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1. F. W. H. M. Merkus. *Pharm. Weekblad* **106**, 69 (1971)
2. F. W. H. M. Merkus. *Nature* **232**, 579 (1971)
3. L. Vollner, D. Bieniek and F. Korte. *Tetrahedron Letters* 145 (1969)
4. E. W. Gill. *J. Chem. Soc.* 579 (1971)
5. T. B. Vree *et al. Clin. Chim. Acta* **34**, 365 (1971)
6. F. W. H. M. Merkus. *Pharm. Weekblad* **106**, 49 (1971)
7. F. W. H. M. Merkus, M. G. J. Jaspers-van Wouw. In press

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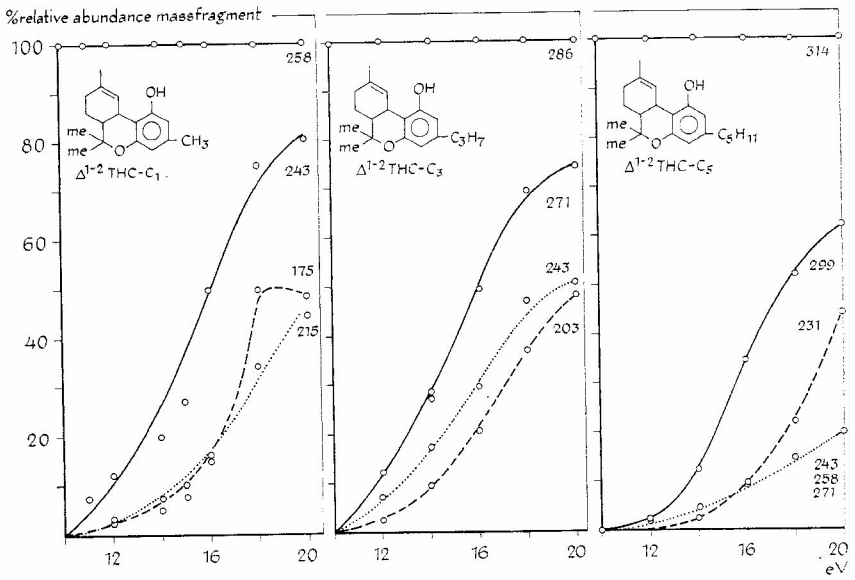
## Identification of the methyl and propyl homologues of CBD, THC and CBN in hashish by a new method of combined gas chromatography-mass spectrometry

Using the LKB-9000 apparatus GC-MS mass spectra were taken of gas chromatographically pure $\Delta^1$-THC and of $\Delta^{1-6}$-THC at different electron voltages (10, 12, 14, 16, 18 and 20 eV). Characteristic graphs for each compound were obtained, when the relative abundance of a particular mass fragment was plotted versus the electron voltage at constant ion source temperature of 250°C. This result suggested a nice identification method for the chemically closely related cannabinoids. From each hashish constituent eluting from the gas chromatograph, the electron voltage-mass fragment intensity graphs (eV-mfi graphs) were constructed. With this technique very characteristic graphs for the major cannabis constituents CBD, $\Delta^1$-THC and CBN were obtained.

In a Nepalese hashish sample 6 compounds were present in a relatively high concentration and from each of these the eV-mfi graphs were constructed. Now it appeared that the graphs of the three compounds, eluting before the CBN, THC and CBN, had the same shape as those of the latter ones, except that each mass fragment was 28 less. As the main fragmentation takes place in the alicylic ringsystem of the cannabinoid molecules, the conclusion must be that we are dealing here with the homologues with a propyl instead of a pentyl side chain [1]. Recently these compounds have been identified via isolation procedures [2, 3, 4].

In a marihuana sample from Brazil two compounds eluting before the propyl-THC and propyl-CBN (no CBD was present) showed again a very similar eV-mfi graph to $\Delta^1$-THC and CBN, but now with a constant mass fragment 56 less. It was concluded that these compounds represent the $\Delta^1$-THC with a methyl side chain, $\Delta^1$-tetrahydrocannabiorcol and the CBN with a methyl side chain, cannabiorcol. See Fig. In a hashish sample of Lebanese origin the methyl homologue of CBD, cannabidiorcol could be identified. These cannabinoids with a methyl side chain (derived from orcinol) have not been identified in cannabis before.




In general it is possible to identify all kinds of derivatives of THC, CBD and CBN by the method described in this communication. The shape of the eV-mfi graphs is always very close to those of the parent compounds. This has been shown for the heptafluorobutyrate, the trifluoroacetate, the trimethylsilyl ether and the methyl ether.

The gas chromatographic behaviour of the methyl, propyl and pentyl homologues is also quite characteristic. There exists a fixed ratio between the retention times of the three, indicating that the side chain on the aromatic ring predominates the gas chromatographic behaviour.

1. T. B. Vree, D. D. Breimer, C. A. M. van Ginneken, J. M. van Rossum, R. A. de Zeeuw, H. Witte. *Clin. Chim. Acta* 34, 365 (1971)
2. L. Vollner, D. Bieniek and F. Korte. *Tetrahedron Letters* 145 (1969)
3. F. W. H. M. Merkus. *Pharm. Weekblad* 106, 69 (1971)
4. E. W. Gill. *J. Chem. Soc. C.* 579 (1971)