XVII.—*The cis- and trans-Modifications of $\alpha\alpha\gamma$ -Trimethylglutaconic Acid.*

By WILLIAM HENRY PERKIN, jun., and ALICE EMILY SMITH, B.Sc.,
1851 Exhibition Scholar of University College, Bangor.

IN a recently published paper (Trans., 1903, , 772), it was shown that when ethyl $\alpha\alpha\gamma$ -trimethylacetonedicarboxylate,

is reduced with sodium amalgam, it is converted into a mixture of the stereoisomeric modifications of β -hydroxy- $\alpha\alpha\gamma$ -trimethylglutaric acid,

Cis, m. p. 115°.

Trans, m. p. 155°.

Both the *cis*- and *trans*-acids, when treated successively with phosphorus pentachloride and diethylaniline, yield *trans*- $\alpha\alpha\gamma$ -trimethylglutaconic acid, which melts at 150°:

The *trans*-hydroxy-acid, when rapidly heated in small quantities, distils without decomposition, whereas the *cis*-hydroxy-acid is readily decomposed on distillation, forming an oily acid (see below) and a neutral crystalline substance, $\text{C}_8\text{H}_{10}\text{O}_3$ (m. p. 88°), and it was suggested

that this latter is probably the anhydride of the *cis*-modification of *αγ*-trimethylglutaconic acid:

We have continued the investigation, and find that this view of the constitution of the substance $\text{C}_8\text{H}_{10}\text{O}_3$ is correct. It is insoluble in aqueous sodium carbonate, but dissolves in warm dilute alkalis, and the solution, on acidifying and extracting with ether, yields *cis-αγ-trimethylglutaconic acid*, $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH} \cdot \text{CO}_2\text{H} \cdot \text{CMe}$, as a colourless, crystalline substance which melts at 125° .

When this acid is treated with bromine, it is readily converted into *cis-βγ-dibromo-αγ-trimethylglutaric acid*,

which melts at 168° and is isomeric with the corresponding *trans*-acid described in the previous paper (*loc. cit.*, p. 779). It was stated above that the *trans*-hydroxy-acid, when heated in small quantities, distils with little decomposition, and we now find that, when considerable quantities of the acid are slowly heated, decomposition sets in, and a semi-solid distillate is obtained which consists of the above-mentioned anhydride of *cis*-trimethylglutaconic acid and an oily acid boiling at about 213° .

The latter is *crotonyldimethylacetic acid*, produced from *αγ*-trimethylglutaconic acid by the elimination of carbon dioxide according to the equation:

Crotonyldimethylacetic acid is also formed in considerable quantities during the preparation of the anhydride of *cis*-trimethylglutaconic acid by the distillation of *cis*-hydroxytrimethylglutaric acid (see above). It is an unsaturated acid which, when digested with dilute sulphuric acid, is converted into the lactone of γ -hydroxy-*αγ*-trimethylbutyric acid,

a substance which has already been described by Anschütz and Gillet (*Annalen*, 1888, 247, 107), who obtained it from *αα*-dimethylævulic acid, $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{COMe}$, by reduction with sodium amalgam and named it *α*-dimethylvalerolactone.

When crotonyldimethylacetic acid is treated with bromine, the colour rapidly disappears, but, even at low temperatures and in the dark, hydrogen bromide is eliminated. The product of this reaction—

TRANS-MODIFICATIONS OF $\alpha\alpha\gamma$ -TRIMETHYLGLUTACONIC ACID. 157

a neutral, crystalline substance melting at 83° —is evidently the *lactone* of β -bromo- γ -hydroxy- $\alpha\alpha\gamma$ -trimethylbutyric acid, produced in the following way :

but the ease with which the dibromo-acid loses hydrogen bromide is very unusual.

cis- $\alpha\alpha\gamma$ -Trimethylglutaconic Acid, $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH} \cdot \text{CMe} \cdot \text{CO}_2\text{H}$.

In preparing this acid, pure *cis*-hydroxytrimethylglutaric acid was rapidly distilled in small quantities and under the ordinary pressure, when carbon dioxide and water vapour were given off and an oily distillate was obtained, which, on cooling, became semi-solid; this mass was cooled in a freezing mixture and collected at the pump on a funnel surrounded with ice and salt, the residue being then left in contact with porous porcelain until the oily impurity had been completely absorbed. By recrystallisation from light petroleum, colourless needles were obtained which melted at 88° .

0.1239 gave 0.2829 CO_2 and 0.0748 H_2O . $\text{C} = 62.7$; $\text{H} = 6.7$.

$\text{C}_8\text{H}_{10}\text{O}_3$ requires $\text{C} = 62.3$; $\text{H} = 6.5$ per cent.

The *anhydride* of *cis*-trimethylglutaconic acid is very readily soluble in chloroform and in ether, less so in cold benzene, and sparingly so in cold light petroleum. The solution in chloroform does not decolorise bromine, and when the benzene solution is mixed with aniline, no crystalline anilic acid separates. The anhydride is almost insoluble in cold water, but it dissolves on warming and is not at once hydrolysed, since, if the solution is rapidly cooled and shaken, a considerable amount of the anhydride crystallises out unchanged. It is insoluble in cold sodium carbonate solution, but dissolves readily in warm dilute aqueous caustic potash, and on acidifying a clear solution is obtained. In order to isolate the very readily soluble *cis*-acid, the liquid was saturated with ammonium sulphate, when the acid separated in needles; the whole was then extracted three times with ether, the ethereal solution dried over calcium chloride and evaporated, and the solid residue purified by recrystallisation from a very small quantity of water.

0.1507 gave 0.3103 CO_2 and 0.0945 H_2O . $\text{C} = 56.2$; $\text{H} = 7.0$.

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

158 MODIFICATIONS OF *ααγ*-TRIMETHYLGLUTACONIC ACID.

cis-ααγ-Trimethylglutaconic acid melts at about 125° with evolution of gas and is readily soluble in water, chloroform, benzene, alcohol, or ether; its solution in aqueous sodium carbonate decolorises permanganate, but not instantaneously. When the acid is exposed to dry bromine vapour for about three hours and the excess of bromine removed over caustic potash in a vacuum desiccator, a solid residue is obtained which crystallises from formic acid (sp. gr. 1·22), in which it is very sparingly soluble, in hard, crystalline crusts. The analysis shows that this acid, which melts at about 168° with decomposition, is *cis-βγ-di-bromo-ααγ-trimethylglutaric acid*, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CHBr}\cdot\text{CMeBr}\cdot\text{CO}_2\text{H}$.

0·1929 gave 0·2180 AgBr. Br = 48·1.

$\text{C}_8\text{H}_{12}\text{O}_4\text{Br}_2$ requires Br = 48·2 per cent.

Crotonyldimethylacetic Acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CHMe}$.

The oily filtrate, which had been separated from the crystals of the anhydride of *cis*-trimethylglutaconic acid, was dissolved in ether and the ethereal solution extracted with sodium carbonate, by which means the crotonyldimethylacetic acid is dissolved, whereas the above anhydride, which is still present in considerable quantities, remains in the ether.

After acidifying and extracting with ether, an oily acid was obtained which distilled at 210—220°, and as this still contained traces of anhydride, the treatment with sodium carbonate was repeated and the acid again distilled, when almost the whole quantity passed over at 213° as a colourless oil having a penetrating and most disagreeable odour.

0·1291 gave 0·3088 CO_2 and 0·1101 H_2O . C = 65·2; H = 9·4.

$\text{C}_7\text{H}_{12}\text{O}_2$ requires C = 65·6; H = 9·4 per cent.

When boiled with 25 per cent. sulphuric acid for a few minutes, crotonyldimethylacetic acid is readily and almost completely converted into the lactone of *γ*-hydroxy-*ααγ*-trimethylbutyric acid,

The product was extracted with ether, the ethereal solution washed with dilute aqueous sodium carbonate, dried over calcium chloride, and evaporated, when a colourless oil remained, which smelt strongly of camphor and crystallised on cooling. The crystals, when left in contact with porous porcelain until quite dry, melted at 48—52°.

0·1760 gave 0·4232 CO_2 and 0·1494 H_2O . C = 65·5; H = 9·4.

$\text{C}_7\text{H}_{12}\text{O}_2$ requires C = 65·5; H = 9·4 per cent.

This lactone has already been prepared by Anschütz and Gillet

(*Annalen*, 1888, 247, 107,) who give 52° as the melting point. Crotonyldimethylacetic acid dissolves in chloroform, and if the solution is treated with bromine at the ordinary temperature the colour disappears, heat is generated, and a considerable quantity of hydrogen bromide is produced. This formation of hydrogen bromide cannot be avoided by keeping the chloroform solution in a blackened test tube at 0° and adding the bromine slowly. On allowing the product of bromination to evaporate spontaneously, a colourless residue is obtained, which crystallises from light petroleum (b. p. $50-60^{\circ}$) in long prisms and melts at $82-83^{\circ}$.

0.3020 gave 0.2748 AgBr. Br = 38.8.

$C_7H_{11}O_2Br$ requires Br = 38.7 per cent.

As stated in the introduction, this substance is evidently the lactone of β -bromo- γ -hydroxy- $\alpha\alpha$ -trimethylbutyric acid.

THE OWENS COLLEGE,
MANCHESTER.