introduce 18.5 ± 1% of ^{13}CO into $[Rh_6(CO)_{15}C]^{2-}$. The ^{13}CO-enriched complex, $[Rh_6(CO)_{15}C]^{2-}$ (42 ± 1% ^{13}CO) was also prepared from CCl_4 and ^{13}CO-enriched $[Rh(CO)_4]^-$ (δ 206.33 ppm, ^1J(Rh–C) 74.7 ± 1 Hz). In both cases the ^{13}C nmr spectra at −70 and +25° were similar (see Figure 1b) and showed the absence of the carbide resonance at 264.7 ppm.

The inequivalent bridging carbonyls both appear as triplets (B, δ 225.2 ppm, ^1J(Rh–C) 30.8 ± 2 Hz; C, δ 236.3 ppm, ^1J(Rh–C) 51.8 ± 2 Hz) whereas the terminal carbonyl resonance (δ_A 198.1 ppm) is a doublet of doublets, which we believe is due to ^1J(Rh$_1$–C$_A$) 77.1 ± 2 Hz and ^2J(Rh$_2$–C$_A$) 3.9 ± 2 Hz (see Figure 2).[9]

In all the above cases the values of the chemical shifts for the carbonyl resonances are similar to those recently reported for related compounds,[10] and generally an increase in rhodium–carbon bond length results in a decrease in ^1J(Rh–CO).

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Sterol Biosynthesis from (3RS, 2R)-[2-^{14}C,2-^{3}H]-Mevalonic Acid in a Yeast Homogenate. Stereochemistry of the C-15 Tritium Atom[1,2]

Sir:

Several years ago we described significant stereochemical differences in the elaboration of sterols by rat liver[3] and by yeast[4] enzymes. These observations were made during the investigation of the biosynthesis of sterols from (3RS, 2R)-[2-^{14}C,2-^{3}H]mevalonic acid (MVA) and (3RS, 2S)-[2-^{14}C,2-^{3}H]MVA by a cell free yeast preparation.[4] It was noticed that in this enzyme system *essentially only* C_{27} sterols were formed and that usually major amounts of radioactivity were incorporated[5,6] into cholesta-5,7,24-trien-3β-ol (1) and 5α-cholesta-7,24-dien-3β-ol (2). The (R)-1a and
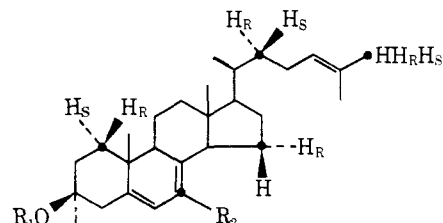
1a, R_1 = H; R_2 = H; H_R = T
b, R_1 = H; R_2 = T; H_S = T
c, 1a acetate
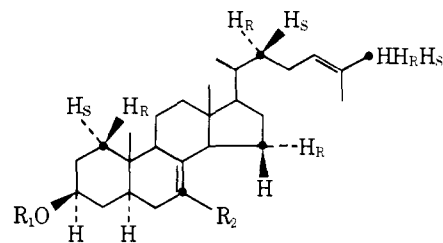
2a, R_1 = H; R_2 = H; H_R = T
b, R_1 = H; R_2 = T; H_S = T
c, 2a acetate
d, R_1 = H; R_2 = H; H_R = T no Δ^{24}

● Carbon atoms derived from C-2 of MVA (^{14}C); T = ^{3}H; H_R and H_S refer to 2 pro R and 2 pro S hydrogens of MVA, respectively.
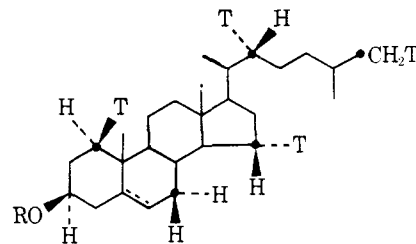
3a, R = H; Δ^5
b, R = Ac; Δ^5
c, R = Ac; no Δ^5, 5α(H)

(R)-2a as well as (S)-1b and (S)-2b each retained four atoms of tritium and five atoms of ^{14}C.[4–6] We have proven[4] that (R)-1a and (R)-2a were *devoid* of tritium atoms at C-7 while the (S)-1b and (S)-2b *retained* tritium atoms at C-7. This observation was in sharp contrast to the situation in rat liver systems[3] in which the transformation of the $\Delta^{8(9)}$ sterol to the Δ^7 isomer proceeds with the loss of a hydrogen derived from 2 pro S of MVA.

It was deduced[4–6] that the yeast (S) metabolites had tritium atoms at C: 1α,7,22, and 26. The (R) metabolites[4–6] had tritium atoms at C: 1β,22 and 26. This left one isotopic hydrogen unaccounted for which was likely to be located[4,12] at C-15. We therefore undertook to determine the location and the stereochemistry of the "fourth" tritium atom of the (R) metabolites.

The homogenate was prepared from aerobically grown yeast as previously reported.[6] The (3RS, 2R)-[2-^{14}C,2-^{3}H]MVA (18 μCi of ^{14}C; ^{3}H: ^{14}C ratio 10.7) was incubated[6] with an aliquot of the homogenate corresponding to 1.5 g of wet cells under an atmosphere of O_2. After conventional work-up[6] the nonsaponifiable residue (1.32 × 10^7 dpm of ^{14}C) was acetylated and resolved into homogeneous trien-acetate (1c) (8.7 × 10^4 dpm) and dien-acetate (2c) (1.06 × 10^6 dpm of ^{14}C). Hydrogenation[7] (EA; Raney-Ni) of a mixture of 2c (4.8 × 10^4 dpm of ^{14}C) and cholesta-5,7-dien-3β-ol acetate resulted in[^{14}C$_5$;^{3}H$_4$]-5α-cholest-7-en-

Table I. Specific Activities of ^{14}C and ^{3}H: ^{14}C Ratios of Yeast Metabolites and Their Transformation Products (See Text)

Compound	Specific activity[a]	^{3}H: ^{14}C ratio — Isotopic	Atomic
MVA[b]	104	10.71	1.00:1
Squalene[b]	491	10.32	5.77:6
2d	7.63	8.72	4.07:5
3a from 2d	1.91	8.65	4.04:5
3b	5.80	8.66	4.04:5
3c	6.00	8.66	4.04:5
3c recovered	6.19	8.63	4.03:5
5	6.04	8.67	4.05:5
4	5.96	6.72	3.14:5

[a] Values $\times 10^4$ dpm; dpm per mmol. [b] The MVA and squalene were counted as the benzyhydrylamide and hexachloride, respectively.

3β-ol acetate (**2d**) (Table I). This confirmed the presence of Δ^7 in the metabolite (**2c**).

We have proven with the use of $(14\alpha,15\alpha)$-$[^{2}H_2]$ and $(8\beta,15\beta)$-$[^{2}H_2]$-5α-cholestanol acetates that their photochemical dehydrogenation to 5α-cholest-14-en-3β-ol acetate in the presence of C_6H_5I Cl_2 involves the overall cis abstraction of the 14α and 15α hydrogen (deuterium) atoms.[8,9] This procedure was employed for the determination of the presence and the stereochemistry of tritium at C-15 of the (R) metabolite (**2c**).

In the absence of an appropriate chemical method for the reduction of **2a** to cholestanol, we opted for a combination of enzymatic and chemical routes.

The (R)-**2a** (5×10^5 dpm of ^{14}C) was incubated with a rat liver preparation[3] to yield $[^{14}C_5,^{3}H_4]$cholesterol (**3a**) (2.2×10^5 dpm of ^{14}C) which was acetylated (**3b**) and then hydrogenated to $[^{14}C_5,^{3}H_4]$cholestanol acetate (**3c**) (Table I). It is apparent that the transformations **2c** → **2a** → **3a** → **3c** proceeded without loss of tritium (Table I). Photochemical dehydrogenation[8,9] of **3c** in benzene in the presence of $C_6H_5ICl_2$ gave cholestanol acetate (**3c**), 5α-cholest-14-en-3β-ol acetate (**4**), and 5α-cholest-9(11)-en-3β-ol acetate (**5**) (Table I).

It is clear that the formation of **4** from **3c** proceeded with the loss of a tritium atom. Since we have proven that the introduction of Δ^{14} involves the abstraction of the 14α- and 15α-hydrogen atoms,[8] it follows that the cholestanol acetate **3c** and hence the (R) metabolites **1a** and **2a** have 15α-tritium atoms. Because the (S) metabolites **1b** and **2b** do not have a tritium[4-6] atom at C-15, it may be inferred that the elimination of the 14α-methyl involves a Δ^{14} intermediate,[10] and that the introduction of this olefinic bond proceeds with the abstraction of a hydrogen originating from 2 pro S of MVA. Considering the fact that the (R) metabolites have a 15α-tritium atom, it follows that the enzymatic reduction of the Δ^{14} proceeds via the trans acquisition of two ionic species of hydrogen at the 14α and 15β positions. In analogy to rat livers[11] it seems likely that a hydride ion (from NADPH) and a proton (from the medium) are added at the 14α and 15β positions, respectively. Finally it may be noticed that the retained 15α-tritium atom in **1a** and **2a** underwent an inversion of configuration with respect to its original orientation in protosterols[12] and lanosterol.

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1,3 Magnetic Exchange in Linear Trimetallic Titanium(III) Complexes

Sir:

Trinuclear metal complexes containing two biscyclopentadienyltitanium(III) species coordinated to a tetrahedral bridging group have been known for some time.[1,2] A representative example is $[Cp_2Ti]_2ZnCl_4 \cdot 2C_6H_6$ which is prepared in benzene by reaction of $[Cp_2TiCl]_2$ with $ZnCl_2$ or from Cp_2TiCl_2 and Zn dust. Crystallization occurs in the form of a dibenzene solvate whose structure has been determined by Vonk[3] and also independently in our laboratory. Similar results are obtained, and our refinement shows a
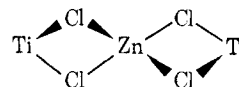
linear unit with a Ti–Zn distance of 3.420 (2) Å, a Zn–Cl–Ti angle of 89.9 (1)°, a Cl–Ti–Cl angle of 82.1 (1)°, and a Ti–Zn–Ti angle of 173.4 (1)°. The Ti–Ti distance is 6.828 (4) Å. We have investigated the magnetic properties of this compound and several analogous ones to liquid helium temperature and wish to report the first example of 1,3 magnetic exchange via a diamagnetic metal atom in a linear trinuclear complex. Gruber, Harris, and Sinn[4] have prepared a series of trinuclear compounds having the potential for this interaction, but did not detect a measurable value for the exchange integral between the terminal metals. Studies of the temperature dependence of the susceptibility of $Ni_3(acac)_6$ have shown that an antiferromagnetic exchange between the terminal nickel atoms via the paramagnetic nickel(II) central metal is necessary to fit the experimental data.[5] In order to study the influence of the nature of the bridging group and cyclopentadienyl rings on the