Synthesis of 3-(ω-Phenylalkyl)catechols, Phenolic Lipids found in Sap of the Burmese Lac Tree, *via* Directed Metallation

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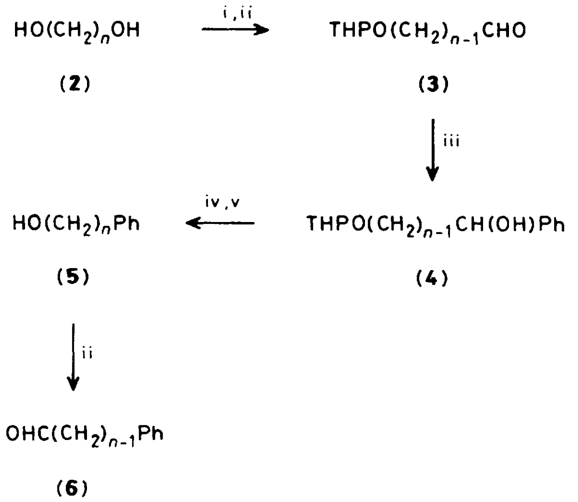
3-(ω-Phenylalkyl)catechols were synthesized *via* directed metallation.

The phenolic lipids 3-(12-phenyldodecyl)catechol (**1a**) and 3-(10-phenyldecyl)catechol (**1b**) were recently isolated from the sap of the Burmese lac tree, *Melanorrhoea ustiate*,[1] but neither their biological activities nor chemical properties are known. We tried to synthesize these lipids to carry out further studies on them. In an earlier work on synthesizing 3-alkylcatechols, *e.g.* urushiol, Yukawa *et al.*[2] alkylated catechol bistetrahydropyranyl ether *via* directed metallation but the yield was not very good. In this communication, we describe a new method of synthesizing these phenolic lipids *via* directed metallation using methoxymethyl ether as the directing group.[3]



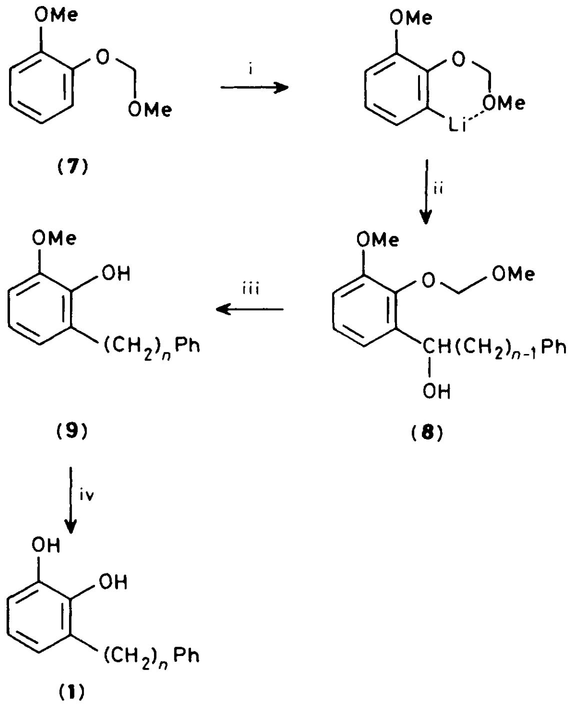
THP = tetrahydropyranyl
a; n = 12, **b**; n = 10

Scheme 1. *Reagents:* i, dihydropyran, p-MeC$_6$H$_4$SO$_3$H, CH$_2$Cl$_2$; ii, (COCl)$_2$, Me$_2$SO, CH$_2$Cl$_2$, Et$_3$N; iii, PhMgBr, Et$_2$O; iv, Et$_3$SiH, CF$_3$CO$_2$H; v, NaOH, MeOH.

Monoprotection of dodecane-1,12-diol (**2a**) with dihydropyran and a catalytic amount of p-MeC$_6$H$_4$SO$_3$H followed by oxidation by Swern's procedure[4] gave the protected aldehyde (**3a**). Treatment of (**3a**) with phenylmagnesium bromide gave the alcohol (**4a**) [30% from (**2a**)]. Hydrogenolysis of (**4a**) with triethylsilane and trifluoroacetic acid[5] followed by hydrolysis with alkali gave the alcohol (**5a**) (59%). Oxidation of (**5a**) by Swern's procedure[4] gave the aldehyde (**6a**) (87%).

When the guaiacol methoxymethyl ether (**7**) was treated with n-butyl-lithium in diethyl ether at room temperature, a white precipitate formed and warming the mixture at 30 °C for 30 minutes resulted in an orange suspension. Addition of the aldehyde (**6a**) to this suspension gave the alcohol (**8a**) (49%). Ionic hydrogenation by Kursanov's procedure[5] gave the phenol (**9a**) (30%). Treatment of (**9a**) with boron tribromide gave 3-(12-phenyldodecyl)catechol (**1a**) (84%), which had physical data identical with those reported by Oshima,[1] thus confirming the structure of the natural product.

3-(10-Phenyldecyl)catechol (**1b**) was also prepared by a similar method from decane-1,10-diol (**2b**) in 2.3% overall yield.



a; n = 12, **b**; n = 10

Scheme 2. *Reagents:* i, Bu^{n}Li, Et$_2$O, 30 °C; ii, (**6**); iii, Et$_3$SiH, CF$_3$CO$_2$H; iv, BBr$_3$, CH$_2$Cl$_2$.

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