Pergamon

Tetrahedron, Vol. 53, No. 2, pp. 659-672, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(96)00998-2

Stereoselective synthesis of five and/or six membered ring hydroxylactones obtained by Lewis acid mediated reaction of γ,δ-epoxy-β-hydroxyesters; access to 5-methylated 2-deoxysugars.

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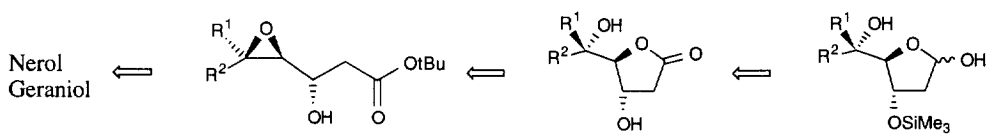
Keywords: optically active γ,δ-epoxy-β-hydroxyesters, lactonisation, furanosides.

Abstract: A stereoselective route to six and/or five membered ring lactones from optically active γ,δ-epoxy-β-hydroxyesters obtained from nerol and geraniol has been developed. The intramolecular cyclization by epoxide ring opening occurred via activation of 6-endo over the usually favoured 5-exo, and the application of this technology to the stereocontrolled synthesis of 5-methylated 2-deoxysugars was achieved. Copyright © 1996 Elsevier Science Ltd

Monoterpenes are often used as starting materials for the synthesis of biologically active molecules such as polyethers ionophores,[1] pheromones[2] and cytotoxic compounds.[3] On the other hand, stereochemically defined substituted γ-butyro-lactones have played a key role in the synthesis of many types of natural products serving as a frame for alkaloids,[4] macrocyclic antibiotics,[5] lignan lactones,[6] pheromones,[7] flavour components,[8] etc.

In connection with a program directed towards the total synthesis of modified deoxysugars[9] and deoxynucleosides, nerol and geraniol were considered as judicious starting materials for the introduction of substituents at C-5'. Oligonucleoside chains including C-5' methylated nucleosides are resistant to nuclease hydrolysis at this modified position.[10] Therefore, the modified 2'-deoxysugars are immediate precursors to nucleoside analogues with potential antiviral activity.[11]



$R^1 = CH_3$ and $R^2 = (CH_2)_2CHC(CH_3)_2$ for nerol
$R^1 = (CH_2)_2CHC(CH_3)_2$ and $R^2 = CH_3$ for geraniol

RESULTS AND DISCUSSION

We have recently shown[12,13] that the stereocontrolled addition of the lithium enolate of *tert*-butylacetate to optically active α,β-epoxyaldehydes leads to γ,δ-epoxy β-hydroxyesters with three defined contiguous chiral carbons. γ,δ-Epoxy-β-hydroxyesters **4**, **5** are obtained in three steps starting from nerol and geraniol (Scheme 1). The synthesis of the diastereoisomers *anti* has been optimised to >99/<1 for **4a/5a** and 94/6 for **4b/5b**. The γ,δ-epoxy β-hydroxyesters **4a**, **4b** can be protected in high yield as their silyl ethers **6a**, **6b** and **7b**.

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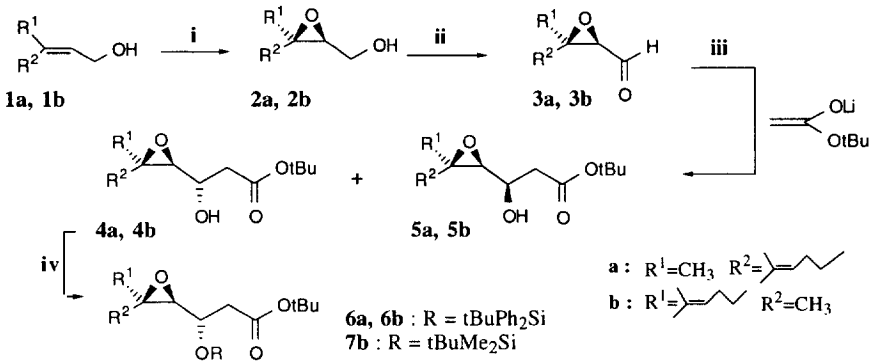
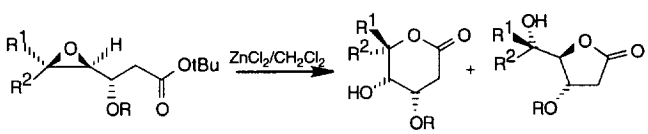


i) CH_2Cl_2, 4 Å molecular sieves, tBuOOH, (+) DET, $Ti(OiPr)_4$, -20°C, 90%, ee 60% (**2a**), 80% (**2b**); ii) CH_2Cl_2, DMSO, Et_3N (5 eq), SO_3-pyridine (5 eq), 90%; iii) Et_2O, LDA, CH_3CO_2tBu, -78°C, or -78°C to +25°C, 80%; iv) DMF, imidazole, $tBuPh_2SiCl$ or $tBuMe_2SiCl$, 90%.

Scheme 1

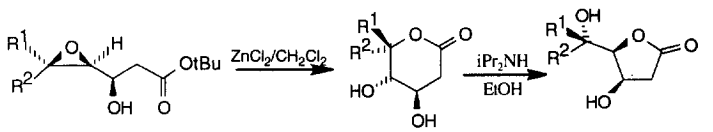


R	R^1	R^2			
H	CH_3		**4a**	**8a**	**9a**
H		CH_3	**4b**	**8b**	**9b**
$tBuPh_2Si$	CH_3		**6a**	**10'a**	**10a**
$tBuPh_2Si$		CH_3	**6b**	**10'b**	**10b**
$tBuMe_2Si$		CH_3	**7b**	**(11'b)**	**11b**

Scheme 2

Compounds **4a** and **4b** were allowed to react with anhydrous $ZnCl_2$ (4 eq) in anhydrous methylene chloride. In 20 minutes a complete reaction occurred with the appearance of two new products, the major products **8a** and **8b** moving slower than the minor ones **9a**, **9b**. The composition of the reaction mixture was calculated from the peak integration of the protons in the ^1H NMR spectra, the ratio being 95/5 in favour of the valerolactones **8a** and **8b**. The major product **8a** starting from **4a** could be crystallised in cold EtOH or Et_2O (yield 75%). HPLC chromatographic separation of the mixture **8b/9b** gave the 6-membered lactone **8b** and the minor product **9b** in a different ratio than the one observed by ^1H NMR (the ratio of isolated compounds depends on the chromatographic column size). This difference led us to suspect the influence of an acidic medium on the formation of the butyrolactones. This idea was further confirmed by action of silica gel or TFA (entries 5 and 6, table 1). The conversion of the six membered rings (**8a, 8b**) into the five membered lactones **9a**, **9b** can also be observed when the reaction medium is treated with acid (entry 6) or with a base such as iPr_2NH (entry 7). In these cases, we can obtain the butyrolactone **9a** as the sole product of

the reaction. Interestingly, when the starting materials are the 3-O-silylated epoxyesters **6a, 6b** and **7b**, no valerolactones can be isolated, but the reaction leads to the butyrolactones **10a, 10b** and **11b** (entries 8, 9, 10). Removal of the silyl protective group of compounds **10a, 10b** and **11b** provides the lactones **9a** and **9b**. This is evidence that these compounds are formed through the opening of the epoxide ring at C-5 even if the corresponding six membered ring lactones **10'a, 10'b, 11'b** are not observed. The silylation of the epoxyester C-3 hydroxyl is the preferred choice to obtain selectively butyrolactones in one pot with high yields.



$R^1 = CH_3$ $R^2 =$ **5a** **12a** **13a**

$R^1 =$ $R^2 = CH_3$ **5b** **12b** **13b**

Scheme 3

The $ZnCl_2$ lactonisation of the minor adducts **5a** and **5b** (entries 2, 4) gives only the six membered rings **12a, 12b**. Their conversion into the corresponding five membered rings **13a, 13b** was achieved by allowing **12a, 12b** to react with diisopropylamine in ethanol. With these two examples, the lactonisations were conducted on the racemic epoxyesters **5a** and **5b**, although the equation above shows only one enantiomer.

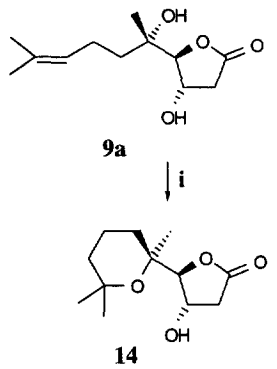
Table 1. Reaction conditions, yields and 6/5 ring ratio lactones obtained from γ,δ-epoxy-β-hydroxyesters.

entry	epoxyester	conditions	lactone	yield %
	N°	$ZnCl_2$, CH_2Cl_2	**6- /5- ring** : ratio	
1	**4a**	20 min	**8a/9a** : >95/<5	100*
2	**5a**	20 min	**12a/13a** :>99/<1	>90*
3	**4b**	20 min	**8b/9b** : >95/<5	100*
4	**5b**	20 min	**12b/13b** :>99/<1	>90*
5	**4a**	20 min then silica gel	**8a/9a** : 40/60	60
6	**4a**	20 min then TFA 2h	**8a/9a** : 0/100	80
7	**4a**	20 min then iPr_2NH 4h	**8a/9a** : 0/100	70
8	**6a**	4h	**10'a/10a** : 0/100	98
9	**6b**	4h	**10'b/10b** : 0/100	95
10	**7b**	4h	**11'b/11b** : 0/100	97

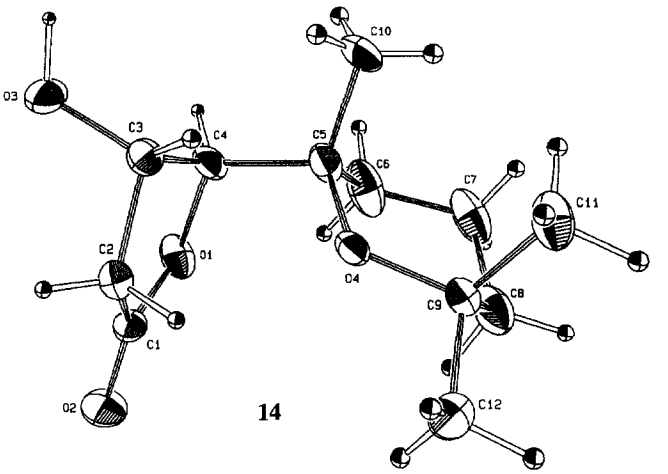
* : Yields according to ^1H NMR spectra of the crude products.

The stereochemistry of the lactonisation reaction has been established by the synthesis of compound **14** which was obtained from **9a** as shown in Scheme 4.

The X-ray crystallographic analysis[14] of **14** proved its structure, and showed that only the absolute configuration at C-5 was inverted relative to its precursor γ,δ-epoxy-β-hydroxyester **4a**.



i) CH_2Cl_2, TFA, 40°C, 2h, 84%

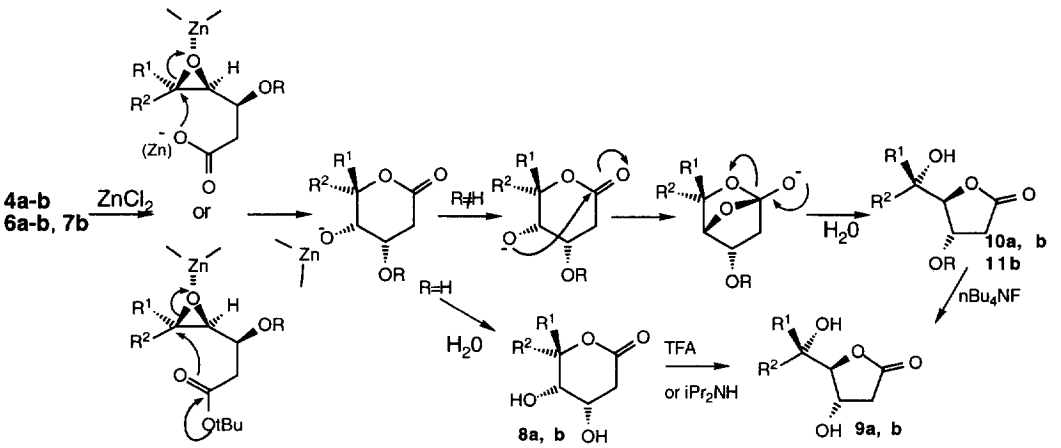


Scheme 4

The mechanism of transformation of epoxyesters (**4a-b**, **6a-b**, **7b**) is outlined below (Scheme 5). Addition of zinc salts[15] or acid (camphorsulfonic acid: CSA)[16,17] to the tert-butylester is known to produce elimination of 2-methylpropene, leading to the *in situ* formation of the carboxylate anion, so that the epoxide ring can be opened either by the carboxylate, or by the ester carbonyl as already reported,[18] by attack on the C-5 carbon of the epoxide leading to the 6-ring lactones **8a**, **8b**. This cyclization reaction (6-endo type) appears to be stereospecific and concerted with epoxide ring opening and configuration inversion at the attacked carbon, since no other diastereoisomers were detectable. Whereas valerolactones **8a**, **8b** (R = H) can be isolated after aqueous work-up, the five membered ring lactones **10a**, **b**, **11b** (R ≠ H) are obtained in the same experimental conditions. The conversion of six membered lactones **10'a,b**, **11'b** (not isolated) to the five membered ring lactones **10a,b**, **11b** is postulated to occur in anhydrous conditions ($ZnCl_2/CH_2Cl_2$), without the participation of an external nucleophile since water does not induce the conversion of the valerolactones when they are present in the medium. Even if the participation of an open form cannot be completely excluded,[18d] it is likely that an intramolecular attack of the carbonyl by the alcoholate would better explain the formation of the butyrolactones, with configuration retention at all the asymmetric centers. The valerolactones **8a**, **8b** (R = H) are probably more stabilised than **10'a,b**, **11'b** (R ≠ H) which might be due to intramolecular hydrogen bonding between the C-3 hydroxyl and the C-4 oxygen. Cyclization of **5a**, **b** proceeds by a similar mechanism.

Ring formation through closure of acyclic precursors is a fundamental and common process. Baldwin[19] has extensively studied these types of reactions and established a set of rules allowing the prediction of the relative ease of various ring closure reactions. According to these rules, and taking into account the tetrahedral geometry of the carbon atom involved in the initial ring closure reaction (carbon

epoxide), we should obtain preferentially the 5-ring lactone by direct intramolecular attack on the C-4 carbon atom (5-exo ring closure) of compounds **4a**, **4b**. The compounds thus obtained would be the diastereoisomers **13a**, **13b** of **9a**, **9b** respectively.



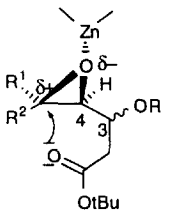
Scheme 5

It is unlikely that the generally more stable 5-ring lactones were formed first and then isomerised to the corresponding **8a**, **8b** (no such evolution was seen during monitoring of the reaction) giving a (**8/9**) 95/5 mixture under our experimental conditions. The regioselectivity of the epoxide ring opening has also been unambiguously established by X-ray crystallographic analysis of the lactone **14**, bearing a tetrahydropyranyl moiety (Scheme 4) and it too favours epoxide ring opening at C-5 (6-endo ring closure) according to the absolute configuration of compound **14** at C-5.

Systematic studies concerning the intramolecular opening of epoxide ring by a primary alcohol as nucleophile for O-heterocycle synthesis[20c] revealed that the regioselectivity of this stereocontrolled reaction is driven by substituent effects. According to these results, reaction regioselectivity can be predicted in agreement with Baldwin's rules and stereoelectronic effects induced by electron rich (or poor) substituents on the epoxide ring. In literature reports[20] the presence, or absence, of the methyl substituent at C-5 did not significantly change the site of the nucleophilic attack. However, as these data were obtained for the specific case of epoxy alcohol cyclization under acidic conditions (catalytic amount of CSA), the regioselectivity of the epoxide ring opening may vary with changes in the reaction conditions, such as with Lewis acid, or basic conditions, as already observed by Nicolaou.[20a] In addition the nucleophilicity difference between primary hydroxyl and carbonyl can also be taken into account to explaining the differences observed with our results (exclusive 6-endo ring closure).

The results obtained are in better agreement with iodolactonisation.[21a] According to Chamberlin,[21b, 22] regioselective ring closure during the iodolactonisation reactions of 4-alkenoic acid derivatives is governed by preferential intramolecular attack of the nucleophile to the more highly substituted carbon atom of the

double bond when the cyclization does not exclusively lead to γ-lactones (5-exo). As the epoxide ring may be considered stereochemically analogous to the iodonium ion (π-complex) intermediate in the iodolactonisation process, the 6-ring lactones **8a**, **8b** are preferentially obtained. In our case the 6-endo ring closure proceeded to produce lactones **8a** (**8b**), via a transition state in which the developing electron-deficient orbital at carbon C-5 of the reacting epoxyester would be stabilised by electron donation from the adjacent methyl substituent (Scheme 6).



$R^1 = CH_3$ and $R^2 = (CH_2)_2CHC(CH_3)_2$
$R^1 = (CH_2)_2CHC(CH_3)_2$ and $R^2 = CH_3$

Scheme 6

The interconversion between the 6-ring and 5-ring lactones has been studied,[23] especially in the case of aldonolactones. In a recent report, Han *et al.*[24] described numerous examples of γ- and δ-lactones, isomerising under strongly acidic media, suggesting that these products are formed through an acid intermediate. In our case, isomerization is occurring under weakly acidic, basic, and especially neutral protic media, such as in methanol.

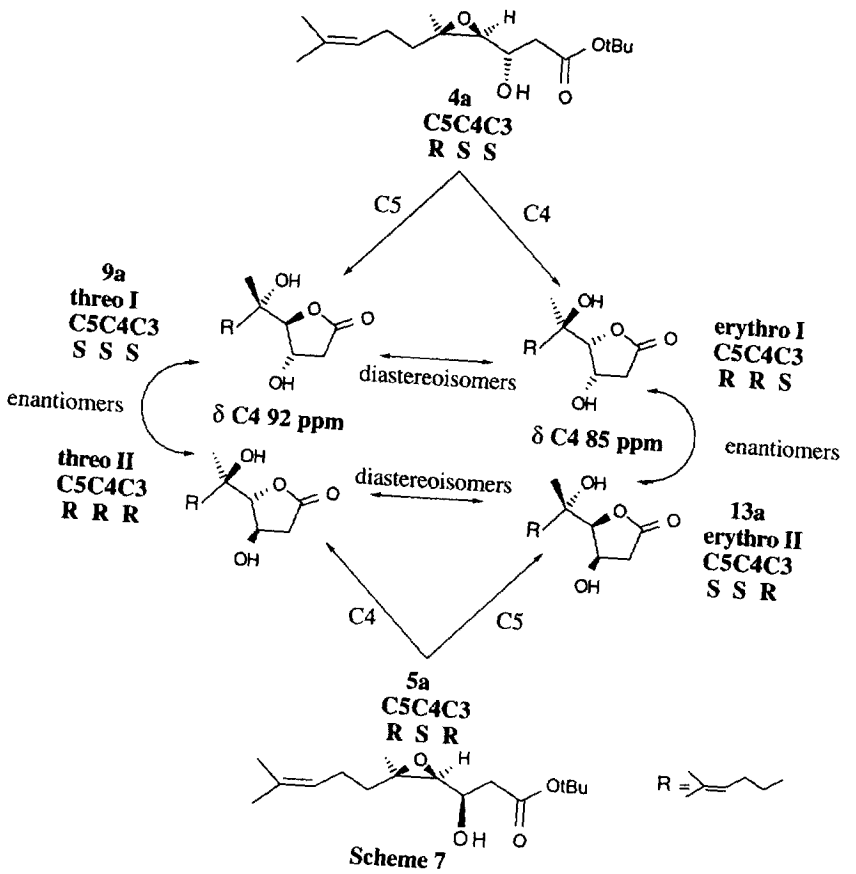
It is noteworthy that ^{13}C NMR data can be used to assign the epoxide ring site of opening during the lactonisation process and then the stereochemistry of the reaction. According to the relative configuration of C-3 and C-4 and since the epoxide ring opening can only occur at C-4 or C-5, only two kinds of butyrolactones *threo* and *erythro* can be synthesized starting from epoxyesters *anti* and *syn* (Scheme 7).

The C-4 chemical shift of the *threo* lactone is downfield to 92 ppm, while the *erythro* one is upfield to 85 ppm (Scheme 7). It must be understood that the C-5 opening of the epoxide ring gives a δ-valerolactone that convert to the γ-butyrolactone as already shown (Schemes 2, 3 and Fig 1).

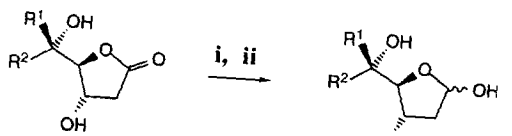
Each epoxyester reported in this publication, through opening at C-5, gives selectively one γ-butyrolactone having a valerolactone as precursor (Schemes 2, 3). For such epoxyesters with an epoxide ring unsymmetrically substituted, the 5-exo ring closure (C4 epoxide ring opening by an attack on the less substituted epoxide ring carbon) does not occur in our experimental conditions.

Other ^{13}C NMR reports[25] showed, that the *threo* γ-butyrolactone C-4 chemical shift is downfield to ≈ 85 ppm) while the *erythro* one is upfield to ≈ 82 ppm, in good agreement with our results. The ^{13}C NMR chemical shift of C-4 can be a helpful way to reveal the regioselectivity of the reaction and to determine the absolute configurations at both C-4 and C-5 of a given butyrolactone.

Finally the butyrolactones **9a**, **9b** were converted into the 3-O-silylated deoxysugars **15a**, **15b** (α/β: 1/1) in 48-65% overall yield (Scheme 8) by reduction of the carbonyl with DIBAH at low temperature.



Scheme 7



i) THF, Et_3N (8 eq), Me_3SiCl (6 eq), 100%;
ii) toluene, DIBAH (2.1 eq), -78°C, 48%-65%.

Scheme 8

No isomerization of the five membered ring lactol into the six membered ring one, as reported in the literature,[24,26,27] was observed. This can be explained in terms of the weak nucleophilicity of the C-5 tertiary hydroxyl function.

We have shown that modified 2-deoxysugars can be obtained in six steps from nerol or geraniol. These sugars have a structural analogy with 2-deoxy-L-ribose, the constituent of DNA. Since stereochemistry at C-5 can be controlled, they can be precursors for the elaboration of 5' substitued 2'-deoxynucleosides.

EXPERIMENTAL

Commercially available reagents were used as supplied. All solvents were distilled prior to use. THF was freshly distilled over sodium before use. $ZnCl_2$ was dried at 150 °C under 0,1 torr pressure for 2 h. Diisopropylamine is distilled and packed over KOH. HPLC chromatography was carried out on a Jobin-Yvon apparatus using Merck 15 µm or Amicon silica (6-35 µm). Infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer. ^1H, ^{13}C NMR spectra were recorded using Bruker AC 250 instrument with TMS as internal reference. Mass spectra were obtained on a Nermag R10-10 mass spectrometer. Optical rotations were measured on a Perkin Elmer 141 polarimeter. Abbreviations used, PE: petroleum ether, EA: ethyl acetate.

General procedure for silylation. To a solution of epoxyester in anhydrous DMF (4 ml/mmol) at r.t. under a nitrogen atmosphere, were added 3 eq of imidazole and 1.5 eq of tert-butyldiphenylchlorosilane or tert-butyldimethylchlorosilane. The mixture was stirred overnight at r.t., quenched with a saturated solution of NH_4Cl (1 ml/mmol) and diluted with Et_2O (8 ml/mmol). The organic layer is washed three times with water (2 ml/mmol) once with brine, dried over $MgSO_4$ and concentrated to leave a residue which was purified on a silicagel column eluted with petroleum ether/ether (PE/Et_2O): 9/1.

Compound 6a. (3R,4R,5S)-9,5-(dimethyl)-3-(tert-butyldiphenylsilyloxy)-4,5-epoxydec-8-enoate tert-butyl. Performed with 3.4 g (12.1 mmol) of **4a**, 5.7 g (11.0 mmol) of **6a** were obtained (Rf = 0.27), 91% yield. IR (film) ν cm^{-1}: 3052-2935 (C-H); 1733 (C=O); 1158-1111 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.72-7.40 (m, 10H, phenyl); 4.75 (t, hept, 1H, J = 7, 1 Hz, =C<u>H</u>-CH_2); 4.03 (td, 1H, J = 8.1, 5.8 Hz, C<u>H</u>OSiPh_2tBu-CH_2CO_2tBu); 2.85 (d, 1H, J = 8.1 Hz, CepMe-Cep<u>H</u>-CHOSiPh_2tBu); 2.60 (d, 2H, J = 5.8 Hz, CH_2CO_2tBu); 1.77 (m, 2H, =CH-C<u>H</u>$_2$); 1.62-1.44 (3s, 15H, OtBu, <u>Me</u>$_2$C=CH); 1.02 (s, 9H, SitBu); 0.98 (s, 3H, CepMe-CepH); 0.81 (m, 2H, =CH-CH_2-C<u>H</u>$_2$). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 170.0, 135.9, 135.9, 129.8, 129.8, 127.9, 127.6, 133.8, 133.2, 131.4, 123.8, 80.5, 67.6, 66.9, 62.4, 42.3, 31.6, 23.4, 28.1, 26.8, 25.6, 17.6, 21.2, 19.3. $[\alpha]_D^{25}$= - 2.5° (c = 1.1, $CHCl_3$).

Compound 6b. (3S,4S,5R)-5,9-(dimethyl)-3-(tert-butyldiphenylsilyloxy)-4,5-epoxydec-8-enoate tert-butyl. Performed with 1.0 g (3.5 mmol) of **4b**, 1.7 g (3.3 mmol) of **6b** were obtained (Rf = 0.33), 93% yield. IR (film) ν cm^{-1}: 3052-2934 (C-H); 1732 (C=O); 1157-1111 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.72-7.39 (m, 10H, phenyl); 4.98 (t, hept, 1H, =C<u>H</u>-CH_2); 4.01 (td, 1H, J = 8; 5.5 Hz, C<u>H</u>OSiPh_2tBu-CH_2CO_2tBu); 2.93 (d, 1H, J = 8 Hz, CepMe-Cep<u>H</u>-CHOSiPh_2tBu); 2.59 (d, 2H, J = 5.5 Hz, CH_2CO_2tBu); 1.84 (m, 2H, =CH-C<u>H</u>$_2$); 1.65-1.54 (2s, 6H, <u>Me</u>$_2$C=CH); 1.43 (s, 9H, OtBu); 1.21 (m, 2H, =CH-CH_2-C<u>H</u>$_2$); 1.03 (s, 9H, SitBu); 0.62 (s, 3H, CepMe-CepH). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 170.0, 136.0, 135.9, 129.7, 127.7, 127.7, 133.7, 133.3, 131.8, 123.7, 80.4, 67.8, 64.9, 62.6, 42.2, 37.6, 23.2, 28.2, 26.6, 25.7, 17.7, 16.2. $[\alpha]_D^{25}$= - 36.8° (c = 1.4, $CHCl_3$). Analysis (calculated/found): %C 73.52 (73.81), %H 8.87 (8.99).

Compound 7b. (3S,4S,5R)-5,9-(dimethyl)-3-(tert-butyldimethylsilyloxy)-4,5-epoxydec-8-enoate tert-butyl. Performed with 2.0 g (8.8 mmol) of **4b**, 3.1 g (7.9 mmol) of **7b** were obtained (Rf = 0.23 eluting with PE/Et_2O: 9.5/0.5), 90% yield. IR (film) ν cm^{-1}: 2933 (C-H); 1732 (C=O); 1090 (C-O). ^1H NMR (250 MHz,

$CDCl_3$) δ ppm: 5.08 (t, hept, 1H, J = 7, 1.5 Hz, =C<u>H</u>); 3.99 (ddd, 1H, J = 8, 8, 4 Hz, CepH-C<u>H</u>OSiMe$_2$tBu-CH$_2$); 2.74 (d, 1H, J = 8 Hz, CepMe-Cep<u>H</u>); 2.55 and 2.47 (ddd, 2H, J = 15.5; 8; 4 Hz, C<u>H</u>$_2$-CO$_2$tBu); 2.06 (q, 2H, J = 8 Hz, =CH-C<u>H</u>$_2$); 1.67 and 1.59 (2s, 6H, <u>Me</u>$_2$C=CH); 1.54 (m, 2H, =CH-CH$_2$-C<u>H</u>$_2$); 1.45 (s, 9H, OtBu); 1.34 (s, 3H, Cep<u>Me</u>-CepH); 0.87 (s, 9H, SitBu); 0.07 (s, 6H, SiMe$_2$). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 170.5, 132.1, 123.6, 80.5, 66.8, 65.2, 62.2, 42.0, 38.3, 25.7, 28.2, 25.7, 18.0, 17.6, 17.0, -4.4 , -4.6, $[\alpha]_D^{25}$= - 21.6° (c = 1.3, $CHCl_3$).

General procedure for lactones synthesis. To a stirred solution of epoxyester in anhydrous CH_2Cl_2 (15 ml/mmol) at r.t. under nitrogen atmosphere, is added 4 eq of dry $ZnCl_2$. When the reaction is completed (20 min for **4a**, **4b** and 4h for **6a**, **6b**, **7b**), the quenching is made by adding a saturated solution of $NaHCO_3$, followed by extraction with CH_2Cl_2, dried over $MgSO_4$ and concentrated to give the crude product.

Compound 8a. (3S, 4S, 5S)-6-[4'-methyl-pent-3'-enyl]-6-methyl-4,5-dihydroxy-2-oxo-1-oxacyclohexane. Starting from 2.0 g (7.0 mmol) of **4a**, the crude product (>95% **8a**, <5% **9a**) is diluted in Et_2O, cooled at - 20 °C then gave 1.2 g (5.3 mmol) of pure crystalline **8a** and a filtrate containing 0.38 g (1.7 mmol) of a mixture **8a** and **9a**. IR (KBr) ν cm^{-1}: 3453-3358 (O-H), 2975 (C-H), 1700 (C=O). ^{1}H NMR (250 MHz, CD_3OD) δ ppm: 5.15 (t, hept, 1H, J = 7; 1 Hz, CH=); 4.26 (ddd, 1H, J = 7; 10; 2.6 Hz, CHOH-C<u>H</u>OH-CH$_2$); 3.74 (d, 1H, J = 2.6 Hz, C<u>H</u>OH-CHOH-CH$_2$); 2.73-2.61 (ddd, 2H, J = 18, 10, 7 Hz, CHOH-C<u>H</u>$_2$-CO); 2.10 (m, 2H, =CH-C<u>H</u>$_2$-CH$_2$); 1.89-1.80 (m, 2H, =CH-CH$_2$-C<u>H</u>$_2$); 1.75 and 1.69 (2s, 6H, <u>Me</u>$_2$C=CH); 1.35 (s, 3H, (O)C<u>Me</u>-CHOH-CHOH). ^{13}C NMR (63 MHz, CD_3OD) δ ppm: 173.2, 132.9, 125.0, 87.2, 71.4, 65.0, 38.8, 34.8, 25.9, 24.3, 23.1, 17.8. $[\alpha]_D^{25}$= - 2,3° (c = 1,4, CH_3CN) ee > 99%, $[\alpha]_D^{25}$= - 1.2° (c = 1.3, CH_3CN) ee = 60%. Analysis (calculated/found): %C 63.14 (62.29), %H 8.83 (8.90).

Compound 8b. (3S, 4S, 5R)-6-[4'-methyl-pent-3'-enyl]-6-methyl-4,5-dihydroxy-2-oxo-1-oxacyclohexane. Lactonisation is performed with 0.5 g (1.8 mmol) of **4b**, to give 0.43 g of crude product containing 97% of **8b**. HPLC purification on silica gel eluting with PE/EA: 2/8 afforded 0.2 g (0.9 mmol) of a mixture **8b** + **9b** and 0.11 g (0.5 mmol) of **8b** (TLC, Rf_{8b} = 0.24, Rf_{9b} = 0.33) **8b** 27% yield, overall yield 78%. IR (film) ν cm^{-1}: 3430 (O-H), 2929 (C-H), 1706 (C=O), 1087 (C-O). ^{1}H NMR (250 MHz, CD_3OD) δ ppm: 5.10 (t hept, 1H, J = 7; 1 Hz, CH=); 4.24 (ddd, 1H, J = 9.5; 6.8; 2.6 Hz, CHOH-C<u>H</u>OH-CH$_2$); 3.75 (d, 1H, J = 2.6 Hz, C<u>H</u>OH-CHOH-CH$_2$); 2.73-2.60 (ddd, 2H, J = 18; 9.5; 6.8 Hz, CHOH-C<u>H</u>$_2$-CO); 2.10 (m, 2H, J = 7 Hz, =CH-C<u>H</u>$_2$-CH$_2$); 1.68 and 1.62 (2s, 6H, <u>Me</u>$_2$C=CH); 1.63-1.59 (m, 2H, =CH-CH$_2$-C<u>H</u>$_2$); 1.43 (s, 3H, (O)C<u>Me</u>-CHOH-CHOH). ^{13}C NMR (63 MHz, CD_3OD) δ ppm: 173.2, 133.3, 124.5, 87.7, 71.4, 65.2, 41.2, 34.9, 25.9, 23.5, 22.3, 17.7.

Procedure for 9a and 9b. After the epoxyester (**4a** or **4b**) disappeared (20 mn), 4 eq of iPr_2NH are added to the reaction medium which 3 h later is filtrated through a pad of silica gel, concentrated and purified by HPLC on silica gel.

Compound 9a. (4S,5S,1'S)-5-[1',5'(dimethyl)-1'-hydroxyhex-4-enyl]-4-hydroxy-2-oxo-1-oxacyclopentane. 2.5 g (8.8 mmol) of **4a** gave 1.6 g (6.8 mmol) of **9a**, 78% yield (eluant PE/EA: 2/8, Rf = 0.33). IR ($CHCl_3$) ν cm^{-1}: 3498 (OH), 3039-2978-2935 (C-H), 1781 (C=O), 1182 (C-O). ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm: 5.10 (t hept, 1H, J = 7.3; 1.5 Hz, =CH); 4.65 (m, 1H, C<u>H</u>O-CHOH-CH$_2$); 4.19 (d, 1H, J = 3.3 Hz, C<u>H</u>O-CHOH-CH$_2$); 2.94 and 2.51 (ddd, 2H, J = 18.5; 7.5; 4 Hz, CH$_2$CO); 2.76 (d, 1H, J = 4.5 Hz, CHO<u>H</u>-CH$_2$); 2.10 (m, 2H, =CH-C<u>H</u>$_2$-CH$_2$); 1.80 (s, 1H, CH$_2$-CMeO<u>H</u>-CHO); 1.68 and 1.61 (2s, 6H, <u>Me</u>$_2$C=CH); 1.65-1.50 (m, 2H, =CH-CH$_2$-C<u>H</u>$_2$); 1.27 (s, 3H, HOCMe-CHO-CHOH). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 176.1, 132.5, 123.5, 92.1, 73.0, 67.8, 38.8, 38.6, 25.7, 22.4, 22.0, 17.7. $[\alpha]_D^{25}$= +17° (c = 0.9 $CHCl_3$). MS

(DCI/NH_3): 246 (M+18, 100%), 229 (M+1, 8.9%). Analysis (calculated/found): %C 63.14 (63.14), %H 8.83 (8.87).

Compound 9b. (4S,5S,1'R)-5-[1',5'(dimethyl)-1'-hydroxyhex-4-enyl]-4-hydroxy-2-oxo-1-oxacyclopentane. 2.3 g (8.1 mmol) of **4b** gave 1.4 g (6.1 mmol) of **9b**, 75% yield (eluant PE/EA: 2/8, Rf = 0.33). IR (KBr) ν cm^{-1}: 3375 (O-H), 2974-2933 (O-H), 1784 (C=O), 1625 (C=C). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 5.10 (t hept, 1H, J = 7.3; 1.5 Hz, =CH); 4.62 (m, 1H, C<u>H</u>O-CHOH-CH_2); 4.17 (d, 1H, J = 3.2 Hz, C<u>H</u>O-CHOH-CH_2); 3.06 (d, 1H, J = 4.6 Hz, CHO<u>H</u>-CH_2); 2.91 and 2.51 (ddd, 2H, J = 18.2; 7.5; 3 Hz, CH_2CO); 2.40 (s, 1H, CH_2-CMeO<u>H</u>-CHO); 2.08 (m, 2H, =CH-C<u>H_2</u>-CH_2); 1.68 and 1.61 (2s, 6H, <u>Me_2</u>C=CH); 1.57 (m, 2H, =CH-CH_2-C<u>H_2</u>); 1.25 (s, 3H, HOCMe-CHO-CHOH). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 178.2, 132.7, 123.6, 92.3, 73.2, 67.6, 38.5, 38.1, 25.7, 22.6, 22.0, 17.7. $[\alpha]_D^{25}$ = -8° (c = 1.6 $CHCl_3$). Analysis (calculated/found): %C 63.14 (62.91), %H 8.83 (8.80).

Procedure for 3-ether silyloxy lactones synthesis 10a, 10b, 11b. To a stirred solution of γ,δ-epoxy-β-silyloxydimethyl or diphenyl tert-butyl ester in anhydrous CH_2Cl_2 under N_2 atmosphere is added 4 eq of dry $ZnCl_2$. The reaction is complete after 4 h, then the usual work up with a saturated solution of $NaHCO_3$ is applied to afford the crude product. The purification was performed on silica gel eluting with PE/EA: 8/2.

Compound 10a. (4R,5R,1'R)-5-[1',5'-(dimethyl)-1'-hydroxyhex-4-enyl]-(tert-butyldimethyl-silyloxy)-2-oxo-1-oxacyclopentane.
Starting from 3.0 g (5.8 mmol) of compound **6a**, after purification (TLC, Rf = 0.26), 2.6 g (5.6 mmol) of **10a** as colourless oil were obtained, 98% yield. IR (film) ν cm^{-1}: 3457 (O-H), 3073-2964 (C-H), 1782 (C=O), 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.65-7.42 (m, 10H, phenyl); 5.05 (t hept, 1H, J = 7; 1 Hz, =CH); 4.56 (ddd, 1H, J = 6.5; 2; 1.5 Hz, OCH-C<u>H</u>OSiPh_2tBu-CH_2); 4.23 (d, 1H, J = 1.5 Hz, OC<u>H</u>-CHOSiPh_2tBu-CH_2); 2.69-2.40 (ddd, 2H, J = 18; 6.5; 2 Hz, CHOSiPh_2tBu-C<u>H_2</u>-CO); 1.95 (m, 2H, =CH-C<u>H_2</u>); 1.67 and 1.60 (2s, 6H, <u>Me_2</u>C=CH); 1.52 (m, 2H, =CH-CH_2-C<u>H_2</u>); 1.06 (s, 9H, tBu); 0.80 (s, 3H, CH_2-COH<u>Me</u>-COH). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 176.3, 135.9, 135.8, 130.2, 128.0, 128.0, 132.8, 132.8, 132.5, 123.5, 92.7, 73.2, 70.0, 39.1, 38.8-22.5, 26.8, 25.7, 17.7, 21.7, 19.1. $[\alpha]_D^{25}$ = + 0.62° (c = 1.1, $CHCl_3$).

Compound 10b. (4S,5R,1'R)-5-[1',5'-(dimethyl)-1'-hydroxyhex-4-enyl]-(tert-butyldiphenyl-silyloxy)-2-oxo-1-oxacyclopentane. Starting from 1.0 g (1.9 mmol) of compound **6b**, after purification (TLC, Rf = 0.21), 0.87 g (1.8 mmol) of **10b** as colourless oil were obtained, 97% yield. IR (film) ν cm^{-1}: 3465 (O-H), 3052-2935 (C-H), 1783 (C=O), 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 7.66-7.46 (m, 10H, phenyl); 4.93 (m, 1H, =CH); 4.56 (ddd, 1H, J = 6.5; 1.5; 1.5 Hz, OCH-C<u>H</u>OSiPh_2tBu-CH_2); 4.22 (d, 1H, J = 1.5 Hz, OC<u>H</u>-CHOSiPh_2tBu-CH_2); 2.65-2.39 (ddd, 2H, J = 18; 6.5; 1.5 Hz, CHOSiPh_2tBu-C<u>H_2</u>-CO); 1.91 (m, 2H, =CH-C<u>H_2</u>); 1.69 and 1.56 (2s, 6H, <u>Me_2</u>C=CH); 1.60 (m, 2H, =CH-CH_2-C<u>H_2</u>)1.16 (s, 3H, CH_2-COH<u>Me</u>-COH); 1.05 (s, 9H, tBu). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 176.2; 135.9, 135.8, 130.2, 128.0, 127.9, 132.9, 132.7, 132.2, 123.7, 93.5, 73.1, 69.7, 39.0, 37.0, 21.9, 26.8, 25.7, 17.7, 22.7, 19.1. $[\alpha]_D^{25}$ = - 7.8° (c = 1.1, $CHCl_3$).

Compound 11b. (4S,5R,1'R)-5-[1',5'-(dimethyl)-1'-hydroxyhex-4-enyl]-(tert-butyldimethyl-silyloxy)-2-oxo-1-oxacyclopentane. Starting from 1.5 g (3.8 mmol) of compound **7b**, after purification (TLC, Rf = 0.22), 1.2 g (3.5 mmol) of **11b** as colourless oil were obtained, 92% yield. IR (film), ν cm^{-1}: 3463 (O-H), 2934-2860 (C-H), 1783 (C=O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 5.09 (t hept, 1H, J = 7; 1.4 Hz, =CH); 4.58 (ddd, 1H, J = 7.2; 3.5; 2.9 Hz, OCH-C<u>H</u>OSiMe_2tBu-CH_2); 4.15 (d, 1H, J = 2.9 Hz, OC<u>H</u>-CHOSiPh_2tBu-CH_2); 2.86-2.39 (ddd, 2H, J = 17.9; 7.2; 3.5 Hz, CHOSiPh_2tBu-C<u>H_2</u>-CO); 2.11 (m, 2H, =CH-C<u>H_2</u>); 1.68 and 1.61 (2s, 6H, <u>Me_2</u>C=CH); 1.56 (m, 2H, =CH-CH_2-C<u>H_2</u>); 1.27 (s, 3H, CH_2-COH<u>Me</u>-COH); 0.08 and 0.07 (2s, 6H,

SiMe2tBu). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 175.8, 132.5, 123.6, 93.1, 73.0, 68.2, 39.3, 37.5, 25.7, 23.2-17.8, 25.6, 17.7, -4.4, -4.9. $[\alpha]_D^{25}$= + 17.9° (c = 1.4, $CHCl_3$). SM (DCI/NH_3): 360 (M+18, 100%), 343 (M+1, 2.69%).

General procedure for removal of the silyl group of lactones 10a, 10b and 11b.
Lactone, in anhydrous THF (2 ml/mmol), at room temperature, is treated with 1.5 eq of nBu4NF, after completion of the reaction (tlc control), THF is removed under reduced pressure. The purification was performed on silica gel eluting with the appropriate solvent (see experimental for **9a** and **9b**). Deprotected lactones **9a** and **9b** are obtained in nearly quantitative yield.

Procedure for 12a, 12b, 13a, 13b synthesis. Same general procedure as previously describe for lactone synthesis. The reaction is quenched after 20 min. A NMR spectrum of the crude products (**12a, 12b**) is recorded, then the crude product is dissolved in EtOH, two equivalents of iPr_2NH are added and the resulting solution is stirred overnight at r.t. This conversion can also be run by adding 2 eq of TFA in CH_2Cl_2 and stirring two hours at room temperature. The five membered rings **13a, 13b** are purified on silica gel.
12a-13a. Starting from 0.60 g (2.11 mmol) of a racemic mixture of **5a**, the $ZnCl_2$ lactonisation gave a crude product containing >99% of **12a** which is converted into **13a** with 79% overall yield (0.38 g, 1.66 mmol) after purification on silica gel eluant EP/AE: 2/8 (TLC, Rf_{12a} = 0.38, Rf_{13a} = 0.42).

Compound 12a. 6-[4'-methyl-pent-3'-enyl]-6-methyl-4,5-dihydroxy-2-oxo-1-oxacyclohexane
IR (film), ν cm^{-1}: 3443 (O-H), 2977-2929 (C-H), 1705 (C=O), 1143 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 5.04 (t hept, 1H, J = 7; 1.3 Hz, =CH-CH_2-CH_2), 4.06 (m, 1H, J = 7.3; 8.6 Hz, CHOH-CHOH-CH_2), 3.53 (m, 3H, CHOH-CHOH-CH_2), 3.07 (dd, 1H, J = 18.3; 7.3 Hz, CHOH-CH_2-CO(O)), 2.63 (dd, 1H, J = 18.3; 8.6 Hz, CHOH-CH_2-CO(O)), 2.10-1.47 (m, 2H, H_7), 1.83 (m, 2H, =CH-CH_2-CH_2), 1.66-1.59-1.46 (3s, 9H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 169.9, 132.6, 122.3, 84.5, 77.1, 65.7, 37.6, 35.4, 25.7, 24.1, 21.5, 17.7.

Compound 13a. 5-[1',5'(dimethyl)-1'-hydroxyhex-4-enyl]-4-hydroxy-2-oxo-1-oxacyclopentane.
IR (film), ν cm^{-1}: 3572-3429 (O-H), 3025-2936 (C-H), 1783 (C=O), 1150 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 5.31 (d, 1H, J = 3.4 Hz, CHOH-CH_2-CO(O)), 5.08 (t hept, 1H, J = 7; 1.4 Hz, =CH-CH_2-CH_2), 4.70 (dddd, 1H, J = 4.1; 1.3 Hz, J = 3.4; 3.4 Hz, CHOH-CH_2-CO(O)), 4.10 (d, 1H, J = 3.4 Hz, CH(O)-CHOH-CH_2), 3.24 (s, 1H, $CH_2(CH_3)$OH-CH(O)-CHOH), 2.69 (dd, 1H, J = 17.5; 4.1 Hz, CHOH-CH_2-CO(O)), 2.63 (dd, 1H, J = 17.5; 1.3 Hz, CHOH-CH_2-CO(O)), 2.03 (m, 2H, =CH-CH_2-CH_2), 1.70 (m, 2H, =CH-CH_2-CH_2), 1.67, 1.60 and 1.38 (3s, 9H, Me). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 176.3, 132.5, 123.3, 84.6, 74.3, 69.7, 40.6, 40.2, 25.7, 22.1, 21.1, 17.7.

12b-13b. Starting from 0.40 g (1.41 mmol) of a racemic mixture of **5b**, the $ZnCl_2$ lactonisation gave a crude product containing > 99% of **12b** which is converted into **13b** with 65% overall yield (0.21 g, 0.91 mmol) after purification on silica gel eluant EP/AE: 5/5 (TLC, Rf_{12b} = 0.14, Rf_{13b} = 0.28).

Compound 12b. 6-[4'-methyl-pent-3'-enyl]-6-methyl-4,5-dihydroxy-2-oxo-1-oxacyclohexane
IR (film), ν cm^{-1}: 3439 (O-H), 2976-2928 (C-H), 1728 (C=O), 1157 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 5.06 (m, 1H, =CH-CH_2-CH_2), 4.08 (m, 1H, J = 7; 9.3 Hz, CHOH-CHOH-CH_2-CO(O)), 3.61 (d, 1H, J = 9.4 Hz, CHOH-CHOH-CH_2-CO(O)), 3.52 (m, 1H, OH), 3.07 (dd, 1H, J = 18.2; 7 Hz, CHOH-CH_2-CO(O)), 2.52 (dd, 1H, J = 18.2; 9.3 Hz, CHOH-CH_2-CO(O)), 2.07 (m, 2H, =CH-CH_2-CH_2), 1.74 (m, 2H, =CH-CH_2-

CH_2), 1.66-1.60-1.30 (3s, 9H, Me). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 169.9, 132.6, 123.3, 84.2, 73.9, 65.9, 39.2, 37.8, 25.8, 21.5, 21.4, 17.8.

Compound 13b. 5-[1',5'(dimethyl)-1'-hydroxyhex-4-enyl]-4-hydroxy-2-oxo-1-oxacyclopentane.
IR (film), ν cm^{-1}: 3579-3432 (O-H), 2979-2939 (C-H), 1777 (C=O), 1147 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 5.24 (s, 1H, OH), 5.12 (t hept, 1H, J = 7.1; 1.4 Hz, =CH-CH_2-CH_2), 4.69 (m, 1H, CHOH-CHOH-CH_2-CO(O)), 4.09 (d, 1H, J = 3.4 Hz, CHOH-CHOH-CH_2-CO(O)), 3.34 (m, 1H, OH), 2.70 (dd, 1H, J = 17.5; 4.2 Hz, CHOH-CH_2-CO(O)), 2.63 (dd, 1H, J = 17.5; 1.2 Hz, CHOH-CH_2-CO(O)), 2.12 (m, 2H, =CH-CH_2-CH_2), 1.78-1.66 (m, 2H, =CH-CH_2-CH_2), 1.69-1.61-1.40 (3s, 9H, Me). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 176.4, 132.6, 123.4, 85.8, 74.2, 69.5, 40.2, 37.1, 25.8, 24.5, 21.8, 17.8.

Compound 14 . (4S, 5S, 1'S)-5-[1',3',3'-trimethyl-2'-0xacyclohexane]-3-hydroxy-2-oxo-1-oxacyclopentane.
To a stirred solution of 0.10 g (0.44 mmol) of lactone **9** in 6.6 ml of anhydrous CH_2Cl_2 under N_2 atmosphere, 2 ml of freshly distilled TFA is added and then the reaction media is heated to refluxing (45 °C). The reaction is complete in 3h, the volatile components are evaporated under reduced pressure, then the residue is purified on silica gel eluting with PE/EA: 5/5 (TLC, Rf = 0.32). 0.084 g (0.37 mmol) of **14** were obtained, 84% yield.
IR ($CHCl_3$), ν cm^{-1}: 3614-3046 (O-H), 2978-2943 (C-H), 1780 (C=O), 1179 (C-O), ^1H NMR (250 MHz, $CDCl_3$) δ ppm: 4.62 (m, 1H, CHOH-CH_2-CO); 3.97 (d, 1H, J = 2.5 Hz, OCH-CHOH-CH_2); 2.91-2.38 (ddd, 2H, J = 18; 7.0, 3.1 Hz, CHOH-CH_2-CO); 2.55 (d, 1H, J = 4 Hz, OH); 1.75-1.69, 1.30 (m, 6H, CH_2-CH_2-CH_2); 1.32, 1.20 and 1.09 (3s, 9H, Me). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 178.2, 93.2, 74.0, 72.3, 68.4, 38.7, 35.9, 28.9, 15.4, 32.4, 27.2, 23.2. $[\alpha]_D^{25}$= - 1.2° (c =1.3, $CHCl_3$). SM (DCI/NH_3): 246 (M+18, 100%), 229 (M+1, 8.97%), 228 (M, 2.95%), 127 (ether cycle, 4.29%). Analyse (calculated/found): %C 63.14 (63.28), %H 8.83 (8.86), mp = 123 °C.

Deoxyfuranosides preparation, general procedure. To a magnetically stirred solution of lactone in anhydrous freshly distilled THF (7 ml/mmol) under N_2 atmosphere, were successively added 8 eq of Et_3N and 6 eq of freshly distilled Me_3SiCl. The reaction is allowed to react at r.t. overnight and then quenched by adding 5 ml of a saturated solution of NH_4Cl. The aqueous layer is extracted 3 times with 20 ml of Et_2O. The combination of the organic phases is washed twice with brine, dried with $MgSO_4$ and the solvents evaporated to afford quantitatively the product of silylation, which was dissolved in anhydrous toluene (2 ml/mmol) cooled to -78 °C and then treated dropwise with 2.1 eq of DIBAH. The reaction is quenched by the addifion dropwise of 5 ml of a saturated solution of NH_4Cl. The aqueous layer is extracted twice with 15 ml of Et_2O. The combined organic solutions is washed twice with brine and dried with $MgSO_4$. After concentration under reduce pressure, the furanosides are purified by HPLC on silica gel eluting with PE/EA: 6/4.

Compound 15a. (4S,5S,1'S)-5-[1',5'(dimethyl)-1'-hydroxyhex-4-enyl]-4-trimethylsilyloxy-2-hydroxy-1-oxa -cyclopentane. Starting from 0.50 g (2.2 mmol) of compound **9a**, after purification (TLC, Rf = 0.49), 0.43 g (1.4 mmol) of **13a** were obtained as a mixture of furanosides anomers (α/β: 1/1), 65% yield. IR (film), ν cm^{-1}: 3392 (O-H), 2960 (C-H), 1110 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: Anomer α: 5.56 (dt, 1H, J = 5.5; 1.7 Hz, CH_2-CHOH-(O)); 5.10 (m, 1H, =CH); 4.38 (dt, 1H, J = 5.7; 2 Hz, OCH-CHOSiMe_3-CH_2); 3.99 (d, 1H, J = 2 Hz, OCH-CHOSiMe_3-CH_2); 3.93 (d, 1H, J = 5.5 Hz, CH_2-CHOH-O); 2.05 (m, 4H, =CH-CH_2-CH_2, CH_2-CHOH-(O)); 1.67-1.61 (2s, 6H, Me_2C=CH); 1.53 (m, 2H, =CH-CH_2-CH_2); 1.17 (s, 3H, CH_2-CMeOH); 0.12 (s, 9H, $SiMe_3$). Anomer β: 5.47 (dd, 1H, J = 10.2; 4.7 Hz, CH_2-CHOH-(O)); 5.10 (m, 1H, =CH); 4.06 (td, 1H, J = 6.5; 4.3 Hz, OCH-CHOSiMe_3-CH_2); 3.89 (d, 1H, J = 4.3 Hz, OCH-CHOSiMe_3-CH_2); 3.87 (d, 1H, J = 10.2 Hz, CH_2-CHOH-O); 2.05 (m, 4H, =CH-CH_2-CH_2, CH_2-CHOH-(O)); 1.67 and 1.61 (2s, 6H, Me_2C=CH); 1.50 (m, 2H, =CH-CH_2-CH_2); 1.18 (s, 3H, CH_2-CMeOH); 0.15 (s, 9H, $SiMe_3$). ^{13}C NMR: (63

MHz, $CDCl_3$) δ ppm: 131.8, 131.6, 124.4, 124.1, 99.5, 98.3, 91.4, 91.6, 72.8, 72.4, 72.3, 71.2, 44.4, 43.2, 40.3, 39.5, 25.7, 17.7, 22.8, 22.5, 22.2, 21.7, 0.19, 0.09.

Compound 15b. (4S,5S,1'R)-5-[1',5'(dimethyl)-1'-hydroxyhex-4-enyl]-4-trimethylsilyloxy-2-hydroxy-1-oxa -cyclopentane. Starting from 0.48 g (2.1 mmol) of compound **9b**, after purification (TLC, Rf = 0.41), 0.31 g (1.0 mmol) of **13b** were obtained as a mixture of furanosides anomers (α/β: 1/1), 48% yield. IR (film), ν cm^{-1}: 3392 (O-H), 2963 (C-H), 1117 (C-O). ^1H NMR (250 MHz, $CDCl_3$) δ ppm: Anomer α: 5.54 (m, 1H, CH_2-CHOH-(O)); 5.10 (t hept, 1H, J = 7; 1.5 Hz, =CH); 4.39 (dt, 1H, J = 5.5; 1.8 Hz, OCH-CHOSiMe_3-CH_2); 4.10 (m, 1H, CH_2-CHOH-O); 4.00 (d, 1H, J = 1.8 Hz, OCH-CHOSiMe_3-CH_2); 2.08 (m, 4H, =CH-CH_2-CH_2, CH_2-CHOH-(O)); 1.68-1.58 (2s, 6H, Me_2C=CH); 1.49 (m, 2H, =CH-CH_2-CH_2); 1.17 (s, 3H, CH_2-CMeOH); 0.11 (s, 9H, SiMe_3). Anomer β: 5.46 (dd, 1H, J = 10.3; 4.5 Hz, CH_2-CHOH-(O)); 5.10 (t hept, 1H, J = 7; 1.5 Hz, =CH); 4.61 (dd, 1H, J = 6.5; 4.5 Hz, OCH-CHOSiMe_3-CH_2); 3.91 (d, 1H, J = 10.3 Hz, OH); 3.78 (d, 1H, J = 4.5 Hz, OCH-CHOSiMe_3-CH_2); 2.06 (m, 4H, =CH-CH_2-CH_2, CH_2-CHOH-(O)); 1.68 (s, 6H, Me_2C=CH); 1.49 (m, 2H, =CH-CH_2-CH_2); 1.21 (s, 3H, CH_2-CMeOH); 0.14 (s, 9H, SiMe_3). ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm: 132.1, 131.8, 124.3, 124.1, 99.4, 98.1, 72.1, 70.8, 92.3, 92.3, 73.0, 72.5, 44.4, 43.2, 38.1, 37.7, 25.7, 24.3, 23.3, 17.8, 22.5, 22.1, 0.16, 0.06.

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Acknowledgement: The authors thank Dr. Victor E. Marquez at NIH/NCI Laboratory of Medicinal Chemistry for his helpful advices and critics, Dr. J. Jaud at the centre d'élaboration des materiaux et d'études structurales for X-ray data determination. We also thank the CNRS and the French MRES for financial support.

(*Received in Belgium* 23 *July* 1996; *accepted* 25 *October* 1996)