

Note

Racemization of (+)-*trans,trans*-Chrysanthemum-dicarboxylic Acid

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The total synthesis of (+)-*trans,trans*-chrysanthemum-dicarboxylic acid, an acidic component of the "pyrethrins", was achieved and the stereochemistry thereof was also established by the synthetic evidence¹⁾. However, nothing about the racemization of the naturally derived chrysanthemum-dicarboxylic acid has been reported since Fujitani²⁾ isolated this acid from Japanese pyrethrum flowers in 1909. In the course of investigations on the synthetic pyrethroids in this laboratory, the present authors have recently succeeded for the first time in the conversion of the naturally derived (+)-*trans,trans*-chrysanthemum-dicarboxylic acid into the corresponding racemate by treating its methylester with potassium methoxide in absolute methanol.

Methyl (+)-*trans,trans*-chrysanthemum-dicarboxylate (1 Mol.) was dissolved in about ten times volume of absolute methanol and was refluxed with an equimolar potassium methoxide (0.5-N) for two hours. In the usual manner, the unchanged methylester was recovered (0.67 Mol.), from which methyl (\pm)-*trans,trans*-chrysanthemum-dicarboxylate, m. p. 79-80° (0.12 Mol.) crystallized out. This was identified by analysis, mixed melting point comparison as well as by IR-spectrum comparison with the authentic specimen.

The filtrate from the crystalline racemate was distilled (0.54 Mol.), also identified as methyl *trans,trans*-chrysanthemum-dicarboxylate and was shown to contain about 18% of the racemate by the polarimetric estimation. The aqueous alkaline solution, after acidification and extraction with ether, yielded a light yellow syrup (0.31 Mol.). The alkaline hydrolysis of a portion of this acidic fraction gave an acid having a dextrorotation which indicated the contamination of *ca.* 18% of racemate.

Therefore, the total racemization in the first run amounted to *ca.* 28% based on the optically active ester employed.

Successive three or four times repetitions of this procedure with the recovered ester sufficed the practically complete racemization of the dextrorotatory ester employed. Potassium can be replaced by sodium, but with a less racemization. Not to mention, the racemic ester afforded, on alkaline hydrolysis (\pm)-*trans,trans*-chrysanthemum-dicarboxylic acid melting at 208°.

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REFERENCES

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- (2) Y. Fujitani, *Arch. exp. Path. Pharm.*, **61** 47 (1909).