

and satisfactory analysis reported for this *p*-bromoanilide it is quite probable that it was contaminated with some of the ortho isomer, as it was prepared by the bromination of isobutyranilide. *p*-Bromoisovaleranilide does not appear to have been described previously in the literature.

CONTRIBUTION FROM THE  
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## COMMUNICATIONS TO THE EDITOR

### THE $\alpha,\beta,\gamma$ -TRIMETHYLGLUTARIC ACIDS

Sir:

In a recent paper Michael and Ross<sup>1</sup> reported the failure to obtain  $\alpha,\beta,\gamma$ -trimethyl- $\alpha$ -carboxyglutaric acid in a crystalline form. I had obtained this acid<sup>2</sup> and reported it as melting at 144–145°. Michael and Ross note that 145° is also the melting point of  $\alpha,\beta$ -dimethyl- $\gamma$ -carboxyglutaric acid, which suggests that the two are identical. The fact is that I obtained  $\alpha,\beta,\gamma$ -trimethylglutaric acid melting at 134° from the decomposition of my acid, whereas  $\alpha,\beta$ -dimethyl- $\gamma$ -carboxyglutaric acid upon decomposition gives  $\alpha,\beta$ -dimethylglutaric acid melting at 87°.<sup>3</sup>

Michael and Ross obtained  $\alpha,\beta,\gamma$ -trimethyl- $\alpha$ -carboxyglutaric acid as a sirup which on distillation gave an acid melting at 115–125°. In my work on these compounds I found that it was necessary to obtain the tricarboxylic acid in a pure state before decomposing it in order to effect the purification of the  $\alpha,\beta,\gamma$ -trimethylglutaric acid. Even so it required ten recrystallizations to reach the melting point of 134°. The compound which Michael and Ross describe as *cis*- $\alpha,\beta,\gamma$ -trimethylglutaric acid, which according to their statement "softened at 115° and melted at 125°," was probably an impure acid identical with mine, which melted at 134°. The liquid which they call *trans*- $\alpha,\beta,\gamma$ -trimethylglutaric acid was, apparently, the same as the liquid remaining in the mother liquors from the crystallization of the acid melting at 134°. Neither their work nor mine is sufficiently complete to characterize this liquid as a definite chemical individual. Inasmuch as modern theory predicts the occurrence of *three* stereoisomeric forms (one racemic and two meso acids) it would, in my opinion, be unfortunate if it should be so described in handbooks.

Michael and Ross attempted to separate their acids into a "*cis*" and a "*trans*" form by converting the "*cis*" form into the anhydride and the imide. Granting free rotation about a single bond *all three* of the possible

<sup>1</sup> Michael and Ross, *THIS JOURNAL*, **52**, 4607 (1930).

<sup>2</sup> Ray, *ibid.*, **50**, 558 (1928).

<sup>3</sup> Thorpe, *J. Chem. Soc.*, **83**, 358 (1903).

compounds should form anhydrides or imides and no direct separation is possible by this method.<sup>4</sup>

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### THE $\alpha,\beta,\gamma$ -TRIMETHYLGLUTARIC ACIDS

Sir:

In the preceding Communication F. E. Ray expresses the opinion that in our recent paper [THIS JOURNAL, 52, 4598 (1930)] (a) certain compounds described were impure and (b) that the method of separation of the  $\alpha,\beta,\gamma$ -trimethylglutaric acids was not valid.

With respect to his first objection, we would draw attention to the fact that the compounds we described were analytically pure and, in the cases where crystalline, were unchanged in melting points after the third crystallization.

Ray prepared his tiglic ester through methylethylmalonic ester, obtained apparently by methylation and ethylation of sodium enol malonic ester. Besides the methylethylmalonic ester, the reaction product would contain monomethyl or ethyl and dimethyl or diethyl malonic esters, which cannot be completely separated by fractional distillation [Michael, *J. prakt. Chem.*, 72, 537 (1905)]. Ray finally obtained a product which boiled at 100° (30 mm.), which is clearly too high for tiglic ester (b. p. 156° (760 mm.)). The addition compound he prepared from this product through sodium enol cyanacetic ester boiled at 150–170° (30 mm.) and this obviously impure material was methylated. By hydrolysis the product gave a solid acid from which by repeated crystallization, a 145° melting acid was isolated. This was considered to be  $\alpha$ -carboxy  $\alpha,\beta,\gamma$ -trimethylglutaric

<sup>4</sup> Since writing this Note, Michael and Ross in a footnote contained in the following Communication to the Editor, p. 1175, have kindly called my attention to a transposition of an analysis in my paper<sup>5</sup> [THIS JOURNAL, 50, 562 (1928)]. The silver salt of  $\alpha,\beta,\gamma$ -trimethyl- $\alpha$ -carboxyglutaric acid was analyzed and found correct (page 562, line 15). Following this is given the titration of the  $\alpha,\beta,\gamma$ -trimethylglutaric acid, C<sub>8</sub>H<sub>14</sub>O<sub>4</sub>. This should, of course, have followed the paragraph which describes the preparation of this acid from the malonic acid derivative for which the analysis of the silver salt is given.

In the hope of identifying this  $\alpha,\beta,\gamma$ -trimethylglutaric acid (m. p. 134°) as the racemic form I have attempted its resolution by means of the brucine and strychnine salts but without success. It may thus be one of the meso forms. As a check to previous work the silver salt of the acid was prepared and analyzed with the following results:

*Anal.* Subs., 0.0450: Ag, 0.0248. Calcd. for C<sub>8</sub>H<sub>12</sub>O<sub>4</sub>Ag<sub>2</sub>: Ag, 55.6. Found: Ag, 55.1.

This leaves no doubt that the acid melting at 134° is  $\alpha,\beta,\gamma$ -trimethylglutaric acid.