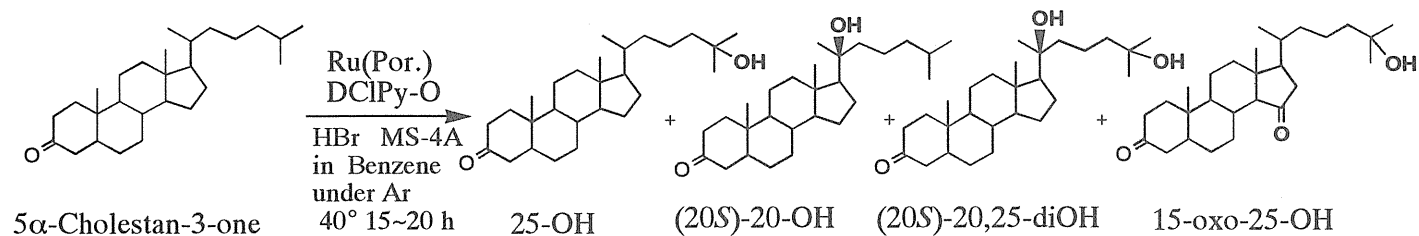


表 1 H₂O₂ の当量数とフェリル型ミオグロビンの吸収極大波長

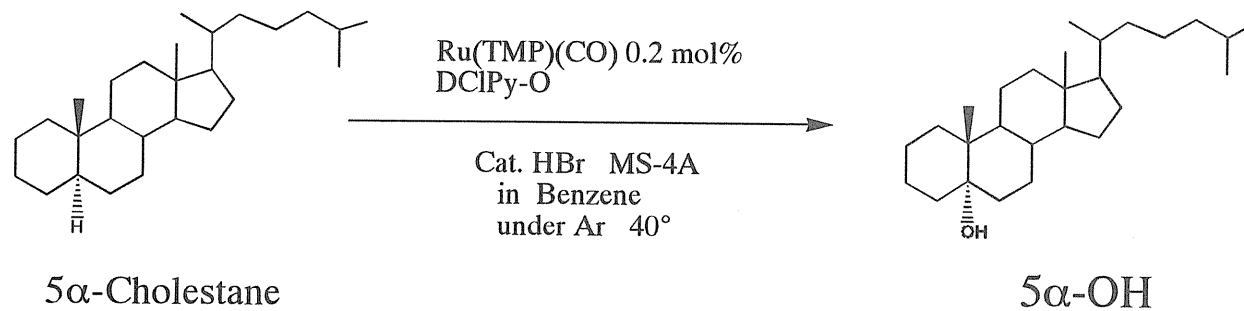
Myoglobin	Eq.	Absorption Maxima/nm		
WT	1.61	421	549	588
S92A	2.62	420	548	589
S92D	1.58	419	551	591
S92E	1.62	416	559	592
S92V	1.76	417	547	583



Catalyst	Reaction Condition		Yield (% , based on substrate)				
	Catalyst (mol%)	DCIPy-O (eq.)	25-OH	(20S)-20-OH	(20S)-20, 15-oxo-25-diOH	15-oxo-25-OH	recovery
Ru(T2,4,6TMPP)(CO)	0.1	3	4	0	0	0	75
Ru(TPP)(CO)	0.5	3	11	0	0	0	57
Ru(TMP)(CO)	0.3	4.5	26	0	7	12	15
Ru(T2,6DCIPP)(CO)	0.2	3	25	19	6	0	33

Reaction mixtures contained catalyst, 0.16 M substrate, 2,6-dichloropyridine *N*-oxide, 16ml/l 47% HBr aq. and 50g/l MS4A in benzene. The reactions were carried out under Ar.

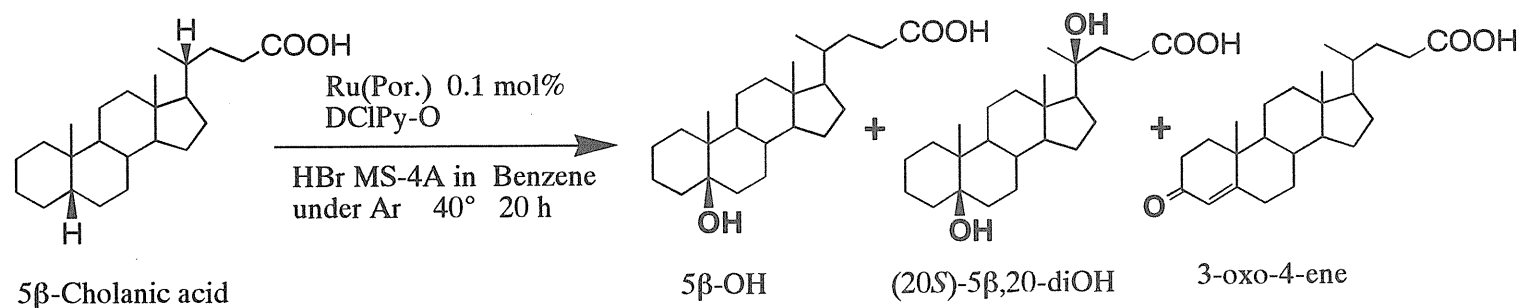
表 2 Oxidation of $5\alpha\text{-Cholestan-3-one}$



Condition	Yield (% , based on substrate)	
	$5\alpha\text{-OH}$	Recovery
DCIPy-O (eq.)		
1.5	28	27
3.0	14	6

Reaction mixtures contained 0.4 mM catalyst, 0.16 M substrate, 2,6-dichloropyridine *N*-oxide, 16 ml/l 47% HBr aq. and 50g/l MS4A in benzene. The reactions were carried out under Ar.

表3 Oxidation of $5\alpha\text{-Cholestane}$



Conditions		Yield (% , based on substrate)			
Catalyst	DCIPy-O (eq.)	5β-OH	(20S)-5β,20-diOH	3-oxo-4-ene	Recovery
Ru-TMP(CO)	1.5	70	8	4	5
Ru-T _{2,6} DCIPP(CO)	1.2	66	0	0	15

Reaction mixtures contained 0.4 mM catalyst, 0.16 M substrate, 2,6-dichloropyridine *N*-oxide, 16 ml/l 47% HBr aq. and 50 g/l MS4A in benzene. The reactions were carried out under Ar.

表 4 Oxidation of 5β-Cholanic acid

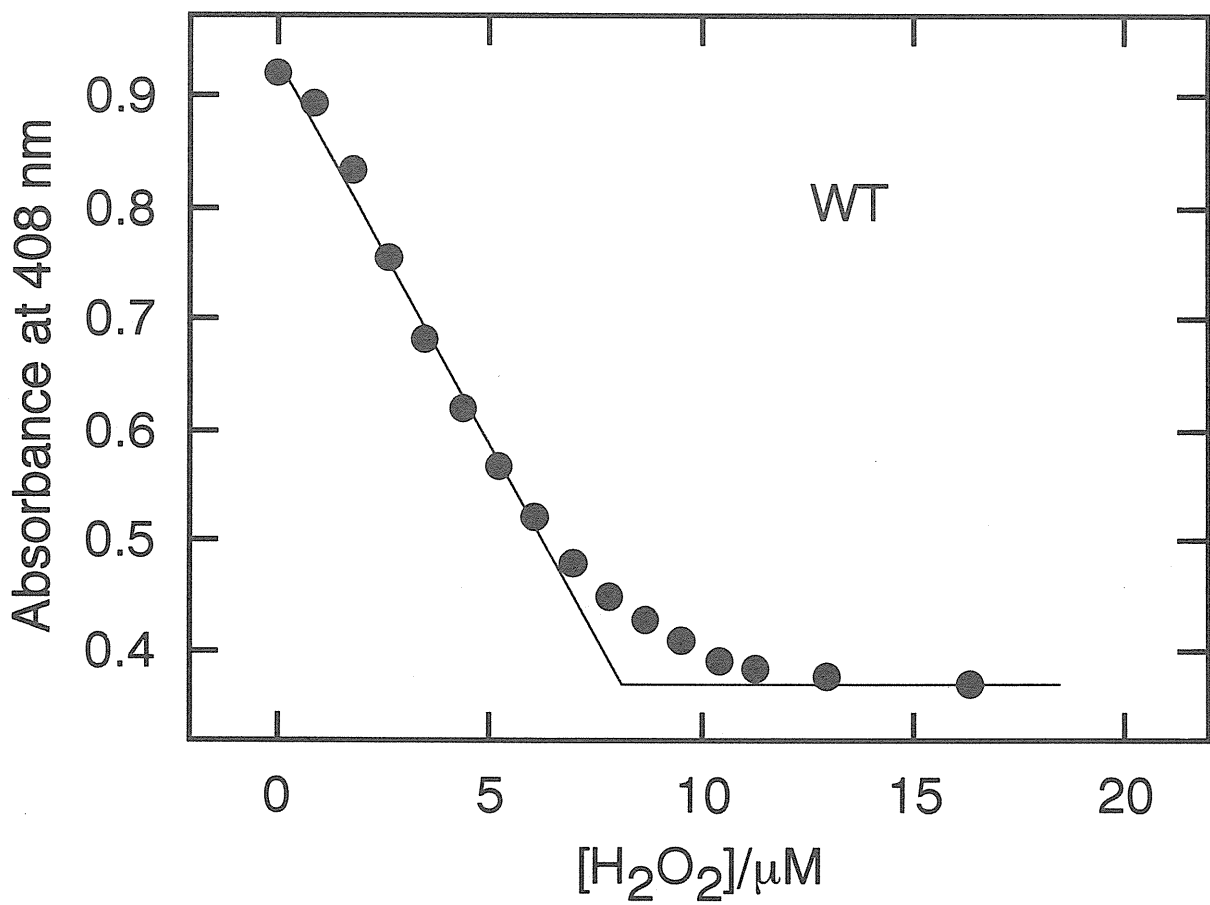
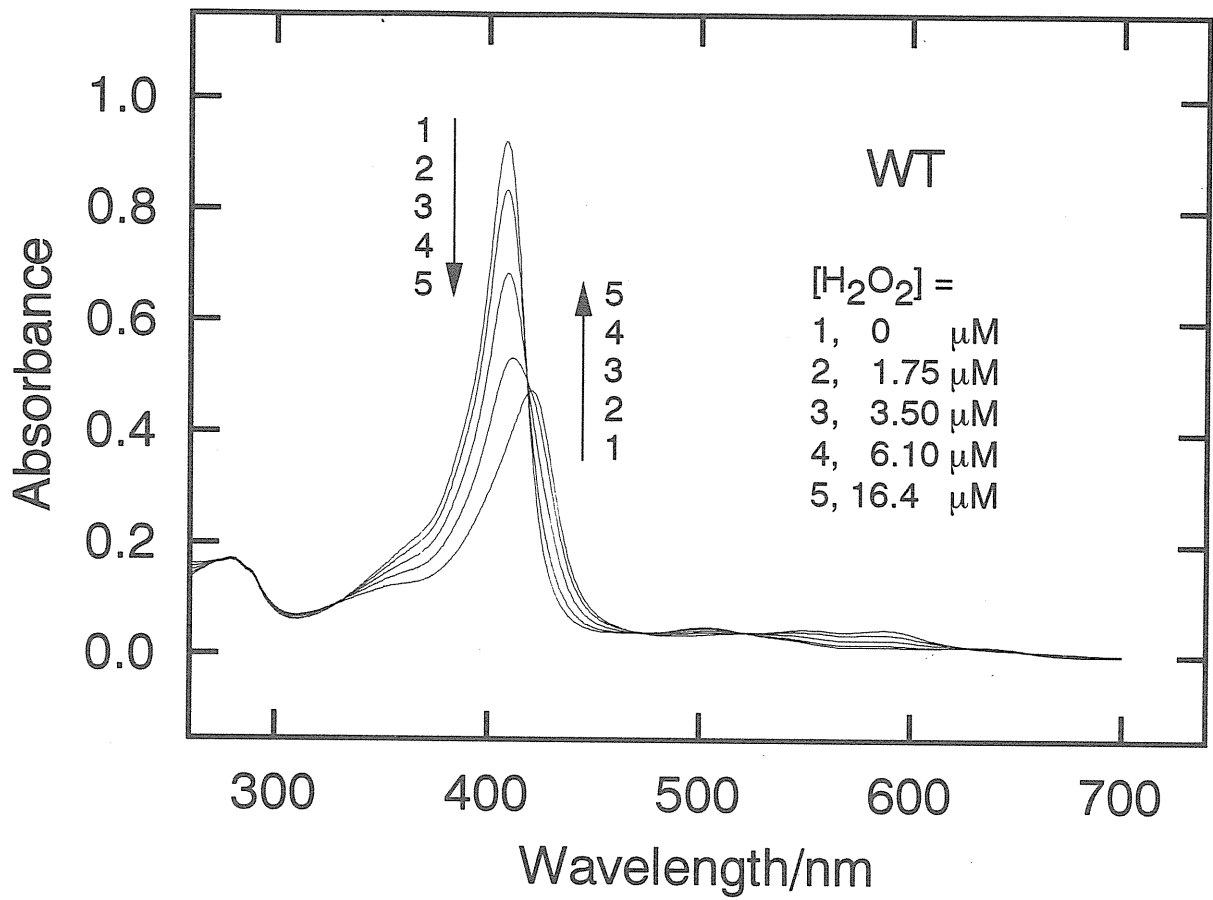


図1 野生型ミオグロビンの過酸化水素滴定

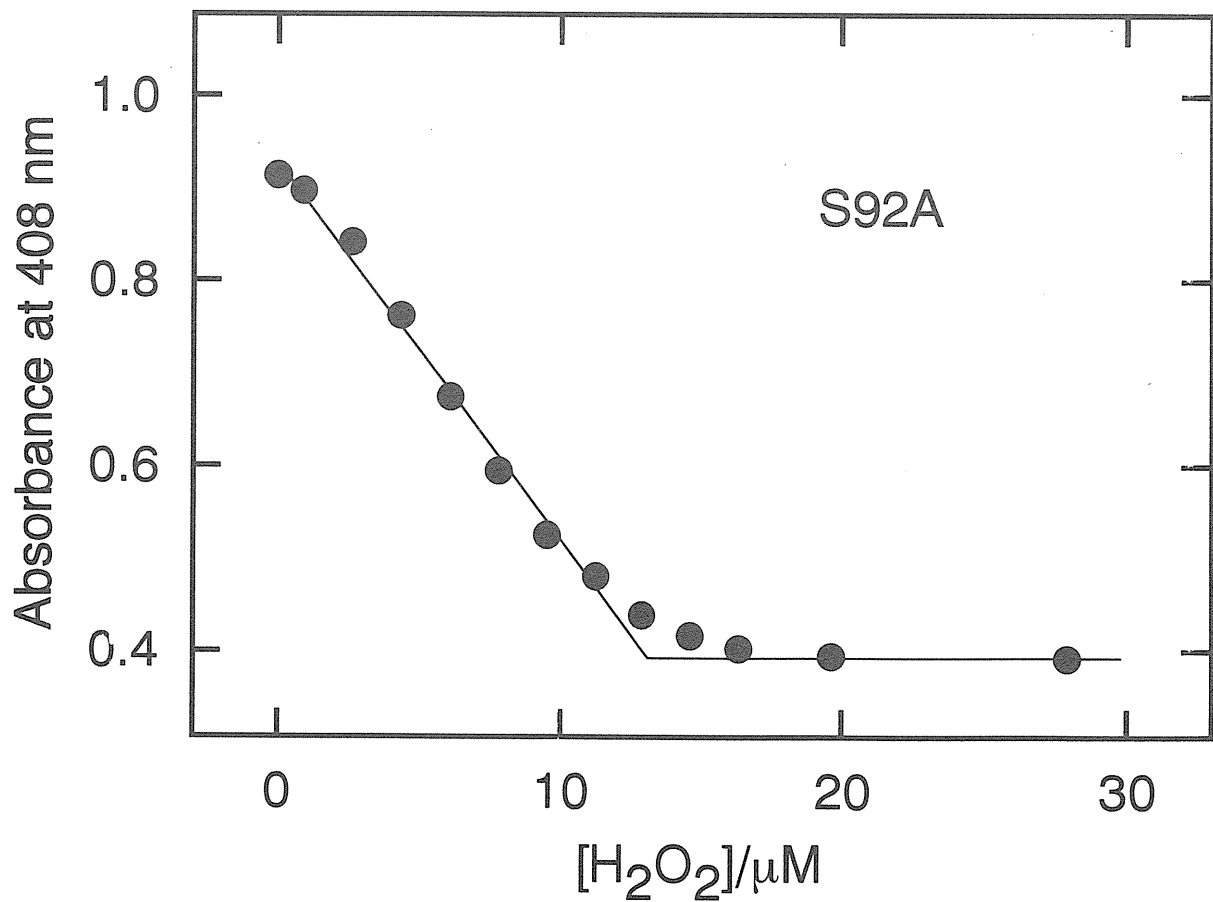
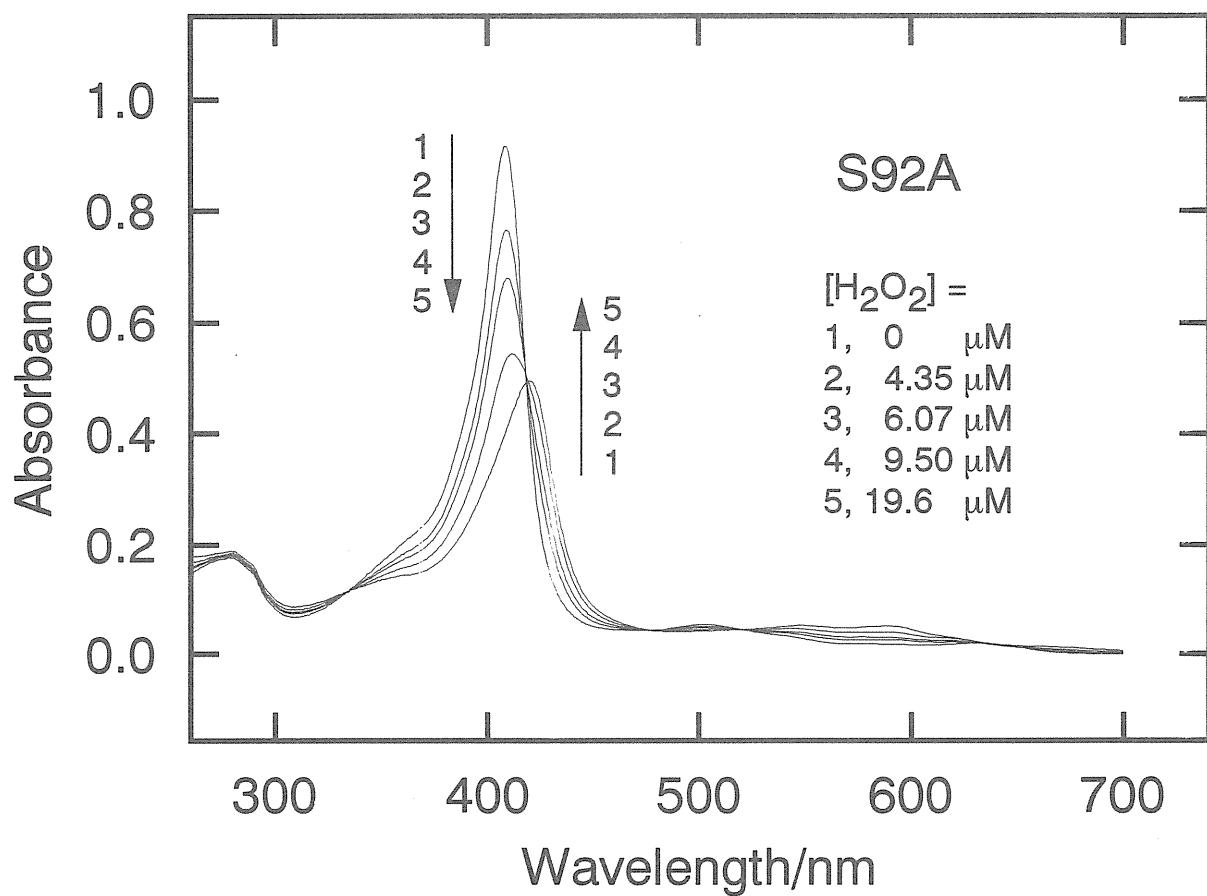


図2 S92Aの過酸化水素滴定

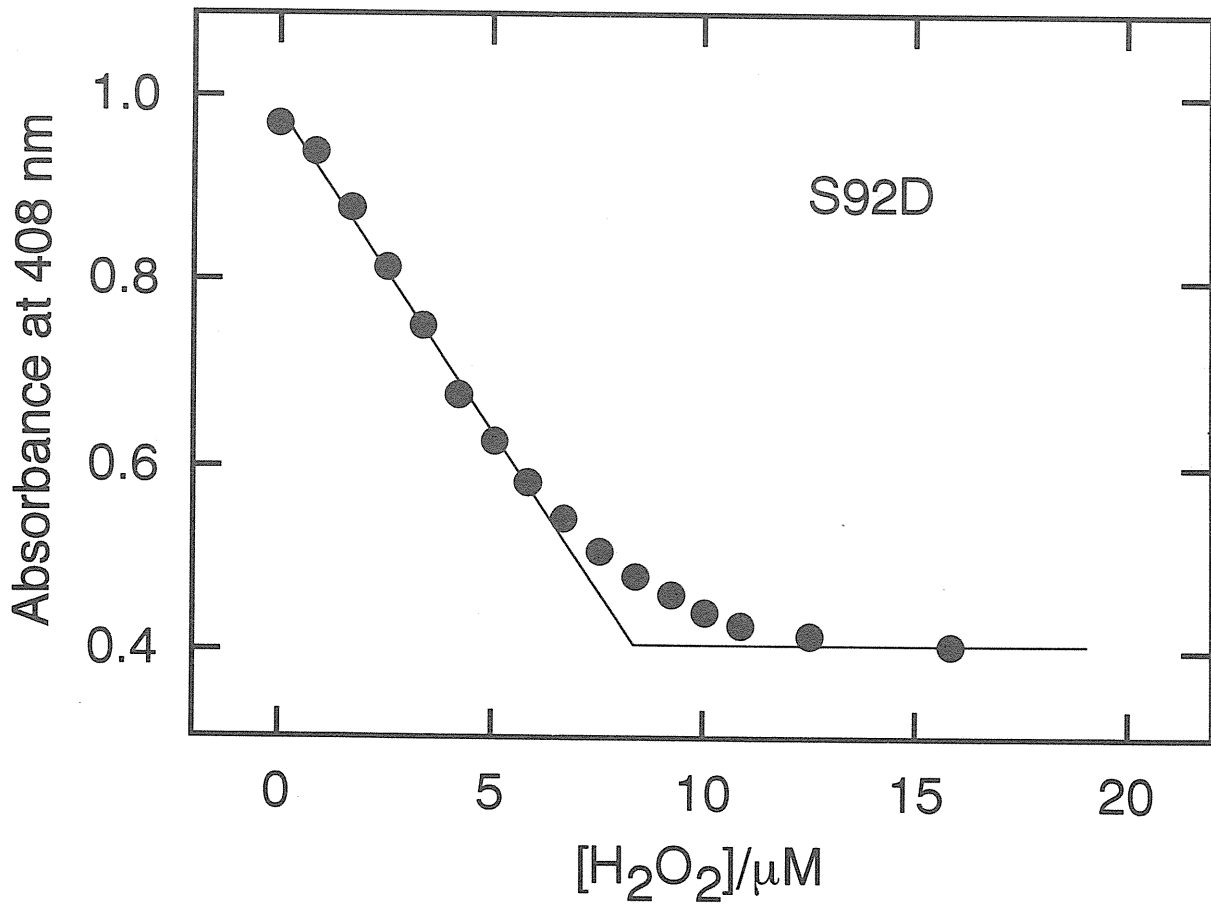
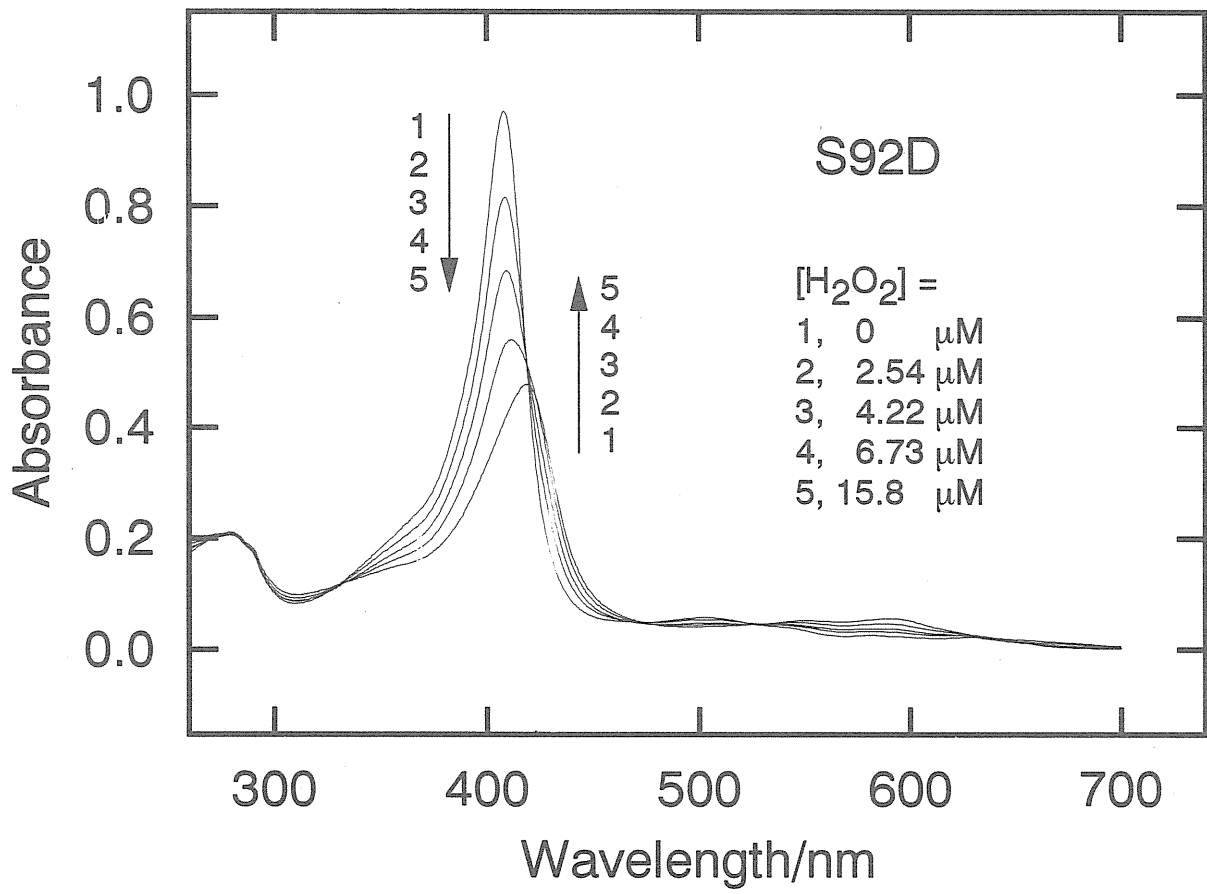


図3 S92Dの過酸化水素滴定

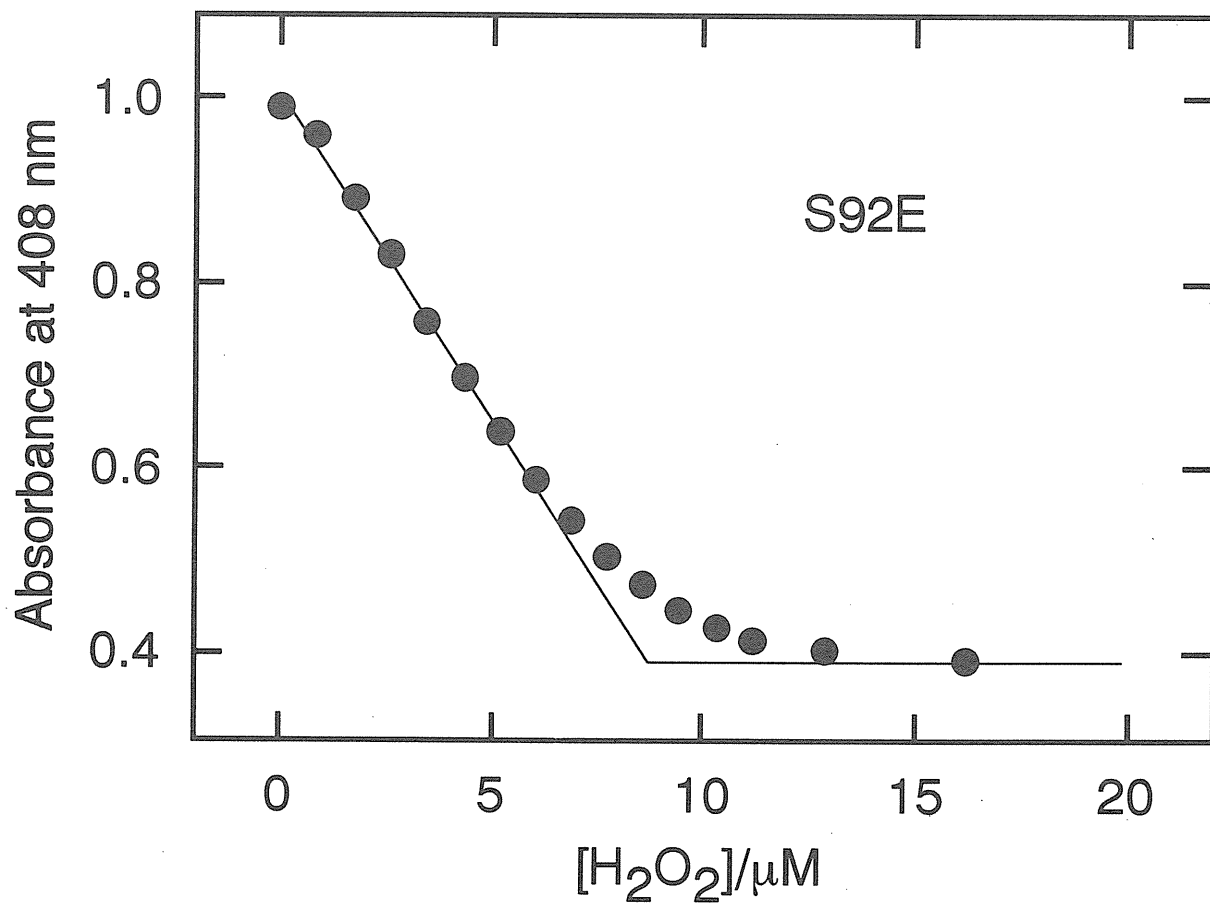
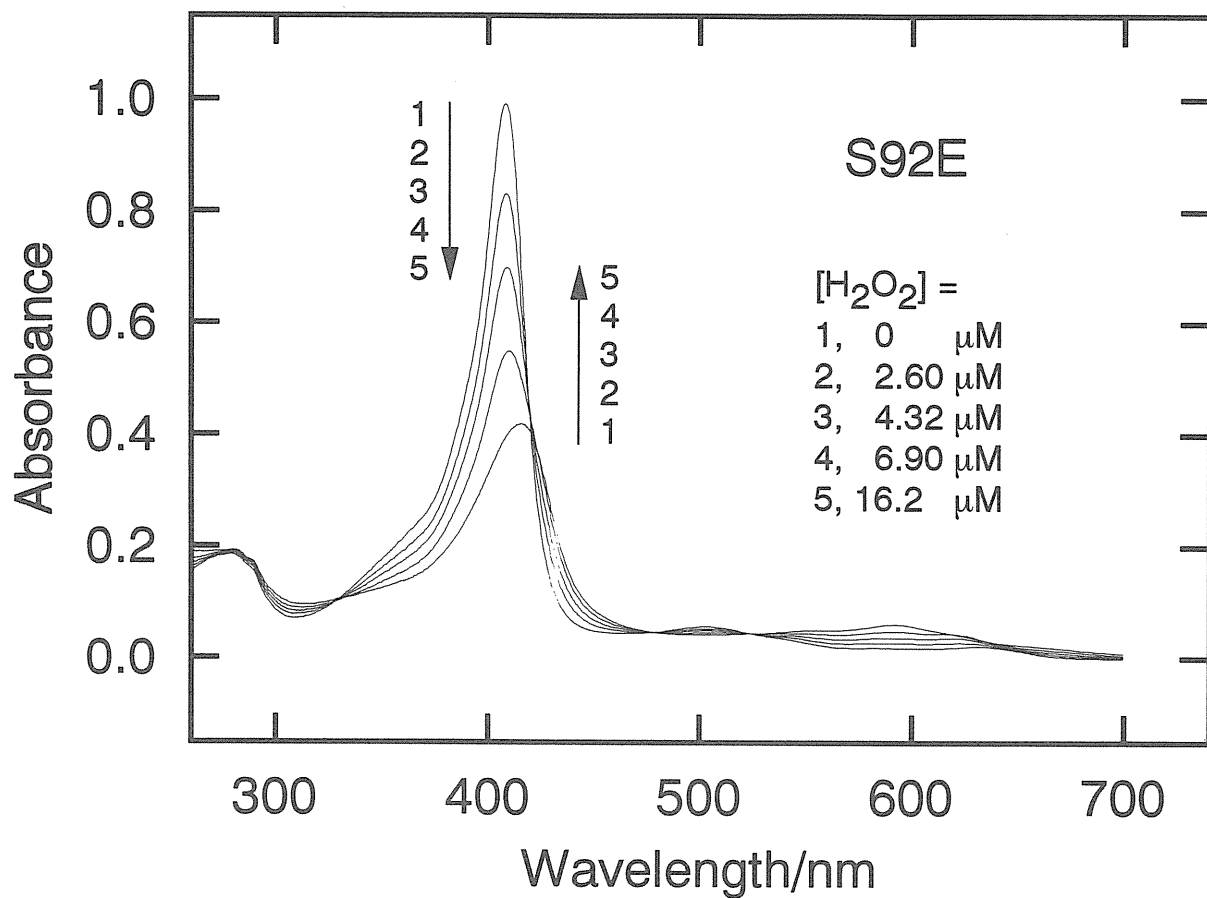


図4 S92Eの過酸化水素滴定

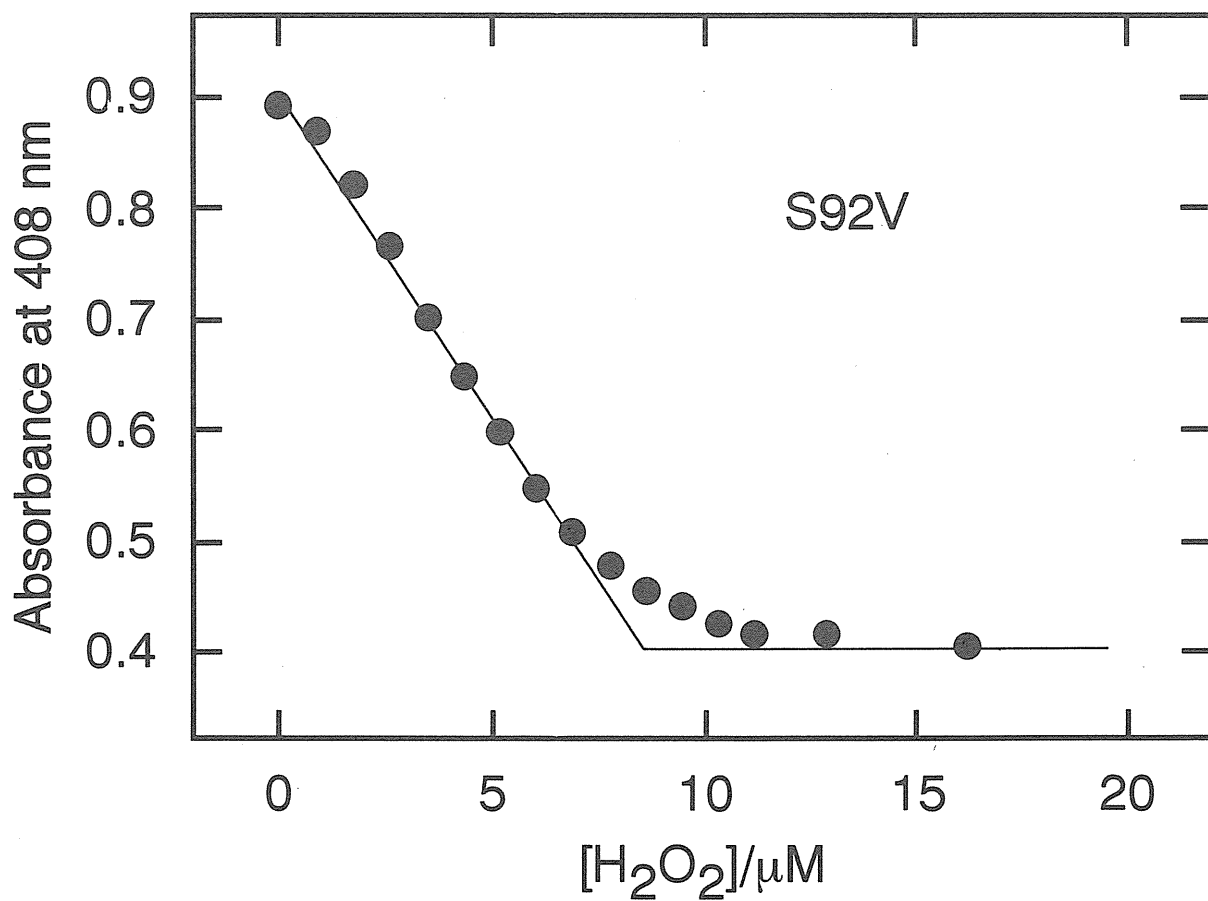
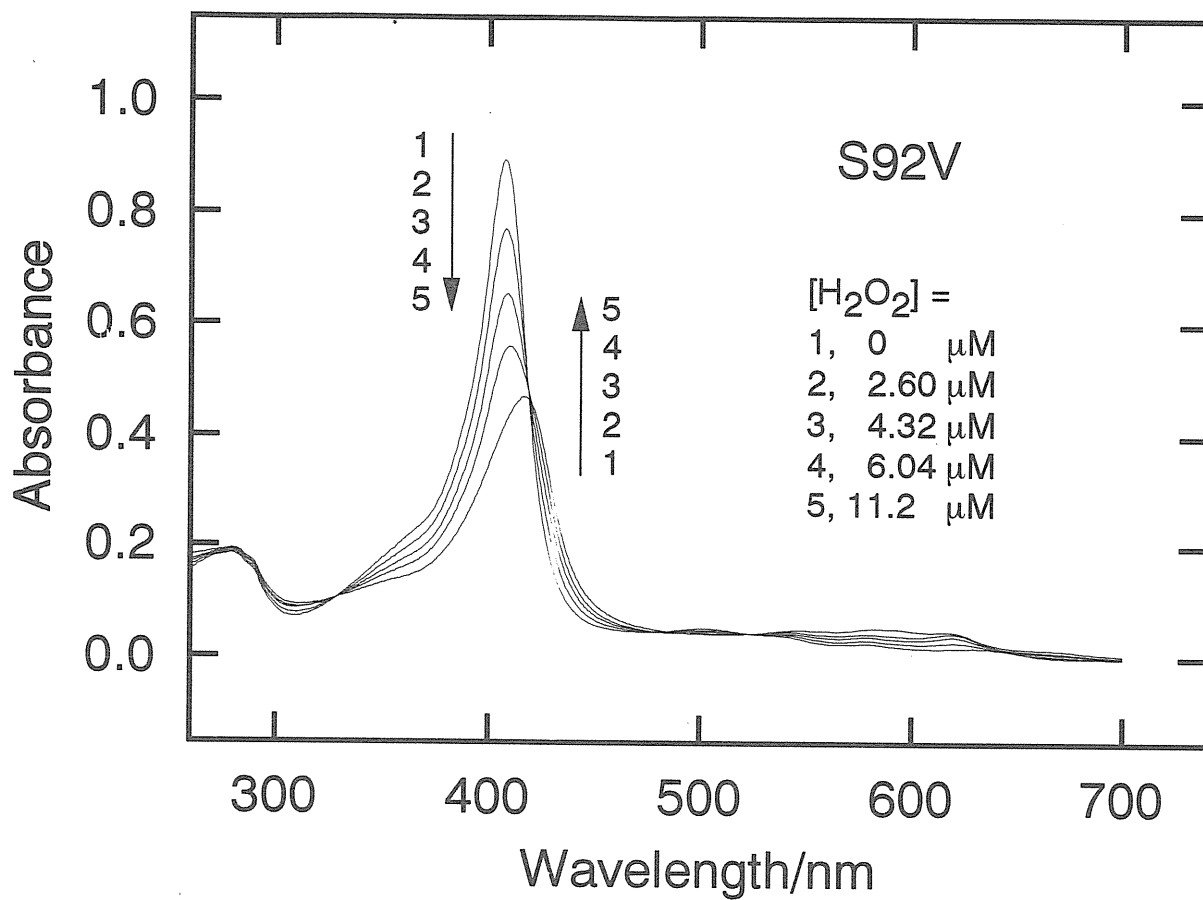
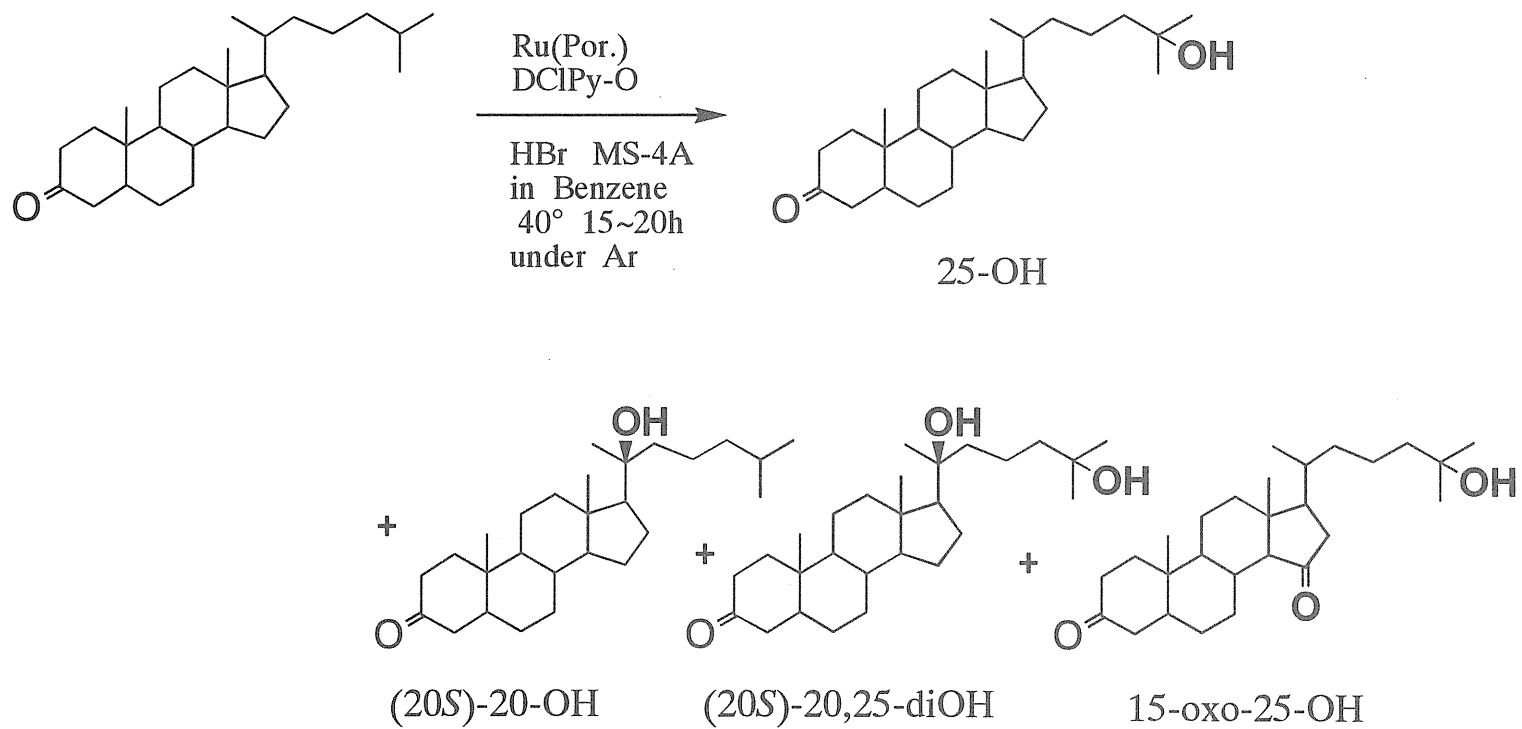
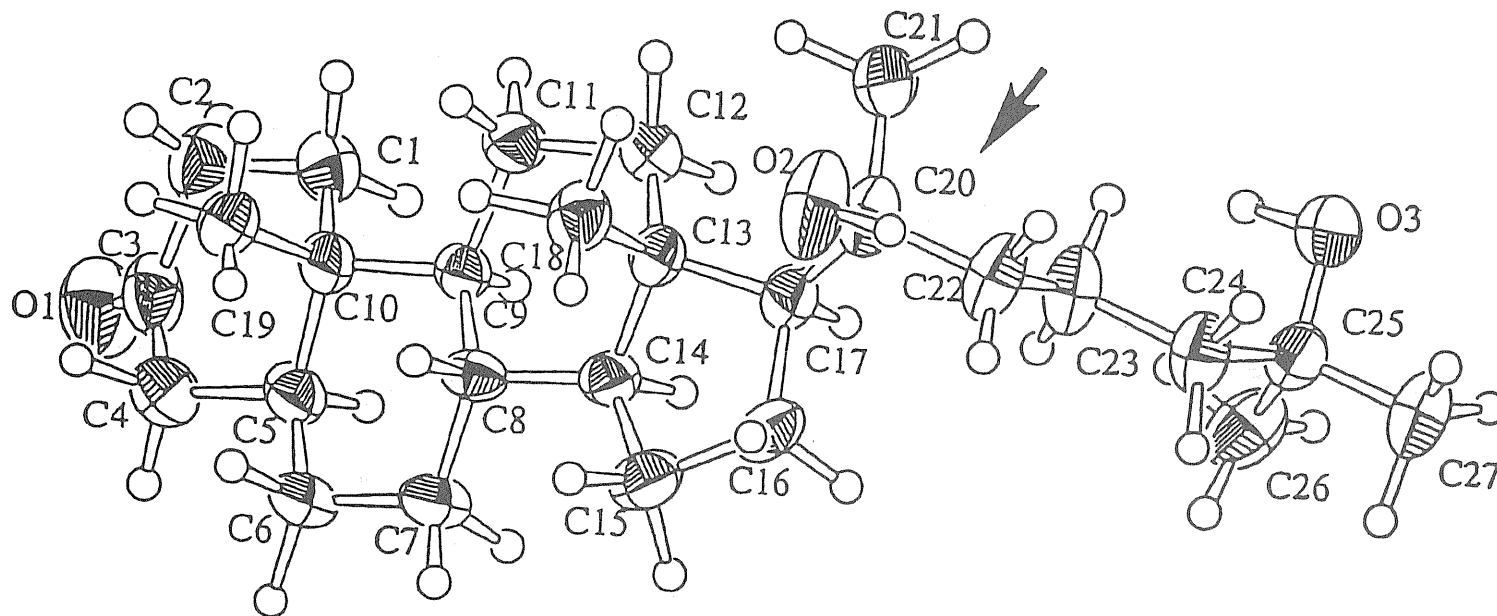


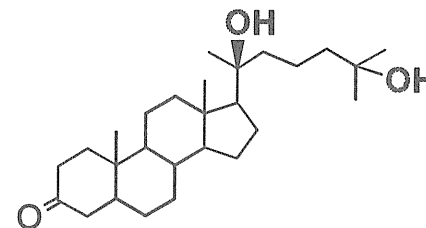
図5 S92Vの過酸化水素滴定



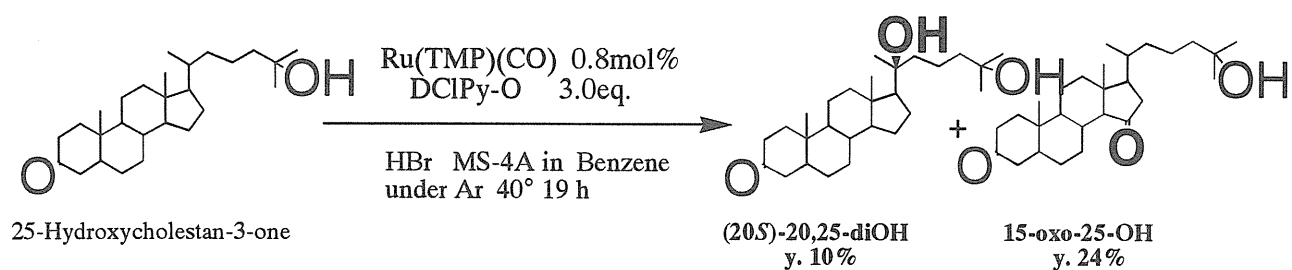
⊠ 6 Oxidation of 5 α -cholestan-3-one



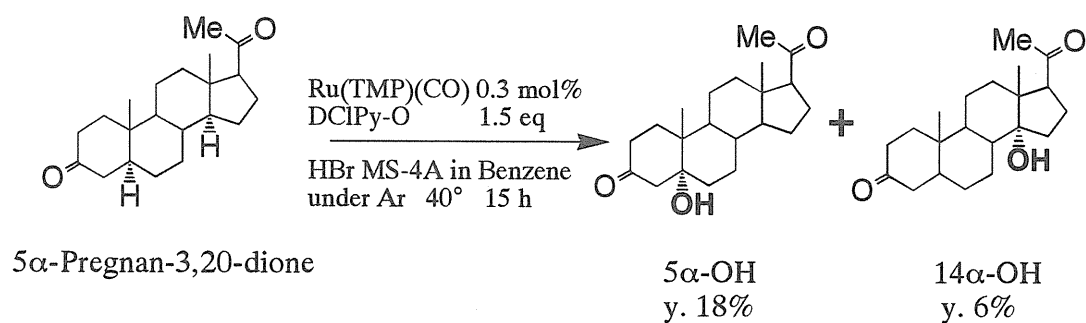
(20*S*)-20,25-Dihydroxycholestan-3-one; C₂₇H₄₆O₃, M=418.66, crystal dimensions (mm): 0.50 x 0.30 x 0.30; monoclinic, space group P2₁, a = 9.889(1), b = 7.5383(6), c = 16.7188(9) Å, β = 101.749(6)°, Z = 2, D_c = 1.139 gcm⁻³, μ(Cu-Kα) = 5.53 cm⁻¹, I = 1.54178 Å, F(000) = 446.00, R = 0.056, R_w = 0.052, T = 293K. 2105 reflections measured on Rigaku AFC7S diffractometer yielded 1978 unique data (2θ_{max} = 120.0°, R_{int} = 0.020, Lorentz-polarization corrections). The structure was solved by direct methods and refined by full-matrix least-squares methods. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.



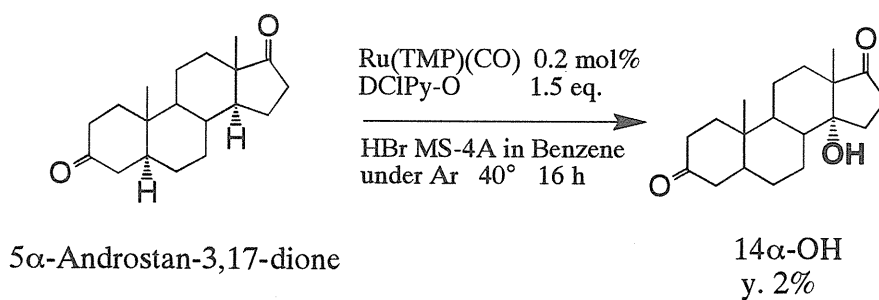
⊗ 7 Molecular diagram of (20*S*)-20,25-dihydroxycholestan-3-one



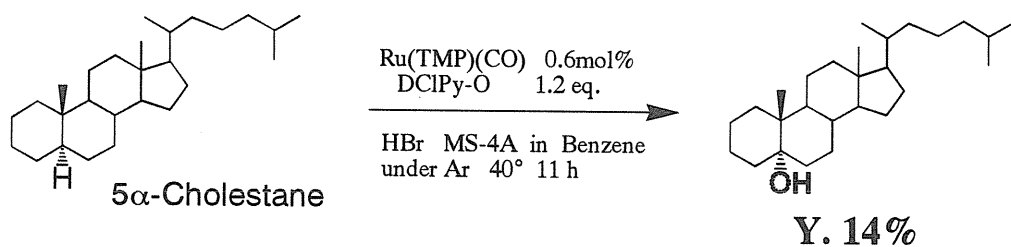
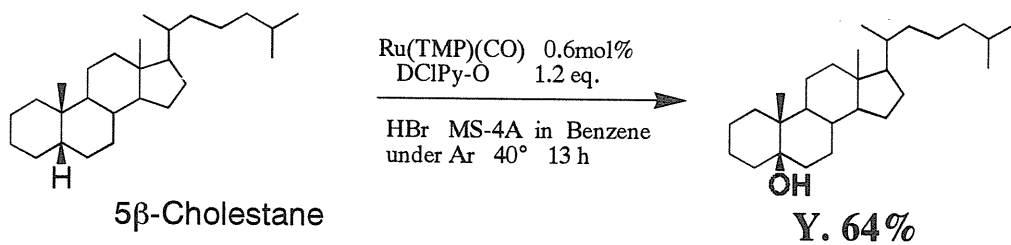
☒ 8 Oxidation of 25-Hydroxycholestan-3-one



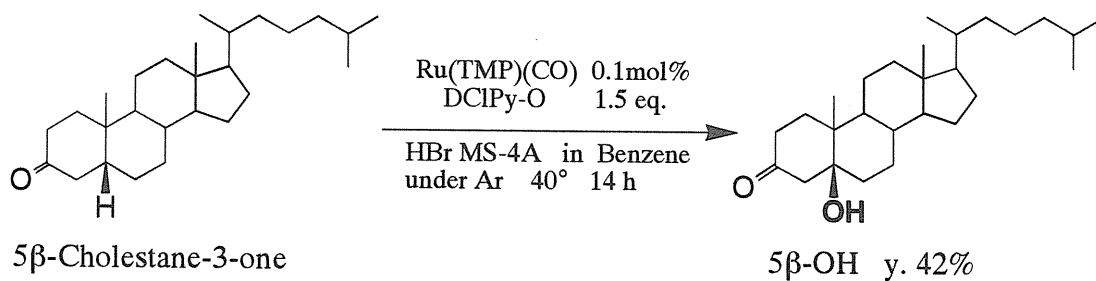
☒ 9 Oxidation of 5 α -Pregnan-3,20-dione



☒ 10 Oxidation of 5 α -Androstan-3,17-dione



☒11 Oxidation of 5 α - and 5 β -Cholestane



☒12 Oxidation of 5 β -cholestan-3-one

