Table I. ^{13}C NMR Spectral Data for Aplasmomycin, Including Relative Enrichments from Labeled Precursors

carbon no.	δ_c[a]	multiplicity[b]	rel enrichment	$^1J_{C-C}$, Hz
1[c]	170.4	s	22.4[c]	64.7
2[d]	78.2	d	18.5[d]	65.2
3[c]	106.0	s	18.5[c]	47.6
4[d]	32.9	d	15.0[d]	47.6
5[c]	28.6	t	17.0[c]	31.7
6[d]	25.0	t	14.0[d]	31.7
7[c]	79.5	d	19.3[c]	39.1
8[d]	39.0	s	12.7[d]	39.1
9[c]	79.3	d	14.9[c]	39.1
10[d]	32.1	t	15.2[d]	39.1
11[c]	128.0	d	13.0[c]	72.1
12[d]	131.8	d	12.5[d]	72.0
13[c]	76.4	d	19.8[c]	34.7
14[d]	36.0	t	14.0[d]	34.7
15	80.4	d		
16	78.2	d		
17	19.4	q		
18[e]	16.5	q	56.6[e]	
19[e]	12.9	q	56.6[e]	
20[e]	21.6	q	56.6[e]	

[a] Chemical shifts are given in parts per million downfield from internal Me_4Si in $CDCl_3$. [b] Multiplicities in the off-resonance decoupled spectrum: s, singlet; d, doublet, t, triplet; q, quartet. [c] These carbon atoms were enriched by [1-^{13}C]acetate and the enrichment is relative to C-17 as 1.0. [d] These carbon atoms were enriched by [2-^{13}C]acetate and the enrichment is relative to C-17 as 1.0. [e] These carbon atoms were enriched by L-[*methyl*-^{13}C]methionine and the enrichment was estimated on the basis of the dilution of the L-[*methyl*-^{14}C]methionine fed with the ^{13}C material.

significant incorporation and enrichment. Kuhn–Roth oxidation of aplasmomycin derived from [2-^{14}C]- and [3-^{14}C]-propionate gave acetic acid samples containing 13.3 and 13.8%, respectively, of the radioactivity of the antibiotic.[9] This suggests that propionate is not incorporated intact, but is converted, with decarboxylation, into acetate via symmetrical intermediates, i.e., succinate and the Krebs cycle. The starter unit of the polyketide, thus, does not originate from propionate.

Pyruvate, succinate, and lactate are not efficient precursors of aplasmomycin. Feeding experiments with [1,3-^{14}C]- and [2-^{14}C]glycerol gave substantial specific incorporations (18–170%). Excess cold acetate or methionine added to the same fermentation with [1,3-^{14}C]glycerol did not decrease the specific incorporation rate. Kuhn–Roth oxidation of the aplasmomycin samples derived from [1,3-^{14}C]- and [2-^{14}C]-glycerol gave sodium acetates containing 31% (of which >⅔ were located in the methyl group) and 54% of the total radioactivity, respectively. This suggests that glycerol may be specifically incorporated into the starter unit, C-1 and C-3 of glycerol probably giving rise to C-15, -15′ and C-17, -17′ of aplasmomycin, and C-2 of glycerol becoming C-16, -16′ of aplasmomycin. In view of the negative results with propionate, pyruvate, succinate, and lactate it seems possible that glycerol is incorporated into aplasmomycin via conversion to methylglyoxal as an intermediate.[10]

The biosynthetic origin of aplasmomycin can therefore be summarized as shown in **I**. Each half of the macrocyclic lactone ring is formed from one glycerol, seven acetate units, and three methyl groups of methionine. Further studies with [1,3-^{13}C]glycerol are in progress to determine whether the starter unit of the polyketide chain is indeed derived from glycerol.

Acknowledgments. We thank Professor Y. Okami, University of Tokyo, for kindly providing *S. griseus* SS-20 and a reference sample of aplasmomycin, Dr. K. Shimada, Hokkaido, University, for his help in procuring Kobu-cha, and Mr. J. Kozlowski of this department for recording many of the NMR spectra. This work was supported by the National Institutes of Health through Research Grant AI 11728. The services of the Purdue University Biological Magnetic Resonance Laboratory, supported by NIH Grant RR 01077 from the Division of Research Resources, are gratefully acknowledged.

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(5) The culture medium contained glucose (1%) and Kobu-cha (1%) at a pH of 7.8. Each precursor was added to ten 100-mL cultures in 500-mL Erlenmeyer flasks. [1-^{13}C]Acetate (400 mg), [2-^{13}C]acetate (440 mg), [1,2-^{13}C]acetate (300 mg), and [$^{13}CH_3$]methionine (440 mg) were added.
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Received May 29, 1979

A Unique Triple Atom Bridge: X-ray Structure of the μ-Selenido-μ-diselenido-bis(tetrachloro)tungstate(V) Ion

Sir:

We believe that Y_2^{2-} units (Y = S or Se) are most easily formed by the oxidation of Y when Y bridges two metal atoms. This appears to be the case with adducts of WCl_3S. Thus the formation of such adducts by reduction of WCl_4S (which has a terminal W=S bond[1]) with excess of ligand gives an adduct in which this terminal bond remains (e.g., $WCl_3S\cdot MeSCH_2CH_2SMe$[2]). On the other hand direct reaction of WCl_3S (which contains W–S–W links) with ligands gives adducts whose infrared spectra indicate the presence of S_2^{2-} groups.[3]

As a part of our study of the chalcogenide halides WCl_3S and WCl_3Se,[4] we have examined the reactions between WCl_3Se and $(AsPh_4)Cl$ in CH_2Cl_2 solution; recrystallization of the soluble product gave brown crystals whose analysis corresponded to $(AsPh_4)_2(W_2Cl_8Se_3)$.[5]

The compound $As_2C_{48}Cl_8H_{40}Se_3W_2$ (M = 1654.34) crystallizes as brown needles in the triclinic system, space group $P\bar{1}$ with a = 12.585 (8), b = 18.151 (9), c = 14.695 (7) Å; α = 112.0 (1), β = 113.7 (1), γ = 100.3 (1)°; U = 2626.03 Å^3; D_m = 2.09 (5), D_c = 2.090 g cm^{-3}; Z = 2; μ = 86.4 cm^{-1}. The intensities of 3277 reflections (2θ < 40°) were collected manually using zirconium filtered Mo Kα radiation and the stationary crystal–stationary counter technique. Data was corrected for absorption and the 2629 reflections significantly

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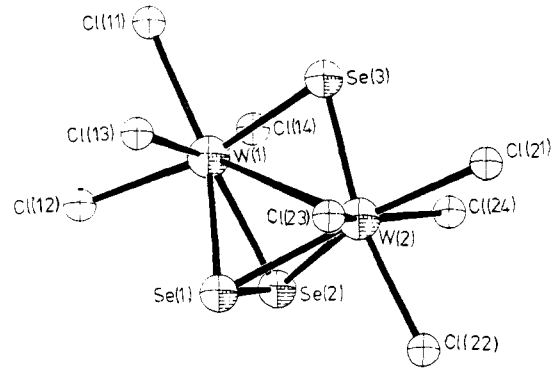

Figure 1. The structure of the $[W_2Cl_8Se(Se_2)]^{2-}$ ion.

above background were used in the final refinement which led to a conventional R factor of 0.0838. The tungsten, selenium, and chlorine atoms were refined anisotropically and the thermal parameters exhibited no noteworthy characteristics.

The asymmetric unit contains two $[AsPh_4]^+$ cations and a $[W_2Cl_8Se_3]^{2-}$ anion (Figure 1). Both metal aroms are bonded to four chlorine atoms and are linked by a bridge consisting of a selenium atom, Se(3), and also an Se_2 group. The anion has approximate C_s symmetry, with the mirror plane containing W(1), W(2), Cl(11), Cl(12), Cl(21), Cl(22), Se(3), and the mid-point of the Se(1)-Se(2) bond. The geometric arrangement around the tungsten atoms of four chlorine atoms, Se(3), and the midpoint Se(1)-Se(2) is approximately octahedral.

The distance between the two tungsten atoms (2.862 (3) Å) suggests the presence of a single metal-metal bond (cf. distances in $[W_3O_2(O_2CR)_6]^{2+}$ (2.75 Å)[6] and $(Et_2NCS_2)(MeO)_2W$-$(\mu$-$S)_2$-$W(MeO)_2(S_2CNEt_2)$ (2.791 (1) Å[7]) to which single bonds have been assigned). Further support for the metal-metal bond is given by the acute angle subtended at the bridging selenium atom Se(3) (73.3 (2)°) (cf. 73.2 (1)° seen in the W(V)-S-W(V)-S fragment[7]).

The tungsten-selenium (Se(3)) distances (2.384 (7)Å to W(1), 2.409 (7) Å to W(2)) are shorter than expected when the tungsten-sulfur distances in $(Et_2NCS_2)(MeO)_2W$-$(\mu$-$S)_2$-$W(MeO)_2(S_2CNEt_2)$ (2.360 (4), 2.319 (4) Å) and the interatomic distances in elemental sulfur (2.012 to 2.087 Å[8]) and selenium (2.375 (5)[9]) are considered. The tungsten to Se_2 group distances are all in the range 2.558 (6) to 2.580 (6) Å.

We have been unable to find literature reports of structures containing a bridging Se_2 group, but examination of the difference between the molybdenum-sulfur distances in the bridges Mo-$(\mu$-$S)_2$-Mo (2.298 (2) to 2.344 (2) Å[10]) and Mo-$(\mu$-$S_2)$-Mo (2.40-2.46 Å[11]) are in accord with the difference between the W-Se(3) and W-Se_2 distances observed here.

The selenium-selenium distance (2.255 (8) Å) is shorter than that seen in Na_2Se_2 (2.38 (5) Å[12]). This shortening of the interatom distance on coordination of Se_2^{2-} is exactly parallel to the changes seen in the disulfide ion which has an interatom distance of 2.13 (5) Å in the ionic compound Na_2S_2[12] that becomes 1.98 Å in $Mo_2Cl_4Cl_{4/2}$-$(\mu$-$S_2)_2$[11], 2.035 (6) to 2.063 (6) Å in $(S_2)_2Mo$-$(\mu$-$S_2)_2$-$Mo(S_2)_2$,[2,13] and 2.03 in Mo_3Cl_4-S-$(\mu$-$S_2)_3$.[11] The valence shell configuration of Y_2^{2-} (Y = S or Se) is $(\sigma s)^2$ $(\sigma^* s)^2$ $(\sigma p)^2$ $(\pi)^4$ $(\pi^*)^4$ and so, when Y_2^{2-} bonds side onto two metal atoms with suitable empty d orbitals π^* to d_π, donation can take place, with a shortening of the Y···Y bond length.

The tungsten-chlorine distances (2.418 (13) to 2.481 (14) Å) are within the range of known tungsten(V)-chlorine terminal bonds. The two independent cations were ordered and the angles between the phenyl rings ranged from 45.5 to 89.1°.

Acknowledgment. We thank the Science Research Council for support of E.M.P.

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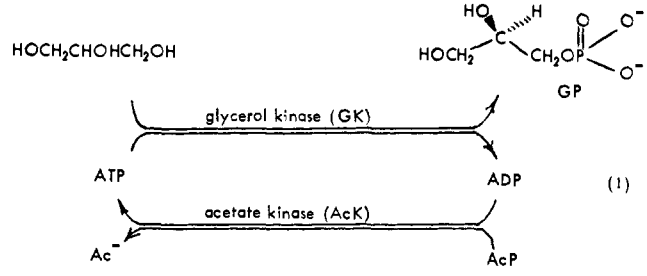
Enzymatic Synthesis of *sn*-Glycerol 3-Phosphate[1]

Sir:

We describe here a practical procedure for the synthesis of *sn*-glycerol 3-phosphate (GP, L-glycerol 3-phosphate) based on enzymatic phosphorylation of glycerol using ATP and glycerol kinase (E.C. 2.7.1.30) (eq 1). The ATP is regenerated



using the recycling system described previously,[2] with acetyl phosphate (AcP) as the ultimate phosphorylating agent.[3] GP is an important intermediate in syntheses of phospholipids.[4] Present preparations of chiral glycerol derivates are based on isolation from natural sources,[5] or on cleavage of the C-3-C-4 bond of derivatives of mannitol.[6] Both types of procedure are capable of generating substantial amounts of materials, but require several steps. The enzymatic synthesis described here requires only a single step, and provides what is probably the most practical method presently available for the preparation of quantities of enantiomerically pure GP.

A representative synthesis was carried out in a 5-L round-bottomed flask equipped with a pH electrode and containing a magnetic stirring bar and 5 g of nylon beads to facilitate stirring. The flask was charged with 1 L of doubly distilled water containing glycerol (110 mmol), ATP (2 mmol), $MgCl_2 \cdot 6H_2O$ (4 mmol), and dithiothreitol (DTT, 10 mmol).[7]

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