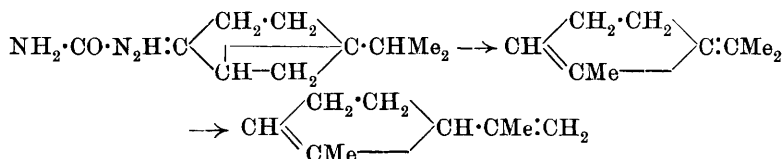


LIII.—*Experiments on the Synthesis of the Terpenes.*
Part XII. Synthesis of Terpins, Terpeneols, and
Terpenes derived from Methylisopropylcyclopentanes,
 $\text{Me} \cdot \text{C}_5\text{H}_8 \cdot \text{CHMe}_2$.

By WALTER NORMAN HAWORTH and WILLIAM HENRY PERKIN, jun.

THE investigation of the naturally occurring members of the camphor and terpene series has shown that almost the whole of these substances are derived, either directly or indirectly, from one of the modifications of methylisopropylcyclohexane, $\text{Me} \cdot \text{C}_6\text{H}_{10} \cdot \text{CHMe}_2$.

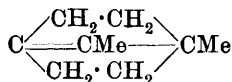
The terpenes derived from natural sources have the composition $\text{C}_{10}\text{H}_{16}$, and a search for lower terpenes of the composition C_9H_{14} , which might possibly be derivatives of methylisopropylcyclopentane, $\text{Me} \cdot \text{C}_5\text{H}_8 \cdot \text{CHMe}_2$, has disclosed only two such substances, and these are of doubtful constitution. Semmler (*Ber.*, 1902, **35**, 2047) found that sabinene ketone, when converted into the semicarbazone and then digested with 25 per cent. sulphuric acid, yields a hydrocarbon, C_9H_{14} (b. p. 165—166°). Since the molecular refraction shows that this hydrocarbon is doubly unsaturated, Semmler suggests that its formation may be assumed to take place in accordance with the scheme :



1-Methyl-2-isopropenyl- Δ^3 -cyclopentene.

Subsequently Semmler (*Ber.*, 1904, **37**, 237) described a hydrocarbon, C_9H_{14} , of boiling point 144—146°, which he obtained from dihydrocamphoryl alcohol, $\text{C}_9\text{H}_{18}\text{O}$, by heating with anhydrous oxalic

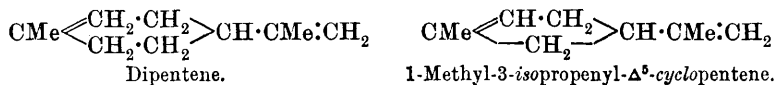
acid, but this substance evidently has the formula C_9H_{16} . The only other terpene from natural sources* which has the composition C_9H_{14} , which we have been able to find, is santene, an optically inactive hydrocarbon which was discovered by F. Müller (*Arch. Pharm.*, 1900, **238**, 366) in the low boiling fractions of sandal wood oil. This hydrocarbon distils at 139–140°, yields a blue nitroso-chloride (m. p. 108°), and a crystalline hydrochloride, $C_9H_{14} \cdot HCl$ (m. p. 80°). Semmler (*Ber.*, 1907, **40**, 4595) subsequently showed that the molecular refraction proves that this substance contains only one double linking, and that it must, therefore, be bicyclic, and this led him to suggest the formula



as probably representing the formula of santene.

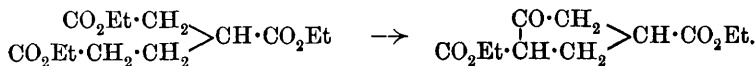
Aschan (*Ber.*, 1907, **40**, 4918) has also recently carefully investigated santene, and confirmed the composition, C_9H_{14} , the boiling point, 140°, the molecular refraction, and has also described other interesting properties of the hydrocarbon.

The consideration of these and of other facts connected with the chemistry of the terpenes led us to think that it would be interesting to attempt the synthesis of terpenes, analogously constituted to dipentene, but containing a closed ring of five-carbon atoms in the place of the six-carbon ring of that hydrocarbon,



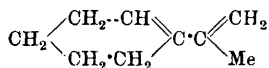
and the present paper contains an account of the experiments which we have made in this direction.

A short time ago (*Trans.*, 1906, **89**, 1641), Kay and Perkin showed that ethyl butane- $\alpha\beta\delta$ -tricarboxylate reacts with sodium with the formation of ethyl cyclopentanone-2:4-dicarboxylate, a decomposition which they formulated thus:

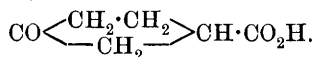


The ester so produced is decomposed by boiling with dilute sulphuric

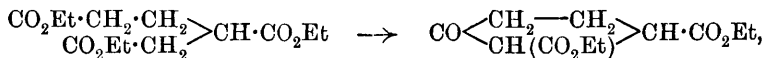
* A terpene, C_9H_{14} , obtained synthetically by Matsubara and Perkin (*Trans.*, 1905, **87**, 637), is $\Delta^3:8(9)$ -normenthadiene (b. p. 161°), and is known to contain a closed chain of six-carbon atoms and to have the constitution:



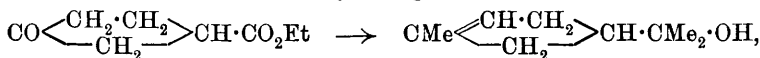
acid, with elimination of carbon dioxide and alcohol, and formation of *cyclopentanone-3-carboxylic acid*,



In continuing these experiments, we have been able to prove (p. 576) that the condensation by means of sodium takes place in a different direction from that represented above, and that the product is in reality *ethyl cyclopentanone-2 : 3-dicarboxylate*,

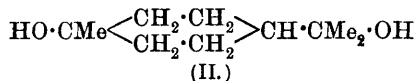
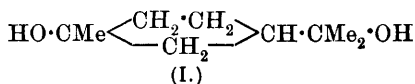


so that this view of this condensation is to be substituted for that given in the earlier paper. This change does not make any difference in regard to the constitution of the keto-acid, since the 2 : 3- and 2 : 4-dicarboxylic esters will both yield the same keto-acid on hydrolysis. We next investigated the action of magnesium methyl iodide on ethyl *cyclopentanone-3-carboxylate*, and obtained a small quantity of 1-*methyl-3-isopropenolcyclopentene*, which distils at 100—105° (30 mm.) and the formation of which may be represented thus :



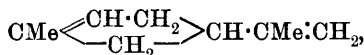
although the double linking (Δ^5) may be in the position Δ^1 .

This carbinol is the terpeneol of the five-carbon series, and, when shaken with dilute sulphuric acid, it is converted into the corresponding terpin, 1-*hydroxy-1-methyl-3-isopropenolcyclopentane* (I),



a crystalline substance which melts at 75°, and is especially interesting on account of its relationship to ordinary terpin (II).

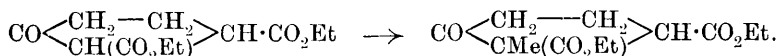
Lastly, a small quantity of a hydrocarbon, 1-*methyl-3-isopropenylcyclopentene*, is produced during the action of magnesium methyl iodide on ethyl *cyclopentanone-3-carboxylate*, which distils at about 150°, and is the representative of dipentene in the pentane series. It is probable that its constitution is represented by the formula



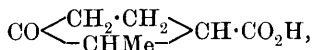
but the position of the double linking in the ring is doubtful.

A second series of experiments, designed with the object of synthesising other terpins, terpeneols, and terpenes of the pentane series, was carried out in the following manner.

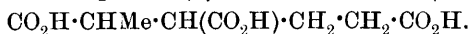
The sodium derivative of ethyl *cyclopentanone-2:3*-dicarboxylate was digested with methyl iodide, and thus converted into *ethyl-2-methylcyclopentanone-2:3*-dicarboxylate,



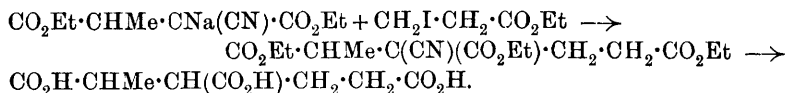
When this ester is hydrolysed by dilute hydrochloric acid, it yields a small quantity of *2-methylcyclopentanone-3-carboxylic acid* (m. p. 95°),



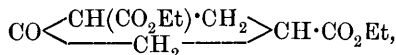
but by far the larger proportion of the ester is further hydrolysed with the formation of *pentane-βγε-tricarboxylic acid* (m. p. 177°),



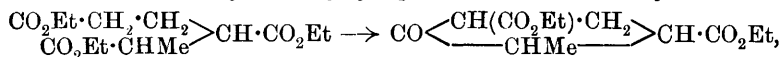
In order to prove the constitution of the latter acid, it was prepared synthetically by digesting the sodium derivative of ethyl cyano-β-methylsuccinate with ethyl β-iodopropionate and subsequently hydrolysing the resulting *ethyl γ-cyanopentane-βγε-tricarboxylate* with concentrated hydrochloric acid:



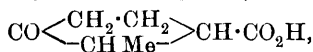
The acid thus synthesised melted at 177°, and was identical with that obtained by the hydrolysis of ethyl *2-methylcyclopentanone-2:3*-dicarboxylate, and this fact clearly proves that the product of the action of sodium on ethyl butane-αβδ-tricarboxylate (Kay and Perkin, *loc. cit.*) must be ethyl *cyclopentanone-2:3*-dicarboxylate, and cannot be ethyl *cyclopentanone-2:4*-dicarboxylate,



as was first thought to be the case, since the latter ester, after methylation, could not yield pentane-βγε-tricarboxylic acid as the product of hydrolysis. When ethyl pentane-βγε-tricarboxylate is treated with sodium, it readily undergoes internal condensation with the formation of *ethyl 2-methylcyclopentanone-3:5*-dicarboxylate,

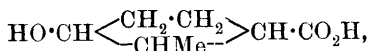


and this ester, on hydrolysis with hydrochloric acid, yields *2-methylcyclopentanone-3-carboxylic acid* (m. p. 95°),

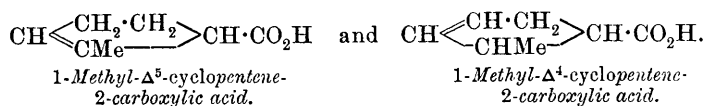


of which mention has already been made, and, indeed, nearly all of this keto-acid which we required in such large quantities for this research was made in this way. When the keto-acid is reduced with

sodium amalgam, it is converted into 2-methylcyclopentanol-3-carboxylic acid,



which, although it is a γ -hydroxy-acid, distils at 182—185° (20 mm.) without conversion into the lactone, a fact which is possibly due to the acid, so obtained, being the *trans*-modification. It reacts readily with hydrobromic acid, and is converted into 5-bromo-1-methylcyclopentane-2-carboxylic acid, $\text{CHBr}\left\langle\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{CHMe} \end{array}\right\rangle\text{CH}\cdot\text{CO}_2\text{H}$, and the ethyl ester of this acid is decomposed by boiling diethylaniline with formation of an oil which was ultimately shown to be a mixture of the esters of the two possible unsaturated acids,

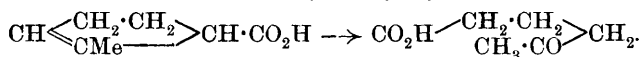


The oily mixture of acids obtained when the ester is hydrolysed could not be separated into the constituents by the fractional crystallisation of such salts as we prepared, and for a long time there seemed to be little prospect of effecting the separation.

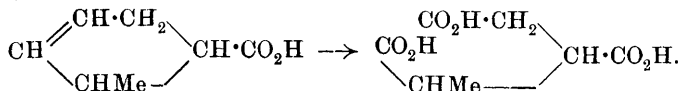
Subsequently, the remarkable fact was discovered that the difference in the rate of esterification of the two isomerides and also in the rate of hydrolysis of the esters is so great that a complete separation can be based on this behaviour.

The Δ^4 -acid esterifies in contact with alcohol and sulphuric acid at the ordinary temperature in a few hours, whereas the esterification of the Δ^5 -acid is not complete after four days, and again the ester of the Δ^4 -acid is hydrolysed by methyl-alcoholic potash in the cold in a few hours, whereas, under the same conditions, hydrolysis of the ester of the Δ^5 -acid is not complete in five days. This difference in behaviour made it possible to work out a complete separation of the two acids, and the details of the method are explained on p. 585. The two acids are strikingly different in their physical properties. One of them is a solid, melts at 131°, and possesses a quite unusual facility in crystallising from solvents; the other is a liquid, distils at 165° (100 mm.), and shows no sign of crystallising when it is cooled in a freezing mixture.

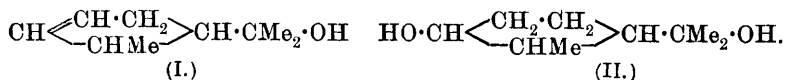
The next step was to determine the constitutions of these acids, and this was done in each case by oxidising with ozone in alkaline solution. In these circumstances, the acid melting at 131° yielded γ -acetobutyric acid; it must therefore be 1-methyl- Δ^5 -cyclopentene-2-carboxylic acid,



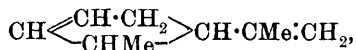
The liquid acid is converted by oxidation, first with ozone and then with chromic acid, into *α*-methyltricarballic acid, a behaviour which clearly proves that it is 1-methyl- Δ^4 cyclopentene-2-carboxylic acid,



The next step was the investigation of the action of magnesium methyl iodide on the ester of the Δ^4 -acid, a process which resulted in the formation of an almost quantitative yield of 1-methyl-2-isopropenol- Δ^4 -cyclopentene (I):



This interesting substance distils at 95° (30 mm.), and resembles terpineol in odour and in the fact that, when shaken with dilute sulphuric acid, it yields the corresponding terpin, namely, 5-hydroxy-1-methyl-2-isopropenolcyclopentane, which crystallises well, melts at 72° , and probably has the constitution (II), but the hydroxyl group in the ring may obviously be situated in the position 4. In one respect in particular, the carbinol differs in a striking way from terpineol. It is well known that terpineol is readily and almost quantitatively converted into dipentene when it is heated with dehydrating agents, but the most unexpected difficulties were encountered in attempting the analogous elimination of water from the carbinol. Ultimately we were able, by employing succinic anhydride as the dehydrating agent, to obtain a small quantity of 1-methyl-2-isopropenyl- Δ^4 -cyclopentene,

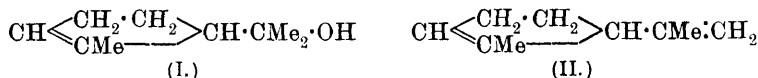


and this interesting hydrocarbon was found to distil at 143 – 145° (770 mm.), and to have an odour closely resembling that of dipentene.

When other dehydrating agents were employed, the product consisted almost entirely of polymerised hydrocarbons, one of which distilled at 170 – 175° (20 mm.), and evidently had the constitution $(\text{C}_9\text{H}_{14})_2$.

The first example of this kind of polymerisation was met with during the investigation of the action of potassium hydrogen sulphate on Δ^3 -normenthenol(8) (Matsubara and Perkin, *Trans.*, 1905, 87, 668), when only a small quantity of $\Delta^{3:8(9)}$ -normenthadiene, C_9H_{14} , was formed, and the product consisted principally of dinormenthadiene, $(\text{C}_9\text{H}_{14})_2$, which distilled at 170 – 172° (16 mm.), or at practically the same temperature as the polymeride mentioned above. Still greater

difficulties were met with in investigating the action of magnesium methyl iodide on the ester of 1-methyl- Δ^5 -cyclopentene-2-carboxylic acid, as in this case only a very small quantity of 1-methyl-2-isopropenol- Δ^5 -cyclopentene (I) is formed, and the product consists

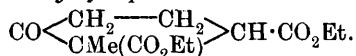


almost entirely of a polymerised terpene, $(\text{C}_9\text{H}_{14})_2$, and of other higher condensation products.

It is unfortunate that it was not found possible to obtain 1-methyl-2-isopropenyl- Δ^5 -cyclopentene (II) in sufficient quantity for characterisation, since this terpene has the constitution which Semmler (*loc. cit.*) suggested for the hydrocarbon which he obtained from sabinene ketone (p. 573).

EXPERIMENTAL.

Ethyl 2-Methylcyclopentanone-2 : 3-dicarboxylate,



In order to prepare this ester, sodium (23 grams) was dissolved in ethyl alcohol (300 c.c.) and, after cooling, 228 grams of ethyl cyclopentanone-2 : 3-dicarboxylate (Kay and Perkin, *Trans.*, 1906, **89**, 1640) were carefully added, the flask being cooled during the addition.

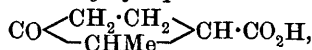
The deep yellow solution was mixed with methyl iodide (150 grams), when little evolution of heat occurred at first, but, on standing, the mixture soon became warm, and gradually the temperature rose to the boiling point. After remaining for two hours, the reaction was completed by heating on the water-bath for an hour, water was then added, and the oily ester extracted with ether. The ethereal solution was well washed, dried over calcium chloride, and evaporated, when a small quantity of the oil was distilled and found to boil at about 170° (18 mm.) :

0.1802 gave 0.3915 CO_2 and 0.1232 H_2O . C = 59.2 ; H = 7.6.

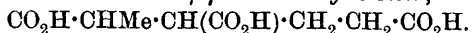
$\text{C}_{12}\text{H}_{18}\text{O}_5$ requires C = 59.5 ; H = 7.4 per cent.

Hydrolysis of Ethyl 2-Methylcyclopentanone-2 : 3-dicarboxylate.

Formation of 2-Methylcyclopentanone-3-carboxylic Acid,



and Pentane- $\beta\gamma\epsilon$ -tricarboxylic Acid,



The curious behaviour of ethyl 2-methylcyclopentanone-2 : 3-dicarboxylate, on hydrolysis with hydrochloric acid, has been discussed

in the introduction (p. 576), and the following experiment has often been repeated and always with the same results. The ester was mixed with three times its volume of dilute hydrochloric acid (1 vol. conc. HCl and 9 vols. of water), and digested in a reflux apparatus for eight hours. When the oil had completely dissolved, the air condenser was removed, from time to time, in order to allow the alcohol to escape; the solution was saturated with ammonium sulphate, and extracted with pure ether, five times by hand and ten times on the shaking machine.* The ethereal extract was dried over calcium chloride and evaporated, and the residual viscid oil, which consisted of a mixture of methylcyclopentanonecarboxylic acid and pentane- $\beta\gamma\epsilon$ -tricarboxylic acid, was esterified by digesting with a 10 per cent. solution of sulphuric acid in alcohol for fifteen hours. The product was mixed with much ether, water was added, and the ethereal layer, after washing with water and dilute sodium carbonate and drying over calcium chloride, was evaporated, and the residual oil fractionated under 20 mm. pressure, when it was somewhat readily separated into two portions distilling at 130—135° and 180—185° respectively.

The lower fraction consists of *ethyl 2-methylcyclopentanone-3-carboxylate* :

0·1310 gave 0·3010 CO₂ and 0·0988 H₂O. C = 62·7 ; H = 8·4.

C₉H₁₄O₃ requires C = 63·5 ; H = 8·2 per cent.

This ester, when hydrolysed with dilute hydrochloric acid, yields *2-methylcyclopentanone-3-carboxylic acid*, which melts at 95°, and the preparation and properties of which are described on p. 582.

The higher fraction is *ethyl pentane- $\beta\gamma\epsilon$ -tricarboxylate* :

0·1279 gave 0·2748 CO₂ and 0·0967 H₂O. C = 58·6 ; H = 8·4.

C₁₄H₂₄O₆ requires C = 58·3 ; H = 8·3 per cent.

A small quantity of this ester was digested with hydrochloric acid for six hours and evaporated to dryness, when a syrup remained which gradually crystallised. The mass was well stirred with a little concentrated hydrochloric acid, transferred to porous porcelain, and the almost colourless residue crystallised from hydrochloric acid, from which the new acid separated as a colourless, sandy powder and melted at 177° :

0·1294 gave 0·2224 CO₂ and 0·0710 H₂O. C = 46·9 ; H = 6·1.

C₈H₁₂O₆ requires C = 47·1 ; H = 5·9 per cent.

That this acid is tribasic was shown by titration with decinormal sodium hydroxide, when 0·1220 required 0·0713 NaOH for neutralisation, whereas this amount of a tribasic acid, C₈H₁₂O₆, should neutralise 0·0719 NaOH.

* The last three extractions yielded a syrupy acid, which crystallised on standing and proved to be almost pure pentane- $\beta\gamma\epsilon$ -tricarboxylic acid.

Synthesis of Pentane- $\beta\gamma\epsilon$ -tricarboxylic Acid,
 $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H},$
from Ethyl Cyano- β -methylsuccinate.

This synthesis was carried out in order to prove that the acid of melting point 177° , obtained as explained in the previous section, is pentane- $\beta\gamma\epsilon$ -tricarboxylic acid, and also because it was found to be the best method for the preparation of the large quantities of this acid required for this research.

Ethyl cyano- β -methylsuccinate, $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ (35.5 grams), prepared from the sodium derivative of ethyl cyanoacetate and ethyl α -bromopropionate by the method recommended by Bone and Sprankling (Trans., 1899, **75**, 853), was converted into the sodium derivative by the addition of sodium (3.9 grams) dissolved in alcohol (60 c.c.) and mixed with ethyl β -iodopropionate (38 grams), the whole being kept as cold as possible during the addition. After remaining overnight, the product was heated on the water-bath for half an hour, mixed with water, extracted with ether, and, after washing with water and drying over calcium chloride, the ether was evaporated and the residual oil fractionated under reduced pressure, when an almost quantitative yield of *ethyl γ -cyanopentane- $\beta\gamma\epsilon$ -tricarboxylate* was obtained as a colourless oil distilling at 212° (25 mm.):

0.2060 gave 8.4 c.c. nitrogen at 14° and 752 mm. $\text{N} = 4.7$.

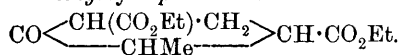
$\text{C}_{15}\text{H}_{23}\text{O}_6\text{N}$ requires $\text{N} = 4.5$ per cent.

The cyano-ester was hydrolysed by digesting in a reflux apparatus with three times its volume of concentrated hydrochloric acid for twenty hours, the condenser being removed every couple of hours for a few minutes in order to allow the alcohol to escape. The clear solution was evaporated to dryness, and the solid residue of acid and ammonium chloride crystallised several times from concentrated hydrochloric acid, from which the *pentane- $\beta\gamma\epsilon$ -tricarboxylic acid* separates as a colourless, sandy powder melting at 177° :

0.1247 gave 0.2137 CO_2 and 0.0685 H_2O . $\text{C} = 46.8$; $\text{H} = 6.1$.

$\text{C}_8\text{H}_{12}\text{O}_6$ requires $\text{C} = 47.1$; $\text{H} = 5.9$ per cent.

That this acid was identical with the tribasic acid, $\text{C}_8\text{H}_{12}\text{O}_6$, obtained as described on page 580, was proved by the fact that a mixture of the two specimens melted at 176 — 177° .

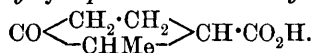
Ethyl 2-Methylcyclopentanone-3 : 5-dicarboxylate,

The sodium derivative of this ketonic ester is readily formed when sodium reacts with ethyl pentane- $\beta\gamma\epsilon$ -tricarboxylate under the following conditions. Sodium (23 grams) is melted under boiling toluene, and vigorously shaken in order to bring it into as fine a state of division as possible, the toluene is poured off, the sodium powder washed with benzene by decantation, and then mixed with ethyl pentanetri-carboxylate (144 grams) dissolved in about 150 grams of pure dry benzene. A long air condenser is attached to the flask, and the mixture gently warmed on the water-bath until a brisk reaction sets in, the flask is then removed from the water-bath, and the reaction allowed to proceed without further external heating, and, indeed, it is sometimes necessary to cool the flask. After about half an hour, the product is heated on the water-bath until the sodium has completely disappeared, an operation which requires usually two and a-half hours. The brown mass is mixed with ether, the sodium derivative decomposed by ice and dilute hydrochloric acid, and the ethereal solution separated. The aqueous solution is twice extracted with ether, the combined ethereal extracts are then well washed with dilute sodium carbonate, which removes much colouring matter,* and dried over calcium chloride. After distilling off the ether and fractionating under reduced pressure, almost the whole quantity passes over at about 180° (25 mm.), and consists of pure *ethyl 2-methylcyclopentanone-3 : 5-dicarboxylate*, the yield being about 70 per cent. of that theoretically possible :

0.2000 gave 0.4346 CO_2 and 0.1368 H_2O . C = 59.3 ; H = 7.6.

$\text{C}_{12}\text{H}_{18}\text{O}_5$ requires C = 59.5 ; H = 7.4 per cent.

This ester is a colourless oil, the alcoholic solution of which gives a violet coloration on the addition of ferric chloride.

2-Methylcyclopentanone-3-carboxylic Acid,

The considerable quantities of this keto-acid which were required for this research were prepared either by the hydrolysis of ethyl

* If the dark-coloured extract is acidified with dilute hydrochloric acid and boiled for 5 hours, a considerable quantity of crude 2-methylcyclopentanone-3-carboxylic acid may be obtained by extraction with ether. It is best purified by conversion into its ester, and, after fractionating this, hydrolysing with dilute hydrochloric acid.

2-methylcyclopentanone-2:3-dicarboxylate (p. 579) or of ethyl 2-methylcyclopentanone-3:5-dicarboxylate (see previous section).

In either case, the ester was digested in a reflux apparatus with four times its volume of 10 per cent. hydrochloric acid until solution was complete, the condenser being removed from time to time in order to allow the alcohol produced to escape. The clear solution was saturated with ammonium sulphate and extracted several times with pure ether, the ethereal solution was dried over calcium chloride, evaporated, and the residue fractionated under reduced pressure, when almost the whole quantity distilled at 190—193° (20 mm.) and crystallised on cooling. The crystalline mass was left in contact with porous porcelain until quite free from oil and then crystallised from ether, in which it is readily soluble, but from the concentrated solution in which it separates in hard, nodular masses :

0·1296 gave 0·2826 CO₂ and 0·0850 H₂O. C = 59·4 ; H = 7·2.

0·1431 „ 0·3091 CO₂ „ 0·0935 H₂O. C = 58·9 ; H = 7·2.

C₇H₁₀O₃ requires C = 59·1 ; H = 7·1 per cent.

2-Methylcyclopentanone-3-carboxylic acid melts at 95°, and is very readily soluble in water and most organic solvents ; it is very sparingly soluble in cold light petroleum, but dissolves readily on warming and separates, when the solution is allowed to cool slowly, as a glistening, satiny mass.

The *semicarbazone* was prepared by adding semicarbazide hydrochloride and sodium acetate to a hot moderately dilute solution of the acid in water. On standing, the clear liquid gradually deposited a mass of crystals, which were collected and crystallised from water, when the semicarbazone was obtained as a sandy powder which decomposes at about 200—202° :

0·1010 gave 17·6 c.c. nitrogen at 14° and 766 mm. N = 20·6.

C₈H₁₃O₃N₃ requires N = 21·2 per cent.

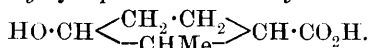
The *Oxime*.—In order to prepare this derivative, the pure acid (2 grams) was dissolved in water, mixed with hydroxylamine hydrochloride (2 grams) and potassium hydroxide (4 grams), and allowed to stand for twelve hours. The solution was acidified, extracted with much ether, the ethereal solution dried over calcium chloride, and evaporated, when a syrup was obtained which soon crystallised. The product was drained on porous porcelain and crystallised from ether, from which the oxime separates in crusts, which soften at 140° and melt at about 155° with gradual decomposition ; at 160°, the substance very rapidly becomes dark brown :

0·1963 gave 15·6 c.c. nitrogen at 18° and 762 mm. N = 9·1.

C₇H₁₁O₃N requires N = 8·9 per cent.

This oxime is readily soluble in water or alcohol, but sparingly so in dry ether, chloroform, or benzene.

2-Methylcyclopentanol-3-carboxylic Acid,



The reduction of 2-methylcyclopentanone-3-carboxylic acid was carried out by treating the solution of the acid (30 grams) in sodium carbonate with 1.5 kilos. of freshly-prepared* sodium amalgam in a bottle fitted with a mechanical stirrer, hydrochloric acid being added from time to time in such a way that the liquid remained always slightly alkaline. The product was acidified with hydrochloric acid, saturated with ammonium sulphate, and extracted at least twelve times with ether on the machine. The first three extractions contained always a small quantity of unchanged keto-acid, and this portion was submitted to further reduction; the other extracts were dried over calcium chloride, evaporated, and the viscid syrup distilled under reduced pressure, when the pure hydroxy-acid passed over at 182—185° (20 mm.):

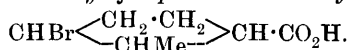
0.1800 gave 0.3874 CO₂ and 0.1316 H₂O. C = 58.7; H = 8.1.

C₇H₁₂O₃ requires C = 58.3; H = 8.3 per cent.

This analysis shows conclusively that, although the substance is a γ -hydroxy-acid, no lactone formation had taken place during distillation; it is therefore probable that the acid prepared by the method described above is the *trans*-modification.

2-Methylcyclopentanol-3-carboxylic acid is a very viscid syrup, which, directly after distillation, sometimes had a pale chartreuse-green colour; it is readily soluble in water.

5-Bromo-1-methylcyclopentane-2-carboxylic Acid,



In order to prepare this acid, 2-methylcyclopentanol-3-carboxylic acid is mixed in a flask with three times its volume of aqueous hydrobromic acid (saturated at 0°), and heated on the water-bath for half an hour. The product will have separated into two layers, the upper one, consisting of the bromo-acid, is often dark brown while hot, and becomes dark blue on cooling. After adding water, the heavy oil is extracted with ether, the ethereal solution well washed with

* The sodium amalgam used in these experiments was always prepared from freshly distilled mercury and carefully cleaned sodium because, if this precaution is not observed, the reduction of the keto-acid is always very slow and incomplete.

water, dried over calcium chloride, and evaporated, when an oil remains which always contains some unsaturated acid produced by elimination of hydrogen bromide. A specimen which had remained for some hours in an evacuated desiccator over sulphuric acid gave the following results on analysis :

0.4131 gave 0.3195 AgBr. Br = 33.0.

$C_7H_{11}O_2Br$ requires Br = 38.6 per cent.

It sometimes happens during the preparation of the bromo-acid that a quantity of crystals separate when the product of the reaction is allowed to remain overnight. These were collected and recrystallised from formic acid, when beautiful, feathery crystals were obtained, which melted at $130-131^\circ$, and were found to consist of pure 1-methyl- Δ^5 -cyclopentene-2-carboxylic acid (see p. 586).

Ethyl Bromomethylcyclopentanecarboxylate.—This ester was prepared by digesting the crude bromo-acid with alcohol containing 10 per cent. of sulphuric acid for six hours on the water-bath. Water was then added, the oily ester extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried over calcium chloride, evaporated, and the ester fractionated under reduced pressure, when it distilled at $160-165^\circ$ (100 mm.) and at about 145° (50 mm.).

Owing to the presence of unsaturated esters (see next section), analysis always gave a percentage of bromine considerably lower than that theoretically required.

Formation and Separation of 1-Methyl- Δ^4 -cyclopentene-2-carboxylic Acid and 1-Methyl- Δ^5 -cyclopentene-2-carboxylic Acid.

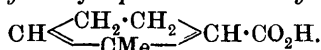
The esters of these unsaturated acids are produced when ethyl 5-bromo-1-methylcyclopentane-2-carboxylate (see the last section) is digested with diethylaniline. The fraction of the crude bromo-ester distilling at $160-170^\circ$ (100 mm.) was gently boiled with three times its volume of pure diethylaniline for two hours, when the elimination of hydrogen bromide proceeded smoothly and with very little darkening. The product was mixed with much ether, the ethereal solution repeatedly extracted with dilute hydrochloric acid, dried over calcium chloride and evaporated, and the residual oil fractionated under reduced pressure, when almost the whole quantity passed over at $120-130^\circ$ (100 mm.). This pungent and very unpleasant smelling oil is a mixture of the esters of the two acids mentioned at the head of this section, and the separation of these acids was accomplished (as explained in the introduction) by taking advantage of the fact that the ester of 1-methyl- Δ^4 -cyclopentenecarboxylic acid is much more readily formed and hydrolysed than that of the 1-methyl- Δ^5 -cyclo-

pentenecarboxylic acid. The separation was readily carried out under the following conditions.

The esters (52 grams) were mixed with a cold solution of potassium hydroxide (30 grams) in methyl alcohol, when it was noticed that the temperature rose slightly, but care was taken that it did not rise at any time above 20°. After remaining overnight, the product was diluted with water, the unchanged ester of the Δ^5 -acid extracted with ether, and the aqueous solution acidified, when an oily acid separated which was extracted with ether. After drying over calcium chloride and evaporating, the oily acid was dissolved in methyl alcohol (200 c.c.) and sulphuric acid (10 c.c.) in the cold, and allowed to remain for twelve hours. Water was then added, the oily ester extracted with ether, and the ethereal extract well agitated with dilute sodium carbonate, when, on acidifying the aqueous extract, about 4 grams of the Δ^5 -acid separated at once in a crystalline and almost pure condition. This process of esterification and hydrolysis was repeated five times, and after the third time it was observed that the acid esterified readily and completely, and that the sodium carbonate extract did not yield any solid acid on acidification.

The oil from the fifth esterification distils constantly at 120—122° (100 mm.), and is pure *ethyl 1-methyl- Δ^4 -cyclopentene-2-carboxylate* (p. 589).

1-Methyl- Δ^5 -cyclopentene-2-carboxylic Acid,



During the process of separation from the Δ^4 -acid by esterification (see the previous section), this acid was obtained partly as the free acid and partly in the form of its ester. The ester was left in contact with a large excess of methyl-alcoholic potash for several days and until hydrolysis was complete, diluted with water, saturated with carbon dioxide, and evaporated until free from alcohol.

When the cold product was acidified with hydrochloric acid, the Δ^5 -acid separated at once in a crystalline condition. In order to purify the crude acid, it is dissolved in sodium carbonate, digested with animal charcoal, and, after filtering and acidifying, the colourless precipitate is collected and crystallised either from ether or light petroleum :

0.1196 gave 0.2932 CO_2 and 0.0870 H_2O . C = 66.8 ; H = 8.1.

$\text{C}_7\text{H}_{10}\text{O}_2$ requires C = 66.7 ; H = 7.9 per cent.

1-Methyl- Δ^5 -cyclopentene-2-carboxylic acid melts at 130—131°, and is readily soluble in ether, alcohol, or hot light petroleum, but sparingly so in water or formic acid in the cold. When its ethereal solution is allowed to evaporate very slowly, it separates in large, striated, four-

sided plates or prisms with bevelled edges, twin crystals being frequent. It is readily soluble in warm formic acid (D 1.20), and crystallises well from this solvent in long, striated plates. The most convenient solvent for recrystallisation is, however, light petroleum (b. p. 100—110°), from which it separates in needles radiating from a point. The solution of the acid in dilute sodium carbonate rapidly decolorises permanganate, and the chloroform solution readily decolorises bromine (see below). It dissolves in concentrated sulphuric acid to a colourless solution, but, when warmed, this rapidly becomes dark reddish-brown, and sulphur dioxide is produced in quantity. The finely-powdered acid dissolves in much hydrobromic acid (saturated at 0°), but without the formation of an additive product, since the solution, especially when exposed to air, deposits crystals of the unchanged acid. This behaviour is unusual, because acids of this kind usually combine with great readiness with hydrobromic acid. The double linking in this methylcyclopentenecarboxylic acid is in the 1:5-position, and it was thought possible that intramolecular change to the 1:2-position might take place on boiling with alkalis, but this does not appear to be the case, since, after digesting with potash, of density 1.3, for ten minutes, the acid was recovered unchanged on the addition of hydrochloric acid.

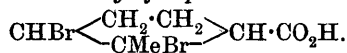
Ethyl Methyl- Δ^5 -cyclopentenecarboxylate.—This ester was prepared by digesting the pure acid (12 grams) with alcohol (100 c.c.) and sulphuric acid (3 c.c.) for three hours, and, after remaining overnight, the product was dissolved in ether, mixed with water, the ethereal solution thoroughly washed with water and dilute sodium carbonate, dried over calcium chloride, evaporated, and the residual oil fractionated under reduced pressure:

0.1378 gave 0.3530 CO_2 and 0.1164 H_2O . C = 69.9; H = 9.1.

$\text{C}_9\text{H}_{14}\text{O}_2$ requires C = 70.1; H = 9.1 per cent.

The ester distils constantly at 133° (100 mm.), and has a penetrating, unpleasant, and very persistent odour, which closely resembles, but is perhaps not quite so pungent as, that of the ester of the Δ^4 -acid (p. 589).

1:5-Dibromo-1-methylcyclopentane-2-carboxylic Acid,



In order to prepare this dibromo-acid, methyl- Δ^5 -cyclopentenecarboxylic acid (0.5 gram) was dissolved in chloroform (10 c.c.), cooled in ice, and bromine added drop by drop, when the colour disappeared rapidly at first, but remained when 0.63 gram had been added.

The end point was, however, not very sharp, and a trace of hydrogen bromide was formed. The amount of acid taken requires 0.64 gram of bromine to form the dibromo-additive product. The solution was poured on a clock glass and left exposed to air until the chloroform had evaporated; the solid residue was then recrystallised from light petroleum (b. p. 70—80°):

0.221 gave 0.2922 AgBr. Br = 56.2.

$C_7H_{10}O_2Br_2$ requires Br = 55.9 per cent.

1:5-Dibromo-1-methylcyclopentane-2-carboxylic acid darkens at about 150°, and decomposes vigorously and becomes black at about 164°.

It is readily soluble in ether, chloroform, or benzene, but sparingly so in light petroleum or formic acid in the cold. When boiled with formic acid, it decomposes vigorously, and the solution becomes violet-black and deposits black flocks on the addition of water.

The dibromo-acid is readily decomposed by boiling with methyl-alcoholic potash, and the solution has an odour of bromoform; it is also decomposed by silver nitrate and nitric acid in the cold with abundant separation of silver bromide.

*Oxidation of 1-Methyl- Δ^5 -cyclopentene-2-carboxylic Acid to γ -Acetobutyric Acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$.**

In this experiment, the pure acid (2 grams) was dissolved in a slight excess of dilute sodium carbonate in a test tube, and ozone led through

* In order to become acquainted with the mechanism of the oxidation of closed chain unsaturated acids by ozone, we experimented, in the first instance, with *iso*-lauronic acid.

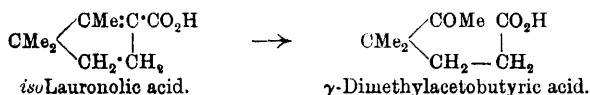
This acid (2 grams) was dissolved in dilute sodium carbonate, and ozone passed for about three hours and until it was no longer absorbed. When the clear solution was acidified, saturated with ammonium sulphate, and extracted with ether in the usual manner, it yielded a syrup which, after remaining in an evacuated desiccator over sulphuric acid for a short time, solidified. After rapidly washing on porous porcelain with light petroleum (b. p. 30—40°), the substance melted at about 47° and proved to be γ -dimethylacetobutyric acid:

0.1297 gave 0.2880 CO_2 and 0.1050 H_2O . C = 60.6; H = 9.0.

$C_8H_{14}O_3$ requires C = 60.8; H = 8.8 per cent.

The acid was dissolved in water, mixed with semicarbazide hydrochloride and sodium acetate, and warmed on the water-bath, when the semicarbazone separated in glistening plates. It crystallised from water as a felted mass of needles, and decomposed vigorously at about 187°. A direct comparison showed that this semicarbazone was identical with that obtained from a specimen of γ -dimethylacetobutyric acid which had been prepared on a previous occasion (Trans., 1898, 73, 844).

The almost quantitative formation of this keto-acid by the oxidation with ozone is probably the most conclusive evidence of the constitution of *isolauronic acid*:



the solution. When the ozone was no longer absorbed and passed freely, the product was acidified, saturated with ammonium sulphate, and extracted five times with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a syrup which yielded bromoform on treatment with bromine and potassium hydroxide, and gave an immediate precipitate with semicarbazide hydrochloride and sodium acetate. The *semicarbazone* was collected and crystallised from water, from which it separated in needles, which softened at 170° and melted at 174—176°. It was found to contain water of crystallisation :*

0·1336 gave 0·2010 CO₂ and 0·0900 H₂O. C = 40·7 ; H = 7·4.

0·1153 ,, 21·2 c.c. nitrogen at 19·5° and 749 mm. N = 20·7.

C₇H₁₃O₃N₃·H₂O requires C = 41·0 ; H = 7·3 ; N = 20·5 per cent.

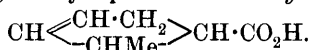
These results seemed to point to a ketonic acid, C₆H₁₀O₃, probably γ -acetobutyric acid, CH₃·CO·[CH₂]₃·CO₂H, and to confirm this the semicarbazone of this acid was prepared from the specimen originally obtained by Bentley and Perkin (Trans., 1896, 69, 1513). It melted at 176°, and, when mixed with the specimen described above, no alteration in the melting point could be detected. The semicarbazone of the acid from the ozone oxidation was decomposed by warming with dilute hydrochloric acid, the acid extracted with ether, and the ethereal solution evaporated, when a syrup was obtained which, on standing in the air, soon crystallised. The crystals were drained on porous porcelain and analysed with the following result :

0·1247 gave 0·2256 CO₂ and 0·0922 H₂O. C = 49·3 ; H = 8·2.

C₆H₁₀O₃·H₂O requires C = 48·7 ; H = 8·1 per cent.

This substance melts at 36° and was proved, by direct comparison, to be the characteristic *hydrate* of γ -acetobutyric acid.

1-Methyl- Δ^4 -cyclopentene-2-carboxylic Acid,



It is explained on p. 585 that this acid esterifies very readily, a property which renders its separation from the Δ^5 -acid a comparatively easy matter. The ester obtained as the result of the fifth fractional esterification distilled constantly at 120—122° (100 mm.), and was pure *ethyl 1-methyl- Δ^4 -cyclopentene-2-carboxylate* :

0·1324 gave 0·3220 CO₂ and 0·0958 H₂O. C = 66·4 ; H = 8·0.

C₇H₁₀O₂ requires C = 66·7 ; H = 7·9 per cent.

* This semicarbazone had been prepared by Bentley and Perkin and dried at 100°, when the specimen gave numbers agreeing with the formula C₇H₁₃O₃N₃.

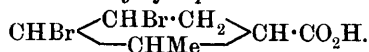
This ester possesses in a marked degree the pungent and most unpleasant odour characteristic of so many of the esters of cyclic unsaturated acids. The pure ester (20 grams) was now mixed with 100 c.c. of 10 per cent. methyl-alcoholic potash, and allowed to remain overnight. Water was then added, the clear solution saturated with carbon dioxide, evaporated until free from alcohol, acidified, the oily acid extracted with ether, and the ethereal solution carefully dried over calcium chloride. The ether was then evaporated, and the acid distilled under reduced pressure, when the whole quantity passed over at 164—165° (100 mm.):

0.1032 gave 0.2634 CO₂ and 0.0870 H₂O. C = 69.7; H = 9.3.

C₉H₁₄O₂ requires C = 70.1; H = 9.1 per cent.

1-Methyl-Δ⁴-cyclopentene-2-carboxylic acid is a viscid oil, and possesses a pungent odour similar to that of the higher fatty acids. It behaves as an unsaturated acid, since its solution in chloroform rapidly decolorises bromine, and the sodium salt instantly decolorises permanganate. When it was boiled with concentrated aqueous potassium hydroxide for five minutes, it became dark brown, and, on acidifying, yielded a liquid acid, so that conversion into the Δ⁵-acid does not appear to take place under these conditions.

4:5-Dibromo-1-methylcyclopentane-2-carboxylic Acid,



In preparing this acid, pure 1-methyl-Δ⁴-cyclopentene-2-carboxylic acid (1.35 grams) was dissolved in three volumes of chloroform, cooled to -10°, and then titrated with a solution of bromine in chloroform. The colour disappeared instantly at first and rather slowly at the close of the reaction, and remained when 1.65 grams had been added, the end point being fairly sharp. Theoretically, 1.7 grams of bromine should be absorbed by 1.35 grams of the unsaturated acid. The product was allowed to evaporate on a clock glass, when a syrup remained which gradually crystallised and became semi-solid. In contact with porous porcelain, the oil was slowly absorbed, and the colourless residue separated from light petroleum (b. p. 50—60°) in crusts which melted, not very sharply, at 106—108°:

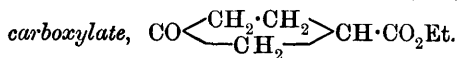
0.2850 gave 0.3740 AgBr. Br = 55.8.

C₇H₁₀O₂Br₂ requires Br = 55.9 per cent.

Oxidation of 1-Methyl- Δ^4 -cyclopentene-2-carboxylic Acid to α -Methyltricarballic Acid, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

This oxidation was carried out by passing ozone into the solution of the sodium salt of the acid, the conditions of experiment being the same as those already described in the case of the Δ^5 -acid. The product was warmed on the water-bath to decompose any unchanged ozonide, acidified, saturated with ammonium sulphate, and repeatedly extracted with ether. When the ether was removed by evaporation, a dark brown oil was obtained, which showed no signs of crystallisation after remaining for several days over sulphuric acid in an evacuated desiccator. It was dissolved in hot water, the solution filtered, and heated on the water-bath with an excess of potassium dichromate and sulphuric acid. After saturating with ammonium sulphate, the green solution was extracted several times with ether on the machine, and the ethereal solution evaporated, when a nearly colourless syrup was obtained which soon became semi-solid. In contact with a little concentrated hydrochloric acid, the oily impurity was soon dissolved, leaving a colourless, crystalline acid, which was drained on porous porcelain and twice recrystallised from hydrochloric acid, from which it separated in small, glistening prisms melting at 177° . That this acid was α -methyltricarballic acid (m. p. 180°) was proved by mixing it with a specimen which had been prepared from the sodium derivative of methylmalonic ester by condensation with fumaric ester (Auwers, Köbner, and Meyenburg, *Ber.*, 1891, **24**, 2891), when the mixture melted at 178 — 180° .

The Action of Magnesium Methyl Iodide on Ethyl cyclopentanone-3-



The *ethyl cyclopentanonecarboxylate* required for these experiments was prepared by digesting the free acid (Kay and Perkin, *Trans.*, 1906, **89**, 1646), in quantities of 50 grams, with a 3 per cent. solution of hydrogen chloride in alcohol (180 grams) for six hours on the water-bath. The product was mixed with three volumes of ether, the ethereal solution repeatedly washed with dilute sodium carbonate, dried over calcium chloride, and evaporated. On fractionation under reduced pressure, the ester distilled constantly at 142 — 143° (40 mm.) as a colourless oil possessing an odour somewhat resembling that of apples :

0.1873 gave 0.4186 CO_2 and 0.1337 H_2O . C = 61.0 ; H = 7.9.

$\text{C}_8\text{H}_{12}\text{O}_3$ requires C = 61.5 ; H = 7.7 per cent.

This ester, in quantities of 30 grams, was slowly added from a dropping funnel to an ethereal solution of magnesium methyl iodide (containing 20 grams of magnesium), the contents of the containing vessel being rapidly stirred by a turbine and the whole carefully cooled with ice and salt. After remaining for four days, the product was cautiously decomposed by ice and very dilute hydrochloric acid, the ethereal layer separated, and the aqueous solution repeatedly extracted with ether. The combined ethereal extracts were dried over calcium chloride and, in order to avoid loss of any volatile hydrocarbon, the ether was slowly distilled off with the aid of a column. The residue was distilled in steam and the distillate,* which contained a considerable quantity of an oil with an odour of peppermint, was extracted with ether, the ethereal solution dried and evaporated as before, and the oil fractionated under reduced pressure.

A good deal of oil passed over below 100° (200 mm.), and there was a large fraction at 100—125° (50 mm.) and a further considerable fraction at 115—125° (15 mm.). After repeated distillation, these fractions yielded a mobile oil, boiling at 150—155° under the ordinary pressure, and a more viscid oil, distilling at 100—105° (30 mm.).

The oil distilling at 150—155° was twice distilled over sodium, when almost the whole quantity passed over at about 150°:

0·1836 gave 0·5990 CO₂ and 0·1955 H₂O. C = 88·9; H = 11·8.

C₉H₁₄ requires C = 88·5; H = 11·5 per cent.

1-*Methyl-3-isopropenylcyclopentene* (compare p. 575) is a colourless oil with a pronounced odour of lemons and peppermint.

It combines with hydrogen bromide and with bromine, but the amount of material available was too small to allow of these additive products being investigated.

The fraction boiling at 100—105° (30 mm.) gave the following results on analysis:

0·1912 gave 0·5374 CO₂ and 0·1930 H₂O. C = 76·7; H = 11·2.

C₉H₁₆O requires C = 77·1; H = 11·3 per cent.

1-*Methyl-3-isopropenylcyclopentene* (compare p. 575) is a rather viscid oil with a strong odour of terpineol and peppermint, it is sparingly soluble in water, and its solution in acetic anhydride gives a deep crimson, nearly as intense as solution of permanganate, on the addition of a drop of sulphuric acid. In order to obtain the corresponding terpin, this oil (5 grams) was shaken with 300 c.c. of 5 per cent. sulphuric acid during several days, and until it had completely dissolved. The clear solution was extracted once with ether to remove any unchanged carbinol, it was then saturated with

* A large quantity of dark-coloured resinous matter remained in the distilling flask.

ammonium sulphate, and extracted ten times, on the machine, with large quantities of ether. The extracts were dried over calcium chloride and evaporated, when a viscid, almost colourless oil was obtained, which on analysis gave numbers closely approximating to those required by the formula $C_9H_{18}O_2$. This syrup, which is probably a mixture of *cis*- and *trans*-modifications, gradually became semi-solid, and, in contact with porous porcelain, the oil was rapidly absorbed, leaving a colourless mass which, after crystallisation from a very small quantity of water, yielded the following results on analysis :

0.1135 gave 0.2813 H_2O and 0.1146 H_2O . C = 67.6 ; H = 11.2.

$C_9H_{18}O_2$ requires C = 68.3 ; H = 11.4 per cent.

1-Hydroxy-1-methyl-3-isopropenolcyclopentane (compare p. 575) softens at 70° and melts at 75° , and is excessively soluble in water, but rather sparingly so in cold ether. It dissolves readily in warm ether, and crystallises slowly from the concentrated solution in feathery groups. Its solution in acetic anhydride gives, with a trace of sulphuric acid, a pink solution which soon fades.

The terpin dissolves in fuming aqueous hydrobromic acid, but the solution soon clouds, and an oil separates which has a penetrating and highly characteristic odour resembling that of sage and carraway seeds.

The Action of Magnesium Methyl Iodide on Ethyl 1-Methyl- Δ^4 -cyclopentene-2-carboxylate, $CH \left\langle \begin{array}{l} CH \cdot CH_2 \\ \text{---} \\ CHMe \end{array} \right\rangle CH \cdot CO_2Et$.

The conversion of this ester into *1-methyl-2-isopropenol- Δ^4 -cyclopentene* takes place almost quantitatively under the following conditions. Magnesium (12 grams) is converted into magnesium methyl iodide in the usual manner, and, after cooling well, ethyl methylcyclopentenecarboxylate (26 grams) is gradually added. There is little action on mixing, but afterwards the liquid gradually comes to the boil. After four hours, the product is cautiously decomposed by water and dilute hydrochloric acid, the ethereal solution washed well, evaporated, and the residue left in contact with methyl-alcoholic potash (10 grams KOH) overnight. Water and ether are then added, and the ethereal solution washed well,* dried over calcium chloride, evaporated, and the residue fractionated under reduced pressure, when almost the whole quantity passes over at 95° (30 mm.) :

0.1212 gave 0.3420 CO_2 and 0.1264 H_2O . C = 76.9 ; H = 11.6.

$C_9H_{16}O$ requires C = 77.0 ; H = 11.4 per cent.

* The aqueous layer yields, on acidification and extraction with ether, a mere trace of unchanged acid, showing that the conversion into the carbinol was practically complete.

1-*Methyl-2-isopropenol- Δ^4 -cyclopentene* is a colourless, viscid liquid, which possesses a very pungent odour of terpineol and peppermint. It yields an intense reddish-brown coloration when a drop of sulphuric acid is added to its solution in acetic anhydride. When the pure substance is quickly added to an acetic acid solution of hydrogen bromide (saturated at 0°), it dissolves with considerable evolution of heat, and the solution becomes purple, then brown, and, finally, dark green.

If, however, the oil is gradually added to the hydrobromic acid solution, cooled in ice, a clear solution is produced, which rapidly clouds and from which an oily layer soon separates. When this mixture is allowed to stand, the lower layer becomes dark brown and the oil a chartreuse-green, and, after twelve hours, the liquid becomes an intense sage-green and the oil red. It is unfortunate that it was not found possible to convert this carbinol into a crystalline urethane or nitroso-chloride, and the only crystalline derivative of any value for its identification is the terpin described below. When the carbinol is mixed with phenylcarbimide and allowed to remain at the ordinary temperature for several days, crystals of diphenylcarbamide slowly separate.

An attempt was made to prepare a crystalline nitroso-chloride by leaving the pure carbinol (1.5 c.c.) in contact with ethyl nitrite (6 c.c. of a 15 per cent. alcoholic solution) and concentrated hydrochloric acid (1.5 c.c.), but the nitroso-chloride produced was a thick syrup. A comparative experiment showed that, under exactly the same conditions, ordinary terpineol is rapidly converted into its crystalline nitroso-chloride.

5-*Hydroxy-1-methyl-2-isopropenolcyclopentane* (see p. 578).—This crystalline terpin is produced in a fairly good yield under the following conditions. The carbinol (10 grams) is shaken on the machine with water (600 c.c.) and sulphuric acid (3 grams), when, even after several days, a considerable brown, oily layer separates on standing.

The product was filtered and extracted once with a little ether,* the aqueous solution was then saturated with ammonium sulphate, and extracted five times on the machine with the same solvent. After drying over calcium chloride and evaporating, the ethereal solution deposited a viscous syrup which gradually crystallised, and, in contact with porous porcelain, a good deal of oily impurity was readily absorbed, leaving a colourless, crystalline mass. The substance was dissolved in much pure ether, filtered, and the filtrate concentrated considerably, when, on standing, groups of colourless

* This ethereal extract yielded, on evaporation, a brown oil which contained, besides unchanged carbinol, a considerable quantity of very high boiling resinous matter.

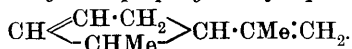
needles separated, which were collected, washed with ether, and dried over sulphuric acid in an evacuated desiccator. The mother liquors of these crystals deposited, on concentration, a further crop of the same substance, and there was no evidence of the presence of an isomeride :

0.1184 gave 0.2964 CO₂ and 0.1250 H₂O. C = 68.3 ; H = 11.7.

C₉H₁₈O₂ requires C = 68.3 ; H = 11.4 per cent.

5-*Hydroxy-1-methyl-2-isopropenolcyclopentane* melts at 70—72°, and is very similar to terpin in appearance. It is excessively soluble in water or alcohol, sparingly so in cold benzene or light petroleum in the cold. It dissolves readily in warm benzene, and separates, on cooling, as an oil which gradually crystallises. When it is warmed with an acetic acid solution of hydrogen bromide (saturated at 0°), it dissolves with slight evolution of heat, and the solution soon clouds and an oil separates. On standing for several days, the oil remains almost colourless, but the solvent becomes an intense brownish-red.

1-*Methyl-2-isopropenyl-Δ⁴-cyclopentene*,



It has been mentioned in the introduction (p. 578) that the elimination of water from 1-methyl-2-isopropenol-Δ⁴-cyclopentene results in the formation, under the most favourable conditions, of only very small quantities of the above terpene, the principal substances always obtained being condensation products of higher molecular weight. When the carbinol is heated with potassium hydrogen sulphate under the usual conditions, it yields principally a high boiling brown oil, and, if anhydrous oxalic acid is employed, the result is a viscid, almost black, product. The carbinol dissolves in anhydrous formic acid with a pink colour, and, when heated on the water-bath, the solution separates into two layers, the lower acid layer is dark brown, whereas the upper oily layer is nearly colourless. If the product is distilled, some methylisopropenylcyclopentene is obtained, but the yield is most unsatisfactory, owing to the formation of large quantities of polymerised hydrocarbons.

Attempts were then made to bring about the elimination of water at the ordinary temperature by leaving the carbinol in contact with a large excess of magnesium methyl iodide for a week, but little action took place and almost the whole of the carbinol was recovered unchanged. The best results were ultimately obtained by heating the carbinol with twice its weight of succinic anhydride* for

* Phthalic anhydride may also be used, but with less satisfactory results.

fifteen minutes and then distilling in steam, when a colourless oil passed over, leaving a dark brown condensation product in the distillation flask.

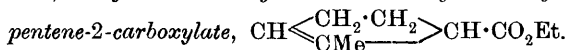
The distillate was extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residue fractionated, first alone and then three times over sodium, when a colourless oil was obtained which distilled at 143—145° (770 mm.):

0.2120 gave 0.6785 CO₂ and 0.2230 H₂O. C = 87.3; H = 11.6.

C₉H₁₄ requires C = 88.5; H = 11.5 per cent.

1-*Methyl-2-isopropenyl-Δ⁴-cyclopentene* has a distinct odour of lemons, and oxidises very readily in the air, a fact which accounts for the somewhat low numbers obtained in the above analysis. When a small quantity of the terpene was placed over water in a tube sealed at one end, the absorption of oxygen took place very rapidly, and overnight the level of the water had risen to almost exactly one-fifth of the volume of the air taken. The solution of the terpene in acetic anhydride gives an intense blood-red coloration when a trace of sulphuric acid is added, and, on warming, the colour changes to violet-black. The terpene does not dissolve in an acetic acid solution of hydrogen bromide (saturated at 0°), but a good deal of heat is liberated, and the oil becomes brown, then blood-red, and, after several hours, a deep sage-green. The dark brown condensation products, obtained in such quantities during the preparation of the terpene, have properties closely resembling those described in more detail in the case of the corresponding experiments in the Δ⁵-series (p. 597). When fractionated, a good deal of a yellowish-brown oil distilled at 170—175° (20 mm.), and evidently consisted of the polymeride, (C₉H₁₄)₂; it oxidised very rapidly in the air, and gave only approximate results on analysis.

The Action of Magnesium Methyl Iodide on Ethyl 1-Methyl-Δ⁵-cyclo-



It has been pointed out in the introduction (p. 579) that this decomposition proceeds abnormally, and gives only a very small yield of the corresponding tertiary alcohol. In several experiments, the pure ester (37 grams) was treated with magnesium methyl iodide (containing 17 grams of magnesium), and the product was left overnight and decomposed by dilute hydrochloric acid in the usual manner.

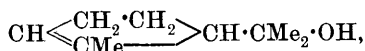
The ethereal solution was washed with dilute sulphurous acid to remove iodine, dried over calcium chloride, and evaporated, when a brown oil was obtained, which, by distillation under reduced pressure, was separated into three fractions: 80—120° (40 mm.),

170—172° (18 mm.), and 225—230° (15 mm.). The lowest fraction yielded, on careful fractionation, a small quantity of a hydrocarbon, distilling at about 147° under the ordinary pressure, and about three grams of an oil boiling at 97—100° (30 mm.). The oil of boiling point 147° is doubtless the terpene, but the quantity was so small and the substance oxidised so rapidly in the air that no analysis was attempted. The oil of boiling point 97—100° (30 mm.) had a strong odour of peppermint, and when dissolved in acetic anhydride gave, on the addition of a trace of sulphuric acid, a red coloration, which was distinctly bluer than that yielded by the corresponding Δ^4 -carbinol (p. 594) under these conditions. The following results were obtained on analysis :

0.1965 gave 0.5450 CO_2 and 0.1940 H_2O . C = 75.7 ; H = 11.0.

$\text{C}_9\text{H}_{16}\text{O}$ requires C = 77.0 ; H = 11.4 per cent.

There can be no doubt that this substance is 1-methyl-2-isopropenol- Δ^5 -cyclopentene,



but the amount of material at our disposal was so small that it was impossible to investigate its properties.

The fraction 170—172° (18 mm.) was distilled over sodium without altering its boiling point and then analysed :

0.1146 gave 0.3613 CO_2 and 0.1200 H_2O . C = 86.0 ; H = 11.6.

$(\text{C}_9\text{H}_{14})_2$ requires C = 88.5 ; H = 11.5 per cent.

Subsequently, it was discovered that this very viscid hydrocarbon is very rapidly oxidised in the air, and this fact accounts for the low numbers obtained in the above analysis. After remaining in a loosely-corked test-tube for a week a second analysis was made, and the substance found to contain only C = 80.1, and H = 10.3.

A small quantity of the hydrocarbon, left in contact with air in a tube over water, absorbed the whole of the oxygen in a few hours. No further experiments were made either with this hydrocarbon or with the higher fraction, 225—230° (15 mm.), mentioned above.

The authors are greatly indebted to the Research Fund Committees, both of the Royal Society and of the Chemical Society, for grants, which have largely defrayed the heavy cost of this investigation.

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