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Nitro Alkanes in Organic Synthesis : An Efficient Stereoselective Synthesis of (+)-Trans Whisky Lactone and (+)-Eldanolide from Nitro Alkane Synthons and Using Bakers' Yeast Reduction as the Key Step

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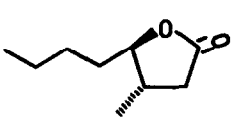
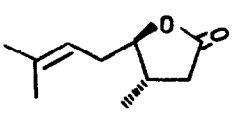
Abstract - *An efficient route using nitroalkane synthon* ***3a*** *and* ***3b*** *for the synthesis of optically pure R-(+)-trans whisky lactone,* ***(+)-9*** *and R-(+)-eldanolide,* ***(+)-10*** *is described. In a key step, bakers' yeast reduction is employed to get the required chirality.*

In recent years aliphatic nitro compounds are emerging as versatile building blocks and intermediates in organic synthesis.[1-8] This is primarily due to the fact that they are easily available, they undergo a variety of carbon-carbon bond forming processes in presence of a suitable base and the nitro group can be converted into a variety of other functional groups. The mechanism and factors influencing the carbon-carbon bond forming reactions of nitro alkanes have been studied extensively by several groups.[9-17]

In this paper we wish to report the enantioselective total synthesis of (+)-trans whisky lactone, (+)-**9** (3S,4R)-3-methyl-4-octanolide, the key flavour of whisky and wine[18,19] and the natural eldanolide (+)-**10** (3S,4R)-3,7-dimethyl-6-octen-4-olide, the pheromone of the male African sugarcane stem borer, *Eldana saccharina* (Wlk.)[20] by using nitroalkane synthons **3a** and **3b**. Although several other procedures are reported for the synthesis of these compounds,[21] this is the first report on their synthesis from nitroalkane synthons.



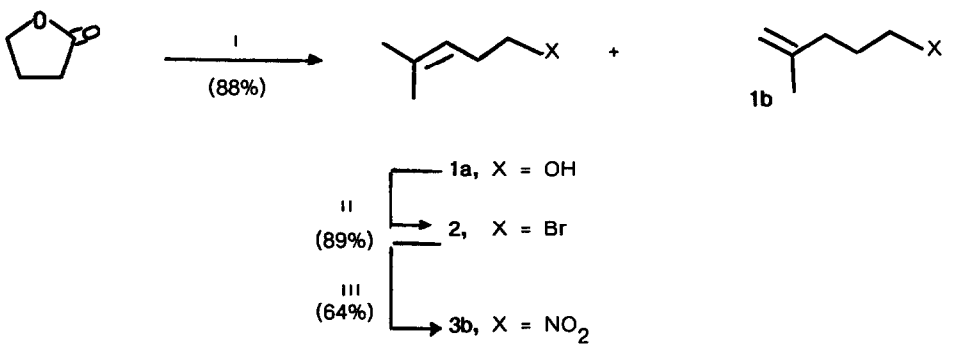
R-(+)-Trans whisky lactone, (+)-**9**



R-(+)-Eldanolide, (+)-**10**

Our method is straight forward and consists of the conjugate addition of primary nitroalkane **3a** and **3b** to acrolein or methyl acrylate in presence of DBU in THF.

Nitroalkane **3b** was obtained readily from butyrolactone. Reaction of methyl magnesium iodide[22] with butyrolactone and distillation of the hydrolyzed aqueous reaction mixture at normal pressure gave a 95:5 mixture of alcohol **1a** and **1b** in 88% yield. Treatment of the crude mixture of **1a** and **1b** with carbon tetrabromide[23] in dichloromethane and in presence of triphenylphosphine gave in 89% yield the essentially pure bromide **2**. Treatment of bromide **2** with sodium nitrite in DMSO gave the desired nitroalkane **3b** in 64% yield (50% overall yield from butyrolactone)(Scheme 1).

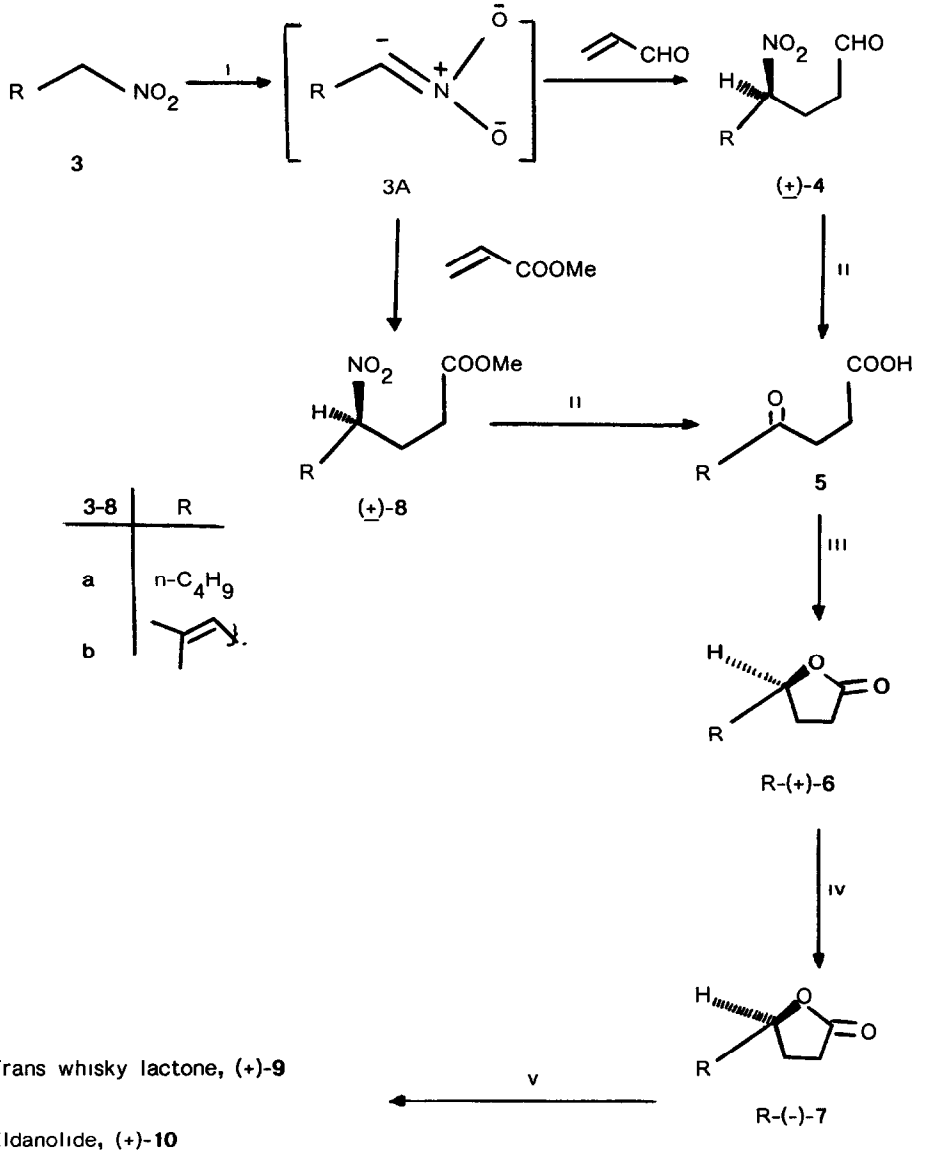


i) MeMgI (2 equiv) ii) $CBr_4/Ph_3P/CH_2Cl_2$ iii) $NaNO_2$/DMSO

Scheme 1

Nitroalkane **3b** is converted with 2 equivalents of DBU in THF to the corresponding dianion 3A. Addition of one equivalent of acrolein gave 4-nitroalkanal, (±)-**4b** in 79% yield which is directly converted to the ketoacid, **5b** in 73% yield by treating with hydrogen peroxide in an aqueous solution of potassium carbonate. In a similar way **3a** is also converted to 4-nitroalkanal (±)-**4a** in 81% yield and then to ketoacid **5a** in 76% yield. The ketoacids **5a** and **5b** are also obtained via an alternative route by first coupling the nitronate dianion 3A with acrylic acid methyl ester and subsequent hydrolysis of the keto ester (±)-**8** with hydrogen peroxide in presence of aqueous potassium carbonate. As illustrated in Scheme 2 reduction of the γ-ketoacids **5a** and **5b** with fermenting bakers' yeast[24] gave R-(+)-4-alkanolide, (+)-**6a**, yield 45%, $[\alpha]_D^{23}$=55.1 (C 1.4 THF); literature[25] $[\alpha]_D$= + 53.3 (C 1.56 THF) and (+)-**6b**, yield 54% $[\alpha]_D^{23}$= + 19.5 (C 1.2 MeOH); literature[26] $[\alpha]_D^{23}$= + 20 (C 1.1 MeOH). Treatment of the chiral lactones (+)-**6a** and (+)-**6b** with LDA/PhSeBr[27] and subsequent treatment with $NaHCO_3/NaIO_4$ gave R-(-)-**7a**, yield 65%, $[\alpha]_D^{23}$=-106° (C = 0.92, $CHCl_3$), literature[28] $[\alpha]_D^{23}$= -108° (C = 0.862, $CHCl_3$) and R-(-)-**7b** yield 70%, $[\alpha]_D^{23}$= -132° (C 1.1 MeOH), literature[26] $[\alpha]^{20}$= -130° (C 0.8 MeOH). Treatment of lactone R-(-)-**7a** and

R-(-)-**7b** with Me_2CuLi at -78°C gave R-(+)-trans whisky lactone, (+)-**9** , yield 75%, $[\alpha]_D^{23}$ = + 80.1 (C 1.6 MeOH), literature[26] $[\alpha]_D^{23}$= + 79.5 (MeOH) and literature[29] $[\alpha]_D^{20}$= + 72.8° (MeOH) and R-(+)-eldanolide, (+)-**10**, yield 80%, $[\alpha]_D^{23}$= + 50.6 (C 1.2 MeOH); literature[26] $[\alpha]_D^{20}$= + 51.5 (C 1.15 MeOH). The optical purity of these lactones have been ascertained by comparison with their specific rotations with that reported in the literature.[18-20]



R-(+)-Trans whisky lactone, (+)-**9**

R-(+)-Eldanolide, (+)-**10**

I) DBU (2 equiv)/THF II) H_2O_2/aq. K_2CO_3 III) Bakers' yeast/H^+

IV) n-BuLi/PhSeBr, $NaHCO_3/NaIO_4$ V) Me_2CuLi/THF, - 78°

Scheme 2

EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR spectra were recorded as neat films on a Perkin-Elmer 237B gratting infra-red spectrometer. Mass spectra were taken on a INCOS 50 GC-MS instrument. ^{1}H NMR spectra unless otherwise stated, were recorded on either a varian T-60 or Jeol FX-90 instrument in $CDCl_3$ using TMS as the internal standard. Chromatographic purifications were done on TLC plates using silica-gel G(E.Merck, India). Optical rotation measurements were done in a automatic polarimeter Model AA-1000 (M/S Optical Activity, U.K). All reactions of air and water sensitive materials were performed in oven dried glasswares and under dry nitrogen.

1-Hydroxy-4-methylpent-3-ene (1a) :

A solution of freshly distilled γ-butyrolactone (11.18g, 0.13 mol) in dry ether (200ml) is added dropwise to a freshly prepared reagent of methyl magnesium iodide prepared from magnesium (7.9g, 0.3 mol) and methyl iodide (45g, 0.3 mmol), while maintaining the temperature below 40°C. After stirring the reaction mixture for another 4 h it is hydrolysed with an ice-cooled saturated solution of ammonium chloride (600ml). The aqueous reaction mixture is distilled under normal pressure and the aqueous distillate is extracted with ether (3 x 100ml). The combined ether extract is dried over anhydrous sodium sulfate and evaporated to yield a liquid which on distillation under reduced pressure gave 11.5g (88%) of a colourless liquid, b.p 100°/5 mm Hg which is a 95:5 mixture of **1a** and **1b** as indicated by its ^{1}H NMR spectrum. A small amount of **1a** is purified by preparative TLC (n-hexane AcOEt, 2:1) to give **1a** as an oil. IR (cm^{-1}) 3400, 2900, and 1610; ^{1}H NMR (δ ppm): 1.7 (br, 6H, $(\underline{CH_3})_2C$ = C), 2.3 (q, J = 6.8Hz, 2H, = CH - $\underline{CH_2}$-), 3.6 (t, J = 7.3Hz, 2H, -$\underline{CH_2}$-OH), 5.0 (t, J = 7.5Hz, 1H, =$\underline{CH}$-); MS (m/z) : 100 (M^+), 82, 68 and 54. Analysis calculated for $C_6H_{12}O$, C = 71.95%, H = 12.08%. Found C = 71.66%, H = 12.1% **1b**, IR (cm^{-1}) : 3400, 2905 and 1610, ^{1}H NMR (δ ppm) : 1.7 (br, 3H, C = CH-$\underline{CH_3}$), 1.9-2.3 (m, 4H, -CH_2-), 3.6 (t, J = 7.3Hz, 2H, -$\underline{CH_2}$-OH), 4.68 (br, 2H, C = CH_2); MS (m/z) 100 (M^+), 82, 68 and 67.

1-Bromo-4-methylpent-3-ene (2)

To a stirred solution of **1** (4g, 40 mmol) and carbon tetrabromide (16.2g, 49 mmol) in dichloromethane (60ml) is added portionwise with ice cooling triphenylphosphine (14.4g, 55 mmol). After addition of triphenylphosphine the reaction mixture is stirred for additional 5 minutes and solvent removed under reduced pressure. Ether (60ml) is added and filtered. The filter cake is washed with ether (3 x 50ml). The combined filtrate and washings are evaporated in rotary evaporator to yield a syrupy liquid which is distilled to give an oil, b.p 52°/17 mm Hg (Literature[1] b.p 56-57/20 mm Hg), yield 5.8g (89%).

4-Methyl-1-nitropent-3-ene (3b) :

A solution of 1-bromo-4-methylpent-3-ene (**2**) (4.89g, 0.03 mmol) in DMSO (20 ml) is added to a mixture of sodium nitrite (3.6g, 0.042 mol) in DMSO (15ml) at r.t. The mixture is stirred at room temperature for 4 hours and then poured into ice-water (100ml) and layered over with petroleum ether (40-60°) (50ml). After separation of the organic layer, the aqueous phase is further extracted with petroleum ether (4 x 50ml). The combined extracts are then washed with water (4 x 50ml) and dried over anhydrous sodium sulfate. The drying agent is removed by filtration and evaporated to yield an oil which is purified by distillation under reduced pressure to yield **3b** as a colourless liquid, b.p 108-113°/5 mm Hg. Yield 2.5g (64%). IR(cm^{-1}) . 2900, 2350, 1650 and 1540; ^1H NMR 1.82 (br, 6H, $(\underline{CH_3})_2$ C = C-), 2.8 (q, J = 7Hz, 2H, $-\underline{CH_2}-CH_2-NO_2$), 4.38 (t, J = 7.0Hz, 2H, $-\underline{CH_2}-NO_2$), 5.2 (t, J = 7Hz, 1H, =CH-). MS (m/z) 130 (M^++1), 83,69,68 and 55. Analysis calculated for $C_6H_{11}NO_2$, C=55.80% H = 8.5%, N = 10.84%. Found C = 55.78%, H = 8.61%, N = 10.83%.

Nitroaldehydes (±)-4a and (±)-4b

General Procedure

A solution of the nitrocompound **3** (0.01 mol) in dry THF (10ml) is cooled to 0°C in an ice-bath and DBU (0.021 mol) is added dropwise while stirring. The reaction mixture is then allowed to reach room temperature over one hour and acrolein (0.015 mol) is added and stirring continued for another 5 to 6 hours at r.t. The reaction mixture is diluted with ether (200ml) and washed with water (3 x 100ml). The ether extract is dried over anhydrous sodium sulfate and evaporated under reduced pressure to yield a residue which is purified by chromatography/distillation.

(±)-**4a**, Colourless liquid b.p. 130°C/0.5 mm Hg, yield 1.4g (81%); IR (cm^{-1}) 1730 and 1545; ^1H NMR (δ ppm). 0.95 (t, J=8Hz, 3H, $\underline{CH_3}-CH_2-$), 1-2.65 (m, 10H, $-\underline{CH_2}-$), 4.2-4.6 (m, $-\underline{CH}-NO_2$), 9.8 (s, 1H, -CHO); MS (m/z) : 174 (M^++1), 128, 113, 98 etc. Analysis calculated for $C_8H_{15}NO_3$, C = 55.47%, H = 8.73% , N = 8.09%. Found C = 55.40%, H = 8.69%, N = 8.1%.

(±)-**4b**, gum, yield 1.46g (79%); IR (cm^{-1}) . 1725 and 1545; ^1H NMR (δ ppm). 1.80 (br, 6H, $(\underline{CH_3})_2$ C=C-), 1.05-2.8 (m, 6H, $-CH_2-$), 4.3-4.81 (m, 1H, $-\underline{CH}-NO_2$), 5.2 (t, J=7.2Hz, 1H, =CH-), 9.83 (s, 1H, -CHO-), MS (m/z) . 186 (M^++1), 139, 110 etc. Analysis calculated for $C_9H_{15}NO_3$; C = 58.36%, H = 8.16%, N = 7.56%. Found C = 58.33%, H = 8.18%, N = 7.58%.

γ-Ketocarboxylic acids 5a and 5b

General Procedure :

A solution of nitroaldehyde (±)-**4a** or (±)-**4b** (5 mmol) in methanol (25ml) is cooled to 0°C in an ice-bath and to this solution is added aqueous 30% hydrogen peroxide (10ml) while stirring. To the resultant solution potassium carbonate (4g) is added and stirring continued at room temperature for 15-20 hours. The solution is then acidified to pH 1 with concentrated hydrochloric acid and extracted with ether (3x50ml). The organic layer is washed with water (50ml) dried over anhydrous sodium sulfate and evaporated. The products are then purified by chromatography.

5a, crystalline solid, yield 0.60g (76%), m.p 46° (literature[25] m.p 47.8-48.2°C); IR(cm^{-1}) 1720 and 1700; ^1H NMR 0.9 (t, J=7Hz, 3H, $\underline{CH_3}$-CH_2), 1.1-2.93 (m, 10H, -CH_2), 8.96 (br, 1H, COO$\underline{H}$), MS (m/z) 158 (M^+), 143, 99, 84 etc.

5b, crystalline solid, yield 0.62g (73%), m.p 63°; IR (cm^{-1}): 3200, 1715, 1705 and 1610; ^1H NMR (δppm): 1.8 (br, 6H ($\underline{CH_3}$)$_2$C=C-), 1.2-2.82 (m, 6H,-$\underline{CH_2}$-), 5.28 (t, J=7Hz, 1H, =$\underline{CH}$-), 9.8 (br, 1H, COO$\underline{H}$); MS (m/z)· 170 (M^+), 125, 110 etc. Analysis calculated for $C_9H_{14}O_3$, C = 63.51%, H = 8.29%. Found C = 63.54%, H = 8.30%.

4-Nitrocarboxylic acid methyl ester (±)-8a and (±)-8b

General Procedure :

Compound (±)-**8** is prepared by using the procedure described for the synthesis of (±)-**4a** and (±)-**4b** but using acrylic acid methyl ester in place of acrolein.

(±)-**8a**, b.p 85/5mm Hg, yield 1.46g (72%); IR(cm^{-1}): 1740, 1715; ^1H NMR (δ ppm). 0.9 (t, J=7Hz, 3H,CH_3-), 1.5-2.1 (m, 4H,-CH_2-), 2.1-2.62 (m, 8H,-CH_2-), 3.56 (s, 3H,-OMe); MS(m/z)· 204, (M^++1), 157, 142, 127, 114 etc. Analysis calculated for $C_9H_{17}NO_4$, C=53.19%, H=8.43%, N=6.89%. Found C = 53.20%, H = 8.44%, N = 6.90%.

(±)-**8b**, gum, yield 1.5g (70%); IR (cm^{-1}): 1745, 1715, 1610 etc. ^1H NMR (δppm): 1.85 (br,6H ($\underline{CH_3}$, C=C-), 1.1-2.8 (m, 6H,-$\underline{CH_2}$-), 3.6 (s, 3H, OMe), 4.6 (m, 1H,-$\underline{CH}$-NO_2), 5.3 (t, J=7Hz, 1H,=$\underline{CH}$-), MS (m/z). 216 (M^++1), 169, 138 and 110. Analysis calculated for $C_{10}H_{17}NO_4$; C=55.80%, H=7.96%, N=6.51%. Found C=55.79%, H=7.99%, N=6.52%.

Asymmetric reduction of γ-ketoacids 5a and 5b with fermenting bakers' yeast :

General Procedure

A suspension of bakers' yeast (125g) and D-glucose (100g) in tap water (350ml) is stirred for 30 minutes at 32°C. A solution of γ -ketoacid (**5a** or **5b**)(7.5mmol) in 7.5ml of 1M NaOH is then added. The reaction mixture is allowed to stand at room temperature for 16 hours and to this is added celite (50g) and filtered. The celite pad is washed with ethyl acetate (150ml). The filtrate is acidified to pH 1 with 2N hydrochloric acid and extracted with ethyl acetate. The extract is dried over anhydrous sodium sulfate and evaporated to yield a gummy residue which is purified by chromatography.

(+)-**6a**, colourless liquid, yield 0.479g (45%), b.p 130-135/17mm Hg (literature,[25] b.p 140-150/22 mm Hg); IR(cm^{-1}): 3200, 1780 etc. ^1H NMR (δ ppm) 0.96 (t, J=6.5Hz,3H,-$\underline{CH_3}$), 1.2-2.3 (m, 8H,-CH_2), 2 4-2.6 (m, 2H,-$\underline{CH_2}$)-C(O)-), 4.02-4.65 (m, 1H,-CH-O-); MS (m/z): 142 (M^+), 127, 113, 99 and 85, $[\alpha]_D^{23}$=+55.1 (C=1.4 THF)(literature[25] $[\alpha]_D$=+53.3 (C=1.56 THF).

(+)-**6b**, gum,yield 0.623g(54%), IR(cm^{-1}). 2970,1780,1211 etc. ^1H NMR(δ ppm)· 1.69(s,3H,$\underline{CH_3}$ -C=), 1.71(s,3H,$\underline{CH_2}$-C=), 1.8-2.8(m,6H,-$\underline{CH_2}$-), 4.6(m,1H,-$\underline{CH}$-O-), 5.18(t,1H,J=7Hz,=$\underline{CH}$-); MS (m/z)· 154(M^+),139,126 and 99 $[\alpha]_D^{23}$=+19.5 (C=1.2 MeOH);(literature[26] $[\alpha]_D^{23}$=+20.0 (C=1.1 MeOH).

α,β-Unsaturated-γ-butyrolactone derivative R-(-)-7a and R-(-)-7b

In a 50ml RB flask absolute dry THF (20ml) is cooled to -78°C under nitrogen. To this cooled solution is added diisopropyl amine (6mmol) followed by n-BuLi (6mmol) (1.5M solution in hexane) with a syringe against a flow of nitrogen. To this solution added lactone (+)-**6a** or (+)-**6b**,(5mmol) in 4ml of THF. The mixture is stirred at the same temperature for another 15 minutes and then phenylselenylbromide (6.2mmol) is added dropwise to this mix-

mixture with a syringe. After 5-10 minutes the cold reaction mixture is poured into a mixture of 0.5N hydrochloric acid and 1.1 ether-pentane mixture (40ml). The organic layer is washed successively with water, saturated sodium bicarbonate solution and saturated brine and dried over sodium sulfate. Evaporation of the organic phase gave a residue, which is treated directly without purification with methanol (60ml), and sodium metaperiodate (8 m mol) with vigorous stirring. After 1-2 hours at room temperature the reaction mixture is poured into a 80:20 mixture of ether-pentane (50ml) and saturated sodium bicarbonate solution (50ml). The organic phase is washed with brine (50ml), water (50ml) and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a residue which is purified by chromatography.

(-)-**7a**, gum, yield 0.910g (65%), IR(cm^{-1}) 1745. ^1H NMR (δ ppm): 0.9 (t, J=7Hz, 3H, $\underline{CH_3}$-CH_2-), 1.2-1.6 (m, 6H,-$\underline{CH_2}$-), 4.7 (m, 1H, $\underline{CH}$-O), 6.1 (dd, J=6&2Hz, 1H, CH=$\underline{CH}$-C(O), 7.5 (dd, J=6&1.7Hz, 1H, $\underline{CH}$=CH-C(O); MS (m/z) 140 (M^+) 125, 111, 97, 83 and 81, $[\alpha]_D^{23}$= -106° (C = 0.92 $CHCl_3$). Literature[28] $[\alpha]_D^{23}$= -108° (C = 0.862 $CHCl_3$).

(-)-**7b**, gum, yield 1.064g (70%), IR (cm^{-1}): 1704, 1750; ^1H NMR (δ ppm). 1.69 (s, 3H, $\underline{CH_3}$-C=), 1.71 (s, 3H, CH_3-C=), 2.15 (m, 2H,-$\underline{CH_2}$-), 4.68 (m, 1H, $\underline{CH}$-O-), 5.14 (t, J=7H z, 1H, C=$\underline{CH}$-), 6.13 (dd, J=6 and 2Hz, 1H, CH=$\underline{CH}$-C(O), 7.5 (dd, J=6 and 1.5Hz,1H, $\underline{CH}$=CH-C(O)-) MS(m/z):152(M^+),137,109,97 and 83;$[\alpha]_D^{20}$=-132°(C=1.1 MeOH); Literature[26] $[\alpha]_D^{20}$=-130° (C = 0.80 MeOH).

Synthesis of (+)-trans-whisky lactone, (+)-9 and R-(+)-Eldanolide, (+)-10 :

General Procedure

To a suspension of cuprous iodide (4mmol) in dry ether (20ml) at 0°C under nitrogen is added 1.5 molar solution of MeLi (8mmol) and the resulting colourless solution is further cooled to -78°C. A solution of the unsaturated lactone (-)-**7a** or (-)-**7b** (5mmol) in ether (10ml) is then added to the cooled solution of lithium dimethyl copper and the mixture is stirred at the temperature for 30 minutes. The mixture is poured into water (200ml) extracted with dichloromethane (3x50ml), dried over anhydrous sodium sulfate and evaporated. Products are purified by chromatography.

(+)-**9**, yield 0.585g (75%), $[\alpha]_D^{23}$= +80.1 (C 1.6 MeOH), literature[26] $[\alpha]_D^{23}$= +79.5 (MeOH) and (+)-**10**, yield 0.672g (80%), $[\alpha]_D^{23}$= +50.6 (C 1.2 MeOH), literature[26] $[\alpha]_D^{20}$=+51.5(C 1.15 MeOH) IR and ^1H NMR data of (+)-**9** and (+)-**10** are identical with data reported.[21]

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