

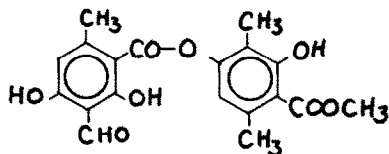
SYNTHESIS OF ATRANORIN

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ATRANORIN is a depside commonly occurring in several species of lichens. Though its structure was elucidated by St. Pfau¹ as an aldehydo depside (I) its synthesis has not till now been accomplished. It has now been done and the results are reported in this communication. In preliminary work, search was made for effective methods of depside synthesis.



In a recent communication² a general method of synthesis of depsides using dicyclohexylcarbodiimide was reported. Even though there was success in a number of cases, some difficulties were experienced in certain condensations and especially when it was applied to the synthesis of atranorin (I). By making use of the carbodiimide for the condensation of 3-formyl-2,4-dihydroxy-6-methylbenzoic acid (haematommic acid) (II) and methyl 2,4-dihydroxy-3,6-dimethylbenzoate (methyl β -orcinol carboxylate) (III) extremely poor yields were obtained. Even though the full amount of dicyclohexylurea separated, haematommic acid could be recovered almost completely.

¹ A.St. Pfau, Helv. Chim. Acta **9**, 650 (1928).

² S. Neelakantan, R. Padmasani and T.R. Seshadri, J. Sci. Industr. Res., India **20B**, 510 (1961).

This may be due to a facile alternative reaction, probably anhydride formation, which is known to take place in carbodiimide synthesis of peptides. In the present case the anhydride should be decomposing easily in the subsequent treatment with aqueous sodium hydrogen carbonate intended to remove any unreacted acidic component. Since this difficulty did not arise so markedly in the other cases of depside synthesis using the carbodiimide, it may be connected particularly with the presence of the aldehyde group in some way. The condensation was also tried with dicarbethoxyhaematommic acid as the acid component. In this case the depside condensation proceeded satisfactorily but the carbethoxy groups of the condensation product could not be removed without affecting the depside linkage and hence atranorin could not be isolated.

In view of the above difficulties there was need for a better reagent for the depside condensation. Bourne et al.³ have reported the use of trifluoroacetic anhydride as a convenient reagent for the synthesis of esters of carboxylic acids. This reagent has now been found to be more suitable for preparing depsides. It has the advantage of being a solvent also besides the condensing agent. During the present study, it was noticed that with equimolecular quantities of the carboxylic and the phenolic components the reaction proceeds smoothly and good yields of the depside are obtained. In a few cases a slight excess of the reagent is used to dissolve the components completely.

The preparation of phenyl benzoate has been taken up as a simple preliminary example though it was earlier prepared by Bourne et al.³ by using an excess of benzoic acid. In depside synthesis it is necessary to avoid this excess. With equimolecular quantities of benzoic acid and phenol in the presence of trifluoroacetic anhydride at a bath temperature

³ E.J. Bourne, M. Stacey, J.C. Tatlow and J.M. Tedder, J. Chem. Soc. 2976 (1949).

