

LI.—*Synthesis and Preparation of Terebic and Terpenylic Acids.*

By W. TREVOR LAWRENCE.

TEREBIC acid, $C_7H_{10}O_4$, and terpenylic acid, $C_8H_{12}O_4$, are the chief products of the oxidation of oil of turpentine, and their investigation has thrown much light on the difficult question of the constitution of the terpenes. The yield of the first of these acids by this process is unsatisfactory, and the author has succeeded in finding a more convenient method for its preparation; he has also succeeded in preparing terpenylic acid synthetically. A short account of these experiments forms the subject of this paper.

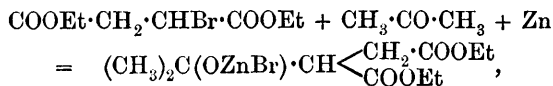
Terebic Acid.

The constitution of terebic acid has been established for some years (Fittig and his pupils, *Annalen*, 1881, 208, 37, 55; 1883, 220, 254; 1884, 226, 363), and is that of the lactone of γ -hydroxyisopropyl

succinic acid, the formula being
$$\begin{array}{c} (CH_3)_2C \text{---} CH \cdot COOH \\ | \qquad \qquad | \\ O \text{---} CO \cdot CH_2 \end{array}$$
 The acid

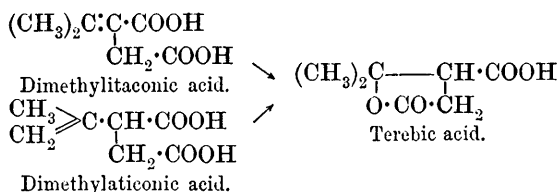
has been prepared synthetically in various ways, of which, however, only two are of practical importance.

Blaise (*Compt. rend.*, 1898, 126, 349) obtained a yield of 10 to 12 per cent. of the theoretical amount of terebic acid by the condensation of ethylic bromosuccinate with acetone in the presence of a zinc copper couple :

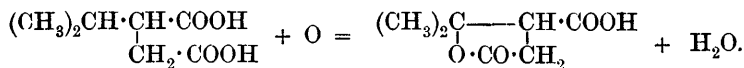


the ethylic salt passing, on hydrolysis, into terebic acid.

Fittig converted dimethylitaconic acid (*Annalen*, 1884, 226, 365) (teraconic acid) and dimethylaticonic acid (*Annalen*, 1899, 304, 220) quantitatively into terebic acid by heating with 50 per cent. sulphuric acid.



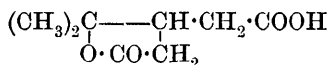
As I required large quantities of terebic acid in order to perform experiments, in conjunction with Dr. A. W. Crossley, on the action of hydrobromic acid on this substance, it was necessary to devise a simpler and more economical method of preparation. Certain considerations, which will be mentioned in discussing terpenylic acid, led me to oxidise isopropylsuccinic acid, in the hope that the reaction would proceed according to the equation :—



Isopropylsuccinic acid can be obtained by various synthetical methods, and forms 20 per cent. of the products of the fusion of camphor or camphoric acid with potash; it is easily oxidised by a mixture of potassium dichromate and sulphuric acid to terebic acid, which crystallises out in a pure condition from the oxidation mixture on cooling. The yield represents 50 to 60 per cent. of that theoretically possible, and a considerable amount of unchanged isopropylsuccinic acid is recovered, so that this method is more economical than any described up to this time.

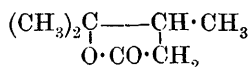
Terpenylic Acid.

The investigations of Fittig (*Annalen*, 1884, 226, 374; 1895, 288, 185), Schryver, and Mahla and Tiemann showed that the constitution of terpenylic acid agrees with the formula suggested by Wallach (*Annalen*, 1890, 259, 321),

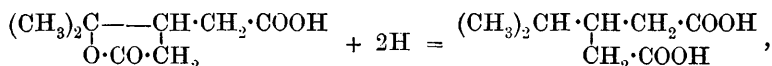


The proof is, briefly, as follows. When terpenylic acid, $\text{C}_8\text{H}_{12}\text{O}_4$, is distilled, teracrylic acid, $\text{C}_7\text{H}_{12}\text{O}_2$, is formed, and this is converted by the action of hydrobromic acid into the isomeric heptolactone.

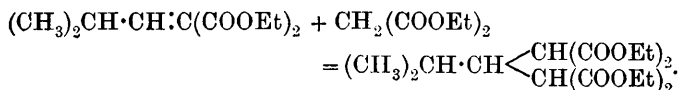
Schryver (*Trans.*, 1893, 63, 1332) synthesised this heptolactone and proved that it had the formula



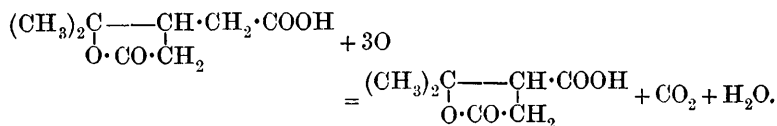
Moreover, the same investigator obtained β -isopropylglutaric acid by reducing terpenylic acid with sodium amalgam :



and prepared this glutaric acid by the condensation of ethylic isobutylene malonate with ethylic malonate :



Finally, Mahla and Tiemann (*Ber.*, 1896, 29, 928), in a paper reviewing the question of the constitution of terpenylic acid, confirmed Wallach's formula by converting this acid into terebic acid by oxidation with potassium permanganate.



The synthesis of this important acid still remained to be effected and is described in the present paper.

The classical researches of R. Meyer (*Annalen*, 1893, 219, 214, 220, &c.), and of Fittig and Bredt (*Annalen*, 208, 1881, 59, &c.), have shown that acids having a tertiary hydrogen atom are capable of direct oxidation to hydroxy-acids by means of potassium permanganate in alkaline solution.

By kind permission of Dr. J. F. Thorpe, I was able to prepare

β -isopropylglutaric acid in considerable quantities (Howles and Thorpe, Proc., 1899, 15, 103), and first attempted its oxidation by the method indicated by R. Meyer, but the acid remained apparently unchanged (compare, however, H. Thron, *Annalen*, 1899, 304, 285), even when dissolved in strong alkali and boiled with excess of 5 per cent. permanganate solution. It was consequently necessary to try other oxidising agents, and it was found that a mixture of potassium dichromate and sulphuric acid oxidised β -isopropylglutaric acid in 24 hours at the temperature of the water-bath, giving a 50 per cent. yield of terpenylic acid, agreeing in every particular with the acid obtained by the oxidation of oil of turpentine.

The synthesis of terpenylic acid has thus been accomplished, and I am at present preparing large quantities of the acid for the purpose of studying, with Professor W. H. Perkin, its behaviour with hydrobromic acid. I also wish to reserve the investigation of the oxidation of α -isopropylglutaric, α -methyl- α -isobutylglutaric and methylisoamylsuccinic acids.

EXPERIMENTAL.

Oxidation of Oil of Turpentine.

The oxidation of oil of turpentine was carried out by Fittig's method, but the products were purified in the following manner. As soon as the oil of turpentine (180 grams) had disappeared from the surface of the chromic acid liquors, these were saturated with ammonium sulphate, extracted several times with ether, and the ether extract distilled with steam to remove acetic and other fatty acids formed; the solution containing the non-volatile acids was then evaporated to a small bulk and left in a vacuum for two days over sulphuric acid. The nearly solid, crystalline mass thus isolated was dried by spreading it on porous plates, and ultimately obtained colourless and dry by transferring it to fresh plates and spreading uniformly by means of a little water.

By extracting these plates, 10 grams of a liquid acid or mixture of acids was obtained, but has not as yet been investigated.

The dry powder consisted of a mixture of terebic and terpenylic acids, and difficulty was anticipated in their separation (compare Mahla and Tiemann, *Ber.*, 1896, 29, 933). It was found, however, that if the finely ground powder was spread on porous plates* and heated in the steam oven at 90°, a complete separation was effected in one operation, the terebic acid remaining as a crystalline powder on the surface of the plate and the terpenylic acid being completely absorbed. The terpenylic acid was recovered with practically no loss

* Extremely absorbent plates were obtained from Messrs. Doulton, of Lambeth.

by extracting the plates with water, and both acids were recrystallised from this solvent. The yield of pure terebic acid represents 5 per cent. and that of terpenylic acid 15 per cent. of the weight of the oil of turpentine oxidised. The terpenylic acid thus obtained melts at 56° to a clear liquid, whereas two specimens of the acid sold as pure contained a considerable amount of terebic acid. My thanks are due to Mr. H. Marsden, a student of the Owens College, for the careful way in which he has conducted this part of the investigation.

Synthesis of Terebic Acid.

A solution of 10 grams of isopropylsuccinic acid (pimelic acid), in 150 c.c. of water, was added to a mixture of 40 grams of potassium dichromate with 55 grams of sulphuric acid, and heated on the water-bath for 56 hours; the mixture, after being left for 2 days, became filled with a white, crystalline substance mixed with crystals of dichromate. The crystals were collected, washed with water, dried on a porous plate, and the finely powdered mixture of terebic acid and potassium dichromate boiled with ether and filtered from the inorganic salt. On evaporating the ether, 5.5 grams of terebic acid were obtained, which, after being purified by recrystallisation from water, melted at 175° , and on analysis gave the following numbers:

0.1241 gave 0.2412 CO_2 and 0.0740 H_2O . $\text{C} = 53.07$; $\text{H} = 6.6$.

$\text{C}_7\text{H}_{10}\text{O}_4$ requires $\text{C} = 53.16$; $\text{H} = 6.33$ per cent.

The identity of the acid was confirmed by mixing some of the synthetical acid with the acid obtained by the oxidation of oil of turpentine; this mixture melted sharply at 174° .

The characteristic barium salt of the hydroxy-acid was also prepared by boiling the solution of terebic acid with excess of baryta, removing the excess of base with carbon dioxide, and precipitating the barium terebinate with alcohol.

0.2113 gave 0.1337 BaSO_4 . $\text{Ba} = 37.2$.

$\text{C}_7\text{H}_{10}\text{O}_5\text{Ba} + 3\text{H}_2\text{O}$ requires $\text{Ba} = 37.53$ per cent.

After the crystals of terebic acid had been filtered off, the chromic acid liquors were saturated with ammonium sulphate, and on extraction with ether, an oil smelling strongly of acetic acid was obtained, which, when left, deposited 2.5 grams of isopropylsuccinic acid.

Synthesis of Terpenylic Acid.

Before the correct oxidising agent was found in chromic acid mixture, an attempt was made to oxidise β -isopropylglutaric acid by means of potassium permanganate and of nitric acid; with fuming

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nitric acid, a liquid acid was obtained, the constitution of which was not determined. A concentrated solution of the acid in strong caustic potash was next treated with excess of a saturated solution of potassium permanganate at the temperature of the water-bath; the acid was, however, recovered unchanged, and no oxidation product could be isolated.

The oxidation of β -isopropylglutaric acid, which led to the formation of terpenylic acid, was carried out as follows: 2.5 grams of pure β -isopropylglutaric acid (m. p. 101°) were dissolved in 15 c.c. of water and added to a mixture of 5 grams of potassium dichromate with 6 grams of sulphuric acid, and heated on the water-bath for 48 hours. At the end of this time, the dark green liquors were saturated with ammonium sulphate and extracted with ether several times; the ethereal solution, on evaporation, yielded a crystalline substance which was recrystallised from water, and gave 1.3 grams of pure terpenylic acid. From the mother liquors, 1 gram of β -isopropylglutaric acid was recovered. The acid was dried over sulphuric acid in a vacuum to remove the water of crystallisation, and on analysis gave the following figures:

0.1603 gave 0.3285 CO_2 and 0.1050 H_2O . $\text{C} = 55.9$; $\text{H} = 7.27$.

0.1144 „ 0.2329 CO_2 „ 0.0742 H_2O . $\text{C} = 55.8$; $\text{H} = 7.2$.

$\text{C}_8\text{H}_{12}\text{O}_4$ requires $\text{C} = 55.8$; $\text{H} = 7.0$ per cent.

Synthetical terpenylic acid agrees in every particular with the oxidation product from oil of turpentine. It crystallises from water with $1\text{H}_2\text{O}$, and melts at 56° ; the water of crystallisation is removed by exposure over sulphuric acid, and the melting point then rises to 89° ; moreover, a mixture of the synthetical acid with the acid obtained by the oxidation of oil of turpentine melts at the same temperature as each of its constituents.

The characteristic silver salt is obtained either by adding excess of silver carbonate to the concentrated solution of the acid and filtering off the excess, or by adding a solution of silver nitrate to the ammonium salt; in both cases, the liquid remains clear for a few minutes, and then becomes filled with the beautiful needles of the silver salt, which is very soluble in hot water.

0.0380 gave 0.0148 Ag. $\text{Ag} = 39.00$.

$\text{C}_8\text{H}_{11}\text{O}_4\text{Ag}$ requires $\text{Ag} = 39.00$ per cent.

To further establish the identity of the synthetical acid, it was oxidised by a 5 per cent. solution of potassium permanganate, according to the method described by Mahla and Tiemann (*loc. cit.*). The mixture of terpenylic and terebic acids extracted from the product of this experiment was recrystallised from water, and the two acids separated by the method indicated earlier in this paper, when it was found

that a considerable proportion of the terpenylic acid had been oxidised to terebic acid melting at 175° .

A proof that the tertiary hydrogen atom in isopropylsuccinic and β -isopropylglutaric acids undergoes oxidation was afforded by attempting to oxidise 5 grams of $\beta\beta$ -dimethylglutaric acid in a similar manner with chromic acid mixture; after 60 hours treatment, the liquors were extracted, and 4.8 grams of unchanged $\beta\beta$ -dimethylglutaric acid, melting at 101° , were obtained. A negative result was also obtained with β -monomethylglutaric acid.

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