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Kyoto University
Resolution of $\pm$-trans-3-(trans-2'-Carboxypropenyl)-2,2-
dimethylcyclopropane-1-carboxylic Acid

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As was described in the previous papers, $(\pm)$-trans-3-(trans-2'-carboxypropenyl)-
2,2-dimethylcyclopropane-1-carboxylic acid, mp. 208°, prepared following our synthetic
scheme, was shown to be the racemic form of the naturally derived chrysanthemum-
dicarboxylic acid by the identity of their infra-red and ultra-violet absorption spectra,
as well as by synthetic and degradative evidence. After the attempts to resolve this ra-
cemic acid into diastereoisomers with commoner alkaloids, we have succeeded in obtaining
the dextrorotatory acid by means of a synthetic optically active base, $a$-phenylethyl-
amine.

The $(-)$-$a$-phenylethylamine salt of the $(+)$-acid obtained pure after fractional
crystallisation had mp. 224-5° and $[\alpha]_{D}^{11}+28.3^\circ$, which did not alter on further recrys-
tallisation. Decomposition of this salt by dilute sulphuric acid gave pure crystalline
$(+)$-trans-3-(trans-2'-carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid,
mp. 163-4°, $[\alpha]_{D}^{11}+70.9^\circ$. The melting point was not depressed when mixed with the
naturally derived chrysanthemum-dicarboxylic acid. The complete synthesis of chrysan-
themum-dicarboxylic acid was thereby achieved.

In one of our experiments to resolve the racemic acid by means of brucine, the
filtrate from the first crop of the brucine salt, when acidified, gave acids with small
dextrorotation.

To a boiling solution of this acids (4.1 g.) in 120 ml. of methanol were added
2.5 g. of $(-)$-$a$-phenylethylamine, having $[\alpha]_{D}^{11}-38.9^\circ$, in 10 ml. of methanol. The
solution was kept overnight and the first crop of salt (2.6 g.) was separated and the
mother liquor evaporated, this procedure being repeated so that five crops were
obtained by successive reduction of the volume.

After successive recrystallisations of these crops and combining crops with approxi-
mately the same rotation to the first crop and recrystallising the combined salt many
times from dilute methanol, there was finally obtained a pure $(-)$-$a$-phenylethylamine
salt of the $(+)$-acid (0.7 g.), mp. 224-5°, $[\alpha]_{D}^{11}+28.3^\circ$ (c, 1.1, l, 1 in methanol).
(Anal. Found C,67.91, H, 8.06, Calcd. for C$_{13}$H$_{26}$O$_2$N, C, 67.69, H, 7.89). Further
recrystallisation did not alter these values. Subsequent decomposition of this salt (0.5
g.) by dilute sulphuric acid gave the pure crystalline (+)-trans-3-(trans-2'-carboxypropenyl)-2,2-dimethylcyclopropane-1-carboxylic acid (0.23 g.), mp. 163-4°, $[\alpha]_D^0 + 70.9^\circ$ ($c$, 3.3, $l$, 1 in ethanol), (Anal. Found C, 60.54, H, 7.19, Calcd. for C$_{10}$H$_{14}$O$_4$, C, 60.59, H, 7.12). The melting point was not depressed when mixed with the naturally derived chrysanthemum-dicarboxylic acid, mp. 164°, $[\alpha]_D^0 + 71.2^\circ$ ($c$, 1.5, $l$, 1 in ethanol). (cf. Standinger and Ruzicka$^2$, $[\alpha]_D^0 + 72.8^\circ$). Di-$p$-phenylphenacylester mp. 151-2°, $[\alpha]_D^0 + 123.3^\circ$ ($c$, 0.9, $l$, 1 in chloroform), (Anal. Found C, 77.51, H, 5.91, Calcd. for C$_{38}$H$_{34}$O$_6$ C, 77.79, H, 5.84)

Further resolution by means of (+)-a-phenylethylamine in order to obtain the enantiomorph laevorotatory acid from the residual salt mixture described above, is now in progress and will be described elsewhere in detail.

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REFERENCES