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Application of the Bichromophoric Exciton Chirality Method to the Stereochemical Elucidation of Acyclic Polyols

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The recently developed technique of bichromophoric derivatization extends the utility of the exciton chirality method. Selective introduction of *two types* of exciton chromophores to two different types of hydroxyl groups gives rise to highly characteristic CD curves. Pairs of chromophores are evaluated for two different applications: 1) an oligosaccharide linkage analysis, and 2) elucidation of stereochemistry in acyclic polyhydroxyl compounds with two or more stereocenters. For the latter application, selective introduction of the 9-anthroate chromophore (λ_{max} = 253 nm) at primary hydroxyls, together with the *p*-methoxycinnamate chromophore (λ_{max} = 311 nm) introduced at secondary hydroxyls of stereocenters, gives rise to highly characteristic CD spectra. Examination by this method of all diastereomeric D-tetrose and D-pentose diethyl dithioacetals indicates that the anthroate/methoxycinnamate bichromophoric approach is a promising method for assignment of stereochemistry in 1,2,3-triols, 1,2,3,4-tetrols, and other polyhydroxylated compounds.

INTRODUCTION

The exciton chirality method has proven to be a powerful tool for the determination of stereochemistry in organic molecules.[1] Compounds containing hydroxyl groups at stereocenters are particularly suitable because they may be derivatized to their *p*-bromobenzoates, and the stereochemistry of these can be assigned in a straightforward manner according to the dibenzoate chirality method. While the method is most widely used for rigid systems such as steroidal glycols, it has also been used for the assignment of configuration in acyclic diols,[2,3] amino alcohols,[4] and diamines.[4] In these cases, however, it is possible to assign only one or, in certain threo cases, only two chiral centers.

An exhaustive study of hexopyranoside tri- and tetrabenzoates demonstrated that the exciton chirality method could be used in an analysis of oligosaccharide linkage patterns.[5] This initial approach, however, necessitated concomitant sugar analysis and mass spectrometry for each resulting monosaccharide subunit. It was later found that addition of a red-shifted chromophore to hexopyranoside *p*-bromobenzoates resulted in complex CD spectra which are unique and characteristic, simultaneously indicating the identity and absolute configuration of the sugar residue in addition to the

linkage pattern.[6] These derivatives may be described as »bichromophoric«, *i. e.* containing *two different types* of chromophores.

When two different types of hydroxyl groups are selectively derivatized with two types of exciton chromophores in a »bichromophoric derivatization«, the CD spectra of such derivatives reflect a greater degree of information than it could be obtained if only a single type of exciton chromophore were used. While a variety of chromophore combinations could be used, we demonstrate here that certain pairings result in more distinctive, and therefore more useful, CD curves.

Finally, we introduce the 9-anthroate ester (λ_{max} = 253 nm) as a new exciton-coupling chromophore which may be introduced to primary hydroxyl groups of acyclic polyols selectively. When used in a »bichromophoric« derivatization together with the *p*-methoxycinnamate chromophore (λ_{max} = 311 nm) at secondary hydroxyls, the resulting derivatives display highly distinctive CD spectra for different stereochemical patterns. The preliminary results reported herein with all acyclic D-tetrose and D-pentose diethyl dithioacetals indicate that the assignment of three chiral centers in an acyclic polyol should be possible with a single CD measurement by using this bichromophoric exciton chirality approach in an empirical manner.

RESULTS AND DISCUSSION

Bichromophoric Derivatizations for Oligosaccharide Linkage Analysis

An oligosaccharide microanalysis which utilizes a bichromophoric derivatization scheme is based upon the differentiation of free hydroxyls from those involved in glycosidic linkages. The derivatization is similar to a variant of the conventional methylation analysis, where permethylation of the oligosaccharide, methanolysis of the glycosidic linkages, and acetylation of the liberated hydroxyls provide partially methylated and acetylated methyl glycosides for g.l.c./m.s. analysis. In the bichromophoric exciton chirality approach, the methyls which tag the free hydroxyls have been replaced with one type of exciton chromophore, and the acetates which tag the linkage positions have been replaced with a second chromophore whose λ_{max} is sufficiently red-shifted from the first.

A general bichromophoric derivatization scheme is represented in Figure 1, where B represents a bromobenzoate or a benzylic ether chromophore, and C represents a cinnamate chromophore. We have completed an exhaustive study of all possible glucoside,[6] galactoside,[7], and mannoside[8] compounds of type I, where B = *p*-bromobenzoate (λ_{max} = 245 nm) and C = *p*-methoxycinnamate (λ_{max} = 311 nm). The bromobenzoate/methoxycinnamate pair proved to be the optimal choice for CD studies, as the 33 possibilities (6 branching, 4 linear, and 1 terminal subunit per glycoside) are all easily distinguished on the basis of their »fingerprint« CD curves. Moreover, while such spectra may be used empirically, it was demonstrated that these characteristic CD spectra can be accurately calculated by the summation of the contributing pairwise chromophore interactions.[6,7]

However, glycosidic bonds in peracylated oligosaccharides are slow to hydrolyze and are subject to acyl migration under such conditions. For these reasons a benzylic ether chromophore which could be introduced by an initial perbenzylation of the oligosaccharide was sought. The *p*-phenylbenzyl (λ_{max} =

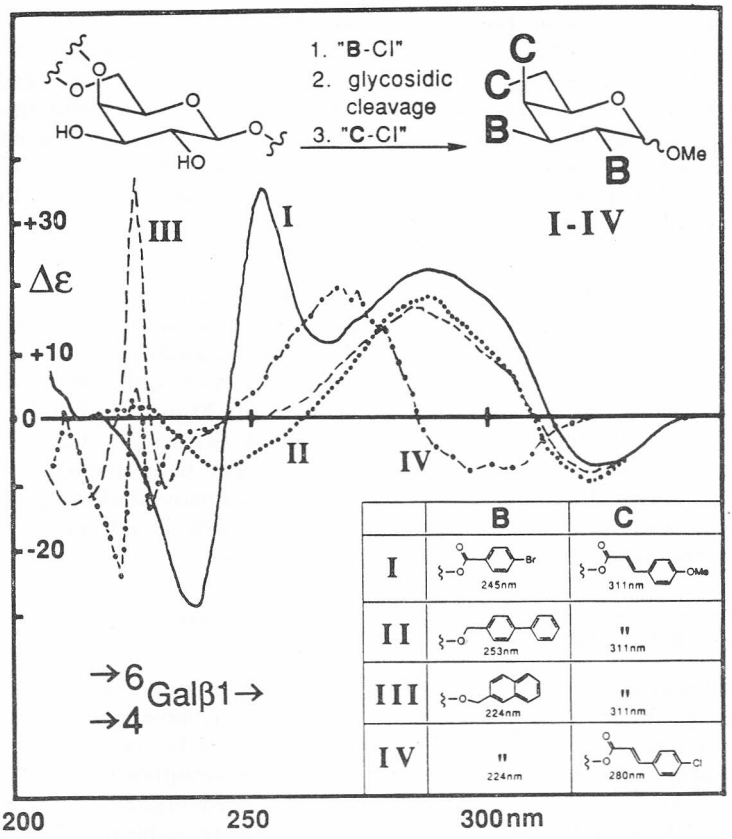


Figure 1. Comparison of the CD spectra from four different bichromophoric derivatizations of a 4,6-linked galactopyranoside residue in an oligosaccharide.

253 nm) chromophore had been thoroughly studied in this regard,[9] and so we investigated its potential in a bichromophoric derivative together with the *p*-methoxycinnamate chromophore (Figure 1, compound *II*). While the cinnamate/cinnamate couplet centered at 311 nm shows little change from that of compound *I*, the Cotton effects in the 250 nm region are relatively small and undefined. Oxidation of the phenylbenzyl ethers to the corresponding phenylbenzoates resulting in a 5—9 fold increase in amplitudes can be achieved with $RuCl_3/NaIO_4$,[9] but this would require an undesired additional step in the derivatization scheme.

The 2-naphthylmethylether ($\lambda_{max} = 224$ nm) was found to be a superior benzylic chromophore. This is due to the fivefold increase of the extinction coefficient compared with the phenylbenzyl chromophore ($\varepsilon = 100{,}000$ *vs.* $\varepsilon = 20{,}000$ for phenylbenzyl). In the analogous bichromophoric galactoside derivative together with the *p*-methoxycinnamate chromophore, the CD spectrum (Figure 1, compound *III*, B = 2-naphthylmethyloxy, C = *p*-methoxycinnamate) exhibits a very strong, distinctive Cotton effect at 225 nm. This is due to the overlapping naphthyl/naphthyl and naphthyl/cinnamate interactions. It

is interesting to note that the naphthyl/methoxycinnamate »hetero« coupling is strong even though their absorption maxima are separated by 86 nm. The magnitude of such coupling could be increased by using a cinnamate whose absorption maximum is less red-shifted, such as the *p*-chlorocinnamate chromophore ($\lambda_{max} = 280$ nm). The corresponding bichromophoric derivative utilizing the naphthyl/chlorocinnamate pair is shown as compound *IV* (Figure 1). The negative cinnamate/cinnamate couplet had now shifted down to be centered about 280 nm. The 220—250 nm region of the spectrum shows smaller yet distinctive maxima due to overlapping effects.

While the napththyl/cinnamate bichromophoric schemes may be workable, the initial pernaphthylmethylation reaction cannot be achieved in near quantitative yield as it would be desirable for a microanalytical technique. The bromobenzoate/methoxycinnamate pair provides not only the most desirable CD curve in the comparisons illustrated by Figure 1, but has already been fully demonstrated to provide an excellent distinction for an oligosaccharide microanalysis. Fortunately, conditions have been recently developed for efficient glycosidic cleavage of per-*p*-bromobenzoylated oligosaccharides without any concomitant acyl migration,[10] and work is currently underway to examine the scope of this derivatization sequence.

Bichromophoric Approach Applied to Chiral Acyclic Polyhydroxylated Compounds

We attempted to apply the same type of bichromophoric derivatization to the difficult problem of assigning stereochemistry in acyclic polyhydroxylated compounds containing several chiral centers. An initial derivatization which would introduce a single, strongly absorbing chromophore exclusively at a primary hydroxyl could be easily followed by a peracylation of the remaining hydroxyls with a red-shifted chromophore. The tri-*p*-biphenylmethyl ether was examined first as a chromophore which could be introduced to primary hydroxyls exclusively. A preliminary assessment of the coupling strength of this group was carried out with (*S*)-1,2-propanediol and the *p*-chlorobenzoate chromophore (see Figure 2, compound *V*).

Even though the absorption maxima of the two chromophores differed by only 13 nm, the resulting CD curve was disappointingly small and indistinctive. Attempts to derivatize the primary hydroxyl to the more strongly absorbing tri-*p*-terphenylmethyl ether proved unsuccessful as the latter group was quite labile.

Having observed the strong, sharp Cotton effects which can be achieved with the naphthyl chromophore (Figure 1, *III*), the 9-anthroic acid ester ($\lambda_{max} = 253$ nm) chromophore was examined since it is a strongly absorbing polyacene ($\varepsilon = 185{,}000$) which was previously demonstrated to exhibit a strong selectivity towards introduction at primary hydroxyls,[11] presumably due to steric interaction with the peri hydrogens of the anthracene ring. The exciton coupling power of the 9-anthroyl group was first examined together with the *p*-bromobenzoate chromophore, again on the (*S*)-1,2-propanediol system. This derivative (*VI*, Figure 2) exhibited a very strong negative couplet, indicating that the anthroyl chromophore was ideed superior to the tri-biphenylmethyl group initially examined. The anthroyl group was next exa-

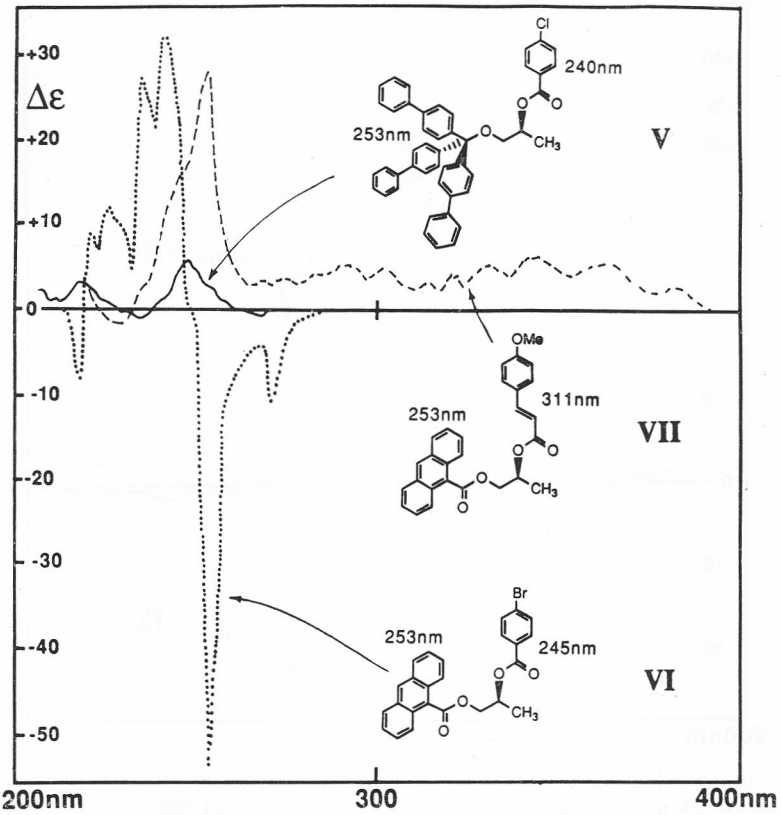


Figure 2. Evaluation of tri-*p*-biphenylmethyl ether *(V)* and 9-anthroate *(VI* and *VII)* groups as exciton chromophores selective for primary hydroxyls using *(S)*-1,2-propanediol.

mined with the *p*-methoxycinnamate chromophore in compound *VII*. The 280—400 nm region of the spectrum (Figure 2, *VII*) is difficult to interpret, presumably due to conformation mixing and additional interactions between the cinnamate chromophore and the transversal ^1L_a bands of the anthroate at 349, 366, and 384 nm. However, this derivative exhibited a strong, sharp positive Cotton effect at 253 nm, and such an effect would serve well to indicate the absolute stereochemistry of the first chiral center at C-2 in a series of two or more adjacent centers.

The 9-anthroyl chromophore was further examined on the (*R*)-1,3-butanediol system (Figure 3). First, together with the *p*-bromobenzoate at position-3 (compound *VIII*), the CD spectrum shows a strong, positive couplet with maxima at 241 and 253 nm. Similarly, the 1-*O*-anthroate 3-*O*-methoxycinnamate (*IX*) also shows a clear positive couplet with maxima at 253 and 289 nm and a strong shoulder at 311 nm. Additionally, small negative Cotton effects at 349, 366, and 384 nm comprise the negative first Cotton effects of couplets between each of them and the methoxycinnamate at 311 nm.

At this stage the 9-anthroate/*p*-methoxycinnamate pair was considered an excellent candidate for discrimination of acyclic polyols with two or more

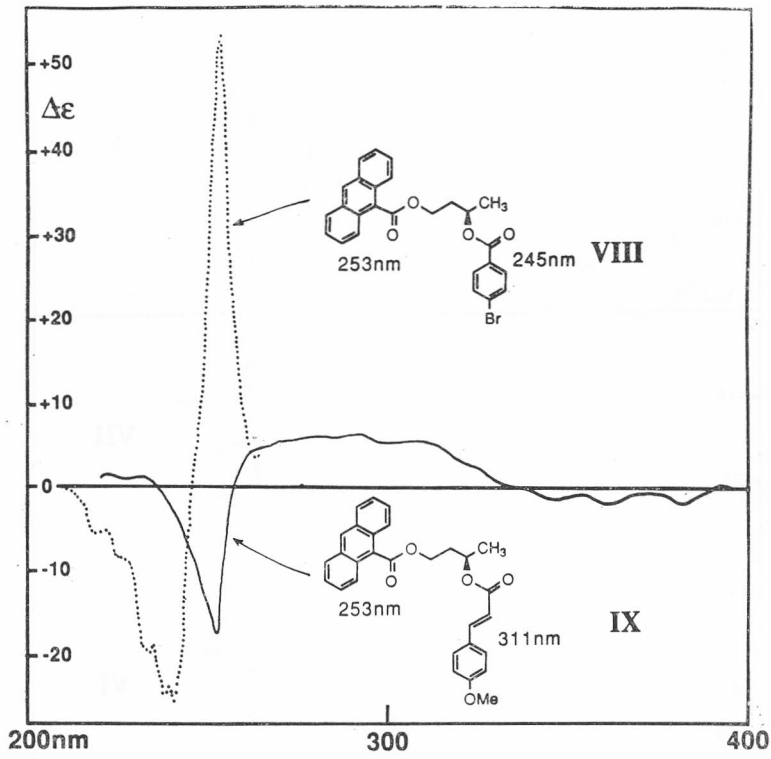
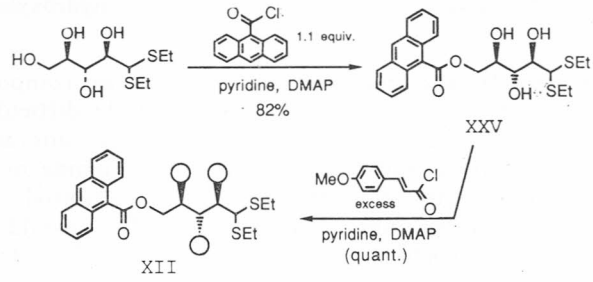


Figure 3. CD spectra of two bichromophoric derivatives of (*R*)-1,3-butanediol where the 9-anthroyl group has been selectively introduced at the primary hydroxyl.



Scheme 1

chiral centers. The derivatization sequence consisted of two simple reactions (Scheme 1): 1) Selective acylation at the primary hydroxyl could be achieved with the 9-anthroyl chloride to afford the monoester in good yield. These anthroate intermediates are highly fluorescent (365 nm active) and therefore easily purified on a small scale by silica chromatography (flash, or with micro quantities, HPLC). 2) Per-*p*-methoxycinnamylation of the remaining secondary hydroxyls could be achieved in high yields, and again the fluorescent anthracene facilitated easy purification. While only 20 nmols of material was

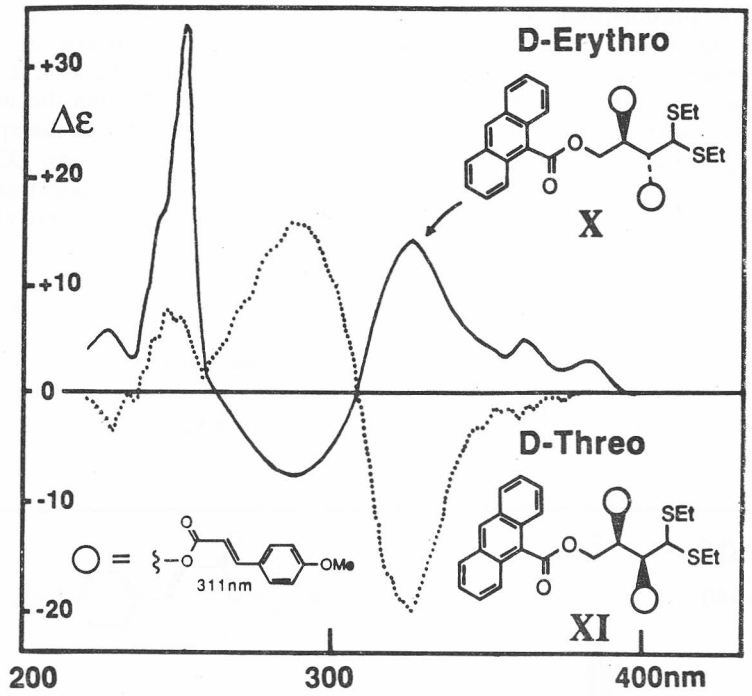


Figure 4. CD spectra of acyclic D-tetrose diastereomers derivatized with the anthroate/methoxycinnamate exciton chromophores.

used to record the CD spectra, larger amounts for detailed NMR studies and other analyses were easily prepared.

As an initial series of chiral acyclic polyols we chose to examine the diastereomeric D-tetrose and D-pentose diethyl dithioacetals, the most readily available compounds of this type.[12] First, in the cases with two chiral centers, the bichromophoric derivatives exhibited very distinctive CD curves (Figure 4). While both curves retain a positive Cotton effect at 253 nm, like the 1,2-diol (Figure 2, *VII*), compared to that of the 1,2-diol (*VII*), it is greater for the D-*erythro* derivative (Figure 4, *X*) and smaller for the D-*threo* derivative (*XI*). The small Cotton effect at 253 nm of *XI* ($\Delta\varepsilon = +6.7$) can be understood as a combination of the positive 253 nm Cotton effect of the 1,2-diol *VII* (Figure 2, $\Delta\varepsilon = +28.3$) and the negative CE of the 1,3-diol *IX* (Figure 3, $\Delta\varepsilon = -18.0$). In addition to these anthroate/cinnamate »hetero« interactions, the spectra also show nice cinnamate/cinnamate »homo« couplets centered about the cinnamate λ_{max}, 311 nm. In this region of the spectra the *erythro* and *threo* diasteromers are also well differentiated.

We next investigated derivatives with three chiral centers. The first two, D-ribo (*XII*) and D-arabino (*XIII*), both have the D-*erythro* configuration at the first two centers (counting from the anthroyl terminus). This D-*erythro* configuration is clearly reflected in the CD curves of both derivatives (Figure 5) by the large positive Cotton effects at 253 nm (Compare with D-*erythro* derivative *X*, Figure 4). The strength of interchromophoric exciton coupling

is inversely proportional to the square of the interchromophoric distance. Thus, the difference between the ribo and arabino derivatives is small at 253 nm because of the greater distance between the anthroate at C-5 and the differentiating cinnamate at C-2. However, a great distinction between the two is clearly seen in the cinnamate/cinnamate coupling region of the spectrum.

A similar trend is noted between the D-*xylo* (*XIV*) and D-*lyxo* (*XV*) derivatives as seen in Figure 6. Both of these have D-*threo* configuration at the first two chiral centers, and this is reflected by the smaller Cotton effects at 253 nm, the *xylo* being somewhat larger than the *threo* (Figure 4, *XI*), and the *lyxo* being somewhat smaller. Again, the two are extremely well differentiated in the cinnamate/cinnamate coupling region, the *xylo* showing a positive couplet centered about 311 nm, and the *lyxo* showing a very large negative couplet. This latter effect is due to the strong coupling between cinnamates at C-4 and C-2. It has been shown previously by Harada and coworkers that such 1,3 interactions have greater amplitudes than 1,2 interactions.[3]

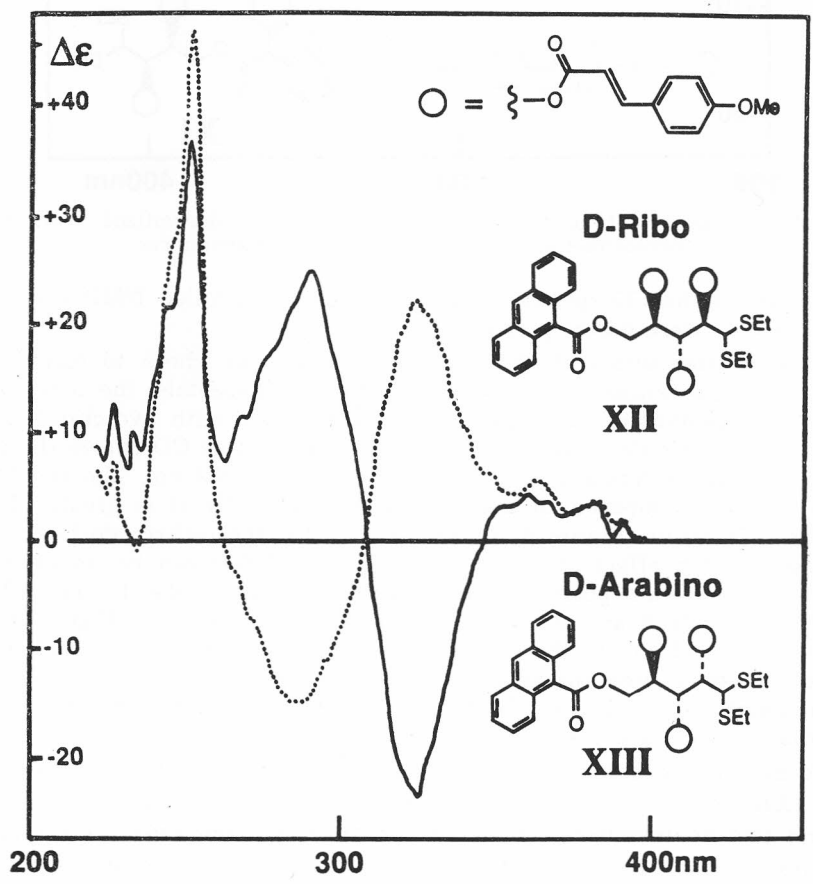


Figure 5. CD spectra comparing the D-ribose and D-arabinose diethyldithioacetals derivatized with the anthroate/methoxycinnamate chromophores

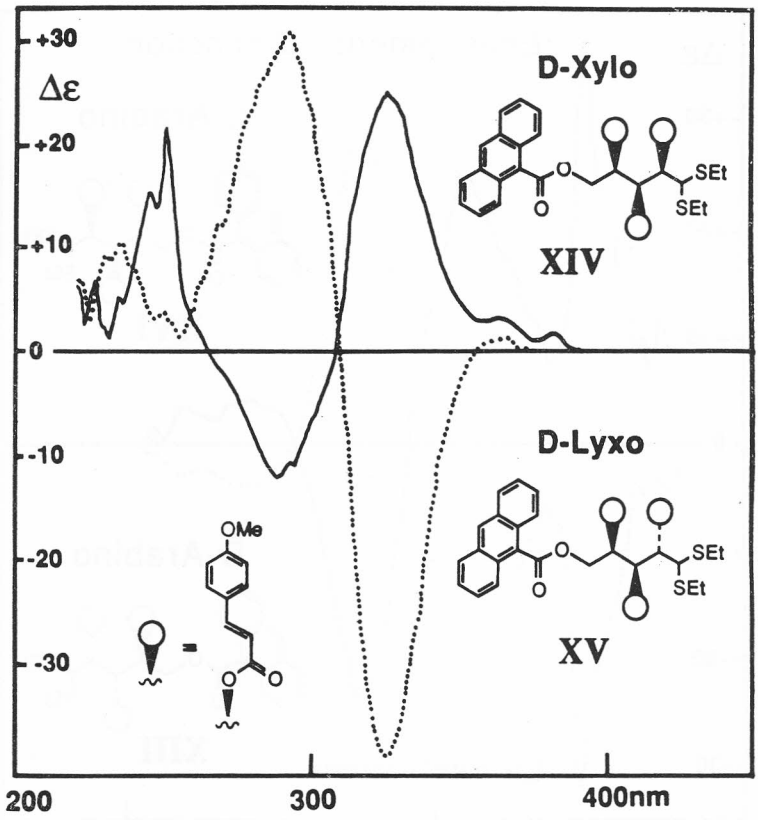


Figure 6. CD spectra comparing the D-xylose and D-lyxose diethyldithioacetals derivatized with the anthroate/methoxycinnamate chromophores.

Finally, the ability of this bichromophoric system to distinguish absolute stereochemistry is illustrated by the comparison of the D-arabino derivative (*XIII*) with the enantiomeric L-arabino derivative obtained from L-arabinose. The strong negative Cotton effect at 253 nm indicates the absolute stereochemistry of the first cinnamate proximal to the anthroate to be (4*S*).

CONCLUSION

The bichromophic exciton chirality method is a powerful technique for stereochemical problems with a higher degree of complexity. The success of the approach in differentiating sugar subunits of oligosaccharides in addition to indicating linkage pattern and absolute stereochemistry suggested its application to another difficult stereochemical problem, the assignment of several chiral centers in an acyclic molecule. These initial findings indicate that the selective bichromorphoric derivatization with anthroate/methoxycinnamate chromophores can provide an easy, empirically-based microanalysis of 1,2,3-triols, 1,2,3,4-tetrols, and other hydroxylation patterns found in natural products or in compounds obtained from their degradation. Work is currently

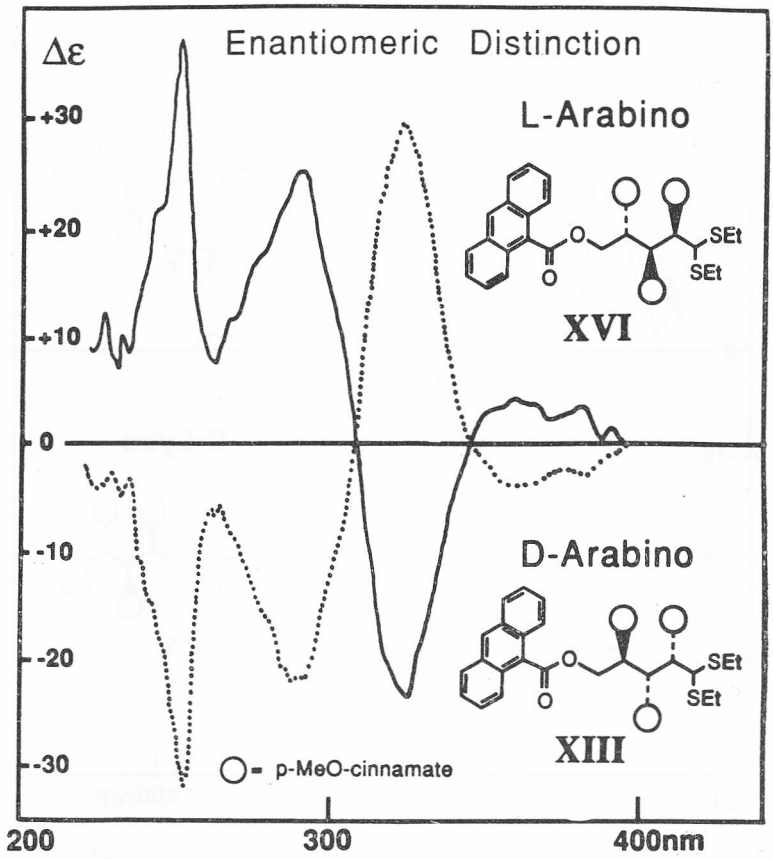


Figure 7. CD spectra of the enantiomeric arabinose diethyldithioacetals derivatized with the anthroate/methoxycinnamate chromophores indicating the ability to assign absolute configuration.

being directed towards assessing the generality of these findings, *e. g.*, in derivatives other than thioacetals which are more closely related to natural products, and towards a more theoretical interpretation of the CD spectra based upon conformational analysis and the recently demonstrated pairwise additivity of such multichromophoric systems.[6]

EXPERIMENTAL

All intermediates and final products were characterized by ^{1}H-NMR (Bruker WM250, 250 MHz). Prior to UV and CD measurements, all samples were purified by HPLC (EtOAc-hexane solvent systems on YMC SiO_2 gel, 5 μm at 2 ml/min) to ensure accuracy of the UV-determined concentrations. (The approximate values were used: anthroate monocinnamates $\varepsilon_{311\,nm} = 28{,}400$; anthroate dicinnamates $\varepsilon_{311\,nm} = 49{,}400$; anthroate tricinnamates $\varepsilon_{311\,nm} = 72{,}400$). UV measurements of 5—15 μM acetonitrile solutions were performed on a Perkin Elmer 320 UV spectrophotometer. CD spectra of the acetonitrile solutions were recorded on a JASCO 500A spectropolarimeter driven by a JASCO DP500N data processor.

The preparation of compound *I* has been previously described.[6] Compounds *II—IV* were prepared by *p*-phenylbenzylation[9] or 2-naphthylation of methyl 4,6-*O*-

benzylidene-α-D-galactopyranoside (XVII) followed by deprotection and acylation of the 4 and 6 positions.

Methyl 2,3-di-O-*(2-naphthylmethyl)-4,6*-O-*benzylidene*-D-*galactopyranosides* (XVIII A, B)

A solution of *XVII* (85 mg) with 2-naphthyl methyl bromide (140 mg, 2.1 equiv.) and 21 mg NaH (2.3 equiv.) was refluxed in dry THF overnight. Removal of the solvent *in vacuo*, followed by preparative TLC (3 : 7 EtOAc-hexane) of half of the crude mixture afforded *XVIIIA* as the major product in addition to a small ammount of the epimeric acetal *(XVIIIB)*.

A: ^{1}H-NMR ($CDCl_3$): 7.9—7.7 (m, 8H, aromatic H's), 7.6—7.4 (m, 8H, aromatic H's), 7.4—7.3 (m, 3H, aromatic H's), 5.46 (s, 1H, acetalic H), 5.06 (d, 12.1 Hz, 1H), 5.01 (d, 12.5 Hz, 1H), 4.92 (d, 12.5 Hz, 1H), 4.87 (d, 12.1 Hz, 1H), 4.80 (d, 3.6 Hz, 1H, H-1), 4.22—4.12 (m, 3H), 4.04 (dd, 3.3, 10.15 Hz, 1H), 3.95 (dd, 1.7, 12.5 Hz, 1H), 3.56 (bs, 1H), and 3.38 (s, 3H, OMe).

B: 7.87—7.7 (m, 8H, aromatic H's), 7.6—7.3 (m, 12H, aromatic H's), 6.26 (s, 1H, acetalic H), 5.20 (d, 12.0 Hz, 1H), 5.06 (d, 11.7 Hz, 1H), 4.95 (d, 11.7 Hz, 1H), 4.90 (d, 12.0 Hz, 1H), 4.79 (d, 3.5 Hz, 1H, H-1), 4.24 (dd, 3.6, 10.1 Hz, 1H, H-2 or H-3), 4.12 (bd, 3.5 Hz, 1H), 3.92 (m, 2H), 3.82 (dd, 1.65, 12.55 Hz, 1H), 3.38 (s, 1H), 3.35 (s, 3H, OMe).

Methyl 2,3-di-O-*(2-naphthylmethyl)*-α-D-*galactopyranoside* (XIX)

To the other half of the crude mixture of *XVIII*, MeOH and a catalytic amount of *p*-toluenesulfonic acid were added. After stirring at room temperature for 5 hours, the MeOH was removed *in vacuo* and the crude mixture was subject to flash chromatography (62 : 38 EtOAc-hexane) to afford 61 mg (86% for two steps) of the deprotected product.

^{1}H-NMR ($CDCl_3$): 7.87—7.67 (m, 8H, aromatic H's), 7.53—7.38 (m, 6H, aromatic H's), 4.96 (bd, 12.0 Hz, 2H), 4.86 (d, 11.7 Hz, 1H), 4.83 (d, 12.3 Hz, 1H), 4.71 (bs, 1H, H-1), 4.06 (bs, 1H), 3.94 (bs, 2H), 3.87 (m, 1H), 3.75 (m, 2H), 3.36 (s, 3H, OMe).

Methyl 2,3-di-O-*(2-naphthylmethyl)*-α-D-*galactopyranoside 4,6-di*-O-*p-methoxycinnamate* (III)

Compound *XIX* was subjected to the standard acylation procedure: excess acid chloride (*p*-methoxycinnamoyl chloride) in dry pyridine with DMAP (dimethylaminopyridine) catalysis. After stirring overnight at room temperature, pyridine was removed *in vacuo* and the crude mixture was subjected to preparative TLC (99 : 1 CH_2Cl_2-MeOH) to provide *III*.

^{1}H-NMR ($CDCl_3$): 7.85—7.65 (m, 8H, aromatic H's), 7.65 (d, 15.9 Hz, 1H, vinylic H), 7.62 (d, 15.9 Hz, 1H, vinylic H), 7.62—7.35 (m, 10H, aromatic H's), 6.87—6.84 (m, 4H, aromatic H's), 6.38 (d, 15.9 Hz, 1H), 6.26 (d, 15.9 Hz, 1H), 5.78 (bd, 3.1 Hz, 1H, H-4), 5.04 (d, 12.5 Hz, 1H), 4.99 (d, 11.5 Hz, 1H), 4.87 (d, 12.5 Hz, 1H), 4.78 (d, 11.5 1H), 4.78 (d, 3.5 Hz, 1H, H-1), 4.32—4.18 (m, 3H), 4.14 (dd, 3.3, 10.0 Hz, 1H), 3.96 (dd, 3.6, 10.0 Hz, 1H), 3.84 (s, 3H, OMe), 3.81 (s, 3H, OMe), and 3.43 (s, 3H, OMe).

Methyl 2,3-di-O-*(2-naphthylmethyl)*-α-D-*galactopyranoside 4,6-di*-O-*p-chlorocinnamate* (IV)

Compound *XIX* was treated with *p*-chlorocinnamoyl chloride under standard acylation conditions. Removal of the pyridine *in vacuo* followed by preparative TLC of the mixture (99 : 1 CH_2Cl_2-MeOH) afforded *IV* in quantitative yield.

^{1}H-NMR ($CDCl_3$): 7.86—7.63 (m, 8H, aromatic H's), 7.62 (d, 16.0 Hz, 1H, vinylic H), 7.62 (d, 16.0 Hz, 1H), 7.51—7.3 (m, 14H, aromatic H's), 6.45 (d, 16.0 Hz, 1H), 6.36 (d, 16.0 Hz, 1H), 5.76 (bd, 3.0 Hz, 1H, H-4), 5.03—4.97 (m, 2H), 4.87 (d, 12.4 Hz, 1H), 4.79 (d, 12.1 Hz, 1H), 4.85 (d, 3.2 Hz, 1H, H-1), 4.34—4.16 (m, 3H), 4.13 (dd, 3.3, 10.0 Hz, 1H), 3.94 (dd, 3.6, 10.0 Hz, 1H), 3.43 (s, 3H, OMe).

(S)-*1*-O-*(Tri*-p-*biphenylmethyl)-1,2-propanediol* (XX)

To a solution of tri-*p*-biphenylmethyl chloride[13] in dry CH_2Cl_2, 1 equivalent of silver triflate was added resulting in a strong red-violet color indicative of the tri-*p*-biphenylmethyl cation. Addition of 3 equivalents of pyridine reduced the color intensity, and upon addition of (*S*)-(+)-1,2-propanediol the color dissipated. After stirring at room temperature for 30 minutes, the reaction mixture was filtered, concentrated *in vacuo*, and subjected to preparative TLC (2 : 8 EtOAc-hexane) to give 8.2 mg (11%) *XX*.

^{1}H-NMR ($CDCl_3$): 7.65—7.25 (m, 27H, aromatic H's), 4.06 (m, 1H, H-2), 3.24 (dd, 3.4, 9.2 Hz, 1H, H-1), 3.12 (dd, 7.8, 9.2 Hz, 1H, H-1'), 2.44 (d, 3.1 Hz, 1H, OH), 1.15 (d, 6.5 Hz, 3H, Me).

(S)-*1-O-(Tri*-p-*biphenylmethyl)-1,2-propanediol 2*-O-p-*chlorobenzoate* (V)

To a solution of *XX* (6 mg) in dry CH_2Cl_2, 3 equivalents of *p*-chlorobenzoyl chloride, 4.5 equiv. pyridine, and 3 equiv. silver triflate were added. After stirring for 2 hours at room temperature the reaction mixture was subjected directly to preparative TLC (3 : 17 EtOAC-hexane) to afford *V*.

^{1}H-NMR ($CDCl_3$): 8.03 (d, 8.6 Hz, 2H), 7.6—7.27 (m, 29H), 5.45 (m, 1H, H-2), 3.38 (dd, 6.1, 10.0 Hz, 1H, H-1), 3.32 (dd, 3.9, 10.0 Hz, 1H, H-1'), 1.39 (d, 6.5 Hz, 3H, Me).

(S)-*1,2-Propanediol 1-(9-anthroate)* (XXI)

(S)-1,2-propanediol (11 mg) was treated with 1.1 equivalents of 9-anthroyl chloride[11] (39 mg) in dry pyridine with DMAP catalysis overnight. After removal of pyridine *in vacuo*, preparative TLC (2 : 3 EtOAc-hexane, 365 nm detection of fluorescent anthroate) afforded compound *XXI* (21 mg) in 50% yield in addition to small amount of diacylated product.

^{1}H-NMR ($CDCl_3$): 8.5 (s, 1H), 8.06—7.95 (m, 4H), 7.56—7.43 (m, 4H), 4.61 (dd, 3.2, 11.2 Hz, 1H, H-1), 4.44 (dd, 7.3, 11.2 Hz, 1H, H-1'), 4.24 (m, 1H, H-2), 2.15 (d, 4.0 Hz, 1H, OH), 1.31 (d, 3H, Me).

(S)-*1,2-Propanediol 1*-O-*(9-anthroate)-2*-O-p-*bromobenzoate* (VI)

Compound *XXI* was treated with excess *p*-bromobenzoyl chloride under standard acylation conditions. Flash chromatography (3 : 7 EtOAc-hexane) of the crude reaction mixture following pyridine removal *in vacuo* afforded *VI* in quantitative yield.

^{1}H-NMR ($CDCl_3$): 8.5 (s, 1H), 8.06—7.9 (m, 6H), 7.63—7.55 (m, 2H), 7.47—7.30 (m, 4H), 5.58 (m, 1H, H-2), 4.80 (d, 4.9 Hz, 2H, H-1's), 1.50 (d, 6.6 Hz, 3H, Me).

(S)-*1,2-Propanediol 1*-O-*(9-anthroate)-2*-O-p-*methoxycinnamate* (VII)

Compound *XXI* (25 mg) was treated with excess *p*-methoxycinnamoyl chloride under the usual conditions. Flash chromatography of the reaction mixture afforded *VII* (35 mg) in 89% yield.

^{1}H-NMR (CD_3CN): 8.57 (s, 1H), 8.07—7.96 (m, 4H), 7.63 (d, 16.0 Hz, 1H), 7.55—7.43 (m, 6H), 6.90 (d, 8.8 Hz, 2H), 6.36 (d, 16.0 Hz, 1H), 5.42 (m, 1H, H-2), 4.87 (dd, 3.5, 11.9 Hz, 1H, H-1), 4.70 (dd, 6.4, 11.9 Hz, 1H, H-1'), 1.37 (d, 6.5 Hz, 3H, Me).

(R)-*1,3-Butanediol 1*-O-*(anthroate)* (XXII)

(R)-1,3-Butanediol (11 mg) was treated with 1 equivalent 9-anthroyl chloride (30 mg) under the usual conditions to afford, after flash chromatography (2 : 3 EtOAc-hexane) a small amount of diacylated product which eluted from the column first, in addition to a 55% yield (20 mg) of the desired monoester *XXII*.

^{1}H-NMR (CD_3CN): 8.48 (s, 1H), 8.04—7.96 (m, 4H), 7.57—7.43 (m, 4H), 4.83 (m, 1H, H-1), 4.68 (m, 1H, H-1'), 4.02 (m, 1H, H-3), 2.02—1.88 (m, 2H, H-2's), 1.27 (d, 6.2 Hz, 3H, Me).

(R)-*1,3-Butanediol 1-O-(9-anthroate)-3-O-p-bromobenzoate* (VIII)

Compound *XXII* was treated with *p*-bromobenzoyl chloride under the usual conditions to afford, after flash chromatography (1 : 3 EtOAc-hexane), compound *VIII* quantitatively.

^{1}H-NMR ($CDCl_3$): 8.47 (s, 1H), 8.02—7.93 (m, 4H), 7.72 (d, 8.7 Hz, 2H), 7.53—7.42 (m, 4H), 7.33 (d, 8.7 Hz, 2H), 5.37 (m, 1H, H-3), 4.86 (m, 1H, H-1), 4.78 (m, 1H, H-1'), 2.26—2.18 (m, 2H, H-2's), 1.40 (d, 3H, Me).

(R)-*1,3-Butanediol 1-O-(9-anthroate)-3-O-p-methoxycinnamate* (IX)

Compound *XXII* was treated with *p*-methoxycinnamoyl chloride under the usual conditions to afford, after flash chromatography (1 : 199 MeOH—CH_2Cl_2) compound *IX* quantitatively.

^{1}H-NMR (CD_3CN): 8.54 (s, 1H), 8.04—7.98 (m, 4H), 7.60—7.46 (m, 5H), 7.37 (d, 8.7 Hz, 2H), 6.86 (d, 8.7 Hz, 2H), 6.22 (d, 16.0 Hz, 1H), 5.17 (m, 1H, H-3), 4.73 (m, 1H, H-1), 4.64 (m, 1H, H-1'), 2.17—2.10 (m, 2H, H-2's), 1.31 (d, 6.4 Hz, 3H, Me).

D-*Erythrose diethyldithioacetal-4-O-(9-anthroate)* (XXIII)

D-Erythrose diethyl dithioacetal[12] (58 mg) was treated with 1 equivalent of 9-anthroyl chloride in dry pyridine with DMAP catalysis overnight. Following removal of pyridine *in vacuo*, the crude mixture was subjected to flash chromatography (1 : 99 MeOH—CH_2Cl_2) to afford 47 mg of compound *XXIII* (43%).

^{1}H-NMR ($CDCl_3$): 8.52 (s, 1H), 8.08—8.00 (m, 4H), 7.55—7.45 (m, 4H), 4.92 (dd, 3.0, 11.6 Hz, 1H, H-4), 4.82 (dd, 5.7, 11.6 Hz, 1H, H-4'), 4.31 (ddd, 3.0, 5.7, 6.7 Hz, 1H, H-3), 4.20 (d, 4.0 Hz, 1H, H-1), 3.86 (dd, 4.0, 6.7 Hz, 1H, H-2), 2.70 (q, 7.4 Hz, 2H, —CH_2—), 8.68 (q, 7.4 Hz, 2H, —CH_2—), 1.26 (t, 7.4 Hz, 3H, Me), and 1.11 (t, 7.4 Hz, 3H, Me).

D-*Erythrose diethyldithioacetal-4-O-(9-anthroate)-2,3-di-O-p-methoxycinnamate* (X)

Compound *XXIII* was treated with excess *p*-methoxycinnamoyl chloride under usual conditions to afford, after pyridine removal and flash chromatography (CH_2Cl_2), compound *X* as the single product.

^{1}H-NMR (CD_3CN): 8.58 (s, 1H), 8.10—7.98 (m, 4H), 7.68 (d, 16.0 Hz, 1H), 7.62 (d, 16.0 Hz, 1H), 7.57—7.44 (m, 8H), 6.96—6.86 (m, 4H), 6.38 (d, 16.0 Hz, 1H), 6.33 (d, 16.0 Hz, 1H), 5.84 (m, 1H, H-3), 5.68 (dd, 5.1, 6.6 Hz, 1H, H-2), 5.10 (dd, 3.0, 12.3 Hz, 1H, H-4), 4.84 (dd, 5.2, 12.3 Hz, 1H, H-4'), 4.26 (d, 5.1 Hz, 1H, H-1), 3.78 (s, 3H, OMe), 3.76 (s, 3H, OMe), 2.73—2.60 (m, 4H, $2CH_2$), 1.19 (t, 7.4 Hz, Me), and 1.17 (t, 7.4 Hz, Me).

D-*Threose diethyldithioacetal-4-O-(9-anthroate)* (XXIV)

D-Threose diethyl dithioacetal[12] (28 mg) was treated with 1.1 equivalent of 9-anthroyl chloride (34 mg) under the usual conditions to give, after pyridine removal and flash chromatography (1 : 99 MeOH—CH_2Cl_2), compound *XXIV* (21 mg) in 40% yield.

^{1}H-NMR ($CDCl_3$): 8.52 (s, 1H), 8.09 (dd, 0.7, 9.2 Hz, 2H), 8.00 (dd, 0.7, 9.2 Hz, 2H), 7.55—7.45 (m, 4H), 4.90 (dd, 7.0, 11.0 Hz, 1H, H-4), 4.60 (dd, 5.2, 11.0 Hz, 1H, H-4'), 4.50 (m, 1H, H-3), 4.06 (d, 9.0 Hz, 1H, H-1), 3.63 (ddd, 9.0, 2.5, 1.6 Hz, 1H, H-2), 3.38 (d, 2.5 Hz, OH), 2.72—2.55 (m, 4H), 1.24 (t, 3H, Me), and 1.21 (t, 3H, Me).

D-*Threose diethyldithioacetal-4-O-(9-anthroate)-2,3-di*-O-p-*methoxycinnamate* (XI)

Compound *XXIV* was treated with excess *p*-methoxycinnamoyl chloride under standard conditions to afford, after removal of pyridine *in vacuo* and flash chromatography (1 : 199 MeOH—CH_2Cl_2), the desired dicinnamate in quantitative yield. ^{1}H-NMR (CD_3CN): 8.55 (s, 1H), 8.07—8.02 (m, 4H), 7.66 (d, 15.9 Hz, 1H), 7.60—7.45 (m, 7H), 7.33 (d, 8.8 Hz, 2H), 6.92—6.84 (m, 4H), 6.37 (d, 15.9 Hz, 1H), 6.14 (d, 15.9 Hz, 1H), 5.92 (m, 1H, H-3), 5.64 (dd, 5.6, 5.8 Hz, 1H, H-2), 5.12 (dd 3.7, 12.4 Hz, 1H, H-4), 4.71 (dd, 4.6, 12.4 Hz, 1H, H-4'), 4.24 (d, 5.8 Hz, 1H, H-1), 3.80 (s, 6H, OMe), 2.72 (q, 7.4 Hz, 2H), 2.60—2.50 (m, 2H), 1.20 (t, 7.4 Hz, 3H, Me), and 1.03 (t, 7.4 Hz, 3H, Me).

D-*Ribose diethyldithioacetal-5*-O-*(9-anthroate)* (XXV)

D-Ribose diethyldithioacetal[12] (34.6 mg) was treated with 1.1 equivalents of 9-anthroyl chloride under the usual conditions to give, after pyridine removal and flash chromatography (1 : 99 MeOH—CH_2Cl_2), compound *XXV* (51 mg) in 82% yield.
^{1}H-NMR ($CDCl_3$): 8.50 (s, 1H), 8.11 (d, 8.6 Hz, 2H), 8.00 (d, 8.6 Hz, 2H), 7.58—7.43 (m, 4H), 4.91 (dd, 5.4, 11.5 Hz, 1H, H-5), 4.83 (dd, 3.3, 11.5 Hz, 1H, H-5'), 4.27 (m, 1H, H-4), 4.24 (d, 3.7 Hz, 1H, H-1), 4.07 (dd, 6.7, 7.8 Hz, 1H, H-3), 3.96 (dd, 7.8 Hz, 1H, H-2), 2.69 (q, 7.4 Hz, 2H, CH_2), 2.63 (q, 7.4 Hz, 2H, CH_2), 1.24 (t, 7.4 Hz, 3H, Me), and 1.23 (t, 7.4 Hz, 3H, Me).

D-*Ribose diethyldithioacetal-5*-O-*(9-anthroate)-2,3,4-tri*-O-p-*methoxycinnamate* (XII)

Compound *XXV* was treated with excess *p*-methoxycinnamoyl chloride under the usual conditions to afford, after pyridine removal and flash chromatography (CH_2Cl_2), compound *XII* as the single product.
^{1}H-NMR (CD_3CN): 8.57 (s, 1H), 8.08—7.95 (m, 4H), 7.75 (d, 16.0 Hz, 1H), 7.66 (d, 16.0 Hz, 1H), 7.63 (d, 16.0 Hz, 1H), 7.56—7.42 (m, 10H), 6.95—6.87 (m, 6H), 6.46 (d, 16.0 Hz, 1H), 6.36 (d, 16.0 Hz, 1H), 6.32 (d, 16.0 Hz, 1H), 5.93 (dd, 4.4, 6.3 Hz, 1H, H-3), 5.77 (m, 1H, H-4), 5.70 (dd, 4.4, 5.3 Hz, 1H, H-2), 5.10 (dd, 2.6, 12.2 Hz, 1H, H-5), 4.93 (dd, 6,9, 12.2 Hz, 1H, H-5'), 4.21 (d, 5.3 Hz, 1H, H-1), 2.74—2.58 (m, 4H, $2CH_2$), 1.17 (t, 7.4 Hz, 3H, Me), and 1.14 (t, 7.4 Hz, 3H, Me).

D-*Arabinose diethyldithioacetal-5*-O-*(9-anthroate)* (XXVI)

D-Arabinose diethyldithioacetal[12] was treated with 1.1 equivalents of 9-anthroyl chloride under the usual conditions to give, after pyridine removal and flash chromatography (1 : 99 MeOH—CH_2Cl_2), compound *XXVI*.
^{1}H-NMR ($CDCl_3$): 8.52 (s, 1H), 8.08 (d, 8.4 Hz, 2H), 7.99 (d, 8.6 Hz, 2H), 7.56—7.43 (m, 4H), 4.89 (dd, 2.7, 11.9 Hz, 1H, H-5), 4.81 (dd, 5.3, 11.9 Hz, 1H, H-5'), 4.18—4.10 (m, 2H), 4.03 (d, 9.3 Hz, 1H), 3.87 (d, 9.3 Hz, 1H), 2.90 (bs, 3H, OH's), 2.68—2.58 (m, 4H, $2CH_2$), 1.24 (t. 7.4 Hz, 3H, Me), and 1.20 (t, 7.4 Hz, 3H, Me).

D-*Arabinose diethyldithioacetal-5*-O-*(9-anthroate)-2,3,4-tri*-O-p-*methoxycinnamate* (XIII)

Compound *XXVI* was treated with excess *p*-methoxycinnamoyl chloride under the usual conditions to afford, after pyridine removal and flash chromatography (CH_2Cl_2), compound *XIII* as the single product.
^{1}H-NMR (CD_3CN): 8.61 (s, 1H), 8.07—8.03 (m, 4H), 7.69 (d, 15.9 Hz, 1H), 7.65 (d, 15.9 Hz, 1H), 7.60 (d, 15.9 Hz, 1H), 7.57—7.40 (m, 10H), 6.92 (d, 8.7 Hz, 2H), 6.89 (d, 8.7 Hz, 2H), 6.83 (d, 8.8 Hz, 2H), 6.40 (d, 15.9 Hz, 1H), 6.35 (d, 15.9 Hz, 1H), 6.32 (d, 16.0 Hz, 1H), 6.00 (dd, 3.4, 6.0 Hz, 1H, H-3), 5.64 (m, 1H, H-4), 5.59 (dd, 3.4, 7.5 Hz, 1H, H-2), 4.99 (dd, 3.6, 12.2 Hz, 1H, H-5), 4.80 (dd, 5.9, 12.2 Hz, 1H, H-5'), 4.15 (d, 7.5 Hz, H-1), 3.80 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.78 (s, 3H, OMe), 2.68—2.53 (m, 4H), 1.15 (t, 7.4 Hz, 3H, Me), 1.07 (t, 7.4 Hz, 3H, Me).

L-*Arabinose diethyldithioacetal-5-O-(9-anthroate)-2,3,4-tri*-O-p-*methoxycinnamate* (XVI)

The L-aribino derivative was prepared analogously to the D-isomer described above. The ^{1}H-NMR, HPLC retention time, and UV spectrum were identical to those of the D-enantiomer.

D-*Xylose diethyldithioacetal-5-O-(9-anthroate)* (XXVII)

D-Xylose diethyldithioacetal[12] (128 mg) was treated with 1.1 equivalents of 9-anthroyl chloride (132 mg) under the usual conditions to give, after pyridine removal and flash chromatography (1 : 99 MeOH—CH_2Cl_2), compound *XXVII* (170 mg) in 74% yield.

^{1}H-NMR ($CDCl_3$): 8.50 (s, 1H), 8.10 (d, 8.5 Hz, 2H), 8.00 (d, 7.9 Hz, 2H), 7.56—7.45 (m, 4H), 4.74 (d, 6.1 Hz, 2H, H-5's), 4.28 (dt, 6.1, 2.4 Hz, 1H, H-4), 4.16 (dd, 2.4, 1.5 Hz, 1H, H-3), 4.07 (d, 9.2 Hz, 1H, H-1), 3.65 (dd, 1.5, 9.2 Hz, 1H, H-2), 2.72—2.57 (m, 4H), 1.23 (t, 7.6 Hz, 3H, Me), and 1.20 (t, 7.4 Hz, 3H, Me).

D-*Xylose diethyldithioacetal-5-O-(9-anthroate)-2,3,4-tri*-O-p-*methoxycinnamate* (XIV)

Compound *XXVII* (28 mg) was treated excess *p*-methoxycinnamoyl chloride under the usual conditions to afford, after pyridine removal and flash chromatography (CH_2Cl_2), compound *XIV* (39 mg) in 69% yield.

^{1}H-NMR (CD_3CN): 8.54 (s, 1H), 8.08—8.00 (m, 4 H), 7.67 (d, 16.0 Hz, 2H), 7.57—7.40 (m, 9H), 7.31 (d, 8.7 Hz, 2H), 6.87—6.82 (m, 6H), 6.38 (d, 15.9 Hz, 1H), 6.31 (d, 16.0 Hz, 1H), 6.17 (d, 15.9 Hz, 1H), 6.06 (dd, 3.9, 5.8 Hz, 1H, H-3), 5.85 (m, 1H, H-4), 5.63 (dd, 5.2, 5.8 Hz, 1H, H-2), 5.00 (dd, 3.7, 12.1 Hz, 1H, H-5), 4.74 (dd, 5.9, 12.1 Hz, 1H, H-5'), 4.19 (d, 5.2 Hz, 1H, H-1), 3.78 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.75 (s, 3H, OMe), 2.73—2.65 (m, 2H), 2.54—2.46 (m, 2H), 1.18 (t, 7.4 Hz, 3H, Me), and 1.03 (t, 7.4 Hz, 3H, Me).

D-*Luxose diethyldithioacetal-5-O-(9-anthroate)* (XXVIII)

D-Lyxose diethyldithioacetal[12] (19 mg) was treated with 1.1 equivalents of 9-anthroyl chloride (20 mg) under the usual conditions to give, after pyridine removal and flash chromatography (1 : 99 MeOH—CH_2Cl_2), compound *XXVIII* (30 mg) in 88% yield.

^{1}H-NMR ($CDCl_3$): 8.49 (s, 1H), 8.07 (d, 7.8 Hz, 2H), 7.99 (d, 8.0 Hz, 2H), 7.54—7.44 (m, 4H), 4.82 (dd, 7.5, 11.4 Hz, 1H, H-5), 4.71 (dd, 4.7, 11.4 Hz, 1H, H-5'), 4.45 (m, 1H, H-4), 4.16 (d, 3.5 Hz, 1H, H-11), 3.99—3.95 (m, 2H, H-3 and H-4), 2.67 (q, 7.4 Hz, 2H), 2.59 (q, 7.5 Hz, 2H), 1.23 (t, 7.4 Hz, 3H, Me), and 1.19 (t, 7.5 Hz, 3H, Me).

D-*Lyxose diethyldithioacetal-5-O-(9-anthroate) 2,3,4-tri*-O-p-*methoxycinnamate* (XV)

Compound *XXVIII* was treated with excess *p*-methoxycinnamoyl chloride under usual conditions to afford, after pyridine removal and flash chromatography (CH_2Cl_2), compound *XV* as the single product.

^{1}H-NMR (CD_3CN): 8.43 (s, 1H), 8.03 (d, 8.1 Hz, 2H), 7.95 (d, 7.8 Hz, 2H), 7.68 (d, 16.0 Hz, 1H), 7.58 (d, 15.9 Hz, 1H), 7.54—7.40 (m, 7H), 7.34 (d, 8.8 Hz, 2H), 7.27 (d, 8.7 Hz, 2H), 6.85 (d, 8.7 Hz, 4H), 6.73 (d, 8.8 Hz, 2H), 6.43 (d, 16.0 Hz, 1H), 6.26 (d, 15.9 Hz, 1H), 6.12 (d, 15.9 Hz, 1H), 5.93 (dd, 1.8, 6.8 Hz, 1H, H-3), 5.82 (m, 1H, H-4), 5.67 (dd, 5.5, 6.8 Hz, 1H, H-2), 5.02 (dd, 4.3, 11.8 Hz, 1H, H-5), 4.75 (dd, 6.3, 11.8 Hz, 1H, H-5'), 4.26 (d, 5.5 Hz, 1H, H-1), 3.79 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.74 (s, 3H, OMe), 2.73—2.58 (m, 4H), 1.18 (t, 7.3 Hz, 3H, Me), and 1.15 (t, 7.3 Hz, 3H, Me).

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SAŽETAK

Primjena metode bikromoforne ekscitonske kiralnosti na stereokemijska određivanja acikličkih poliola

William T. Wiesler i Koji Nakanishi

Nedavno razvijena tehnika bikromoforne derivatizacije proširuje upotrebljivost metode ekscitonske kiralnosti. Selektivno uvođenje *dva tipa* ekscitonskih kromofora u dvije različite vrste hidroksilnih skupina uzrokuje vrlo karakteristične CD krivulje. Parovi kromofora provjereni su za dvije različite primjene: 1) analizu veze u oligosaharidu, i 2) određivanje stereokemije acikličkih polihidroksi-spojeva sa dva ili više stereocentara. Kod ove posljednje primjene, selektivno uvođenje 9-antroatnog kromofora (λ_{max} = 253 nm) na primarne hidroksilne skupine, zajedno s *p*-metoksicinamatnim kromoforom (λ_{max} = 311 nm) uvedenim na sekundarne hidroksilne skupine na stereocentrima, uzrokuje vrlo karakteristične CD spektre. Ispitivanje tom metodom diastereomernih ditioacetala svih D-tetroza i D-pentoza pokazuje da je antroatni/metoksicinamatni bikromoforni pristup obećavajuća metoda za određivanje stereokemije 1,2,3-triola i 1,2,3,4-tetrola, kao i drugih polihidroksiliranih spojeva.