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Acyclic 1,2-/1,3-Mixed Pentols. Synthesis and General Trends in Bichromophoric Exciton Coupled Circular Dichroic Spectra

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Abstract: The synthesis of all eight configurational isomers of acyclic 1,2,3,4,6-pentols belonging to the 2*R* enantiomeric series is described. The 1-anthroyl-2,3,4,6-*p*-methoxycinnamates of these pentols give rise to unique exciton coupled circular dichroic spectra in the range of 220-380 nm. Comparisons with the CD of corresponding bichromophoric derivatives of the lower homologous tetrols, 1-anthroyl-2,3,4-*p*-methoxycinnamates led to a predictable general trend in which only minor differences result from 1,3-*syn* extensions whereas major differences result from 1,3-*anti* extensions.

INTRODUCTION

There exists no general microgram scale method for determining the absolute and relative configurations of acyclic 1,2-polyols, 1,3-polyols (skipped polyols) and mixed 1,2-/1,3-mixed polyols. These moieties exist as such in a large number of natural products, e.g., hopanoids, or in numerous antibiotics, particularly the polyene microlides; in the antibiotics, the polyol moieties can be isolated by a combination of hydrolysis, ozonolysis, periodate oxidation, etc. We have recently been developing bichromophoric exciton coupled circular dichroic methods[1,2] for microscale configurational assignments of different types of acyclic 1,2- and 1,3-polyols and aminopolyols containing terminal primary hydroxyl or amino groups. In this bichromophoric method, two selectively introduced chromophores couple to give rise to "fingerprint" CD curve, which can be reproduced by summation of all interacting basis set pairs; this pairwise additivity principle was first fully demonstrated with glycopyranoside derivatives.[2,3] In the case of 1,2-acyclic polyols derived from sugars, the terminal hydroxyl and remaining hydroxyls groups are derivatized as anthroates and *p*-methoxycinnamates, respectively,[4] to give a CD library of triols, tetrols and pentols.[5] The method was further extended to aminobacteriohopanes which carry acyclic side-chain moieties consisting of aminotetrols and pentols.[6] The bichromophoric approach has also been extended, together with a CD library, to 1,3-polyols with a terminal 1,2-diol group, i.e., 1,2,4-triols, 1,2,4,6-tetrols and 1,2,4,6,8-pentols.[7] Both in 1,2-polyol and 1,3-polyols, a general trend is seen which makes it possible to predict the CD of unknown cases; this is particularly facile with the skipped polyols.

Two general reiterative NMR and/or CD methods for 1,3-polyol absolute configurational assignments that can be extended to longer systems[8,9] including a difference CD approach[10] has been described. An NMR

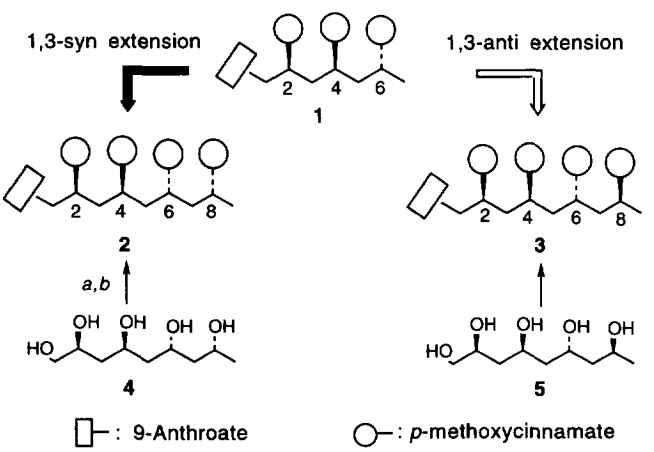
method for relative configurational assignments of 1,3-polyols has also been described.[11] However, they depend on multistep transformations not suited for microscale manipulations, or have limited applicabilities.

None of the methods, including the coupled CD methods described above, are applicable to mixed 1,2-/1,3-polyol systems which have been found recently in new hopanoids;[12] furthermore, these moieties exist in masked forms in polyene macrolides, e.g., primycin,[13] myxovirescin,[14] octacomycin,[15] pentamycin.[16] In order to facilitate microscale structural studies of such compounds, we describe the synthesis and CD of mixed polyols, which is followed by an application.[12]

RESULTS AND DISCUSSION

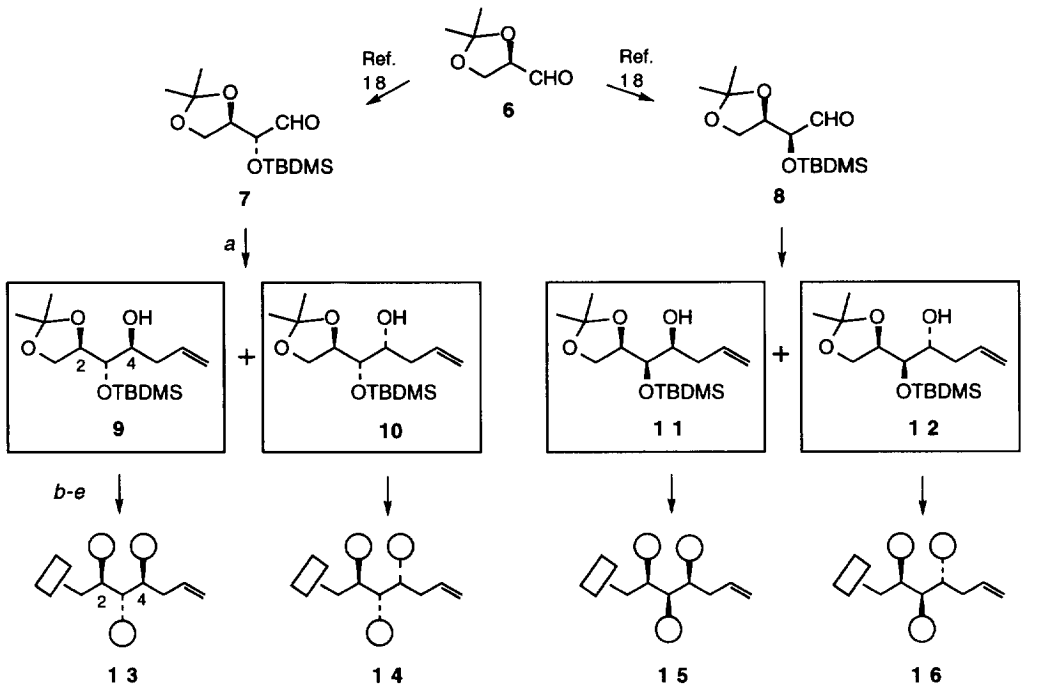
Synthesis of ω-Monoanthroate Per-p-methoxycinnamates

Skipped pentol peracylates 2 and 3. These were prepared from corresponding acyclic pentols **4** and **5**,[7b] respectively (**Scheme 1**).



Scheme 1. a) 9-anthroyl tetrazole, DBU, MeCN, 8 h, 50%;
b) *p*-methoxycinnamoyl imidazole, DBU, MeCN, 4 h, 88%.

Allylic tetrol peracylates 13-16. Propanal acetonide **6** (**Scheme 2**), obtained from (D)-mannitol,[17] was diastereoselectively converted into 3α and 3β alcohols **7** and **8** by the procedure developed by Dondoni.[18] Acetonides **7** and **8**, upon treatment with allylmagnesium bromide gave diastereomeric pairs **9/10** and **11/12**, respectively, each pair of which was separated by repeated silica gel chromatography using 10-11% ether/hexane mixture as eluate. Since pairs **9/10** and **11/12** could not be differentiated by NMR, the stereochemistry was determined from the CD data (**Figure 3**, see later on in the text). Diastereomers **9-12** were converted into the corresponding bichromophoric derivatives **13-16** (**Scheme 2**) by desilylation, acetonide cleavage, anthroylation of primary hydroxyl with 9-anthroyltetrazole and percinnamoylation of the three secondary hydroxyls with *p*-methoxycinnamoylimidazole. The assignment of absolute configuration was



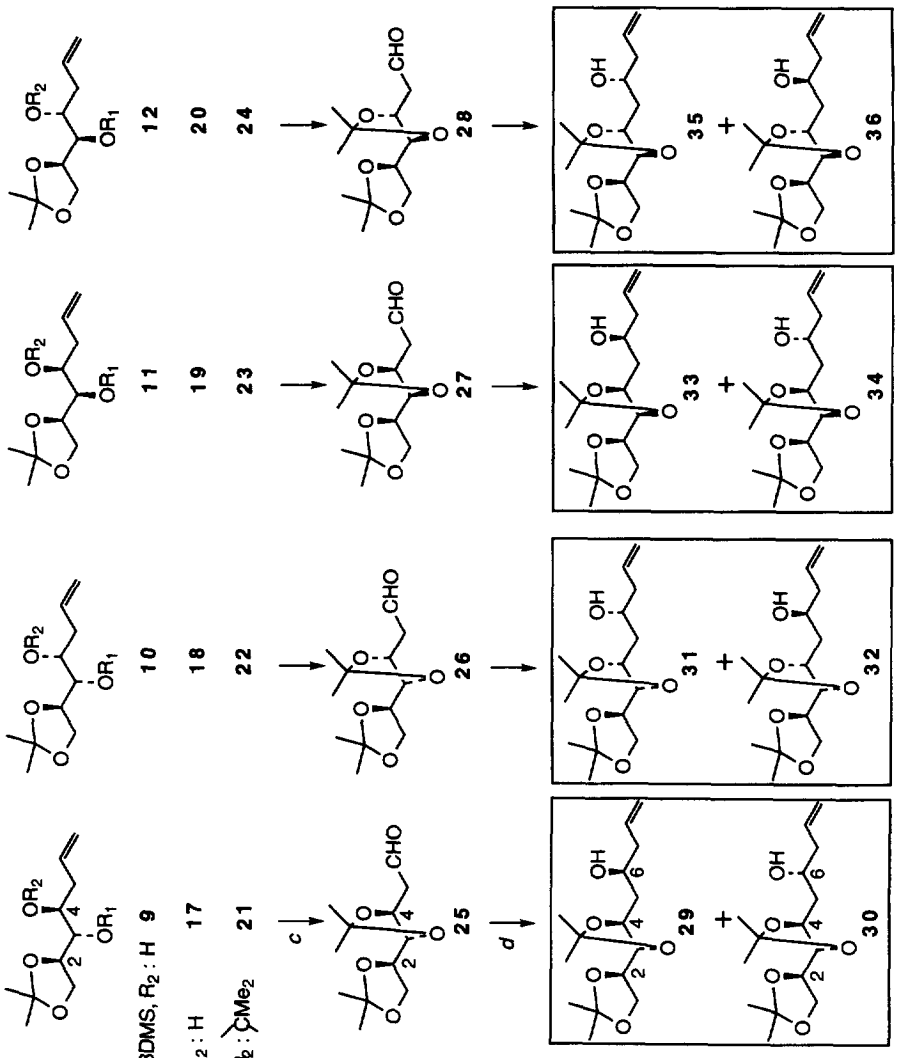
Scheme 2. a) CH_2=$CHCH_2MgBr$, THF, -30°C, 15 min., then 0°C, 45 min.; b) 1.0 M tetrabutylammonium fluoride in THF, rt., 5.5 h, 70%; c) MeOH, CH_3COCl, rt., 2 h; d) 9-anthroyl tetrazole, DBU, MeCN, 8 h, 53%; e) *p*-methoxycinnamoyl imidazole, DBU, MeCN, 4 h, 88%.

achieved by comparison of the CD of **13-16** with those of authentic ethyl tetrols (**13r-16r**) measured in acetonitrile[5a] and in methylcyclohexane.[5b]

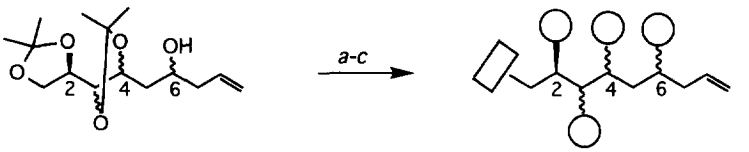
Mixed pentol derivatives 37-44. A three step conversion of acetonides **9-12** (**Scheme 3**) afforded aldehydes **25-28** as precursors of the skipped and mixed 1,2-/1,3-pentols. Thus silyl derivatives **9-12** were first desilylated to diol acetonides **17-20** and then converted into bisacetonides **21-24**. The latter upon ozonolysis yielded bisacetonide aldehydes **25-28**. Treatment of aldehydes **25-28** with allylmagnesium bromide at -30°C afforded, respectively, the 1,3-*syn*- and 1,3-*anti*- hydroxyl extended pairs, **29/30, 31/32, 33/34** and **35/36**. All pairs were separated into respective diastereomers by silica gel chromatography, except for the pair **33/34**, which was separated after chromophoric derivatization.

The pentol bisacetonides **29** and **30, 31** and **32**, and **35** and **36** were converted into bichromophoric derivatives, **37** and **38**, **39** and **40**, and **43** and **44**, respectively, where the primary hydroxyl groups were anthroylated and secondary hydroxyl groups were cinnamoylated (**Scheme 4**). In the case of the inseparable diastereomeric pair **33/34**, the mixture was first subjected to chromophoric derivatization and then base-line separated into diastereomers **41** and **42** by 3μ-silica HPLC column and 2% THF/CH_2Cl_2.

The *syn* versus *anti* extension at C-6 was determined by NMR as follows (**Figure 1**). The ^{1}H-NMR J constants of 5-H and the extent of 7-H's chemical shifts difference in the three diastereomeric pentol

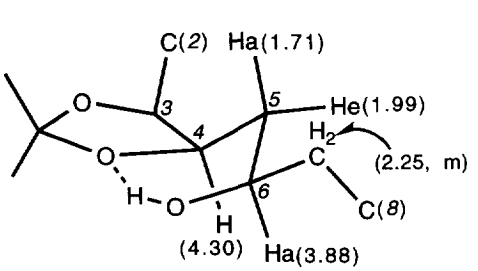


Scheme 3. a) 1.0 M tetrabutylammonium fluoride in THF, rt., 5.5 h, 70%; b) p-TsOH, CH3OC(CH3)2OCH3, 3.5 h, 83%; c) O3, Ph3P, -78°C, 93%; d) CH2=CHCH2MgBr, THF, -30°C, 15 min., then 0°C, 45 min..

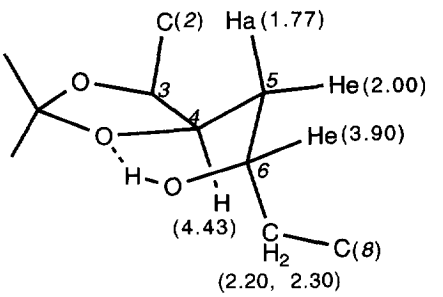


29 : 3α, 4β, 6β	**30** : 3α, 4β, 6α	**37** : 3α, 4β, 6β	**38** : 3α, 4β, 6α
31 : 3α, 4α, 6α	**32** : 3α, 4α, 6β	**39** : 3α, 4α, 6α	**40** : 3α, 4α, 6β
33 : 3β, 4β, 6β	**34** : 3β, 4β, 6α	**41** : 3β, 4β, 6β	**42** : 3β, 4β, 6α
35 : 3β, 4α, 6α	**36** : 3β, 4α, 6β	**43** : 3β, 4α, 6α	**44** : 3β, 4α, 6β

Scheme 4. a) MeOH, CH_3COCl, rt., 2 h; b) 9-anthroyl tetrazole, DBU, MeCN, 8 h, 53%; c) *p*-methoxy-cinnamoyl imidazole, DBU, MeCN, 4 h, 88%.



(35a) $J_{5a,5e}$ 13.9; $J_{5a,4}$ 11.3; $J_{5a,6a}$ 9.0



(36a) $J_{5a,5e}$ 13.7; $J_{5a,4}$ 11.0; $J_{5a,6a}$ 2.6

Figure 1. Conformations **35a** and **36a** and NMR data of 1,3-*syn*- and 1,3-*anti*- extended bisacetonides **35** and **36**, respectively.

bisacetonides **29/30**, **31/32**, and **35/36** led to the C-6 stereochemical assignments. This is exemplified by the pair **35a** (*syn*) and **36a** (*anti*). The upfield 5-H signal of homoallylic alcohol **35** at 1.71 ppm exhibits two large vicinal coupling constants, $J_{4,5}$ 11.3 and $J_{5,6}$ 9.0, in addition to J_{gem} 13.9 Hz; the two 7-H appears as a single 2H multiplet centered at 2.25 ppm. In contrast, the upfield 5-H of **36a** at 1.77 ppm has $J_{4,5}$ 11.0 and $J_{5,6}$ 2.6, in addition to the J_{gem} 13.7 Hz; the 7-H's appear as two multiplets at 2.20 and 2.30 ppm. This difference can be rationalized by the fact that in the *syn*-extended **35a**, the C-7 homoallylic group adopts a quasi equatorial conformation with respect to the intramolecular H-bonded ring; this leads to a large $J_{5,6}$ of 9.0 Hz. In the *anti*-extended **36a**, the H-bonded ring causes C-7 to assume a quasi axial orientation, and hence 6-H becomes quasi equatorial, leading to the small $J_{5,6}$ of 2.6 Hz. This is corroborated by the observation of an NOE between the 1.77 ppm 5-H and the 3.90 ppm 6-H signals. The 7-methylene protons in **35a** has a greater degree of freedom to rotate around C(6)-C(7) in comparison to the 7-methylene in **36a**, thus giving rise to the difference in the two 7-H signals mentioned above. Similar trends were observed in the pairs **29/30** and **31/32**.

General Trends in CD

CD of skipped pentol derivatives 2 and 3. The CD curves of these derivatives are compared with the lower homologous tetrol derivative **1**[7a] in two solvents, the nonpolar methylcyclohexane and the more polar acetonitrile (**Figure 2**). It was noted earlier that bisacylates which are in 1,3-*syn* relation do not couple.[19] This was accounted for by the fact that acyclic 1,3-bisacylates adopt the planar zig-zag form as their most stable conformation, and that the related electric transition moments of the acylates are parallel and hence exhibit no exciton coupling.[20] This trend is clearly seen in the present 1,3-*syn* extension of tetrol derivative **1** to pentol derivative **2**, where the CD curves are similar. The positive Cotton effect (CE) at ca. 252 nm reflects the 2β-configuration,[4] while the negative couplet centered at 300 nm is due to the 4,6-dicinnamate moiety which constitutes a counter-clockwise twist.

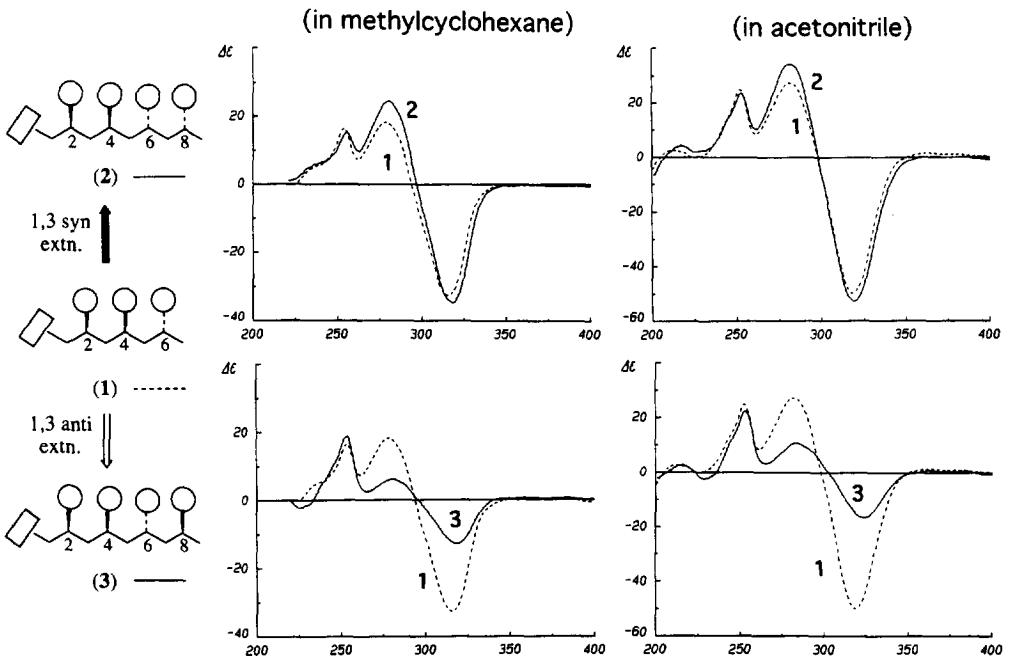


Figure 2. CD spectra of 1,3-skipped tetrol and pentol bichromophoric derivatives **1** (dashed), **2**, and **3** (solid) in methylcyclohexane and acetonitrile.

In the case of 1,3-*anti* extensions,**1**→ **3**, the terminal and penultimate acylates are gauche-oriented and hence this extension reflects the coupling corresponding to their screw sense. Namely, in **3**, the projection angle of the acylates at C-6 and C-8 is counter-clockwise or negative (by definition), which in turn gives rise to a negative contribution to the split (bisignate) CD curve. This trend is clearly seen in the higher pentol derivative as well. Thus, the CD of the anti-extended pentol derivative **3**, except for the positive CE at 250 nm diagnostic of the 2β-configuration,[4] is different from that of the lower homolog, i.e., intensity of the 300 nm negative couplet of **1** is greatly reduced because of the positive screw sense of the 6,8-acylates.

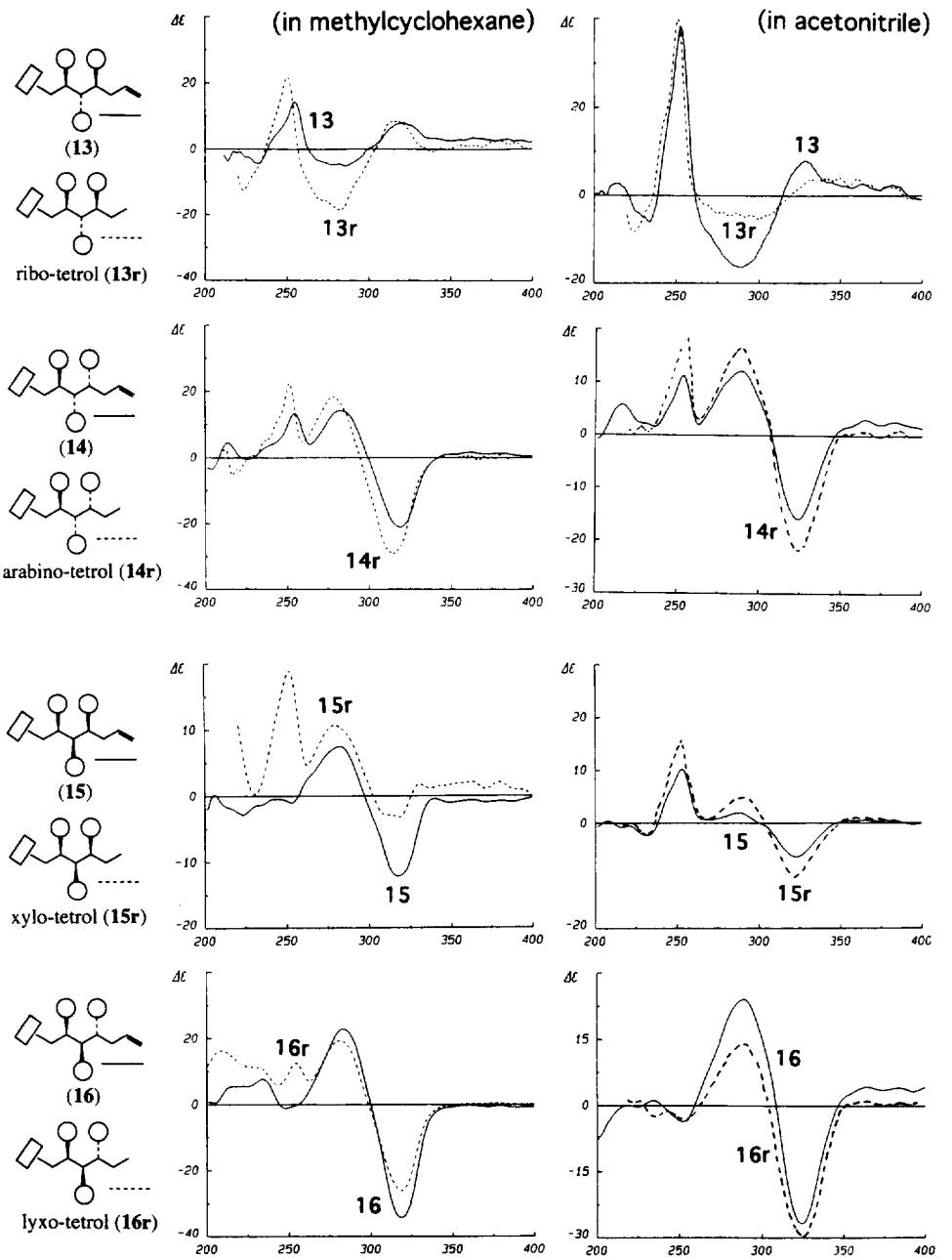


Figure 3. CD spectra of bichromophoric derivatives of allylic tetrol **13-16** (solid) and reference ethyl tetrol **13r-16r** (dashed) in methylcyclohexane and acetonitrile.

Configurational assignments of 1,2-tetrol derivatives 13-16. Comparisons of the CD of bichromophoric anthroate/methoxycinnamate derivatives of 1,2-acyclic polyols with corresponding reference curves are occasionally not straightforward (**Figure 3**). In such cases the following general process should be taken: *measure CD in both the nonpolar methylcyclohexane and the more polar acetonitrile, and then draw conclusions from the solvent showing greater similarity.*

This is exemplified in the xylo- and lyxo derivatives **15/15r** ("r" for reference) and **16/16r**, respectively. It was noted earlier[5,6] that the CD of homologous 1,2-polyol bichromophoric derivatives followed clearer systematic trends when measured in methylcyclohexane than in acetonitrile. It was therefore unexpected that the CDs of the xylo and lyxo series, allylic-**15**/ethyl-**15r** and allylic-**16**/ethyl-**16r** showed better agreement in acetonitrile than in methylcyclohexane; the reason for this is unclear. Thus it is recommended that the CDs in both solvents should be compared.

Table 1. CD (λ_{ext} nm/$\Delta\varepsilon$) Data of Bichromophoric Derivatives of Acyclic Polyols with 2β-Configuration in Methylcyclohexane and Acetonitrile.

Entry	Compd	CD [λ_{ext} ($\Delta\varepsilon$)] in $C_6H_{11}CH_3$	CD [λ_{ext} ($\Delta\varepsilon$)] in CH_3CN
1	**1**	254(+16.4), 278(+18.2), 316(-32.6)	252(+24.9), 280(+27.2), 318(-49.9)
2	**2**	255(+15.5), 279(+24.5), 319(-34.7)	252(+24.1), 280(+34.1), 320(-52.8)
3	**3**	254(+18.8), 280(+6.2), 319(-12.8)	252(+22.3), 282(+10.7), 323(-16.5)
4	**13**	254(+14.5), 284(-5.0), 320(+8.0)	252(+38.2), 287(-16.3), 327(+8.0)
5	**13r**	250(21.9), 282(-18.3), 315(+8.4)	253(+41), 287(-9), 322(+10)
6	**14**	254(+13.3), 281(+14.2), 318(-21.1)	252(+11.2), 288(+12.1), 323(-15.9)
7	**14r**	252(+22.4), 278(+18.4), 315(-29.0)	253(+18), 287(+6), 322(-26)
8	**15**	252(-1.0), 282(+7.5), 316(-12.1)	252(+10.3), 286(+2.0), 322(-6.3)
9	**15r**	252(+18.9), 280(+10.7), 318(-3.2)	253(+24), 287(+6), 322(-15)
10	**16**	252(-0.3), 282(+23.0), 318(-34.2)	251(-3.6), 288(+24.2), 323(-26.8)
11	**16r**	254(+12.6),281(+19.4),319(-26.1)	253(-6),287(+20),322(-31)
12	**37**	254(+26.7), 288(-7.2), 325(+7.1)	252(+37.5), 278(+0.3), 312(-11.8)
13	**38**	254(+23.7), 279(+17.2), 317(-31.9)	252(+36.5),283(+26.3),321(-59.9)
14	**39**	255(+10.1), 280(+29.5), 318(-29.8)	252(+13.1), 285(+25.8), 322(-30.2)
15	**40**	254(+18.6), 297(+9.9), 326(-5.0)	252(+14.9), 277(-5.7), 310(+15.5)
16	**41**	254(+9.0), 293(-0.1), 320(-4.6)	252(+14.1), 288(-0.8), 323(-5.9)
17	**42**	254(+6.4), 279(+16.2), 315(-24.4)	252(+12.4), 281(+10.1), 317(-24.6)
18	**43**	256(-1.9), 280(+24.7), 318(-29.9)	254(-3.8), 284(+20.6), 322(-26.7)
19	**44**	252(+2.0), 295(+3.2), 316(+5.4)	257(-3.0), 279(-5.3), 318(+16.0)

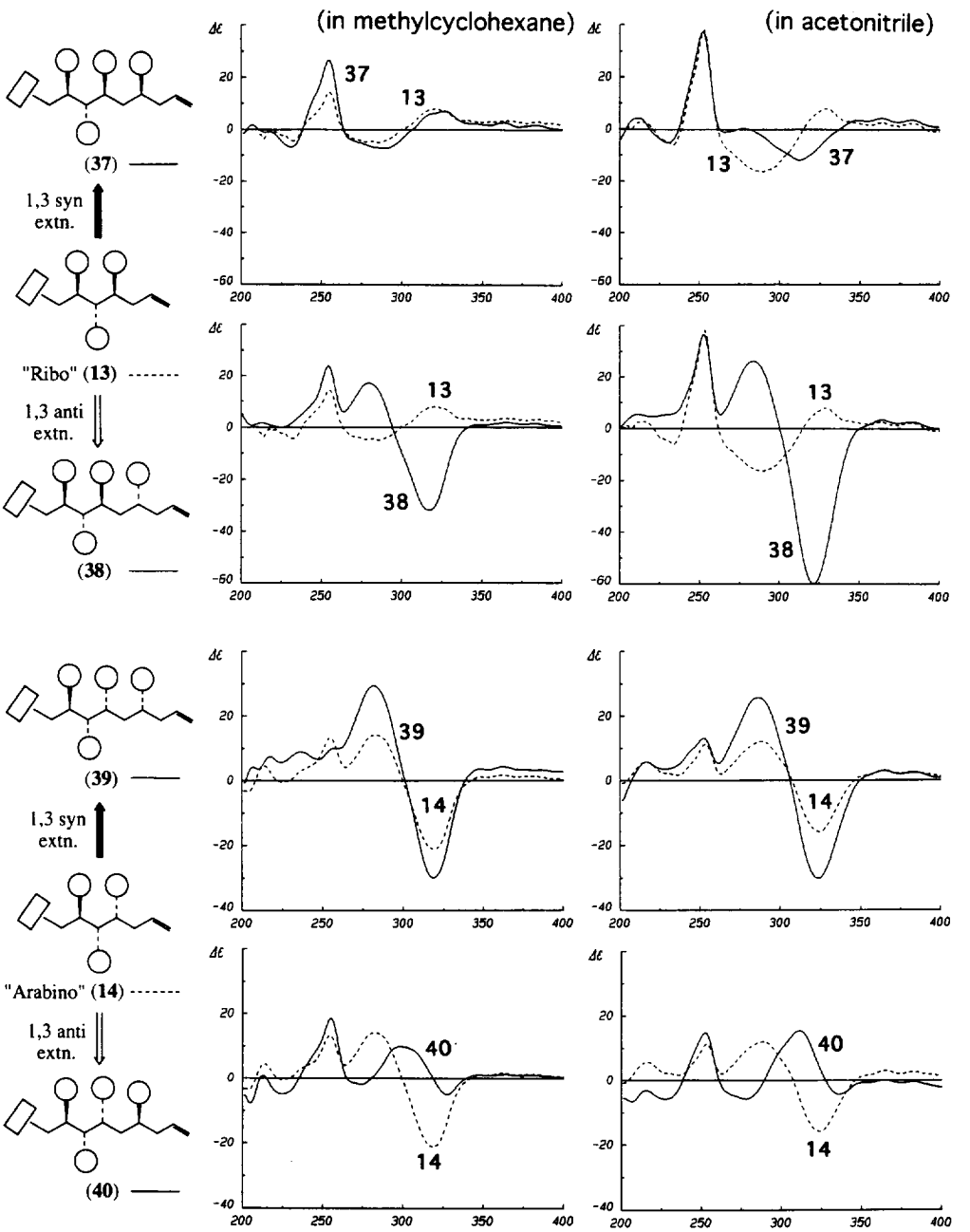


Figure 4. CD spectra of bichromophoric derivatives of allylic tetrol **13-16** (dashed) and 1,2-/1,3-mixed pentol **37-44** (solid) in methylcyclohexane and acetonitrile.

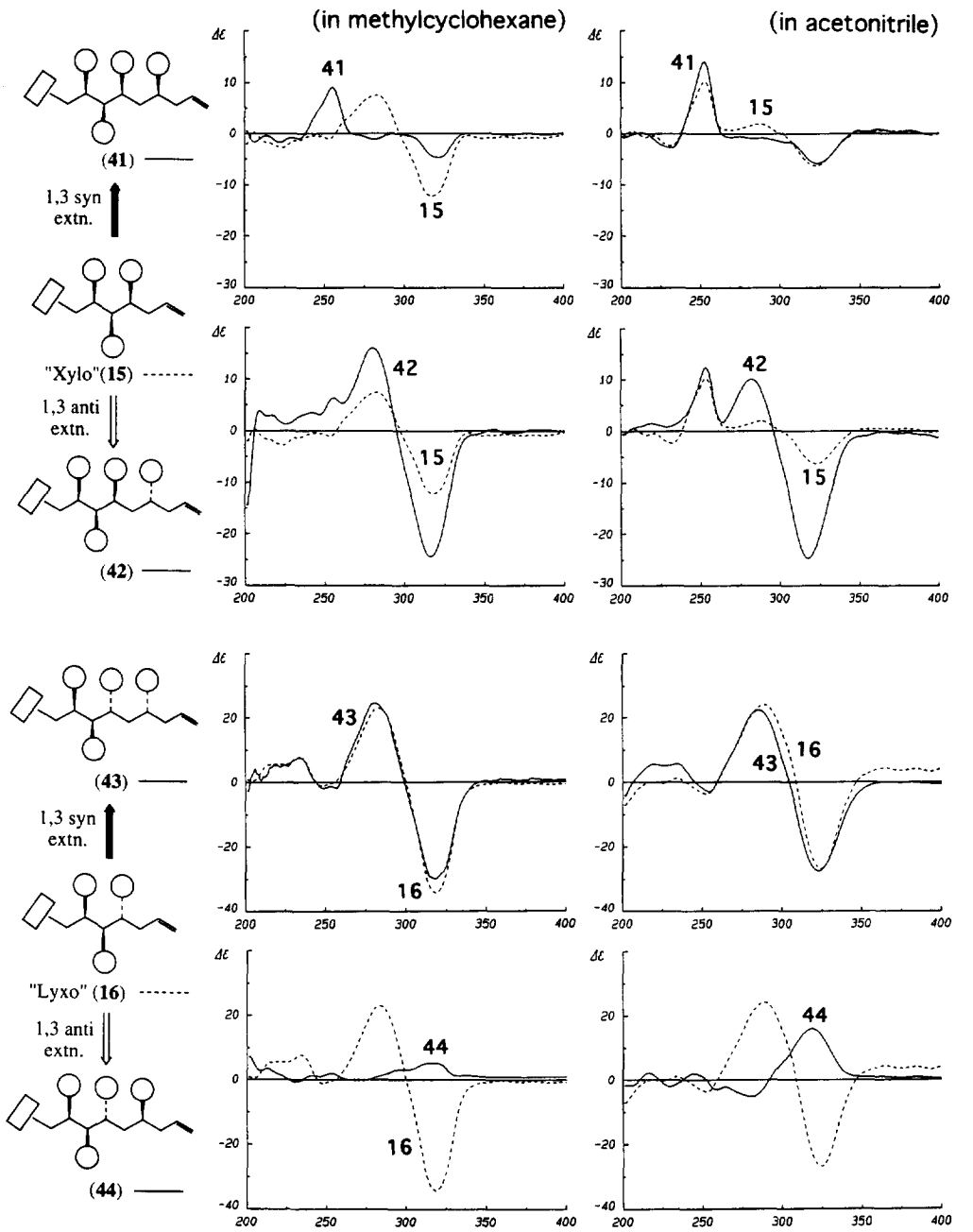


Figure 4. (continued).

CD of mixed pentol derivatives 37-44. The italicized comments mentioned above, i.e., measurements in two solvents, apply here as well when comparing the spectra with their lower homologs. The CD spectra of eight diasteromers **37-44**, measured in methylcyclohexane and in acetonitrile, are compared with the four parent tetrol derivatives **13-16** on **Table 1** and **Figure 4**. The following trend emerges from this comparison.

i) 1,3-*syn* extension: The CD spectra of 1,3-*syn* extended mixed pentol derivatives **37**, **39**, **41** and **43** closely resemble those of parent tetrols **13-16**. The 1,3-*syn* extensions exert only a weak effect arising from 1,3-interactions in the pairwise additivity interactions. However, the curves do not necessarily show similarity in both solvents. As mentioned earlier, because of the inherent conformational flexibility of these acyclic compounds with lipophilic acylate branches, configurational correlations are more reliable upon comparisons of CD measured in both the nonpolar methylcyclohexane and the more polar acetonitrile. For example, the CDs of *syn*-extended **37** and "ribo" **13** are similar in methylcyclohexane (MC) but not in acetonitrile (AN). On the other hand, for a similar *syn*-extended **41**, the CD is similar to the reference precursor **15** in AN but not in MC.

ii) 1,3-*anti* extension: In contrast to *syn*-extensions, the CDs of 1,3-*anti* extended mixed pentol derivatives **38**, **40**, **42**, and **44** differ significantly, but in a predictable pattern, from those of parent tetrols **13-16**. Without exception, the 1,3-*anti* extension contributes a strong exciton spilt CE, the sign of which reflects the screw sense between the newly introduced 1,3-extension.

iii) the 252 nm Cotton effect (CE): The sign of the anthroate CE at 252 nm is primarily dependent upon the C-2 configuration.[4] A clear positive CE at 252 nm (positive shorter wavelength counterpart of a negative couplet) is diagnostic for a 2β-configuration and for an anticlock-wise twist between 1-anthroate/2-cinnamate transition moments. This CD band is distinctly positive in 2β,3α 1,2-type polyols, e.g. in "ribo" **13**, "arabino" **14**, as well as in the 1,3-extended mixed polyols compounds **37-40** prepared in this study. The uniformly positive sign is due to fact that both 1-anthroate/2β-methoxycinnamate and 1-anthroate/3α-methoxycinnamate both exhibit positive 252 bands. The intensity of this band is solvent dependent and is generally stronger in AN than in MC, e.g., **37** and **38**.

In contrast, in the 2β,3β mixed polyols **15**, **16**, **41-44**, the 252 nm CE is variable, ranging from weakly positive to weakly negative; this is because the 1-anthroate/3β-methoxycinnamate moiety has a negative CE in this region. The 252 nm CE represents the shorter wavelength wing of a split CD which is generally much more intense than the longer wavelength wing; however, the reason for this difference in intensities of the two wings is currently under study.

CONCLUSION

CD curves of all eight diastereomers **37-44** with mixed 1,2- and 1,3-acylate functions are characteristic and give rise to predictable trends for each stereochemical pattern. These reference curves and general trends can be used for configurational assignments of other 1,2- and 1,3-mixed polyols of the same type. The microscale application of the results described above to the determination of absolute configuration of two new bacteriohopanepentols isolated from cyanobacterium *Nostoc* PCC 6720 is described in the following paper.

EXPERIMENTAL SECTION

General. Solvents used for reactions were reagent grade. Anhydrous solvents were freshly distilled (THF from Na/benzophenone; CH_2Cl_2 and acetonitrile from CaH_2). Unless otherwise stated, reagents were obtained from commercial sources and were used as such. Moisture sensitive reactions were carried out in oven-dried glassware under argon. Thin-layer chromatography (TLC), Analtech Silica Gel GHLF plates (250 μm thickness), was used for monitoring reactions.

ICN silica gel (32-63 mesh) was employed for flash chromatography. HPLC purifications were performed using either Rainin or waters HPLC system equipped with a Rainin Dynamax model UV-D detector or diode array detector, respectively. Solvents used for chromatographic separation were HPLC grade.

All ^1H NMR spectra were measured in $CDCl_3$ on a Varian VXR 400 and are reported in parts per million (δ) relative to $CHCl_3$ (7.24 ppm) as internal reference, with coupling constants (J) reported in Hertz (Hz). Low-resolution and high-resolution FAB mass spectra were measured on a JEOL JMS-DX 303 HF mass spectrometer using glycerol matrix and Xe ionizing gas. CI mass spectra were measured on a NERMAG R10-10 spectrometer with NH_3 as ionizing gas. UV-VIS and CD spectra were recorded in methylcyclohexane and acetonitrile (spectroscopic grade) solutions on a Perkin-Elmer Lambda 4B UV/VIS spectrophotometer and JASCO J-720 spectropolarimeter, respectively. Smoothing (Discrete Fourier Transform procedure) and other manipulations of CD spectra were carried out with in house developed software.

Representative procedure for preparation of bichromophoric derivatizatives of polyols (Method A): (2*S*,4*S*,6*R*,8*R*)- and (2*S*,4*S*,6*R*,8*S*)-1-*O*-anthroyl-2,4,6,8-tetra-(*O*-*p*-methoxycinnamoyl)-nonane-1,2,4,6,8-pentols (2) and (3).

i) Anthroylation: To **4** (or **5**) (5 mg, 24.3 mmol) in acetonitrile (0.5 ml) was added 9-anthroyltetrazole (13.3 mg, 48.5 mmol) and DBU (7 μl, 48.5 mmol). The reaction mixture was stirred at room temperature for 8 h and concentrated. The yellow residue was purified by silica gel flash chromatography (8% MeOH/CH_2Cl_2) to give 5.0 mg of pentol-1-anthroate in 50% yield.

ii) Cinnamoylation: To 1-anthroate of **4** (or **5**) (5 mg, 12.2 mmol) in acetonitrile (0.5 ml) was added *p*-methoxycinnamoyl imidazole (22.6 mg, 97.6 mmol) and DBU (11 μl, 73.2 mmol). The reaction mixture was stirred at room temperature for 4 h. After removal of solvent, the residue was purified by silica gel flash chromatography (30% EtOAc/Hexane) to give 11.3 mg of **2** (or **3**) in 88% yield. FAB-HRMS for $C_{64}H_{60}O_{14}$, calcd 1052.3980, found 1052.3990 for **2** and 1052.3960 for **3**.

Representative procedure for Grignard addition (Method B): (2*R*,3*S*,4*S*)- and (2*R*,3*S*,4*R*)-1,2-*O*-isopropylidene-3-*tert*-butyldimethylsilyl-6-heptene-1,2,3,4-tetrols (9) and (10). To a solution of aldehyde **7** (428 mg, 1.56 mmol) in CH_2Cl_2 (8 ml) at -30°C was added 1.0 M THF solution of allylmagnesium bromide (1.72 ml). The mixture was maintained at -30°C for 45 min. and then at 0°C for 15 min.. It was diluted with CH_2Cl_2 (20 ml), the organic phase was washed with water (10 ml x 2), brine (20 ml), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel. The two diastereomers **9** (230 mg, 47%) and **10** (220 mg, 46%) were isolated in pure form upon elution with 10 and 11% ether/hexane, respectively.

(9). ^{1}H-NMR δ 0.08 (S, 3H, Si-Me), 0.09 (S, 3H, Si-Me), 0.87 (S, 9H, Si-*t*-Bu), 1.32 (S, 3H, Me), 1.37 (S, 3H, Me), 2.20 (m, 1H, H-5), 2.30 (m, 1H, H-5'), 3.73 (m, 1H, H-4), 3.78 (m, 1H, H-3), 3.80 (m, 1H, H-1), 4.00 (dd, 1H, *J* = 8.0, 6.1 Hz, H-1'), 4.10 (m, 1H, H-2), 5.08 (m, 2H, H-7, 7'), 5.84 (m, 1H, H-6) ; CI-MS (NH_3) *m/z* 317 $(m+1)^+$, 334 $(M+18)^+$.

(10). ^{1}H-NMR δ 0.08 (S, 3H, Si-Me), 0.09 (S, 3H, Si-Me), 0.87 (S, 9H, Si-*t*-Bu), 1.32 (S, 3H, Me), 1.39 (S, 3H, Me), 2.20 (m, 1H, H-5), 2.30 (m, 1H, H-5'), 3.61 (m, 1H, H-4), 3.74 (dd, 1H, *J* = 6.4, 2.8 Hz, H-3), 3.78 (dd, 1H, *J* = 7.9, 6.9 Hz, H-1), 4.02 (dd, 1H, *J* = 8.1, 6.3 Hz, H-1'), 4.10 (m, 1H, H-2), 5.08 (m, 2H, H-7, 7'), 5.86 (m, 1H, H-6) ; CI-MS (NH_3) *m/z* 317 $(m+1)^+$, 334 $(M+18)^+$.

(2*R*,3*R*,4*S*)- and (2*R*,3*R*,4*R*)-1,2-*O*-isopropylidene-3-*tert*-butyldimethylsilyl-6-heptene-1,2,3,4-tetrols (11) and (12). The two compounds were prepared from allylmagnesium bromide addition to aldehyde **8** by the procedure described in method B. They were purified by flash chromatography. Compound **11** was eluted with 10-11% and compound **12** with 11-13% ether/hexane (87% overall yield of 1:1 mixture of **11** and **12**).

(11). ^{1}H-NMR δ 0.09 (S, 3H, Si-Me), 0.12 (S, 3H, Si-Me), 0.90 (S, 9H, Si-*t*-Bu), 1.32 (S, 3H, Me), 1.39 (S, 3H, Me), 2.25 (m, 1H, H-5), 2.45 (m, 1H, H-5'), 3.69-3.76 (m, 2H, H-3, 4), 3.95 (dd, 1H, *J* = 8.4, 6.6 Hz, H-1), 4.06 (dd, 1H, *J* = 8.4, 6.3 Hz, H-1'), 4.19 (m, 1H, H-2), 5.16 (m, 2H, H-7, 7'), 5.85 (m, 1H, H-6) ; CI-MS (NH_3) *m/z* 317 $(m+1)^+$, 334 $(M+18)^+$.

(12). ^{1}H-NMR δ 0.08 (S, 3H, Si-Me), 0.09 (S, 3H, Si-Me), 0.88 (S, 9H, Si-*t*-Bu), 1.33 (S, 3H, Me), 1.41 (S, 3H, Me), 2.20 (m, 1H, H-5), 2.37 (m, 1H, H-5'), 3.61-3.68 (m, 2H, H-3, 4), 3.81 (dd, 1H, *J* = 8.3, 7.9 Hz, H-1), 3.98 (dd, 1H, *J* = 8.4, 6.6 Hz, H-1'), 4.19 (m, 1H, H-2), 5.11 (m, 2H, H-7, 7'), 5.85 (m, 1H, H-6) ; CI-MS (NH_3) *m/z* 317 $(m+1)^+$, 334 $(M+18)^+$.

(2*R*,3*S*,4*S*)-1,2-*O*-isopropylidene-6-heptene-1,2,3,4-tetrols (17). Compound **9** (130 mg, 0.41mmol) was stirred in 1.0 M solution of tetrabutylammonium fluoride in THF (0.85 mol) for 5.5 h. The solvent was removed under reduced pressure and the residue was column chromatographed (silica gel, 50% ether/hexane) to afford tetrol acetonide **17**, 70% yield.

Tetrol acetonides **18-20** were prepared from **10-12**, respectively, by using the same desilylation procedure.

Bichromophoric derivatization of 17-20 to 13-16 (Method C): (2*R*,3*S*,4*S*)-1-*O*-anthroyl-2,3,4-tri-(*O*-*p*-methoxycinnamoyl)-heptene-1,2,3,4-tetrol (13).

i) Acetonide cleavage: To a methanolic solution (0.5 ml) of tetrol acetonide **17** (2.5 mg) was added 2-3 drops of acetyl chloride. The mixture was stirred for 2 h. The solvent was removed under reduced pressure and the residue was dried overnigh *in vacuo* . The tetrol thus obtained was subjected to anthroylation without further purificaion.

ii) Anthroylation: The tetrol obtained from earlier step was monoanthroylated according to method A (i). The monoanthroate derivative was purified over a short silica gel column (5% MeOH/ether). The overall yield of steps (i) and (ii) is 53%.

iii) Cinnamoylation: Tetrol 1-anthroate was then cinnmoylated with *p*-methoxycinnamoyl imidazole using the procedure described earlier, method A (ii). Silica gel chromatography (55% ether/hexane) afforded compound **13** (72%). A small amount of the sample for CD measurement was further purified on HPLC (3μ

YMC silica gel, 25% ethyl acetate/hexane); FAB-MS 846 (M^+); FAB-HRMS for $C_{52}H_{46}O_{11}Na$, calcd 869.2938, found 869.2969.

Bichromophoric derivatives **14, 15, 16** were prepared from the corresponding compounds **10, 11, 12** respectively, by using the above procedure for **13** (method C).

(2*R*,3*S*,4*R*)-1-*O*-anthroyl-2,3,4-tri-(*O*-*p*-methoxycinnamoyl)-heptene-1,2,3,4-tetrol (14). HPLC (3μ YMC silica gel, 25% ethyl acetate/hexane); FAB-MS 846 (M^+); FAB-HRMS for $C_{52}H_{46}O_{11}$, calcd 846.3040, found 846.3021.

(2*R*,3*R*,4*S*)-1-*O*-anthroyl-2,3,4-tri-(*O*-*p*-methoxycinnamoyl)-heptene-1,2,3,4-tetrol (15). HPLC (3μ YMC silica gel, 25% ethyl acetate/hexane); FAB-MS 846 (M^+); FAB-HRMS for $C_{52}H_{46}O_{11}$, calcd 846.3040, found 846.3041.

(2*R*,3*R*,4*R*)-1-*O*-anthroyl-2,3,4-tri-(*O*-*p*-methoxycinnamoyl)-heptene-1,2,3,4-tetrol (16). HPLC (3μ YMC silica gel, 25% ethyl acetate/hexane); FAB-MS 846 (M^+); FAB-HRMS for $C_{52}H_{46}O_{11}Na$, calcd 869.2938, found 869.2949.

(2*R*,3*S*,4*S*)-1,2:3,4-bis(*O*-isopropylidene)-6-heptene-1,2,3,4-tetrol (21). *p*-Toluenesulfonic acid (2 mg) was added to a stirred solution of compound **17** (0.247 mmol) in 2,2-dimethoxypropane (2 ml). The mixture was stirred at ambient temperature for 3.5 h. The solvent was removed and the residue was chromatographed over a short silica column (11% ether/hexane) to afford the tetrol diacetonide **21** (83%); CI-MS (NH_3) 243 $(M+1)^+$, 260 $(M+18)^+$.

Tetrol diacetonides **22-24** were synthesized from **18-20,** respectively, using the same procedure.

(2*R*,3*S*,4*R*)-1,2:3,4-bis(*O*-isopropylidene)-6-heptene-1,2,3,4-tetrol (22). Purification by silica gel chromatography (11% ether/hexane) afforded **22** (81%); CI-MS 243 $(M+1)^+$, 260 $(M+18)^+$.

(2*R*,3*R*,4*S*)-1,2:3,4-bis(*O*-isopropylidene)-6-heptene-1,2,3,4-tetrol (23). Purification by silica gel chromatography (10% ether/hexane) yielded **23** (82%); CI-MS (NH3) 243 $(M+1)^+$, 260 $(M+18)^+$.

(2*R*,3*R*,4*R*)-1,2:3,4-bis(*O*-isopropylidene)-6-heptene-1,2,3,4-tetrol (24). Purification by silica gel chromatography (12% ether/hexane) gave **24** (82%); CI-MS (NH3) 243 $(M+1)^+$, 260 $(M+18)^+$.

(2*R*,3*S*,4*S*)-1,2:3,4-bis(*O*-isopropylidene)-6-hexanal-1,2,3,4-tetrol (25). Into a solution of compound **21** (8.5 mg, 0.035 mmol) in CH_2Cl_2 : MeOH (4 : 1, 12 ml) maintained at -78°C was bubbled O_3 for 2-3 min until the solution turned deep blue. Then triphenylphosphine was added (46 mg, 0.18 mmol) and the mixture was stirred for 10 min. at -78°C and 45 min. at 0°C. The mixture was concentrated under reduced pressure. Purification (silica gel column, 10% ether/hexane) afforded compound **25** (93%); CI-MS (NH3) 245 $(M+1)^+$, 262 $(M+18)^+$.

Ozonolysis of compounds **22-24** under the same conditions yielded aldehydes **26-28**, respectively.

(2*R*,3*S*,4*R*)-1,2:3,4-bis(*O*-isopropylidene)-6-hexanal-1,2,3,4-tetrol (26). Chromatography over silica gel (15% ether/hexane) afforded **26** (88%); CI-MS (NH3) 245 $(M+1)^+$, 262 $(M+18)^+$.

(2*R*,3*R*,4*S*)-1,2:3,4-bis(*O*-isopropylidene)-6-hexanal-1,2,3,4-tetrol (27). Silica gel chromatography (10% ether/hexane) gave **27** (87%); CI-MS (NH3) 245 $(M+1)^+$, 262 $(M+18)^+$.

(2*R*,3*R*,4*R*)-1,2:3,4-bis(*O*-isopropylidene)-6-hexanal-1,2,3,4-tetrol (28). Purification on silica gel (12% ether/hexane) yielded **28** (85%); CI-MS (NH3) 245 $(M+1)^+$, 262 $(M+18)^+$.

Grignard addition of allylmagnesiumbromide to the aldehydes 25-28. Pentols diacetonides **29-36** were synthesized from the corresponding aldehydes **25-28** by Grignard reaction with allylmagnesium bromide according to the procedure described earlier (method B). Each aldehyde yields a mixture of two diastereomeric pentol diacetonides in almost equal amounts.

(2*R*,3*S*,4*S*,6S)- and (2*R*,3*S*,4*S*,6*R*)-1,2:3,4-bis(*O*-isopropylidene)-8-nonene-1,2,3,4,6-pentols (29) and (30). Compound **25** (8 mg, 0.032 mmol) gave a mixture of **29** and **30** after the Grignard reaction. The two isomers were separated on silica gel column with 17% ether/hexane (42% each).
(29). ^{1}H-NMR δ 1.32 (S, 6H, 2-Me), 1.37 (S, 3H, Me), 1.40 (S, 3H, Me), 1.70 (ddd, 1H, *J* = 14.3, 9.4, 9.2 Hz, H-5a), 1.91 (ddd, 1H, *J* = 14.0, 3.5, 2.9 Hz, H-5e), 2.27 (m, 2H, H-7, 7'), 3.88 (m, 1H, H-1), 3.90 (m, 1H, H-6), 3.96 (m, 1H, H-1'), 4.05 (m, 1H, H-2), 4.09 (dd, 1H, *J* = 8.1, 5.9 Hz, H-3), 4.38 (ddd, 1H, *J* = 9.8, 5.4, 4.3 Hz, H-4), 5.10 (m, 2H, H-9, 9'), 5.80 (m, 1H, H-8); CI-MS (NH_3) *m/z* 287 $(m+1)^+$, 304 $(m+18)^+$.
(30). ^{1}H-NMR δ 1.31 (S, 3H, Me), 1.34 (S, 3H, Me), 1.37 (S, 3H, Me), 1.38 (S, 3H, Me), 1.88 (m, 2H, H-5a, e), 2.28 (bm, 2H, H-7, 7'), 3.81 (m, 1H, H-6), 3.90 (dd, 1H, *J* = 8.2, 5.5 Hz, H-1), 4.03 (m, 2H, H-1', 3), 4.11 (m, 1H, H-2), 4.41 (m, 1H, H-4), 5.10 (m, 2H, H-9, 9'), 5.82 (m, 1H, H-8) ; CI-MS (NH_3) *m/z* 287 $(m+1)^+$, 304 $(m+18)^+$.

(2*R*,3*S*,4*R*,6*R*)- and (2*R*,3*S*,4*R*,6*S*)-1,2:3,4-bis(*O*-isopropylidene)-8-nonene-1,2,3,4,6-pentols (31) and (32). Separation of these two diastereomers was achieved by silica gel chromatography , compound **31** and **32** being eluted with 21% and 24 % ether/hexane, respectively (40% each).
(31). ^{1}H-NMR δ 1.32 (3H, S, Me), 1.34 (S, 3H, Me), 1.37 (S, 3H, Me), 1.38 (S, 3H, Me), 1.63 (ddd, 1H, *J* = 14.3, 9.6, 9.6 Hz, H-5a), 1.94 (ddd, 1H, *J* = 14.3, 2.9, 2.9 Hz, H-5e), 2.26 (m, 2H, H-7, 7'), 3.56 (dd, 1H, *J* = 8.0, 7.9 Hz, H-3), 3.91 (bm, 1H, H-6), 3.94 (dd, 1H, *J* = 8.4, 4.8 Hz, H-1), 4.00 (ddd, 1H, *J* = 8.4, 6.0, 4.8 Hz, H-2), 3.96 (m, 1H, H-1), 4.05 (m, 1H, H-2), 4.12 (dd, 1H, *J* = 8.4, 6.0 Hz, H-1'), 5.07 (m, 2H, H-9, 9'), 5.83 (m, 1H, H-8); CI-MS (NH_3) *m/z* 287 $(m+1)^+$, 304 $(m+18)^+$.
(32). ^{1}H-NMR δ 1.32 (3H, S, Me), 1.34 (S, 3H, Me), 1.38 (S, 6H, 2-Me), 1.78 (ddd, 1H, *J* = 14.5, 7.5, 2.7 Hz, H-5e), 1.90 (ddd, 1H, *J* = 14.3, 9.0, 3.9 Hz, H-5a), 2.27 (bm, 2H, H-7, 7'), 3.60 (m, 1H, H-3), 3.91 (bm, 1H, H-6), 3.92 (dd, 1H, *J* = 8.4, 5.1 Hz, H-1), 4.01 (m, 1H, H-2), 4.11 (dd, 1H, *J* = 8.4, 6.1 Hz, H-1'), 4.16 (ddd, 1H, *J* = 7.6, 7.5, 3.9 Hz, H-4), 5.06 (m, 2H, H-9, 9'), 5.80 (m, 1H, H-8); CI-MS (NH_3) *m/z* 287 $(m+1)^+$, 304 $(m+18)^+$.

(2*R*,3*R*,4*S*,6*S*)- and (2*R*,3*R*,4*S*,6*R*)-1,2:3,4-bis(*O*-isopropylidene)-8-nonene-1,2,3,4,6-pentols (33) and (34). Compounds **33** and **34** could not be separated even after repeated column chromatography over silica gel (84%). This mixture was therefore separated after bichromophoric derivatization (see below).

(2*R*,3*R*,4*R*,6*R*)- and (2*R*,3*R*,4*R*,6*S*)-1,2:3,4-bis(*O*-isopropylidene)-8-nonene-1,2,3,4,6-pentols (35) and (36). These two diastereomers were easily separated on silica gel column, compound **35** and **36** being eluted with 30% and 38% ether/hexane, respectively (84%).
(35). ^{1}H-NMR δ 1.35 (S, 3H, Me), 1.36 (S, 3H, Me), 1.43 (S, 3H, Me), 1.51 (S, 3H, Me), 1.71 (ddd, 1H, *J* = 13.9, 11.3, 9.0 Hz, H-5a), 1.99 (bs, 1H, H-5e), 2.25 (m, 2H, H-7, 7'), 3.62 (dd, 1H, *J* = 7.8, 7.6 Hz, H-1), 3.88 (dddd, 1H, *J* = 8.9, 6.2, 5.8, 2.9 Hz, H-6), 4.00 (dd, 1H, *J* = 8.0, 6.4 Hz, H-1'), 4.06 (dd, 1H, *J* = 6.7, 6.3 Hz, H-3), 4.13 (m, 1H, H-2), 4.30 (ddd, 1H, *J* = 11.3, 6.2, 2.6 Hz, H-4), 5.00 (m, 2H, H-9, 9'), 5.81 (m, 1H, H-8); CI-MS (NH_3) *m/z* 287 $(m+1)^+$, 304 $(m+18)^+$.
(36). ^{1}H-NMR δ 1.35 (S, 3H, Me), 1.38 (S, 3H, Me), 1.43 (S, 3H, Me), 1.48 (S, 3H, Me), 1.77 (ddd, 1H, *J* = 13.7, 11.9, 2.7 Hz, H-5a), 2.00 (bs, 1H, H-5e), 2.20 (m, 1H, H-7), 2.30 (m, 1H, H-7'), 3.64 (dd, 1H, *J* = 7.8, 7.7 Hz, H-1), 3.90 (bs, 1H, H-6), 4.02 (dd, 1H, *J* = 8.0, 6.4 Hz, H-1'), 4.07 (dd, 1H, *J* = 6.5, 6.3 Hz, H-3), 4.13 (m, 1H, H-2), 4.43 (ddd, 1H, *J* = 10.9, 6.1, 2.7 Hz, H-4), 5.12 (m, 2H, H-9, 9'), 5.78 (m, 1H, H-8); CI-MS (NH_3) *m/z* 287 $(m+1)^+$, 304 $(m+18)^+$.

Bichromophoric derivatization of pentol diacetonides 29-36 to 37-44. Bichromophoric derivatives **37-40**, **43**, and **44** were prepared from the pentol diacetonides **29-32**, **35**, and **36** by acetonide cleavage, anthroylation and cinnamolytion (method C). The products were purified over silica gel column (4% MeOH/ether) in 40-45% overall yield. A small fraction of the flash chromatography purified samples were further purified by HPLC for CD and high-resolution FAB mass spectra. In the case of the diastereomeric pair **33** and **34**, the mixtures was subjected to acetonide cleavage and bichromophoric derivatization. The resultant derivatives **41**, **42** were separated by HPLC.

(2*R*,3*S*,4*S*,6*S*)-1-*O*-anthroyl-2,3,4,6-tetra-(*O*-*p*-methoxycinnamoyl)-8-nonene-1,2,3,4,6-pentol (37). HPLC (5μ alltech silica gel, 26% ethyl acetate/hexane); FAB-MS 1050 (M^+); FAB-HRMS for $C_{64}H_{58}O_{14}$, calcd 1050.3830, found 1050.3853.

(2*R*,3*S*,4*S*,6*R*)-1-*O*-anthroyl-2,3,4,6-tetra-(*O*-*p*-methoxycinnamoyl)-8-nonene-1,2,3,4,6-pentol (38). HPLC (5μ alltech silica gel, 31% ethyl acetate/hexane); FAB-MS 1050 (M^+); FAB-HRMS for $C_{64}H_{58}O_{14}$, calcd 1050.3830, found 1050.3857.

(2*R*,3*S*,4*R*,6*R*)-1-*O*-anthroyl-2,3,4,6-tetra-(*O*-*p*-methoxycinnamoyl)-8-nonene-1,2,3,4,6-pentol (39). HPLC (3μ YMc silica gel, 28% ethyl acetate/hexane); FAB-MS 1050 (M^+); FAB-HRMS for $C_{64}H_{58}O_{14}$, calcd 1050.3830, found 1050.3870.

(2*R*,3*S*,4*R*,6*S*)-1-*O*-anthroyl-2,3,4,6-tetra-(*O*-*p*-methoxycinnamoyl)-8-nonene-1,2,3,4,6-pentol (40). HPLC (5μ alltech silica gel, 26% ethyl acetate/hexane); FAB-MS 1050 (M^+); FAB-HRMS for $C_{64}H_{58}O_{14}$, calcd 1050.3830, found 1050.3845.

(2*R*,3*R*,4*S*,6*S*)-1-*O*-anthroyl-2,3,4,6-tetra-(*O*-*p*-methoxycinnamoyl)-8-nonene-1,2,3,4,6-pentol (41). HPLC (3μ YMC silica gel, 2% THF/CH_2Cl_2, retension time of 6.234 min); FAB-MS 1050 (M^+); FAB-HRMS for $C_{64}H_{58}O_{14}$, calcd 1050.3830, found 1050.3837.

(2*R*,3*R*,4S,6*R*)-1-*O*-anthroyl-2,3,4,6-tetra-(*O*-*p*-methoxycinnamoyl)-8-nonene-1,2,3,4,6-pentol (42). HPLC (3μ YMC silica gel, 2% THF/CH_2Cl_2, retension time of 5.287 min); FAB-MS 1050 (M^+); FAB-HRMS for $C_{64}H_{58}O_{14}$, calcd 1050.3830, found 1050.3860.

(2*R*,3*R*,4*R*,6*R*)-1-*O*-anthroyl-2,3,4,6-tetra-(*O*-*p*-methoxycinnamoyl)-8-nonene-1,2,3,4,6-pentol (43). HPLC (5μ alltech silica gel, 27% ethyl acetate/hexane); FAB-MS 1050 (M^+); FAB-HRMS for $C_{64}H_{58}O_{14}$, calcd 1050.3830, found 1050.3830.

(2*R*,3*R*,4*R*,6*S*)-1-*O*-anthroyl-2,3,4,6-tetra-(*O*-*p*-methoxycinnamoyl)-8-nonene-1,2,3,4,6-pentol (44). HPLC (5μ alltech silica gel, 25% ethyl acetate/hexane); FAB-MS 1050 (M^+); FAB-HRMS for $C_{64}H_{58}O_{14}$, calcd 1050.3830, found 1050.3842.

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