

ploying 1) neutral paper, 2) boric acid impregnated paper, and as developers 1) hypophase of chloroform, ethanol, water (8:2:1) and 2) epiphase of benzene, ethanol and boric acid saturated water (6:2:1). Only a single spot corresponding to that of taxifolin was observed on spraying with bisdiazotised benzidine.

The ligroin solution B was evaporated and the residue dissolved in ether (700 ml) and shaken successively with a saturated aqueous solution of sodium bicarbonate (3 × 200 ml), a 10% sodium carbonate solution (4 × 300 ml) and a 5% potassium hydroxide solution (3 × 200 ml). Evaporation of the residual ether solution yielded a neutral fraction (6 g) which was subjected to distillation with steam. Only about one gram of a terpene-like volatile oil was obtained and a semisolid non-volatile fraction which were not further investigated.

Acidification and ether extraction of the aqueous solutions yielded a bicarbonate soluble fraction (1.1 g), a "carbonate fraction" (26 g) and an "alkalifraction" (1.8 g) of which only the carbonate fraction was investigated. It crystallised readily and yielded after recrystallisation from light petroleum (b. p. 40–60°) pure β -thujaplicin (25.8 g, 2.2%) m. p. 52.5–53° (mixed m. p.). Cu-complex: from chloroform crystals m. p. 93–94° (containing solvent of crystallisation) resolidifying and again melting at 165.5–165.7°. Paperchromatographic tests employing sodium borate impregnated paper and butanol, ethanol, water (5:1:4) or benzene, ligroin (b. p. 80–120°) as developers indicated the absence of carvacrol in the mother liquor. There was an extremely weak spot corresponding to α -thujaplicin.

2. *Extraction with ligroin.* The ground wood (100 g) was extracted continuously with hot ligroin for 15 hours. The extract (2.3 g) was an oil which easily crystallised. By dissolution in dilute potassium hydroxide solution and precipitation with hydrochloric acid a yield of 1.6 g of practically pure β -thujaplicin was obtained.

3. *Extraction with alkali.* The ground wood (100 g) was mixed with a 2% solution of potassium hydroxide (500 ml). After fifteen minutes the mixture was filtered and this operation repeated twice. The combined extracts were acidified with hydrochloric acid and shaken with ether. In this manner a fraction insoluble in ether (4 g) and a fraction soluble in ether were obtained. The latter was distilled *in vacuo* (10 mm) yielding a volatile product (2.5 g) which crystallised directly and from which pure β -thujaplicin (2.1 g) was isolated.

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The Diastereomers of α -Methyl- α' -ethyl-glutaric Acid

GERD BENZJ

Chemical Institute, University of Uppsala, Sweden

In connection with an investigation into configurative relations in progress at this institute Schotte¹ has studied the infrared absorption spectra of the two isomers of α -methyl- α' -ethyl-glutaric acid. As early as 1946 these isomers were prepared by the author and this communication describes the method used.

The separation of the two isomers was performed by making use of the different solubility of their acid calcium salts and after several recrystallisations from water they melted at 83.5–84.5° and 105.5°, respectively. According to Schotte¹ the configuration of the low melting acid is probably mesoid and that of the high melting racemoid. On mixing the two isomers in about equal quantities, the mixed melting point was 62.5–64°. Owing to shortage in material only a few mixed melting points could be obtained but these suggest an eutectic at about 62° with approximately 40% high melting acid.

Another method of separation has been used by previous authors²⁻⁴, viz. by converting the mixture of diastereomeric α -methyl- α' -ethyl-glutaric acids to the imides which are then separated and hydrolysed. The high melting acid thus prepared was reported² to melt at 107°, the low melting product must, however, still have been a

mixture of the two acids according to the melting points given ³⁻⁴: 63°, 70–71° and 72–73°.

Preliminary experiments indicated that the resolution of the two α -methyl- α' -ethyl-glutaric acids into optical antipodes could be made by means of their strychnine salts.

Experimental. Methyl ethyl-glutaric acid was prepared in two ways:

1. By adding methyl methacrylate to an alcoholic solution of diethyl ethylmalonate in the presence of sodium ethoxide, methyl ethyl 1-ethyl-3-methyl propan-1,1,3-tricarboxylate boiling at 160–162°/7 mm was formed (45 %).

2. By condensing ethyl α -bromoisobutyrate with diethyl ethylmalonate according to Rydon ², when diethyl 1-ethyl-3-methylpropan-1,1,3-tricarboxylate is formed (68 %).

The methyl ethyl glutaric acid was obtained by refluxing these esters with an excess of constant boiling hydrochloric acid for about 25 hours, evaporating to dryness and heating the residue at 170° during three hours. The resulting mixture of isomers melted at 67–74° and was recrystallised from water.

Several experiments indicated, that the best method for separating the two isomers was to dissolve the mixture in five times its own weight of water and at 40–50° add calcium carbonate in an amount corresponding to 75 % of what is required for the acid calcium salt. From the precipitate the high melting acid was obtained after acidification and extraction

with ether and melted, after several recrystallisations from water, at 105.5°. [Found: equiv. wt. (by titration) 87.1. $C_8H_{14}O_4$ requires equiv. wt. 87.1]. The low melting acid was prepared in the same way from the filtrate and gave, after recrystallisations from water, a melting point of 83.5–84.5°. [Found: equiv. wt. (by titration) 87.4. $C_8H_{14}O_4$ requires equiv. wt. 87.1]. 28.7 g mixture gave 11.35 g high melting acid and 15.4 g low melting acid.

Before taking the mixed melting points the acids were dissolved in dry acetone and after evaporation dried in vacuum over P_2O_5 .

% High melting acid	m. p.
27.4	62–68°
52.1	64–73°
76.6	81–91°

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