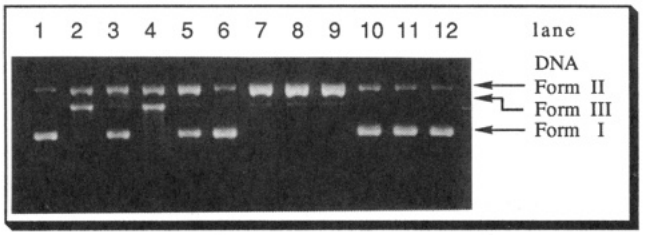


**Figure 2.** Cleavage of ΦX174 supercoiled DNA by Fe(II)-**4**, Fe(II)-bleomycin $A_2$, and Fe(II)-deglycobleomycin $A_2$. Solutions contained 0.25 μg of ΦX174 supercoiled DNA ($1.4 \times 10^{-8}$ M) in 50 mM Tris-HCl, pH 8 containing 10 mM 2-mercaptoethanol. The DNA cleavage reactions were run for 60 min at 25 °C, and electrophoresis was conducted at 50 V (2.5 h) on a 1.0% agarose gel. Lane 1, control ΦX174 DNA 95% Form I (supercoiled), 5% Form II (relaxed); lanes 2–3, 1 and 0.2 μM Fe(II)-bleomycin $A_2$; lanes 4–6, 5, 1, and 0.2 μM Fe(II)-deglycobleomycin $A_2$; lanes 7–10, 50, 10, 5, and 1 μM Fe(II)-**4**; lanes 11–12, 5 and 1 μM Fe(II), control. Form I = supercoiled DNA, Form II = relaxed DNA (single-strand cleavage). Form III = linear DNA (double-strand cleavage).

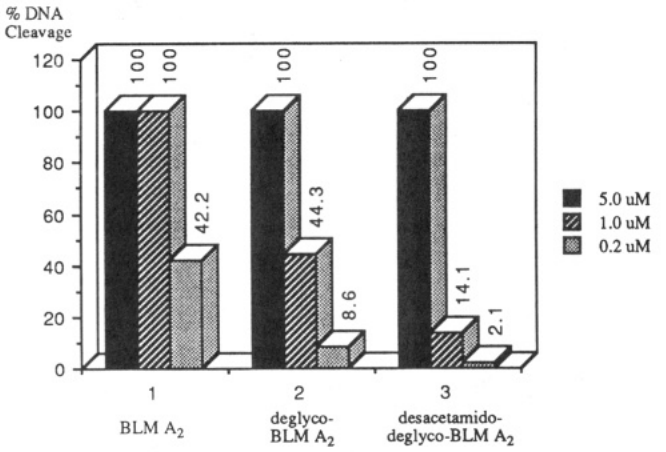


**Figure 3.** Comparison of the relative efficiency of cleavage of supercoiled ΦX174 RFI DNA by Fe(II)-bleomycin $A_2$, Fe(II)-deglycobleomycin $A_2$, and Fe(II)-**4**.

A preliminary study of the ability of the Fe(II) complex of **4** to cleave duplex DNA was conducted through examination of single-strand and double-strand cleavage of supercoiled φX174 RFI DNA (Form I) to produce relaxed (Form II) and linear (Form III) DNA, respectively. Like Fe(II)-bleomycin $A_2$[17] and deglycobleomycin $A_2$[17], Fe(II)-**4** produced both single- and double-strand cleavage of φX174 RFI DNA, Figure 2. The direct comparison of the efficiency of DNA cleavage by Fe(II)-**4** and Fe(II)-deglycobleomycin $A_2$ permits the assessment of the relative importance and functional role of the pyrimidoblamic acid C2 acetamido side chain. Although the side chain has been shown not to be intimately involved in the metal chelation, it has been suggested to contribute to the efficiency of DNA cleavage by constituting one side or component of the oxygen binding pocket thereby sterically shielding or protecting the activated and reactive iron-oxo intermediate.[1] Consistent with this latter suggestion, Fe(II)-deglycobleomycin $A_2$ proved to be 3–5× more effective than Fe(II)-**4** in its efficiency for producing the cleavage of supercoiled φX174 RFI DNA, Figure 3 [relative efficiency: bleomycin $A_2$ (1), deglycobleomycin $A_2$ (0.5–0.2), **4** (0.2–0.05)]. Under the conditions of the assay, both Fe(II)-deglycobleomycin $A_2$ and Fe(II)-**4** produced little or no cleavage at 0.2 μM, significant cleavage at 1 μM, and complete cleavage at 5 μM. Both agents proved to be slightly less efficient that Fe(II)-bleomycin $A_2$ which produced significant cleavage of the supercoiled DNA at concentrations as low as 0.2 μM with complete cleavage of the DNA at 1 μM. Consistent in each of multiple assays, Fe(II)-deglycobleomycin $A_2$ proved at least as effective in producing linear DNA resulting from double-stranded DNA cleavage as Fe(II)-bleomycin $A_2$ itself which in turn generally proved more effective than Fe(II)-**4**. Detailed studies of the DNA cleavage properties of Fe(II)-**4** including additional comparison of its duplex DNA cleavage efficiency and selectivity with that of bleomycin $A_2$, deglyco bleomycin $A_2$, and structurally related analogs are in progress and will be reported in due course.

(17) Boger, D. L.; Menezes, R. F.; Yang, W. *Biomed. Chem. Lett.*, in press.

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**Supplementary Material Available:** Experimental details, full physical and spectroscopic characterization for **8–14**, **16**, **17**, **20**, and **3–4**, and two tables detailing studies of the [4 + 2] cycloaddition reactions of **5** and the reduction of **9** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

## A Practical Preparation of α-Alkoxylithium Reagents: Synthesis of Syn or Anti 1,3-Diols

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*Received May 19, 1992*

*Summary:* Phenylthio acetals **3** are easily prepared from β-hydroxy aldehydes and can be reduced to anti alkyllithiums **7** and subsequently equilibrated to syn alkyllithiums **9** with excellent stereoselectivity and in good overall yield. A practical preparation of **3** and a reductive lithiation procedure using catalytic naphthalene makes these alkyllithium reagents conveniently available on a multigram scale.

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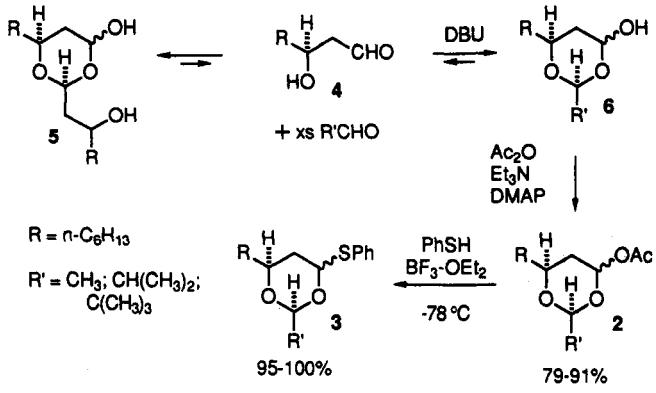
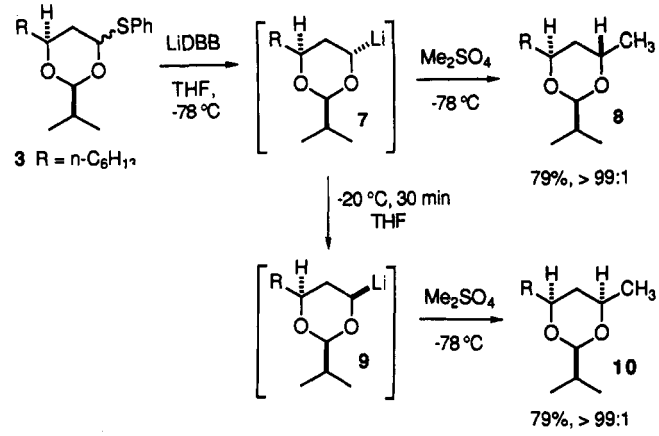
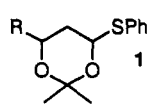
**Scheme I**



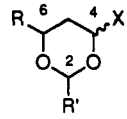

**Scheme II**




Alternating (1,3,5...) polyol chains are found in a variety of interesting natural products including the polyene macrolide antibiotics.[2] As part of a program to develop practical new methods for the convergent syntheses of these polyols, we have previously reported the preparation of 6-alkyl-2,2-dimethyl-4-(phenylthio)-1,3-dioxanes, **1**, and their use as 1,3-diol synthons.[3] Unfortunately, synthesis of **1** requires expensive reagents and is not easily generalized. We now report a new 1,3-diol synthon, phenylthio acetal **3**, where the nascent diol is protected as an aldehyde acetal rather than a ketone acetal that serves as a convenient precursor to stereochemically defined alkyllithium reagents. These alkyllithium reagents react with most electrophiles with retention of configuration. Synthon **3** is easily prepared on large scale using inexpensive reagents and can be reduced to syn or anti alkyllithium reagents with good selectivity and yield using lithium di-*tert*-butylbiphenylide (LiDBB) *or, more conveniently, lithium metal with 5 mol % naphthalene.*



**1**



**2** X=OAc
**3** X=SPh

Simple β-hydroxy aldehydes exist preferentially as asymmetric dimers **5** rather than as the corresponding free aldehydes **4**, Scheme I. A number of dimeric β-hydroxyaldehydes have been reported,[4] and several examples of dimers incorporating two different aldehydes, e.g., isobutyraldehyde and its aldol product, are known.[5] We became intrigued with this dimeric structure because it contains the 4-hetero-substituted 6-alkyl-1,3-dioxane ring system of synthon **1**, and yet it forms spontaneously from the free aldehyde. One of the β-hydroxy aldehydes participates in the desired sense but the other acts as a simple aldehyde, in essence protecting the first β-hydroxy aldehydes as a cyclic acetal. If the simple aldehyde component of the dimeric structure **5** could be exchanged with an inexpensive aldehyde, the resulting cyclic hemiacetal **6** would be a readily accessible, potentially valuable intermediate in 1,3-diol synthesis.

Racemic 3-hydroxynonanal[6] forms a crystalline dimer **5** that was used to develop this chemistry, Scheme I. Combining dimer **5** with excess trimethylacetaldehyde and a variety of bases[7] led to the identification of DBU as a uniquely effective catalyst for this exchange process. As the number of equivalents of trimethylacetaldehyde was increased, more of the cyclic hemiacetal **6** [R′ = $C(CH_3)_3$] was formed until a maximum conversion was reached at 8–10 equiv. Acetaldehyde and isobutyraldehyde gave similar results with the exchange reaction being fastest with acetaldehyde and slowest with trimethylacetaldehyde. Acetone gave no exchange product under these conditions, presumably due to an unfavorable equilibrium.[8] The reactions could be followed by TLC, and in the case of isobutyraldehyde the cyclic hemiacetal **6** [R′ = $CH(CH_3)_2$] was isolated by column chromatography and gave satisfactory IR and $^1H$ and $^{13}C$ NMR spectral data. Each of the cyclic hemiacetals **6** was prone to revert to dimer **5** on standing. The less hindered acetals decomposed more readily. In general, the hemiacetals **6** were not isolated but were acylated in situ by addition of $Ac_2O$, $Et_3N$, and DMAP to give acetates **2** in 79–95% overall yield.[9] The acetates **2** gave sulfides **3** in 95–100% yield on treatment with $BF_3$·$OEt_2$ and thiophenol at −78 °C. Acetates **2** were formed as a mixture of isomers at the anomeric [C(4)] position, but with a single relative configuration at the C(2) and C(6) positions.[10] Acetals **3** were initially formed with

(1) Camille and Henry Dreyfus Teacher-Scholar 1990–1995. Alfred P. Sloan Research Fellow 1992–1993. McKnight Land-Grant Professorship, 1990–1993.

(2) Omura, S.; Tanaka, H. In *Microlide Antibiotics: Chemistry, Biology and Practice*; Omura, S., Ed.; Academic Press: New York, 1984; pp 351–404.

(3) (a) Rychnovsky, S. D. *J. Org. Chem.* **1989**, *54*, 4982–4984. (b) Rychnovsky, S. D.; Mickus, D. E.; *Tetrahedron Lett.* **1989**, *30*, 3011–3014.

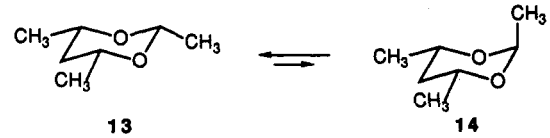
(4) (a) Andersson, R.; Theander, O.; Westerlund, E. *Carbohydr. Res.* **1978**, *61*, 501–509. (b) Duke, C. C.; MacLeod, J. K.; Williams, J. F. *Carbohydr. Res.* **1981**, *95*, 1–26. (c) Cloux, R.; Schlosser, M. *Helv. Chim. Acta* **1984**, *67*, 1470–1474.

(5) (a) Saunders, R. H.; Murray, M. J.; Cleveland, F. F. *J. Am. Chem. Soc.* **1943**, *65*, 1714–1717. (b) Spath, E.; Lorenz, R.; Fruend, E. *Chem. Ber.* **1943**, *76*, 1196–1208. (c) Alexander, E. R.; Marvell, E. N. *J. Am. Chem. Soc.* **1950**, *72*, 1396. (d) Hine, J.; Houston, J. G.; Jensen, J. H. *J. Org. Chem.* **1965**, *30*, 1184–1188. See also: Osipowicz, B.; Jablonski, L.; Mejer, S. *Pol. J. Chem.* **1985**, *59*, 1081–1087.

(6) Prepared by hydrolysis (20:5:1 THF/$H_2O$/HOAc) of 3-[(trimethylsilyl)oxy]nonanal: Rychnovsky, S. D.; Zeller, S.; Skalitzky, D. J.; Griesgraber, G. *J. Org. Chem.* **1990**, *55*, 5550–5551.

(7) The bases used include pyridine, $Et_3N$, imidazole, DBU, NaH, and $K_2CO_3$.

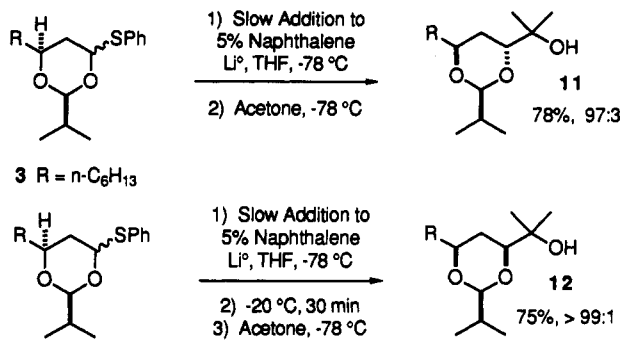
(8) The equatorial 2-methyl dioxane **13** is favored over the axial 2-methyldioxane **14** by >3.5 kcal/mol, and the increased strain associated with an axial 2-methyl group provides an estimate of the difference in stability between cyclic acetals and cyclic acetonides formed from 1,3-diols. See: Eliel, E. L.; Knoeber, Sr. M. C. *J. Am. Chem. Soc.* **1968**, *90*, 3444–3458.



**13** **14**

(9) New compounds were characterized by $^1H$ and $^{13}C$ NMR, IR and C,H analysis; See supplementary material for listings.

**Scheme III**




an axial phenylthio group, but prolonged exposure to the reaction conditions resulted in approximately a 1:1 mixture at the phenylthio position. The phenylthio acetal **3** [R′ = $CH(CH_3)_2$] was prepared in quantitative yield from dimer **5** on a 40-g scale.[11] Studies with the phenylthio acetal **3** [R′ = $CH(CH_3)_2$] are described below, but similar results were obtained with phenylthio acetals **3** [R′ = $CH_3$] and **3** [R′ = $C(CH_3)_3$].[9]

Phenylthio acetals **3** are effective precursors to stereochemically defined alkyllithium reagents **7** and **9**. Addition of **3** [R′ = $CH(CH_3)_2$] in THF to LiDBB[12] in THF at −78 °C gave the axial alkyllithium **7**, which upon alkylation with dimethyl sulfate gave the protected anti 1,3-diol **8** in 79% yield and >99:1 selectivity.[3,13] The yields were slightly better when **3** was added slowly to the LiDBB solution, probably due in part to more effective temperature control. The equatorial alkyllithium reagent **9** was prepared by equilibrating a solution of the axial alkyllithium **7** by warming to −20 °C for 30 min with careful temperature control.[3b,13b] Recooling the reaction mixture to −78 °C and treatment with dimethyl sulfate gave the protected syn 1,3-diol **10** in 79% yield and >99:1 stereoselectivity.[14] An unanticipated benefit of using the much more accessible acetal protected synthons **3** rather than the previously described[3] acetonide protected synthons **1** is the more effective equilibration of the corresponding alkyllithium reagents. Acetal **3** gave a higher yields (79% vs 47–65%) and better stereoselectivity (>99:1 vs 95:5) than acetonide **1** in the equilibrium and coupling of the corresponding equatorial alkyllithium reagents. The more effective equilibration is a result of fewer side reactions of the acetal **9** compared with the corresponding acetonide, presumably due to reduced ring strain.[7]

The major practical limitation in using these stereochemically defined alkyllithium reagents is that 2 equiv of an aromatic radical anion, preferably lithium di-*tert*-butylbiphenylide, are required to generate them, and the resulting 4,4′-di-*tert*-butylbiphenyl must then be separated from the product by chromatography. Several alkyllithium preparations have been reported using lithium metal and an aromatic catalyst, but to date none of these have involved configurationally stable anions.[15] We applied the procedure recently reported by Yus and Ramon[15e] using lithium powder and 5 mol % naphthalene to the preparation of **7** with limited success. The stereoselectivity was 97:3, and the yield of acetone adduct **11** was only 54%. An examination of the side products suggested that proton transfer between alkyllithium **7** and **3** was responsible for the reduced yield. This problem could be largely overcome by adding **3** to the lithium/naphthalene mixture over several hours using a syringe pump, Scheme III. Using 5% naphthalene, a 3 h addition of **3** and acetone as an electrophile gave anti acetone adduct **11** in 78% yield as a 97:3 mixture of isomers.[16] The alkyllithium reagent **9** was generated by the same procedure but with an added equilibration step and trapped with acetone to give the syn adduct **12** in 75% yield and >99:1 selectivity.[17] Tributyltin chloride can be used as an electrophile with similar results.[9] The reductive lithiation of **3** using of 5 mol % naphthalene and lithium powder shows a slightly lower stereoselectivity than stoichiometric LiDBB reductions but is much more convenient for large-scale synthesis.

The new 1,3-diol synthons **3** are easily prepared on large scale from β-hydroxy aldehydes and are effective precursors to syn and anti 1,3-diols. Both syn and anti alkyllithium reagents are available in 75–80% yield and >99:1

(10) The anomers of compounds **2** were separated, and both anomers [R′ = $CH_3$, $CH(CH_3)_2$, $C(CH_3)_3$] showed NOE's between the protons at C(2) and C(6), confirming their cis relationship.

(11) **Preparation of Phenylthio Acetal 3 [R′ = $CH(CH_3)_2$].** 3-hydroxynonanal (**5**) (21.9 g, 138.4 mmol, 1.0 equiv), isobutyraldehyde (101.2 g, 1403 mmol, 10 equiv), and DBU (10.0 mL, 66.9 mmol, 0.5 equiv) were dissolved in 600 mL of THF, and the solution was stirred overnight. The reaction vessel was placed in a 23 °C water bath, and DMAP (560 mg, 4.58 mmol, 3.3 mol %), $Et_3N$ (60 mL, 431 mmol, 3 equiv) and $Ac_2O$ (33 mL, 350 mmol, 2.5 equiv) were added. After 1.5 h the reaction was quenched by slow addition of saturated $NaHCO_3$. The mixture was extracted with ether (500 mL), and the organic layer was washed (1N $NaHSO_4$, brine), dried ($MgSO_4$), and concentrated under reduced pressure. Vacuum distillation gave 38.7 g (142.1 mmol, 100%) of acetate **2** [R′ = $CH(CH_3)_2$] (bp 105–110 °C (0.25 Torr)). This material was combined with thiophenol (21.5 mL, 209 mmol, 1.5 equiv), dissolved in 500 mL of $CH_2Cl_2$, and cooled to −78 °C. $BF_3{\cdot}OEt_2$ (42.5 mL, 345 mmol, 2.5 equiv) was added dropwise, and after 2 h the reaction was quenched with 1 N NaOH and the solution warmed to rt. The mixture was extracted with ether (1 L), and the organic layer was washed (2 × 1 N NaOH, brine), dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was filtered through a plug of silica gel with 5% *t*-BuOMe/hexanes and concentrated under reduced pressure. Vacuum distillation gave 45.1 g (139.8 mmol, 100%) of phenylthio acetal **3** [R′ = $CH(CH_3)_2$] (bp 143–145 °C (0.25 Torr)).

(12) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924–1930.

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(14) The product ratios were assigned by GC analysis. The stereochemistry was assigned by hydrolysis to the 1,3-diol, acetonide formation, and $^{13}C$ NMR analysis. The acetonide prepared from **8** shows acetonide methyl signals at 24.9 and 25.0 ppm, whereas the acetonide prepared from **10** shows acetonide methyl signals at 19.8 and 30.3 ppm. Rychnovsky, S. D.; Skalitzky, D. J. *Tetrahedron Lett.* **1990**, *31*, 945–948. See supplementary material for details.

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(16) **Preparation of Anti Acetone Adduct 11 Using Lithium Metal with 5 mol % Naphthalene.** Lithium powder (325 mesh, 234 mg, 3.7 mmol, 5.4 equiv) and naphthalene (39.6 mg, 0.31 mmol, 5 mol %) were suspended in 40 mL of THF. The solution was stirred at 0 °C for 10 min after the purple color persisted and then cooled to −78 °C. Phenylthio acetal **3** [R′ = $CH(CH_3)_2$] (2.01 g, 6.23 mmol, 1.0 equiv) was dissolved in 6 mL of THF and added via syringe pump (2.7 mL/h) over 3 h. The syringe was rinsed with 2.0 mL of THF, and the reaction was stirred for an additional 15 min. Acetone (2.0 mL, 27.2 mmol, 4.4 equiv) was added, and the solution was allowed to warm to rt overnight. The reaction was quenched with $H_2O$, and the mixture was extracted with ether (100 mL). The organic layer was washed (2 × 1 N NaOH, brine), dried ($MgSO_4$), and concentrated under reduced pressure. The resulting oil was purified by flash chromatography ($SiO_2$, 5–10% ethyl acetate/hexanes) to give 172 mg (0.80 mmol, 13%) of simple reduction product as a light yellow oil and 1.33 g (4.88 mmol, 78%) of the acetone adducts **11** and **12** as a 97:3 mixture favoring the anti adduct.

(17) **Preparation of Syn Acetone Adduct 12 Using Lithium Metal with 5 mol % Naphthalene.** The anion from 509.3 mg of phenylthio acetal **3** [R′ = $CH(CH_3)_2$] (1.58 mol, 1.0 equiv) was prepared as above from 84.3 mg of lithium powder (12.1 mmol, 7.7 equiv) and 9.3 mg of napthalene (0.073 mmol, 5 mol %). After slow addition of **3** to the lithium/naphthalene suspension the reaction stirred at −78 °C for 15 min and then warmed to exactly −20 °C for 30 min. The reaction mixture was then recooled to −78 °C, and acetone (500 μL, 6.8 mmol, 4.3 equiv) was added. The reaction was quenched and worked up as above to give 44.5 mg (0.21 mmol, 13%) of the simple reduction product as a light yellow oil and 320.6 mg (1.18 mmol, 75%) of only syn acetone adduct **12** as a light yellow oil.

stereoselectivity by appropriate choice of reaction conditions, and the reductive lithiations can be performed with lithium metal and a catalytic amount of naphthalene. We are currently investigating the use of phenylthio acetal 3 and acetate 2 in radical and cationic carbon–carbon bond forming reactions. These synthons herald a rich new area for practical polyol synthesis.

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**Supplementary Material Available:** Representative procedures and full characterization for all new compounds (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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# Perovskone: A Triterpene with a Novel Carbon Skeleton from *Perovskia abrotanoides*†

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*H.E.J. Research Institute of Chemistry, University of Karachi, Karachi-75270, Pakistan, and Department of Chemistry, University of Baluchistan, Quetta, Pakistan*

*Received April 24, 1992*

*Summary:* A new triterpene, perovskone (1) with a novel carbon skeleton, was isolated from the whole plant of *Perovskia abrotanoides* (Labiatae). The structure of 1 was established on the basis of 2D NMR spectroscopic studies and single-crystal X-ray diffraction analysis. A possible biogenetic route for 1 was also suggested.

*Perovskia abrotanoides*, Karel syn. *P. artemisioides* Boiss (Labiatae) occurs in Baluchistan and North West Frontier provinces of Pakistan.[1] The plant is used as a cooling medicine and has been studied for essential oils.[2-4] Antibacterial activities of the essential oils have also been reported.[4]

Perovskone (1), a novel triterpene, was isolated from plant material collected from the Baluchistan province.[5] The molecular formula of perovskone (1), $C_{30}H_{42}O_3$, was determined by its high-resolution electron-impact mass spectrum ($m/z$ 450.3120 amu), indicating 10 degrees of unsaturation in the molecule. The UV spectrum displayed an intense absorption at 270 nm, indicating extending conjugation in the molecule. The IR spectrum showed bands at 1660, 1620, and 1120 $cm^{-1}$ revealing the presence of an $\alpha,\beta$-unsaturated carbonyl, olefinic, and ether functionalities. $^{13}C$ NMR (broad-band and DEPT)[6] experiments revealed all 30 carbons attached to a total of 42 hydrogen atoms, with seven methyl, eight methylene, five methine, and 10 quaternary carbon atoms (Table I). The $^1H$ NMR spectrum ($CDCl_3$) (Table I) contained five three-proton singlets at $\delta$ 0.79, 0.82, 1.34, 1.50, and 1.65 which could be assigned to five tertiary methyl groups. Two three-proton doublets at $\delta$ 1.01 and 1.10, due to two secondary methyl groups, were also present. A multiplet at $\delta$ 5.32 indicated the presence of an olefinic proton.

Deshielded $^{13}C$ NMR resonances at $\delta$ 201.2 (C), 124.0 (C), and 169.5 (C) indicated the presence of an $\alpha,\beta$-unsaturated ketone functionality containing a tetrasubstituted double bond and an oxygen substituent at the $\beta$-position. Olefinic resonances at $\delta$ 120.2 (CH) and 136.3 (C) revealed a trisubstituted double bond. Three more downfield signals at $\delta$ 88.8 (C), 89.3 (C), and 96.4 (C) indicated the presence of carbons containing oxygen func-

**Table I. $^1H$ and $^{13}C$ NMR Assignments for Perovskone (1)[a]**

| carbon no. | $^1H$ (ppm) | $^{13}C$ (ppm) |
|---|---|---|
| 1 | 1.12 (m), 1.32 (m) | 42.1 ($CH_2$) |
| 2 | 1.42 (m), 1.70 (m) | 19.7 ($CH_2$) |
| 3 | 1.60 (m), 1.80 (m) | 42.8 ($CH_2$) |
| 4 | | 33.7 (C) |
| 5 | 0.85 (m) | 53.9 (CH) |
| 6 | 1.36 (m), 1.55 (m) | 21.7 ($CH_2$) |
| 7 | 1.30 (m), 2.00 (dd, $J$ = 8.0, 14.4 Hz) | 41.2 ($CH_2$) |
| 8 | | 48.4 (C) |
| 9 | | 54.0 (C) |
| 10 | | 88.8 (C) |
| 11 | | 96.4 (C) |
| 12 | | 169.5 (C) |
| 13 | | 124.0 (C) |
| 14 | | 201.2 (C) |
| 15 | 3.08 (hept, $J$ = 7.1 Hz) | 24.4 (CH) |
| 16 | 1.10 (d, $J$ = 7.1 Hz) | 20.6 ($CH_3$) |
| 17 | 1.01 (d, $J$ = 7.1 Hz) | 19.8 ($CH_3$) |
| 18 | 0.82 (s) | 32.1 ($CH_3$) |
| 19 | 0.79 (s) | 21.9 ($CH_3$) |
| 20 | 1.74 (d, $J$ = 13.5 Hz)<br>2.53 (d, $J$ = 13.5 Hz) | 54.4 ($CH_2$) |
| 21 | 1.55 (m), 2.72 (dd, $J$ = 7.0, 15.1 Hz) | 35.7 ($CH_2$) |
| 22 | 5.32 (m) | 120.2 (CH) |
| 23 | | 136.3 (C) |
| 24 | 2.42 (br t, $J$ = 9.2 Hz) | 48.6 (CH) |
| 25 | 1.24 (m), 2.11 (ddd, $J$ = 7.4, 7.8, 12.6 Hz) | 33.5 ($CH_2$) |
| 26 | 2.34 (dd, $J$ = 7.4, 12.6 Hz) | 54.0 (CH) |
| 27 | | 89.3 (C) |
| 28 | 1.34 (s) | 24.4 ($CH_3$) |
| 29 | 1.65 (s) | 27.2 ($CH_3$) |
| 30 | 1.50 (br s) | 20.1 ($CH_3$) |

[a] Spectra were recorded in $CDCl_3$ at 500 ($^1H$) and 75 ($^{13}C$) MHz. Chemical shifts are in ppm from internal TMS. $^{13}C/^1H$ Correlations are based on HMQC and hetero COSY experiments.

† Dedicated to Professor Salimuzzaman Siddiqui on his 94th birthday.

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