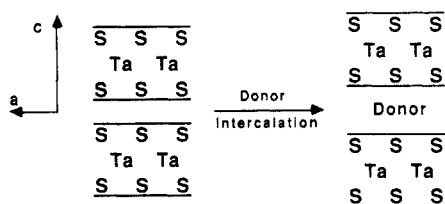


Scheme I



metallic materials it may be possible to image the surface sulfur atoms.

All imaging studies were carried out by using a modified commercial instrument (Digital Instruments, Santa Barbara, CA) and platinum-iridium tips; the STM was operated in the constant current mode.¹ Images were recorded in real-time on an analogue storage oscilloscope (without digital processing) and then photographed. Single crystals of 1T-TaS₂¹¹ were cleaved along the VdW bonded planes to yield atomically flat surfaces that are suitable for STM imaging. A typical example of a room temperature tunneling image for 1T-TaS₂ is shown in Figure 1a. In this top-view image the white spots, corresponding to peaks in the tunneling conductivity, form a hexagonal array with a peak spacing of 11.6 ± 0.2 Å. These peaks correspond to the expected periodic variation in electron density of the CDW state.^{9,10} Notably, the hcp surface sulfur plane, which has a sulfur-sulfur spacing of 3.35 Å, is not observed in this image, clearly demonstrating the importance of the electronic properties for this material.

To better understand the importance of this electronic contribution to the observed images we have taken advantage of the fact that a variety of electron donor compounds, such as amines and alkali metals, can be intercalated between the weakly bonded sulfur planes of TaS₂ (Scheme I).¹² The driving force for these intercalation reactions is believed to be a charge transfer to the tantalum d-band.¹³ We have investigated both the ethylenediamine (EDA) and lithium intercalation complexes of 1T-TaS₂. Diffraction studies¹³ of these complexes have shown that the only major structural change that occurs following intercalation is an expansion along the crystallographic *c*-axis.

The moderately air-stable EDA intercalation complex of 1T-TaS₂, TaS₂-1/4EDA, and the air-sensitive Li complex, Li-TaS₂, were prepared by using published procedures.^{13,14} A top view of the EDA complex recorded at the same resolution as TaS₂ is shown in Figure 1b. Although the CDW peaks are also prominent in this image (large white spots with a 11.5 ± 0.2 Å separation), smaller peaks are visible around the CDW maxima. The spacing between these peaks, 3.3 ± 0.2 Å, agrees closely with the S-S spacing;⁸ we assign these satellite peaks to the surface sulfur atoms. A reasonable explanation of these results is that by increasing the carrier concentration via the charge-transfer reaction,¹³ the metallic character of the material is enhanced.¹⁵ In support of this conclusion we find that the STM images of Li-TaS₂ show more atomic structure than TaS₂-1/4EDA.¹⁶ Clusters of peaks with

a peak-peak separation of 3.3 Å, the expected S-S spacing, can be clearly distinguished in Figure 1c; the spacing between these clusters is 10.5 ± 0.2 Å. These observations are consistent with the greater charge transfer in the Li system ($\approx 1e^-/\text{Li}$ is donated)^{13b} versus the EDA intercalation complex.¹⁷ The 10.2 Å periodicity in the clusters of atomically resolved peaks suggests that the CDW is still present in Li-TaS₂; the reduction in the CDW wavelength is also consistent with electron donation to the Ta d-band. Studies designed to obtain a more quantitative understanding of these effect of charge transfer on the images of TaS₂ are currently in progress.

In summary, we have shown for the first time that it is possible to delineate the electronic and structural contributions to STM images by utilizing charge-transfer intercalation reactions which systematically perturb a materials electronic properties. We believe that our approach and other well-defined chemical strategies will be useful in general for probing the structural and the electronic information contained in tunneling images. Studies such as these will be crucial for developing STM as a useful tool to probe the local molecular details of surface reactivity in situ.

Acknowledgment. We thank Prof. F. DiSalvo and P. Rauch for samples of TaS₂, the reviewers for helpful comments, and S. Kelly for help in setting up the inert atmosphere STM. C.M.L. acknowledges support from a Dreyfus New Faculty Award.

(17) A quantitative value for the degree of charge transfer in TaS₂-1/4EDA is not known; however, in the related NbS₂-1/2pyridine system 0.2 e⁻/nitrogen was reported to be transferred: Ehrenfreund, E.; Gossard, A. C.; Gamble, F. R. *Phys. Rev. B* 1972, 5, 1708.

A Novel Chiral Route to Substituted Tetrahydrofurans. Total Synthesis of (+)-Verrucosidin and Formal Synthesis of (-)-Citreoivridin

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Verrucosidin (1), a potent neurotoxin isolated from the fungus *Penicillium verrucosum* var. *cyclopium* by Burka and co-workers,¹ has been assigned structure 1 on the basis of the chemical, spectroscopic, X-ray crystallographic, and synthetic studies.^{2,3} Verrucosidin (1) is structurally related to citreoivridin (2),^{4,5} asteltoxin,⁶ and aurovertin B⁷ which are potent inhibitors of mitochondrial ATPase activity.^{4,8} The combination of their characteristic molecular architectures and their potent biological activities has stimulated significant synthetic efforts.^{9,10} We wish

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(14) The TaS₂-1/4EDA and Li-TaS₂ samples were prepared by reaction of single crystals of 1T-TaS₂ with EDA (140 °C) and BuLi (45 °C), respectively, in sealed tubes for 2-3 days. TaS₂-1/4EDA was imaged in air immediately after cleaving a crystal; greater stability was obtained by covering the freshly cleaved surface with an inert oil.^{5c} The air-sensitive Li-TaS₂ samples were handled at all times in a Ar-filled glovebox; surfaces were cleaved and either imaged under Ar or oil. Images were recorded over many areas of several independent samples with different STM tips for both the EDA and Li systems; Figure 1 (parts b and c) is representative of these recorded data.

(15) If 1T-TaS₂ had a normal metallic electronic structure, only the hcp surface sulfur atoms would be visible in the tunneling images.

(16) It is unlikely that this atomic structure is due to direct observation of the lithium because it is disordered at room temperature (F. DiSalvo, personal communication).

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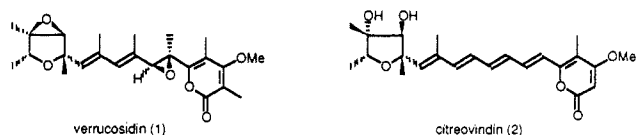
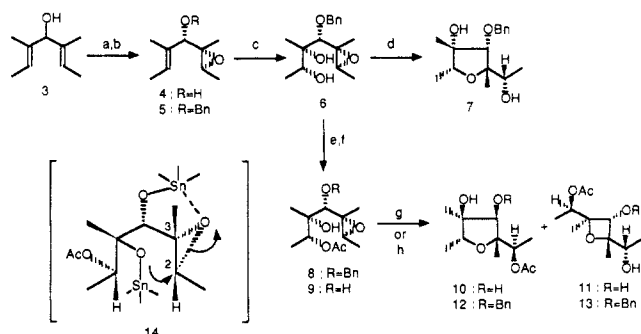
(5) Yamamura and co-workers have isolated more than 10 metabolites of *Penicillium citreoivridine* B. related to citreoivridin, see: Nishiyama, S.; Shizuri, Y.; Toshima, H.; Ozaki, M.; Yamamura, S.; Kawai, K.; Kawai, N.; Furukawa, H. *Chem. Lett.* 1987, 515 and earlier papers.

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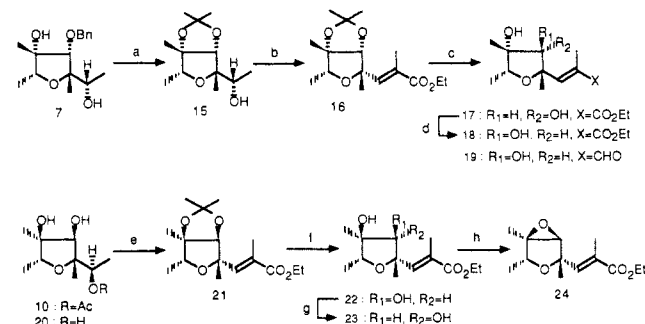
Chart 1

Scheme I^a

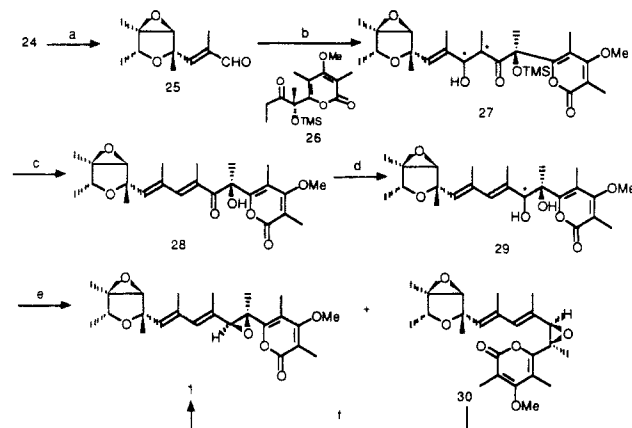
^a (a) Ti(O-*i*-Pr)₄, L(+)-DIPT, *t*-BuOOH, CH₂Cl₂, -40 °C, 74%; (b) C₆H₅CH₂Br, NaH, *n*-Bu₄NI (15 mol%), DMF, 88%; (c) OsO₄ (5 mol%), NMO, 50% aqueous acetone, 0 °C; (d) CSA (catalyst), CH₂-Cl₂, 89% overall from **5** (94:4:2); (e) Ac₂O, pyridine, 88%; (f) H₂, 20% Pd(OH)₂/C, EtOH, quantitative; (g) 2.6 equiv SnCl₄, CH₂Cl₂, -50 °C, 89% (10:11=48:1), 92% (12:13=2:1); (h) 2.6 equiv of BF₃·Et₂O, CH₂Cl₂, -30 °C, 80%.

to report here the first total synthesis of (+)-verrucosidin (**1**).

The latent symmetry in the carbon skeleton of the tetrahydrofuran unit of **1** allowed us to start the synthesis from asymmetric epoxidation of a σ -symmetrical prochiral divinylcarbinol derivative.¹¹ The titanium tartrate mediated asymmetric epoxidation¹² of the divinylcarbinol **3**, prepared by addition of *cis*-2-butenyllithium¹³ to methyl formate (50% based on *cis*-2-bromo-2-butene), took place enantio- and diastereoselectively to give the epoxy alcohol **4**,¹⁴ with an optical purity of >95% ee.¹⁵ After benzylation, hydroxylation¹⁶ of **5** proceeded with high diastereoselectivity (>15:1)¹⁷ to afford the diol **6** which was directly

Scheme II^a

^a (a) (i) H₂, 20% Pd(OH)₂/C, EtOH, (ii) CSA (catalyst), Me₂C(OMe)₂, acetone, reflux, 90% overall; (b) (i) MsCl, pyridine, DMAP (catalyst), (ii) DBU, toluene, 200 °C (sealed tube), (iii) O₃-Me₂S, CH₂Cl₂, -78 °C then Ph₃P=C(Me)CO₂Et, 61% overall; (c) Amberlite IR-120 resin (H⁺ form), 50% aqueous MeOH, 82%; (d) (i) SO₃·pyridine, Et₃N, DMSO, CH₂Cl₂, (ii) NaBH₄, THF, -78 °C to -30 °C, 80% overall (17:18=1:4); (e) (i) K₂CO₃, MeOH, (ii) a-ii, (iii) b-i, (iv) b-ii, (v) b-iii, 50% overall; (f) 80% aqueous AcOH, reflux, quantitative; (g) d, 80% overall (22:23=1:12); (h) (i) b-i, (ii) NaOEt, EtOH, 75% overall.

Scheme III^a

^a (a) (i) DIBALH, CH₂Cl₂, -78 °C, (ii) MnO₂, CH₂Cl₂, 97% overall; (b) 26, LHMDS, THF, -78 °C, 10 min, 60% (87% based on the consumed starting materials); (c) (i) MsCl, DMAP, CH₂Cl₂, (ii) DBU, CH₂Cl₂, (iii) CsF, EtOH, 82% overall; (d) LAH, THF, -90 °C, 81% (4:1); (e) c-i, 64% (1:30=2:3); (f) (i) 1 N H₂SO₄, THF, (ii) c-i, 60% overall (1:30=1:3).

used for the next reaction.¹⁸ Treatment of **6** with a catalytic amount of D-10-camphorsulfonic acid led to stereo- and regio-selective "exo-mode cyclization"^{19,20} to give the tetrahydrofuran **7** together with two unidentified isomers in a ratio¹⁷ of 94:4:2. On the other hand, treatment of the acetate **9**, prepared from **5** via **6** and **8**, with SnCl₄ at -50 °C led to stereo- and regioselective "endo-mode cyclization" to give the tetrahydrofuran **10** and the oxetane **11** in a ratio²¹ of 48:1. It is interesting to add that this SnCl₄-mediated cyclization of the benzyl ether **8** resulted in rather poor regioselection to give a 2:1 mixture²¹ of the tetrahydrofuran **12** and the oxetane **13**, while the BF₃·Et₂O-mediated cyclization of **8** proceeded with the opposite regioselectivity to give the oxetane **13** as a sole product. These results suggest that tight complexation

(18) Upon purification by silica gel chromatography, **6** cyclized partially to **7**.

(19) The preferred formation of **7** in the five exo-trigonal manner can be interpreted in terms of the Baldwin's rule, see: Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* 1976, 734. Baldwin, J. E.; Cutting, J.; Dupont, W.; Kurse, L.; Silberman, L.; Thomas, R. C. *J. Chem. Soc., Chem. Commun.* 1976, 736.

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(21) Determined by 500 MHz ¹H NMR analysis.

(9) Synthesis of citreoviridin: (a) Nishiyama, S.; Shizuri, Y.; Yamamura, S. *Tetrahedron Lett.* 1985, 26, 231. (b) Williams, D. R.; White, F. H. *J. Org. Chem.* 1987, 52, 5067. (c) Suh, H.; Wilcox, C. S. *J. Am. Chem. Soc.* 1988, 110, 470. Synthesis of citreoviridin: (d) Shizuri, Y.; Nishiyama, S.; Shigemori, H.; Yamamura, S. *J. Chem. Soc., Chem. Commun.* 1985, 292. (e) Williams, D. R.; White, F. H. *Tetrahedron Lett.* 1985, 26, 2529. (f) Bowden, M. C.; Patel, D.; Pattenden, G. *Tetrahedron Lett.* 1985, 26, 4793. (g) Hatakeyama, S.; Matsui, Y.; Suzuki, M.; Sakurai, K.; Takano, S. *Tetrahedron Lett.* 1985, 26, 6485. (h) Trost, B. M.; Lynch, J. K.; Angle, S. R. *Tetrahedron Lett.* 1987, 28, 375. Synthesis of asteltoxin: (i) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* 1985, 106, 4186. Synthesis of aurovertin B: (j) Nishiyama, S.; Toshima, H.; Kanai, H.; Yamamura, S. *Tetrahedron Lett.* 1986, 27, 3643. Synthesis of citreoviridinol and neocitreoviridinol: (k) Nishiyama, S.; Toshima, H.; Yamamura, S. *Chem. Lett.* 1986, 1973. Synthesis of episcitreoviridinol: ref 5.

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(15) Determined by 500 MHz ¹H NMR analysis of the (R)-MTPA ester derivatives of the epoxidation products obtained from the reaction of **3** with the Sharpless reagents derived from (+)- and (-)-DIPT.

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(17) Determined by HPLC analysis (ODS column, 3:1 MeCN-H₂O).

of the epoxy alcohol moiety to the metal center allows the hydroxy group to attack the epoxide in "endo-mode" rather than in "exo-mode" due to preferential polarization of the carbon-oxygen bond of C-2 position as in **14**.²²

The next phase of our efforts involved introduction of the requisite C-2 side chain and inversion of the C-3 chiral center. Debenzylation of **7** followed by selective protection as its acetonide afforded the acetonide **15**. Upon sequential dehydration, ozonolysis, Wittig reaction,²³ and deprotection,^{9d} **15** yielded the α,β -unsaturated ester **17**. According to the method developed by Yamamura and co-workers,^{3,9b} the C-3 hydroxyl group of **17** was then inverted through the oxidation-reduction sequence to give the diol **18**. The diol **18** thus obtained was identical in every respect (¹H NMR, IR, MS, α D, mp) with the authentic sample which we have previously prepared.^{9b} Since **18** has already been converted to (+)-citroviridin (**19**),^{9b} a key intermediate in the synthesis of (-)-citroviridin (**2**),^{9a,c} the synthesis of **18** constitutes a formal synthesis of (-)-citroviridin (**2**) as well as (+)-citroviridin (**19**).

Having established the method for the construction of the properly functionalized tetrahydrofuran unit, the synthesis of verrucosidin (**1**) was then investigated. Hydrolysis of the tetrahydrofuran **10** gave the triol **20** which was converted to the acetonide ester **21**²⁴ in the same manner as described for the preparation of **16**. Successive deprotection, inversion of the C-3 hydroxyl group, and formation of the epoxide through mesylation served to transform **21** to the epoxy ester **24**.

The epoxy ester **24** was successively subjected to reduction and oxidation to afford the aldehyde **25**. Aldol reaction of **25**²⁵ with the lithium enolate of the ketone **26**,²⁶ generated through the action of lithium hexamethyldisilazide, gave the aldol **27** as an inseparable diastereoisomeric mixture. Upon dehydration followed by desilylation, **27** yielded the enone **28** as a sole product. Reduction of **28** with LAH at -90 °C proceeded stereoselectively to give an inseparable 4:1 epimeric mixture²¹ of the diol **29**. Finally, mesylation²⁸ of this epimeric mixture of **29** directly furnished (+)-verrucosidin (**1**) and its stereoisomer **30** in a ratio²¹ of 2:3. ²⁹ The synthetic substance, mp 90-92 °C, [α]_D²⁶ +92.9° (c 0.42, MeOH), was identical with natural verrucosidin (**1**), mp 90-91 °C, [α]_D²⁶ +92.4° (c 0.25, MeOH), by spectroscopic (¹H and ¹³C NMR, IR, MS, UV) and chromatographic comparisons. It is worthwhile to mention that acid treatment of **30** followed by mesylation afforded a 1:3 mixture²¹ of verrucosidin (**1**) and **30** giving the procedure for recycling **30**.

Acknowledgment. We are grateful to Professor Shosuke Yamamura, Keio University, for providing spectra of synthetic intermediates. We also thank Professor Thomas M. Harris, Vanderbilt University, for a generous gift of natural verrucosidin and its ¹H NMR spectrum.

(22) For Lewis acid mediated nucleophilic opening of epoxy alcohols, see: Caron, M.; Sharpless, K. B. *J. Org. Chem.* **1985**, *50*, 1557. Molander, G. A.; Shubert, D. C. *J. Am. Chem. Soc.* **1987**, *109*, 576.

(23) Ireland, R. E.; Norbeck, D. W. *J. Org. Chem.* **1985**, *50*, 2198.

(24) The corresponding methyl ester, [α]_D¹⁸ +25.6° (c 0.72, CHCl₃) [lit.³ +23.6° (c 1.04, CHCl₃)], prepared by ester exchange reaction of **21** (KOH, MeOH), exhibited spectra properties (¹H NMR, IR, MS) in accord with those of the authentic methyl ester prepared by Yamamura and co-workers.³

(25) White, C. T.; Heathcock, C. H. *J. Org. Chem.* **1981**, *46*, 191.

(26) The ketone **26** was prepared in enantiomerically pure form from 6-ethyl-4-hydroxy-3,5-dimethyl-2-pyrone²⁷ (15 steps, 20% overall). Details of the synthesis will be reported in due course.

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(28) Upon mesylation (MsCl, *n*-BuLi, THF, -78 °C), retro-aldol reaction took place to give (-)-verrucosin (74%), [α]_D²⁷ -28.6° (c 0.30, MeOH) [lit.² [α]_D²⁷ -23.5° (c 0.40, MeOH)], whose spectral properties (¹H NMR, IR, MS) were identical with those reported.²

(29) Reduction of **28** with NaBH₄-CeCl₃³⁰ at -30 °C in methanol proceeded with opposite stereoselectivity giving a 1:4 epimeric mixture²¹ of **29** (96%) which, upon mesylation, gave **1** and **30** in a ratio²¹ of 1:5 (70%). These results suggest that the epoxide formation should involve not only the S_N2 type of reaction pathway but also a solvolytic reaction pathway where the isomer **30** would be produced preferentially. On the basis of this mechanistic consideration, we assumed that the major isomer of the LAH reduction of **28** might be the anti isomer.

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Supplementary Material Available: Optical rotations and spectral and analytical data for **4**, **5**, **7-13**, **15-18**, **21-24**, **26**, **28**, and **30** (4 pages). Ordering information is given on any current masthead page.

On the Water Content of Micelles: Infrared Spectroscopic Studies¹

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While experimental and theoretical studies²⁻⁷ continue to advance our understanding of micellar structure, the question of water penetration into the micellar interior remains somewhat unsettled.^{8,9} Recent calculations³ show that even though water molecules penetrate deeply into micelles, the central core is devoid of water. In this communication, direct experimental evidence is presented which confirms the recent calculations on micelles of sodium octanoate: these micelles do contain a central core devoid of water, while at the same time water penetrates at least up to position 7 of the octanoate chain.

Infrared spectroscopy is well suited to detect hydrogen bonding.¹⁰⁻¹³ In particular, such an interaction between a carbonyl group (acceptor) and water (donor) is used here to detect the presence of water in micelles. Sodium 7-oxooctanoate (7-oxo-Na-C₈)¹⁴ is the "probe", and the C=O stretching band of the keto group is used as the "sensor". There are many advantages in using a molecule such as sodium 7-oxooctanoate as the probe; e.g., it is a surfactant by itself,¹⁵ its cmc (\approx 0.25 M) is similar to that of Na-C₈; the C=O group in keto surfactants has been shown to provide a realistic measure of the polarity of the environment of micelles¹⁷ and lipid bilayers;¹⁸ and it may be safely assumed that individual molecules of 7-oxo-Na-C₈ are able to adopt all conformations adopted by those of Na-C₈.

(1) Issued as NRCC publication no. 29042.

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