

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

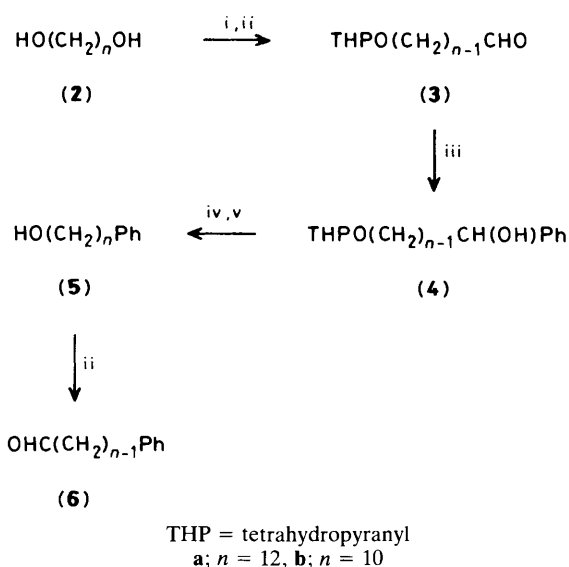
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3-( $\omega$ -Phenylalkyl)catechols were synthesized *via* directed metallation.

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*,<sup>1</sup> 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-alkyl-

catechols, *e.g.* urushiol, Yukawa *et al.*<sup>2</sup> 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.<sup>3</sup>

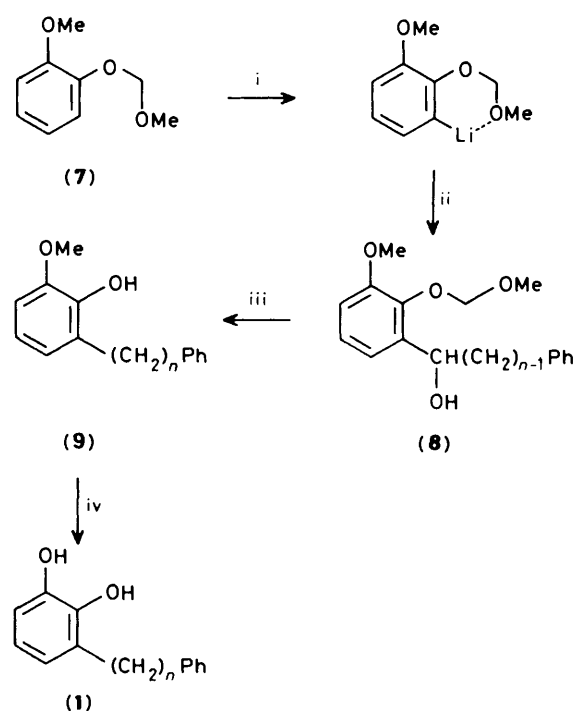


**Scheme 1.** Reagents: i, dihydropyran, *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, CH<sub>2</sub>Cl<sub>2</sub>; ii, (COCl)<sub>2</sub>, Me<sub>2</sub>SO, CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>3</sub>N; iii, PhMgBr, Et<sub>2</sub>O; iv, Et<sub>3</sub>SiH, CF<sub>3</sub>CO<sub>2</sub>H; v, NaOH, MeOH.

Monoprotection of dodecane-1,12-diol (**2a**) with dihydropyran and a catalytic amount of *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H followed by oxidation by Swern's procedure<sup>4</sup> 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<sup>5</sup> followed by hydrolysis with alkali gave the alcohol (**5a**) (59%). Oxidation of (**5a**) by Swern's procedure<sup>4</sup> 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<sup>5</sup> 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,<sup>1</sup> 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<sup>n</sup>Li, Et<sub>2</sub>O, 30 °C; ii, (**6**); iii, Et<sub>3</sub>SiH, CF<sub>3</sub>CO<sub>2</sub>H; iv, BBr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>.

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## References

- 1 Y. Du, R. Oshima, Y. Yamauchi, and J. Kumanotani, *J. Chem. Soc., Chem. Commun.*, 1985, 630.
- 2 T. Hanafusa and Y. Yukawa, *Nippon Kagaku Zasshi*, 1966, **87**, 202.
- 3 I. Kubo, T. Kamikawa, and I. Miura, *Tetrahedron Lett.*, 1983, **24**, 3825.
- 4 A. J. Mancuso, S.-L. Huang, and D. Swern, *J. Org. Chem.*, 1978, **43**, 2480.
- 5 D. N. Kursanov, Z. N. Parnes, and N. M. Loin, *Synthesis*, 1974, 633.