and Mrs. Joyann Serauskas. Column chromatography and thin layer chromatography were accomplished under the direction of Mr. R. T. Nicholson and Mr. B. G. Smith, Mr. W. W. Aksamit and staff provided the vpc results. We are grateful to Dr. J. W. Ahlberg and staff for both spectral data and elemental analyses.

# Badgerin, a New Germacranolide from *Artemisia arbuscula* ssp. *arbuscula*

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*Received April 20, 1971*

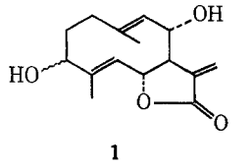
Samples of *Artemisia arbuscula* ssp. *arbuscula*, collected in Montana, contained tatridin-A (**1**) and a new germacranolide which was named badgerin. Structure **2** was assigned to the new lactone on the basis of its spectral properties and chemical reactions.

The sesquiterpene lactones of three subspecies of big sagebrush (*Artemisia tridentata*) were investigated[2] in this laboratory as a part of our program on chemical constitutents of sagebrush in Montana.[2-4] One of the subspecies, *A. tridentata* ssp. *vaseyana*, collected from several locations in this state gave the same sesquiterpene lactones that have been isolated from *A. arbuscula* Nutt. ssp. *arbuscula* collected in another location.[5] This prompted us to investigate the sesquiterpene lactones of a Montana plant known as *A. arbuscula* ssp. *arbuscula*.

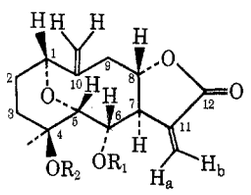
## Results and Discussion

Different samples of this plant were collected from a 1 square mile area near Badger Pass and extracted with chloroform. Tlc analysis of the extracts gave a consistent pattern for the sesquiterpene lactone contents, which were quite different from those reported earlier for *A. arbuscula* ssp. *arbuscula*.[5]

Extensive chromatographic separation of the lactones from the combined chloroform extracts resulted in the isolation of two pure crystalline lactones along with some gummy fractions and a crystalline mixture. One of the two crystalline lactones was identified as tatridin-A[6] (**1**) by its physical constants, spectral properties and ultimately by tlc and mixture melting point with an authentic sample. The other crystalline lactone was an unknown compound. It was named badgerin and assigned the structure **2** on the basis of the following considerations.



**1**



**2**, $R_1 = R_2 = H$
**3**, $R_1 = R_2 = Si(Me)_3$
**4**, $R_1 = Ac$; $R_2 = H$
**5**, $R_1 = R_2 = Ac$

**Composition and Functional Groups.**—Mass spectroscopy and elemental analysis showed the molecular weight of 280 and the empirical formula of $C_{15}H_{20}O_5$. The compound had an $\alpha,\beta$-unsaturated $\gamma$-lactone, as shown by uv end absorption, ir bands at 1766 and 1639 $cm^{-1}$, and the nmr spectrum discussed later (see Table I, **2**). There were two hydroxyl groups, with an ir band at 3378 $cm^{-1}$, which formed a di(trimethylsilyl) ether derivative (**3**). One of these hydroxyl groups was readily acetylated to give a monoacetate compound (**4**) and was proved to be secondary (see Table I and the following nmr discussions). The monoacetate showed an ir band at 3510 $cm^{-1}$ for a free hydroxyl group. However, it could not be oxidized by chromium trioxide–acetic acid[7,8] or by Jones[9] reagent, indicating the tertiary nature of the remaining hydroxyl group.

The lactone moiety and the hydroxyl groups account for four of the five oxygen atoms present. Since no other functional group could be detected it became evident that the fifth oxygen must form an oxide ring. The oxide ring could not be cleaved on treatment with acetic anhydride and *p*-toluenesulfonic acid,[10] or acetic anhydride and sulfuric acid,[11] indicating the presence of an unusually stable ring structure. This almost ruled out the possibility of a labile epoxide ring in favor of a more stable structure such as a pyran derivative. Under the employed drastic acetylating conditions, however, the free hydroxyl groups in badgerin were acetylated to give a crystalline diacetate (**5**).

Badgerin was not oxidized by sodium metaperiodate even after 48 hr, nor did it form a benzeneboronate derivative on treatment with benzeneboronic acid,[12] showing that the two hydroxyl groups are neither adjacent nor are likely to be 1,3-diaxially oriented.

Other than the methylene group conjugated to the lactone carbonyl function, badgerin had another double bond and on hydrogenation it absorbed 2 mol of hydrogen. The hydrogenation product, which lacked olefinic protons in its nmr spectrum, unfortunately proved

(1) Established through a grant from Hoerner–Waldorf Corp. of Montana.
(2) F. Shafizadeh, N. R. Bhadane, M. S. Morris, R. G. Kelsey, and S. N. Khanna, *Phytochemistry*, **10**, 2745 (1971).
(3) F. Shafizadeh and W. Bukwa, *ibid.*, **9**, 871 (1970).
(4) F. Shafizadeh and A. B. Melnikoff, *ibid.*, **9**, 1311 (1970).
(5) M. A. Irwin and T. A. Geissman, *ibid.*, **8**, 2411 (1969).
(6) T. A. Geissman, private communication.
(7) L. F. Fieser, *J. Amer. Chem. Soc.*, **70**, 3237 (1948).
(8) W. Herz and G. Hogenauer, *J. Org. Chem.*, **27**, 905 (1962).
(9) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *ibid.*, 2555 (1953); C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).
(10) W. Herz, P. S. Subramaniam, P. S. Santhanam, K. Aota, and A. L. Hall, *J. Org. Chem.*, **35**, 1453 (1970).
(11) M. A. Irwin and T. A. Geissman, *Phytochemistry*, **8**, 305 (1969).
(12) F. Shafizadeh, G. D. McGinnis, and P. S. Chin, *Carbohyd. Res.*, **18**, 357 (1971).

TABLE I

NMR SPECTRAL DATA FOR BADGERIN AND DERIVATIVES[a]

| Compd | C-13 $H_b$ | C-13 $H_a$ | C-10 $=CH_2$ | C-8 H | C-7 H | C-6 H | C-5 H | C-4 $CH_3$ | C-1 H | Miscellaneous |
|---|---|---|---|---|---|---|---|---|---|---|
| 2[b] | 6.13 | 6.07 | 5.18, 4.99 | 3.95 | 3.36 | 4.40 | 2.85 | 1.60 | 4.33 | 2.00 |
| | (d, 3.5) | (d, 3.5) | (bs, $W_{1/2}$ = 4) | (td, 10, 2) | (br) | (dd, 8.5, 2) | (d, 2) | (s) | (nr) | hydroxyls |
| 3[c] | 6.16 | 5.75 | 5.28, 5.03 | 4.07 | 3.21 | 4.32 | 2.67 | 1.43 | 4.37 | 0.10, 0.20 |
| | (d, 3.5) | (d, 3.5) | (bs, $W_{1/2}$ = 4) | (td, 10, 2) | (br) | (dd, 8.5, 2) | (d, 2) | (s) | (nr) | $[OSi(Me)_3]_2$ (s) |
| 4[c] | 6.15 | 5.42 | 5.42, 5.15 | 4.21 | 3.65 | 5.35 | 3.03 | 1.27 | 4.48 | 2.22 |
| | (d, 3.5) | (mx) | (mx) (d, 2) | (td, 10, 2) | (br) | (mx) | (d, 2) | (s) | (nr) | acetate |
| 4[b] | 6.10 | 5.47 | 5.22, 5.03 | 4.10 | 3.60 | 5.80 | 3.07 | 1.50 | 4.37 | 2.10 |
| | (d, 3.5) | (d, 3.5) | (bs, $W_{1/2}$ = 4) (d, 2) | (td, 10, 2) | (br) | (dd, 8.5, 2) | (d, 2) | (s) | (nr) | acetate |
| 5[c] | 6.12 | 5.40 | 5.40, 5.13 | 4.20 | 3.50 | 5.62 | 3.48 | 1.48 | 4.47 | 2.10, 1.96 |
| | (d, 3.5) | (mx) | (mx) (d, 2) | (td, 10, 2) | (br) | (dd, 8.5, 2) | (d, 2) | (s) | (nr) | acetates |

[a] These data were obtained with a Varian HA-60 nmr spectrometer. TMS was used as an internal standard for compounds **2**, **4**, and **5** and $CHCl_3$ for **3**. Chemical shifts are quoted in $\delta$ (parts per million) and the signals are denoted by s, singlet; d, doublet; dd, doublet of doublets; td, triplet of doublets; br, broad signal; nr, narrow signal; bs, broad singlet; mx, mixed signal. Figures in parenthesis denote coupling constants in cycles per second. [b] Pyridine-$d_5$ was used as the solvent. [c] $CDCl_3$ was used as the solvent for these spectra and in the double irradiation experiments.

to be a mixture and could not be isolated as pure isomers.

The nmr spectrum of badgerin (see Table I, **2**) showed the following features: a low-field pair of doublets at 6.13 and 6.07 ppm (2 H, $J$ = 3.5 Hz) for methylene protons of the $\alpha,\beta$-unsaturated $\gamma$-lactone[2,5,13] (C-13 $H_b$ and C-13 $H_a$); two broad singlets at 5.18 and 4.99 ppm (2H, $W_{1/2}$ = 4 Hz), characteristic of unconjugated *exo*-methylene vinyl protons[2,8] (C-10 $=CH_2$); three protons which appeared to represent OCH groups including a triplet of doublets at 3.95 ppm ($J$ = 10, 2 Hz) for the lactone proton (C-8 H) and a doublet of doublets at 4.40 ppm ($J$ = 8.5, 2 Hz for C-6 H) on a narrow signal at 4.33 ppm (C-1 H); a broad signal centered at 3.36 ppm (C-7 H); a doublet at 2.85 ppm (1 H, $J$ = 2 Hz) also representing an OCH group as discussed later (C-5 H); a narrow singlet at 2 ppm which collapsed on $D_2O$ exchange signifying the hydroxyl proton(s); and a sharp singlet at 1.60 ppm (3 H) indicating a methyl group on a carbon attached to oxygen (C-4 $CH_3$).

The above data indicated a germacranolide structure (**2**) with the following groups: an $\alpha,\beta$-unsaturated lactone, one secondary hydroxyl group, one tertiary hydroxyl group, one oxide ring, and an unconjugated *exo*-methylene.

**Position of the Lactone Ring and the Secondary Hydroxyl Group.**—The biosynthetic pathways involved in the conversion of *trans*-farnesyl pyrophosphate to sesquiterpene lactones including eudesmanolides, guaianolides, and germacranolides generally lead to lactone ring enclosure at C-6 or C-8.[14]

As noted before, the conjugated methylene protons, C-13 $H_b$ and C-13 $H_a$, in badgerin gave characteristic nmr signals at 6.13 and 6.07 ppm. In the nmr spectra of the disilyl compound, the monoacetate, and the diacetate (see Table I, **3**, **4**, and **5**), the signal from one of the methylene protons, C-13 $H_b$, remained almost unchanged, while the position of the other proton, C-13 $H_a$, shifted upfield to 5.75, 5.42, and 5.40 ppm, respectively. The near equivalence of C-13 protons in badgerin and the upfield shift of one of them after the substitution is characteristic of an $\alpha$-oriented hydroxyl group in the $\beta$ position to the lactone methylene group in a variety of sesquiterpene lactones investigated.[15] Although in most of these compounds the lactone ring is enclosed at C-6 and the free hydroxyl group is at C-8, the possibility of the reverse situation, that is, lactone closure at C-8 and the free hydroxyl group at C-6, should be also considered.

The doublet of doublets at 4.40 ppm in badgerin representing an OCH proton shifted downfield in the monoacetate derivative (**4**, Table I) and merged with other signals at 5.42 ppm so that only a part of it could be seen as a narrow doublet at 5.35 ppm. This characteristic downfield shift indicated that the proton (C-6 H) is located under a secondary hydroxyl group that has been acetylated.[16] The coupling constants of the lactone proton (C-8 H, $J$ = 10, 2 Hz, Table I) and the proton under the adjacent secondary hydroxyl group (C-6 H, $J$ = 8.5, 2 Hz, Table I) indicated the presence of either C-8 $\alpha$-hydroxyl and C-6 $\alpha$-lactone or C-6 $\alpha$-hydroxyl and C-8 $\alpha$-lactone. In the former case opening and reclosing of the lactone should result in changing to the more stable C8 enclosure, while the latter structure should remain unchanged.[17] Badgerin was recovered unchanged on opening and reclosing of the lactone moiety, thus showing that the lactone is enclosed at C-8 and the secondary hydroxyl group is at C-6.

**Positions of the Tertiary Hydroxyl, the Unconjugated Methylene, and the Methyl Functions.**—The C-6 proton showed a doublet of doublets ($J$ = 8.5, 2) suggesting that it had only two neighboring protons, one at C-7 and the other at C-5. The narrow doublet at 2.85 ppm in badgerin which shifted to 3.03 ppm in the monoacetate was assigned to C-5 H because irradiation of this proton in the monoacetate collapsed the C-6 H doublet to a singlet and *vice versa*.

The C-5 H doublet shifted further downfield to 3.48 ppm in the diacetate.[10] These shifts, which are more clearly observed by comparing the spectra of the disilyl,

(13) W. Herz, H. Watanabe, M. Miyazaki, and Y. Kishida, *J. Amer. Chem. Soc.*, **84**, 2601 (1962).

(14) W. Herz in "Recent Advances in Phytochemistry," Vol. 1, T. J. Mabry, Ed., Appleton-Century-Crofts, New York, N. Y., 1968, p 231.

(15) H. Yoshioka, T. J. Mabry, M. A. Irwin, and T. A. Geissman, *Tetrahedron*, **27**, 3317 (1971).

(16) J. N. Shoolery and M. T. Rogers, *J. Amer. Chem. Soc.*, **80**, 5121 (1958); N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 77.

(17) H. Yoshioka, W. Renold, and T. J. Mabry, *Chem. Commun.*, 147 (1970).

the monoacetate and the diacetate compounds in chloroform solution [Table I, **3**, **4** (in $CDCl_3$) and **5**], indicated that the C-5 proton is located between the two hydroxyl groups. This means that the tertiary hydroxyl group is at C-4. In the germacranolide skeleton the methyl and methylene groups could be either at C-4 or C-10. The presence of the tertiary hydroxyl group at C-4 leads to the assignments of methyl group to the same position and the methylene group to C-10.

**Position of the Oxide Ring.**—The nmr spectrum of badgerin showed three protons between 3.7 and 4.6 ppm and one proton at 2.85 ppm which could be attributed to an OCH system. Two protons at 3.95 and 4.40 ppm have been assigned to C-8 H and C-6 H, respectively. This leaves the C-5 proton at 2.85 ppm and another proton (C-1 H) at 4.33 ppm for the two ends of the oxide bridge. Irradiation of the latter proton in the diacetate compound affected the C-10 methylene protons, indicating that it is located at C-1 or C-9 allylic positions. Position 9 was eliminated because the lactone proton, C-8 H, showed a triplet of doublets which on irradiation of C-7 H in the diacetate collapsed to another complex signal[18] indicating the presence of two protons at C-9. This showed that the oxide ring must form a bridge between C-1 and C-5.

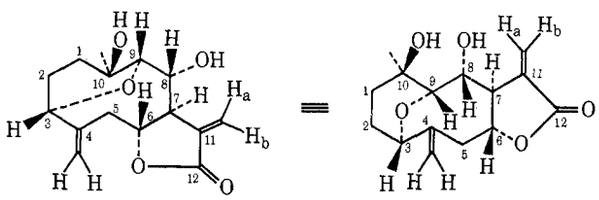
The C-1 and C-5 protons gave narrow signals, indicative of equatorially (or pseudoequatorially) oriented bonds. Construction of a chemical model showed that these equatorially oriented protons have the $\beta$ configuration and the oxide bridge involves C-1$\alpha$,C-5$\alpha$ bonds.

The above data account for configuration of all the asymmetric centers except C-4. The configuration of the hydroxyl group at C-4 was determined from solvent-induced chemical shifts of the C-6 H and C-4 $CH_3$ signals in the nmr spectra of the monoacetate compounds.

In $CDCl_3$ (see **4**, Table I) the signals for C-6 H and C-4 $CH_3$ appeared at 5.35 and 1.27 ppm, respectively. However, when pyridine-$d_5$ (see **4**, Table I) was used as the solvent, the C-6 H signal showed a downfield shift of 0.45 ppm to appear at 5.80 ppm, and the C-4 $CH_3$ signal showed a downfield shift of 0.23 ppm to appear at 1.5 ppm. These solvent shifts indicated that the C-6 H and C-4 $CH_3$ bonds must lie in the same planes as the C-4 O and C-6 O bonds respectively.[19,20] In other words the hydroxyl groups at C-4 and C-6 are trans. Since the C-6 OH, as noted before, is $\alpha$, the C-4 OH, or the tertiary hydroxyl group, must be $\beta$ oriented. The trans configuration of the hydroxyl group explained the failure of badgerin to form a benzeneboronate derivative. Also, it could be seen from a chemical model that the eclipsed conformation of C-6 H and C-4 OH forms a dihedral angle of somewhat more than 60° between C-6 H and C-5 H which is consistent with the observed weak coupling ($J$ = 2 Hz) between these protons.

**Absolute Configuration.**—The above data give the structure of badgerin and the relative configuration of all the asymmetric centers. However, they do not establish the absolute configuration of the compounds because all the spectroscopic and chemical properties that have been considered are equally applicable to the mirror image of the proposed structure.

It is interesting to note that the above structure is based on the application of the relactonization rule[17] established for germacranolides. It could be argued that the new compound with an oxygen bridge between C-1 and C-5 may behave differently so that the relactonization rule is no longer applicable. Under these circumstances the alternative possibility, that is, lactone closure to C-6, must be considered. If the lactone ring is closed at C-6, then the other functional groups on the germacranolide skeleton must be located as shown in structure **6** in order to accommodate the observed chemical and spectroscopic properties. At the first sight structure **6** seems totally different from the proposed structure of badgerin (**2**). However, closer observation indicates that despite the differences in numbering, structures **2** and **6** are actually mirror images. Consequently, the position of the lactone ring will be known when one of the enantiomers is related to a compound with known absolute configuration or *vice versa*. This situation is remarkably similar to the configurational relationships that were used by Emil Fischer at the turn of the century for determining the stereoisomerism of the monosaccharides.



**6**

## Experimental Section[21]

**Isolation of Tatridin-A** (**1**).—Three samples of *A. arbuscula* ssp. *arbuscula*[22] were collected from a one square mile area near Badger Pass, Montana (T. 7 S, R. 11 W, Section 11, elevation 6319 ft), in August 1970. Dried twigs and foliage of the samples (400 g each) were separately extracted with chloroform and worked up in the usual manner.[2,23] The resulting crude dark syrups, about 25 g from each sample, were found to have the same sesquiterpene lactone pattern by tlc and were combined together. The combined syrup was dissolved in a small amount of benzene and chromatographed over 1 kg of silica gel, using benzene and benzene–ethyl acetate mixtures of increasing polarity as the eluents. The first 4 l. of benzene and 9 l. of the solvent mixtures (9:1, 8:2, 7:3) eluted colored gums. The following eight 150-ml aliquots of the mixed solvents (6:4) furnished a gum which crystallized from chloroform–ether and gave a mixture of two compounds. The next ten 150-ml aliquots of benzene–ethyl acetate (1:1) contained a transparent gum which crystallized from chloroform–ether to give 800 mg of colorless needles of tatridin-A, mp 150–160°. Azeotropic removal of the crystallization solvent and recrystallization from methanol gave another crystalline form, mp 176–177°, alone or in admixture with an authentic sample:[24] $[\alpha]^{18}D$ −49° ($c$ 1.1, EtOH); mass spectrum $m/e$ 264 ($M^+$); uv end absorption; ir bands at 3333 (hydroxyl), 1762 ($\gamma$-lactone), 1666, 1647, 890 $cm^{-1}$ (unsaturation); nmr spectrum in pyridine-$d_5$, doublets of doublets at 6.50, 6.35 ppm

(18) M. F. L'Homme, T. A. Geissman, H. Yoshioka, T. H. Porter, W. Renold, and T. J. Mabry, *Tetrahedron Lett.*, 3161 (1969).

(19) K. Tori, Y. Hamashima, and K. Takamizawa, *Chem. Pharm. Bull.*, **12**, 924 (1964).

(20) C. R. Narayanan, N. R. Bhadane, and M. R. Sarma, *Tetrahedron Lett.*, 1561 (1968).

(21) All melting points are uncorrected. The uv and ir spectra were recorded on Coleman–Hitachi EPS-3T and Beckman IR-5 spectrophotometers, respectively.

(22) Samples were collected and identified by M. S. Morris, Professor of Range Management, University of Montana.

(23) T. A. Geissman, T. Stewart, and M. A. Irwin, *Phytochemistry*, **6**, 901 (1967).

(24) The authentic sample was obtained from Professor T. A. Geissman as the methanol solvate, mp 178–179°.

(1 H each, $J$ = 3, 1.5 Hz, C-11 $=CH_2$) situated on a broad base of hydroxyl signals from 6.0 to 6.7 ppm, broad doublets at 5.20 and 5.32 ppm (1 H each, $J$ = 9.5 Hz, C-5 H and C-9 H), a complex signal from 4.4 to 5.1 ppm (3 H, C-3 H, C-6 H, C-8 H), a broad signal at 3.0 ppm (1 H, C-7 H), and two narrow doublets at 1.88 and 1.68 ppm (3 H each, $J$ = 1.5 Hz, C-4 and C-10 $CH_3$).

**Isolation of Badgerin (2).**—The materials remaining in the chromatographic column after removal of tatridin-A were further eluted with ten 150-ml portions of the same solvent mixture. The tlc analysis of the eluents showed a single spot, but the gummy product, 5 g, obtained on removal of the solvents could not be crystallized and glc analysis of a silylated sample indicated the presence of two closely related components which remain unidentified.

Continued elution in the same manner gave 1.5 g of a transparent gum, which crystallized from chloroform–ether to give 200 mg of needles of badgerin: mp 207–208°; $[\alpha]^{18}D$ +8.50 ($c$ 1.165, EtOH), mass spectrum $m/e$ 280 ($M^+$), 262 (M − 18); uv end absorption; ir bands at 3378 (hydroxyl), 1766 ($\gamma$-lactone), 1639 $cm^{-1}$ (unsaturation).

*Anal.* Calcd for $C_{15}H_{20}O_5$: C, 64.28; H, 7.14. Found: C, 64.05; H, 7.27.

A solution of badgerin in pyridine-$d_5$ gave the nmr spectrum recorded in Table I. Further elutions of the column gave colored gums which could not be crystallized.

**Di(trimethylsilyl) Derivative of Badgerin (3).**—Badgerin (50 mg) was treated with Tri-Sil reagent (3 ml). The resulting solution was warmed for a few minutes and allowed to stand for 1 hr. The excess solvent was then removed under reduced pressure and the residue was extracted with carbon tetrachloride. Removal of the solvent from the filtered extract left a residue which was used for the spectroscopic investigations. The nmr spectrum of this compound is given in Table I.

**Badgerin Monoacetate (4).**—Badgerin (50 mg) was dissolved in pyridine (2 ml) and acetic anhydride (2 ml) and kept overnight. Removal of solvents under reduced pressure and crystallization of the residue from methanol afforded a monoacetate derivative (4): yield 40 mg; mp 197–199°; ir bands at 3510 (hydroxyl), 1766 ($\gamma$-lactone), 1718, 1245 $cm^{-1}$ (acetate).

*Anal.* Calcd for $C_{17}H_{22}O_6$: C, 63.35; H, 6.83. Found: C, 63.57; H, 6.88.

**Badgerin Diacetate (5).**—A solution of 50 mg of badgerin in 10 ml of acetic anhydride was treated with a drop of concentrated sulfuric acid.[10] After a few minutes the solution was poured over crushed ice and allowed to stand for 1 hr. It was then extracted with chloroform (five 20-ml portions). The extract was washed with sodium bicarbonate solution and water. Removal of the solvent left a solid which was recrystallized from ethanol to give 40 mg of a diacetate (5): mp 189–190°; mass spectrum $m/e$ 364 ($M^+$); ir bands at 1776 ($\gamma$-lactone), 1740 and 1250 $cm^{-1}$ (acetate).

*Anal.* Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.59. Found: C, 62.29; H, 6.68.

This compound was also obtained in good yield when badgerin (40 mg) was refluxed in acetic anhydride (5 ml) with $p$-toluenesulfonic acid[10] (30 mg) for 1.5 hr.

**Hydrogenation of Badgerin.**—A solution of 56 mg of badgerin in 25 ml of ethanol was stirred with 10% Pd/C catalyst in a hydrogen atmosphere. The reaction was complete in 2 hr after absorption of 2 mol of hydrogen. The catalyst was then filtered and the filtrate was concentrated to a residue which showed three overlapping tlc spots. The nmr spectrum of this mixture lacked signals for olefinic protons.

**Relactonization of Badgerin.**[25]—Badgerin (~10 mg) was dissolved in 1 ml of 10% aqueous sodium hydroxide solution by gentle warming. The solution was then cooled in ice and the solvent was removed under vacuum without heating. The solid residue was dissolved in 2 ml of glacial acetic acid and the solution was again evaporated under high vacuum without heating. The residue obtained was taken in cold water and extracted repeatedly with chloroform. Removal of chloroform under vacuum gave badgerin quantitatively.

**Attempted Oxidation of Badgerin Monoacetate. A.**—The monoacetate (28 mg) was dissolved in 4 ml of glacial acetic acid and treated with 10 mg of chromium trioxide.[7,8] The reaction mixture was monitored by tlc. There was no change after 8 hr, when the reagent was destroyed by methanol and the starting monoacetate was recovered quantitatively.

**B.**—The monoacetate recovered from the above experiment (25 mg) was dissolved in 20 ml of acetone (purified by distillation from $KMnO_4$ and stored over $K_2CO_3$) and Jones reagent[9] was added dropwise with stirring until a persistent orange color developed. Stirring was continued for 20 min, after which the excess reagent was destroyed with methanol and the starting monoacetate was recovered quantitatively.

**Attempted Periodate Oxidation of Badgerin.**—Badgerin (14 mg, $0.5 \times 10^{-4}$ mol) was suspended in a solution of sodium metaperiodate (21.4 mg, $1 \times 10^{-4}$ mol) in distilled water (10 ml). The reaction was monitored by periodic titrations of the mixture and a blank. No appreciable amount of periodate was consumed in 48 hr. The reaction mixture was then extracted with $CHCl_3$ ($5 \times 10$ ml) and removal of the solvent left a residue which was identical with the starting material.

**Attempted Preparation of Benzeneboronate Derivative.**—Badgerin (42 mg) and benzeneboronic acid (22 mg) were added to 30 ml of benzene and refluxed for 8 hr in a Dean–Stark apparatus.[12] The main bulk of benzene was then removed and dry ligroin was added to the remaining solution. This gave a fine precipitate that was filtered and identified as badgerin.

**Registry No.**—**2**, 32557-05-4; **3**, 32557-06-5; **4**, 32557-07-6; **5**, 32557-08-7.

**Acknowledgments.** —The authors are grateful to Professors T. A. Geissman for an authentic sample of tatridin-A, T. J. Mabry for spectral data of sesquiterpene lactones, M. S. Morris for collection and identification of the plant materials, W. L. Waters for nmr decoupling experiments, and R. J. Spangler for mass spectra. They also thank Hoerner–Waldorf Corporation of Montana and Forest and Conservation Experiment Station of the University of Montana for financial support.

(25) W. Renold, H. Yoshioka, and T. J. Mabry, *J. Org. Chem.*, **35**, 4264 (1970).