Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. VI. Studies on the Oxidation of Dihydroshonanic Acid with Ozone and Potassium Permanganate.

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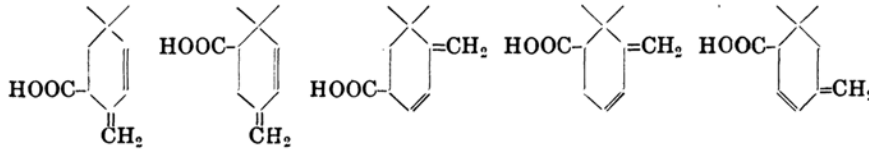
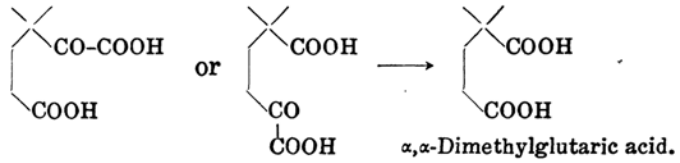
In the previous communication the author has reported that the constitution of shonanic acid should be represented by one of the following formulæ:



I. II. III. IV. V.

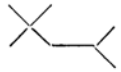
The present communication deals with the studies on the oxidation products of dihydroshonanic acid with ozone and potassium permanganate and as a result of these investigations the author has come to the conclusion that the acid must be represented by the formula III.

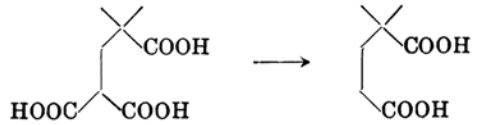
The ozonisation of dihydroshonanic acid and the subsequent decomposition of the ozonide, followed by the treatment with dilute nitric acid, furnished a dibasic ketonic acid of the formula $C_8H_{12}O_5$, which on further oxidation with perhydrol gave α,α-dimethylglutaric acid. These facts show that this dibasic ketonic acid may be represented by either VI or VII.



VI. VII. α,α-Dimethylglutaric acid.

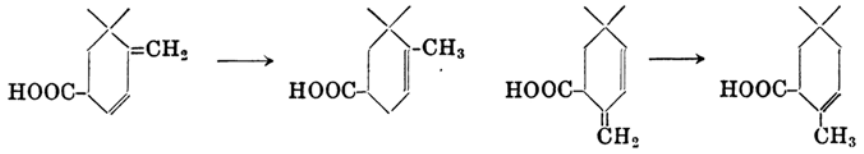
The oxidation of dihydroshonanic acid with potassium permanganate gave a crystalline dihydroxy-dihydroshonanic acid $C_{10}H_{18}O_4$ (m.p. 161–161.5°) together with a liquid dibasic ketonic acid with the formula $C_{10}H_{16}O_5$. On examination, the latter proved to be a chain compound and its optical activity revealed the presence of at least one asymmetric

carbon atom. It could be prepared from the former by oxidizing it with lead tetracetate as described by R. Criegee, L. Kraft and B. Rank[1] and subjecting the resulting aldehydic acid to the action of alkaline perhydrol. The ketonic acid was evidently a methyl ketonic acid as it could be converted into tribasic acid $C_9H_{14}O_6$ by digestion with sodium hypochlorite. This tribasic acid, on oxidation with dilute nitric acid, gave α,α-dimethylglutaric acid and another tribasic acid of the formula $C_8H_{12}O_6$, which was easily transformed into α,α-dimethylglutaric acid on treatment with hot concentrated hydrochloric acid. It naturally follows that the tribasic acid $C_8H_{12}O_6$ should be represented by VIII and as consequence an arrangement  in the molecule of dihydroshonanic acid is to be expected.



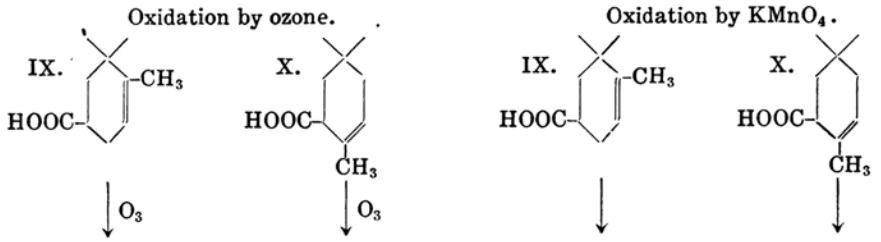
VIII. α,α-Dimethylglutaric acid.

There are two possible constitutional formulæ for dihydroshonanic acid which are capable of explaining the facts mentioned above, the one is IX which should be derived from III while the other is X transformed from I.

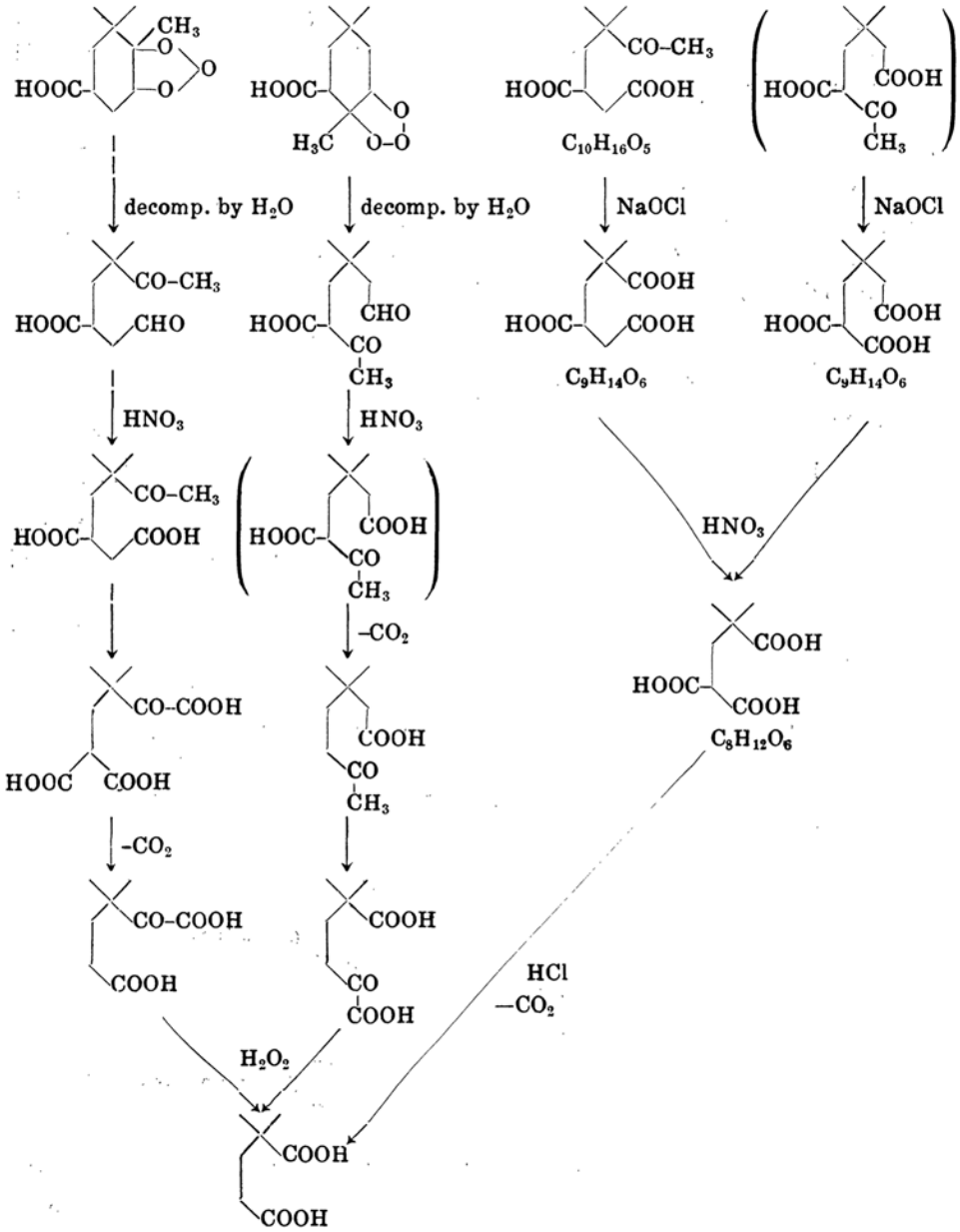


III. IX. I. X.

Oxidation by ozone. Oxidation by $KMnO_4$.



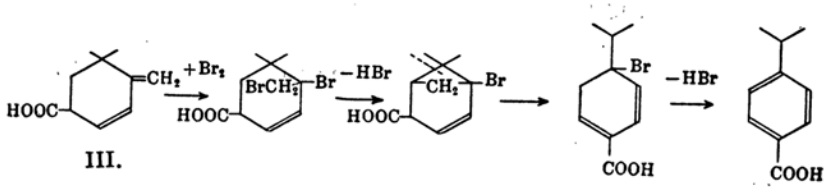
(1) *Ann.*, **507** (1933), 159.



The compound put in parentheses may not exist as free acid as it is a β-ketonic acid and consequently may transform into monoketo-monocarboxylic acid of the formula $C_9H_{16}O_3$ with liberation of carbon dioxide. For this reason the formula X seems not suitable for the constitution

of dihydroshonanic acid, whilst the constitution IX fulfils all the requirements of this compound. Now, the author will choose the formula III for shonanic acid by the two following reasons.

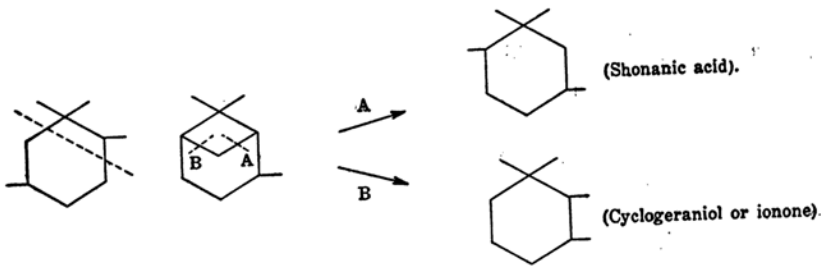
(1) The fact that by distillation under reduced pressure shonanic acid dibromide gives rise to *p*-cuminic acid, can very easily be explained by assuming the formula III as shown by the following scheme (as for the mode of addition of bromine see the second paper[2]), while the formula I necessitates to assume an extravagant migration of the carboxyl group in order to explain this conversion.



III. *p*-Cuminic acid

(2) The fact that shonanic acid can be esterified with fairly good yield (from 10 g. of the acid 9.3 g. of the ester), indicates that in shonanic acid the carbon atom in the ortho-position to its carboxyl group is unsubstituted.

The skeleton of III may be regarded as consisting of two isoprene nuclei as shown below whilst this structure may be considered as derived from pinane by cleavage of four-membered ring system at A. It is noteworthy that if the splitting of the four-membered ring occurs at B, the resulting skeleton represents that of cyclogeraniol or ionone.



Attention must also be drawn to the interesting fact that an acid of the structure closely related to pinene, the most widely distributed constituent of various essential oils, especially in those of coniferous trees, was found as the prevailing constituent of the conifer *"Libocedrus formosana,* Florin" or "Shônan-Boku".

(2) This Bulletin, **12** (1937), 233.

Experimental.

I. Separation of dihydroshonanic acid. Dihydroshonanic acid was separated by fractionation of the acidic portion obtained as by-product during the preparation of dihydroshonanyl alcohol by the reduction of ethyl shonanate with sodium and ethyl alcohol (see the fourth paper[3]).

140 g. of the material was subjected to fractional distillation under reduced pressure using Widmer's fractionating column. After three successive rectifications, the following fractions were obtained.

Fr. No.	B.p./6 mm.	d_4^{20}	n_D^{30}	α_D^{20}	Wt.(g.)	Wt.(%)
1	-137°	—	1.4796	—	3	2.17
2	137-138°	1.007	1.4798	−5.28°	43	31.16
3	138-139°	1.012	1.4800	−5.20°	32	23.19
4	139-140°	1.012	1.4810	−5.20°	18	13.04
5	140-141°	1.015	1.4824	−4.68°	7	5.07
6	141-144°	1.017	1.4834	−3.68°	4	2.90
7	144-147°	Crystallized	—	—	12	8.69
8	147-150°	,,	—	—	14	10.14
9	Residue				5	3.64

The main fractions 2 and 3 mainly consisted of dihydroshonanic acid. Further rectifications gave a distillate with the following properties: b.p. 138.7°/6 mm.; d_4^{30} 1.009; n_D^{30} 1.4795; α_D^{24} −5.26°; M.R. obs. 47.26, calculated for $C_{10}H_{16}O_2$ 47.30; Acid value 333.97, calculated for $C_{10}H_{16}O_2$ 333.3. (Found: C, 71.60; H, 9.49. Calculated for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52%. Analysis of the silver salt: Ag, 39.32. Calculated for $C_{10}H_{15}O_2Ag$: Ag, 39.27%.)

Amide. The amide was prepared in white leaflets by the interaction of the acid chloride and aqueous ammonia. It was recrystallized once from 60% ethyl alcohol when it melted at 130°.

II. Oxidation of dihydroshonanic acid with potassium permanganate. 20 g. of the acid was dissolved in 600 c.c. of 1% caustic soda solution and 800 c.c. of 1.5% potassium permanganate solution was added drop by drop with vigorous stirring. After all the permanganate solution had been added, the reaction mixture was saturated in cold with carbon dioxide and then warmed on the water-bath for an hour until the permanganate has been completely consumed. The precipitate of manganese dioxide was filtered off and the filtrate was evaporated to a smaller bulk on the water-bath in an atmosphere of carbon dioxide. The solution was then slightly acidified with 5N hydrochloric acid, and the soft crystalline mass appeared was filtered and dried on a porous plate. Yield 8 g.

The crystalline substance thus separated represented dihydroxy-dihydroshonanic acid (A). A liquid acidic substance made appearance on further addition of 5N

(3) This Bulletin, **12** (1937), 253.

hydrochloric acid to the filtrate which was extracted with ether, and the ethereal solution was precipitated by the addition of light petroleum ether. The portion precipitated was separated and left to cool in an ice-box. A little dihydroxy-dihydroshonanic acid crystallized out, which was filtered off, washed with petroleum ether and dried. The viscous liquid acid obtained after the separation of the crystalline acid and evaporation of the solvent was found to consist mainly of ketonic acid of the formula $C_{10}H_{16}O_5$ (B).

Dihydroxy-dihydroshonanic acid. The crystalline acid (A) was insoluble in petroleum ether, ether and chloroform, difficultly soluble in water, but soluble in hot alcohol. The purified acid (recrystallized from hot water or alcohol) melted at 161–161.5°. The silver salt was found to dissolve readily in water. Acid value 276.22, calculated for $C_{10}H_{18}O_4$ 277.23. (Found: C, 59.09; H, 8.95. Calculated for $C_{10}H_{18}O_4$: C, 59.41; H, 8.91%.)

The liquid acid ($C_{10}H_{16}O_5$). The yield of the liquid acid (B) amounted to about 10 g. Its reactions were decidedly aldehydic. Thus it was dissolved in an excess of caustic soda solution, 5 c.c. of 30% perhydrol was added and left over night at ordinary temperature. The acid recovered from this alkaline solution was a viscous fluid with a faint reddish brown colour, which was then esterified by warming it with 30 c.c. of alcohol containing 4% hydrochloric acid.

The ethereal solution of the ester was washed with water then with 5% sodium carbonate solution successively, dried over anhydrous sodium sulphate and the ether was distilled off. The residual ester was fractionated twice under reduced pressure.

Fr. No.	B.p.	d_4^{30}	n_D^{30}	α_D^{28}	Vol. (c.c.)
1	113–116°/13 mm.	0.9738	1.4497	−6.3°	2.0
2	116–118°/13 mm.	0.9844	1.4499	−5.8°	1.0
3	118°/13 mm.— 130°/3 mm.	—	—	—	1.1
4	130–140°/3 mm.	1.057	1.4583	−1.18°	3.5
5	140–150°/3 mm.	1.060	1.4563	−1.03°	2.0
6	over 150°/3 mm.	—	—	—	0.3

Judging from its physical properties as well as from its odour, fraction 1 appeared to be the ethyl ester of the unchanged dihydroshonanic acid, while the main fractions 4 and 5 were once more rectified under reduced pressure and a fraction with the following properties was obtained: b.p. 276°/758 mm.; d_4^{30} 1.059; n_D^{30} 1.4584; α_D^{28} −1.08°; M.R. obs. 70.14, calculated for $C_{14}H_{24}O_5$ 70.08; saponification value 429.3, calculated for $C_{14}H_{24}O_5$ (diethyl ester) 411.8. (Found: C, 61.85; H, 8.88. Calculated for $C_{14}H_{24}O_5$: C, 61.7; H, 8.8%.)

Application of Criegee's method on dihydroxy-dihydroshonanic acid. 10 g. of the acid was dissolved in warm benzene and 22 g. of lead tetracetate was added in small portions with vigorous stirring, filtered while hot from the precipitate and the precipitate was washed several times with ether. Then the benzene-ethereal solution was shaken with water in order to remove acetic acid liberated from lead tetracetate,

and evaporated. The viscous acid thus obtained was readily soluble in ether and alcohol but sparingly in petroleum ether. As the substance showed reactions of aldehyde its alkaline solution was treated with 5 c.c. of 30% perhydrol at 40–50°, when the reddish brown colour of the solution turned into yellow. The acid recovered as usual from this alkaline solution showed no tendency of solidification so that it was esterified by warming with 30 c.c. of alcohol containing 4% hydrochloric acid and the ester thus prepared showed the following properties: b.p. 274°/757 mm., 132–134°/2 mm.; d_4^{30} 1.054; n_D^{30} 1.4579; α_D^{30} −1.34°; saponification value 431.3, calculated for $C_{14}H_{24}O_5$ (diethyl ester) 411.8. (Found: C, 62.42; H, 8.98. Calculated for $C_{14}H_{24}O_5$: C, 61.7; H, 8.8%.)

The physical properties of the ethyl ester of the acid agreed well with those of the ester of the liquid acid $C_{10}H_{16}O_5$ (B) obtained by the oxidation of dihydroshonanic acid and was proved to be the same ketonic dicarboxylic acid by its behaviours toward oxidizing agents.

Oxidation of liquid acid $C_{10}H_{16}O_5$. The acid resulting from the saponification of the ethyl ester mentioned above was a viscous sticky substance but showed no tendency to crystallize. In order to ascertain whether the ketonic group in the molecule of the acid is an acetyl group or not, the substance was next subjected to oxidation with sodium hypochlorite, when a tricarboxylic acid should be obtained if the substance under investigation be a compound containing acetyl group.

To a solution of 4 g. of the substance dissolved in 20 c.c. of 10% sodium hydroxide solution, 8 c.c. of sodium hypochlorite solution (ca. 5.6%) was added in small portions with stirring. The reaction proceeded with evolution of heat and the smell of chloroform was perceived during the course of the reaction. After all the hypochlorite solution had been consumed the reaction mixture was refluxed for about half an hour on the water-bath, then it was evaporated to a smaller bulk and the acidic substance was recovered as usual. The ethereal solution (100 c.c.) of the acid was then stirred with 50 c.c. of water under reflux condenser at 40–50° for half an hour and the water layer separated. On evaporating the aqueous solution on the water-bath, a syrupy acid was obtained (yield 2.6 g.) which remained fluid even when kept cool for a week. The purification of the crude substance thus obtained could not be accomplished further by distillation but from the result of analysis of the silver salt and from its acid value, the substance seemed likely to represent a tribasic acid of the formula $C_9H_{14}O_6$. Acid value 744.8, calculated for $C_9H_{14}O_6$ 770.6. Analysis of the silver salt: Ag, 59.43. Calculated for $C_9H_{11}O_6Ag_3$: Ag, 60.11%. The difference between the theoretical and the experimental values may be attributed to the presence of a little unchanged acid.

Oxidation of the tricarboxylic acid $C_9H_{14}O_6$. With a view to obtain a C_8-acid, the tribasic acid obtained above was oxidized with dilute nitric acid. A mixture of 4 g. of the substance and 40 c.c. of nitric acid (d = 1.12) was warmed under reflux for 2 hours and then evaporated on the water-bath to a smaller bulk. On cooling, it deposited a little crystalline acid, which was filtered, dried on a porous plate and was purified by reprecipitation from benzene solution by the addition of light petroleum ether. Yield 0.4 g. It melted at 83° and was found to be identical with α,α-dimethylglutaric acid by melting in admixture with authentic specimen. The liquid acidic portion after removal of α,α-dimethylglutaric acid was esterified with 20 c.c. of 7% alcoholic hydrochloric acid and the ester formed was fractionally distilled under reduced pressure.

Fr. No.	B.p./5mm.	d_4^{30}	n_D^{30}	Vol. (c.c.)
1	95–103°	—	1.4228	0.2
2	103–107°	0.9946	1.4286	0.6
3	107–135°	—	—	0.3
4	135–149°	1.043	1.4328	1.3

Fraction 2 was saponified as usual and after evaporating the alkaline solution on the water-bath nearly to dryness it was acidified with 2N hydrochloric acid, and the organic acid set free was extracted with ether. After removal of ether remained syrupy mass, which, on boiling with conc. hydrochloric acid for a while in a test tube and subsequent cooling, turned into a crystalline mass. The crude crystals, dried on a porous plate, melted at 74–78°, and after recrystallization from benzene melted at 82.5° and was confirmed to be identical with α,α-dimethylglutaric acid by examining the mixed melting point.

Fraction 4 was analysed without further rectification owing to the scarcity of the material. Saponification value 567.0, calculated for $C_{14}H_{24}O_6$ (triethyl ester) 583.3. (Found: C, 58.77; H, 8.49. Calculated for $C_{14}H_{24}O_6$: C, 58.33; H, 8.33%.)

The analytical data showed that the fraction consisted mainly of the triethyl ester of a tricarboxylic acid $C_8H_{12}O_6$. The free acid was regenerated from the neutral solution resulting from the determination of the saponification value. The solution was evaporated nearly to dryness on the water-bath and was acidified with hydrochloric acid and the free organic acid liberated was extracted with chloroform, dried over anhydrous sodium sulphate, and evaporated. The residue showed no tendency to crystallize even when kept ice-cold for several days. Then it was gently heated with conc. hydrochloric acid for about half an hour under reflux as in the previous case. On cooling, a minute quantity of crystals made appearance, so that the heating was continued for further 3 hours and kept cool over night in an ice-box. The crystalline acid thus deposited was filtered, and dried on a porous plate. It melted at 87° when purified by reprecipitation from chloroform solution by the addition of light petroleum ether and proved to be identical with α,α-dimethylglutaric acid. Thus it should be concluded that the free tricarboxylic acid has transformed into α,α-dimethylglutaric acid by elimination of one mol of carbon dioxide therefrom.[4]

III. Ozonolysis of dihydroshonanic acid. A well-cooled solution of 10 g. of the acid in 100 c.c. of carbon tetrachloride was treated with ozonized oxygen (containing ca. 5% ozone) at a rate of 20–25 l. per hour. The ozonide formed was crystalline and remained suspended in the solution. It was filtered, washed with carbon tetrachloride, heated to gentle boiling with 100 c.c. of 3.5% solution of sodium carbonate, and then a calculated quantity of 3% perhydrol was added drop by drop with constant stirring in order to oxidize the aldehyde group into the carboxyl, meanwhile sodium carbonate solution being added little by little to maintain the reaction mixture

(4) Analogous with the case of preparation of α,α-dimethylsuccinic acid [Leukart, *Ber.*, **18** (1885), 2550] or α,α-dimethyladipic acid [Blanc, *Bull. soc. chim.*, [4], **3** (1890), 288] from isobutane-α,α,β-tricarboxylic acid or α,α-dimethyl-α′-carboxy-adipic acid respectively.

slightly alkaline. The acidic substance recovered (amounted to ca. 9 g.) from the reaction mixture was a viscous substance with a light reddish brown colour and showed positive reaction toward Schiff's reagent and Tollens' solution. As the substance remained liquid even when kept cold for several days, it was directly oxidized by heating it with dilute nitric acid (d = 1.12) on the water-bath for 2 hours, evaporated, and esterified by warming with 50 c.c. of ethyl alcohol containing 4% hydrochloric acid. The ester formed was fractionally distilled under reduced pressure.

Fr. No.	B.p./2mm.	d_4^{21}	n_D^{21}	α_D^{21}	Wt.(g.)
1	78–135°	0.9722	1.4614	−0.8°	1.8
2	135–140°	1.082	1.4570	−0.3°	5.2

Fraction 2 was once more rectified and the portion 138–140°/6 mm. was collected, which showed the following properties: d_4^{29} 1.083; n_D^{29} 1.4535; α_D nil; M.R. obs. 60.96, calculated for $C_{12}H_{20}O_5$ 60.88; saponification value 474.5, calculated for $C_{12}H_{20}O_5$ (diethyl ester) 459.0. (Found: C, 59.13; H, 8.41. Calculated for $C_{12}H_{20}O_5$: C, 59.0; H, 8.2%.)

Preparation of the semicarbazone. The ester gave a crystalline semicarbazone melting at ca. 149° without any purification, which when purified by one recrystallization from 60% alcohol melted at 154–156°. The further purification from the same solvent was impossible. (Found: N, 14.26. Calculated for $C_{13}H_{23}O_5N_3$: N, 13.95%.)

Preparation of α,α-dimethylglutaric acid from ketonic diethyl ester $C_{12}H_{20}O_5$. 3 g. of the viscous liquid acid obtained by saponification of the diethyl ester mentioned above was dissolved in 60 c.c. of caustic soda solution, to which 40 c.c. of 30% perhydrol was added with constant stirring at 40–50°. When the peculiar reddish brown colour of the solution disappeared, the reaction mixture was evaporated on the water-bath, acidified with dilute hydrochloric acid and organic acid set free was extracted with chloroform. On removal of chloroform there remained a yellowish sticky substance, which turned into a crystalline mass on warming with conc. hydrochloric acid as in the previous cases. The crystalline acid was also identical with α,α-dimethylglutarc acid.

In conclusion, the author wishes to thank Prof. Kinzô Kafuku for his kind advices and suggestions rendered during the course of this work.

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