

NOTE

Geometrical Isomers of Chrysanthemum Dicarboxylic Acid*

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In the previous paper¹⁾ the authors have tried the synthesis of chrysanthemum dicarboxylic acid, the acidic component of pyrethrin II and cinerin II, by our routes, i.e. addition of ethyl diazoacetate to ethyl $\alpha\delta$ -dimethyl- β -hydroxy- $\Delta\gamma$ -hexenoate (route A), or to ethyl $\alpha\delta$ -dimethylsorbate (route B), and by route A we have obtained a dicarboxylic acid $C_{10}H_{14}O_4$ (mp. 180° , after recrystallisation mp. $185-6^\circ$, *p*-phenylphenacylester mp. 151°). At first we regarded this as a racemic isomer of synthetic chrysanthemum dicarboxylic acids, but the IR spectrum showed the absence of the typical absorption for cyclopropane. This acid absorbed 1.95 mol. hydrogen on catalytic hydrogenation, giving $C_{10}H_{18}O_4$ (mp. $94-5^\circ$, *p*-phenylphenacylester mp. $106-7^\circ$) and UV absorption (λ_{max} $274 m\mu$, ϵ 29700) showed that this acid contained the system $-C=C-C=C-COOH$. Among ozonisation products, acetone was isolated as 2,4-dinitrophenylhydrazone. Thus, this acid is considered to be $\alpha\delta$ -dimethyl- γ -carboxymethylsorbic acid. This was obtained also by route B.

In route B, $\alpha\delta$ -dimethylsorbic acid $C_8H_{12}O_2$ (λ_{max} $273 m\mu$, ϵ 22300, *p*-phenylphenacylester mp. 103°) was obtained by dehydration of the corresponding β -hydroxyester with phosphorus pentoxide in benzene, followed by hydrolysis. This acid absorbed 1.97 mol. hydrogen on catalytic hydrogenation, giving $\alpha\delta$ -dimethylcaproic acid (bp. 116° at 13 mm., amide mp. 103° , *p*-phenylphenacylester mp. 66°), and stereochemical consideration suggests the *trans* configuration of this acid in spite of the lack of experimental evidences. Two kinds of dicarboxylic acid $C_{10}H_{14}O_4$, mps. $207-8^\circ$ and $208-9^\circ$, were isolated from the adduct, resulted from addition of ethyl diazoacetate to ethyl $\alpha\delta$ -dimethylsorbate. The former 208° acid gave *dl-trans* caronic acid (mp. 212°) and pyruvic acid (as 2,4-dinitrophenylhydrazone mp. 218°) on ozonisation and the comparison with authentic specimens showed no depression of mps. UV absorption (λ_{max} $237 m\mu$, ϵ 15400) was identical with that of natural chrysanthemum dicarboxylic acid (λ_{max} $238 m\mu$, ϵ 15300) and IR spectrum in Nujol

* When these experiments were in progress and nearing completion we learnt by Dr.S.H.Harper's communication, that he also had synthesised these geometrical isomers of chrysanthemum dicarboxylic acids by the same routes²⁾

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mull (Fig. 1) was closely identical with that of natural acid and thus, this is the racemic form of the natural chrysanthemum dicarboxylic acid.

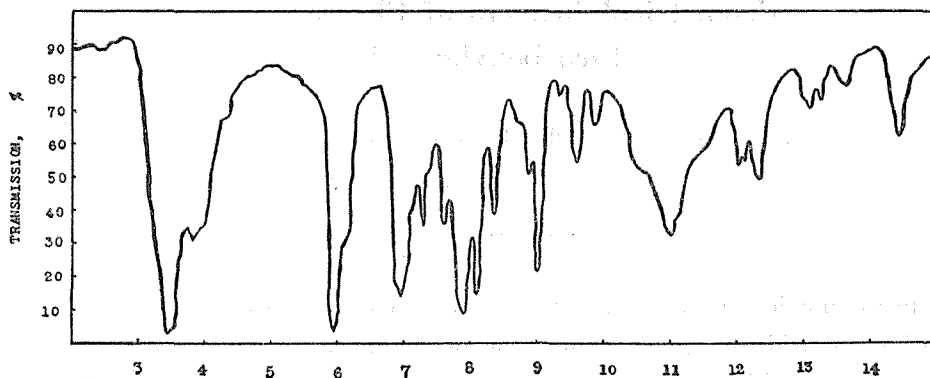


Fig 1.

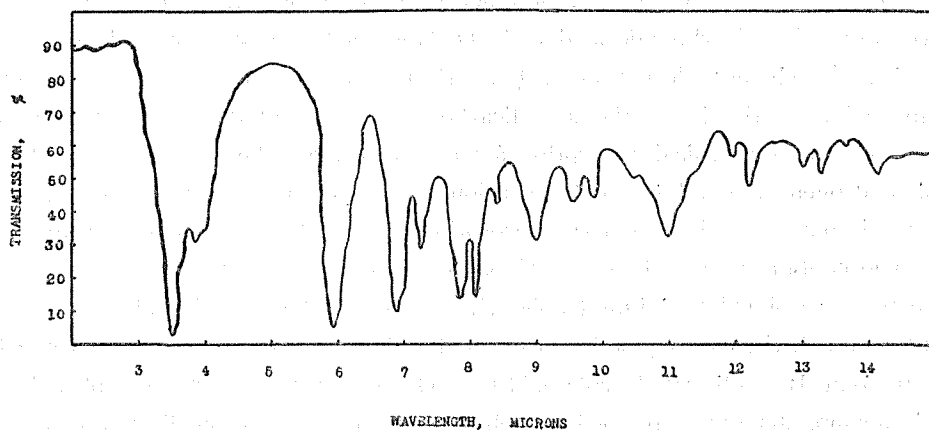


Fig 2.

The latter 208-9° acid showed a depression of mp. when mixed with the former 208° acid and gave *dl-cis* caronic acid (mp. 173-4°) as well as pyruvic acid on ozonisation. IR spectrum of this acid in Nujol mull (Fig. 2) was very similar to those of 208° acid and of natural acid, but UV absorption (λ_{max} 242 $m\mu$, ϵ 15700) was not identical. This 209° acid is the *cis*-isomer (with reference to the cyclopropane) of the former 208° acid. Mps. were uncorrected. Further studies are now in progress and will be described in details elsewhere.

REFERENCES

- (1) Y.Inouye et al. : *Botyu-Kagaku*, **19**, 35-7, 102-5 (1954).
- (2) S.H.Harper et al. : *Chemistry and Industry*, **1954**, 1538-9.