the SEM and in an electron microprobe demonstrated that they were Al_2O_3 (*2*). The spheres were colorless and are pure Al_2O_3, with no impurities at the 0.5 percent detection level. Typical particles are shown in Fig. 1. The aluminum oxide spheres (AOS's) did not have perfect spherical symmetry, but departures from sphericity were usually small. Highly oblate, prolate, or dumbbell shapes were not observed. Some of the AOS's had smaller spheres bonded to their surfaces. Many of the larger spheres had brain-textured surfaces suggestive of multicrystalline interiors.

The spatial density of AOS's is shown in Fig. 2. Although ~ 90 percent of the collected particles ≤ 6 μm were Al_2O_3, the size distribution was so steep that for sizes larger than 10 μm, the AOS's became a minority among collected particles. Most of the collected particles > 10 μm had elemental compositions like those of primitive meteorites (*1*), or they were opaque, irregular particles composed of Al with minor amounts of Fe, Cu, and sometimes other elements. The irregular Al particles may be contaminants, but because they were not found on control surfaces, we suspect they may be stratospheric and genetically related to the AOS's.

The pure Al_2O_3 composition of the AOS's suggests an exotic source. While it is conceivable that a few spheres could be produced by high-temperature condensation in meteor wakes, we believe the most reasonable source is solid-fuel rocket exhaust. Powdered aluminum is an additive put in solid rocket fuels to increase specific impulse. During combustion the aluminum is oxidized, and laboratory experiments (*3*) have shown that Al_2O_3 spheres are the major particulate in the exhaust. That rockets are definite contributors of Al_2O_3 to the stratosphere was proved by U-2 sampling flights through the exhaust plumes of two Titan III rockets (*4*, *5*). The collections were made at 20 km and yielded large quantities of Al_2O_3 spheres virtually identical to the AOS's normally collected as background aerosol. Both the Titan III and the background Al_2O_3 spheres have identical elemental abundances and optical properties, and in the SEM many of the spheres from both sources have brain-textured surfaces or adhering surface blebs or spherules. The total mass of background AOS's appears to be compatible with the solid-fuel rocket source. Assuming that our density measurements are representative of the entire earth we estimate that the total mass of AOS's > 2 μm in the stratosphere is on the order of 10^8 g.

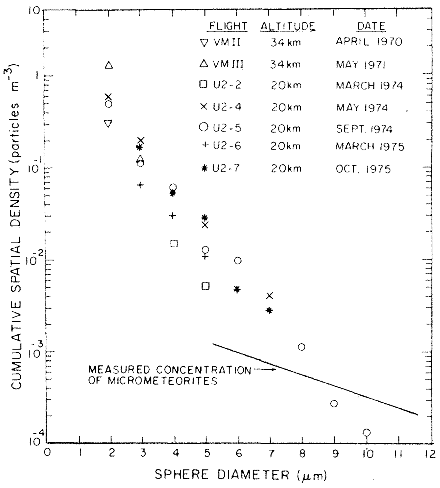

Fig. 2. Spatial density of AOS's measured at 34 km with balloons and at 20 km with NASA U-2 aircraft. The particle diameters are uncertain by ~ 1 μm because of the difficulty of optically measuring the diameters of small transparent spheres. The errors due to counting statistics are comparatively unimportant, except for the point at 10 μm, which is based on only two particles. The accuracy of the points at 2 μm is uncertain because of microscope counting difficulties and uncertainties in the collection efficiency for 2-μm particles.

Our measurements indicate that for the past 6 years AOS's have been the dominant stratospheric aerosol in the size range 3 to 8 μm. Within a factor of ~ 5, or possibly much less, the spatial density has been constant between 20 and 35 km in the atmosphere. Apparently the concentration has been maintained in quasi-equilibrium by injections of new material from solid-fuel rockets. Because of the altitudes of the collections and the low fall speeds of the particles [0.1 cm/sec for 2-μm AOS's (*6*)] there can be little doubt that the aerosol is a hemispherical if not global phenomenon. Possible climatological effects of Al_2O_3 from the solid-fuel boosters of the space shuttle have been evaluated by Hofmann *et al.* (*7*).

Our new measurements indicate that the composition of the stratospheric aerosol is strongly size-dependent. In the submicrometer region the majority of particles are the well-known sulfate aerosol (*8*). For the size range bounded by 8 μm and approximately 3 μm the majority of particles are Al_2O_3. Particles larger than 10 μm are largely extraterrestrial in origin (*1*) and are similar in composition to primitive meteorites.

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Prostaglandin B_1: The L-Shaped Prostaglandin

Abstract. *The crystal and molecular structure of prostaglandin B_1 (PGB_1) has been determined. The conformation is L-shaped, with the α and ω side chains roughly perpendicular to one another. This arrangement differs from the "hairpin" or approximately parallel disposition of side chains observed for other prostaglandins. The ω chain, which normally turns at the 15-hydroxyl back toward the α chain, is fully extended. The conformation is stabilized by the conjugation of the dienone chromophore. The 15-hydroxyl, which is normally directed away from the centroid of the prostaglandin in the hairpin model, is turned inward in L-shaped PGB_1. The low biological activity of PGB_1 in many systems and especially its inhibition of the metabolizing enzyme 15-hydroxyprostaglandin dehydrogenase may be attributable directly to the observed L-shape conformation.*

Studies of prostaglandin conformation by single crystal diffraction techniques (*1*–*5*) suggest that a conformational characteristic of the active prostaglandins is the hairpin alignment of the α (C-1 through C-7) and ω (C-13 through C-20) side chains. In addition to diffraction studies, spectral studies (*6*) of the conformations of prostaglandins in solution also suggest the importance of the hairpin model of active prostaglandins. With this in mind, the crystal structure of prostaglandin B_1 (PGB_1) (**1**), a generally less active prostaglandin and a noncompetitive inhibitor of the major metabolizing enzyme 15-hydroxyprostaglandin dehydrogenase

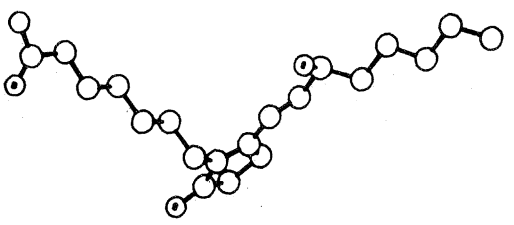


Fig. 1 (left). The conformation of prostaglandin B_1. The oxygen atoms are indicated by a small dot in the center of atom outline.

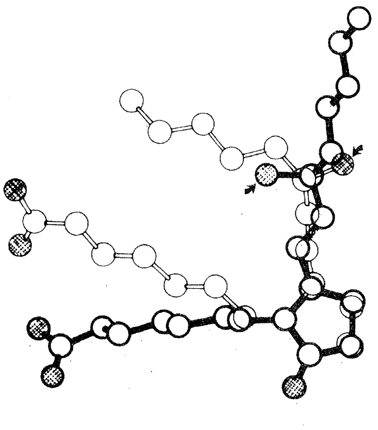


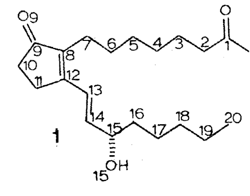
Fig. 2 (right). The structures of PGB_1 (dark line) and the monoclinic form of PGA_1 (light line) superimposed at the cyclopentenone rings. The hatched atoms are oxygens. The 15-hydroxyls are indicated by the arrows.

(PGDH), has been determined in order to see whether there are gross or subtle differences in the conformations of active and inactive prostaglandins. Our study indicates that the conformation of PGB_1 differs radically from that of all other prostaglandins studied up to now by diffraction techniques.

The molecular structure shown (*7*) in Fig. 1 illustrates the nearly perpendicular disposition of the side chains. The ω chain, which normally turns back in toward the α chain at the 15-hydroxyl, is fully extended. The hydroxyl, which normally extends out from the centroid of the prostaglandin molecule, is turned inward. The observed conformation is stabilized by the conjugation of the dienone system extending from O(9) through the Δ^{8-12} and Δ^{13-14} double bonds and possibly to the hydroxyl group. The torsion angles in progression are O(9)=C(9)-C(8)=C(12), 177°; C(9)-C(8)=C(12)-C(13), 179°; C(8)=C(12)-C(13)=C(14), -174°; C(12)-C(13)=C(14)-C(15), 177°; C(13)=C(14)-C(15)-O(15), 2°. The bond lengths C(9)-C(8), 1.47 Å; C(12)-C(13), 1.45 Å; and perhaps C(14)-C(15), 1.50 Å, are shorter than expected for formal single C-C bonds. The *syn*-periplanar arrangement of the 15-hydroxyl oxygen is unique; for all other prostaglandins the O(15) oxygen is +*anti*clinal with respect to C-13; that is, the torsion angle C(13)-C(14)-C(15)-O(15) is approximately +120°. This difference is probably a consequence of the dienone system, also unique to B prostaglandins. The plane of the α chain is approximately perpendicular to the plane of the ring. The cyclopentenone ring itself is essentially planar. The internal ring torsion angles range from 0° about the double bond to ±5° about the C(9)-C(10) and C(10)-C(11) bonds, respectively.

The structure of PGB_1 is shown (Fig. 2) superimposed upon the structure of PGA_1 (monoclinic) (*1*). Like other natural prostaglandins, PGA_1 (**2**) is a substrate for PGDH (*8*), which inactivates prostaglandins by oxidizing the 15-hydroxyl to a 15-keto function. Prostaglandins B_1 and B_2 (**3**) are noncompetitive inhibitors of PGDH. The PGA_1 (monoclinic) geometry of the 15-hydroxyl with respect to the exocyclic double bond and ring is representative of the geometry observed for PGA_1 (orthorhombic) (*2*), PGE_1 (**4**) (*3*), $PGF_{1\beta}$ (**5**) (*4*), and PGE_2 (**6**) (*5*), all substrates for PGDH. In each case the hydroxyl is directed away from the center of the molecule. The exception is PGB_1, the only natural inhibitor of PGDH.

In a recent review (*8*) of the properties of PGDH the question was raised: does the PGB_1 Δ^{8-12} bond "move the ω-alkyl side chain away from the substrate site and if so is it moved into a position which sterically inhibits binding?" To these questions a partial answer seems to be that the side chains move with respect to what we observe for substrate prostaglandins. Although the inhibitory characteristics of PGB_1 have not been definitively related to its binding at the substrate site, and nonspecific fatty acid effects have not been ruled out, it is reasonable to conclude that the shift in conformation from the hairpin model of the substrate prostaglandins to an L-shaped model of a noncompetitive inhibitor is a sufficient condition to explain the behavior of PGB_1 in the PGDH system.



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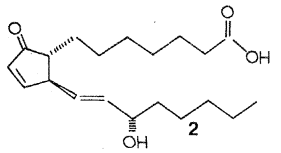

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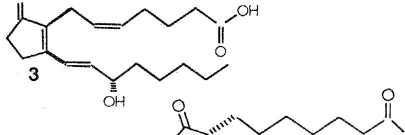

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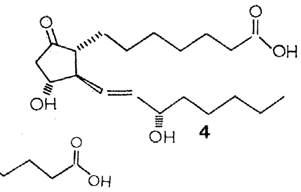

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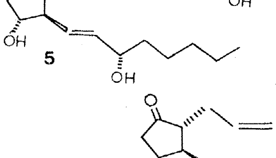

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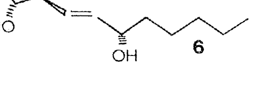

6

Crystals of PGB_1 are orthorhombic, space group $P2_12_12_1$, with $a = 18.744(2)$, $b = 23.017(1)$, $c = 4.6935(4)$ Å; volume = 2025 Å^3. A single crystal of excellent quality was screened optically and by x-ray Weissenberg photography for quality, approximate cell constants, and space group. A total of 2447 data, of which 1252 are considered observed, were measured in the θ-2θ scan mode on an automatic kappa geometry diffractometer with CuKα radiation and base width $(1.2 + 0.2 \tan\theta)°$. The crystal structure was determined by routine multisolution tangent refinement techniques (*9*). The current residuals are $R = 0.108$ and $R_W = 0.124$. Addition of hydrogen atoms and further refinement is expected to lower the residual significantly.

In summary, the conformation of PGB_1 differs markedly from the hairpin observed for other prostaglandins. It is likely that the conformation is stabilized by the conjugation of the dienone system. The observed conformation suggests that the noncompetitive inhibition of PGDH by PGB_1 is a consequence of the protection of the 15-hydroxyl group which extends in toward the center of the molecule.

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