, 144.0, 135.9, 128.6 (3 C), 125.7 (2 C), 121.6, 75.1, 62.1, 55.0, 26.2.

ESI-MS: *m/z* = 239 $[M + Na]^+$.

(6*R*)-6-[(1*S*,2*R*)-1-Hydroxy-2-methoxy-2-phenylethyl]-5,6-dihydro-2*H*-pyran-2-one (1; 8-Methoxygoniodiol)

Eu(OTf)$_3$ (6.1 mg, 0.01 mmol) was added to a stirred solution of lactone (*S*)-**2** (20 mg, 0.09 mmol) in MeOH (0.6 mL) at r.t.. After 5 h, the solvent was removed under vacuum, and the residue was purified by flash column chromatography [silica gel, hexane–EtOAc (6:4)] to give a white solid; yield: 22 mg (96%); mp 99 °C; $[\alpha]_D^{25}$ +23.9 (*c* 0.6, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42–7.33 (m, 5 H), 6.97 (ddd, *J* = 9.7, 6.4, 2.1 Hz, 1 H), 6.04 (ddd, *J* = 9.7, 2.8, 0.7 Hz, 1 H), 4.95 (ddd, *J* = 12.8, 3.8, 1.5 Hz, 1 H), 4.38 (d, *J* = 8.8 Hz, 1 H), 3.61 (dd, *J* = 9.0, 1.5 Hz, 1 H), 3.22 (s, 3 H), 2.83 (ddt, *J* = 18.4, 12.8, 2.1 Hz, 1 H), 2.25 (dddd, *J* = 18.4, 6.2, 3.8, 0.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 145.9, 138.5, 128.6 (2 C), 128.5, 127.8 (2 C), 120.8, 81.9, 76.1, 74.8, 56.7, 26.1.

ESI-MS: *m/z* = 249 $[M + H]^+$, 271 $[M + Na]^+$.

HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{14}H_{16}NaO_4$: 271.09408; found: 271.09363.

Acknowledgment

The author thanks the Council of Scientific and Industrial Research, Ministry of Science and Technology, New Delhi, for funding the project ORIGIN (CSC-0108).

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561491.

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