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Author	江口, 早苗(Eguchi, Sanae) 海老原, 公代(Ebihara, Kimiyo) 森崎, 益雄(Morisaki, Masuo)
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## A New Method for Introducing the 14-Hydroxymethyl Group into the Steroidal Nucleus\*

Sanae EGUCHI, Kimiyo EBIHARA and Masuo MORISAKI

江口早苗, 海老原公代, 森崎益雄

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 7 $\beta$ -hydroxylanostane derivative. As an alternative, we have now developed a convenient method for introducing the 14-hydroxymethyl group into the steroidal nucleus.

The methoxymethyl (MOM) ether of cholest-7-en-3 $\beta$ -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 7 $\alpha$ -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  $-78^{\circ}\text{C}$  to ambient temperature induced a smooth [2,3]-sigmatropic rearrangement to give the 14-hydroxymethyl derivative in 79% yield. Removal of the MOM group with dilute HCl gave 14 $\alpha$ -hydroxymethyl-7-cholesten-3 $\beta$ -ol (98%). Similarly, 4,4-dimethyl-7-cholesten-3 $\beta$ -ol was transformed into the 32-hydroxy-7-lanosten-3 $\beta$ -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.

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