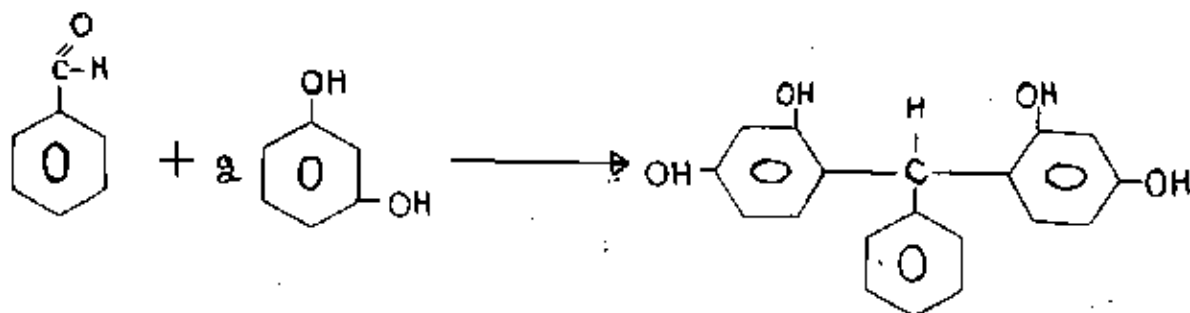


4 DISCUSSION

In assigning the structural formula to thailandine, the following experimental facts have been taken into account besides the essential functional groups as diagnosed by conventional physical methods, i.e. the unusual stability of the molecule and the formation of red color in alkaline solution. The determination of the exact molecular weight of thailandine was attempted by mass spectrometric method, but unfortunately, the compound could not be vaporized in the mass spectrometer. For this reason, the osmometric method of molecular weight determination was resorted to and the molecular weight found to be 1505.

The proposed structure for thailandine corresponds to a compound of high molecular weight and is calculated as 1514 from the formula proposed. The agreement between experimental and theoretical molecular weights is quite good and the proposed structure is adopted on this basis.

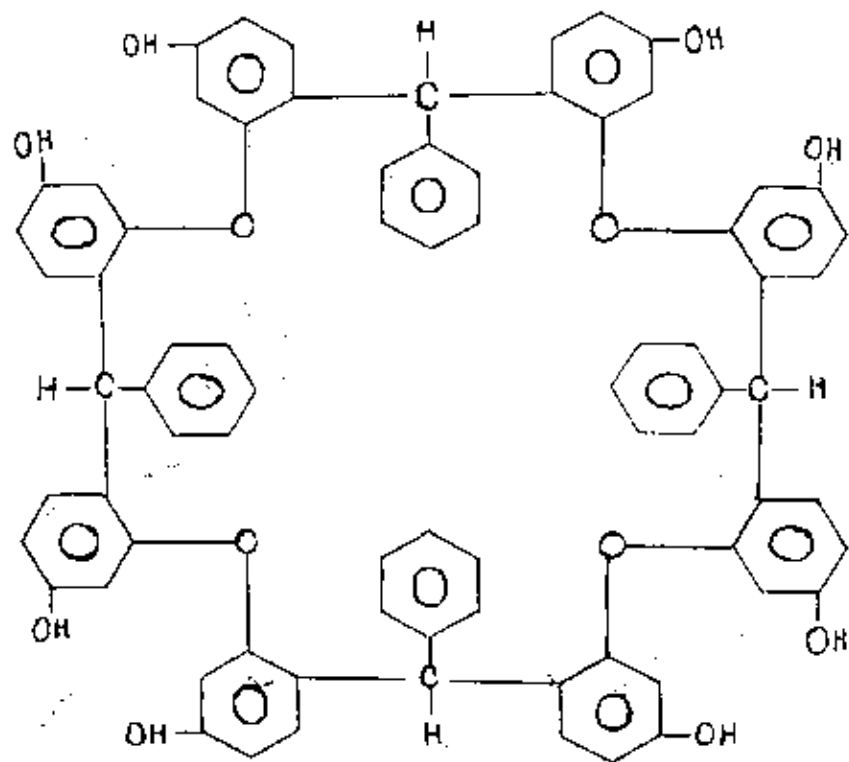
Thailandine contains triphenyl methyl nuclei as revealed by the characteristic I.R. absorptions at 1200 and 1280 cm.^{-1} (1). It is logical, therefore, to assume that they arise by the condensation between one mole of benzaldehyde and two moles of resorcinol via the crossed aldol condensation followed by elimination of water. The position of condensation should be ortho-para to both of the hydroxyl groups of the resorcinol molecules in accordance with orientation rules as shown below :



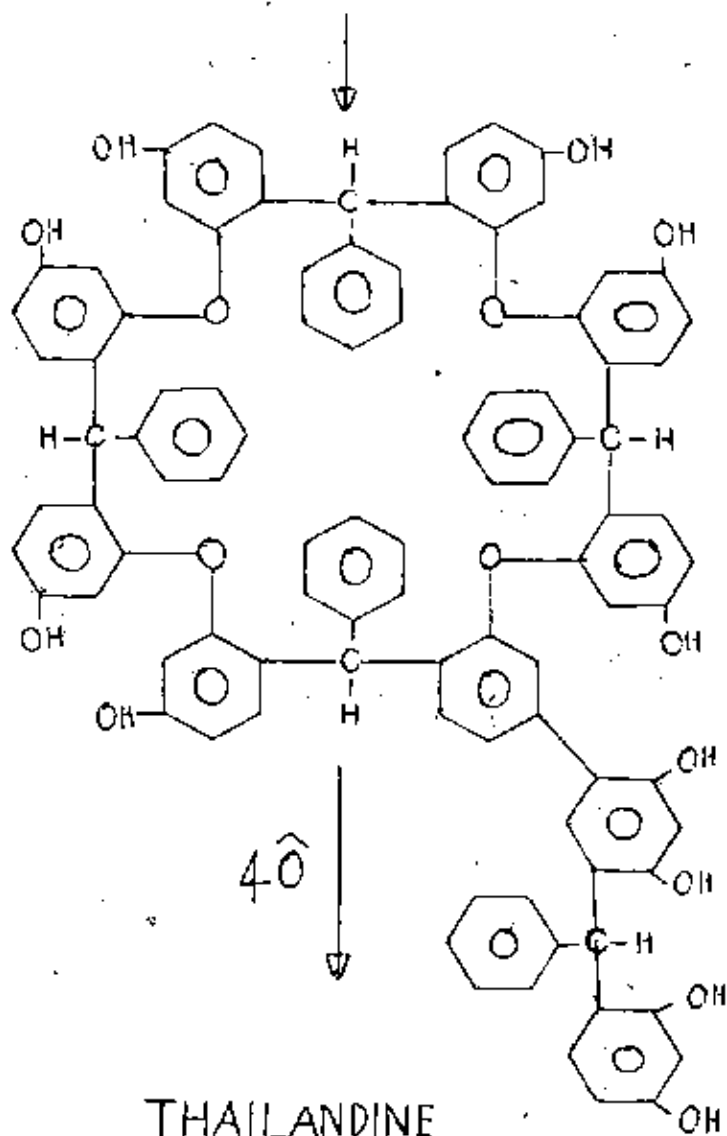
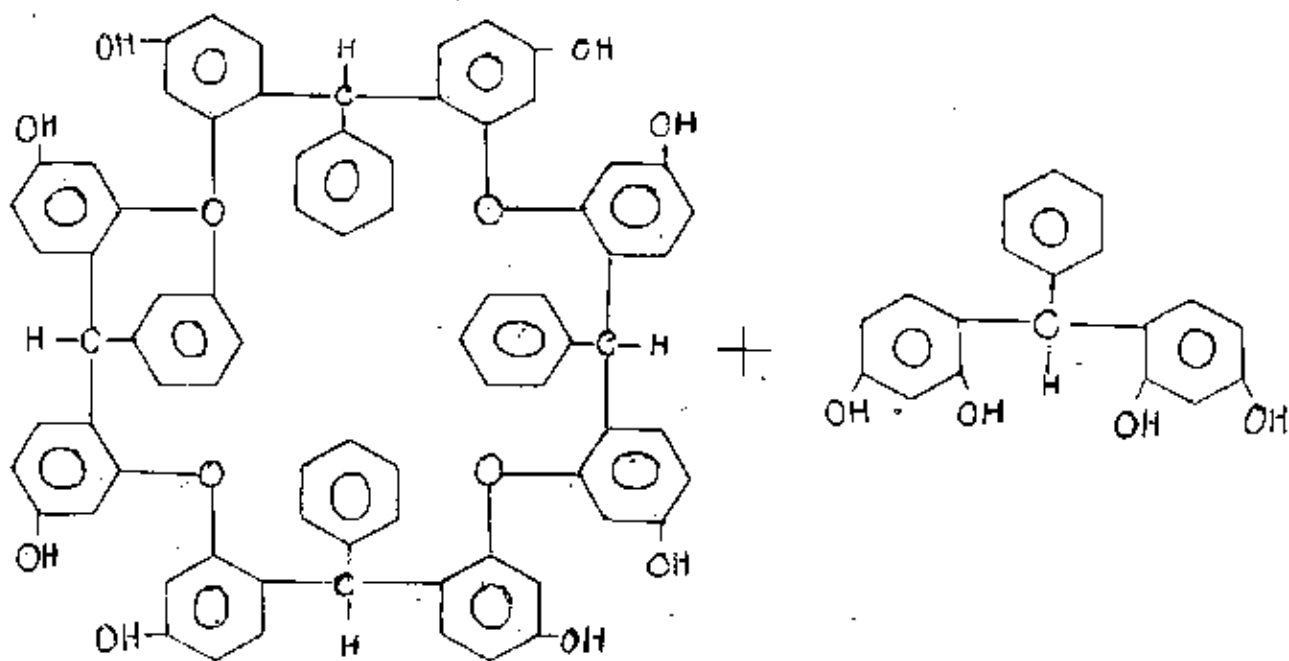
The resulting triphenyl methane derivatives can then condense intermolecularly to form the large molecule of thailandine. Elemental analyses establish that five of these molecules should condense with the loss of water to form thailandine. We here postulate the formation of cyclictetramer by the condensation of four of these molecules to form the main skeleton of thailandine while the fifth molecule condenses at this skeleton to form a branching of biphenyl derivative.

The presence of the biphenyl system with ortho and para hydroxyls in the molecule of thailandine is postulated to account for its red color in alkali. We postulate it to arise by the condensation between one hydroxyl group of the skeleton tetramer and a hydrogen atom at the ortho-para position to the two hydroxyl groups of a dihydroxy benzene ring of the dihydroxy-diphenylmethane as shown below. This, however, remains an open question since we have been unable to isolate any degradation product possessing biphenyl structures. The position of condensation is immaterial in view of the symmetrical structure of the skeleton ring.

006941



CYCLICTETRAMER



THAILANDINE

The two hydroxyl groups indicated by asterisks in the above proposed structure will form phenoxide ions in alkali which can accordingly resonate among the various structures, causing a bathochromic shift that renders the solution deep red. In acid, however, the phenoxide ions revert to the phenolic form, less resonance is operative and the red color is lost. The stability of thailandine towards acid and alkaline hydrolysis is consistent with the proposed aromatic ether structure. The compound was recovered unchanged upon refluxing in alkali for 3 days. It can be brominated easily, a typical reaction of phenol. As a phenolic and alcoholic compound, thailandine can be methylated by dimethyl sulfate in alkali to tri-deca methyl derivative. The compound also forms benzoyl and acetyl derivatives. The proposed structure was further supported by degradation of thailandine in conc. HNO_3 which afforded a pale-yellow solid whose elemental analysis agreed with the structure of *m*-nitro benzoic acid.

In the proposed structure, it becomes necessary to postulate the uptake of an oxygen atom for each of the four triphenyl methyl carbons of the skeleton tetramer to form hydroxyl groups in order to account for the relatively high oxygen content of thailandine shown by microanalysis as well as by n.m.r. spectrum. This is not unreasonable since triphenylmethyl derivatives are oxidized easily to their

carbinol derivatives(5). From elemental analyses, one triphenylmethyl carbon must be left unoxidized and is postulated to be the one shown by asterisk in view of the fact that it is hindered by the phenyl group and the two hydrogen-bonded hydroxyls. The structure of thailandine is therefore postulated as shown on page 8 .

The I.R. spectrum shows characteristic absorption bands for the main groups as shown in Table 2, which is consistent with the assigned structure. It should be mentioned that the complex asymmetry of the compound makes it difficult to confirm the structure by the n.m.r. spectrum, as important fine structures are lacking. The number of different protons diagnosed by n.m.r. however, are in accord with the assigned structure. The evidence of the elemental analyses and the molecular weight determination, together with the I.R. and n.m.r. spectra lend good support to the structure proposed for this compound.

Analogous compounds can be prepared by using sulfanilic acid in place of 6-methyl-2-aminopyridine.