358. *Lanceol, a Sesquiterpene Alcohol from the Oil of* Santalum lanceolatum. *Part I.*

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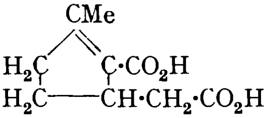
DURING an examination of the essential oil from the wood of *Santalum lanceolatum* one of us (Penfold, *J. Proc. Roy. Soc. New South Wales*, 1928, **62**, 60; 1932, **66**, 240) isolated a new sesquiterpene alcohol, $C_{15}H_{24}O$. We have now studied the reactions of this alcohol, for which we suggest the name *lanceol.* We derive the trivial name in this instance from the botanical name of the variety of the wood and not, as is customary, from the species name, since there appears to be no structural relationship between the α- and β-santalols and lanceol.

Lanceol is a primary alcohol, since it reacts with phthalic anhydride in benzene solution to yield a hydrogen phthalate, characterised by the preparation of a crystalline *strychnine* salt, m. p. 103—105°. It can be identified most readily by means of the *allophanate,* m. p. 114—115°. It is monocyclic, titration with camphoric acid peroxide showing the presence of three ethylenic linkages : these cannot be conjugated, since the alcohol does not react with α-naphthaquinone, nor is it reduced by sodium in ethyl-alcoholic solution. On oxidation with chromic acid lanceol gives, in very poor yield, an aldehyde, $C_{15}H_{22}O$, from which two derivatives, the *semicarbazone*, m. p. 151—152°, and the p-*nitrophenylhydrazone*, m. p. 135—136°, were prepared.

On oxidation of lanceol with ozone in either acetic acid or ethyl acetate formaldehyde was obtained in considerable quantity. Hydroxyacetone appeared to be present amongst the products volatile in steam after decomposition of the ozonide, the phenyl- and the 2 : 4-dinitrophenyl-osazone being isolated. It is considered unlikely that these osazones arise alternatively from the presence of methylglyoxal, since the formation of this substance would involve the presence originally of the system :CMe·CH: containing conjugated ethylenic linkages. Extraction with ether of the non-volatile products gave an oil having strong reducing properties, which showed no tendency to crystallise. If this oil was treated with alkali, or preferably oxidised further with silver oxide, a mixture of acids was obtained which partly crystallised. In the liquid acid mixture lævulic acid was identified by esterification with diazomethane and fractional distillation, methyl lævulate being characterised by the preparation of the semicarbazone, m. p. 148°, the 2 : 4-dinitrophenylhydrazone, m. p. 139—141°, and the *phenylsemicarbazone*, m. p. 115°.

The crystalline *acid*, m. p. 174°, which was readily isolated in a pure state owing to its sparing solubility in ethyl acetate and ether, had the composition $C_9H_{12}O_4$, was optically inactive, and its alkaline solution immediately decolorised potassium permanganate. On oxidation with ozone it gave δ-acetylbutane-αβ-dicarboxylic acid (III), m. p. 119—120° (Meldrum and Perkin, J., 1908, **93**, 1427), identified by comparison with an authentic specimen and by oxidation with sodium hypobromite to butane-αβδ-tricarboxylic acid. The formation of δ-acetylbutane-αβ-dicarboxylic acid with the loss of one carbon atom suggested that the acid $C_9H_{12}O_4$ was either 1-*methyl*-Δ^1-cyclo*pentene-2-carboxylic-3-acetic acid* (I) or 1-*methyl*-Δ^1-cyclo*hexene-2 : 4-dicarboxylic acid* (II). These acids were synthesised; they melt at 200—202° and 193—195° respectively, and cannot therefore be identical with the oxidation acid.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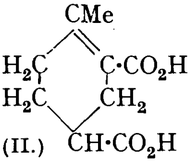
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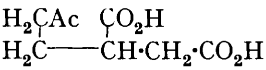
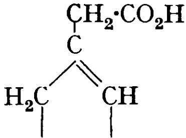

(III.)

The only other acids which could give (III) on ozonolysis are represented by (IV), (V), and (VI). Since the acid, m. p. 174°, seems to be stable to hot alkali, we regard (IV) and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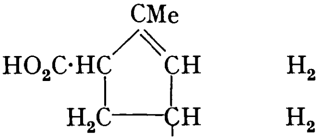
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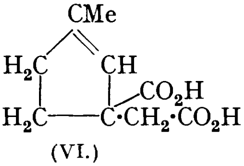
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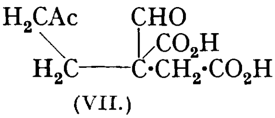
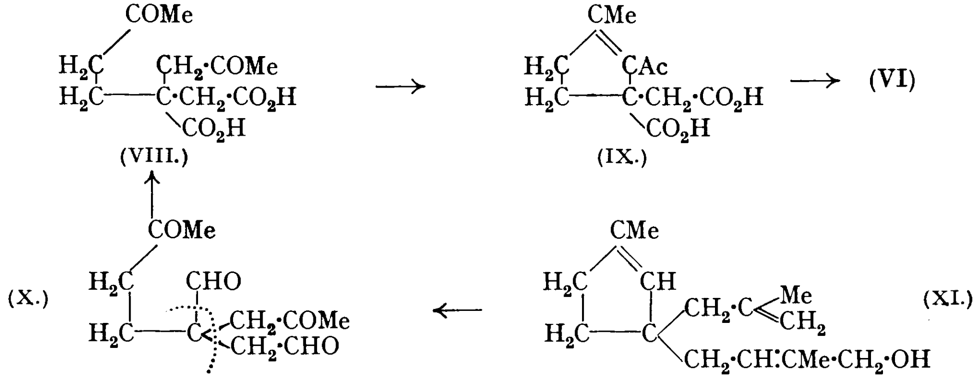

(VII.)

(V), containing as they do an ethylenic linkage in the βγ-position to a carboxyl group, as extremely improbable. If (VI) correctly represents the unsaturated acid, the oxidation to (III) must proceed *via* the aldehyde (VII) or the related malonic acid. We have been unable to obtain any evidence of the presence of the malonic acid or the aldehyde, since, even if the oxidation was effected in acetic acid solution and the solvent removed at room temperature, only the keto-dicarboxylic acid was obtained. It is possible that the aldehyde (VII) is unstable and we regard (VI) therefore as the most probable representation of the unsaturated acid, although we are unable to furnish a rigid proof of this. In view of its importance the synthesis of the acid (VI) is being studied.

This structure being tentatively accepted for the unsaturated acid, it is now necessary to consider its relationship to the parent alcohol and also how its formation can be reconciled with the three other products of the oxidation, formaldehyde, hydroxyacetone, and lævulic acid.

Regarding 1-methyl-Δ^1-*cyclo*pentene-3-carboxylic-3-acetic acid (VI), two possibilities arise, either that it is a primary oxidation product retaining an ethylenic linkage unattacked by ozone, or that it is a secondary product. For the reason given below, we regard the latter alternative as the more probable and we suggest that the acid is formed by the cyclisation of the diketone (VIII) to yield (IX), which then loses an acetyl group, giving (VI).



(VIII.) (IX.) (VI) (X.) (XI.)

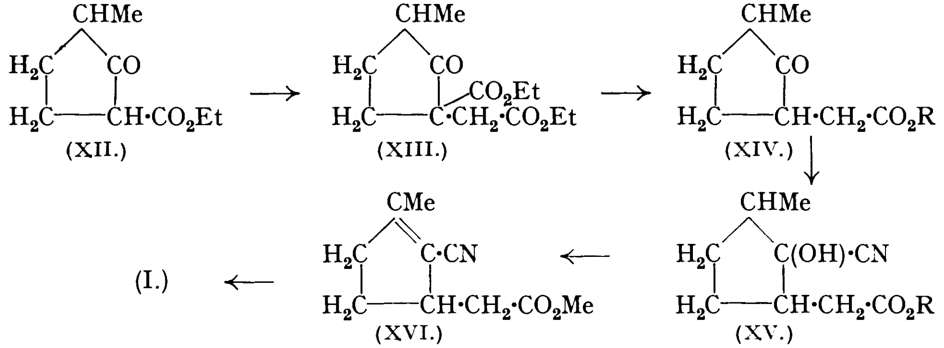
It might be anticipated that (IX) would be sufficiently stable to permit of its isolation and it is not improbable that it is present amongst the products of the oxidation. Esterification of the liquid acids gives a high-boiling fraction which is ketonic, but we were unable to prepare any crystalline derivatives, either from the ester or from the acid obtained by hydrolysis. On the basis of (VIII) we suggest as a working hypothesis for further investigation that lanceol is represented by (XI), the primary products of the oxidation being the diketo-dialdehyde (X), formaldehyde, and hydroxyacetone. (X) would be capable of cyclisation in many directions: this may account for the difficulties encountered in isolating homogeneous oxidation products.

The alternative possibility that 1-methyl-Δ^1-*cyclo*pentene-3-carboxylic-3-acetic acid is a primary product leads also to (XI) for lanceol, with the slight modification that an *iso*propylidene group replaces the *iso*propenyl group. On ozonolysis the modified form of (XI) should then yield (VI) directly (the *cyclo*pentene ring, *ex hypothesi*, not being attacked), hydroxyacetone, and acetone. However, in spite of a careful search, we could not detect acetone after oxidation with either ozone or potassium permanganate.

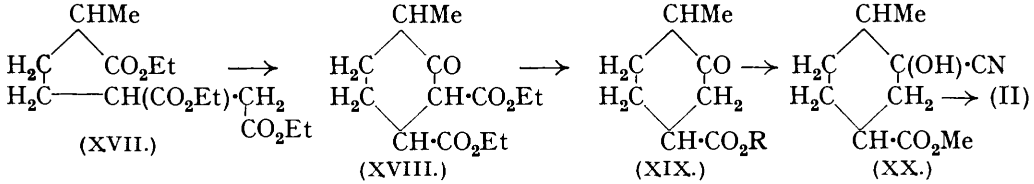
There remains to account for the production of lævulic acid. We have been unable to devise any formula which will account for its formation in a simple and obvious manner and yet be in harmony with the other evidence available. We suggest that lævulic acid results from the oxidative breakdown of (X) at the dotted line by the hydrogen peroxide formed during the decomposition of the ozonide. Drastic degradations of this type by the action of ozone are uncommon, but have been recorded previously (*inter alia*; Ruzicka, Zimmermann, and Huber, *Helv. Chim. Acta*, 1936, **19**, 346). Finally, the formula (XI) proposed for lanceol contains three isoprene residues combined in a somewhat unusual manner.

The unsaturated cyclic acids (I) and (II) were synthesised *via* the *hydroxy-nitriles* (XV) and (XX), which were prepared from the methyl esters of the keto-acids (XIV; R = Me) and (XIX; R = Me).

By the condensation of ethyl sodio-1-methyl*cyclo*pentan-2-one-3-carboxylate (XII) (Dieckmann, *Annalen*, 1901, **317**, 73) with ethyl bromoacetate, *ethyl* 3-*carbethoxy*-1-*methyl*-cyclo*pentan*-2-*one*-3-*acetate* (XIII) was prepared; this, on hydrolysis with dilute sulphuric acid, gave 1-methyl*cyclo*pentan-2-one-3-acetic acid (XIV; R = H) as an oil, which was purified through its *semicarbazone*, m. p. 175—176°. Fractional crystallisation showed, as was to be expected, that the keto-acid was a mixture of *cis*- and *trans*-forms, but only one semicarbazone was obtained pure. By treatment of the *methyl* ester with anhydrous hydrogen cyanide the *hydroxy-nitrile* (XV) was prepared, which was dehydrated with thionyl chloride and pyridine to the cyclo*pentene cyano-ester* (XVI). Hydrolysis of the latter with hydrochloric acid gave the *cyclo*pentene acid (I) together with a small quantity of the related *cyano-acid*, m. p. 216°. The constitution of (I) was confirmed by its oxidation with ozone to δ-acetylbutane-αβ-dicarboxylic acid.



The keto-acid (XIX; R = H) has been described by Meldrum and Perkin (*loc. cit.*), who prepared it from *p*-toluic acid. We now find that it can be prepared conveniently in accordance with the scheme given below. When ethyl 3-carbethoxy-1-methyl*cyclo*pentan-2-one-3-acetate (XIII) was digested with sodium ethoxide, ring fission occurred with the formation of *ethyl hexane-αβε-tricarboxylate* (XVII), which gave, on cyclisation with sodium, *ethyl 1-methyl*cyclo*hexan-2-one-2 : 4-dicarboxylate* (XVIII), from which by hydrolysis with dilute sulphuric acid the keto-acid (XIX; R = H) was obtained in excellent yield. The acid was apparently a mixture of *cis*- and *trans*-isomerides, but its structure was proved by the preparation of the semicarbazone and oxime, which had the melting points recorded by Meldrum and Perkin, and also by its oxidation with chromic acid to δ-acetylbutane-αβ-dicarboxylic acid. As would be anticipated, the *cyclo*pentanone acid (XIV) was not formed. The *methyl* ester of (XIX; R = Me) was converted into the *cyclo*hexene acid (II) in a manner similar to that used for the preparation of the *cyclo*pentene acid, but the reaction proceeded very much less smoothly. In the hydrolysis of the nitrile considerable dehydrogenation occurred and in addition to the *cyclo*hexene acid (II), the aromatic acid, its *nitrile*, m. p. 162—163°, and its acid *amide*, m. p. 285°, were obtained. The actual yield of the *cyclo*hexene acid was small, but sufficient was prepared to confirm its structure by oxidation wlth ozone to δ-acetylbutane-αβ-dicarboxylic acid.



EXPERIMENTAL.

Lanceol.—The *alcohol*, which was purified by conversion into its gummy hydrogen phthalate and recovery by hydrolysis with alkali, was a somewhat viscid, colourless oil with only a faint odour. It had b. p. 175—176°/17 mm., $d_{15^\circ}^{15^\circ}$ 0·9474, $n_D^{25^\circ}$ 1·5074, $[\alpha]_{5461}$ − 77·4°, $[\alpha]_{5780}$ − 67·8° (Found : C, 81·8; H, 10·8. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9%). With percamphoric acid the alcohol absorbed oxygen equivalent to 2·75 ethylene linkages. Catalytic hydrogenation of the alcohol or of its hydrogen phthalate yielded a mixture, the boiling-point range indicating the presence of much hydrocarbon. It was unaffected by heating with alcoholic potassium hydroxide at 150° for 5 hours, and after dehydrogenation with selenium at 300° for 40 hours the product failed to yield a crystalline picrate. The *allophanate* crystallised from alcohol in soft needles, m. p. 114—115° (Found : C, 67·1; H, 8·4; N, 9·4. $C_{17}H_{26}O_3N_2$ requires C, 66·7; H, 8·5; N, 9·0%). The hydrogen phthalate gave a *strychnine* salt, which crystallised from *cyclo*hexane in needles, m. p. 103—105° (Found : C, 74·6; H, 7·3. $C_{44}H_{50}O_6N_2$ requires C, 75·2; H, 7·1%).

Oxidation of Lanceol.—(i) *With chromic acid.* The alcohol (3 g.) in acetic acid (5 c.c.) was treated with chromic acid (1 g.) in acetic acid (5 c.c.). Oxidation proceeded vigorously, but the product, b. p. 165—175°/15 mm., was not homogeneous and contained only a small percentage of aldehyde. The *semicarbazone* crystallised from methyl alcohol in irregular prisms, m. p. 151—152° (Found : C, 70·1; H, 9·2. $C_{16}H_{25}ON_3$ requires C, 69·8; H, 9·1%); the p-*nitrophenylhydrazone* separated from acetic acid in balls of terra-cotta needles, m. p. 135—136° (Found : C, 71·0; H, 7·5. $C_{21}H_{27}O_2N_3$ requires C, 71·4; H, 7·6%); the oxime was an oil. (ii) *With ozone.* The alcohol (10 g.) in ethyl acetate (130 c.c.), cooled in ice, was ozonised, the issuing gases being led through water, this water subsequently being shown to contain formaldehyde in considerable quantity by the dimedone test. The solvent was evaporated under diminished pressure, and the ozonide decomposed by boiling with water. Volatile products were removed by steam distillation, about 1 l. of distillate being collected. From the distillate the phenyl- and the 2 : 4-dinitrophenyl-osazone of hydroxyacetone, m. p. 141—142° and 300° respectively, were prepared. The liquid in the distilling flask was cooled and treated with solutions of silver nitrate (20 g.) and sodium hydroxide (10 g.). After standing overnight, the solution was filtered, concentrated on the water-bath, acidified, and extracted continuously with ether. After separation, drying, and evaporation of the ether, the oil obtained partly solidified. It was triturated with a little ethyl acetate and filtered from the acid (*A*) (1·8 g.). Evaporation of the ethyl acetate and repetition of the treatment with solvent yielded further small quantities of (*A*), the final evaporation of the solvent leaving an oil (*B*). The *acid* (*A*) crystallised from water in small irregular plates, m. p. 174°, unaltered by further crystallisation (Found : C, 58·9; H, 6·3. $C_9H_{12}O_4$ requires C, 58·7; H, 6·5%). The acid was readily soluble in alcohol, acetone and hot water, very sparingly so in ether, ethyl acetate and benzene. It was unaltered when heated with sulphuric acid (90%) at 100°. When heated with acetyl chloride, it gave a crystalline anhydride, m. p. about 148°, which crystallised from ether–benzene in rosettes of prisms. The anhydride was, however, very unstable and on further crystallisation it gradually reverted to the parent acid. The *di*-p-*phenylphenacyl* ester crystallised from methyl alcohol in balls of needles, m. p. 105—106° (Found : C, 77·4; H, 5·5. $C_{37}H_{32}O_6$ requires C, 77·6; H, 5·6%).

The oil (*B*) gave amorphous or gummy precipitates with carbonyl reagents, and with sodium hypobromite in alkaline solution it gave a milky precipitate. It was esterified with diazomethane, and the esters distilled. A fraction (1·2 g.), b. p. 90—105°/15 mm., yielded the semicarbazone, m. p. 148°, the *phenylsemicarbazone*, m. p. 115° (Found : N, 15·8. $C_{13}H_{17}O_3N_3$ requires N, 16·0%), and the 2 : 4-dinitrophenylhydrazone, m. p. 139—141°, of methyl lævulate, the m. p.'s being unchanged by admixture with authentic specimens. A viscid fraction (3·6 g.), b. p. 195—225°/15 mm., yielded some of the acid (*A*), m. p. 174°, on hydrolysis, but no other solid derivatives could be obtained from this or the small intermediate fractions.

In separate experiments in which the ozonolysis was carried out in ethyl acetate or in carbon tetrachloride solution, the solution after decomposition of the ozonide was made alkaline and distilled through a short column into a water–acetic acid solution of *p*-nitrophenylhydrazone. No acetone could be detected.

Oxidation of the Acid (A).—The acid (0·7 g.) in sodium carbonate solution (carbonate 1 g.; water 10 c.c.) was treated with ozone until the solution no longer decolorised potassium permanganate. After the addition of a few drops of hydrogen peroxide the solution was kept overnight, concentrated, acidified, and extracted with ether. The oil remaining after evaporation of the solvent rapidly crystallised. For purification the keto-acid was converted into the semicarbazone, which crystallised from water in well-formed prisms, decomp. 180° (Found : C, 44·1; H, 6·0. Calc. : C, 44·1; H, 6·1%). The acid, regenerated from the semicarbazone by hydrolysis with dilute sulphuric acid, crystallised from ether in cubes, m. p. 119—120°, both alone and after admixture with δ-acetylbutane-αβ-dicarboxylic acid (Found : C, 51·3; H, 6·0. Calc. : C, 51·1; H, 6·4%). The keto-acid was oxidised with sodium hypobromite to butane-αβδ-tricarboxylic acid, which after crystallisation from acetone–chloroform had m. p. 116—118°, both alone and in admixture with an authentic specimen.

*Ethyl 3-Carbethoxy-1-methyl*cyclo*pentan-2-one-3-acetate.*—Ethyl 1-methyl*cyclo*pentan-2-one-3-carboxylate (16·5 g.) was added to finely divided sodium (2·3 g.) in benzene (64 c.c.) and heated on the water-bath for 4 hours. Ethyl bromoacetate (13 g.) was added to the cooled solution, and the condensation effected by heating for a further 4 hours. After the addition of water and ether, the ether–benzene layer was separated and dried, and the solvent removed. The *ester* then distilled as a mobile oil, b. p. 173—175°/19 mm. (yield, 75%) (Found : C, 60·5; H, 7·9. $C_{13}H_{20}O_5$ requires C, 60·9; H, 7·8%).

1-*Methyl*cyclo*pentan*-2-*one*-3-*acetic Acid*.—The above-mentioned ester (92 g.), sulphuric acid (90 g.), and water (600 c.c.) were heated under reflux for 10 hours; aqueous sodium hydroxide (sodium hydroxide 40 g.) was added to the cooled solution, which was finally made alkaline with sodium carbonate. After extraction with ether to remove neutral products, the alkaline solution was acidified and repeatedly extracted with ether; evaporation of the dried extract finally gave the acid (55 g.) as an oil. The acid was purified by conversion into the semicarbazone, (56 g.), which separated as a crystalline powder, m. p. 163°. The filtrate gave on digestion with dilute sulphuric acid an oil (11·7 g.), which was not further examined. The *semicarbazone* (36·4 g.), purified by fractional crystallisation from methyl alcohol, in which it was somewhat sparingly soluble, separated in fine needles, m. p. 175—176° (Found : C, 50·6; H, 6·8. $C_9H_{15}O_3N_3$ requires C, 50·7; H, 7·0%). From the mother-liquors a more readily soluble semicarbazone was isolated, which could not be obtained pure. Hydrolysis of the semicarbazone (36 g.) with dilute sulphuric acid gave the pure keto-acid (27·5 g.) as a colourless oil showing no tendency to crystallise. The *phenylsemicarbazone* crystallised from methyl alcohol in long needles, decomp. 175—176° (Found : N, 14·9. $C_{15}H_{19}O_3N_3$ requires N, 14·5%). The *methyl* ester was a mobile oil, b. p. 123°/20 mm. (Found : C, 63·6; H, 8·2. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2%).

Methyl 2-*Hydroxy*-2-*cyano*-1-*methyl*cyclo*pentane*-3-*acetate*.—The methyl ester (16 g.) was added to hydrogen cyanide obtained from potassium cyanide (100 g.) (Wade and Panting, J., 1898, **73**, 256) at 0°. After the addition of a drop of potassium cyanide solution the mixture was kept at this temperature overnight, a little dilute sulphuric acid added, and the excess of hydrogen cyanide removed by means of the pump. The residual oil was dissolved in ether, and the solution dried; the *hydroxy-ester* remaining after removal of the solvent had b. p. 166°/20 mm. (yield, 70%) (Found : N, 7·4. $C_{10}H_{15}O_3N$ requires N, 7·1%).

1-*Methyl*-Δ^1-cyclo*pentene*-2-*carboxylic*-3-*acetic Acid*.—The hydroxy-ester (7·8 g.) in pyridine (6·3 g.) was cooled in salt–ice, and freshly distilled thionyl chloride (10·3 g.) added during 30 minutes. On cautious warming on the water-bath, vigorous evolution of gas occurred; the reaction was controlled in the early stages by removal from the water-bath and cooling in ice. After 1 hour's heating, ice was added, the mixture poured into dilute hydrochloric acid, and the unsaturated nitrile extracted with ether. The ethereal extract was washed with dilute sulphuric acid, aqueous sodium hydroxide, and dried, and the solvent removed. The residual deep brown oil, which contained a small quantity of a crystalline solid, was distilled under diminished pressure (18 mm.), the nitrile being obtained as an oil, b. p. 140—145°. For hydrolysis the nitrile (6 g.) was digested with hydrochloric acid (30 c.c.) for 3 hours, a crystalline solid separating. The cyclo*pentene acid* separated from hot water (charcoal) in needles, m. p. 200—202°, unaltered by further crystallisation (Found : C, 58·6; H, 6·6; *M*, 184·4. $C_9H_{12}O_4$ requires C, 58·7; H,6·5%; *M*, 184). The acid was readily soluble in the ordinary organic solvents except ligroin; its alkaline solution was unstable to potassium permanganate. On oxidation in sodium carbonate solution with ozone, followed by hydrogen peroxide, it gave in quantitative yield δ-acetylbutane-αβ-dicarboxylic acid, m. p. 119—120°, both alone and in admixture with an authentic specimen. The semicarbazone, after crystallisation from water, had m. p. 177—179°.

Evaporation of the hydrochloric acid solution from which the *cyclo*pentene acid had been separated gave a gummy solid, which was extracted with acetone to separate the ammonium chloride. The acetone left on evaporation a brown oil, which slowly solidified and then crystallised from methyl alcohol in needles. 2-*Cyano*-1-*methyl*-Δ^1-cyclo*pentene*-3-*acetic acid* decomposed at 216° after sintering at 212° (Found : C, 65·6; H, 6·7. $C_9H_{11}O_2N$ requires C, 65·5; H, 6·7%).

Ethyl Hexane-αβε-*tricarboxylate*.—Ethyl 3-carbethoxy-1-methyl*cyclo*pentane-2-one-3-acetate (69 g.) was mixed with sodium ethoxide (sodium 1·2 g.; ethyl alcohol 24 c.c.) and heated on the water-bath for 2·5 hours. The cooled solution was poured into a mixture of ether and water, the ethereal extract separated, washed with water, and dried, and the ether evaporated. The *triethyl* ester (59 g.) had b. p. 188°/18 mm. (Found : C, 59·6; H, 8·5. $C_{15}H_{26}O_6$ requires C, 59·6; H, 8·6%). Hydrolysis of the ester with hydrochloric acid gave the tribasic acid as a crystalline cake, which did not lend itself to purification.

Ethyl 1-*Methyl*cyclo*hexan*-2-*one*-3 : 4-*dicarboxylate*.—The above-mentioned ester (52 g.)

was added slowly to finely divided sodium (6·4 g.) and heated on the water-bath for 1 hour; xylene (50 c.c.) was then added, and the heating continued for a further hour at 140°. After the addition of alcohol (10 c.c.) and water to the cooled reaction mixture, the solution was acidified with dilute hydrochloric acid, ether added, the ether–xylene extract separated, washed with sodium carbonate solution, and dried, and the solvents removed. The *keto-ester* (31 g.), b. p. 185°/30 mm., gave a deep blue colour with alcoholic ferric chloride (Found: C, 60·9; H, 7·7. $C_{13}H_{20}O_5$ requires C, 60·9; H, 7·8%).

1-*Methyl*cyclo*hexan-2-one-4-carboxylic Acid.*—The keto-ester (30 g.) was digested with dilute sulphuric acid (acid 80 g.; water 200 c.c.) for 40 hours and the cooled solution, after saturation with ammonium sulphate, was extracted with ether. Evaporation of the solvent gave a crystalline acid (15·4 g.) which, after crystallisation from ether, had m. p. 85—90° and was evidently a mixture of the *cis*- and the *trans*-modification of the keto-acid (Found: C, 61·6; H, 7·8. Calc.: C, 61·5; H, 7·7%). The semicarbazone had m. p. 195—197° and the oxime decomposed at 193° (Meldrum and Perkin, *loc. cit.*, give m. p. 193—195° and 193—195° respectively). The constitution of the acid was confirmed by its oxidation with chromic acid to δ-acetylbutane-αβ-dicarboxylic acid. The *methyl* ester had b. p. 132°/21 mm. (Found: C, 63·7; H, 8·4. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2%).

*Methyl 2-Hydroxy-2-cyano-1-methyl*cyclo*hexane-4-carboxylate.*—The *hydroxy-nitrile*, prepared in a similar manner to the *cyclo*pentane nitrile described above, had b. p. 191°/25 mm. (Found: N, 7·6. $C_{10}H_{15}O_3N$ requires N, 7·1%).

1-*Methyl*-Δ^1-cyclo*hexene-2* : *4-dicarboxylic Acid.*—The nitrile was dehydrated with thionyl chloride and pyridine under conditions similar to those adopted in the case of the *cyclo*pentane isomeride. The product, b. p. 160—215°/29 mm., contained halogen and it was therefore digested with pyridine for 1 hour; the recovered oil had b. p. 155—160°/22 mm. and was free from chlorine. The cyano-ester (5·7 g.) was mixed with methyl-alcoholic potassium hydroxide solution (potassium hydroxide 8 g.) and heated on the water-bath; after some minutes, a crystalline potassium salt separated. The solution was cooled, the salt (*A*) collected, and the filtrate (*B*) heated on the water-bath for 36 hours, evolution of ammonia having then ceased. The salt (*A*) was dissolved in water, and the solution evaporated to remove traces of alcohol, cooled, and acidified. The solid deposited (1·7 g., m. p. 140—190°) was ground with cold ethyl acetate, and the sparingly soluble portion (A_1) (0·39 g.) removed. Evaporation of the solvent gave 2-*cyano*-p-*toluic acid*, which crystallised from water in long fine needles, m. p. 162—163° (Found: C, 67·2; H, 4·5. $C_9H_7O_2N$ requires C, 67·1; H, 4·3%). The nitrile was readily hydrolysed to the dibasic acid, m. p. 319—320°, by warming at 125—130° with equal parts of water and sulphuric acid. The *amide* (A_1 above) crystallised from alcohol in soft prisms, decomp. 285° (Found: C, 60·3; H, 5·1. $C_9H_9O_3N$ requires C, 60·3; H, 5·0%).

The solution (*B*) was diluted with water and acidified after the alcohol had been removed on the water-bath. The amorphous solid (B_1) which separated was collected and after crystallisation from alcohol had m. p. 319—320° and was identified as methyl*iso*phthalic acid. Extraction of the filtrate from (B_1) with ether gave an oil (2·6 g.), which partly crystallised on trituration with water. The solid (B_2), m. p. 130—180°, was purified by crystallisation first from ethyl acetate and finally from hot water. 1-*Methyl*-Δ^1-cyclo*hexene-2* : *4-dicarboxylic acid* crystallised in irregular prisms, m. p. 193—195° (Found: C, 58·5; H, 6·6; *M*, 185. $C_9H_{12}O_4$ requires C, 58·7; H, 6·5%; *M*, 184). The structure of the acid was confirmed by its oxidation with ozone to δ-acetylbutane-αβ-dicarboxylic acid, the semicarbazone of which had m. p. 177° both alone and in admixture with an authentic specimen. The mother-liquor from which the *cyclo*hexene acid had been separated contained a more soluble acid, m. p. about 158—160°, which was not obtained pure (Found: C, 59·2; H, 6·5%). It is possible that this was the lactonic acid, but the quantity available was insufficient for purification.

We are indebted to the Government Grants Committee of the Royal Society, the Chemical Society, and Imperial Chemical Industries, Ltd., for grants.

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[*Received, August 19th,* 1936.]