diffraction analysis was performed.

Crystals of **4** were grown from concentrated toluene solutions, carefully layered with methylcyclohexane at −40 °C, and its structure was determined from diffraction data collected at −170 °C.[16] The molecular geometry with selected distances and angles is shown in Figure 3. The bridging hydrogens did *not* appear in the final difference Fourier but must be located in the cavity below the bridging chlorides. **4** may be described as a quadruply bridged tantalum(IV) dimer with a metal–metal single bond of 2.621 (1) Å. The terminal Cl_2P_2 units and the bridging ligands are in a mutually staggered arrangement so that the coordination about each tantalum is roughly square antiprismatic. The molecular symmetry is very close to C_s (mirror symmetry), although this is not imposed by the space group. The solid-state phosphine stereochemistry agrees very well with that predicted on the basis of solution NMR measurements. The two angles, Ta(2)–Ta(1)–P(9) and Ta(2)–Ta(1)–P(10), are equal [117.6 (1)°], as are the two Ta(1)–P_{eq} distances [2.635 (3) and 2.646 (3) Å]. The axial phosphines are clearly nonequivalent. The Ta(1)–Ta(2)–P(11) and Ta(1)–Ta(2)–P(12) angles are 130.6 (1) and 103.2 (1)°, respectively. P(11), which is adjacent to the chloride bridges and trans to the bridging hydrides, is 2.665 (3) Å from Ta(2) while the Ta(2)–P(12) distance is significantly shorter, 2.610 (3) Å. The bridging chlorine angles, Ta(1)–Cl(3,4)–Ta(2), are very acute and average 61.8°. There is one exceptionally short nonbonded intramolecular contact. The two bridging chlorines are separated by 3.072 Å, well below the van der Waals limit. Full details of the two structures described here will be reported in a future publication.

Finally, we note that **2**, dissolved in toluene, reacts readily and cleanly with ethylene (20 psi) at 25 °C (eq 4) to give a royal blue

$$Ta_2Cl_6(PMe_3)_4 + C_2H_4 \xrightarrow{PhCH_3} 2TaCl_3(PMe_3)_2(C_2H_4) \qquad (4)$$

diamagnetic crystalline solid, **5**. Elemental analyses and a mass spectrum[17] of this volatile compound establish it as the monomeric tantalum(III) ethylene complex, $TaCl_3(PMe_3)_2(C_2H_4)$. A trans,mer geometry is indicated by ^{31}P, ^{13}C, and ^1H NMR measurements.[18] **5** has been reported previously by Schrock and co-workers[19] from the reaction of the tantalum alkylidene complex, *trans,mer*-$Ta(CHCMe_3)Cl_3(PMe_3)_2$, with ethylene. It is not obvious why only one isomer should form in eq 4. Low-temperature reactions of **2** with C_2H_4 which may bear on this question are in progress.

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Supplementary Material Available: Fractional coordinates and thermal parameters for $Ta_2Cl_6[P(CH_3)_3]_4$ and $Ta_2Cl_6[P(CH_3)_3]_4H_2$ (6 pages). Ordering information is given on any current masthead page.

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(15) (a) The only structural report we are aware of is the neutron diffraction analysis[15b] of $H_8Re_2(PEt_2Ph)_4$, a complex with four bridging hydrides. (b) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

(16) $Ta_2Cl_6(PMe_3)_4H_2$ crystallizes in the monoclinic space group $P2_1/n$ with a = 13.650 (4), b = 11.285 (3), c = 22.479 (8) Å, β = 125.45 (1)°; V = 2820.95 Å^3 and ρ(calcd) = 2.074 g cm^{-3} for mol wt 880.9 and z = 4. Diffraction data were collected at −170 °C by a θ–2θ scan technique using equipment described elsewhere.[8] Data were corrected for absorption (μ = 84.6 cm^{-1}) and the structure was solved by a combination of Patterson, difference Fourier, and full-matrix least-squares refinement techniques. All atoms, with the exception of the bridging hydrogens, were located and their positional and thermal parameters (anisotropic for Ta, Cl, P and C; isotropic for H) refined. The resulting discrepancy indices are R_F = 6.21% and R_{wF} = 4.83% for those 5153 reflections with $F_o \geq 2.33\sigma(F_o)$. The limits of data collection were 5° < 2θ < 55° (Mo Kα radiation).

(17) Anal. Calcd for $TaCl_3P_2C_8H_{22}$: C, 20.55; H, 4.74; Cl, 22.75. Found: C, 20.40; H, 4.78; Cl, 22.67. The mass spectrum of **5** (electron impact, 45 eV) did not show the parent ion (P) but P minus C_2H_4 and P minus (C_2H_4 + PMe_3) were observed with the correct isotope patterns expected for $TaCl_3(PMe_3)_2$ and $TaCl_3(PMe_3)$, respectively.

(18) JEOL FX90Q data. ^1H NMR (ppm, C_6D_6, 89.56 MHz) 2.84 (t, 4, C_2H_4, J_{PH} = 2.0 Hz), 1.45 ("virtual triplet", 18, P–CH_3, J_{PH}(apparent) = 4.0 Hz). $^{13}C\{^1H\}$ NMR (ppm from Me_4Si, C_6D_6, 22.50 MHz) 59.09 (poor t, C_2H_4, J_{PC} ~3.9 Hz), 14.45 ("virtual triplet", P–CH_3, J_{PC} (apparent) = 13.7 Hz). $^{31}P\{^1H\}$ NMR (ppm from H_3PO_4, C_6D_6, 36.20 MHz) −10.1 (s, P–CH_3).

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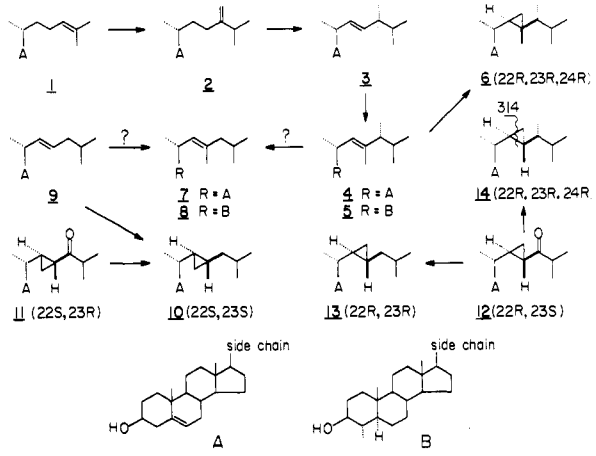
Isolation and Structure Elucidation of 22(*S*),23(*S*)-Methylenecholesterol. Evidence for Direct Bioalkylation of 22-Dehydrocholesterol[1]

Sir:

A unique feature of certain marine sterols—never encountered among terrestrial counterparts—is the occurrence of bioalkylation of the cholesterol side chain at positions 22 and 23. Gorgosterol (**6**)[2] is the first recorded example, and we hypothesized[2,3] that its biosynthetic precursor is brassicasterol (**3**), itself derived by the conventional C-24 bioalkylation from desmosterol (**1**).[4,5] This



implied the existence of an intermediate 23,24-dimethyl-Δ^{22}-sterol whose subsequent isolation[6,7] (e.g., **5** and **4**) added plausibility

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Table I. ^{1}H NMR Chemical Shifts of the Methyl Groups of Natural and Synthetic Isomers of 22,23-Methylenecholesterol and of Natural and Synthetic Isomers of Demethylgorgosterol[a]

sterol	methyl groups					
	C_{19}	C_{18}	C_{21}	C_{26}	C_{27}	C_{28}
22,23-methylenecholesterol (10) (natural)	1.004	0.621	0.995 (6.6)	0.913 (6.9)	0.889 (6.8)	
synthetic 10 (22*S*,23*S*)	1.004	0.623	0.995 (6.7)	0.912 (7.2)	0.890 (6.6)	
synthetic 13 (22*R*,23*R*)	1.006	0.626	0.951 (6.6)	0.894 (6.6)	0.894 (6.6)	
demethylgorgosterol (14) (natural)	1.005	0.640	0.920 (6.1)	0.913 (6.3)	0.889 (6.9)	0.858 (6.9)
synthetic 22*R*,23*R*,24*R*	1.005	0.640	0.920 (6.2)	0.913 (6.4)	0.889 (6.9)	0.858 (6.9)
synthetic 22*R*,23*R*,24*S*	1.006	0.650	0.888 (7.1)	0.868 (7.1)	0.854 (6.9)	0.710 (6.9)
synthetic 22*S*,23*S*,24*R*	1.004	0.622	1.006 (6.3)	0.881 (7)	0.872 (6.3)	0.799 (6.9)
synthetic 22*S*,23*S*,24*S*	1.005	0.621	1.002 (6.4)	0.898 (6.8)	0.898 (6.8)	0.867 (6.8)

[a] In parts per million; coupling constants of doublets, in hertz, in parentheses.

to our hypothesis for the biosynthesis of gorgosterol (**6**), consisting of *a series of bioalkylation steps starting with conventional C-24 methylation of a Δ precursor* (**1**).

More recenly, two 23-*mono*methyl-Δ^{22}-sterols have been isolated (**8**[8] and **7**[9,10]) which present a new biosynthetic problem. As we pointed out elsewhere,[9] such 23-monomethylsterols could either arise by biodealkylation[11] of 23,24-dimethyl-Δ^{22}-sterols (e.g., **4**→**7**) or by *direct bioalkylation of a* Δ^{22} *double bond* (e.g., **9**→**7**). Hitherto, this process has not been observed in nature, but it should be noted that Δ^{22}-unsaturated sterols [especially 22-dehydrocholesterol (**9**)] are very common in the marine environment.[5] We should now like to present evidence which suggests strongly that such bioalkylation of an isolated Δ^{22} double bond is possible.

In our continuing search for new marine sterols of biogenetic interest, we have encountered in various marine organisms [e.g., *Dysidea* and *Xestospongia* species (Porifera) and *Siphonoborgia* species (Alcyonacea)] small amounts of an apparently widely distributed Δ^5-sterol[12] which has hitherto escaped detection because it is isomeric with the very common 24-methylenecholesterol (**2**)[5] and exhibits a virtually identical mass spectrum with a base peak at m/z = 314. Such a peak is generally considered to be diagnostic[13] of a $\Delta^{24(28)}$ double bond (via a McLafferty rearrangement), but is also very prominent[14,15a] in sterols with a 22,23-cyclopropane ring (sed wavy line in **14**). In point of fact, the new sterol [mp 165 °C; $[\alpha]_D$-104.6° ($CHCl_3$); M^+ = 398.35501 ($C_{28}H_{46}O$)] showed no olefinic NMR (360 MHz) peaks other than the C-6 proton signals (5.35 ppm), but displayed four cyclopropyl protons (2 H, 0.18–0.22 ppm, complex, and 2 H, 0.36–0.40 ppm, complex) in addition to the methyl signals listed in Table I. These data are consistent with a 22,23-methylenecholesterol (**10**, **13**) structure, which we had predicted earlier[3] might occur in nature. In order to confirm this structure and establish its absolute configuration, we performed a Wolff–Kishner reduction of the previously synthesized[16] 3β-hydroxy-22,23-methylene-5-cholesten-24-one (**11**), whose absolute configuration (22*S*,23*R*)[18] had been established unambiguously by X-ray analysis. The resulting product, **10** (22*S*,23*S*), proved to be indistinguishable by NMR (see Table I) and mass spectra as well as GLC mobility from the naturally occurring marine sterol. However, since it was not certain that the 22*S*,23*S* (**10**) and 22*R*,23*R* (**13**) isomers could be differentiated by such criteria, it was necessary to prepare an authentic sample of the second isomer **13**. This was accomplished by Wolff–Kishner reduction of 3β-hydroxy-22(*R*),23(*S*)-methylene-5-cholesten-24-one (**12**), which in turn was obtained by acid-catalyzed treatment (zinc acetate/glacial acetic acid) of 6β-methoxy-3α,5-cyclo-22(*R*),23(*S*)-methylenecholestan-24-one.[17] Its 22*R*,23S configuration is secure,[18] because **12** has been related[17] to natural demethylgorgosterol (**14**) whose absolute configuration (22*R*,23*R*,24*R*) has been established[15b] by X-ray analysis. The mass spectra and GLC mobility [oven temperature 260 °C; retention time (relative to cholesterol) OV-17 = 1.27, OV-25 = 1.31, SE-52 = 1.22] of both isomers **10** and **13** were identical, but as shown in Table I, the small but definite chemical shifts of the C-21 signals detectable in the 360-MHz spectra serve to distinguish them. The utility of such NMR measurements for differentiating among such isomers is further documented in Table I by the four isomers of demethylgorgosterol (**14**).[15–17] The chemical shift differences of the 21-methyl signal can definitely be related to the stereochemistry of the cyclopropane ring and are only slightly affected by the C-24 stereochemistry in the demethylgorgosterol isomers.

Therefore, our newly isolated 22(*S*),23(*S*)-methylenecholesterol (**10**) has the opposite configuration from naturally occurring demethylgorgosterol (**14**)[15] and cannot be derived from **14** by biodealkylation of the C-24 substituent. We believe that our present results constitute the strongest evidence to date that bioalkylation of the Δ^{22} double bond of a sterol side chain is possible in the absence of a C-24 substituent. This in turn greatly increases the likelihood that the recently isolated[8–10] 23-methyl-Δ^{22}sterols **7** and **8** arise by direct biomethylation of Δ^{22}-sterol precursors (e.g., **9**) or via isomerization of 22,23-methylene progenitors (e.g., **10**).

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