Stereochemistry of the Phthiocerols

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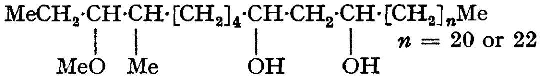
Summary The asymmetric centre bearing the methyl branch (C-4 of phthiocerol A) is assigned *S*-configuration.

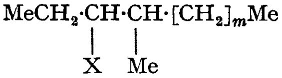
IN connection with structural studies of phthiocerol, reduction utilising successively hydrogen iodide, zinc amalgam, and hydrogenation gave an optically inactive hydrocarbon phthiocerane[1] which was subsequently shown to be a mixture of 4-methyltetratriacontane and 4-methyldotriacontane.[2]

We have converted material consisting essentially of phthiocerol A (I),[3] by the sequence shown below through the previously unreported compounds (IIa—c), into the hydrocarbon (IId); the specific rotation of the latter was in agreement with that of synthetic *R*-(—)-4-methyltritriacontane, $[\alpha]_D^{23}$ — 0·6°.[4] It thus follows that the asymmetric centre at C-4 of phthiocerol A has *S*-configuration.



$$\mathrm{MeCH_2{\cdot}\underset{MeO}{CH}{\cdot}\underset{Me}{CH}{\cdot}[CH_2]_4{\cdot}\underset{OH}{CH}{\cdot}CH_2{\cdot}\underset{OH}{CH}{\cdot}[CH_2]_{\mathit{n}}Me} \qquad n = 20 \text{ or } 22$$

(I)



$$\mathrm{MeCH_2{\cdot}\underset{X}{CH}{\cdot}\underset{Me}{CH}{\cdot}[CH_2]_{\mathit{m}}Me} \qquad m = 27 \text{ or } 29$$

(II)

	X	M.p.	$[\alpha]_D^{20}(CHCl_3)$
(IIa)	OMe	57°	$-0{\cdot}5°$
(IIb)	OAc	59°	$+1{\cdot}8°$
(IIc)	OH	75°	$-4{\cdot}9°$
(IId)	H	60°	$-0{\cdot}6°$

$$(\mathrm{I}) \xrightarrow{\text{(i), (ii)}} (\mathrm{IIa}) \xrightarrow{\text{(iii)}} (\mathrm{IIb}) \xrightarrow{\text{(ii)}} (\mathrm{IIc}) \xrightarrow{\text{(iv), (ii)}} (\mathrm{IId})$$

(i) Toluene-*p*-sulphonyl chloride, (ii) $LiAlH_4$, (iii) HBr–AcOH, (iv) $MeSO_2Cl$

Satisfactory i.r., n.m.r., and mass spectra have been obtained for the compounds listed.

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[4] S. Ställberg-Stenhagen and E. Stenhagen, *J. Biol. Chem.*, 1950, **183**, 223.