

Table II. Chemical Shift Data for Samples of [3-²H₁] Allylthiourea in the Presence of Eu(fod)₃

| pre-cursor | resonance positions of allylthiourea, ppm | | | | rel intens of D _A and D _B |
|------------|---|----------------|----------------|----------------|---|
| | H _A | H _B | D _A | D _B | |
| 24 | 5.33 | 5.57 | 5.36 | 5.57 | D _A :D _B ≈ 1:4 |
| 25 | 5.39 | 5.62 | 5.38 | 5.60 | D _A :D _B ≈ 5:1 |

harvested and homogenized, and the homogenate was incubated at 37 °C for 12 h. Radioinactive allyl isothiocyanate was then added as carrier and labeled allyl isothiocyanate recovered by steam distillation. Treatment of the allyl isothiocyanate with ammonia produced crystalline allylthiourea (**5**, Scheme I) that was recrystallized to constant specific activity and constant ratio. The results of the three incorporation experiments are summarized in Table I (experiment numbers 1-3). The data clearly show that homomethionine is transformed into allylglucosinolate with the stereospecific removal of the 4 *pro-S* hydrogen atom.¹⁷

The second stage of the stereochemical analysis required determination of the spatial orientation of the 5 *pro-R* and 5 *pro-S* hydrogen atoms of homomethionine at C-3 of **5**. This determination was achieved by means of precursor incorporation experiments with DL-[5(*S*)- and 5(*R*)-²H₁]homomethionine. The synthesis of these chirally deuterated forms of the amino acid is summarized in Scheme IV. 3-Carbomethoxypropionyl chloride¹⁸ was converted to the acetal ester **18** by using methods previously devised in our laboratories.¹⁹ **18** was reduced with lithium aluminum deuteride and the resulting dideutero alcohol oxidized with PCC to give the deuterated aldehyde **19**. Reduction of **19** with the adduct derived from 9-borabicyclononane and (-)- or (+)- α -pinene¹¹ yielded the [1(*R*)- and 1(*S*)-²H₁] alcohols **20** and **21** (43%). The stereochemistry assigned to **20** and **21** follows from literature precedents.¹¹⁻¹⁴ Alcohols **20** and **21** were mesylated and the mesyl groups displaced with sodium methylthiolate (81%). If it is assumed that the displacement proceeds with inversion of configuration, then the alcohols **20** and **21** should produce the chiral thioethers **22** and **23**, respectively. Finally, **22** and **23** were converted to DL-[5(*S*)- and 5(*R*)-²H₁]homomethionine (**24**, **25**) by removal of the acetal functions and Bücherer synthesis (37%).

The two chirally deuterated forms of homomethionine were each mixed with DL-[2-¹⁴C]-**2** and the doubly labeled precursors administered to *A. lapathifolia* in the usual way. Workup after 24 h yielded radioactive allylthiourea in each case (Table I, experiment numbers 4, 5). Location of the deuterium label in each of the two samples of allylthiourea was accomplished by ²H NMR. The ¹H NMR spectrum of unlabeled allylthiourea at 90 mHz in CDCl₃ exhibits a multiplet at δ ca. 5.9 assignable to H_C, while H_A and H_B overlap to form a multiplet at δ ca. 5.3. Addition of Eu(fod)₃ resolves the multiplet at δ 5.3 into two doublets whose coupling constants ($J_{AC} = 9.3$ Hz, $J_{BC} = 17.3$ Hz) show that H_B has shifted downfield relative to H_A. The deuterium labeling pattern of the two samples of allylthiourea isolated in experiments 4 and 5 was elucidated by comparing the 400-mHz ¹H NMR spectrum of each sample in the presence of Eu(fod)₃ with the corresponding 61.4-mHz ²H NMR spectrum. The results of this comparison are shown in Table II. It can be seen that [5(*S*)-²H₁]homomethionine (**24**) yielded allylthiourea with most of the deuterium label present at the chemical shift position of H_B. Conversely, [5(*R*)-²H₁]homomethionine (**25**) gave allylthiourea with the higher level of deuterium enrichment at the chemical shift position of H_A.²⁰ From these observations and the data in

Table I, one can conclude that the conversion of [3-(methylthio)propyl]glucosinolate (**3**) into allylglucosinolate (**1**) proceeds by an anti elimination process. The possibility of a pericyclic elimination via the sulfoxide **4** is therefore ruled out.²¹

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Registry No. [1-¹⁴C]-**1**, 81624-87-5; [4(*RS*)-³H,2-¹⁴C]-**2**, 81624-88-6; [4(*R*)-³H,2-¹⁴C]-**2**, 81655-15-4; [4(*S*)-³H,2-¹⁴C]-**2**, 81655-16-5; [5(*R*)-²H,2-¹⁴C]-**2**, 81624-89-7; [5(*S*)-²H,2-¹⁴C]-**2**, 81624-90-0; DL-[2-¹⁴C]-**2**, 15995-78-5; [1-¹⁴C]-**3**, 81624-91-1; (*R*)-**4**, 27303-31-7; [³H-¹⁴C]-**5**, 81624-92-2; (\pm)-**6**, 81624-93-3; **7**, 81624-94-4; (*R*)-**8**, 81655-17-6; (*S*)-**9**, 81655-18-7; **10**, 81624-95-5; (*R*)-**11**, 81643-40-5; (*S*)-**12**, 81624-96-6; **13**, 81624-97-7; **14**, 81624-98-8; **14** aldehyde, 81624-99-9; DL-**15**, 81625-00-5; (*R*)-DL-**16**, 81625-01-6; (*S*)-DL-**17**, 81625-02-7; **18**, 81625-03-8; **19**, 81625-04-9; (*R*)-**20**, 81625-05-0; (*S*)-**21**, 81625-06-1; (*S*)-**22**, 81625-07-2; (*R*)-**23**, 81625-08-3; (*S*)-DL-**24**, 81625-09-4; (*R*)-DL-**25**, 81625-10-7; (*Z*)-[3-²H₁-a¹⁴C]-**5**, 81625-11-8; (*E*)-[3-²H₁-¹⁴C]-**5**, 81625-12-9; 1-chloro-3-(methylthio)propane, 13012-59-4; [1-¹⁴C]-3-(methylthio)propanenitrile, 81625-13-0; [1-¹⁴C]-3-(methylthio)propanoic acid, 81625-14-1; phenyl isocyanate, 103-71-9; [7-³H,4-¹⁴C]-1-phenyl-4-thio-5-allylbiuret, 81625-15-2; benzyloxyacetaldehyde, 60656-87-3.

(20) The presence of deuterium at both the H_A and H_B positions of the two allylthiourea samples is expected since the optical purity of the (+)- and (-)- α -pinene used in the 9-BBN reductions is ca. 80%.

(21) An anti elimination proceeding via sulfoxide **4** remains a viable possibility.

Total Synthesis of the First Molecular Möbius Strip

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Chemical topology, as defined by Wasserman in 1961,¹ deals with certain kinds of novel isomerism that may occur upon formation of macrocyclic rings.² As first discussed by Wasserman¹ and later by Schill,³ one may conceive of classes of molecules, including knotted rings and linked rings (catenanes), with interesting topological properties. In addition, a favorite subject of topology for mathematicians and chemists alike involves the properties of the Möbius strip, the one-sided, one-edged "isomer" of a cylinder with a single 180° twist about its long axis. In principle, it should be possible to prepare such structures by total synthesis. These interesting speculations have captured the imaginations of many chemists; however, of the structures mentioned above, only syntheses of catenanes have actually been demonstrated to date.^{1,3,4} In this communication, we report an efficient total synthesis of the first molecular Möbius strip (**2**)⁵ and its cylindrical isomer (**3**) via high-dilution cyclization of the tris-(tetrahydroxymethylene) (THYME) diol ditosylate (**1**) (Scheme I).

(1) (a) Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961**, *83*, 3789-3795. (b) Wasserman, E. *Sci. Am.* **1962**, *207*, 94-100.

(2) Mathematically, chemical topology deals with geometrical properties of molecules that remain invariant upon continuous deformation in three-dimensional space.

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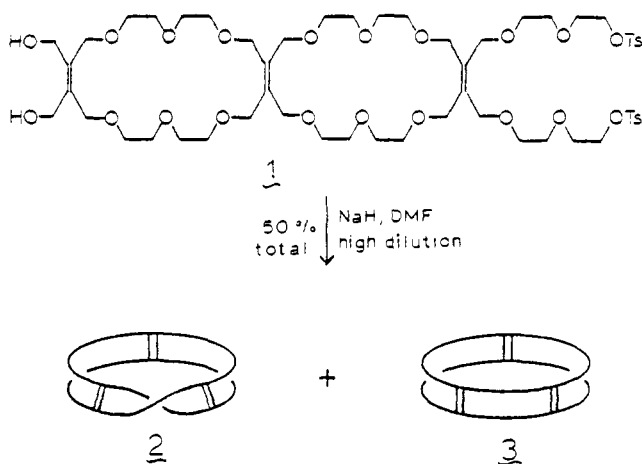
(5) The structure of macrotetracyclic polyether **2** may be considered as a graph possessing three four-sided figures. The surface defined by these figures is a Möbius strip. Though only a single enantiomer is shown, compound **2** formed in this manner is racemic.

(17) The degree of tritium retention in experiments 1-3 is slightly higher than that expected on the basis of experimental error. In order to ascertain if this slight excess might be due to a radiochemical contaminant, the allylthiourea obtained in experiment 3 was derivatized with phenylisocyanate to give 1-phenyl-4-thio-5-allylbiuret. After chromatography and recrystallization the tritium to carbon-14 ratio of the biuret was the same as that of the allylthiourea. The presence of a radiochemical impurity therefore seems unlikely.

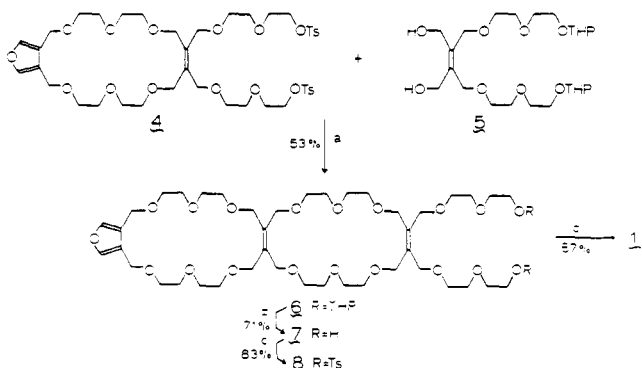
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Scheme I



Scheme II



^a 0.01 M in DMF, 10 molar equiv, NaH, room temperature, 48 h. ^b Dowex 50W-X12, CH₃OH/CH₂Cl₂, reflux, 18 h. ^c TsCl/pyr, 0 °C, 18 h. ^d (1) Pt anode, CH₃CN/aq NaHCO₃, trace LiBF₄, argon ebullition; (2) NaBH₄, 50% EtOH/H₂O.

Diol ditosylate **1** is prepared as shown in Scheme II by utilizing our recently reported strategy for synthesis of linear arrays of crown ether rings fused by the THYME unit.⁶ Intermolecular coupling of the readily available ditosylate **4**⁶ and diol **5**⁶ gives bis(crown ether) **6**⁷ in good yield. Conversion of bis(THP ether) **6** to ditosylate **8**⁷ via diol **7**⁷ is straightforward. Application of our method for generation of the THYME diol function then gives diol ditosylate **1** in satisfactory yield.

Examination of molecular models (CPK) suggests that treatment of diol ditosylate **1** with base under high-dilution conditions where intermolecular reactions are rare should afford two isomeric tetracyclic products, Möbius strip **2** and cylinder **3**, in approximately equal amounts. In principle, more highly twisted isomers may also result, but CPK models indicate such reactions are sterically disfavored.

In the event, addition of a dry DMF solution of diol ditosylate **1** to a suspension of oil-free sodium hydride in dry DMF over 12 h followed by removal of solvent at reduced pressure, aqueous work up (dichloromethane), flash chromatography⁸ of the crude product of Woelm N III alumina (32–63 μm), and elution with 50% dichloromethane/tetrahydrofuran then tetrahydrofuran gives only two products: a high *R_f* oil (TLC, alumina, tetrahydrofuran, *R_f* 0.65), and a low *R_f* solid (TLC, alumina, tetrahydrofuran, *R_f* 0.35, mp 107–108 °C after recrystallization from ethyl acetate/hex-

anes). The isolated yields of chromatographed products are 22% and 24%, respectively (average of four runs). The low *R_f* solid is shown unequivocally to be tris(THYME) cylinder **3**⁷ by single-crystal X-ray analysis.⁹ Consistent with its high symmetry (*D*_{3h}), THYME cylinder **3** shows only two resonances in the ¹H NMR spectrum,¹⁰ a broad singlet for the OCH₂CH₂O protons and an AB quartet for the allylic methylene protons, and only four carbon resonances in the ¹³C NMR spectrum.

We propose the tris(THYME) Möbius strip **2** as the only reasonable structure for the high *R_f* oil produced in this reaction. The symmetry of Möbius strip **2** is quite novel and deserves some comment before a description of the spectral properties. The highest symmetry any single conformation of compound **2** may possess is *C*₂. The molecule should, however, be conformationally mobile, as indicated by CPK models. Given this flexibility, there are many conformations with *C*₂ symmetry. But there are two fundamentally different kinds of *C*₂ conformations. One is represented by the drawing in Scheme I. The *C*₂ axis passes through the center of one of the double bonds, perpendicular to the axis of the double bond. In the other, the double bonds may be considered to move one-sixth of a circuit about the strip, affording a conformation in which one of the double bonds is "in the twist", and the *C*₂ axis passes through both olefinic carbons of that double bond. When viewed as a nonrigid system, compound **2** belongs to molecular symmetry group *C*₆ × *C*₂, a group of order 12 which is isomorphic to the point group *D*₆.¹¹ Interestingly, this high degree of symmetry implies the Möbius molecule **2** should have qualitatively identical spectral properties with cylinder **3** as is, in fact, observed.¹⁰ All chemically equivalent carbons of **2** are homotopic. However, even with the exchanges caused by molecular flexibility, the pairs of geminal protons lying on the single edge of the Möbius strip are diastereotopic.

The unlikely possibility that the high *R_f* oil is an oligomeric cylindrical molecule, also consistent with the observed NMR spectra, is ruled out by mass spectrometry and gel permeation chromatography. Thus, Möbius strip **2** and cylinder **3** show similar, but not identical, chemical ionization mass spectra, both giving very strong protonated molecular ions.¹² Upon chromatography on both 100- and 500-Å Waters μSytragel columns (toluene solvent), compounds **2** and **3** have identical retention times and are retained longer than the bicyclic furan ditosylate **8**. Both **2** and **3** show well-resolved peaks (*R_f* 1.0) upon coinjection with compound **8** on the 500-Å column. This result is expected given the high degree of connectivity of tetracyclic polyethers **2** and **3** relative to bicyclic compound **8**.

Since the Möbius strip **2** is chiral, whereas cylinder **3** is not, the NMR spectra of these compounds may be qualitatively different in a chiral environment. Specifically, the olefinic carbons of both **2** and **3** are homotopic. Thus, since cylinder **3** is achiral, only a single olefinic carbon resonance may be observed in a chiral environment. Racemic Möbius strip **2**, however, may show two

(9) Crystals of cylinder **3** were grown from a concentrated ethyl acetate/hexane solution; space group *PI-C*₁ (No. 2) with *a* = 11.841 (6) Å, *b* = 17.390 (9) Å, *c* = 11.551 (6) Å, *α* = 95.46 (4)°, *β* = 107.65 (4)°, *γ* = 91.30 (4)°, *V* = 2253 (2) Å³, *d*_o = 1.26 g/mL, *d*_c = 1.27 g/mL for *Z* = 2. Three-dimensional X-ray data were collected on a Nicolet PI automated four-circle diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and *θ*-2*θ* scans. Of the 5294 reflections measured in the full sphere up to 2*θ* = 35°, 2372 were determined to be observed [*F*_o² > 3.0σ(*F*_o²)]. The structure was solved by direct methods (MULTAN 78) and was refined with full-matrix least-squares procedures. All atoms were treated isotropically. Five atoms, involving two chains, exhibited disorder. No attempts were made to locate hydrogen atoms. At convergence, the residuals were *R* = 0.12 and *R*_w = 0.14. Full details of the structure analysis will be reported.

(10) Möbius strip **2**: ¹H NMR (CDCl₃) δ 3.65 (br s, 2 H, OCH₂CH₂O), 4.18, 4.29 (AB q, 1 H, *J* = 11.8 Hz, allylic methylene); ¹³C NMR (CDCl₃) δ 137.26, 70.91, 69.60, 68.56. THYME cylinder **3**: ¹H NMR (CDCl₃) δ 3.67 (br s, 2 H, OCH₂CH₂O), 4.16, 4.29 (AB q, 1 H, *J* = 11.8 Hz, allylic methylene); ¹³C NMR (CDCl₃) δ 136.68, 70.89, 69.77, 67.90.

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(12) Equal concentrations of Möbius strip **2** and cylinder **3** (2 mg/50 mL) in 1:1 acetonitrile/water were injected via a Hewlett-Packard bomb linked to an LC probe interfaced to the CI ion source of a Hewlett-Packard 5985 mass spectrometer. High ion currents were obtained in each case: (**2**) *m/z* 865 (33%, PH⁺), 391 (100%); (**3**) *m/z* 865 (100%, PH⁺), 391 (48%).

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(7) All new compounds except **2** and **3** were purified by flash chromatography on silica gel. All new compounds showed consistent ¹H and ¹³C NMR and IR spectra and gave satisfactory combustion analyses except **2**, which, after several attempts, gave a combustion analysis 0.5% low in carbon. These data are included in the supplementary material.

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olefinic carbon resonances in such an environment. Indeed, the ^{13}C NMR spectrum of cylinder **3** shows but a single olefinic carbon resonance in CDCl_3 saturated with (+)-2,2,2-trifluoro-9-anthrylethanol,¹³ while two olefinic carbon peaks are resolved ($\Delta\delta = 1.9$ Hz at 62.9 MHz) in the spectrum of Möbius strip **2** under identical conditions. The chirality of compound **2** represents a novel example of optical isomerism. There are no chiral centers, and no molecular rigidity is required to keep the optical antipodes of **2** nonequivalent. They owe their distinct character to connectivity only, and yet they have identical connectivity.

In conclusion, we have prepared and characterized the first molecular Möbius strip: a unique structure with novel and esthetically pleasing symmetry properties. Studies on resolution of compound **2**, cleavage of the double bonds of **2** and **3**, and extension of the synthesis to other topologically interesting structures, including more highly twisted cylinders, catenanes, knots, and multiply looped catenanes, are in progress.

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Registry No. **1**, 81617-29-0; (\pm)-**2**, 81617-30-3; **3**, 81617-31-4; **6**, 81617-32-5; **7**, 81617-33-6; **8**, 81617-34-7.

Supplementary Material Available: Spectral and analytical data on all new compounds reported, a listing of atomic positional and thermal parameters, and a drawing for the crystal structure of cylinder **3** (5 pages). Ordering information is given on any current masthead page.

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Picosecond Study of the Photodissociation of a Model Hemoprotein Compared to Hemoglobin

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We communicate the results of a comparative study of picosecond photodissociation experiments on the CO derivatives of hemoglobin, hemoglobin subunits, and unstrained chelated protoheme **1**-CO shown in Figure 1. These results suggest that the differences in the initial stages of the photodissociation for these molecules may be correlated with the geometry of the heme pocket, possibly the position of the proximal imidazole, although other geometrical effects cannot be ruled out at this time. Our objective in this study is to establish grounds for additional experiments of this type on the CO and O₂ forms of modified model compounds with the aim of determining the effect of heme geometry and/or strain on the photodissociation process. Such studies will be of importance in gaining additional insight,^{1,3} from the perspective

of photodissociation dynamics,^{4,5} into effects of tertiary heme structure on the affinity of the heme for the sixth axial ligand in the T and R forms of hemoglobin.^{6,7}

The picosecond absorption experiments reported here were conducted by pumping the Q band of the various heme-porphyrin complexes with use of the second-harmonic 530-nm light generated from a mode-locked neodymium-phosphate glass laser. The absorption changes in the Soret region were recorded over a 42-nm band width at certain fixed-time delays between the pump and probe pulses. Our double-beam sample-reference system was equipped with a triple spectrograph and a channel-plate intensified dual wide-area diode array detector. This detector was interfaced to a computer-based data acquisition system.² A comprehensive analytical and experimental evaluation of this apparatus can be found elsewhere.⁸ The hemoglobin and isolated chains were prepared by using standard procedures.⁹⁻¹¹ Purity of the CO, O₂, and deoxy derivatives was checked spectroscopically as well as by using electrophoresis. All samples were maintained at 5 °C at pH \sim 7.45 in 0.025 M Bistris-Tris buffer. The sample concentrations were adjusted to give a Soret absorbance of \sim 1.2 in a 1-mm path for HbCO and \sim 1.0 for **1**-CO. Traylor and co-workers discuss the synthesis and purification of unstrained protoheme **1**, which we used in CTAB solution at ambient temperature. They have also shown that the spectroscopic, thermodynamic, and kinetic properties of unstrained chelated protoheme are almost identical to R-state hemoglobin.³

Figure 1 shows our results on the initial stages of the photodissociation for protoheme **1**-CO and for HbCO at various delays, between the 530-nm optical pump pulse and the Soret interrogation pulse, ranging from -8 to 24 ps. Each of these pulses has a width (FWHM) of \sim 8 ps. The spectra recorded from -8 to +8 ps are in a temporal range where there is varying, but considerable, pump-probe pulse overlap. For the spectra recorded at negative delay, the peak of the probe pulse precedes the peak of the pump pulse. Earlier work in this area^{4,5} has shown that the difference spectrum¹² having a minimum centered at 418 nm is due to the bleaching of the CO compound, while the spectrum with maximum at \sim 436 nm corresponds to the appearance of the deoxy compound and/or photoproduct. Taking into account these facts and the noise limitations stated in Figure 1, comparison of the spectra at various delays reveals some important similarities and differences between these compounds in the early stages of photodissociation. The -7 and -8 ps spectra indicate that both compounds have undergone measurable bleaching with very little

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