

methyl substitution at the C-1 atoms has little effect in **3** and **4** ( $X = {}^{13}\text{CH}_3$ ), whereas substitution at the C-2 or C-3 atom decreases  ${}^3J_{\text{CC}}(180^\circ)$  by the same amount because of the equivalence of these positions. As a consequence, the equality of the calculated results and the near equality of the experimental results for 2-methyladamantane and 1-methyladamantane (**10** and **13**, respectively;  $X = {}^{13}\text{CH}_3$ ) is a unique situation in which the two  $\gamma$ -methylenes give equal contributions to  ${}^3J_{\text{CC}}(180^\circ)$ . Any change in the nature of  $X$  from a methyl or methylene group is expected to lead to different values of  ${}^3J_{\text{CX}}(180^\circ)$  for **10** and **13**. Because the interactions between hydrogens make negative contributions to the couplings, it is reasonable to expect that vicinal  ${}^3J_{\text{CX}}$  for **10** would be consistently greater in magnitude than the values for **13**. This is the case for all of the experimental data obtained for the two compounds. For example, the vicinal  ${}^{13}\text{C}$ - ${}^{13}\text{C}$  coupling constants for **10** and **13** with  $X = {}^{13}\text{CO}_2\text{H}$  are 4.2 and 3.6 Hz, respectively;<sup>6,7</sup> for  $X = {}^{13}\text{CH}_2\text{OH}$  the values are 3.54 and 3.27 Hz, respectively.<sup>13</sup> In the more complex physical situation in which  $X = {}^{119}\text{Sn}(\text{CH}_3)_3$  the experimental values are 60.0 and 51.1 Hz, respectively.<sup>14</sup> It seems likely that the recognition of the substituent  $\gamma$ -methyl effect will prove to be important in understanding other types of vicinal coupling involving  ${}^{13}\text{C}$ .<sup>15,16</sup>

**Acknowledgments.** This research was supported in part by the Robert A. Welch Foundation. Services of the University of Arizona Computer Center are gratefully acknowledged.

## References and Notes

- D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984-2990 (1964).
- D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315-5318 (1967).
- M. Barfield, S. A. Conn, J. L. Marshall, and D. E. Miller, *J. Am. Chem. Soc.*, **98**, 6253-6260 (1976).
- J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960-2964, 2965-2970 (1968).
- Contributions to vicinal  ${}^{13}\text{C}$ -H and  ${}^{13}\text{C}$ - ${}^{13}\text{C}$  coupling constants from orbital and spin-dipolar terms are thought to be quite small: A. C. Blizard and D. P. Santry, *J. Chem. Phys.*, **55**, 950-963 (1971); see ref 6.
- V. Wray, *J. Am. Chem. Soc.*, **100**, 768-770 (1978).
- J. L. Marshall and D. E. Miller, *J. Am. Chem. Soc.*, **95**, 8305-8308 (1973).
- M. Barfield, I. Burfitt, and D. Doddrell, *J. Am. Chem. Soc.*, **97**, 2631-2634 (1975).
- Conformational and substituent effects on  ${}^3J_{\text{CH}}$  have been investigated by R. E. Wasylshen and T. Schaefer, *Can. J. Chem.*, **51**, 961-973 (1973).
- Conformational and substituent effects on  ${}^3J_{\text{CC}}$  have been discussed in ref 3 and 8.
- Conformational and substituent effects on  ${}^3J_{\text{CF}}$  have been discussed by V. Wray, *J. Chem. Soc., Perkin Trans. 2*, 1598-1605 (1976).
- In previous studies, where coupling paths were of qualitative interest,<sup>3</sup> it was found to be sufficient to set the appropriate overlap integrals equal to zero; see J. L. Marshall, S. R. Walter, M. Barfield, A. P. Marchand, N. W. Marchand, and A. L. Segre, *Tetrahedron*, **32**, 537-542 (1976). However, because of the small effects of interest in this investigation, it seemed appropriate to eliminate the remaining terms as well; see V. Mamayev and Kh. Orazberdeiv, *Dokl. Akad. Nauk USSR*, **220**, 877-880 (1975).
- J. L. Marshall, S. A. Conn, and M. Barfield, *Org. Magn. Reson.*, **9**, 404-407 (1977).
- D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, C.-H. Lee, R. J. Mynott, J. L. Considine, H. G. Kuivila, and R. H. Sarma, *J. Am. Chem. Soc.*, **96**, 1640-1642 (1974).
- W. Kitching, D. Praeger, D. Doddrell, F. A. L. Anet, and J. Krane, *Tetrahedron Lett.*, 759-762 (1975).
- G. E. Buchanan and C. Benezra, *Can. J. Chem.*, **54**, 231-237 (1976).

M. Barfield\*

Department of Chemistry, University of Arizona  
Tucson, Arizona 85721

J. L. Marshall,\* E. D. Canada

Department of Chemistry, North Texas State University  
Denton, Texas 76203

M. R. Willcott, III

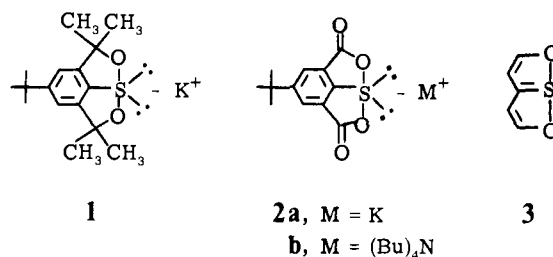
Department of Chemistry, University of Houston  
Houston, Texas 77004

Received July 11, 1978

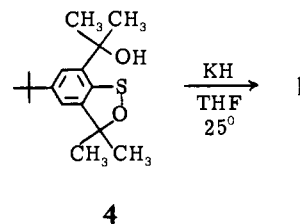
## Tricoordinate Hypervalent Sulfur Species. Sulfuranide Anions<sup>1</sup>

Sir:

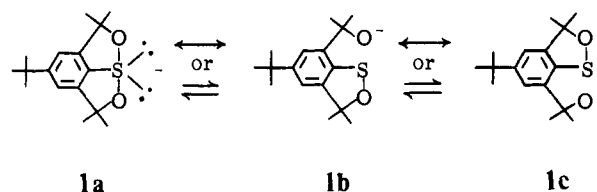
Over the past twenty years interest in trithiapentalene (6a-thiathiophene) and its derivatives, a class of tricoordinate sulfur(IV) species, has continued at a high level,<sup>2</sup> primarily reflecting chemists' fascination with the unusual chemical bonding in these compounds. Recently, a series of tricoordinate sulfuranes with apical halogen and equatorial  $\pi$ -acceptor ligands has been prepared by Arduengo and Burgess.<sup>3</sup> We now report the synthesis of tricoordinate anionic sulfurane salts **1** and **2**, salts of sulfuranide anions, and their reactions with electrophiles.



Compound **1**,<sup>4</sup> an anionic analogue of **3**<sup>5</sup> lacking its  $\pi$ -electron system, was obtained as a white precipitate by treatment of a THF solution of sultene **4**<sup>6</sup> with 1 equiv of KH.



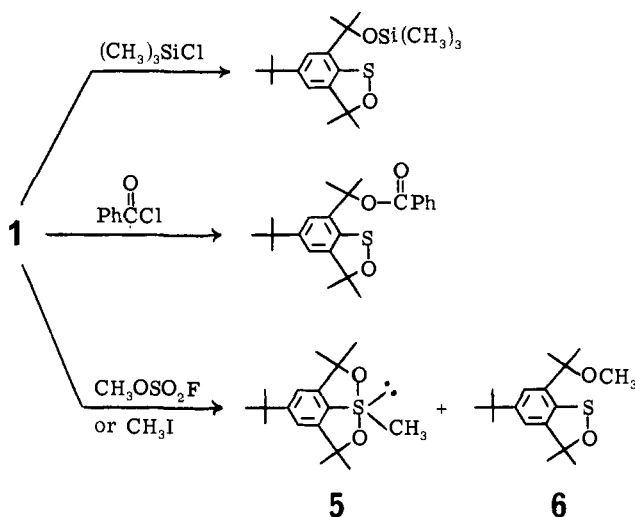
The structure of the anion of **1** may, a priori, be represented as a resonance hybrid of structures **1a**, **1b**, and **1c** or as an equilibrium mixture of structures of different geometries which may also be represented by **1a**, **1b**, and **1c**. Even at temperatures as low as  $-70^\circ\text{C}$  no evidence was seen in the  ${}^1\text{H}$  NMR spectra of **1** for unsymmetrical structures such as **1b** or **1c**.



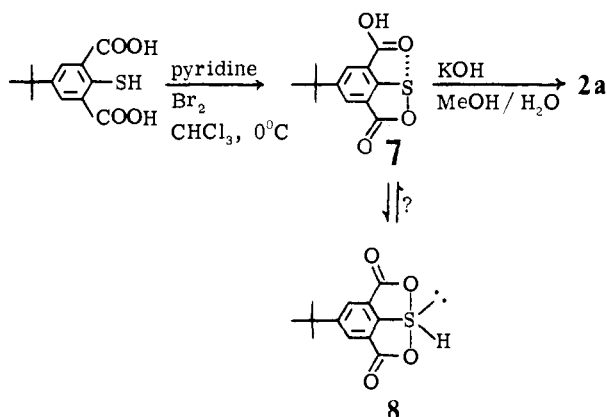
The  ${}^1\text{H}$  NMR spectrum of **1** shows substantial upfield shifts of all peaks ( $\delta$  ( $\text{Me}_2\text{SO}-d_6$ ) 6.68 (s, 2, ArH), 1.25 (s, 9,  $t$ - $\text{C}_4\text{H}_9$ ), 1.20 (s, 12,  $\text{OCCH}_3$ ) when compared with that of **4** ( $\delta$  ( $\text{Me}_2\text{SO}-d_6$ ) 7.03-6.99 (m, AB pattern, 2, ArH), 5.70 (s, 1, OH), 1.48 (s, 6,  $\text{OCCH}_3$ ), 1.41 (s, 6,  $\text{OCCH}_3$ ), 1.31 (s, 9,  $t$ - $\text{C}_4\text{H}_9$ )). This suggests negative charge delocalization into the benzene ring as well as the apical alkoxy ligands. The sharp singlet for the ring protons of **1** in THF solution, with 18-crown-6 as solubilizing agent, does not exhibit any sign of broadening even at  $-70^\circ\text{C}$ . In contrast, the aromatic ring protons of **4** have been found to be nonequivalent at room temperature.<sup>6</sup>

Reaction of a THF suspension of **1** with trimethylsilyl chloride or benzoyl chloride produces exclusively O-substituted products. Treatment with methyl fluorosulfonate or methyl iodide affords a mixture of sulfurane **5**<sup>7</sup> and sultene **6** (Scheme 1) in a ratio of 1:2 and 10:1, respectively. These results can be explained by applying the principle of hard and soft acids and

Scheme I



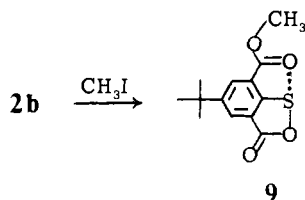
Scheme II



bases<sup>8</sup> since **1** is an ambident nucleophile with soft (S) and hard (O) loci for reaction with electrophiles.

The carbonyl analogue of **1** (**2a**) was prepared by reaction of cyclic sulfenyl carboxylate **7**<sup>9</sup> with methanolic KOH, as shown in Scheme II.

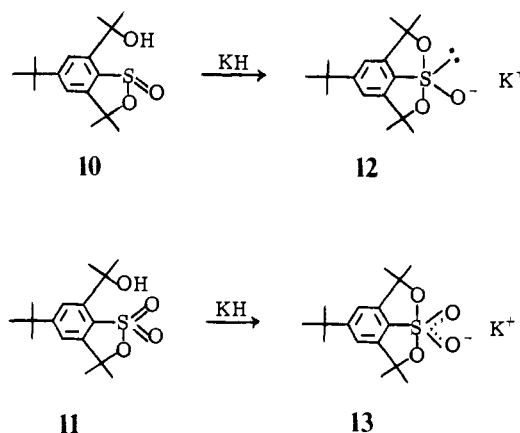
The infrared spectrum of **7** ( $\text{C}=\text{O}$  peaks at 1736 and 1670  $\text{cm}^{-1}$ ) is consistent with this structure rather than the hydrosulfurane tautomer, **8**. In contrast, the infrared spectrum of the analogous tetrabutylammonium salt (**2b**) in chloroform solution shows only a single carbonyl absorption at 1638  $\text{cm}^{-1}$  consistent with the postulated symmetrical structure of the anion. Reaction of **2b** with  $\text{CH}_3\text{I}$  gave only **9**, with no product



from nucleophilic attack at the sulfur atom detectable by NMR. Compound **9** shows infrared peaks at 1739 and 1670  $\text{cm}^{-1}$  ( $\text{CHCl}_3$ ) similar to those of **7**. (The carbonyl stretching frequencies quoted for **7** and **9** are consistent with the O-S interactions represented by the dotted lines in these structures, interactions expected<sup>10</sup> to lower the  $\text{C}=\text{O}$  stretching frequency of the carbonyl involved.)

Sultene **4** was successively oxidized by *m*-chloroperbenzoic acid to sultine (**10**) and sultone (**11**). Treatment of **10** and **11**

with KH in ether affords white precipitates of **12** and **13**, respectively, or their open chain analogues. The NMR spectra of the more soluble **10** and **11** show singlets for the aromatic protons in the presence of NaOH.



Further work on the structures of these hypervalent sulfur anions and their reactions with other electrophiles is underway in our laboratory.

The NMR spectroscopic evidence which we have presented is consistent with the symmetrical structures postulated for **1** and **2**. The alternative formulation of rapidly equilibrating unsymmetrical forms such as **1b** and **1c** cannot rigorously be ruled out. A similar ambiguity exists in interpretation of the experiment showing predominantly S-methylation of **1**. While electrophilic attack at the sulfur of a sulfuranide anion is expected, electrophilic attack on the sulfur of sulfonate esters such as **1b** is also possible. The short time scale of infrared spectroscopy ( $\sim 10^{-13}$  s) makes the observation of a single carbonyl stretching frequency in **2** more convincing evidence for a symmetrical sulfuranide structure for these species.<sup>10,11</sup>

**Acknowledgment.** This research was supported in part by a grant from the National Science Foundation (MPS75-17742), in part by fellowships from Abbott Laboratories, the Uniroyal Co., and the University of Illinois for P.H.W.L., and in part by Departmental Instrumentation Grants from the National Science Foundation and the National Institutes of Health.

## References and Notes

- (1) Part 37 in a series of sulfuranides. For part 36, see J. C. Martin, *ACS Symp. Ser.*, **No. 69**, 71 (1978). Presented, in part, as a Plenary Lecture at the 8th International Symposium on Organic Sulfur Chemistry, Portoroz, Yugoslavia, June 20, 1978.
- (2) For recent reviews, see R. Gleiter and R. Gygas, *Top. Curr. Chem.*, **63**, 49 (1976); R. J. S. Beer in "Organic Compounds of Sulphur, Selenium, and Tellurium", Vol. 3, D. H. Reid, Ed., The Chemical Society, London, 1975, p 494.
- (3) A. J. Arduengo and E. M. Burgess, *J. Am. Chem. Soc.*, **99**, 2376 (1977).
- (4) Elemental analyses of new compounds are within 0.4% of theoretical values except those of **12** and **13**. Calcd for **12** ( $\text{C}_{16}\text{H}_{23}\text{O}_3\text{SK}$ ): C, 57.45; H, 6.93. Found: C, 56.12; H, 6.91. Calcd for **13** ( $\text{C}_{16}\text{H}_{23}\text{O}_4\text{SK}$ ): C, 54.83; H, 6.61. Found: C, 55.28; H, 6.93.
- (5) D. H. Reid and R. G. Webster, *J. Chem. Soc., Chem. Commun.*, 1283 (1972).
- (6) The synthesis of **4** has been previously reported: P. H. W. Lau and J. C. Martin, *J. Chem. Soc., Chem. Commun.*, 521 (1977).
- (7) The chemical properties of **5** and the corresponding sulfuranide oxide have been reported earlier: P. H. W. Lau and J. C. Martin, *J. Am. Chem. Soc.*, **99**, 5490 (1977).
- (8) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
- (9) The thermal stabilities of **7** and **9** are in marked contrast to the analogue, prepared by L. Field, P. M. Giles, Jr., and D. L. Tuleen, *J. Org. Chem.*, **36**, 623 (1971), which lacks the second carboxyl group.
- (10) P. Livant and J. C. Martin, *J. Am. Chem. Soc.*, **99**, 5761 (1977), have discussed the variation of carbonyl stretching frequency in carboxylsulfuranides as a function of the symmetry of the three-center four-electron bond.
- (11) After this manuscript was written, Professor W. Walter called our attention to a very recent paper (W. Walter, B. Krische, G. Adiwidjaja, and J. Voss, *Chem. Ber.*, **111**, 1685 (1978)) in which analogues to **7** and **9** are described which lack the *tert*-butyl substituent. While infrared spectroscopic studies of both analogues and an X-ray crystallographic study of the analogue of

**9** provided evidence for O-S interactions similar to those that we postulate, no evidence was obtained for symmetrical species such as the anions described here.

Patrick H. W. Lau, J. C. Martin\*

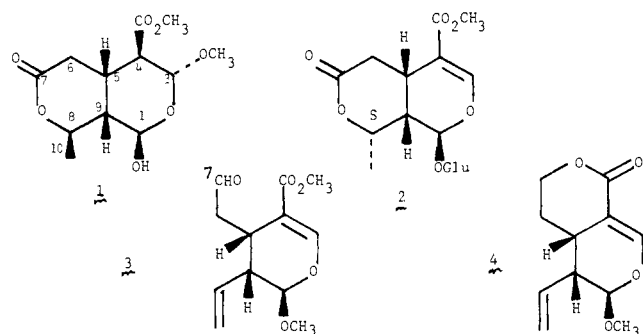
Roger Adams Laboratory, Department of Chemistry  
University of Illinois, Urbana, Illinois 61801

Received July 11, 1978

## Revision of the Structure of Xylomollin

Sir:

The structure of xylomollin was reported in 1976 to be **1**, a secoiridoid hemiacetal acetal isolated from an East African tree and found to have insect antifeedant and other biological activities.<sup>1</sup> Its structural assignment was based almost solely on NMR and mass spectral data, which, by analogy to all known iridoid structures,<sup>2</sup> appeared to justify that **1** was related to 8(*S*)-secoiridoids like kingside (**2**)<sup>3</sup> and sarracenin,<sup>4</sup> but having the 8(*R*) configuration. However, it seemed to us that

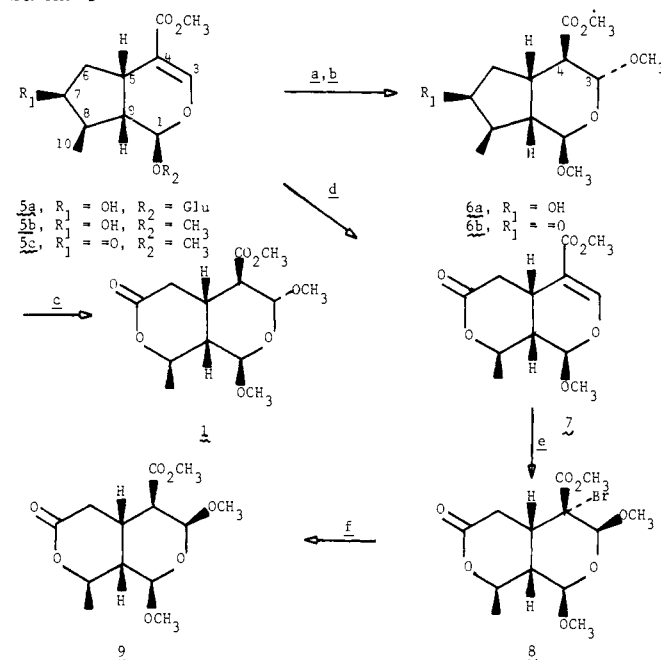


the  $^3J_{H_5H_9}$  value of 10 Hz found for **1** was too large for a *cis*-fused decalin system in view of some NMR data obtained during our recent total synthesis of the secoiridoid aglucone acetals, 1-methoxysecologanin (**3**) and 1-methoxyswerside (**4**).<sup>5</sup> We thus considered that xylomollin could actually be a *trans*-fused iridoid. This appears to be true since partial synthesis of (-)-1-OMe-**1** and its C-3 epimer (**9**) has provided spectral evidence that xylomollin is not **1**.

The strategy for the partial synthesis of **1** was based on its possible biomimetic relationship to (-)-loganin (**5a**), from which two tactical developments were pursued to provide the target molecules. Addition of methanol to (-)-1-methoxyloganin aglucone (**5b**)<sup>6</sup> or (-)-1-methoxylogan-7-one (**5c**)<sup>6</sup> was effected cleanly under basic conditions (Scheme I) to give **6a** (71%; mp 91–92 °C (Skelly B–Et<sub>2</sub>O);  $[\alpha]^{24.5}_D -56.0^\circ$  (c 3.3 mg/mL, MeOH)) or **6b** (58%; mp 81–82 °C (Skelly B–Et<sub>2</sub>O);  $[\alpha]^{24.5}_D -169.8^\circ$  (c 18 mg/mL, MeOH)) as colorless, crystalline solids.<sup>8</sup> The addition was clearly *cis* as judged by the appearance of a doublet ( $\delta_H$  4.85 ( $^3J_{H_3H_4} = 8.3$  Hz)) for the new acetal proton in **6a** and in **6b** ( $\delta_H$  4.93 ( $^3J_{H_3H_4} = 8.5$  Hz)). Presumably the expected *trans* diaxial addition of methanol is not observed because of the ease of the reversibility of the reaction, although **6a,b** itself appeared to be in equilibrium with **5b,c** since extended reaction times did not increase the amount of the **6a,b** formed relative to unreacted **5b,c**. Conversion of **6a** to **6b** (quantitative) with Cr(VI) and/or subsequent Baeyer–Villiger oxidation gave (-)-1-OMe-**1** (60–70%; mp 99–100.5 °C (Et<sub>2</sub>O);  $[\alpha]^{24.5}_D -102^\circ$  (c 12.2 mg/mL, MeOH)).

Alternatively, Baeyer–Villiger oxidation of **5c** to **7** (50–60%; mp 84–85 °C (Skelly B–Et<sub>2</sub>O);  $[\alpha]^{24.5}_D -46.0^\circ$  (c 0.87 mg/mL, MeOH)) followed by bromomethoxylation<sup>9</sup> of the enol double bond gave **8** (75%; glass;  $[\alpha]^{24.5}_D -3.8^\circ$  (c 3.15 mg/mL, MeOH)). The addition of bromine at C-4 was clearly

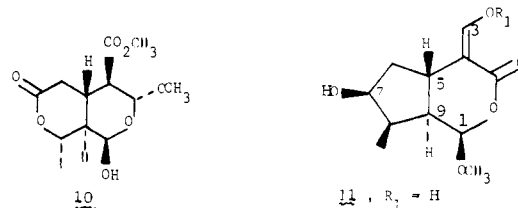
## Scheme I



<sup>a</sup> Mg(OMe)<sub>2</sub> (10 equiv), MeOH (0.5 M), reflux 6–72 h. <sup>b</sup> Pyridinium chlorochromate (1.7 equiv), CH<sub>2</sub>Cl<sub>2</sub> (1.8 M), 25 °C, 1 h. <sup>c</sup> *m*-ClpBzA (3 equiv), NaHCO<sub>3</sub> (7 equiv), CH<sub>2</sub>Cl<sub>2</sub> (3 M), 25 °C, 4 h. <sup>d</sup> *m*-ClpBzA (1.2 equiv), NaHCO<sub>3</sub> (3 equiv), CH<sub>2</sub>Cl<sub>2</sub> (0.1 M), 25 °C, 20 h. <sup>e</sup> NBS (1 equiv), MeOH (0.2 M), 0 → 25 °C, 30 min. <sup>f</sup> (*n*-Bu)<sub>3</sub>SnCl (2 equiv), NaBH<sub>4</sub> (7 equiv), absolute EtOH (0.015 M), *hν*, 15 °C, 45 min.

evident in the <sup>1</sup>H NMR spectrum of **8**: downfield shift of the carbomethoxy resonance ( $\Delta\delta$  0.09), and the appearance of new singlets at  $\delta$  3.44 (C-3 OCH<sub>3</sub>) and 5.16 (H-3). This is shown to occur with the *trans* diaxial endo stereochemistry by analogy to the known stereoselectivity of bromomethoxylation of pentaacetyl **5a**;<sup>10</sup> the axial C-1 OMe must effectively inhibit formation of the intermediate bromonium ion on the exo face of **7**. Reductive debromination of **8** under free-radical conditions using Corey's catalytic (*n*-Bu)<sub>3</sub>SnH method<sup>11</sup> resulted in an ~1:1 mixture of **9** and its C-4 epimer (50%).<sup>12</sup> The formation of two C-4 epimers is consistent with equilibration of the intermediate radical before it can be reductively captured.

Since (-)-1-OMe-**1** and (-)-**9** were prepared from (-)-loganin, whose absolute configuration has been secured by X-ray crystallography,<sup>10b</sup> these two secoiridoid diacetals must have the 5(*S*),8(*R*),9(*S*) absolute stereochemistry originally assigned to **1**. However, synthetic 1-OMe-**1** has an  $^3J_{H_5H_9}$  of 4.8 Hz and **9**, 4.0 Hz, consistent with an approximately *gauche* relationship of the bridgehead hydrogens in a *cis*-decalin system.<sup>13</sup> This and other spectral data<sup>1</sup> lead us to propose that xylomollin's structure be revised to **10**, a 5(*S*),8(*S*),9(*R*)-



secoiridoid, in which the all-*trans* diaxial orientation of the methine hydrogens is more consistent with the reported <sup>1</sup>H NMR coupling constant data than is **1**.<sup>14</sup> Consequently, xylomollin is the first example of a *trans*-fused iridoid to be found in Nature. Its biogenesis probably parallels that of **2** and mornonside, the 7-hemiacetal analogue of **2**,<sup>3a</sup> which are de-