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.

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

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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 α,β-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 δ 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 δ 1.01 and 1.10, due to two secondary methyl groups, were also present. A multiplet at δ 5.32 indicated the presence of an olefinic proton.

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) 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.

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

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

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(1) Nasir, E.; Ali, S. I. *Flora of West Pakistan*; Fakhri Printing Press: Karachi; 1972; p 628.

(2) Chopra, R. N.; Nayar, S. L.; Chopra, I. C. *Glossary of Indian Medicinal Plants*; CSIR: New Delhi, 1956; p 189.

(3) Kirtikar, K. R.; Basu, B. D. *Indian Medicinal Plants*; Indian Press: Allahabad, 1918; p 1031.

(4) Hasan, M.; Iqbal, R.; Ullah, I.; Haq, I. U. *Islamabad J. Sci.* **1978**, *5*(1–2), 22–5 (Engl.) *Chem. Abstr.* **1980**, *93*, 230915b.

0022-3263/92/1957-4339$03.00/0

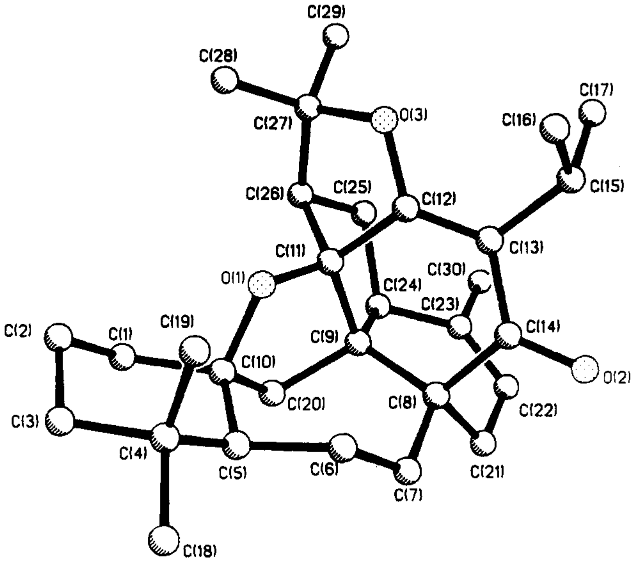
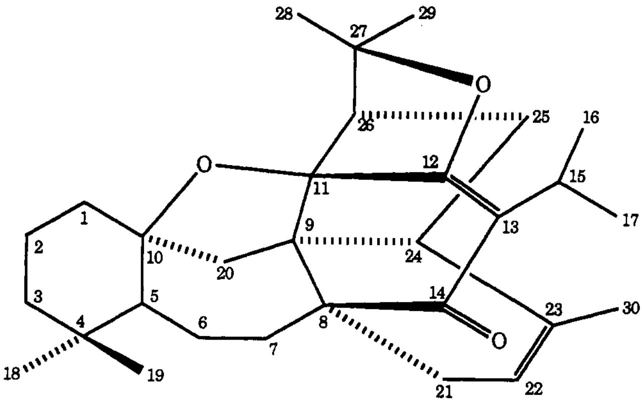


Figure 1. A computer-generated perspective drawing of the final X-ray model of perovskone (1). Hydrogens are omitted for clarity.

tions. The absence of additional carbonyl resonances implied that perovskone (1) must have seven rings, including two cyclic ethers, in order to satisfy its unsaturation number.



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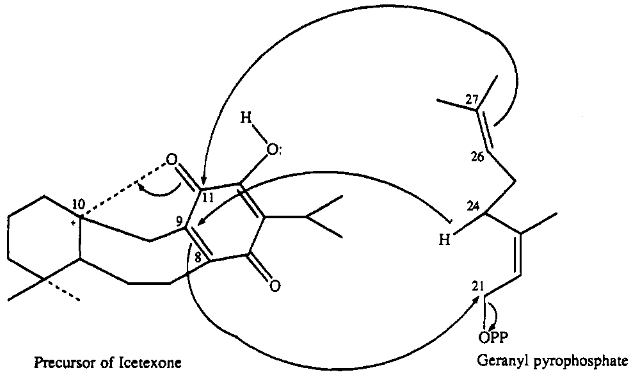
It was not possible to accommodate all of the identified fragments with any known triterpene carbon skeleton, so the structure of perovskone (1) was solved by single-crystal X-ray diffraction analysis. A suitable crystal, which belonged to the orthorhombic space group $P2_12_12_1$, with accurate lattice constants of a = 8.654 (1) Å, b = 15.989 (3) Å, c = 18.719 (3) Å and Z = 4, was selected for this purpose. All unique reflections with $2\theta \leq 112°$ were collected with $2\theta:\theta$ scans and CuKα radiation (1.541 78 Å). A total of 1510 (77%) had $|F_o| \geq 6\sigma(F_o)$ and were used in subsequent calculation. The structure was solved by using direct methods and refined by full-matrix least-squares techniques to a conventional discrepancy index of 0.040 (Rw = 0.057) for the observed data.[7,8] A computer-generated perspective drawing of the final X-ray model of perovskone is given in Figure 1. No absolute configuration is implied. The O-3, C-12, C-13, C-14, and O-2 are in perfect conjugation as reflected by the shorter bond lengths of O-3–C-12 (1.35 Å) and C-13–C-14 (1.46 Å) single bonds and relatively longer bond lengths of C-12–C-13 (1.34 Å) and C-14–O-2 (1.23 Å) double bonds.

Scheme I. Proposed Biosynthesis of Perovskone (1)



Two-dimensional NMR (J-resolved, COSY 45°, HETCOR, NOESY) and inverse 2D NMR (heteronuclear multiple quantum coherence and homonuclear multiple bond connectivity) experiments[6] were performed for unambiguous chemical shift assignments of carbons and protons of the skeleton. The heteronuclear correlations and $^1H/^1H$ coupling constants are summarized in Table I.

Perovskone (1) is the first member of a new class of triterpene, for which we suggest the name perovskane. Perovskone is an extremely interesting target for biosynthetic studies. Its biogenesis may proceed through the addition of geranylpyrophosphate to an icetexone precursor[9] with the formation of carbon–carbon bonds between C-21 and C-8, C-24 and C-9, C-26 and C-11, and carbon oxygen bonds (Scheme I). The numbering of the skeleton is based on biogenetic arguments.

Acknowledgment. We thank Dr. R. B. Tareen, Asst. Prof., Department of Botany, University of Baluchistan, Quetta, for the identification of the plant material.

Supplementary Material Available: X-ray crystallographic data for 1 (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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(5) The whole plant material (18 kg) was collected in Ziarat, Baluchistan, in Aug 1989. The plant was identified by Dr. R. B. Tareen, Asst. Prof., Department of Botany, University of Baluchistan, Quetta. A voucher specimen has been deposited in the Department's herbarium. The crushed plant material was soaked in n-hexane (40 L). The hexane extract was evaporated to a gum under vacuum. The resulting gum (100 g) was loaded on a silica gel (1 kg, 70–230 mesh size) column and eluted with n-hexane to yield 1 with several minor components. Recrystallization from MeOH yielded 1 as colorless crystals (90 mg): $[\alpha]^{25}_D$ = +94° (c 0.07, $CHCl_3$); mp 192 °C; yield 0.0005%, R_f = 0.49 (silica gel card Riedel de Haen, Art. No. 37341 $CHCl_3$–C_6H_{14} (1:1)).

(6) Atta-ur-Rahman. *One and Two Dimensional NMR Spectroscopy*; Elsevier Science Publishers: New York, 1989.

(7) Sheldrick, R. G. *SHELXTL PLUS, Structure Solving Package*; Nicolet: Madison, 1986.

(8) The Nicolet R3m/V (now Siemens) diffractometer connected with digital MicroVax II computer was used in crystallographic work. Crystal data: $C_{30}H_{42}O_3$, MW 450, orthorhombic, space group $P2_12_12_1$, a = 8.654 (1) Å, b = 15.989 (3) Å, c = 18.719 (3) Å, Z = 4, V = 2590.2 (8) Å^3, Dc = 1.156 g/cm^3, radiation CuKα (λ = 1.5418 Å). Crystal dimensions: 0.35 × 0.30 × 0.27 mm. Intensity data: $\theta:2\theta$ scan type 2θ = 0.0–112°, graphite monochromator, yielded 1962 unique reflections, out of which 1510 $|F_o| \geq 6\sigma(F_o)$ were judged observed. The structure was solved by direct methods and refined by full-matrix least-squares methods for final discrepancy index of 0.040 (Rw = 0.057). Hydrogen atoms were included at their calculated positions.

(9) Watson, W. H.; Taira, Z.; Dominguez, X. A. Gonzales, H.; Guiterrez, M.; Aragon, R. *Tetrahedron Lett.*, **1976**, 29, 2501–2502.