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Asymmetric Total Synthesis of (+)-Goniotriol and (+)-Goniofufurone

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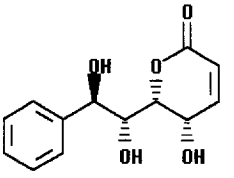
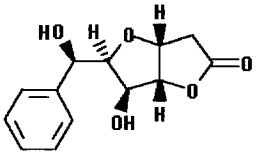
Abstract: The Enantioselective synthesis of two antitumor styryl lactones, (+)-goniotriol and (+)-goniofufurone, have been completed starting from cinnamyl alcohol in ten and eleven steps with an overall yield of 21% and 12%, respectively.

(+)-Goniotriol **1** was isolated from the leaves and twigs of *Goniothalamus sesquipedalis* (Annoaceae)[1] and from the stem bark of *Goniothalamus giganteus*(Annonaceae)[2], whereas (+)-goniofufurone **2** has been extracted from the stem bark of *Goniothalamus giganteus*[3]. Both of them were shown to have significant cytotoxic activities toward human tumor cells[2,3]. Because of their cytotoxicity as well as the interesting heterocyclic skeletons, several groups have paid attention to the synthesis of these two styryl lactones[4-7].



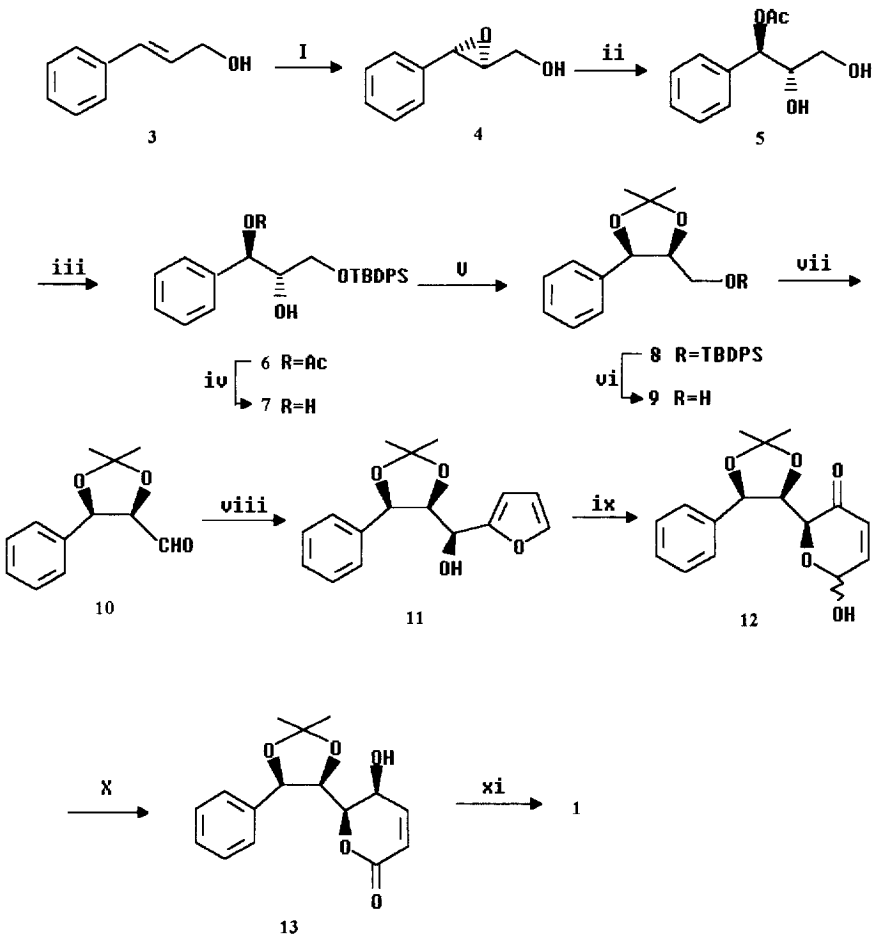
1



2

Fig. 1

As part of our work on styryl lactones, we have reported a total synthesis of (+)-goniopypyrone from methyl cinnamate[8]. Recently, we also described the enantioselective synthesis of another natural product, (+)-8-*epi*-goniofufurone, from the same starting material[9]. Herein, we present the enantioselective synthesis of goniotriol **1** and goniofufurone **2** from cinnamyl alcohol as a new synthetic route to styryl lactones.



Scheme 1. Reagents and conditions: i, TBHP, L-(+)-DIPT, Ti(O*i*-Pr)$_4$, CH_2Cl_2, -20-0°C, 86%; ii, Ti(OAc)(O*i*-Pr)$_3$, $CHCl_3$, -20-0°C, 3h, 90%; iii, TBDPSCl, imidazole, THF, r.t., 24h, 94%; iv, K_2CO_3, MeOH, H_2O, r.t., 2h, 85%; v, $MeC(OMe)_2$, *p*-TsOH, CH_2Cl_2, r,t. 8h, 91%; vi, *n*-Bu_4NF, THF, r.t, 2h, 95%; vii, DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2, -78--20°C; viii, 2-furyllithium, THF, -78-0°C, 74% from **9**; ix, TBHP, $VO(acac)_2$, CH_2Cl_2, 0°C, 12h, 86%; x, CrO_3, HOAc, 25-30°C, 15min. ; then, *i*-PrOH, $NaBH(OAc)_3$, -5-0°C, 69%; xi, TFA, THF, H_2O, r.t., 90%.

The route to goniotriol **1** is illustrated in scheme 1. The asymmetric epoxidation of cinnamyl alcohol **3** using Sharpless reagent[10] yielded 2,3-epoxyalcohol **4** in 86% yield, m.p. 50-51°C, $[\alpha]_D^{20}$ -50.9(C, 1.3, $CHCl_3$) {lit[11].m.p. 51-52°C, $[\alpha]_D^{20}$ -51.7(C,1.2,$CHCl_3$)}. Highly regioselective cleavage of oxirane ring of **4** with tri(isopropoxy)titanium acetate[12] successfully afforded acetate **5** in 90% yield. Selective protection of primary hydroxy group of **5** with *tert*-butylchlorodiphenylsilane provided the silyl ether **6** in 94% yield. Deacetylation of **6** with potassium cabonate in methanol and water gave the diol **7** in 83% yield. Protection of the diol **7** with

2,2-dimethoxy propane in the presence of *p*-toluene sulphonic acid followed by desilylation with tetrabutylammonium fluoride provided the alcohol **9** in 86% overall yield from **7**. Swern oxidation afforded the aldehyde **10**, which, due to its instability, was immediately treated with 2-furyllithium[13] to give the *syn*-adduct **11** as colorless prisms in 74% yield, m.p. 90-91°C, $[\alpha]_D^{20}$ +14.3(C,1.0, $CHCl_3$), together with the *anti*-adduct as an oil in 2.4% yield, $[\alpha]_D^{20}$ -78.7(C,0.6, $CHCl_3$). The ratio of *syn* to *anti* adduct was ca. 30:1. The highly *syn*-selective addition of 2-furyllithium to **10** was due to the space obstruction of the phenyl ring, so that the 2-furyllithium could attack the carbonyl group from the back face of **10** (Fig.2).

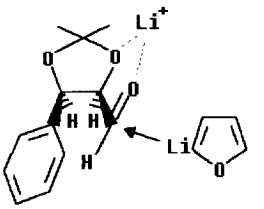
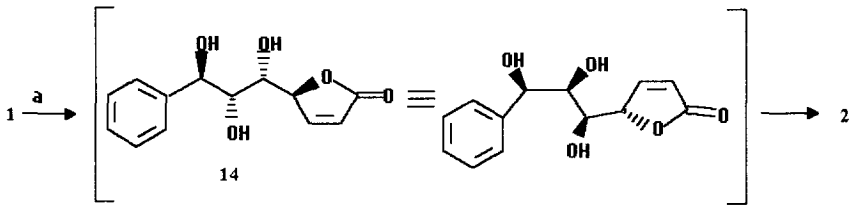


Fig. 2

Oxidation of furylmethanol **11** with *tert*-butylhydroperoxide(TBHP) in the presence of $VO(acac)_2$ afforded the hydropyranone **12** as a mixture of α- and β-anomers. Succeeding oxidation of the anomeric mixture with chromium(VI) oxide in acetic acid followed by immediate reduction with sodium triacetoxyborohydride[14] in one pot furnished the crude allyl alcohol **13**, which was recrystallized with ethyl acetate-hexane to give pure **13** in 60% yield, m.p. 157-158°C, $[\alpha]_D^{20}$ -75.3(C,0.6, $CHCl_3$). Finally, deprotection of **13** with trifluoroacetic acid smoothly provided the desired **1** (90%yield) as colorless prisms, m.p. 170-171°C, $[\alpha]_D^{20}$ +120.7(C,1.1, MeOH) {lit.[2], m.p. 170°C, $[\alpha]_D^{20}$ +121(MeOH)}.

Treatment of **1** with a catalytic amount of 1,8-diazabicyclo[5,4,0] undec-7-ene(DBU) in THF brought about the ring transformation to provide (+)-goniofufurone **2** directly[7], m.p. 153-154°C, $[\alpha]_D^{20}$ +8.9(C, 0.4,



Scheme 2. Reagents and conditions: a., DBU, THF, r.t., 4 days, 56%.

EtOH){lit.[3] m.p. 152-154°C, $[\alpha]_D^{20}$ +9(C, 0.5, EtOH)}. The cyclization pathway probably involved a two-step sequence in which the six-membered lactone was converted into the five-membered lactone **14** and then **14** was cyclized to form the bicyclic skeleton through an intramolecular Micheal addition (Scheme 2).

In summary, as our further work on styryl lactones, we have developed a new route to (+)-goniotriol and (+)-goniofufurone starting from cinnamyl alcohol .

Experimental

All m.p.s were uncorrected. ^{1}HNMR spectra were recorded on a Bruker AM300 instrument with TMS as internal standard. Mass spectra were obtained from HP5890A spectrometer. IR spectra were taken for solid samples in KBr pellets and for liquid samples on film, on a Shimadzu-440 spectrophotometer. Optical rotations were measured on a Perkin-Elmer 241MC polarimeter.

(2S,3S)-2,3-epoxy-3-phenyl-1-propanol **4**

A mixture of powdered and activated 4A molecular sieves (0.5g, 15-20wt% based on substrate) and dichloromethane(40ml) was cooled to -5°C. L-(+)-diisopropyl tartrate(0.4g, 2mmol) and titanium(IV) isopropoxide(0.3g, 1 mmol) were added sequentially. After cooling to -20°C, *tert*-butyl hydroperoxide (30mmol, 5ml 6.06 M in dichloromethane) was added and the mixture was stirred for 10min. Cinnamyl alcohol **3** (2.68g, 20mmol in 3ml of dichloromethane) was added dropwise in 1h. After being stirred for 1h at -15°C to -5°C, water(6ml) was added. The mixture was stirred for 30-60min and allowed to warm room temperature. 30% Aqueous solution of sodium hydroxide saturated with sodium chloride was added. After being vigorously stirred for 1h, the mixture was filtered and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2x20ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography [ethyl acetate-hexane(1:9)] to afford **4** as a white solid(2.58g, 86%), m.p. 50-51°C, $[\alpha]_D^{20}$-50.9 (c,1.3, $CHCl_3$) {lit[11]. m.p. 51-52°C, $[\alpha]_D^{20}$ -51.7(C,1.2,$CHCl_3$)}, IR ν 3350(-OH), 1260(epoxy) cm^{-1}; ^{1}HNMR($CDCl_3$): 7.25-7.37 (5H, m, Ph), 4.03(1H, d, *J*=12.5Hz, 1-H), 3.92(1H, d, *J*=2.0Hz, 3-H), 3.79(1H, d, *J*=12.5Hz,1-H), 3.22(1H, m, *2*-H), 2.17(1H, br, -OH); *m/z*(EI): 150(M^+),132 (M^+-H_2O), 119(M^+-CH_2OH). Anal. Calcd for $C_9H_{10}O_2$: C,71.98; H,6.71. Found: C,72.05; H,6.45.

(2S,3R)-3-acetoxyl-3-phenyl-1,2-propanediol **5**

To a solution of **4**(330mg, 2.2mmol) in anhydrous chloroform(15ml), tri(isopropoxy)titanium acetate in chloroform(1M, 3.3ml, 3.3mmol) was added at -20°C under N_2. After being stirred for 3h at -20°C to 0°C, the reaction was quenched with acetone 10ml and water (2ml). The mixture was stirred for 30min, and the resultant precipitate was filtered. The filtrate was dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography[ethyl acetate-hexane(2:3)] to afford **5** (415mg,90%) as a colourless oil, $[\alpha]_D^{20}$ -77.2 (c,1.9,$CHCl_3$), IR ν 3350(-OH),1720(C=O),1600(Ph) cm^{-1}; ^{1}HNMR($CDCl_3$): 7.29 -7.36(5H, m, Ph), 5.72(1H, d, *J*=6.8Hz, 3-H), 3.93(1H, m, *J=6.8*,3.2Hz, 2-H), 3.67 (1H, dd, *J*=11.7,3.2Hz, 1-H), 3.57(1H, dd, *J*=11.7,6.1Hz, 1-H), 2.60(2H, br, -OH), 2.08(3H, s, CH_3). *m/z* (EI): 211(M^++1), 195(M^+-OH), 150(M^+-HOAc). HRMS Calcd for $C_{11}H_{14}O_3$: 210.0933. Found: 210.0937.

(2S,3R)-2-hydroxy-3-acetoxyl-3-phenylpropanyl tert-butyldiphenylsilyl ether **6**

To a stirred solution of **5**(172mg, 0.819mmol) and imidazole(90mg, 1.323mmol) in dry THF(10ml) was added *tert*-butyl diphenylsilyl chloride(0.28ml, 1.06mmol) at room temperature. The mixture was stirred for 24h at the same temperature, and water (5ml) was added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2x20ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography[ethyl acetate-hexane(1:14)] to afford **6** (343mg, 94%) as a colourless oil, $[\alpha]_D^{20}$ -34.2 (c,1.3, $CHCl_3$), IR ν 3400(-OH), 1730(C=O), 1580(Ph) cm^{-1}. ^{1}HNMR(CD_3COCD_3): 7.28-7.73(15H, m, 3xPh), 5.98(1H, d, *J*=5.5Hz, 3-H), 4.12(1H, m, *J*=5.5,5.3Hz, 2-H), 3.76(1H, dd, *J*=10.4,5.3Hz, 1-H), 3.66(1H, dd, *J*= 10.4,5.3Hz, 1-H), 2.02(3H, s, CH_3), 1.07(9H, s, Bu^t). *m/z*(EI): 431(M^+-OH), 331(M^+-HOAc-Bu^t), 311. HRMS Calcd for $C_{23}H_{23}O_4Si(M^+-Bu^t)$: 391.1343. Found: 391.1353.

(2S,3R)-2,3-dihydroxy-3-phenylpropanyl tert-butyldiphenylsilyl ether **7**

To a stirred solution of **6**(80mg, 0.178mmol) in methanol and water(9:1, 5ml) was added potassium cabonate(74mg, 0.536mmol). After being stirred for 2h at room temperature, water(20ml) was added. The mixture was extracted with ethyl acetate (2x20ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography[ethyl acetate-hexane(1:9)] to afford **7** (58mg,83%) as a colourless oil, $[\alpha]_D^{20}$ -9.6(c,1.2, $CHCl_3$), IR ν 3400(-OH), 1590(Ph) cm^{-1}. ^{1}HNMR (CD_3COCD_3): 7.22-7.74(15H, m, 3xPh), 4.81(1H, d, *J*=5.5Hz, 3-H), 3.95(1H, m, *J*= 5.5, 5.4, 5.6Hz, 2-H), 3.81(1H, dd, *J*=10.3, 5.6Hz, 1-H), 3.75(1H, dd, *J*=10.3,5.4Hz, 1-H), 1.05(9H, s, Bu^t). *m/z*(EI): 406(M^+), 349(M^+-Bu^t). Anal. Calcd for $C_{25}H_{30}O_3Si$: C,73.85; H,7.43. Found: C,73.64; H,7.43.

(2S,3R)-2,3-isopropylidenyloxy-3-phenylpropanyl tert-butyldiphenylsilyl ether **8**

To a stirred solution of **7**(189mg, 0.465mmol) and *p*-toluene sulphonic acid(2mg) in dichloromethane(8ml) was added 2,2-dimethoxypropane(0.23ml, 1.4mmol). After being stirred for 12h at room temperature, aqueous solution of sodium bicarbonate(4ml) was added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2x20ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography[ethyl acetate-hexane(1:19)] to afford **8** (189mg, 91%) as a colourless oil, $[\alpha]_D^{20}$ -79.6 (c,1.5,$CHCl_3$), IR ν 3010 ,1590(Ph), 1100, 1050(C-O) cm^{-1}. ^{1}HNMR(CD_3COCD_3): 7.28-7.59(15H, m, 3xPh), 5.37(1H, d, *J*=7.0Hz, 3-H), 4.60(1H, ddd, *J*=7.0,6.0,1.0Hz, 2-H), 3.33(2H, dd, *J*=6.0,1.0Hz, 2x1-H), 1.54(3H, s, CH_3), 1.43(3H, s, CH_3), 0.92(9H, s, Bu^t). *m/z*(EI) 431(M^+-CH_3), 331(M^+-Me_2CO-Bu^t), 253. HRMS Calcd. for $C_{21}H_{19}O_2Si(M^+-Me_2CO-Bu^t)$: 331.1157. Found: 331.1147.

(2S,3R)-2,3-isopropylidenyloxy-3-phenyl-1-propanol **9**

To a stirred solution of **8**(108mg, 0.242mmol) in THF(5ml) was added tetrabutylammonium fluoride in THF(1M, 0.29ml 0.29mmol). After being stirred for 2h at room temperature, water (5ml) was added. The

organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2x20ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography[ethyl acetate-hexane(1:6)] to afford **9** (47mg, 94%) as prisms, m.p. 57-58°C, $[\alpha]_D^{20}$ -112.3(c,1.3,$CHCl_3$), IR ν 3200(-OH),1050(C-O) cm^{-1}. ^{1}HNMR($CDCl_3$): 7.29-7.35(5H, m, Ph), 5.31(1H, d, *J*=7.0Hz, 3-H), 4.45(1H, ddd, *J*=7.0,8.0,4.6Hz, 2-H), 3.23(1H, dd, *J*=11.7,8.0Hz, 1-H), 3.10(1H, dd, *J*=11.7,4.6Hz, 1-H), 2.0(1H, br, -OH), 1.64(3H, s, CH_3), 1.49(3H, s, CH_3). *m/z*(EI): 193(M^+-CH_3), 177(M^+-CH_2OH). Anal. Calcd for $C_{12}H_{16}O_3$: C,69.20; H,7.74. Found: C,69.10; H,7.61.

(1S,2R,3R)-1-(2-furyl)-2,3-isopropylidenyloxy-3-phenyl-1-propanol **11**

A solution of oxalyl chloride (0.256 ml, 3.259 mmol) in dichloromethane (6 ml) was stirred and cooled to -60°C. Dimethylsulfoxide(0.508ml, 6.79mmol) in dichloromethane(2ml) was added dropwise. After 10 min, a solution of **9** (565mg, 2.716mmol) in dichloromethane (4ml) was added dropwise at -78°C. The reaction mixture was allowed to warm to -40°C for 5 min. After the solution was cooled to -78°C, triethylamine (1.015ml, 7.46mmol) was added. The resulting suspension was stirred for 1h at -78°C to -20°C, and then saturated aqueous solution of sodium dihydrogen phosphate (40ml) was added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2x20ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure to give a crude aldehyde **10** which was unstable. A small amount of the sample was purified for NMR data, ^{1}HNMR (CD_3COCD_3): 9.15(1H, d, *J*=3.0Hz, -CHO), 7.28-7.40(5H, m, Ph), 5.64(1H, d, *J*=7.7Hz, 3-H), 4.73(1H, dd, *J*=7.7,3.0Hz, 2-H), 1.70 (3H, s, CH_3), 1.55(3H, s, CH_3). The aldehyde was used immediately for next reaction without purification.

To a stirred solution of 2-lithiumfuran in THF (50ml) which was prepared from furan(0.8ml) and 2M *n*-BuLi in THF (3ml), was added **10** dropwise in THF (10 ml) at -78°C. After being stirred for 2h at -78°C to -40°C, the reaction mixture was quenched with saturated aqueous ammonium chloride. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2x20ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography [ethyl acetate-hexane(1:9)]. The first fraction gave the *anti*-adduct(18mg, 2.4%) as a colourless oil, $[\alpha]_D^{20}$ -78.7(c,0.6,$CHCl_3$), ^{1}HNMR(CD_3COCD_3): 7.30-7.50(6H, m, Ph, furyl), 6.31(1H, dd, *J*=1.8,3.1Hz, furyl), 6.21(1H, d, *J*=3.1Hz, furyl), 5.38(1H, d, *J*=6.6Hz, 3-H), 4.70(1H, dd, *J*=9.3,6.6Hz, 2-H), 4.21(1H, d, *J*=9.3Hz, 1-H), 1.52(3H, s, CH3), 1.41(3H, s, CH3). The second fraction gave the *syn*-adduct **11** (551mg, 74%) as colourless prisms. m.p. 90-91°C $[\alpha]_D^{20}$ +14.3(c,1.0,$CHCl_3$). IR ν 3400(-OH),1600(Ph),1050(C-O) cm^{-1}; ^{1}HNMR(CD_3COCD_3): 7.08-7.29(6H, m, Ph, furyl), 6.19(1H, dd, *J*=1.8,3.3Hz, furyl), 5.89(1H, d, *J*=3.3Hz, furyl), 5.22(1H, d, *J*=7.0Hz, 3-H), 4.85(1H, dd, *J*=7.0, 8.0Hz, 2-H), 4.17(1H, d, *J*=8.0Hz, 1-H),1.65(3H, s, CH_3), 1.50(3H, s, CH_3); m/z(EI):274(M^+), 216 (M^+-Me_2CO), 199(M^+-Me_2CO-OH); Anal. Calcd for $C_{16}H_{18}O_4$: C,70.06; H,6.61; Found: C,70.26; H, 6.61.

(2S)-6-hydroxy-2-[(1R,2R)-1,2-isopropylidenyloxy-2-phenylethyl]-2,6-dihydropyran-3-one **12**

To a stirred solution of **11**(100mg, 0.365mmol) and $VO(acac)_2$ (2mg, 0.0074mmol) in CH_2Cl_2(8ml) was added TBHP (0.1ml, 0.65mmol,6.5M in CH_2Cl_2) at 0°C. The solution was stirred for 10h at 0°C, and Me_2S(0.08ml) was added at 0°C. After being stirred for 30min at 0°C, water(10ml) was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2x20ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography[ethyl acetate-hexane(1:4)] to afford **12** (91mg, 86%) as inseparable mixture of α– and β-anomers. IR ν 3400(-OH), 1690(C=O), 1620, 1600(Ph) cm^{-1}. ^{1}HNMR (CD_3COCD_3): 7.24-7.57(5H, m, Ph), 6.91(1H, dd, *J*=10.2,3.8Hz, 5-H), 5.93(1H, d, *J*=10.2Hz, 4-H), 5.58(1H, d, *J*=3.8Hz, 6-H), 5.46(1H, d, *J*=7.0Hz, 8-H), 4.96(1H, dd, *J*=7.0,2.6Hz, 7-H), 3.99(1H, d, *J*=2.6Hz, 2-H), 1.57(3H, s, CH_3), 1.42(3H, s, CH_3). *m/z*(EI) 289(M^+-1), 275(M^+-CH_3), 233(M^++1-Me_2CO), 215(M^+-Me_2CO-OH). HRMS Calcd for $C_{16}H_{18}O_5$ 290.1130. Found: 290.1132.

(5S,6R)-5-hydroxy-6-[(1R,2R)-1,2-isopropylidenyloxy-2-phenylethyl]-5,6-dihydropyran-2-one **13**

To a stirred solution of **12** (82mg, 0.283mmol) in acetic acid(2ml) was added chromium(VI) oxide (34mg, 0.34mmol) in acetic acid(3ml). After being stirred for 15 min at 25~30°C, isopropanol(10ml) was added, and the reaction mixture was stirred at room temperature for a further 5 min. The resulting mixture was cooled to -10°C, and freshly prepared sodium triacetoxyborohydride (prepared from 200mg $NaBH_4$ and 6ml acetic acid below 10°C) was added. The reaction mixture was stirred for 1h at the same temperature and poured into water(50ml) and dichloromethane (20ml). The organic layer was separated, and the aqueous layer was extracted with dichloromethane(2x20ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography[ethyl acetate-hexane(1:3)] to afford **13**(57mg,69%), which was recrystallized with ethyl acetate-hexane to give pure **13** in 60% yield, m.p. 157-158°C, $[\alpha]_D^{20}$ -75.3 (C,0.6, $CHCl_3$). IR ν 3400(-OH), 1720(C=O) cm^{-1} ; ^{1}HNMR(CD_3COCD_3): 7.34-7.51(5H, m, Ph), 6.70(1H, dd, *J*=9.7,5.6Hz, 4-H), 5.89(1H, d, *J*=9.7Hz, 3-H), 5.33(1H, d, *J*=7.0, 8-H), 4.90(1H, dd, *J*=7.0,7.9Hz, 7-H), 4.09(1H, dd, *J*=7.9,3.2Hz, 6-H), 3.38(1H, dd, *J*=3.2,5.6Hz, 5-H), 1.61(3H, s, CH_3), 1.47(3H, s, CH_3). *m/z*(EI): 275(M^+-CH_3), 233(M^++1 -Me_2CO), 215(M^+-Me_2CO-OH). Anal, Calcd for $C_{16}H_{18}O_5$: C,66.19, H, 6.25; Found: C, 66.16, H, 6.26.

(+)-Goniotriol **1**

To a stirred solution of **13** (25mg,0.086mmol) in THF-H_2O(2:1,3ml) was added trifluoroacetic acid(1ml). After being stirred for 6h at room temperature, water (5ml) was added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate(3x20ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was purified by flash chromatography[ethyl acetate-hexane(2:1)] to give **1**(19mg,90%) as colourless prisms , m.p. 170-171°C; $[\alpha]_D^{20}$ +120.7(c, 1.1,MeOH) {lit[2], m.p. 170°C, $[\alpha]_D^{20}$ +121(MeOH)}. IR ν 3400(-OH), 1710(C=O) cm^{-1} ; ^{1}HNMR (CD_3OD): 7.26-7.47(5H, m, Ph), 7.00(1H, dd, *J*=9.7,5.8Hz, 4-H), 6.08(1H, d, *J*=9.7Hz, 3-H), 4.74(1H, d, *J*=7.9Hz, 8-H), 4.59(1H, t, *J*=3.8,3.2Hz, 6-H), 4.43(1H, dd, *J*=5.8,3.2Hz, 5-

H), 4.18(1H, dd, J=7.9,3.8Hz, 7-H). *m/z*(EI): 251(M^++1), 233(M^+ +1-H_2O), 215(M^++1-2H_2O). Anal, Calcd for $C_{13}H_{14}O_5$: C,62.39, H, 5.63; Found: C, 61.99, H, 5.44.

(+)-Goniofufurone **2**

To a stirred solution of **13** (12mg, 0.048mmol) in THF (6ml), was added DBU(3ul, 0.05%v/v) at room temperature. After being stirred for 4 days at room temperature, the reaction mixture was filtered through a pad of silica gel, and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography[ethyl acetate-hexane(2:1)] to give **2**(7mg,58%) as white solid, m.p. 153-154°C; $[\alpha]_D^{20}$ +8.9(c, 0.4, EtOH) {lit.[3] m.p. 152-154°C, $[\alpha]_D^{20}$ +9(C,0.5, EtOH)}. IR ν 3400(-OH), 1750(C=O) cm^{-1}; ^{1}HNMR ($CDCl_3$): 7.34-7.44(5H, m, Ph), 5.19(1H, J=4.8Hz, 8-H), 5.10(1H, m, J=5.4,4.2,1.0Hz, 4-H), 4.84(1H, dd, J=4.2,0.4Hz, 5-H), 4.39(1H, dd, J=2.7,0.4Hz, 6-H), 4.08(1H, dd, J=4.8,2.7Hz, 7-H), 2.74(1H, dd, J=18.8,5.4Hz, 3a-H), 2.66(1H, dd, J=18.8,1.0Hz, 3b-H). *m/z*(EI): 251(M^++1), 233(M^++1-H_2O), 215(M^++1-2H_2O). HRMS, Calcd for $C_{12}H_{12}O_4$(M^+-OH): 233.0740; Found:233.0737.

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