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# FIRST SYNTHESIS OF THE DIFURANSESQUITERPENE ATHANASIN AND THE ELUCIDATION OF ITS RELATIVE AND ABSOLUTE CONFIGURATION

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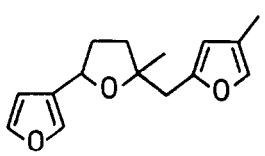
*Key Words* *Difuransesquiterpene, natural product synthesis, special furan building blocks, relative and absolute configuration, optical rotations*

***Abstract:*** *The synthesis of the naturally occurring difuransesquiterpene athanasin is described Employing Seebach's method of "self-reproduction of chirality", the chiral oxirane* ***6*** *is built up, which is successively connected with suitable furan building blocks Cyclization of the resulting diols* ***14 a/b*** *gives the enantiomerically pure diastereomers* ***1a*** *and* ***1b***
*Comparison of their spectroscopic data with athanasin after separation allows the elucidation of the natural product's relative and absolute configuration*

## INTRODUCTION

Investigating the asteraceae *Athanasia crithmifolia* L and *Athanasia parvifolia* L for new compounds in 1972, Bohlmann and Rao[1] isolated among other furansesquiterpenes an optically active one, for which they proposed the structure given below



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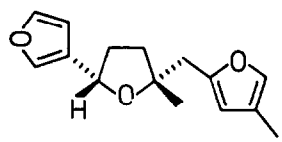
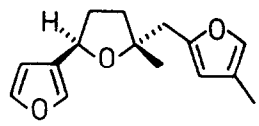
This difuransesquiterpene was called athanasin and has been found later in *Stilpnophytum linifolium* (Thunb ) Less and *Eumorphia sericea* by Bohlmann and Zdero[2,3] Its relative and absolute configuration, however, has never been determined
The value of optical rotation $[\alpha]_D^{20}$ −29 6° (c= 2 30, $CHCl_3$) given for 1 could not be reproduced when the original sample was purified recently and measured again $[\alpha]_D^{20}$ −1 93° (c=1 84 $CHCl_3$)

In this paper we present a short and effective synthesis of the enantiomerically pure diastereomers **1a** and **1b**



1a



1b

## RESULTS AND DISCUSSION

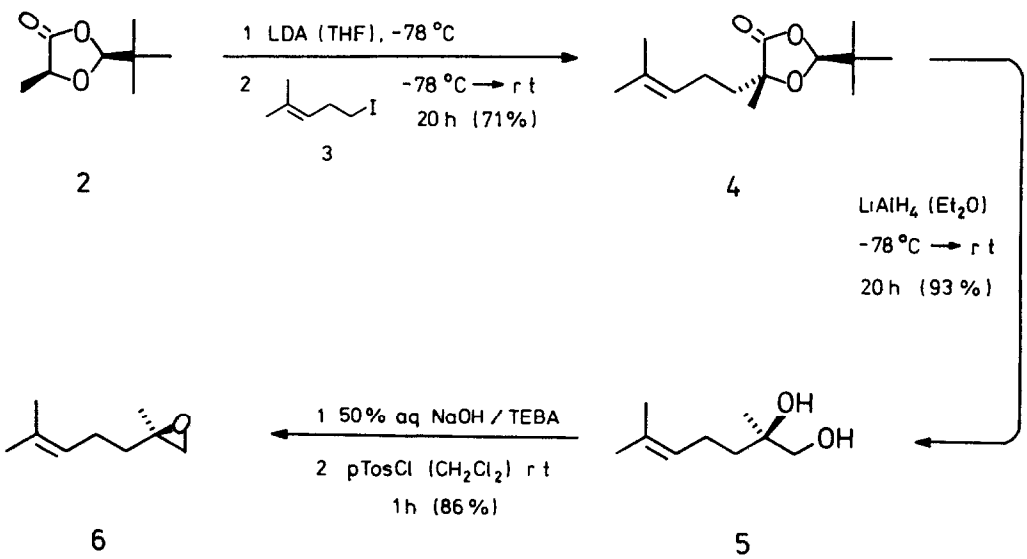
To establish a definite stereochemistry at the disubstituted centre of the tetrahydrofuran ring, Seebach's[4,5] method of "self-reproduction of chirality" using (2*S-cis*)-2-(1,1-dimethylethyl)-5-methyl-1,3-dioxolan-4-one (**2**) was employed (Scheme 1)

The dioxolanone **2** was treated with lithium diisopropylamide (LDA) in absolute tetrahydrofuran (THF) and alkylated with homoprenyliodide (**3**), which had been synthesized according to Ref 6-9

$^1$H-NMR- and GC-spectra of the substituted dioxolanone **4** showed no diastereomeric impurities

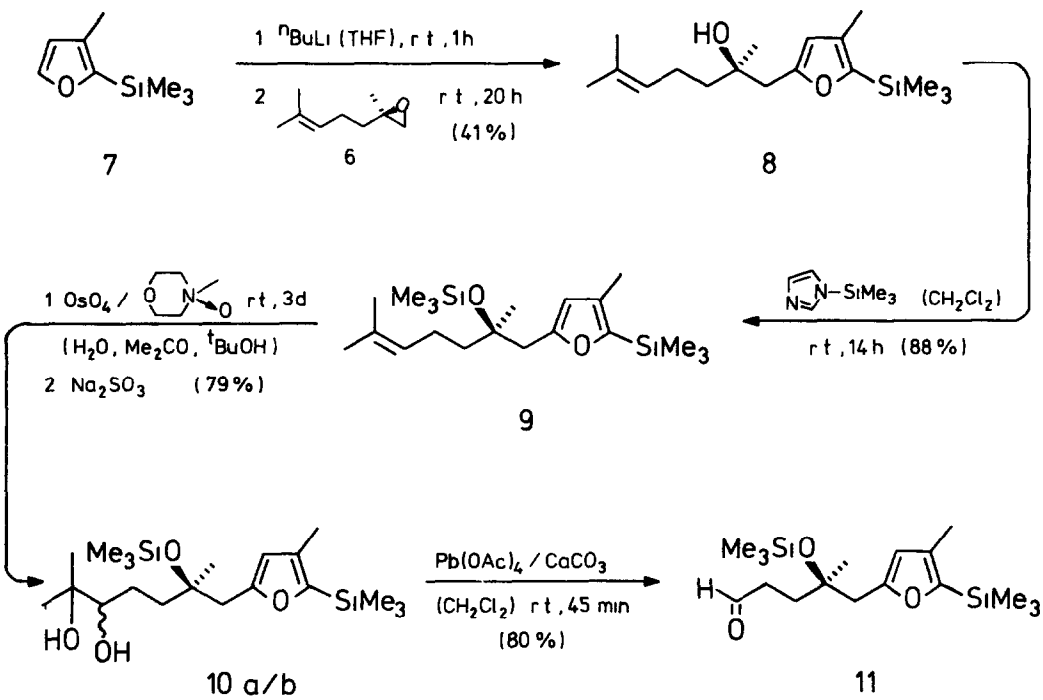
Dioxolanone **4** was reduced to the diol **5** with lithium aluminum hydride in absolute diethyl ether

The ring closure to the oxirane **6** was carried out applying a recently described phase transfer-catalyzed one-pot procedure[10] a solution of the diol **5** in dichloromethane had been vigorously stirred for 15 minutes with benzyltriethylammonium chloride (TEBA) and 50% aqueous sodium hydroxide, before a solution of *p*-toluenesulfonyl chloride (*p*TosCl) in dichloromethane was added




Scheme 1

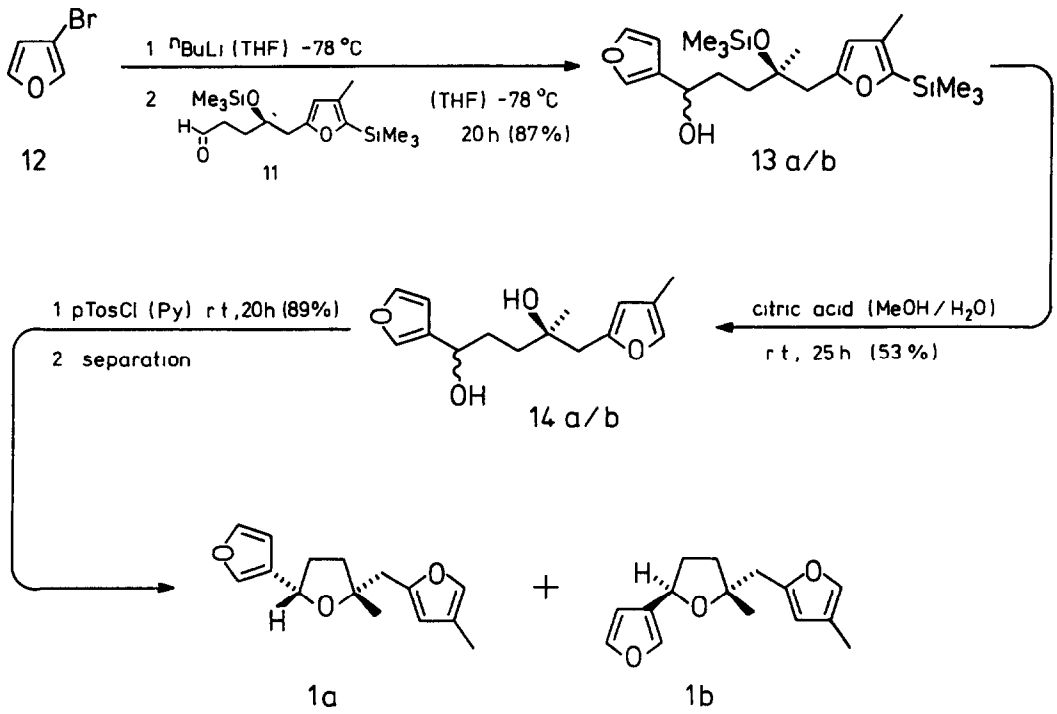
To introduce the 4-methyl-2-furanyl moiety, 3-methyl-2-(trimethylsilyl)furan (**7**) was employed, the preparation of which we reported in this journal[11] (Scheme 2)
**7** was lithiated with *n*-butyllithium in THF and was treated with the oxirane **6** to the alcohol **8**, which had to be protected as trimethylsilyl ether This protection required a stronger silylating reagent than the usually applied system trimethylsilyl chloride/triethylamine N-(Trimethylsilyl)imidazole, which was added to a solution of the dry alcohol **8** in absolute dichloromethane at room temperature, gave the silylether **9** in good yields
An ozonolysis had been intended for the generation of the aldehyde **11**, however the furan moiety was attacked even by one equivalent ozone at −78 °C Thus the double bond had to be cleaved by the known two-step method diolization by catalytic amounts of osmium tetroxide in *t*-butanol, water and acetone as well as N-methylmorpholine-N-oxide afforded the diols **10 a/b** Cleavage of the diols **10 a/b** into aldehyde **11** as the second step did not succeed with sodium periodate in diethyl ether/water, because this system was too acidic and effected partial fission of the trimethylsilyl ether Therefore lead tetraacetate in absolute dichloromethane was used with an excess of calcium carbonate to neutralize the liberated acetic acid[12]




Scheme 2

The 3-furanyl moiety was now introduced by halogen metal exchange[11] of 3-bromofuran with *n*-butyllithium in absolute THF at −78 °C and subsequent coupling with the aldehyde **11** (Scheme 3) The diastereomeric difuran alcohols **13 a/b** were desilylated under mild conditions with citric acid in methanol/water yielding the diols **14 a/b**
The difuran diols **14 a/b** underwent cyclization when treated with *p*-toluenesulfonyl chloride in absolute pyridine

The diastereomers **1a** and **1b** were successfully separated by repeated flash column chromatography
Structure **1a** was assigned to the more polar substance by NOE-measurements irradiation with the $^1$H-NMR frequency of the methyl protons at the tetrahydrofuran ring caused an intensity increase of the doublet-doublet signal of the proton highlighted in the formula, whereas for the less polar substance no change could be observed




Scheme 3

The measurements of the optical rotations yielded

**1a** $[\alpha]_D^{20}$ −1 82° (c = 1 11 , $CHCl_3$)

**1b** $[\alpha]_D^{20}$ +20 9° (c = 2 30, $CHCl_3$)

athanasin $[\alpha]_D^{20}$ −1 93° (c = 1 84 , $CHCl_3$)

From the comparison of the spectroscopic data and optical rotations of the naturally occurring with the synthesized material it is concluded that athanasin has the structure **1a**

## EXPERIMENTAL

*General remarks* Boiling points (b p) are uncorrected air-bath temperatures of the Kugelrohr distillations Spectra were recorded on the following instruments $^1$H-NMR. Bruker WM 400 (400 MHz, $CDCl_3$ as internal standard), MS. Varian MAT 711 and 44 S (EI operating with an ionisation potential of 70 eV, DI direct inlet, HR. high resolution, GC-MS using a semipolar 20 m SE 54 glass capillary column, initial temp 100 °C, rate of heating 25 °C /min) IR Beckman spectrophotometer IR 4230 Optical rotations were determined with a Perkin-Elmer 241 MC polarimeter

All reactions involving lithium derivatives were carried out with dried flasks under nitrogen atmosphere Tetrahydrofuran (THF) and diethyl ether were distilled from potassium benzophenon ketyl Thin layer chromatography was performed on silica gel (Merck Kieselgel 60 $F_{254}$) and aluminum oxide (Merck Aluminiumoxid 60 $F_{254}$ neutral) on aluminum foils with visualization by UV (254 nm) and $KMnO_4$-spray reagent Column chromatography was performed using glass columns packed with aluminum oxide 60 (neutral, 63-200 μm, containing 7% of water) and silica gel 60 (230-400 mesh ASTM i e 40-63 μm)

*(2S-trans)-2-(1,1-Dimethylethyl)-5-methyl-5-(4-methyl-3-pentenyl)-1,3-dioxolan-4-one (4)* 20 ml (32 mmol) *n*-Butyllithium (1 6 M in hexane) is added to a stirred, -78 °C cold solution of 3 4 g (33 6 mmol) diisopropylamine in 200 ml abs THF After 15 min 4 8 g (30 3 mmol) of dioxolanone **2**, dissolved in 20 ml abs THF, is added dropwise After stirring for 30 min at -78 °C, 7 5 g (35 7 mmol) homoprenyliodide (**3**) is added dropwise and the mixture is allowed to warm to room temp (r t) over a period of 20 h The reaction mixture is poured into 200 ml diethyl ether, washed with 20 ml saturated $Na_2S_2O_3$ solution and 100 ml water and dried over $MgSO_4$ The solvent is removed in vacuo Distillation of the residue afforded 5 16 g **4** (71%) **B.p.** 80 °C / 0 075 mmHg $[\alpha]_D^{20}$ +30 2° (c=2 40, $CHCl_3$) **$^1$H-NMR** ($CDCl_3$) δ (ppm) 5 18 (s, 1 H), 5 08 (tr sept, J=7+1 Hz, 1 H), 2 20-2 00 (m, 2 H), 1 82-1 69 (m, 2 H), 1 67 (br s, 3 H) 1 60 (br s, 3 H), 1 44 (s, 3 H), 0 95 (s, 9 H) **GC-MS** m/e 154 (14%), 137 (18%), 111 (52%), 110 (50%), 109 (72%), 69 (100%), 57 (80%) **IR** ($CCl_4$) ν ($cm^{-1}$) 2980s 2940m, 2920m, 2880m, 1805s, 1645m, 1495m, 1390w, 1185s, 1150m, 1090m, 1000m

*(2R)-2,6-Dimethyl-5-heptene-1,2-diol (5)* 2 4 g (10 mmol) **4** in 12 ml abs diethyl ether is added dropwise to a mixture of 0 7 g (18 mmol) lithium aluminum hydride and 120 ml abs diethyl ether under nitrogen at −78 °C The reaction mixture is allowed to warm to r t over a period of 20 h At 0 °C 0 7 ml water, 0 7 ml 15% aqueous NaOH and 2 1 ml water are added The precipitate is filtered and decocted thrice with 300 ml dichloromethane in all The combined organic layers are dried with $MgSO_4$, the solvent is evaporated in vacuo Distillation gives 1 47 g **5** (93%) **B.p.** 82 °C / 0 1 mmHg $[\alpha]_D^{20}$ +1 7° (c=2 76, $CHCl_3$) **$^1$H-NMR** ($CDCl_3$) δ (ppm) 5 11 (tr sept, J=7+1 5 Hz, 1 H), 3 46 (d, J=11 Hz, 1 H), 3 39 (d, J=11 Hz, 1 H), 2 04 (br q, J=7 Hz, 2 H), 1 68 (d, J=1 5 Hz, 3 H), 1 61 (br s, 3 H), 1 54 (ddd, J=14+9+7 Hz, 1 H), 1 48 (ddd, J=14+9+7 Hz, 1 H), 1 17 (s, 3 H) **GC-MS** m/e 140 (14%), 109 (94%), 82 (24%), 75 (14%), 69 (100%), 67 (36%), 57 (24%) **IR** ($CCl_4$) ν ($cm^{-1}$) 3600m,br, 3470m,br, 2990s, 2950s, 2900m, 1620w, 1475m, 1400m, 1135m 1065s

*(2R)-2-Methyl-2-(4-methyl-3-pentenyl)oxirane (6)* The mixture of 400 mg (2 53 mmol) **5**, 21 mg (0 09 mmol) benzyltriethylammonium chloride in 5 ml dichloromethane and 1 3 ml of 50% aqueous NaOH is vigorously stirred at r t for 15 min At 0 °C a solution of 500 mg (2 62 mmol) *p*-toluenesulfonyl chloride in 2 5 ml dichloromethane is added The reaction mixture is allowed to warm up to r t over a period of 2 h The two layers are separated and the organic layer is washed with water, before it is dried with $MgSO_4$ After evaporation distillation afforded 306 mg **6** (86%) **B.p** 80 °C /14 mmHg $[\alpha]_D^{20}$ −7 6° (c=2 33, $CHCl_3$) **$^1$H-NMR** ($CDCl_3$) δ (ppm) 5 08 (tr sept, J=7+1 5 Hz 1 H), 2 62 (d, J=5 Hz, 1 H), 2 57 (d, J=5 Hz, 1 H), 2 07 (br q, J=7 5 Hz, 2 H), 1 68 (d J=1 5 Hz, 3 H) 1 63 (ddd, J=14+8+7 5, 1 H), 1 60 (br s, 3 H) 1 51 (ddd, J=14+9+7 5 Hz 1 H), 1 31 (s 3 H) **GC-MS** m/e 109 (54%), 82 (72%), 69 (64%), 67 (100%), 55 (40%) **IR** ($CCl_4$) ν ($cm^{-1}$) 3060w 3000s, 2960s, 2940s, 2890w, 1640w, 1470s, 1410s, 1400m 1390m, 1130m 1100m, 930w

*(αR)-α,4-Dimethyl-α-(4-methyl-3-pentenyl)-5-(trimethylsilyl)-2-furanethanol (8)*

9 6 ml (15 36 mmol) *n*-Butyllithium in hexane are added dropwise to a stirred solution of 2.20 g (14 26 mmol) **7** in 20 ml abs THF at 0 °C The mixture is stirred at r t. for 1 h, cooled down to 0 °C Then a solution of 2 00 g (14 26 mmol) **6** in 5 ml abs THF is added dropwise After warming up to r t over a period of 20 h, the mixture is poured into 100 ml diethyl ether, washed twice with brine and dried over $MgSO_4$ After evaporation of the solvent, the residue is chromatographed on aluminum oxide [diethyl (*t*-butylmethyl) ether petrolether 40/60 = 2 25(1 ) 9] Educt containing fractions are collected 1 73 g **8** (41%) are obtained $[\alpha]_D^{20}$ −4 2° (c=2 17, $CHCl_3$) **$^1$H-NMR** ($CDCl_3$) δ (ppm) 5 94 (s, 1 H), 5 11 (tr sept, J=7+1 5 Hz, 1 H), 2 78 (d, J=15 Hz, 1 H), 2 74 (d, J=15 Hz, 1 H), 2 09 (br q, J=8 Hz, 2 H), 2 06 (s, 3 H), 1 68 (br s, 3 H), 1 62 (br s, 3 H), 1 49 (ddd, J=14+8+7, 1 H), 1 44 (ddd, J=14+7 5+6 5, 1 H), 1 18 (s, 3 H), 0 26 (s, 9 H) **GC-MS** m/e 168 (72%), 153 (80%), 109 (38%), 75 (42%), 74 (30%), 73 (100%), 69 (70%) **IR** ($CCl_4$) ν ($cm^{-1}$) 3600m, 2970s, 2930m, 2920m, 1610m, 1460m, 1400m, 1390m, 1385m, 1375m, 1260s, 1130m, 995m, 860s

*(2R)-5-[2,6-Dimethyl-2-[(trimethylsilyl)oxy]-5-heptenyl]-3-methyl-2-(trimethylsilyl)furan (9)*

990 mg (7 05 mmol) N-(Trimethylsilyl)imidazole (TMSIM) are added to a solution of 1 73 g (5 87 mmol) of the dry alcohol **8** in 12 ml abs dichloromethane at 0 °C under nitrogen The mixture is allowed to warm up to r t over a period of 14 h After evaporation of the solvent the residue is digested with cold *n*-pentane for several times The combined solvents are evaporated and the residue is chromatographed on aluminum oxide [ petrolether 40/60 ] 1 89 g **9** (88%) are obtained $[\alpha]_D^{20}$ +11 0° (c=2 50, $CHCl_3$) **$^1$H-NMR** ($CDCl_3$) δ (ppm) 5 89 (s, 1 H), 5 10 (tr sept, J=7+1 5 Hz, 1 H), 2 78 (d, J=15 Hz, 1 H), 2 72 (d, J=15 Hz, 1 H), 2 08 (br q, J=8 Hz, 2 H), 2 06 (s, 3 H), 1 68 (br s, 3 H), 1 61 (br s, 3 H), 1 45 (ddd, J=14+9+7 Hz, 1 H), 1 40 (ddd, J=14+9+7 Hz, 1 H), 1 24 (s, 3 H), 0 25 (s, 9 H), 0 09 (s, 9 H) **GC-MS** m/e 199 (46%), 131 (10%), 75 (14%) 73 (36%), 69 (100%) **IR** ($CCl_4$) ν ($cm^{-1}$) 2970s, 2940m, 1605m, 1460m, 1400m, 1385m, 1260s, 1135m, 1060s, 995w, 855s

*(6R)-2,6-Dimethyl-7-[4-methyl-5-(trimethylsilyl)-2-furanyl]-6-[(trimethylsilyl)oxy]-2,3-heptanediol (10 a/b)*

A mixture of 1 83 g (5 mmol) **9** in 5 ml *t*-butanol, 13 mg (51 μmol) osmium tetroxide, dissolved in diethyl ether, 1 17 g (7 6 mmol) N-methylmorpholine-N-oxide, dissolved in 8 ml water and 16 ml acetone, is stirred for 3 d at r t To reduce the osmium derivatives, 280 mg (2 22 mmol) $Na_2SO_3$, dissolved in 2 ml water, is added and the mixture is stirred for 30 min The dark precipitate is filtered over a small column with neutral aluminum oxide washing the residue with acetone After evaporation under reduced pressure the residue is dissolved with water, saturated with NaCl and extracted five times with dichloromethane The organic layers are dried with $MgSO_4$ , and after removal of the solvent the residue is chromatographed on aluminum oxide [diethyl (*t*-butylmethyl) ether petrolether 40/60 = 2 (1 ) 1 ] 1 58 g **10 a/b** (79%) are isolated **$^1$H-NMR** ($CDCl_3$) δ (ppm) 5 89/5 88 (s, 1 H), 3 37-3 30 (m, 1 H), 2 85/2 81 (d, J=14 Hz, 1 H), 2 76 (d, J=14 Hz, 1 H), 2 05 (s, 3 H), 1 76-1 40 (m, 4 H), 1 28/1 26 (s, 3 H), 1 21 (s, 3 H), 1 16 (s, 3 H), 0 25 (s, 9 H), 0 13/0 12 (s, 9 H) **GC-MS** m/e 143 (100%), 125 (34%), 75 (36%), 74 (28%), 73 (100%) **IR** ($CCl_4$) ν ($cm^{-1}$) 3580m, 3430m,br , 2970s, 1610m, 1400m, 1385m, 1260s, 1085m, 1020m, 995w, 855s

*(γR)-γ,4-Dimethyl-5-(trimethylsilyl)-γ-[(trimethylsilyl)oxy]-2-furanpentanal (11)*

3 64 g (8 15 mmol) Lead tetraacetate, dissolved in 50 ml abs dichloromethane, is added dropwise to a stirred mixture of 1 63 g (4 07 mmol) **10 a/b** and 4 62 g (46 mmol) dried calcium carbonate in abs dichloromethane at r t under nitrogen After 45 min the reaction mixture is poured into saturated sodium carbonate (50 ml) The organic layer is separated and the aqueous layer is extracted thrice with dichloromethane The combined organic layers are washed with water and dried over $MgSO_4$ Chromatography on aluminum oxide [diethyl (*t*-butylmethyl) ether petrolether 40/60 = 1(1 ) 2 ] affords 1 11 g **11** (80%) $[\alpha]_D^{20}$ +11 4° (c=1 57, $CHCl_3$) **$^1$H-NMR** ($CDCl_3$) δ (ppm) 9 74 (t, J=2 Hz, 1 H), 5 88 (s, 1 H), 2 81 (d, J=14 Hz, 1 H), 2 74 (d, J=14 Hz, 1 H), 2 54 (dddd, J=15+9+7+2 Hz, 1 H) 2 49 (dddd, J=15+9+7+2 Hz, 1 H) 2 05 (s, 3 H), 1 77 (ddd, J=14+9+7 Hz, 1 H), 1 72 (ddd, J=14+9+7 Hz, 1 H), 1 27 (s, 3 H), 0 24 (s, 9 H), 0 10 (s 9 H) **GC-MS** m/e 174 (16%), 173 (62%), 83 (30%), 75 (36%), 74 (24%), 73 (100%) 55 (16%) **IR** ($CCl_4$) ν ($cm^{-1}$) 2970s, 2900m, 2820w 2730w, 1735s 1610m 1400m, 1385m, 1260s, 1150m, 1070m, 995w, 855s

*(δR)-α-(3-Furanyl)-δ,4-dimethyl-5-(trimethylsilyl)-δ-[(trimethylsilyl)oxy-2-furanpentanol (13 a/b)*

1 5 ml (2 40 mmol) *n*-Butyllithium, 1 6 M in hexane, is added dropwise to a −78 °C cold stirred solution of 330 mg (2 25 mmol) 3-bromofuran (**12**) in 1,5 ml abs THF After 1 h at −78 °C 511 mg (1 50 mmol) aldehyde **11** , dissolved in 1 5 ml abs THF, is added dropwise After 20 h at −78 °C, the reaction mixture is quenched with brine and diluted with diethyl ether The layers are separated and the aqueous is extracted with diethyl ether twice It is dried over $MgSO_4$ Chromatography on aluminum oxide [diethyl (*t*-butylmethyl) ether petrolether 40/60 = 1 (1) 3 ] affords 533 mg **13 a/b** (87%) **$^1$H-NMR** ($CDCl_3$) δ (ppm) 7 37 (br s, 2 H), 6 39 (m, 1 H), 5 88/5 87 (s, 1 H), 4 63 (m, 1 H), 2 83/2 82 (d, J=14 5 Hz, 1 H), 2 76/2 74 (d, J=14 5 Hz, 1 H), 2 05 (s, 3 H), 1 89 (m, 2 H), 1 60-1 35 (m, 2 H), 1 27/1 25 (s, 3 H), 0 25 (s, 9 H), 0 12/0 10 (s, 9 H). **GC-MS** m/e 223 (6%), 152 (10%), 151 (62%), 133 (6%), 105 (6%) 75 (28%), 74 (24%), 73 (100%) **IR** ($CCl_4$) ν ($cm^{-1}$) 3620m, 3430w,br , 2960s, 2940m, 2910m, 2880m, 1605m, 1510m, 1400m, 1385m, 1260s, 1175m, 1135m, 1070s, 995m, 890s, 860s

*(4R)-1-(3-Furanyl)-4-methyl-5-(4-methyl-2-furanyl)-1,4-pentanediol (14 a/b)*

20 ml Of a solution of 50 ml abs methanol, 10 ml water and 500 mg citric acid are stirred together with 340 mg (0 83 mmol) **13 a/b** at r t during 25 h Brine is added, and the aqueous layer is extracted five times with diethyl ether The combined organic layers are washed with saturated $NaHCO_3$ solution and brine and dried over $MgSO_4$ Evaporation of the solvent under reduced pressure gives 116 mg **14 a/b** (53%) **$^1$H-NMR** ($CDCl_3$) δ (ppm) 7 38 (br s, 2 H), 7 10 (br s, 1 H), 6 40 (br s, 1 H), 5 97 (s, 1 H), 4 67/4 65 (tr, J=6 5 Hz, 1 H), 2 78/2 77 (d, J=15 Hz, 1 H), 2 72 (d, J=15 Hz, 1 H), 1 99 (s, 3 H), 1 94-1 83 (m, 2 H), 1 65 (ddd, J=15+8+7 Hz, 1 H), 1 52 (ddd, J=15+9+7 Hz, 1 H), 1 19/1 18 (s, 3 H) **GC-MS** m/e 151 (78%), 109 (26%), 108 (28%), 97 (26%), 96 (100%), 95 (88%), 81 (30%), 79 (28%), 77 (22%), 67 (28%), 65 (18%) **IR** ($CCl_4$) ν ($cm^{-1}$) 3600m, 3420m,br , 2970m, 2960m, 2940s, 1620m, 1550m, 1505m, 1395m, 1385m, 1375m, 1175s, 1130s, 1040m, 985w, 965w, 890s

*(2R-trans)-2,3,4,5-Tetrahydro-5-methyl-5-[(4-methyl-2-furanyl)methyl]-2,3'-bifuran (1 b) and (2S-cis)-2,3,4,5-Tetrahydro-5-methyl-5-[(4-methyl-2-furanyl)methyl]-2,3'-bifuran (athanasin) (1 a)*

968 mg (5 08 mmol) *p*-Toluenesulfonyl chloride in 2 ml abs pyridine are added to a solution of 337 mg (1 27 mmol) **14 a/b** in 3 ml abs pyridine The resulting mixture is stirred at r t for 20 h Brine is added , the mixture is stirred for 10 min and then extracted four times with petrolether 40/60 The combined extracts are washed twice with 1 M hydrochloric acid, once with saturated $NaHCO_3$ solution and brine Evaporation of the solvent and chromatography on aluminum oxide [diethyl (*t*-butylmethyl) ether petrolether 40/60 = 2 (1) 4 ] afford 278 mg **1 a/b** (89%) 100 mg of **1 a/b** were separated on flash silica gel (10 g) under slight pressure (1 drop/2 s ) Fractions containing both diastereomers are collected and repeatedly separated [ diethyl ether petrolether 40/60 = 1 30 ] NOE measurements showed that the more polar substance eluating second has structure **1 a** Its spectroscopic data are in accord with those of "Athanasin" **1 a** $[\alpha]_D^{20}$ −1 82° (c=1 11 , $CHCl_3$), [-1 93° (c=1 84 , $CHCl_3$) for "Athanasin" ] **$^1$H-NMR** ($CDCl_3$) δ (ppm) 7 37 (m, 2 H), 7 09 (m, 1 H), 6 33 (m, 1 H), 5 96 (s, 1 H), 4 93 (dd, J=8+6 Hz, 1 H), 2 85 (d, J=15 Hz, 1 H), 2 80 (d, J=15 Hz, 1 H), 2 22-2 09 (m, 2 H), 2 00 (d, J=1 Hz, 3 H), 1 81-1 69 (m, 2 H), 1 29 (s, 3 H) **HR-MS** found 246 125595, calculated for $C_{15}H_{18}O_3$ 246 125595 **GC-MS** m/e 246 (2%), 152 (10%), 151 (100%), 109 (12%), 95 (20%) **IR** ($CCl_4$) ν ($cm^{-1}$) 2980s, 2940s, 2880m, 2870m, 1505m, 1465w,br , 1390m, 1180s, 1140m, 1100m, 1045s, 975w, 945m, 890s **1 b** $[\alpha]_D^{20}$ +20 9° (c=2 30 , $CHCl_3$) **$^1$H-NMR** ($CDCl_3$) δ (ppm) 7 37 (m, 2 H), 7 09 (m, 1 H), 6 37 (m, 1 H), 5 98 (s, 1 H), 4 86 (dd, J=8+6 Hz, 1 H), 2 86 (d, J=15 Hz, 1 H), 2 80 (d, J=15 Hz, 1 H), 2 19-2 11 (m, 1 H), 2 11-2 02 (m, 1 H), 2 00 (d, J=1 Hz, 3 H), 1 97-1 87 (m, 1 H), 1 82-1 75 (m, 1 H), 1 31 (s, 3 H) **HR-MS** found 246 125595 calculated for $C_{15}H_{18}O_3$ 246.125595 **GC-MS** m/e 246 (2%), 152 (10%), 151 (100%), 109 (12%), 95 (20%) **IR** ($CCl_4$) ν ($cm^{-1}$) 2980s, 2940s, 2890m, 2870m, 1510m, 1465m, br , 1390m, 1270m, 1180s, 1140m, 1105m, 1060m, 1050m, 970w, 940m, 895s

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