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Synthesis of 14α-Methylcholesterol*

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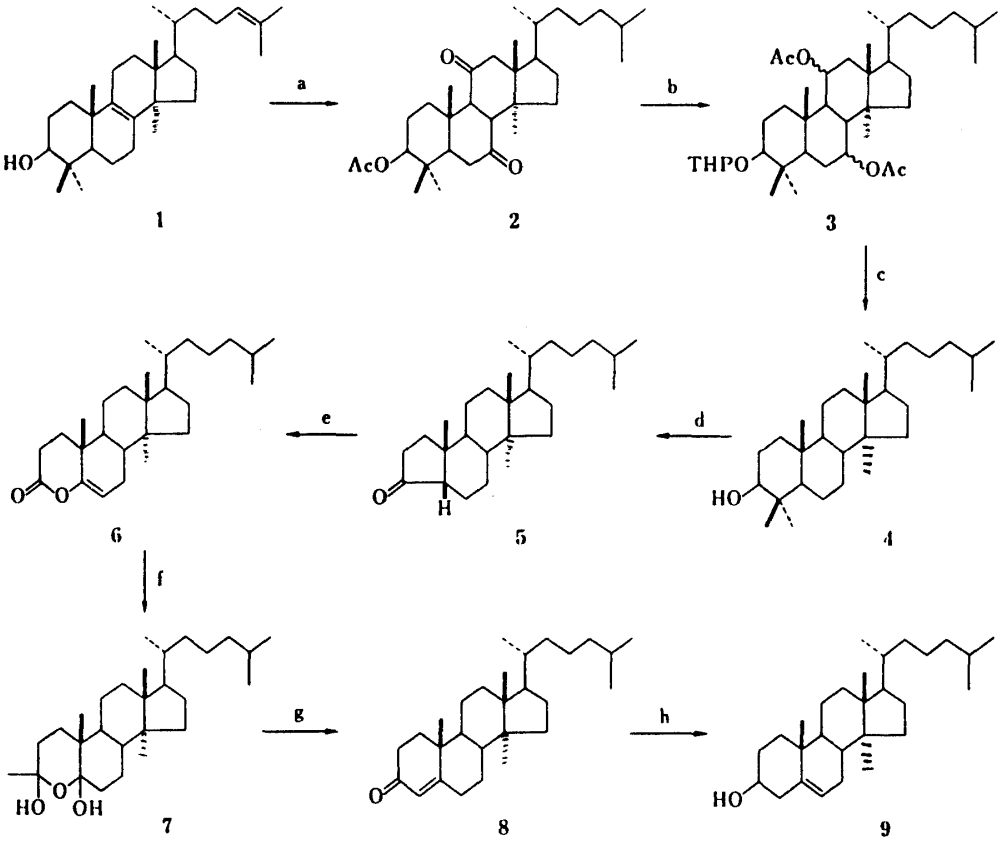
Lanosterol (**1**), through a conventional four step sequence (catalytic hydrogenation, acetylation, chromic acid oxidation, reduction with zinc-acetic acid) was converted to the 7,11-diketone (**2**) in 59% yield. We avoided the hazardous Wolff-Kishner reduction to remove the 7,11-oxygen function of **2** and instead, deacetoxylation of the 7,11-diacetate (**3**) was performed. Thus the latter, derived from **2** by successive saponification, tetrahydropyranyl ether formation, $LiAlH_4$ reduction and acetylation with acetic anhydride-



(a) i, H_2/Pd-C/AcOEt; ii, Ac_2O/pyr.; iii, CrO_3/AcOH; iv, Zn/AcOH.
(b) i, KOH/MeOH; ii, dihydropyran/Amberlyst 15/CH_2Cl_2; iii, $LiAlH_4$/THF; iv) Ac_2O/DMAP/pyr.
(c) i, Na/HMPA/*tert*-BuOH; ii, HCl/MeOH-CH_2Cl_2.
(b) i, PCl_5/*n*-hexane; ii, O_3/CH_2Cl_2 and then Zn/AcOH; iii, KOH/MeOH.
(e) i, CF_3COOH/CH_2Cl_2; ii, Jones oxid.; iii, $Ac_2O/HClO_4$. (f) CH_3MgI/Et_2O-C_6H_6. (g) NaOH/MeOH.
(h) i, $CH_2=C(OAc)Me$/*p*-TsOH; ii, $NaBH_4$/MeOH-THF.

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pyridine in the presence of 4-dimethylaminopyridine, was subjected to reaction with sodium in hexamethylphosphoric triamide/*tert*-butanol. Subsequent acid treatment afforded lanostanol (**4**) in 61% overall yield from **2**. Transformation of **4** into the enol lactone (**6**) *via* the A-nor -ketone (**5**), was effected essentially by the reported method in 18% yield. Grignard reaction of **6** with methyl magnesium iodide gave the masked 1,5-diketone (**7**) in 75% yield. The latter had neither carbonyl absorption (infrared and carbon-13 nuclear magnetic resonance) nor an olefinic bond (^{1}H- and ^{13}C-NMR), and was much more polar than the starting enol lactone (**6**) on thin layer chromatography. Other NMR signals as well as the mass spectral peak at *m/z* 416 (M-18) strongly suggested the dihemiacetal structure (**7**), although its stereochemistry remained undetermined. Alkaline treatment of **7** gave the 3-oxo-4-one (**8**). Enol acetylation of **8** with isopropenyl acetate/*p*-toluenesulfonic acid, followed by reduction with $NaBH_4$ furnished 14α-methylcholesterol (**9**,42%), together with its 3-epimer (4%). The spectroscopic data of **9** unequivocally established the structure.