after the deposition of each layer, an ultrathin oxide layer may also be formed which may be an important factor in increasing the resistivity.

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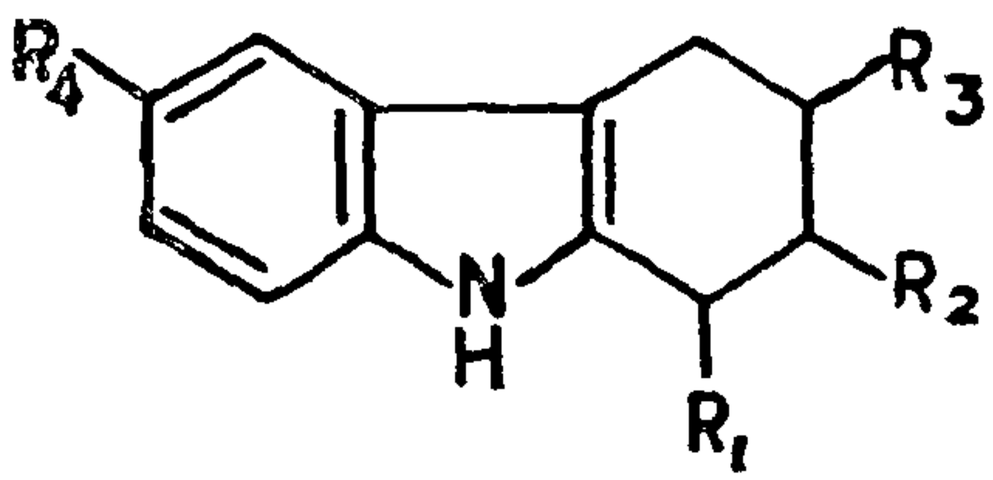
STUDIES ON THE INSECTICIDAL AND ANTIMICROBIAL PROPERTIES OF SOME CARBAZOLE DERIVATIVES

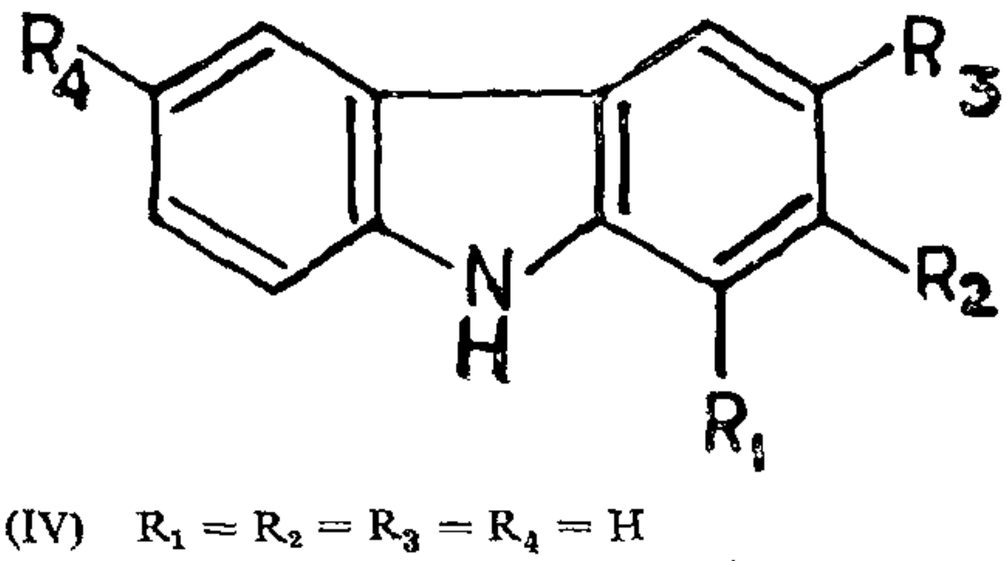
CARBAZOLE derivatives are biologically active displaying antibacterial and antifungal activities[1,2]. These were synthesised by Borsche method[3] and Japp-Klingemann reaction[4]. According to the Borsche's modified method of Fischer Indole Synthesis, the condensation of phenyl hydrazine hydrochloride with appropriate cyclohexanone derivatives, in the presence of sodium acetate, yielded the corresponding hydrazones, which on cychlisation in presence of aqueous sulphuric acid, afforded the corresponding tetrahydrocarbazole derivatives (I, II, and III). The tetrahydrocarbazole derivatives, on chloranil dehydrogenation, furnished the appropriate carbzole derivatives (IV, VI and VII). Compound (V) was prepared in the same way, but the corresponding tetrahydrocarbazole had not been isolated in the pure state.

Carbazole compounds were also prepared by Japp-Klingemann reaction. The reaction of aniline hydrochloride with 2-hydroxymethylene cyclohexanone derivatives furnished the corresponding substituted hydrazones, which on indolisation in acidic medium afforded the corresponding 1-oxo-1, 2, 3, 4-tetrahydrocarbazole derivatives (VIII, IX and X). On Wolff-Kishner reduction (Huang-Minlon modified method) the oxo-derivatives furnished the corresponding tetrahydrocarbazole derivatives (I, II and III), which on chloranil dehydrogenation afforded carbazole derivatives (IV, VI and VII).

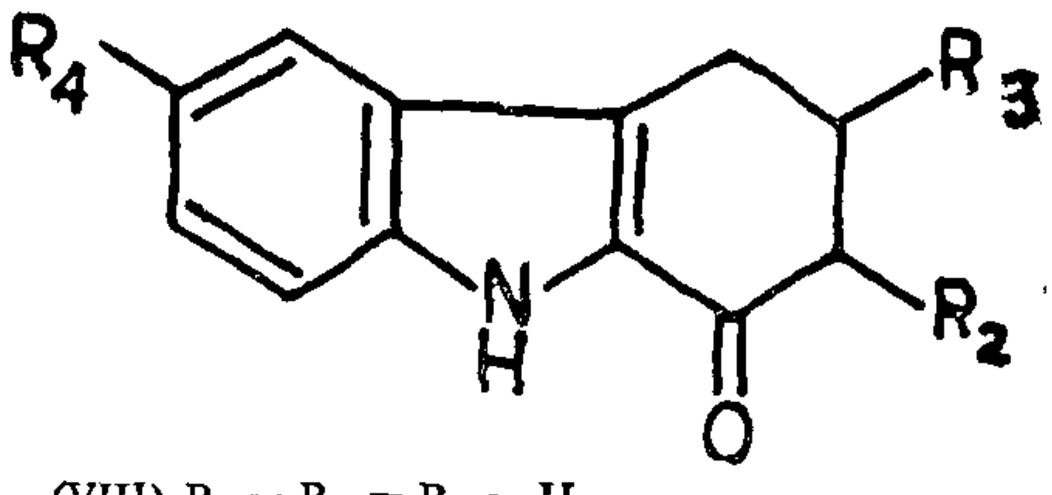
Two carbazole alkaloids glycozoline[5] (XI) and glycozolidine[6,7] (XII) were isolated from the root-bark of *Glycosmis pentaphylla* (Retz.) DC. Glycozoline (XI) on demethylation by HBr furnished 3-methyl-6-hydroxy-carbazole[5] (XIII) and glycozolidine on similar treatment furnished 2-methoxy-3-methyl-6-hydroxy-carbazole[6,7] (XIV).



(I) $R_1 = R_2 = R_3 = R_4 = H$
(II) $R_1 = R_3 = R_4 = H$, $R_2 = Me$
(III) $R_1 = R_2 = R_4 = H$, $R_3 = Me$



(IV) $R_1 = R_2 = R_3 = R_4 = H$
(V) $R_2 = R_3 = R_4 = H$, $R_1 = Me$
(VI) $R_1 = R_3 = R_4 = H$, $R_2 = Me$
(VII) $R_1 = R_2 = R_4 = H$, $R_3 = Me$
(XI) $R_1 = R_2 = H$, $R_3 = Me$, $R_4 = OMe$
(XII) $R_1 = H$, $R_2 = R_4 = OMe$, $R_3 = Me$
(XIII) $R_1 = R_2 = H$, $R_3 = Me$, $R_4 = OH$
(XIV) $R_1 = H$, $R_2 = OMe$, $R_3 = Me$, $R_4 = OH$



(VIII) $R_2 = R_3 = R_4 = H$
(IX) $R_2 = Me$, $R_3 = R_4 = H$
(X) $R_2 = R_4 = H$, $R_3 = Me$

Insecticidal properties of these fourteen carbazole derivatives in comparison with DDT were studied by spraying directly 10 ml ethanolic solution of each compound at 0·5% concentration on house-flies (*Musca domestica* L.) collected in wire-cages. In a separate cage house-flies were sprayed with 10 ml

alcohol (control). The cages were well ventilated; after 10 minutes food and water were supplied to the flies. After 24 hours the percentage of mortality was counted. Four replications were made at each concentration. All the experiments were carried out at 35 ± 1° C.

Studies of the insecticidal properties reveal that the mortality of house-flies are highest in DDT (97%). Next to DDT we have the toxicity of tetrahydrocarbazole (I), 2-methyl tetrahydrocarbazole (II) and 3-methyl tetrahydrocarbazole (III) (*ca.* 84·3%). The toxicity of these tetrahydrocarbazole derivatives (I, II, III) are greater than those of the corresponding carbazole derivatives (IV, VI and VII). The toxicity of (I), (II) and (III) are more or less the same. But the presence of oxo group in 1-position of tetrahydrocarbazole derivatives diminishes their toxicity. Of the 1-oxo-tetrahydro-derivatives, the toxicity of 1-oxo-tetrahydrocarbazole (VIII) > 1-oxo-2-methyl-tetrahydrocarbazole (IX) > 1-oxo-3-methyl-tetrahydroacarbazole (X). Carbazole (IV), 1-methyl carbazole (V), 2-methyl carbazole (VI), 3-methyl carbazole (VII), glycozolidine (XII) and 1-oxo-3-methyl-tetrahydrocarbazole (X) have more or less the same degree of toxicity, but the toxicity of 2-methoxy-3-methyl-6-hydroxy carbazole (XIV) is much lower. Glycozoline (XI) and 3-methyl-6-hydroxy carbazole (XIII) have little or no toxicity.

The glycozolidine (XII) is toxic but glycozoline (XI) is not. Hence the introduction of another methoxy group in the 2-position of glycozolidine makes the resultant compound toxic. If the methoxy group at the 6-position of glycozolidine (XII) be converted to hydroxy group, the resultant compound becomes less toxic. Moreover, the toxicity of carbazole derivatives is highly enhanced by the presence of partially reduced nucleus.

The inhibitory effects of the ten synthetic carbazole compounds (I to X) were studied against ten microbes, *viz.*, (*a*) *Microsporum gypseum*, (*b*) *Candida albicans*, (*c*) *Epidermophyton floccusam*, (*d*) *Tricophyton rubrum*, (*e*) *Alternaria solani*, (*f*) *Aspergillus niger*, (*g*) *Helminthosporium sativum*, (*h*) *Curvularia lunata*, (*i*) *Escherichia coli* and (*j*) *Staphylococcus aureus* by agar diffusion method. The agar medium was at first inoculated with a 24 h. old culture of the test organism. Filter paper discs (6 mm dia) saturated with the solution of the carbazole derivatives (10 mg/ml) in ethanol were placed on the agar plate. The zones of inhibition around the discs were measured after an incubation period of 24 hours at 35° ± 1° C. The antimicrobial activity of the carbazole derivatives was measured from the zone of inhibition.

Though carbazole (IV) has no pronounced activity on microbes, the presence of methyl group in the 1-position of the carbazole nucleus enhances its activity. But the methyl group at the 2 or 3 positions of the carbazole nucleus does not enhance its activity to a marked extent, *i.e.*, (V) is active on the microbes but not (VI) and (VII). Tetrahydrocarbazoles (I, II and III) (particularly III), show pronounced activity. But the presence of oxo group in the 1-position of the 2-methyl and 3-methyl tetrahydrocarbazole derivatives decreases their activity in comparison to that of 2-methyl and 3-methyl tetrahydrocarbazole derivatives.

These investigations clearly show that tetrahydrocarbazoles (I, II, III and VIII) are not only toxic to house-flies, but also have ant fungal and antibacterial activities. Generally, insecticidal properties are enhanced due to the pressence of partially reduced heterocyclic moiety, but at the same time the fungicidal properties are reduced. But in the case of the above carbazole derivatives it is seen that due to the presence of partially reduced moiety both the insecticidal and antimicrobial properties are enhanced.

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SYNTHESIS OF NEW ANTICOAGULANTS AS RODENTICIDES AND THEIR TOXICITY AGAINST BLACK RAT (*RATTUS RATTUS* LIN.)

Introduction

THE advent of anticoagulent rodenticides in 1950 marked a turning point in rodent control strategy as it offered three main advantages, such as bait being