

NEW INDOLE TRIMER

Hisashi Ishii, Keiko Murakami and Yasuoki Murakami  
Faculty of Pharmaceutical Sciences, Chiba University  
1-33, Yayoi-cho, Chiba, Japan

It is well known that indole itself was easily polymerized under various acidic conditions to give a dimer and/or a trimer. A sole compound (1) [known trimer: mp 173-177° or mp 110-113°] has been known as a trimer until now and its structure was proposed by Smith and Noland. Recently, in the course of studies on the advanced Fischer indolization, we occasionally obtained another trimer (2) [New trimer: mp 186.5-187.2° or mp 105-107°] on treatment of a benzene solution of indole with TSOH. Acetylation of the new trimer (2) afforded the mono N-acetyl derivative (3), mp 168.5-171°.

Inspection of the NMR spectra of the new trimer (2) and its acetate (3) revealed the presences of an  $\text{ArCH}_2\text{CH}$ , an aromatic primary amine and two indolic NH groups. The mass spectra of these compounds (2 and 3) show a common base peak at  $m/e$  245 corresponding to a bisindolylmethine ion. These data could be also explained by the formula which was allocated for the known trimer (1) until now.

In the trial of the Vilsmeier reaction of the acetyl new trimer (3) and the acetyl known trimer (4), the former (3) gave the mono formyl derivative (5), mp 252-255°, but the latter (4) resulted in the recovery of the starting material. These evidences clearly show that the new trimer (2) has an unsubstituted indolic  $\text{C}_3$ -position but the both indolic  $\text{C}_3$ -positions of the known trimer (1) should be substituted. These evidences allowed us to depict the structures of the new trimer and the known trimer as the formula 2 and 1, respectively.

We also found that, although the condensation of o-nitrophenylacetaldehyde with indole in AcOH gave a compound (6), which could be converted to the known trimer (1) as reported by Noland, the same treatment of these compounds in the presence of  $\text{ZnCl}_2$  gave a mixture of 6 and its isomer which could be introduced to the new trimer (2).

