in ethyl acetate–hexane at 5 °C afforded clear crystalline needles in 3 days.

Preparation of 14. 13 (0.6 mg) was reacted with dry C_5H_5N/Ac_2O (100 μL each) overnight at ambient temperature. 14 was purified by HPLC: column, RP C_4 (0.9 × 30 cm); solvent, 0.1% TFA in H_2O–0.1% TFA in MeCN (85:15) to (linear gradient, 30 min) 0.1% TFA in H_2O–0.1% TFA in MeCN (30:70); flow, 5 mL/min; detection, UV (225 nm); FABMS, m/z 464 (M^+).

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Supplementary Material Available: FAB mass spectra of 1–14, ^1H, ^{13}C, and DEPT NMR spectra of 4, NMR spectra of 11 in CD_3OD (HOM2DJ resolved, COSYPS, HETCOR, DEPT, "quaternary only", COLOC, RELAYH) and in C_5D_5N (^1H, ^{13}C, COSYPS), and the X-ray structure of 12 (30 pages). Ordering information is given on any current masthead page.

Isolation and Identification of Two New Metabolites from Silver Leaf Fungus *Stereum purpureum*

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Two new sterpurene sesquiterpenes have been isolated from *Stereum purpureum* and identified as 4,12-dihydroxysterpurene (1) and 5,12-dihydroxysterpurene (3) mainly on the basis of mass spectra and extensive nuclear magnetic resonance spectrometry of compounds 1 and 3 and their diacetate derivatives 2 and 4.

The fungus *Stereum purpureum*, which causes the so-called silver leaf disease of a variety of fruit trees and scrubs, grows slowly on a malt extract broth to produce a complex mixture of sesquiterpene metabolites belonging to a new structural type among the sesquiterpenoids. *S. purpureum* was grown in malt extract–dextrose–peptone liquid culture. Extraction of the culture broth with dichloromethane provided crude metabolites which caused "silvering" in mountain ash seedings.[1,2] The crude metabolites were first separated by TLC and further purified by column chromatography over silica gel to give a viscous, yellow product, followed by preparation of their diacetate derivatives and final purification by HPLC using two different solvent systems.

Compound 1 has the same skeleton as 4,12-dihydroxysterpurene. The IR spectrum of 1 shows a characteristic hydroxyl absorbance at 3586 cm^{-1} ($CHCl_3$). Two proton signals disappear from the ^1H-NMR spectrum of 1 upon addition of D_2O, indicating the presence of two hydroxyl groups. The remaining functionality of the 4,12-dihydroxysterpurene skeleton (three quaternary methyls, a fully substituted double bond) was established from examination of ^1H- and ^{13}C-NMR, NOE, and COSY spectra of 1 and/or 2. For example, the 400-MHz ^1H-NMR spectrum of 1, analyzed in detail in the Experimental Section, includes an AB quartet at 4.50 ppm (allylic primary alcohol) and a multiplet at 4.33 ppm (secondary alcohol); these signals serve to confirm the locations of the two hydroxyl groups. The ^1H-NMR and ^1H–^1H COSY spectra of 1 show the presence of three methyl groups (1.03, 1.07, and 1.25 ppm), an isolated allylic methylene group (2.25 ppm, C-11), an allylic methine proton (2.75 ppm, C-3) coupled to two otherwise isolated methylene groups (C-7 and C-9), an isolated 4-spin system corresponding to two methine protons (C-3 and C-4), and a methylene group (C-5) on a cyclobutane ring. These data thus establish the fundamental 4,12-dihydroxysterpurene skeleton.

Compound 1 readily forms a diacetate 2 when treated with acetic anhydride–pyridine. 2 was first separated by TLC and then repeatedly purified through HPLC. In the ^1H-NMR of 2, the hydrogens on carbons bonded to oxygen are moved downfield to 4.58 (2 H, s, H-12) and 4.43 (1 H, m, H-4) ppm. Singlets at 141.9 and 127.5 ppm in the APT-^{13}C NMR spectrum of 2 correspond to the fully substituted double bond of the allylic alcohol. The 400-MHz ^1H-NMR spectrum and COSY of 2, analyzed in the Experimental Section, include an isolated allylic methylene group (C-11) and an allylic methine proton (C-8) coupled to two methylene groups (four protons on C-7 and C-9). This produces the multiplet at 2.75 ppm. In addition, an isolated 4-spin system on the cyclobutane ring appears. These data further confirm the fundamental carbon skeleton of 1.

The mass spectrum of 1 shows a very weak molecular ion at m/z 236 (0.6); its exact mass measurement m/z 236.1772 corresponds to the molecular formula $C_{15}H_{24}O_2$ (required 236.1776), indicating four double-bond equivalents. Its striking characteristic peaks appear at M – 18, M – 44, and 159. The peak m/z 192 (M – 44), shown by high-resolution measurements to be due to reaction i and then cleavage of the cyclobutane ring with loss of C_2H_4O

(1) Westcott, C. *Plant Disease Handbook*, 3rd ed.; Van Nostran Reinhold, Toronto, 1971; p 354.
(2) Hepting, G. H. *Agriculture Handbook*; Agriculture Forest Service: Washington, DC, 1981; No. 386, pp 61, 84, 90, 236.

0022-3263/92/1957-2313$03.00/0

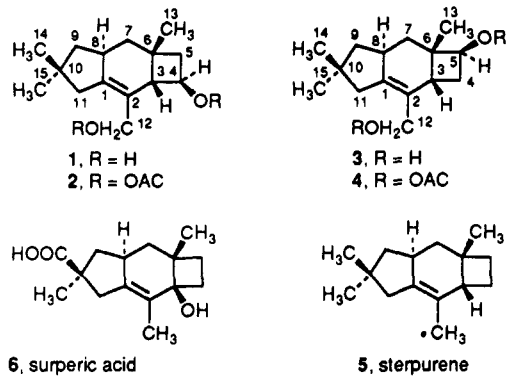


Figure 1.

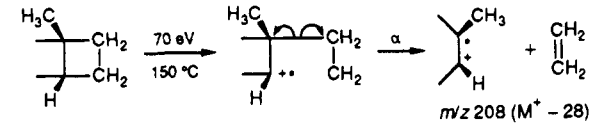
Table I. Important ^{1}H-NMR Data and NOE Results of Compounds 2 and 4

compd 2		compd 4	
protons irradiated (ppm)	protons obtaining NOE increment (ppm)	protons irradiated (ppm)	protons obtaining NOE increment (ppm)
H-15 (1.03)	H-9a (1.74)	H-15 (1.04)	H-9a (1.74)
H-14 (1.07)	H-9b (1.15)	H-14 (1.07)	H-9b (1.09)
H-13 (1.25)	H-3 (2.46)	H-13 (1.13)	H-3 (2.27)
	H-5b (1.76)		(no H-5b)
	H-7b (0.69)		H-7b (0.72)
H-9b (1.15)	H-7b (0.69)	H-9b (1.09)	H-7b (0.72)
	H-14 (1.07)		H-14 (1.07)
H-8 (2.75)	H-5a (2.27)	H-8 (2.76)	H-5a (4.95)
	H-7a (1.68)		H-7a (1.68)
	H-9a (1.74)		H-9a (1.74)
H-5a (2.27)	H-8 (2.75)	H-5a (4.95)	H-8 (2.76)
H-4a (4.43)	H-5a (2.27)	H-4a (2.45)	H-5a (4.95)
H-3 (2.46)	H-13 (1.25)	H-3 (2.27)	H-13 (1.13)

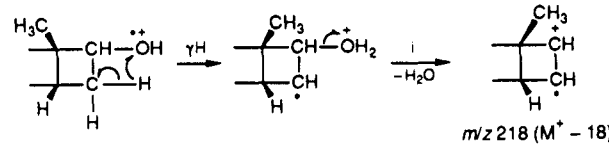
is a characteristic cleavage of compounds with the sterpurene skeleton. The MS of 2 shows a weak molecular ion peak at m/z 320 (0.86); the exact mass measurement is 320.1983, corresponding to the molecular formula $C_{19}H_{28}O_4$ (calcd 320.1988), indicating six double-bond equivalents. The characteristic peaks and their exact masses in the mass spectrum of 2 corresponded to the following: M − 60 ($C_{17}H_{24}O_2$, calcd 260.1776, found 260.1772), M − 86 ($C_{15}H_{22}O_2$, calcd 234.1620, found 234.1624), M − 120 ($C_{15}H_{20}$), and 174 ($C_{13}H_{18}$).

Using the above data, the assignment of structure 1 was completed by a series of NOE experiments on the diacetate 2. We can observe the NOEs in 2 along two paths, one is from H-14 (1.07 ppm, methyl group on C-10) to the H-9b hydrogen (1.15 ppm H-9b), from this hydrogen to H-7b (0.69 ppm), and from H-7b to H-13 (1.25 ppm, methyl on C-6), and finally from H-13 across to H-3 (2.46 ppm). The other path under the molecular plane is from H-15 (1.03 ppm, methyl group on C-10) to H-9a (1.74 ppm), from this hydrogen to H-8 (2.57 ppm, methine proton on C-8), and from this hydrogen to H-5a (2.27 ppm); the NOE of H-5a with H-4a (4.33 ppm) is also apparent. The highest field signal, a double doublet at 0.69 ppm, can be compared with that of the sterpuric acid 6,[3] where this high-field signal is also attributed to one of the hydrogens on C-7. From these NOE results, listed in Table I, we can establish the cis relationship of H-3 to the methyl group on C-6, the location and stereochemistry of the secondary hydroxyl group on C-4, the cis fusion of the six- and four-membered rings, and the configuration at C-8. The molecular skeleton of 1 is coincident with its parent sterpurene 5 and compound 6; the latter's structure has been confirmed by an X-ray crystallographic study.[3,4]

Scheme I



Scheme II



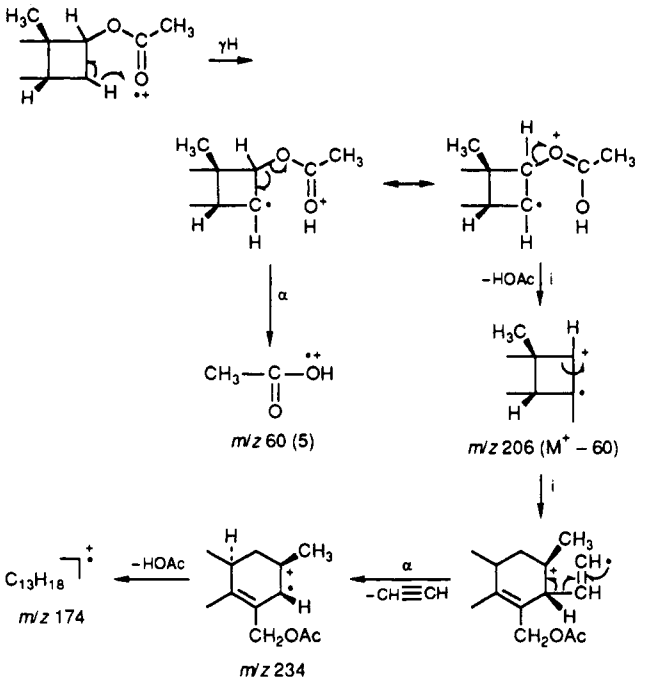
5,12-Dihydroxysterpurene, the other metabolite isolated, is assigned as 3. The structure of this new compound was deduced through IR, ^{1}H- and ^{13}C-NMR, and mass spectral determination of 3 and 4, analyzed in detail in the Experimental Section. The IR spectrum of 3 shows only a characteristic hydroxyl group peak (35–92 cm^{-1}, $CHCl_3$). The ^{1}H-NMR of 3 is similar to that of 1, also including an AB quartet around 4.00 ppm (allylic primary alcohol) and a triplet around 4.17 ppm (secondary alcohol coupled with two hydrogens on C-4), indicative of the presence of a hydroxymethyl group and a hydroxymethylene group.

Brief treatment of 3 with acetic anhydride–pyridine affords the diacetate 4. The 400-MHz ^{1}H-NMR and the 100-MHz ^{13}C-NMR spectra of 3 show the C-12 methylene group now appearing as a singlet at 4.48 ppm, and the other hydrogen on C-5 is also moved downfield to 4.95 ppm (1 H, t, J = 8.2 Hz). The spectrum also shows the presence of three methyl group signals at 1.04, 1.06, and 1.14 ppm corresponding to the C-15, C-14, and C-6 methyl groups, respectively, an isolated allylic methylene group (C-11), and an allylic methine proton (C-8) coupled to two methylene groups on C-7 and C-9. All data reported herein established the positions and the fundamental 5,12-dihydroxysterpurene carbon skeleton.

The mass spectrum of 3 shows a very weak molecular ion at m/z 236 (04); the exact mass found for 3 was 236.1778, corresponding to the molecular formula $C_{15}H_{24}O_2$ (calcd 236.1776) and indicating four double equivalents. The exact mass found for 4 was 320.1982, corresponding to the molecular formula $C_{19}H_{28}O_4$ (calcd 320.1988). The mass spectra of 3 and 4 are quite different from those congeners[3,5] of sterpurene which lack a hydroxyl group on C-4 or C-5 of the cyclobutane ring, like 1. Except for a M − 18 peak, 3 displays a striking characteristic peak at M − 44 (m/z 192), shown by high-resolution measurements to be due to the loss of C_2H_4O from the cyclobutane ring. This is the common α cleavage which is favored at the more substituted bond in the cyclic aliphatic alcohols. This peak provides a means to distinguish this mass spectrum from those compounds which lack a hydroxyl group on C-4 or C-5 and can help to locate the position of the secondary alcohol. The m/z 44 and 192 (M − 44) peaks may be explained by α-cleavage and inductive cleavage (reaction i) as shown in Scheme I; the M − 18 peak is rather weak and can be explained by Scheme II. The mass spectrum of 4 displays two striking peaks at M − 60 and M − 120 due to the loss of two molecules of acetic acid in succession. The base peak m/z 174 can be explained by Scheme III; first, the loss of a molecule acetic acid; second, cleavage of the cyclobutane followed by loss of a molecule acetylene;

(3) Ayer, W. A.; Saeedi-Ghomi, M. H. *Can. J. Chem.* **1981**, *59*, 2536.
(4) Ayer, W. A.; Saeedi-Ghomi, M. H.; Eggan, D. V.; Tagle, B.; Clardy, T. *Tetrahedron* **1981**, *37*(1), 379.
(5) Abell, C.; Leech, A. P. *Tetrahedron Lett.* **1987**, *28*, 4887.

Scheme III



and third, the loss of another molecule of acetic acid.

The assignment of the stereochemistry in **3** was also based on a series of NOE experiments and ^{13}C-NMR and double quantum[6] experiments with its diacetate **4**. The most significant of NOEs are from H-13 across to H-3, which establishes the cis fusion of six- and four-membered rings, and from H-8 to the proton adjacent to the secondary hydroxyl group on C-5, which locates it at that center. An NOE between H-8 with H-5a also enables the stereochemistry at C-8 to be assigned. The more important results of these NOE experiments are listed in Table I.

APT-^{13}C-NMR of **3** is extremely informative in identifying its structure; a detailed analysis of the ^{13}C-NMR spectrum of **3** is provided in the Experimental Section. The ^{13}C-NMR spectrum shows the presence of two fully substituted olefinic carbons (141.3 and 130.7 ppm), three methyl groups, five methylene groups, three methine groups, and two quaternary carbons for a total of 15 carbons. Among them, we can observe two carbons attached to oxygen (67.9 and 62.5 ppm). These results are otherwise in accord with the structure **3** formulated. Thus, the structure **3** was completely established by this data.

Experimental Section

^{1}H-NMR, ^{13}C-NMR, NOE, and COSY were determined in CD_2Cl_2 with TMS as internal standard. Column chromatography was carried out using Machery Nagel Kieselgel 60 (50 g/1 g of substrate). Preparative layer chromatography (PLC) was carried out on 20 × 20 silica gel G (E. Merck 0.75-mm layers) plates. All solvents were distilled prior to use. All compounds for which spectral data were reported showed a single spot by TLC analysis using at least two solvent systems.

Growth of *Stereum purpureum* and Extract of Metabolites. The fungus was grown in still culture at room temperature (23 ± 1 °C) on an aqueous liquid medium containing malt extract (2.5%), dextrose (1.3%), and peptone (0.07%) in 12 1.5-L Fernbach flasks, containing 400-mL per flask. The innoculation (*S. purpureum* strain C-663, Northern Forest Research Centre, Edmonton, Canada) was worked up in the usual manner. After 30 days growth, the mycelium was moved by filtration with a plastic sieve, and the broth was extracted with dichloromethane (3 × 330 mL/L of broth); the extract was washed with water then brine, dried (anhydrous Na_2SO_4), and evaporated under reduced pressure to give a viscous yellow oil (0.65–0.70 g).

(6) Piantini, U.; Sorensen, O. W.; Ernst, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6800.

Table II. Comparison of ^{1}H-NMR Data (Partial)

	compds (ppm, peaks, *J*, Hz)			
^{1}H	1	3	5	6
H-7b	0.69, dd, 12.5, 5.1	0.72, dd, 12.8, 5.6	0.69, dd, 130, 110	0.88, dd, 13.0, 11.0
H-7a	1.68, dd, 12.8, 11.1	1.68, dd, 12.5, 11.4	1.85, m	1.85, dd, 13.0, 6.0
H-8	2.75, m	2.76, m	2.65, m	2.61, m
H-11b	2.29, d, 14.4	2.43, d, 13.3	2.10, m (2 H)	2.68, d, 17.0
H-11a	2.20, d, 14.4	2.23, d, 13.3	(Ibid.)	2.25, d, 17.0
H-13	1.25, s (3 H)	1.13, s (3 H)	1.23, s (3 H)	1.20, s, (3 H)

Isolation of 1 and 3. The dichloromethane extracts (0.30 g) from above were first separated by TLC (elution with CH_2Cl_2–EtOA (1:1)) and then were further chromatographed over silica gel (elution with hexane–EtOA (3:1) or dichloromethane–acetonitrile (4:1)) yielding 15 mg of 4,12-dihydroxysterpurene **1** as a viscous light yellow oil, R_f 0.23 in hexane–EtOA (3:1), and 18 mg of 5,12-dihydroxysterpurene **3**, R_f 0.37 in the same solvent system.

Spectral Data for 1. IR: 3586 cm^{-1} (OH). ^{1}H-NMR: 4.52 (1 H, d, *J* = 8.8 Hz, H-12), 4.40 (1 H, d, *J* = 8.8 Hz, H-12), 4.33 (1 H, m, H-4), 2.75 (1 H, br m, H-8), 2.46 (1 H, br d, *J* = 16.3 Hz, H-3), 2.29 (1 H, br d, *J* = 14.4 Hz, H-11), 2.27 (1 H, m, H-5a), 2.20 (1 H, br d, *J* = 11.4 Hz, H-11), 1.76 (1 H, m, H-5b), 1.74 (1 H, dd, *J* = 5.2, 12.8 Hz, H-9a), 1.68 (1 H, dd, *J* = 5.1, 12.8 Hz, H-7a), 1.25 (3 H, s, methyl on C-6, i.e., H-13), 1.15 (1 H, dd, *J* = 12.8, 5.2 Hz, H-9b), 1.07 (3 H, s, H-14, methyl on C-10), 1.03 (3 H, s, H-15), 0.69 (1 H, dd, *J* = 12.8, 11.1 Hz, H-7b). Note that H-15 is the methyl group on the same face as H-8 and H-5a. The assignments of coupling partners were verified by double irradiation, COSY experiments, and an NOE study (similarly hereinafter). The MS (70 eV, direct inlet at 180 °C) of **1** shows the following peaks: *m/z* 236 (M, 0.6), M – 18 (M – H_2O, 7.5), M – 44 (27), 159 (100), 105 (75).

Spectral Data for 3. IR: 3592 cm^{-1} (OH). ^{1}H-NMR: 4.17 (1 H, t, *J* = 7.6 Hz, H-5a), 4.07 (1 H, d, *J* = 11.5 Hz, H-12), 3.93 (1 H, d, *J* = 11.5 Hz, H-12), 2.76 (1 H, br m, H-8), 2.45 (1 H, m, H-4a), 2.34 (1 H, d, *J* = 13.3 Hz, H-11b), 2.27 (1 H, br d, *J* = 15.4 Hz, H-3), 2.23 (1 H, d, *J* = 13.3 Hz, H-11a), 2.03 (1 H, m, H-4b), 1.86 (1 H, dd, *J* = 12.5, 5.6 Hz, H-7a), 1.74 (1 H, dd, *J* = 13.3, 11.6 Hz, H-9a), 1.13 (3 H, s, H-13), 1.09 (1 H, dd, *J* = 13.3, 5.6 Hz, H-9b), 1.07 (3 H, s, H-14), 1.04 (3 H, s, H-15), 0.72 (1 H, dd, *J* = 12.5, 11.4 Hz, H-7b). H-15 is the methyl group on the same face as H-8 and H-5a. Again, one of the protons of the C-7 methylene group is at abnormally high field (0.72 ppm). This is also reminiscent of compounds **1** and **6** where this high-field signal is also attributed to one of the hydrogens on C-7. APT-^{13}C-NMR (ppm): 141.3 (s, C-1), 130.7 (s, C-2), 67.9 (d, C-5), 62.5 (t, C-12), 48.2 (t, C-4), 44.1 (s, C-10), 43.8 (t, C-11), 37.6 (d, C-3), 37.4 (t, C-7), 37.3 (t, C-9), 37.1 (s, C-6), 34.3 (d, C-8), 30.1 (q, C-13), 29.2 (q, C-14), and 21.4 (q, C-15). *m/z*: 236.1778 (M, calcd 236.1776), 218.1679 (M – H_2O, calcd 218.1671), 192 (M – 44), 159 (basic peak), 105 (78).

Acetylation of 1 and 3. Acetic anhydride (0.3 mL) was added to a solution of diol **1** (6 mg) in pyridine (0.6 mL). The reaction mixture was stirred at room temperature for 1 h, and then toluene (8 mL) was added and the solvents were evaporated under reduced pressure (1.33 × 10^2 Pa), separated by TLC followed by further purification by HPLC twice (first elution with EtOA–hexane (5:95) then with CH_2Cl_2–Et_2O (93:7)), yielding 4 mg of pure diacetate derivative **2**. Acetylation of **3** has been completed under the same conditions as **1**, yielding 5 mg of pure diacetate **4**.

Spectral Data for Diacetates 2 and 4. IR spectrum of **2**: hydroxyl signals disappear, but it shows the carbonyl signal of the ester at 1723 cm^{-1}, other important peaks at 1440, 1365, 1220, 1160, 982 cm^{-1}. ^{1}H-NMR of **2** shows very similar properties to that of **1** except that the protons on carbons bonded to oxygen are moved downfield to δ 4.58 (2 H, s, H-12) and 4.43 (1 H, m,

H-4) and two methyl (acetylmethyl groups) signals appeared at 2.02 (3 H, acetyl in $-COCH_3$, attached to C-4). MS of **2** (m/z): 320 (M, 0.86), 260 (M - 60, 14), 234 (M - 86, 58), 200 (M - 120, 54), 174 ($C_{13}H_{18}$, 100). From the double quantum filtered COSY of **2**, we can also discover the coupling between H-4a (4.43) and H-3 (2.46), H-5a (2.27) and H-5b (1.75), H-11a (2.20) and H-11b (2.29), and H-7a (1.68) and H-7b (0.69 ppm). The NOE data of **2** are listed in Table I.

MS (m/z) of **4**: 320 (M, 0.56), 260 (M - 60, 20), 200 (M - 120, 40), 185 (26), 174.1404 ($C_{13}H_{18}$, calcd 174.1408, 100), 159 (93), 86 (21), 60 (5). IR of **4**: 1730 cm^{-1} (C=O), hydroxyl signal disappeared. Its ^1H-NMR shows quite similar peaks to that of **3** except that the protons on carbons bonded to oxygen are moved downfield (see above) and the two methyl groups (acetylmethyl groups attached to C-12 and C-5) signals appeared at 2.01 and 1.99 ppm. ^1H-^1H COSY of **4** are presented in the Introduction. NOE results for **4** are listed in Table I.

The structures of **1** and **3** were further confirmed by comparison of the spectral data with surperic acid **6** and their parent sterpurene **5**. The comparable ^1H-NMR data for them are listed in Table II.

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Registry No. 1, 138835-50-4; 2, 138835-52-6; 3, 138835-51-5; 4, 138835-53-7.

Regioselective Bromination and Fluorination of Apogossypol Hexamethyl Ether

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Apogossypol hexamethyl ether (**3**) was brominated upon treatment with any of a number of brominating agents. Each reagent gave a different bromo derivative. Thus, the reaction of **3** with bromine in CCl_4 with ultrasound irradiation gave **4** in 71% yield. When treated with bromine and iron powder in CCl_4 at -5 °C, **3** afforded **5** in 65% yield. The reaction of **3** with pyridinium bromide perbromide in 1,2-dichloroethane at 65-70 °C furnished **6** in 70% yield. Treatment of **3** with NBS in DMF at room temperature afforded **7** in 30% yield. Treatment of **4** and **5** with potassium fluoride and 18-crown-6 in acetonitrile at room temperature furnished **8** and **9**, respectively. An attempt to introduce trifluoromethyl groups at the 8 and 8′ positions of **4**, by treatment with cuprous iodide and sodium trifluoroacetate, failed and gave only **10**. Interestingly, but unexpectedly, **11** and **12** were produced upon treating **4** with silver(I) fluoride.

Introduction

Gossypol (**1**),[1,2] a toxic pigment present in cotton seed, was first isolated, in the form of its crystalline acetic acid complex, by Marchlewski.[3] Its structure was deduced by Adams and co-workers[4] in 1938, but it was not until 1957 that Shirley and Dean[5] provided the first conclusive proof of the structure of gossypol by independently synthesizing its two derivatives apogossypol hexamethyl ether (**3**) and desapogossypol hexamethyl ether. Over the next 20 years, evidence that gossypol and its derivatives have vlue as anticancer agents, antibiotics, and pesticides gradually accumulated.[2] In 1978, Chinese investigators reported gossypol to be an effective male antifertility agent.[6] This revelation generated enormous interest and, furthermore, suggested that fluoro derivatives of gossypol might also be biologically active. Herein, we describe the synthesis of several bromo derivatives of apogossypol hexamethyl ether. Such compounds should prove to be valuable as starting materials for the synthesis of novel compounds structurally related to gossypol, in particular those that contain fluorine.

Results and Discussion

Gossypol (**1**), when treated with base, provides apogossypol (**2**), which can be readily methylated to furnish the corresponding hexamethyl ether **3**.[4,5,7,8] We found that **3** can be brominated by treatment with any of a number of brominating agents. Each reagent gives a different bromo derivative. For example, the bromination of **3** by treatment with bromine in CCl_4 at room temperature gave a separable mixture of **4**, **5**, and **6**. The ratio of these three products did not change significantly as the reaction temperature was increased. However, when a CCl_4 solution of **3** and bromine was irradiated with ultrasound, only the tetrabromide **4** was produced, and in 71% yield. The reaction of **3**, bromine, and iron powder at -5 °C gave the tribromide **5** as the main product (65% yield). Interestingly, when **3** was allowed to react with pyridinium bromide perbromide in 1,2-dichloroethane at 65-70 °C, the dibromide **6** was produced in 70% yield. Treatment of **3** with the NBS-DMF complex[9] at room temperature pro-

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