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A STEREOSPECIFIC SYNTHESIS OF OPTICALLY PURE (-)-α-MULTISTRIATIN

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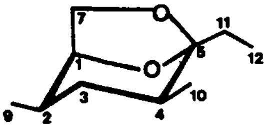
Abstract : *An efficient stereo- and enantiospecific synthesis of (-)-α-multistriatin from (L)-malic acid is described. The key steps of this synthesis are the stereoselective alkylation of the hydroxylactone 5 and the acid equilibration of the esters 9 and 10.*

α-Multistriatin, one of the essential components of the aggregation pheromone of the European elm bark beetle, "*Scolytus multistriatus*", the principal vector of Dutch elm disease in Europe and North America, was isolated and synthesized in racemic form by Silverstein and coworkers (1). The first enantioselective synthesis, carried out by Mori, showed that the absolute configuration of the pheromone component was 1S, 2R, 4S, 5R as shown in 1 (2). More recently the two enantiomers of α-multistriatin were prepared and it was shown that the only the (-) enantiomer is biologically active (3).

Most of the previous syntheses have been non-stereoselective leading to mixtures of diastereoisomers of 1 in various amounts (4). Because these isomers are not isolable by



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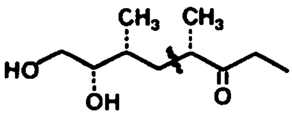

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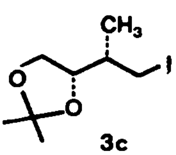
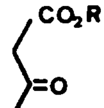


3c

+



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conventional liquid chromatography, the pure α-multistriatin was only obtained by using preparative VPC. The only totally stereospecific syntheses were long and tedious routes, using carbohydrates as starting material (5).

We report here a short and efficient new method to prepare optically pure (-)-α-multistriatin. Retrosynthetic analysis shows that this compound may be prepared by cyclization of the ketodiol 2. To obtain this intermediate, we were faced with the double problem of 1,2 and 1,3 relative induction. The approach which was used in this synthesis involves the coupling reaction of an iododioxolan 3c, which possesses the correct configuration at C-1 and C-2 of multistriatin with the carbanion derived from a β-ketoester 4.

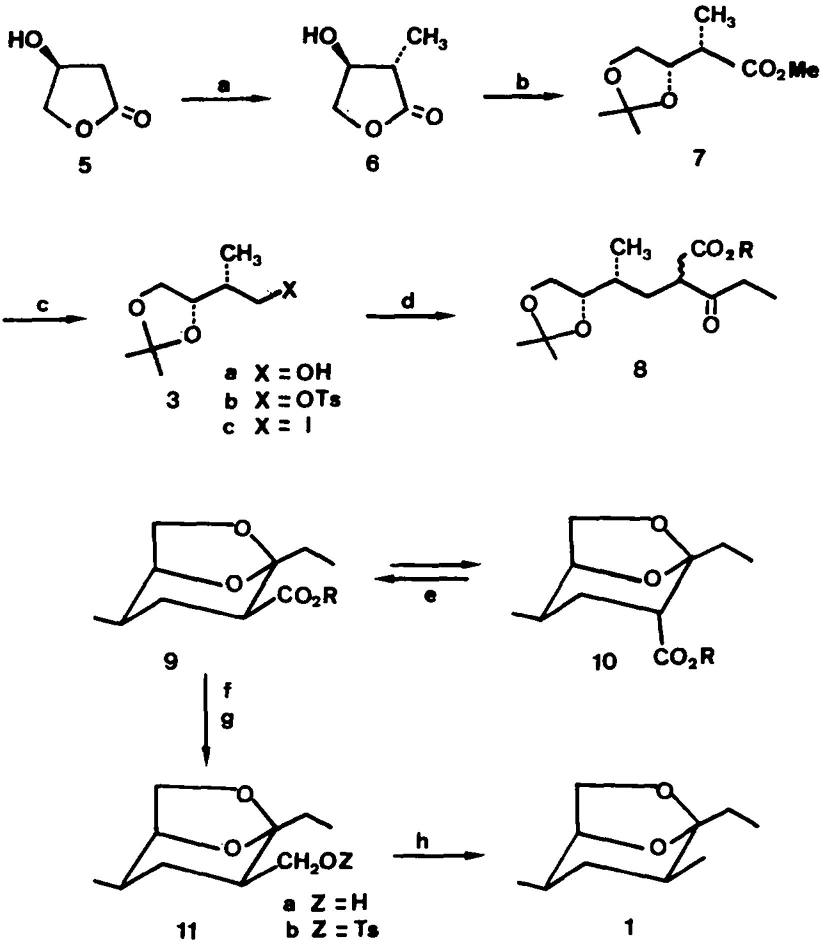
Although it is possible to epimerize the C-4 center in acidic medium, it must be pointed out that α-multistriatin (methyl at C-4 in equatorial position) and γ-multistriatin (methyl at C-4 in axial position) are not separated by conventional liquid chromatographic methods. It was thus necessary to use another approach in order to control the configuration at C-4. We anticipated that the replacement of the methyl by an ester group would perhaps solve that problem.

In order to prepare the iodocompound 3c, we planned to use the stereoselective alkylation of β-hydroxylactones (6). It was previously shown that by using two equivalents of LDA at -78°C, it is possible to obtain the trans lactone after alkylation. However, due to the presence of HMPT, the methylated lactone was isolated as the O-methyl ether.

By operating at very low temperature (-95°C, 24 h), we succeeded in obtaining the free alkylated lactone 6 without this O-methyl ether (cis/trans ratio : 2/98). This reaction was carried out using a hydroxylactone prepared by reduction of the hemiester derived from malic acid in three steps (total yield : 84 %) by an original pathway that we have previously published (7).

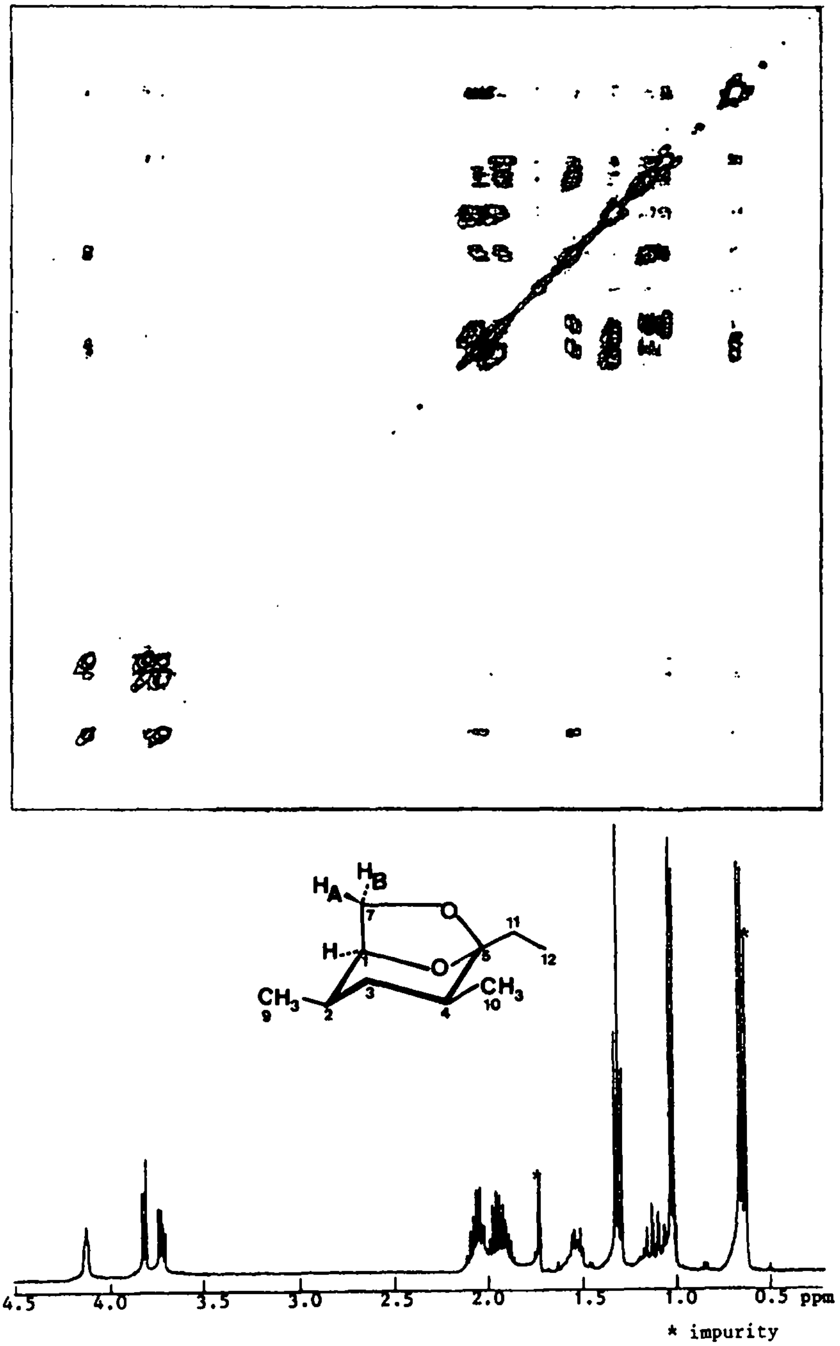
The lactone 6 was then opened under acidic conditions and transformed into the protected diol 7 (dimethoxypropane in methanol : 75 %). The iodide 3c was obtained in 90 % yield from the dioxolan 7 by lithium aluminium hydride reduction followed by tosylation and iodine exchange. The condensation with the β-ketoester 4 (R = Et or iPr) was achieved by using phase transfer catalysis. The two diastereoisomers were quantitatively cyclized at room temperature in dilute hydrochloric acid to give the esters 9 and 10 in a 1/1 ratio. Equilibration was carried out by heating this mixture in aqueous acid for four hours. The 9/10 ratio was thus transformed into a 75/25 mixture which was analysed by VPC on a capillary column. The esters 9 and 10 were easily separated by flash-chromatography and their stereochemistry determined by 2D NMR. The minor compound 10 was again equilibrated so that it was possible to obtain the pure ester 9 in 79 % yield.

To complete the synthesis of α-multistriatin, it was now necessary to transform the ester function into a methyl group. The ester 9 was reduced by lithium aluminium hydride and further transformed into the tosylate 11b. The reduction of this tosylate was achieved by using sodium borohydride in DMSO (9), a method which proved to be superior over the conventional lithium aluminium reduction which affords a noticeable amount of the alcohol 11a. It must be outlined that



a) 2 LDA, CH$_3$I, THF , - 95°C, 24h (65 %) ; b) (CH$_3$)$_2$C(OCH$_3$)$_2$,H$^+$, CH$_3$OH (75 %) ; c) LiAlH$_4$; TsCl, Pyr. and NaI, acetone (90 %) ; d) NaOH 50 %, nBu$_4$N$^+$HSO$_4^-$, 4 (75 %) ; e) HCl 3N, 50°C, CH$_3$CN, 4h ; f) LiAlH$_4$ (90 %) ; g) TsCl, Pyr (85 %) ; h) NaBH$_4$, DMSO, 50°C, 3h (70 %).

the reaction of this alcohol with a triphenylphosphine-carbon tetrabromide mixture affords both the equatorial and the axial bromides in a 75/25 ratio. Finally pure α-multistriatin was obtained in 70 % yield from tosylate 11b. The spectral properties of this compound (mass spectrometry, ^{1}H, ^{13}C) were identical with those reported for α-multistriatin (1b,1c,8).However in previous works, NMR



2D ^1H-^1H COSY (δ-δ) spectrum of multistriatin in C_6D_6 (400 MHz)

spectra were recorded in deuterochloroform and the attribution of some protons was not very clear. By operating in benzene and using the 2D technique, it was possible to determine very accurately the chemical shift of each proton.

The optical rotation ($[\alpha]_D^{22}$ - 45° ; hexane, c = 2.0) was in good agreement with literature values (5). Furthermore, capillary VPC analysis indicated that this material contained > 99 % of the desired isomer.

EXPERIMENTAL

Products were purified by flash chromatography (Kieselgel 60 Merck ; 0.040-0.060 mm ; solvent : cyclohexane/ethyl acetate) and analysed by gas chromatography (10 % SE30, 3 m column), thin layer chromatography (silica gel 60 F 254), and distillation. ^{1}H NMR spectra were recorded on a Bruker WP 80 or on a Cameca TSN 250 or on Bruker AM 400 operating at 400.13 MHz for ^{1}H and 100.56 MHz for ^{13}C. Deuterochloroform was used as solvent with tetramethylsilane as internal standard. Mass spectra were recorded on a Nermag R 10-10 (fitted with a CPV-mass coupling ; column : CP Sil 5, 40 m).

(2S,3S)-(-)-2-Methyl-3,4-dihydroxybutanoic acid-1,4-lactone 6

To a dry flask containing 122.5 mmol of lithium diisopropylamide (prepared from 17.3 ml (122.5 mmol) of diisopropylamine and 55 ml of 2.2 M nBuLi in hexane) in 300 ml of THF at - 100°C was added a solution of 5 g (49 mmol) of hydroxylactone 5 in 200 ml of THF. After 45 mn, 9.2 ml (147 mmol) of methyl iodide in 150 ml of THF was added at this temperature. After two days at - 100°C the reaction was quenched with 100 ml of saturated ammonium chloride solution, brought to ambient temperature, and extracted with ether. The ether layer was washed with a saturated sodium chloride solution, dried over $MgSO_4$ and concentrated. Flash column chromatography (cyclohexane/AcOEt 20/80) afforded 3.7 g (65 %) of pure methylated lactone 6 (6). b.p. 163-165°C/15 Torr $[\alpha]_D^{20}$ = -58° (c = 2.87 ; methanol): ee > 97 % (HPLC of MTPA ester). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.52 (d, J=7.5 Hz, 3H, CH_3) ; 2.58 (dq, J=7.7,5.5 Hz, 1H, $\underline{CH}CH_3$) ; 3.12 (s, 1H, OH) ; 4.10 (dd, J=10.0,5.0 Hz, 1H) ; 4.30 (m, 1H, $\underline{CH}OH$) ; 4.50 (dd, J=10.0,6.0 Hz, 1H, CH_2O). ^{13}C NMR ($CDCl_3$) δ 12.85 ; 43.15 ; 73.47 ; 75.02 ; 179.38. Mass spectrum m/z (rel intensity, %) 116,(3) ; 98,(4) ; 58,(64) ; 57,(100) ; 55,(14).

(2'S,4S)-(+)-Methyl-2'-(2,2-dimethyl-1,3-dioxolan-4-yl)-propanoate 7

A solution of 11.6 g (0.1 mol) of hydroxylactone 6 and 1 g of p. toluenesulfonic acid monohydrate in 10 ml of 2,2-dimethoxypropane, 2 ml of methanol and 10 ml of acetone was stirred and refluxed for 3 hr, then cooled, diluted with ether and washed with saturated aqueous $NaHCO_3$ solution. The organic solution was dried over $MgSO_4$ and evaporated in vacuo. The crude oil was chromatographied on silica gel (hexane/AcOEt 80/20) to afford 14.1 g (75 %) of pure 7. $[\alpha]_D^{20}$ = 20° (c = 2.9 ; hexane). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.27 (d, 3H, J=7 Hz, $\underline{CH_3}CH$) ; 1.35 (s, 3H, acetonide CH_3) ; 1.40 (s, 3H, acetonide CH_3) ; 2.58 (m, 1H, $\underline{CH}CH_3$) ; 3.60 (s, 3H, OCH_3) ; 3.7-4.0 (m, 3H, $O\underline{CH}\underline{CH_2}O$). ^{13}C NMR ($CDCl_3$) δ 173.9 ; 108.9 ; 76.7 ; 68.0 ; 51.7 ; 43.5 ; 26.7 ; 25.9 ; 13.9. Anal. cald. for $C_9H_{16}O_4$: C, 57.43 ; H, 8.57. Found : C, 57.12 ; H, 8.68.

(2'R,4S)-(-)-2'-(2,2-Dimethyl-1,3-dioxolan-4-yl) propan-1'-ol 3a

A solution of 7 (14.1 g, 75 mmol) in 150 ml of dry ether was added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (5 g) in dry ether (20 ml). The mixture was stirred for 1 hr at room temperature. The solution was hydrolysed with 4.9 ml of water, 4.9 ml of 4N NaOH and 14.8 ml of water and stirred for 30 mn at room temperature. The mixture was filtered and the filter cake was thoroughly washed with ether. The combined ether solution was dried over $MgSO_4$ and concentrated in vacuo to afford 11.9 g (99 %) of pure product 3a. $[\alpha]_D^{20}$ = -9° (c = 2.3 ; hexane) ; Litt. (3). ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.97 (d, 3H, J=7.5 Hz, $\underline{CH_3}CH$) ; 1.32 (s, 3H, acetonide CH_3) ; 1.41 (s, 3H, acetonide CH_3) ; 1.80 (m, 1H, $C\underline{H}CH_3$) ; 2.55 (s, 1H, OH) ; 3.52 (d, 2H, J=6.0 Hz, CH_2OH) ; 3.7 - 4.1 (m, 3H, $OC\underline{H}C\underline{H}_2O$).

(2'R,4S)-(-)-2'-(2,2-Dimethyl-1,3-dioxolan-4-yl)-1'-tosyloxypropane <u>3b</u>

9.53 g (51 mmol) of pTsCl was added to a stirred and ice-cooled solution of <u>3a</u> (8 g, 50 mmol) in 50 ml of dry pyridine. After 2 hr at 0°C, the mixture was poured into 1N HCl solution and extracted with ether. The ether solution was washed with 1N HCl, $CuSO_4$ solution, dried over $MgSO_4$ and concentrated in vacuo to give 15.5 g of crude product. Chromatography on silica gel (cyclohexane/AcOEt 60/40) afforded 13.5 g (90 %) of pure product. $[\alpha]_D^{20}$ = 10° (c = 4.49 ; hexane); Litt.(3). ^1H NMR (80 MHz, $CDCl_3$) δ 0.98 (d, J=6.5 Hz, 3H, $C\underline{H}_3CH$) ; 1.28 (s, 3H, acetonide CH_3) ; 1.32 (s, 3H, acetonide CH_3) ; 1.98 (m, 1H, $C\underline{H}CH_3$) ; 2.40 (s, 3H, CH_3Ar) ; 3.55 (t, J=6 Hz, 1H, $OCHC\underline{H}_2O$) ; 3.9-4.0 (m, 4H, CH_2OTs, $OC\underline{H}C\underline{H}_2O$) ; 7.2-7.6 (4H, aromatic protons).

(2'S,4S)-(-)-2'-(2,2-Dimethyl-1,3-dioxolan-4-yl)-1'-iodo-propane <u>3c</u>

A solution of 13.5 g (45.3 mmol) of the tosylate <u>3b</u> in 30 ml of acetone was stirred with 13.6 g (90.6 mmol) of sodium iodide for 24 hr. The solution was filtered and poured into 50 ml of water and extracted with ether. The organic phase was dried over $MgSO_4$ and evaporated in vacuo to afford 12.1 g of crude oil. Chromatography on silica gel (cyclohexane/AcOEt90/10) afforded 12 g (98 %) of pure product. $[\alpha]_D^{20}$ = -2.6° (c = 3.09 ; hexane) ; Litt. (3). ^1H NMR (80 MHz, $CDCl_3$) δ 1.06 (d, 3H, J=6.0 Hz, $C\underline{H}_3CH$) ; 1.35 (s, 3H, acetonide CH_3) ; 1.43 (s, 3H, acetonide CH_3) ; 1.75 (m, 1H, $C\underline{H}CH_3$) ; 3.07 (dd, J=7.0,12.1 Hz, 1H, CH_2I) ; 3.20 (dd, J=6.0,12.1 Hz, 1H, CH_2I) ; 3.60 (m, 1H, CH_2O) ; 4.0 (m, 2H, $OC\underline{H}C\underline{H}_2O$).

General procedure for the condensation

57.8 g (0.17 mol) of tetrabutylammonium hydrogeno-sulfate was added to a cooled solution of 13.6 g (0.34 mmol) of sodium hydroxide in 80 ml of water. This mixture was added to a cooled stirred solution of 24.5 g (0.17 mol) of ethyl acetoacetate and 11.5 g (42.4 mmol) of alkyl iodide in 160 ml of chloroform. The solution was stirred for 2 hr at room temperature. The chloroform was dried over $MgSO_4$ and evaporated in vacuo ; the tetrabutylammonium iodide was precipitated by adding ether to the residue. The solution was filtered and ether was evaporated to give 9.2 g (75 %) of <u>8</u>. This one was further employed without purification.

The same procedure was used for the isopropylic ester (yield : 93 %).

(1S,2R,4S,5R)-(-)-5-Ethyl-2-methyl-4-ethoxycarbonyl-6,8-dioxabicyclo[3.2.1]octane <u>9</u>

9.2 g (32.2 mmol) of <u>8</u> was added to a solution of 3N HCl (20 ml) in 60 ml of acetonitrile. The solution was heated at 50°C for 4 hr and extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give 7.88 g of crude oil. Chromatography on silica gel (hexane/AcOEt 90/10) afforded 4.90 g (75 %) of the equatorial diastereoisomer and 1.63 g (25 %) of the axial diastereoisomer. Equatorial diastereoisomer <u>9</u> : $[\alpha]_D^{20}$ = -60° (c = 2.13 ; hexane). ^1H NMR (250 MHz, $CDCl_3$) δ 0.85 (d, 3H, J=6.9 Hz, CH_3(9)) ; 0.95 (t, 3H, J=7.3 Hz, CH_3 (12)) ; 1.23 (t, 3H, J=6.9 Hz, CH_3(ester)) ; 1.70 (m, 1H, H (3 ax)) ; 1.75 (q, 1H, J=7.1 Hz, CH_2 (11)) ; 1.80 (m, 1H, H (3eq)) ; 2.00 (m, 1H, H(2)) ; 2.72 (dd, 1H, J=5.85,11.3 Hz, H(4)) ; 3.73 (dd, 1H, J=5.1,7.6 Hz, H(7B)) ; 4.03 (d, 1H, J=7.0 Hz, H(7A)) ; 4.12 (m, 2H, CH_2(ester)) ; 4.24 (m, 1H, H (5)). Mass spectrum m/z (rel intensity, %) 228 (0.4), 183 (0.4), 171 (0.7), 154 (1.6), 128 (5), 81 (15), 57 (100), 55 (70). Anal. cald. for $C_{12}H_{20}O_4$: C,63.14 ; H,8.83. Found : C,62.90; H,8.66. Axial diastereoisomer <u>10</u> : $[\alpha]_D^{20}$ = 25.6° (c = 1.92 ; hexane). ^1H (250 MHz, $CDCl_3$) δ 0.82 (d, 3H, J=7.1 Hz, CH_3 (9)) ; 0.95 (t, 3H, J=7.4 Hz, CH_3 (12)) ; 1.25 (t, 3H, J=7.2 Hz, CH_3 (ester)) ;

1.50 (m, 1H, H (3ax)) ; 1.80 (q, 2H, J=7.0 Hz, CH_2 (ester)) ; 1.85 (m, 1H, H (3eq)) ; 2.5 (m, 1H, H (2)) ; 2.68 (dd, J=6.1 Hz, H (4)) ; 3.65 (ddd, 1H, J=8.0,5.0,1.0 Hz, H (7B)) ; 3.92 (d, J=8.0 Hz, H (7A)) ; 4.13 (q, 1H, J=7.2 Hz, CH_2 (ester)) ; 4.39 (m, 1H, H(1)). Mass spectrum m/z (rel intensity, %) 228 (1.5), 183 (1.4), 171 (3.2), 154 (7.8), 81 (23), 57 (100), 55 (30). The same procedure was used for the isopropylic ester to give 9 + 10 in 90 % yield.

(1S,2R,4R,5R)-5-Ethyl-2-methyl-4-hydroxymethyl-6,8-dioxabicyclo[3.2.1]octane 11a

A solution of 4.43 g (19.4 mmol) of 9 in dry ether (10 ml) was added to a stirred suspension of $LiAlH_4$ (1.11 g ; 29.5 mmol) in 5 ml of dry ether at 10°C. The mixture was stirred at room temperature for 1hr. The solution was hydrolysed with 1.15 ml of water, 1.15 ml of NaOH 4N and 3.45 ml of water and stirred for 30 mn at room temperature. The mixture was then filtered and the filtered cake was thoroughly washed with ether. The combined ether solution was dried over $MgSO_4$ and concentrated in vacuo to give 11a (3.3 g ; 90 %) as an oil. This one was employed without purification. ^1H NMR (250 MHz, $CDCl_3$) δ 0.87 (d, 3H, J=7.0 Hz, CH_3 (9)) ; 0.96 (t, 3H, J=7.5 Hz, CH_3 (12)) ; 1.48 (m, J=12.0 Hz, 1H, H (4)) ; 1.69 (m, 1H, H (3ax)) ; 1.83 (q, J=7.5 Hz, 2H, CH_2 (11)) ; 1.91 (m, 1H, H (3eq)) ; 2.11 (m, 1H, H (2)) ; 2.37 (s, 1H, OH) ; 3.49 (dd, 1H, J=3.5,11.0 Hz, H (7B)) ; 3.73 (m, 2H, $\underline{CH_2}OH$) ; 3.98 (d, 1H, J=8.0 Hz, H (7A)) ; 4.29 (m, 1H, H(1)). Anal. cald. for $C_{10}H_{18}O_3$: C,64.49 ; H,9.74. Found : C, 64.61 ; H, 9.80.

(1S,2R,4R,5R)-(−)-5-Ethyl-2-methyl-4-tosyloxymethyl-6,8-dioxabicyclo[3.2.1]octane 11b

8.45 g (44 mmol) of pTsCl was added to a stirred and ice-cooled solution of 3.3. g (17.7 mmol) of 11a in dry pyridine (5 ml), 300 mg of DMAP and 50 ml of CH_2Cl_2. After 12 hr at room temperature the mixture was poured into $NaHCO_3$ and extracted with ether. The organic solution was washed with a saturated $CuSO_4$ solution, dried over $MgSO_4$ and concentrated in vacuo to give 5.7 g of crude product. Chromatography on silica gel (cyclohexane/AcOEt 90/10) afforded 5.13 g (85 %) of a white solid 11b which was recristallised in diisopropylic ether. $[\alpha]_D^{20} = -31°$ (c=2.2; EtOH). ^1H NMR (250 MHz, $CDCl_3$) δ 0.82 (d, J=7.0 Hz, 3H, CH_3 (9)) ; 0.88 (t, J=7.5 Hz, 3H, CH_3(12)); 0.96 (m, J=12.0 Hz, 1H, H (4)) ; 1.60 (dq, J=7.5,3.0 Hz, 2H, CH_2 (11)) ; 1.74 (m, 1H, H (3ax)) ; 2.00 (m, 1H, H (2)) ; 2.12 (m, 1H, H (3eq)) ; 2.46 (s, 3H, CH_3Ar) ; 3.68 (m, 2H, CH_2OTs) ; 3.84 (d, J=7.5 Hz, H (7A)) ; 4.06 (dd, J=10.0,6.0 Hz, 1H, H(7B)) ; 4.22 (m, 1H, H (1)) ; 7.4 ; 7.8 (aromatic protons). Anal. cald. for $C_{17}H_{24}O_5S$: C, 55.98 ; H, 7.11. Found : C, 56.10 ; H, 6.95.

(−)-α-multistriatin

A solution of 4 g (11.7 mmol) of 11b and 2 g (53 mmol) of $NaBH_4$ in 20 ml of dimethylsulphoxide was heated for 3 hr at 50°C, diluted with water and extracted with ether. The organic solution was washed with NaCl, dried over $MgSO_4$ and concentrated in vacuo to give 1.9 g of crude product. Flash chromatography on silica gel (ether/pentane 5/95) afforded 1.4 g (70 %) of pure (−)-α-multistriatin. $[\alpha]_D^{20} = -45°$ (c = 2 ; hexane). The 2D spectrum was measured on 2 mg in C_6D_6. The spectral widths in F(1) and F(2) are 1750 Hz. 256 increments (16 transients) of 1K data points were recorded. Zero fillings was applied once in F(1). The fid were multiplied by a square sinebell in both dimensions before Fourier transform. The pulse sequence was taken from the Bruker Library. ^1H NMR (400 MHz, C_6D_6) δ0.65 (d, J=7.0 Hz, 3H, CH_3 (9)) ; 1.02 (d, J=7.0 Hz, 3H, CH_3(10));

1.10 (m, 1H, H (3ax)) ; 1.30 (t, J=7.8 Hz, 3H, CH_3 (12)) ; 1.52 (m, 1H, H(3eq)) ; 1.8 - 2.1 (m, 2H, CH_2 (11)) ; 1.80 (m, 1H, H (4)) ; 2.10 (m, 1H, H (2)) ; 3.70 (dd, J=5.5,7.5 Hz, 1H, H (7A)) ; 3.82 (d, J=7.5 Hz, 1H, H (7B)) ; 4.13 (m, 1H, H (1)). ^{13}C NMR ($CDCl_3$) δ 7.13, 16.32, 16.73, 23.05, 33.09, 34.79, 37.16, 65.16, 78.76, 110.33. Mass spectrum m/z (rel intensity, %) 57 (100), 96 (10), 128 (8), 170 (4).

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