The *X*-Ray Structure of Dibromocannabicyclol: Structure of Bicyclomahanimbine

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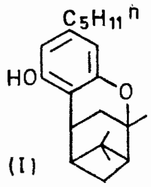
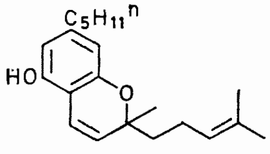
Summary The structure of cannabicyclol is confirmed as (III) *via* an *X*-ray study of dibromocannabicyclol; the result suggests that the structure of bicyclomahanimbine should be revised to (VI).

CANNABICYCLOL (cannabipinol) is an extractive of hashish (*Cannabis sativa* L.) originally formulated (I).[1] It was shown to be formed synthetically in the pyridine-catalysed condensation of citral with olivetol.[2] Cannabichromene

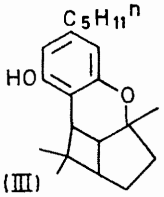
(II), also formed in the reaction, can be converted into cannabicyclol by heat,[2] acid conditions,[3,4] or photochemically,[5] and as a result of n.m.r. examination and these synthetic studies we revised the structure of cannabicyclol to (III).[2,5] This structural revision has not found acceptance in all quarters. Kane and Razdan[6] criticise formulation (III), and suggest that in the absence of further experimental data the structure and stereochemistry (I) should not be discarded. We regard their structural and mechanistic criticisms[6,7] as unsound, and in further support of (III) report the *X*-ray structure of dibromocannabicyclol.



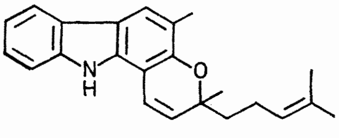
(I)



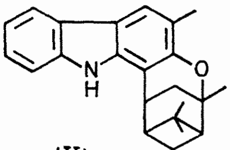
(II)



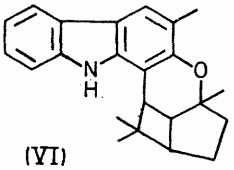
(III)



(IV)

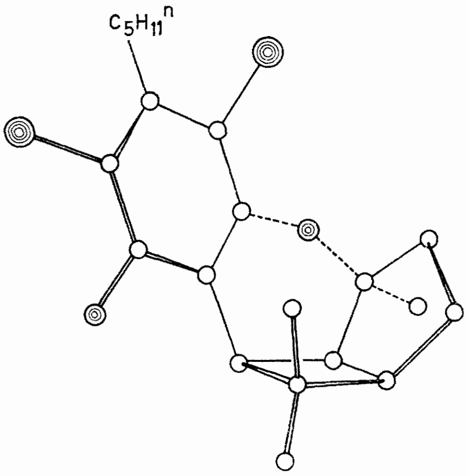


(V)



(VI)

Dibromocannabicyclol, $C_{21}H_{28}Br_2O_2$ was prepared by bromination in dioxan and crystallised at $-20°$ from light petrol (b.p. 40—60°). It formed triclinic crystals, m.p. 73—74°, space group $P\bar{1}$, with $a = 9{\cdot}14$, $b = 10{\cdot}20$, and $c = 15{\cdot}51$ Å; $\alpha = 112°56'$, $\beta = 87°12'$, and $\gamma = 116°0'$. There was one molecule with petrol in the asymmetric unit. The crystal was mounted in a sealed capillary tube to prevent decomposition, and the *X*-ray intensities were measured on a linear diffractometer, with 2531 reflections considered observed. A Patterson synthesis located the bromine positions. The first Fourier synthesis showed the remaining 23 non-hydrogen atoms and refinement was continued to $R = 9{\cdot}6\%$ using the least-squares (block-diagonal) method. A difference map is now being examined to locate petrol of crystallization. The resulting structure is shown in the Figure, and confirms structure (III).



FIGURE

Recently the alkaloid mahanimbine (IV) from *Murraya koenigii* has been synthesised[8] by application of our chromenylation procedure.[2,9] Along with mahanimbine, an isomeric alkaloid, bicyclomahanimbine, has been found, and this can be formed from (IV) by mild acid treatment.[10] Bicyclomahanimbine has been formulated[10] as (V), apparently through acceptance of Kane and Razdan's suggestion.[6] Its mode of formation from (IV) indicates structural revision to (VI).

Added in proof. A similar revision is required for the recently described carbazole alkaloid bicyclomahanimbicine.[11]

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