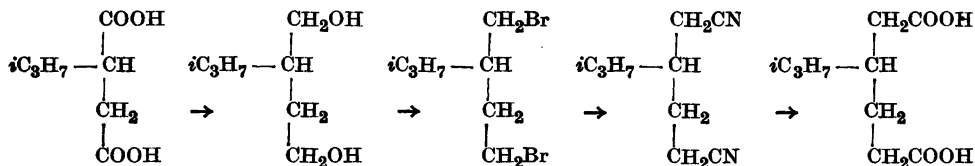


## The Steric Connections of $\beta$ -*iso*-Propyladipic Acid

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Optically active  $\beta$ -*iso*-propyladipic acid is in several cases obtained on degradation of terpenoid compounds, *e. g.* limonene<sup>1</sup> and phellandral<sup>2</sup>, and its steric connections are therefore of special interest for the stereochemistry of the terpene group. Von Braun and coworkers have resolved the racemic acid into the optical antipodes<sup>1</sup> and made several attempts to relate it to the *iso*-propylsuccinic acid<sup>3</sup>. It had previously been found, that (+)- $\beta$ -methyladipic acid could be degraded to (+)-methylsuccinic acid<sup>4</sup>, but corresponding experiments with the *iso*-propyl derivative were unsuccessful. They also tried to go the opposite way:



The initial reduction could be accomplished either by sodium in alcohol or catalytically with copper chromium oxide catalyst at high temperature and pressure. Both methods are, however, known to

cause racemisation of an asymmetric carbon atom in  $\alpha$ -position and the products obtained were completely inactive.

Reduction of carboxylic acids to primary alcohols can now be performed very smoothly with *lithium aluminium hydride* in ethereal solution<sup>5</sup>. This reaction could be expected to proceed without loss of activity. Racemic and dextro-rotatory *iso*-propylsuccinic acid were therefore treated with lithium aluminium hydride according to Nystrom and Brown<sup>5</sup>. The resulting diols were, without further purification, successively converted to dibromides, dicyanides and dicarboxylic acids using familiar methods. The ultimate yields were rather poor, but the acids obtained could be identified as racemic and dextro-rotatory  $\beta$ -*iso*-propyladipic acid. A closer investigation of the different steps might lead to a better yield.

16 g of racemic *iso*-propylsuccinic acid yielded 1.85 g of crude  $\beta$ -*iso*-propyladipic acid. After recrystallisations from water,

benzene and hydrochloric acid, there remained 1.52 g with m. p. 82.5—83.5°.

0.1207 g: 12.11 ml 0.1060 N NaOH. —  
27.63 mg: 58.25 mg CO<sub>2</sub> and 21.14 mg H<sub>2</sub>O.  
C<sub>9</sub>H<sub>16</sub>O<sub>4</sub> (188.2)  
Calc. Equiv. wt 94.1 C 57.43 H 8.57  
Found » » 94.0 » 57.49 » 8.56

concentration 1 : 200 and *p,p'*-dihydroxy-diphenylsulphone to possess only a slight bacteriostatic activity (1 : 4000).

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8 g of pure (+)-*iso*-propylsuccinic acid having  $[\alpha]_D^{25} = +22.9^\circ$  in aqueous solution<sup>6</sup> gave 0.91 g of crude  $\beta$ -*iso*-propyladipic acid. After recrystallisations from water and hydrochloric acid, there remained 0.55 g having m. p. 71—73°.

0.1196 g: 11.98 ml 0.1060*N* NaOH. —  
0.4092 g neutralised with NaOH and  
made up to 5.00 ml with water:  $\alpha_D^{25} = +$   
0.425°.

Equiv. wt. Calc. 94.1 Found 94.2  
 $[\alpha]_D^{25} = + 5.2^\circ$ ;  $[M]_D^{25} = + 9.8^\circ$ .

On comparison with the values given by Von Braun and Werner<sup>1</sup>, this preparation seems to contain about 90 % of (+)-acid and 10 % of (—)-acid. As the rotatory power is very low and the data of these authors refer to much more concentrated solutions, this estimation is very approximate. It can however be stated that an optically active carboxylic acid can in this way be converted to a higher homologue without material loss of activity. As the asymmetric carbon atom is not involved in the reactions, (+)-*iso*-propylsuccinic acid and (+)- $\beta$ -*iso*-propyladipic acid must be sterically related.

The latter acid may be obtained from (+)-limonene<sup>1</sup>, and this terpene is thus sterically connected to the alkylsuccinic acids. On the other hand, (+)-limonene is sterically related to (+)-fenchone and (+)-camphor<sup>7, 8</sup>, which have previously been connected to the alkylsuccinic acids by aid of  $\alpha$ -*iso*-propylglutaric acid<sup>9</sup>. These earlier results are corroborated by the present investigation. A further discussion of these matters and a more detailed account of the experiments will be published later.

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## Electron Diffraction of Cyclooctatetraene Vapour

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The most direct way for determining the molecular structure of cyclooctatetraene would be the use of interferometric methods based either on X-rays or electrons. Reports on interferometric investigations were published in 1947 by the present authors<sup>1</sup> and by Kaufman, Fankuchen and Mark<sup>2</sup>. The conclusions, however, to which the present authors were led using the electron diffraction sector method were quite different from those reached by Kaufman *et al.* using X-ray crystallographic methods.

In order to check our results two new analyses were carried out, the first with the same material used in our previous investigation (a sample prepared by prof. A. Langseth), the second using new material obtained from The British Oxygen Company. The computation work associated with the second of these new analyses was carried out by a new member of the staff who had no knowledge about the results of the two first analyses. In Fig. 1

the  $\frac{\sigma(r)}{r}$ -curve obtained in the very first analysis (A) is compared with those of the two new analyses (B and C). The C-C-C-angle is determined by the ratio of the *r*-values of the two first high maxima of the

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