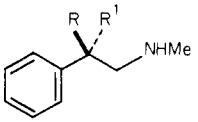
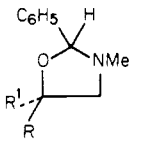
the limits of the ^1H NMR spectroscopic method used.[9] The deuterated amides **3a** and **3b** have been prepared in a study on the stereochemistry of the biological hydroxylation β to the nitrogen atom which is expected to occur in *N*-methyl-2-phenylethylamine in the biosynthesis of the alkaloid halostahine **4** in *Halostachys caspica*,[10] from β-*S* [β-^2H] halostahine **6** and from



4, R = OH; R^1 = H
5, R = OH; R^1 = ^2H
6, R = ^2H; R^1 = OH

the β-*R* isomer **5** through palladium-catalyzed ring opening of the oxazolidines **7** and **8**, respectively, a reaction known to proceed with inversion of configuration at the benzylic carbon.[11]



7, R = C_6H_5; R^1 = ^2H
8, R = ^2H; R^1 = C_6H_5

The values of β are about 2 orders of magnitude smaller than those observed for chiral secondary alcohols.[5] Values of the pitches were determined by means of the Grandjean–Cano method, which is based on the observation of the discontinuity lines appearing when a cholesteric mesophase is inserted in a cell of variable thickness.[12,13] A drop of cholesteric solution was put between the planoconvex lens and a glass plate,[14] both previously rubbed with tissue paper; the rubbing directions of the lens and plate were kept parallel to each other.[16] The preparation was observed with the polarizing microscope and showed the Grandjean–Cano disclinations as concentric circles. The separation of the disclination circles gives the pitch (*P*) through the relation[16]

$$r^2/2R = (n - \tfrac{1}{2})p/2 \qquad n = 1, 2, 3$$

where *R* is the radius of the lens and *r* the radius of the disclination circles. The handedness of the helices was deduced by placing a drop of the cholesteric solution between a glass plate rubber as before and a lens with concentric surface alignment (circular rubbing). With these boundary conditions, a double-spiral disclination appears; a right-handed helix gives a left-handed double spiral and vice versa.[17] The measurements were carried out between 16 and 19 °C.[18]

The concentrations were varied between 6 and 10 (mole of solute/mole of solution). The β values were constant within the experimental errors. No coexistence of cholesteric and isotropic phases were observed below 20 °C. The method requires only two drops of solution and a very small amount of chiral derivative.

Acknowledgment. We thank CNR (Rome) for financial support and Miss Anna Zaghini for technical assistance.

(9) (a) C. Fuganti, D. Ghiringhelli, and P. Grasselli, *J. Chem. Soc., Chem. Commun.*, 846 (1975); (b) D. Coggiola, C. Fuganti, D. Ghiringhelli, and P. Grasselli, *ibid.*, 143 (1976).

(10) G. P. Men'shikov and G. M. Borodina, *J. Gen. Chem. USSR (Engl. Transl.)*, **17**, 1569 (1947); *Chem. Abstr.* 2245 (1948).

(11) (a) C. Fuganti, D. Ghiringhelli, and P. Grasselli, *J. Chem. Soc., Chem. Commun.*, 1152 (1972); (b) L. Bernardi, C. Fuganti, and D. Ghiringhelli, *Gazz. Chim. Ital.*, **98**, 836 (1968).

(12) F. Grandjean, *C. R. Hebd. Seances Acad. Sci.*, **172**, 71 (1921).

(13) R. Cano, *Bull. Soc. Fr. Mineral Cristallogr.*, **911**, 20 (1968).

(14) It is important to coat both the lens and glass plate with aligning agents such as [(methylamino)propyl]triethoxysilane[15] in order to facilitate the measurements.

(15) F. J. Kahn, *Appl. Phys. Lett.*, **22**, 8 (1973).

(16) G. Heppke and F. Oestreicher, *Z. Naturforsch., A*, **32**, 899 (1977).

(17) G. Heppke and F. Oestreicher, *Mol. Cryst. Liq. Cryst. Lett.*, 245 (1978).

(18) Attempts to detect the chiralities by means of circular dichroism[5] failed owing to the strong linear dichroic effects.

Biosynthetic Intermediates to the Macrocyclic Trichothecenes

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The trichothecene group of terpenoid antibiotics may be classed into two distinct types: simple and macrocyclic.[1] We recently reported the isolation of trichodermadiene (**1**),[2] a compound whose structure is intermediate between these two classes in that the C4 ester side chain is analogous in structure to a portion of the macrocyclic ring [as in roridin E (**2**)],[3] but **1** is not macrocyclic. We now wish to report the isolation of a series of new trichothecenes related to both the simple and macrocyclic trichothecenes. Also, we present evidence that these new trichothecenes lie along the biosynthetic pathway to the macrocyclic trichothecenes.[4]

During the course of the workup of a large scale fermentation of *Myrothecium verrucaria*,[6] we isolated three sets of epimeric pairs of new trichothecenes, one set of which upon hydrolysis gave trichodermol (**3**) while the other two sets upon hydrolysis gave verrucarol (**4**). By a combination of ^1H and ^{13}C NMR spectroscopy and mass spectroscopy, it was evident that the former pair of isomers was related to trichodermadiene (**1**) in that the pendant C-6′, C-7′ epoxy group was hydrated yielding trichodermadienediols A (**5**) and B (**6**).[7] The absolute stereochemistry at C-6′ and C-7′ in **5** and **6** was established by transesterification (methanol) to give methyl esters **11** and **12**, respectively, whose absolute configurations have been established by total synthesis.[8]

(1) (a) Bamburg, J. R.; Strong, F. M. *Microb. Toxins* **1971**, *7*, 207. (b) Bamburg, J. R. *Adv. Chem. Ser.* **1976**, *149*, 144–162. (c) Doyle, T. W.; Bradner, W. T. In "Anticancer Agents Based on Natural Product Models"; Cassidy, J. M., Douros, J., Eds. Academic Press: New York, 1980; Chapter 2.

(2) Jarvis, B. B.; Midiwo, J. O.; Stahly, G. P.; Pavanasasivam, G.; Mazzola, E. P. *Tetrahedron Lett.* **1980**, 787.

(3) Tamm, Ch. *Fortschr. Chem. Org. Naturst.* **1974**, *31*, 63.

(4) The details of the biosynthesis of the various component parts of the macrocyclic trichothecenes have been worked out through the elegant work of Professor Tamm.[5]

(5) Tamm, Ch. In "Mycotoxins in Human and Animal Health"; Rodricks, J. V., Hesseltine, C. V., Mehlman, M. A., Eds., Pathotox Publishers: Park Forest South, IL, 1977; pp 209–228.

(6) Conducted at the Frederick Cancer Research Center under the supervision of Mr. Richard Geoghegan on *M. verrucaria*, ATCC No. 24571.

(7) **5**: mp 184–185 °C (EtOAc–petroleum ether); $[\alpha]^{28}D$ +26.3° (*c* 0.39, $CHCl_3$); UV_{max} (MeOH) 260 nm (log ϵ 4.53); mass spectrum (chemical ionization, methane gas reagent) *m/e* 405.2263 (M^+ + H, calcd 405.2277); ^1H NMR ($CDCl_3$) δ 0.76 (3 H, s, 14-H), 0.98 (3 H, s, 15-H), 1.13 (3 H, *d*, *J* = 6 Hz, 8′-H), 1.74 (3 H, s, 16-H), 2.60 (1 H, dd, *J* = 8 and 15 Hz, 3α-H), 3.03 (2 H, AB, *J* = 4 Hz, 13-H), 3.66 (1 H, d, *J* = 5 Hz, 11-H), 3.87 (1 H, d, *J* = 5 Hz, 2-H), 4.06 (1 H, m, 6′-H), 5.44 (1 H, d, *J* = 5 Hz, 10-H), 5.73 (1 H, d, *J* = 11 Hz, 2′-H), 6.09 (1 H, dd, *J* = 6 and 16 Hz, 5′-H), 6.64 (1 H, dd, *J* = 11 1 and 11 Hz, 3′-H), and 7.65 (1 H, dd, *J* = 11 and 16 Hz, 4′-H). **6**: an oil; $[\alpha]^{28}D$ −15.8° (*c* 0.80, $CHCl_3$); UV_{max} (MeOH) 260 nm (log ϵ 4.55); mass spectrum (chemical ionization, methane gas) *m/e* 405.2252 (M^+ + H calcd 405.2277); ^1H NMR ($CDCl_3$) δ 0.74 (3 H, s, 14-H), 0.98 (3 H, s, 15-H), 1.16 (3 H, d, *J* = 6 Hz, 8′-H), 1.73 (3 H, s, 16-H), 2.62 (1 H, dd, *J* = 8 and 15 Hz, 3α-H), 3.04 (2 H, AB, *J* = 4 Hz, 13-H), 3.66 (1 H, d, *J* = H_s, 11-H), 3.88 (1 H, d, *J* = 5 Hz, 2-H), 4.30 (1 H, m, 6′-H), 5.44 (1 H, d, *J* = 5 Hz, 10-H), 5.72 (1 H, d, *J* = 11 Hz, 2′-H), 6.16 (1 H, dd, *J* = 6 and 16 Hz, 5′-H), 6.66 (1 H, dd, *J* = 11 and 11 Hz, 3′-H), and 7.64 (1 H, dd, *J* = 11 and 16 Hz, 4′-H).

(8) Tulshian, D. B.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1981**, *103*, following paper in this issue.

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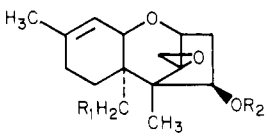


1, R_1 = H; R_2 = COCH=CHCH=CHCH(O)CHCH$_3$ (c, t, (*R*), (*R*))

3, R_1 = R_2 = H

4, R_1 = OH; R_2 = H

5, R_1 = H; R_2 = COCH=CHCH=CHCHOHCHOHCH$_3$ (c, t, (*S*), (*S*))

6, R_1 = H; R_2 = COCH=CHCH=CHCHOHCHOHCH$_3$ (c, t, (*S*), (*R*))

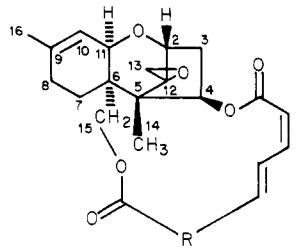
7, R_1 = OH; R_2 = COCH=CHCH=CHCHOHCHOHCH$_3$ (c, t, (*S*), (*S*))

8, R_1 = OH; R_2 = COCH=CHCH=CHCHOHCHOHCH$_3$ (c, t, (*S*), (*R*))

9, R_1 = OCOCH=C(CH$_3$)CH$_2$CH$_2$OH (*E*); R_2 = COCH=CHCH=CHCHOHCHOHCH$_3$ (c, t, (*S*), (*S*); 1″ 2″ 3″ 6″ 4″ 5″)

10, R_1 = OCOCH=C(CH$_3$)CH$_2$CH$_2$OH (*E*); R_2 = COCH=CHCH=CHCHOHCHOHCH$_3$ (1′ 2′ 3′ 4′ 5′ 6′ 7′ 8′; c, t, (*S*), (*R*))

c = cis, t = trans



roridin E (**2**), R = CH=C(CH$_3$)CH$_2$CH$_2$OCH(Cl)CHOHCH$_3$ (*E*)

roridin A, R = CHOHCHCH$_3$CH$_2$CH$_2$OCH(Cl)CHOHCH$_3$

verrucarin A, R = CHOHCHCH$_3$CH$_2$CH$_2$OC(=O)=O

MeOC(=O)CH=CHCH=CHCHOHCHOHCH$_3$ (c, t, (*S*), (*S*))

11

MeOC(=O)CH=CHCH=CHCHOHCHOHCH$_3$ (c, t, (*S*), (*R*))

12

The second set of epimers formed triacetates (pyridine–acetic anhydride), and again by a combination of NMR and mass spectroscopy the structures were shown to be trichoverrols A (**7**) and B (**8**).[9] The last set of epimers also formed the triacetates, but ^{13}C NMR spectroscopy showed the presence of 29 carbon atoms. The proton NMR spectra of these new compounds closely resemble the ^{1}H NMR spectrum of roridin E (**2**);[3] however, the ^{13}C spectra cannot be accommodated by any reasonable structure in which roridin E type structures possess three hydroxyl groups.[10] The structural assignments were made firm by relating the methyl esters obtained by methanolysis to those synthesized by Fraser-Reid and Tulshian.[8] These new trichothecenes, named trichoverrins A (**9**) and B (**10**),[11] are unique in that they possess all the necessary elements to be macrocyclic and yet are nonmacrocylic.[12]

Two interesting questions about these compounds are (1) what is their role, if any, in the biosynthesis of the macrocyclic trichothecenes and (2) how do the biological activities, especially those associated with the trichoverrins, compare with the bioactivities of the macrocyclic trichothecenes? Here we present data addressing the first question, and we have preliminary data on the second one, which suggest that the bioactivity of the trichoverrins more closely resembles that of the simple trichothecenes rather than that of the macrocyclic trichothecenes.[13]

An observation which struck us as interesting was that the observed ratio of the isolated A:B epimers was the same (1:2) for all three sets of epimers, and, therefore, these compounds appeared to be biosynthetically related to one another. Futhermore, trichoverrins A and B appear as likely candidates for precursors to roridin E and/or isororidin E,[15] since ring closure–dehydration of trichoverrins A and/or B would lead to roridin E and/or isororidin E. In separate experiments, 100 mg each of trichoverrins A (**9**) and B (**10**) were subjected to 7 days of aerobic incubation (1 L of each) with a resting culture of *M. verrucaria*.[16] From each of these experiments, ca. 50 mg each of recovered trichoverrin was isolated along with 12 mg of verrucarin A and 5 mg of verrucarin B. TLC and high-performance LC analysis indicated that appreciable amounts of roridin A and isororidin E also were present; however, compounds **5**–**8** were absent. Furthermore, in each case, the recovered trichoverrin was uncontaminated with its epimer, suggesting that **9** and **10** undergo conversion to the macrocycles via a common, and as yet undetermined, intermediate. A control experiment with the resting culture but without added trichoverrins yielded only trace amounts of verrucarins and roridins.[17] These experiments strongly support the thesis that the

(9) **7**: mp 177–179 °C (EtOAc-petroleum ether); $[\alpha]^{28}_D$ + 37.7° (*c* 0.45, $CHCl_3$); UV_{max} (MeOH) 260 nm (log ε 4.56); mass spectrum (chemical ionization, methane gas reagent) *m/e* 421.2226 (M^+ + H, calcd 421.2226); ^{1}H NMR ($CDCl_3$) δ 0.84 (3 H, s, 14-H), 1.19 (3 H, d, *J* = 6 Hz, 8′-H), 1.72 (3 H, s, 16-H), 2.46 (1 H, dd, *J* = 8 and 15 Hz, 3α-H), 3.00 (2 H, AB, *J* = 4 Hz, 13-H), 5.49 (1 H, d, *J* = 5 Hz, 10-H), 5.73 (1 H, d, *J* = 11 Hz, 2′-H), 6.66 (1 H, dd, *J* = 11 and 11 Hz, 3′-H), and 7.62 (1 H, dd, *J* = 11 and 16 Hz, 4′-H). **8**: an oil; $[\alpha]^{28}_D$ −3.3° (*c* 0.39, $CHCl_3$); UV_{max} (MeOH) 260 nm (log ε 4.53); mass spectrum (chemical ionization, methane gas reagent) *m/e* 421.2232 (M^+ + H, calcd 421.2226); ^{1}H NMR ($CDCl_3$) δ 0.84 (3 H, s, 14-H), 1.16 (3 H, d, *J* = 6 Hz, 8′-H), 1.74 (3 H, s, 16-H), 2.47 (1 H, dd, *J* = 8 and 15 Hz, 3α-H), 3.07 (2 H, AB, *J* = 4 Hz, 13-H), 4.18 (1 H, m, 6′-H), 5.50 (1 H, d, *J* = 5 Hz, 10-H), 5.74 (1 H, d, *J* = 11 Hz, 2′-H), 6.67 (1 H, dd, *J* = 11 and 11 Hz, 3′-H), and 7.61 (1 H, dd, *J* = 11 and 16 Hz, 4′-H).

(10) The chemical shifts of carbons 5″ and 6′ which flank the macrocyclic ether oxygen atom in the roridins are found ca. 8–10 ppm upfield in the trichoverrins relative to the corresponding resonances in the roridins (e.g., roridin E). Thus, ^{13}C NMR spectroscopy is an excellent means by which the trichoverrins can be distinguished from the roridins.

(11) **9**: mp 78–79 °C (EtOAc-petroleum ether); $[\alpha]^{28}_D$ −21.5° (*c* 0.39, $CHCl_3$); UV_{max} (MeOH) 260 nm (log ε 4.60); mass spectrum (chemical ionization, methane gas reagent) *m/e* 533.2714 (M^+ + H, calcd 533.2754); ^{1}H NMR ($CDCl_3$) δ 0.82 (3 H, s, 14-H), 1.21 (3 H, d, *J* = 6 Hz, 8′-H), 1.74 (3 H, s, 16-H), 2.53 (1 H, dd, *J* = 8 and 15 Hz, 3α-H), 3.04 (2 H, AB, *J* = 4 Hz, 13-H), 4.18 (2 H, s, 15-H), 5.52 (1 H, d, *J* = 5 Hz, 10-H), 5.75 (1 H, d, *J* = 11 Hz, 2′H), 5.90 (1 H, s, 2″-H), 6.67 (1 H, dd, *J* = 11 and 11 Hz, 3′-H), and 7.63 (1H, dd, *J* = 11 and 16 Hz, 4′-H). **10**: an oil; $[\alpha]^{28}_D$ −32.2° (*c* 0.57, $CHCl_3$); UV_{max} (MeOH) 260 nm (log ε 4.53); mass spectrum (chemical ionization, methane gas reagent) *m/e* 533.2722 (M^+ + H, calcd 533.2754); ^{1}H NMR ($CDCl_3$) δ 0.82 (3 H, s, 14-H), 1.15 (3 H, d, *J* = 6 Hz, 8′-H), 1.70 (3 H, s, 16-H), 2.48 (1 H, dd, *J* = 8 and 15 Hz, 3α-H), 3.04 (2 H, AB, *J* = 4 Hz, 13-H), 4.18 (2 H, s, 15-H), 5.51 (1 H, d, 5 Hz, 10-H), 5.73 (H, d, *J* = 11 Hz, 2′-H), 5.93 (1 H, s, 2″-H), 6.68 (1 H, dd, *J* = 11 and 11 Hz, 3′-H), 7.58 (1 H, dd, *J* = 11 and 11 Hz, 3′-H), 7.58 (1 H, dd, *J* = 11 and 16 Hz, 4′-H).

(12) Note that the A series (**5**, **7**, and **9**) and B series (**6**, **8**, and **10**) differ in configuration at C7′. This is also the analogous center of epimerization in the antileukemic baccharinoids (Kupchan, S. M. et al., *J. Org. Chem.* **1977**, *81*, 4221) which are closely related to roridins in structure. To date, the stereochemistry at positions analogous to C6′ and C7′ (see structure **10**) in roridins has not been established.

(13) The macrocyclic trichothecenes are perhaps the most toxic compounds known which contain only carbon, hydrogen, and oxygen atoms.[3] Both roridin A and verrucarin A are toxic at dose levels of 1–2 mg/kg in the in vivo P388 mouse leukemia test.[1c] Compounds **5**–**10** exhibited no toxicity (or activity) in this test system at dose levels of 32 mg/kg down to 1 mg/kg.[14] These data clearly show the importance of the macrocyclic ring system with respect to toxicity.

(14) We thank Dr. T. W. Doyle, Bristol Laboratories, Syracuse, NY, for making these data available to us.

(15) Matsumoto, M.; Minato, H.; Tori, K.; Ueyama, M. *Tetrahedron Lett.* **1977**, 4093.

(16) These experiments were performed with **9** and **10** which had been carefully purified by preparative high-performance LC (2–5% $MeOH/CH_2Cl_2$ gradient on a Whatman Magnum 9 silica gel column).

trichoverrins lie along the biosynthetic pathway to the macrocyclic trichothecenes. There are a number of details yet to be worked out including the point at which further elaboration of the double bond in the C-15 ester group occurs and at which point on the biosynthesis path the roridins and verrucarins diverge. The discovery of the role played by the trichoverrins in the biosynthesis of the macrocyclic trichothecenes suggests that conversion of verrucarol[19] to the highly biologically active macrocyclic trichothecenes via trichoverrins is a viable synthetic route. These and other aspects of this work currently are under investigation.

Acknowledgment. This investigation was supported by Grant Number CA 259667-01, awarded by the National Cancer Institute, DHHS. G. P. Stahly thanks Gillette Corporation for a fellowship. We thank Dr. Gary McCluskey of the Frederick Cancer Research Center, Frederick, MD, for mass spectral measurements.

(17) This experiment was repeated by using a mixture of [^{14}C]trichoverrin A and B (1 mg in 20 mL of culture).[18] The crude fermentation extract was subjected to TLC followed by autoradiographic analysis of the plate. A number of radioactive bands corresponding in descending order in R_f to verrucarins A, B, and J, isororidin E, and roridin A were clearly evident. Although this experiment supports the conclusions drawn from the preparative experiment, use of specifically labeled trichoverrin would yield a more definitive result.

(18) These experiments used ^{14}C-labeled trichoverrins synthesized by feeding ^{14}C-labeled sodium acetate to a culture of *M. verrucaria* (ATCC No. 24571). The experiments involving the biotransformations of **9** and **10** were conducted with a mutant strain of *M. verrucaria* developed by UV irradiation of the fungus obtained from the American Type Culture Collection; for details see G. Pavanasasivam, Ph.D. Thesis, University of Maryland, 1980.

(19) Readily available anguidine[1] has been transformed in high yield to verrucarol: see Tulshian, D. B.; Fraser-Reid, B. *Tetrahedron Lett.*, in press.

A Synthetic Route to the C4 Octadienic Esters of Trichothecenes from D-Glucose

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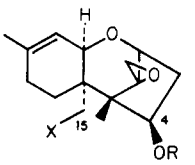
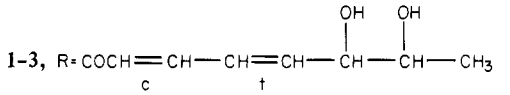
Received July 21, 1980

Considerable attention is currently focused upon the trichothecene family of sesquiterpenes owing, in part, to the wide range of biological activities displayed by this group of natural products.[1,2] This is particularly true for the macrocyclic members in which an intricate concentration of ether–ester–olefin–alcohol functionalities connects the C4 and C15 hydroxyl groups of the tricyclic backbone. Changes in the type and/or orientation of the functionalities elicit profound biological effects, judging from the wide spectrum of activities found in the various verrucarins and roridins.[2] Impressive gains in synthetic methodology relating to the tricyclic backbone have been reported[3] but, by contrast, there have been no reports concerning the components of the macrocyclic "ribbon".

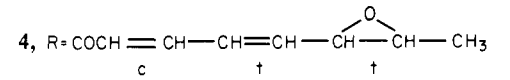
Impetus for appropriate methodology comes from the work of Jarvis et al. in the preceding communication, describing the novel esters, trichodermadinediols A and B (**1A** and **1B**), trichoverrols A and B (**2A** and **2B**), and trichoverrins A and B (**3A** and **3B**).[4]





1-3, R = COCH=CH–CH=CH–CH(OH)–CH(OH)–CH$_3$ (c, t)

1, (A and B) X = H
2, (A and B) X = OH
3, (A and B) X = OCOCH=C(CH$_3$)–(CH$_2$)$_2$OH (*E*)



4, R = COCH=CH–CH=CH–CH(O)–CH–CH$_3$ (c, t, t)

4, X = H

c = cis, t = trans

These "incomplete macrocycles", **1–3**, are reminiscent of trichodermadiene (**4**) reported earlier from the same laboratory.[5] The characterization undertaken by these workers revealed only the gross structures of the C4 esters. In this communication we outline a simple synthetic program that establishes structural details of the pendant C4 esters in **1–4** and which makes this class of dienic esters available with control of chiral as well as geometric centers.

Our synthetic approach (Scheme I) emanated from previous work in our laboratory which showed that triacetyl-D-glucal **5a** was converted into a mixture of pseudoglucal **6a** and the hydroxy aldehyde **7a** upon treatment with boiling water.[6,7] These substances are readily separated, but fractionation is unnecessary, since free-radical scavengers or darkness suppresses the formation of **7a**.[6] On the other hand, the excellent procedure of Perlin and co-workers affords **7a** in virtually quantitative yield,[8] an encouraging circumstance since the contiguous ene–diol moiety of **7** permits a synthesis that determines the stereochemistries, *absolute and relative*, of the C4 esters of compounds **1–4**.

Accordingly triacetyl-D-glucal[9] (**5a**) was converted into the 6-deoxy analogue **5b** (four steps in 51% overall yield),[10] which was subjected to the Perlin transformation,[8] whereby **7b** was obtained in 95% yield. In a similar way, triacetyl-D-galactal **8**[12] was converted into the D-threo analogue **9**.

A number of procedures for obtaining the dienic esters were tested on the aldehyde **7a** and the results, which are shown in Table I, speak for themselves. With regard to the desired cis,trans isomer **11**, the best procedure (entry 2) was found to be that of Peterson,[13] while the Horner–Emmons reagent (entry 1) used with such success in Kishi's laboratory[14] was very disappointing. Similarly the aldehydes **7b** and **9** were converted into the isomers **13a** and **14a**, respectively, which were deacetylated to **13b** and **14b** with sodium methoxide.[11]

The optical rotations of the dienes **13b** and **14b** being −42.06° and −48.00° are uncomfortably close, but fortunately their NMR

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(11) All new compounds gave satisfactory NMR, UV, and IR spectra and elemental analysis and/or high-resolution MS.
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