Title	A new method for introducing the 14-hydroxymethyl group into the steroidal nucleus
Sub Title	
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Publisher	共立薬科大学
Publication year	1989
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.34 (1989.) ,p.82- 82
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000034- 0082

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A New Method for Introducing the l4-Hydroxymethyl Group into the Steroidal Nucleus*

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Standard sample of the 32-oxygenated lanostane compounds which are key intermediates of cholesterol and ergosterol biosynthesis, have been available only through Barton-Kalvoda reaction of the appropriate 7β -hydroxylanostane derivative. As an alternative, we have now developed a convenient method for introducing the l4hydroxymethyl group into the steroidal nucleus.

The methoxymethyl (MOM) ether of cholest-7-en-3 β -ol was oxidized to the $7\alpha,8\alpha$ -epoxide with m-chloroperbenzoic acid, which was then treated with borontrifluoride etherate in tetrahydrofuran (THF), yielding the 7α -hydroxy-8(14)-ene system in 65% yield. When this allylic alcohol was deprotonated (KH/THF) and alkylated with iodotrimethyltin, the corresponding stanylmethyl ether was formed in 71% yield. Treatment of the ether with excess n-butyllithium in THF at -78°C to ambient temperature induced a smooth [2,3] -sigmatropic rearrangement to give the 14hydroxymethyl derivative in 79% yield. Removal of the MOM group with dilute HCl gave 14α -hydroxymethyl-7-cholesten- 3β -ol (98%) . Similarly, 4,4-dimethyl-7cholesten- 3β -ol was trnsformed into the 32-hydroxy-7-lanosten- 3β -ol. Conversion of these 7-ene compounds into the biologically more important 8-ene isomer has already been established. Thus the present procedures pave a convenient way leading to various 32-oxygenated sterols.

^{*} 本報告は Chem. Pharm. Bull., 36, 4638-4639 (1988) に発表.