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Received December 3, 1956.

Mass Spectrometric Determination of the Structure of Phthiocerol

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The position of the methoxyl group in phthiocerol previously inferred from mass-spectrometric and X-ray data [1] has now been confirmed by a mass-spectrometric study of synthetic 3-methoxy-4-methylheptene-6. The spectrum of this molecule, like that of phthiocerol, shows an intense peak at $m/e = 73$, arising from cleavage between carbon atoms 3 and 4.

A similar study of the parent hydrocarbon, phthiocerane [2], definitely settles the structure of this hydrocarbon in favour of 4-methyltetratriacontane and not 4-methyltritriacontane, which previously appeared more likely [3-5]. The mass-spectrum shows a small parent peak at $m/e = 492$ corresponding to $C^{35}H^{72}+$ (ionized unfragmented molecule), and very strong peaks at $m/e = 449$ and $m/e = 421$ corresponding to $C_{32}H_{65}+$ and $C_{30}H_{61}+$, respectively, arising from cleavage on both sides of the tertiary carbon atom in position 4.

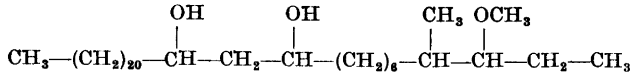
Parts of the mass-spectra of phthiocerol, 16,17-dihydroxydotriacontane, and 2,4-dihydroxyeicosane are shown in Fig. 1. A comparison between the spectrum of phthiocerol and those of the two synthetic glycols shows that phthiocerol is an 1,3-glycol as previously demonstrated by Demarteau-Ginsburg and Lederer [6] and excludes the possibility that phthiocerol is an 1,2-glycol. In the spectrum of 17,19-dihydroxyeicosane (2,4-dihydroxyeicosane) the C_{15}-alkene peaks $C_{15}H_{30}+$ and $C_{15}H_{28}+$ are considerably stronger than the corresponding peaks in the C_{14}- and C_{16}-groups. In the phthiocerol spectrum the $C_{20}H_{40}+$ and $C_{20}H_{38}+$ peaks are similarly increased, indicating the presence of a hydroxyl group in position 22. In phthiocerol the C_{27}- and C_{28}-groups of peaks are very weak, but a comparison with 17,19-dihydroxyeicosane is of course not possible as this molecule is too short. A comparison with the spectrum of 16,17-dihydroxydotriacontane, where the C_{20}- and C_{21}-groups of peaks are weak, does indicate, however, that phthiocerol has no hydroxyl group in position 25 or 26 from the normal chain end of the molecule.

Through the kind co-operation of Professor E. Lederer we have been able to make mass-spectrometric and monolayer studies of the acidic long-chain product obtained by Mme Demarteau-Ginsburg by oxidation of phthiocerol. The sample was found to consist of a mixture of about equal amounts of n-C_{22}- and n-C_{24}-acid together with smaller amounts of n-C_{21}- and n-C_{23}-acid. The presence of behenic acid supports the conclusion that phthiocerol has a hydroxyl group in position 22.

The presence of n-tetracosanoic acid appears more difficult to explain. This acid might arise from elimination of the hydroxyl group in position 22 before cleavage of the chain between the 24th and 25th carbon atom. It is hoped to settle this question by the study of oxidation products of a suitable synthetic 1,3-glycol.

Phthiocerol would thus have the empirical formula $C_{35}H_{69}(OH)_2OCH_3$ and be one of the sixteen theoretically possible stereoisomers of 3-methoxy-4-methyl-11,13-dihydroxytetratriacontane.

The mass-spectra of phthiocerol preparations from a virulent human strain of



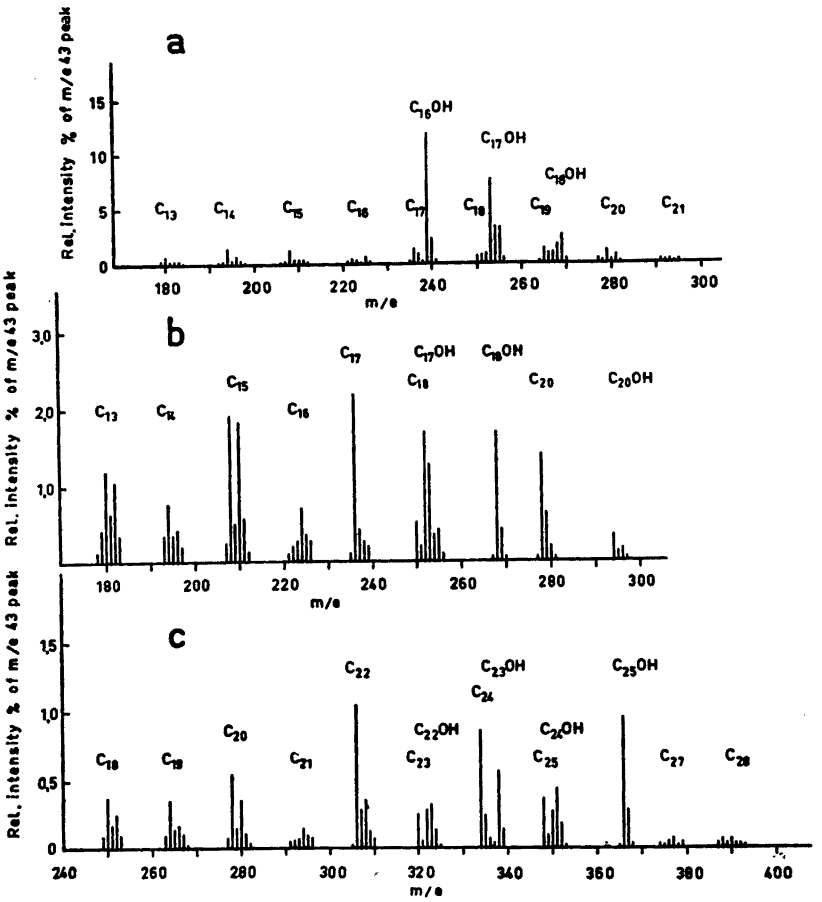


Fig. 1. Part of the mass-spectrum of a) 16,17-dihydroxydotriacontane b) 2,4-dihydroxyeicosane (17,19-dihydroxyeicosane). The two stereoisomers studied give closely similar spectra. c) phthiocerol from B.C.G.-strain of *M. tuberculosis*.

tubercle bacilli and from a B.C.G. strain were essentially similar.

We are indebted to Professor R. J. Anderson of Yale University and Professor E. Lederer of Institut de Biologie physico-chimique, Paris, for samples of phthiocerol. We wish to thank Mr. K. Serck-Hanssen for the synthetic 1,3-glycols and Mr. L. Ahlquist for assistance in the preparation of other synthetic material used for comparison. The expenses of this work have been defrayed in part by grants from the *Swedish Medical Research Council*.

Full details of this work will be published later.

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Received December 6, 1956.