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Preparation of the Laevorotatory Enantiomer of Methylallylacetic Acid

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The dextrorotatory form of methylallylacetic acid ((+)-2L-methyl- $\Delta^{4:5}$ -pentenoic acid) was first obtained by Ställberg-Stenhagen¹ by resolution of the racemic acid *via* the quinine salt. The configuration was determined by Ställberg-Stenhagen and Stenhagen², who oxidized the (+)-acid to (–)-methylsuccinic acid. The laevorotatory enantiomer has so far not been reported in the literature. In connection with work on the synthesis of phthiocerol in this laboratory, both enantiomers were needed for the synthesis of the different stereoisomeric forms of the 3-methoxy-4-methyl-grouping of the phthiocerol molecule³. It has now been found that the laevorotatory enantiomer of methylallylacetic acid ((–)-2D-methyl- $\Delta^{4:5}$ -pentenoic acid) can be obtained *via* the (+)-1-phenylethylamine salt. The optical rotation found was numerically equal to that reported for the dextrorotatory enantiomer^{4,5}.

Experimental. (–)-2D-Methyl- $\Delta^{4:5}$ -pentenoic acid. Partially resolved laevorotatory acid (43 g, $\alpha_D^{25} - 5.3^\circ$ (undiluted, *l* 1)), obtained from the mother liquor of the first crystallization of the quinine salt of

the dextrorotatory enantiomer, was dissolved in ether (700 ml) and a solution of (+)-phenylethylamine (44.5 g) in ether (800 ml) was added cautiously (heat is evolved during the formation of the salt). Crystallization was allowed to take place overnight at a temperature of -15° . The salt crystallized in the form of long thin needles. Acid isolated from the mother liquor of this crystallization had an optical rotation of $\alpha_D^{25} - 2.2^\circ$ (undiluted, *l* 1). The salt was recrystallized from successively smaller volumes of ether and the course of the resolution followed by measuring the rotation of acid isolated from the mother liquors. Nine crystallizations were needed before the rotation attained the constant value $\alpha_D^{25} - 7.80^\circ$ (undiluted, *l* 1). Decomposition of the salt gave 6.6 g of (–)-methylallylacetic acid of b.p. $87-88^\circ$ at 12 mm; n_D^{25} 1.4275, n_D^{18} 1.4305; d_4^{25} 0.946; R_D calcd. 31.02, found 31.01.

Optical rotation: $\alpha_D^{25} - 7.80^\circ$ (undiluted, *l* 1); $[\alpha]_D^{25} - 8.25^\circ$; $[M]_D^{25} - 9.41^\circ$.

The specimen of the dextrorotatory enantiomer, prepared in the course of the present work had $[\alpha]_D^{25} + 8.25^\circ$. Ställberg-Stenhagen⁴ gives $\alpha_D^{20} + 7.88^\circ$ (undiluted, *l* 1), which corresponds to $[\alpha]_D^{20} + 8.28^\circ$. Fray and Polgar⁵ give $[\alpha]_D^{19} + 8.24^\circ$.

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