The constitution of umbellulone. [Pt. I] / by Frank Tutin.

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Publication/Creation

London : Wellcome Chemical Research Laboratories, [1906]

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No. 61

THE CONSTITUTION
OF
UMBELLULONE

BY

FRANK TUTIN

(From the Transactions of the Chemical Society, 1906)

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CXIII.—*The Constitution of Umbellulone.*

By Frank Tutin.

In the course of a chemical examination of the essential oil of Californian Laurel (*Umbellularia Californica*), Power and Lees (Trans., 1904, **85**, 629) isolated a new ketone, which they designated "umbellulone." This ketone was shown to have the formula $C_{10}H_{14}O$, and to contain only one ethylenic linking, which indicated the presence of two closed rings. Power and Lees also showed that umbellulone behaves abnormally when treated with semicarbazide or hydroxylamine, for not only does the usual reaction with the carbonyl group take place on treatment with either of these reagents, but a molecule of the base also becomes attached to the carbon atoms of the ethylenic linking. This behaviour has been shown by Harries and his pupils (*Ber.*, 1897, **30**, 230), by Tiemann (*Ber.*, 1897, **30**, 251, and 1900, **33**, 562), and by Rupe and Schlochoff (*Ber.*, 1903, **36**, 4377) to be a property of those ketones which contain an ethylenic linking in the *αβ*-position with respect to the carbonyl group. It was therefore indicated that umbellulone was an *αβ*-unsaturated cyclic ketone containing two closed rings.

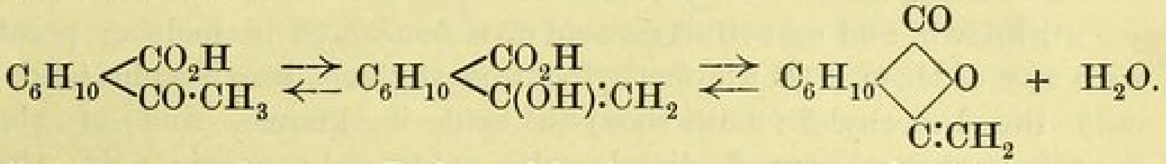
The behaviour of umbellulone towards certain reagents was further studied by Lees (Trans., 1904, **85**, 639), and the results obtained by him may be summarised as follows:

On treatment with bromine, umbellulone formed a liquid dibromide, which, on distillation under diminished pressure, gave solid dibromodihydroumbellulone, $C_{10}H_{14}OBr_2$, an unsaturated liquid monobromoumbellulone, $C_{10}H_{13}OBr$, and a small amount of a hydrocarbon, $C_{10}H_{14}$. The unsaturated monobromoumbellulone, on reduction with zinc dust and acetic acid, yielded a saturated ketone, $C_{10}H_{16}O$, whilst on submitting dibromodihydroumbellulone to a similar treatment monobromodihydroumbellulone, $C_{10}H_{15}OBr$, was obtained; the latter, on reduction with sodium in alcohol, gave tetrahydroumbellulol, $C_{10}H_{20}O$. It was also stated that "umbellulone is readily oxidised by potassium permanganate, yielding a lactone, $C_9H_{12}O_2$, together with several acids which were not further investigated."

As Mr. Lees has been unable to continue the investigation of this ketone, the author, in agreement with him, has further studied the derivatives of umbellulone, more especially the products of its oxidation with potassium permanganate. The present communication embodies the results obtained, and the conclusions which may be drawn from them respecting the constitution of this ketone.

Throughout this investigation it has been borne in mind that the material available for the greater part of the work could not be regarded as a pure substance, as it represented a fraction of the essential oil collected over a range of 10 degrees. Control experiments were therefore made with the use of pure umbellulone which had been regenerated from its semicarbazido-semicarbazone, and the compounds here described as derivatives of umbellulone are only such as were obtained from the pure ketone.

When umbellulone, $C_{10}H_{14}O$, is oxidised with cold permanganate, a *monocarboxylic keto-acid*, $C_9H_{14}O_3$ (b. p. 193—195°/50 mm.; m. p. 102°), is the principal product. This has been designated *umbellulonic acid*. It yields a crystalline oxime (m. p. 169—170°), and evidently contains the group $-CO\cdot CH_3$, since, on warming with iodine in presence of sodium carbonate, it readily gives iodoform. The umbellulonic acid thus obtained is associated with smaller amounts of acids of higher boiling point, but these could not be isolated in a state of purity owing to the presence of oxidation products derived from substances other than umbellulone contained in the fraction of oil employed. When this mixture of acids is slowly distilled under 20 mm. pressure, water is eliminated, and a portion of the umbellulonic acid passes into an *unsaturated lactone*, $C_9H_{12}O_2$ (b. p. 129—135°/50 mm.), which, on solution in potash, again yields the keto-acid. This lactone is, in fact, produced by the elimination of water from the enolic modification of umbellulonic acid.



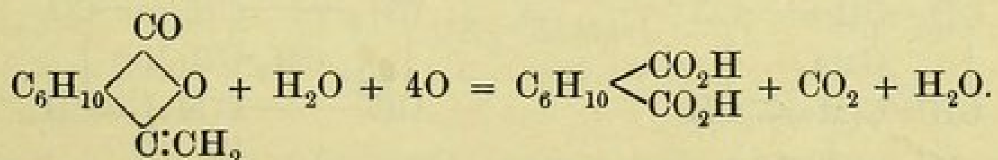
Umbellulonic acid. Enolic modification. Lactone.

The change from keto-acid to lactone also takes place, but to a less extent, when pure umbellulonic acid is distilled under diminished pressure. The explanation of the phenomenon, that a larger proportion of umbellulonic acid becomes converted into lactone on distilling the crude mixture of acids than when the pure acid alone is distilled, probably lies in the fact that the acids associated with the umbellulonic acid in the former case are of higher boiling point, and also give rise to anhydrides * which assist in the abstraction of water and formation of the lactone. This supposition receives support from the fact that umbellulonic acid was found to pass into the lactone on boiling with acetic anhydride.

This unusual change from keto-acid into unsaturated lactone, and *vice versâ*, is accompanied by a remarkable change in optical rotation, as the former has $[\alpha]_D + 377{\cdot}6°$ and the latter $[\alpha]_D - 210{\cdot}58°$.

From the formation of umbellulonic acid, $C_6H_{10}(CO_2H)CO{\cdot}CH_3$, by the oxidation of umbellulone, $C_{10}H_{14}O$, it would appear that the latter contains the complex $C_6H_{10}{<}\begin{matrix}CO\text{—}\\ CMe\end{matrix}{>}CH$.

The lactone, when shaken into an emulsion with water, is readily oxidised by potassium permanganate, giving a quantitative yield of a polymethylene dicarboxylic acid, $C_8H_{12}O_4$ (m. p. 120—121°; $[\alpha]_D - 89{\cdot}7°$), for which the name *umbellularic acid* is proposed.



The lactone. Umbellularic acid.

Umbellularic acid passes into the anhydride (b. p. 167—169°/50 mm.) when heated to about 150°, and is remarkably stable, for all further

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* Umbellularic acid is probably present.

attempts to break down the molecule resulted in failure. It was therefore impossible to obtain more direct evidence regarding the constitution of umbellularic acid, but the following considerations afford indirect evidence, which may be considered fairly conclusive.

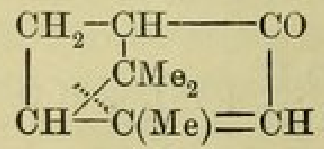
The general properties, and especially the great stability, of umbellularic acid indicate that it is one of the tetra-, penta-, or hexamethylene dicarboxylic acids. The latter consideration may be at once dismissed, as the four possible hexamethylene dicarboxylic acids are all known, and umbellularic acid does not agree in melting point with any of them. Of the methylpentamethylene dicarboxylic acids, only the 1-methyl-3 : 3-dicarboxylic acid is known, and of the dimethyltetramethylene * dicarboxylic acids only norpic acid, the 2 : 2-dimethyl-1 : 3-dicarboxylic acid, is known, with neither of which is umbellularic acid identical.

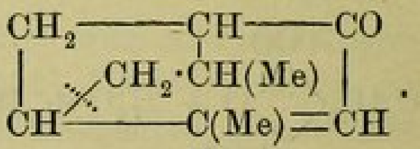
By the bromination of umbellulone and subsequent distillation of the product, Lees obtained, in addition to products containing bromine, a small amount of a hydrocarbon, $C_{10}H_{14}$, but expressed the opinion that this compound was derived from some substance other than umbellulone contained in the oil employed. This hydrocarbon has now been obtained from pure umbellulone, and has been identified as *p*-cymene.

Although the formation of *p*-cymene from umbellulone cannot very well be traced by any cycle of direct chemical changes, it would appear probable that the molecule of umbellulone contains a carbon skeleton which is capable of yielding a compound having methyl and *iso*propyl groups in the para-position without undergoing any profound structural change.

Any structural formula which would represent the constitution of umbellulone must, therefore, fulfil the following conditions. In the first place, it must contain a dimethyltetramethylene or a methylpentamethylene ring. United to this ring there must be the group $-CO\cdot CH\colon CMe-$, and, lastly, it must have a carbon framework capable of yielding, in a simple manner, paramethyl and *iso*propyl groups.

The only formulæ which are capable of fulfilling these conditions are the following :


I.


II.

Both of these compounds would yield paramethyl and *iso*propyl groups through the rupture of the diagonal bridge by the addition of

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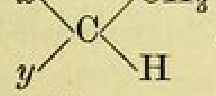
* The possibility of the occurrence of an ethyl group need not be considered, as this group does not occur among natural terpene derivatives and allied compounds.

hydrogen at the place indicated by the dotted line. A ketone of formula (I) contains a dimethyltetramethylene ring, and, on oxidation, would yield a norpic acid; whilst one of formula (II) contains a methylpentamethylene ring and would give 1-methylpentamethylene 3 : 5-dicarboxylic acid.

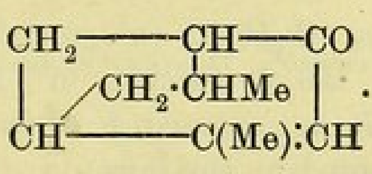
Umbellularic acid is, therefore, either a stereoisomeride of norpic acid or of 1-methylpentamethylene 3 : 5-dicarboxylic acid.

Norpic acid gives no anhydride and is apparently the *trans*-modification of inactive 2 : 2-dimethyltetramethylene 1 : 3-dicarboxylic acid. Umbellularic acid readily yields an anhydride, therefore it apparently represents a *cis*-modification, and it has not been found possible either to racemise it or to convert it into the corresponding *trans*-acid. It was therefore impossible directly to decide whether umbellularic acid is *l*-*cis*-norpic acid, but for the following reasons it appears extremely improbable. In the first place, if umbellularic acid is *l*-*cis*-norpic acid, then umbellulonic acid is *d*-pinononic acid, and this compound would not differ in boiling point from the inactive pinononic acid obtained by Wagner by the oxidation of pinene; whereas the methyl ester of Wagner's acid boils at 130—135°/14 mm. (*Ber.*, 1896, **29**, 881), and the ethyl ester of umbellulonic acid at about 130° under 20 mm. pressure.

In addition to this, if umbellulone is a keto-pinene (formula I), it would be expected that the norpic acid derived from it would become racemised, just as inactive norpic acid is obtained from active pinene; whereas umbellularic acid is not only optically active, but it has been found impossible to racemise it.

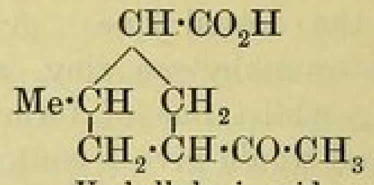
It would therefore appear probable that umbellularic acid is not *l*-*cis*-norpic acid, but *l*-1-methylpentamethylene 3 : 5-dicarboxylic acid, and that its persistent optical activity is due to the stable asymmetric group , which is contained in this compound, but not in norpic acid.

Umbellulone is therefore most probably represented by the formula

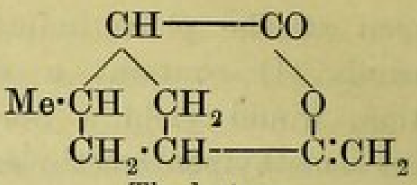


That is, "an *αβ*-unsaturated cyclic ketone containing two closed rings," as was indicated by the observations of Power and Lees (*loc. cit.*).

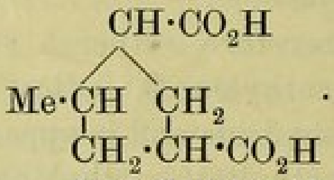
The products obtained by the oxidation of umbellulone would then have the following constitution:



Umbellulonic acid.



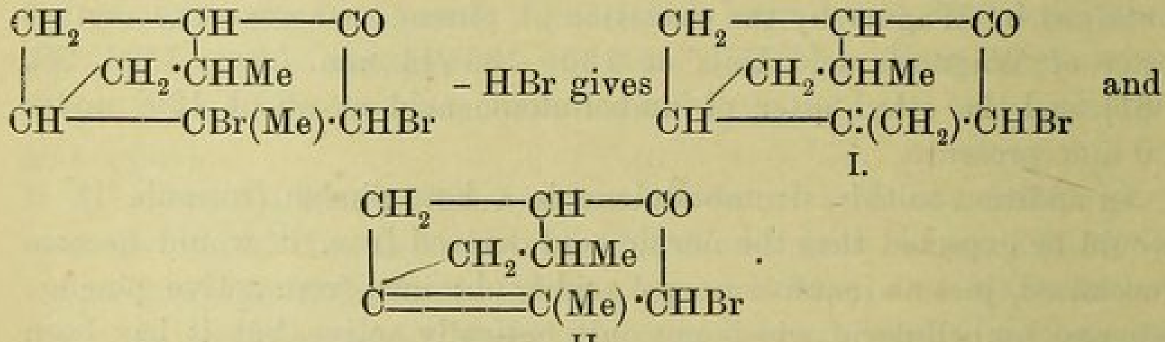
The lactone.



Umbellularic acid.

The above constitutional formula offers a ready explanation of the behaviour of umbellulone on treatment with bromine and subsequent distillation of the product.

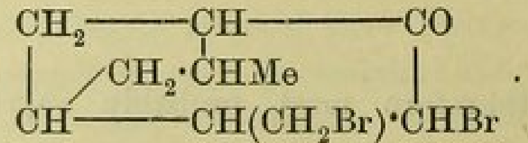
The liquid obtained by the treatment of umbellulone with bromine represents the compound formed by the direct addition of the halogen to the carbon atoms of the ethylenic linking. This compound, on distillation, eliminates hydrogen bromide in two ways:



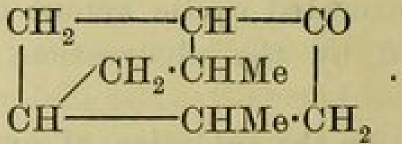
I.

II.

One of these unsaturated compounds (probably II) is incapable of recombining with the hydrogen bromide, and represents the monobromoumbellulone. The other compound immediately unites with the elements of hydrogen bromide, and yields the solid dibromodihydroumbellulone, which is therefore probably represented by the formula



The saturated ketone, $C_{10}H_{16}O$ (m. p. of semicarbazone, 177°), obtained by Lees by the reduction of monobromoumbellulone, $C_{10}H_{13}OBr$, and which it is proposed to name *a-dihydroumbellulone*, will therefore be represented by the formula



By the reduction of umbellulone itself with sodium and alcohol and subsequent oxidation of the resulting alcohol with a limited amount of chromic acid, a ketone, $C_{10}H_{16}O$ (m. p. of semicarbazone, 155—156°), is obtained, for which the name *β-dihydroumbellulone* is proposed. This ketone has an odour almost indistinguishable from that of pulegone, and is unsaturated; it is evident, therefore, that when umbellulone is reduced by sodium and alcohol, the ethylenic linking remains unattacked, whilst one of the carbon rings becomes ruptured by the addition of two atoms of hydrogen.

The rupture of one of the closed rings contained in bromodihydroumbellulone, $C_{10}H_{15}OBr$, was shown by Lees to take place when this compound is reduced by sodium and alcohol, but the "tetrahydroumbellulol" obtained is undoubtedly a mixture, as the ketone resulting from its oxidation yielded semicarbazones of m. p. 150° and 171° respectively. It is impossible to say whether this mixture consists of structural or only stereo-isomerides.

EXPERIMENTAL.

The umbellulone employed in this investigation was obtained from the essential oil of *Umbellularia Californica*, which had been specially distilled for this purpose. It was found to have the following constants: $d = 0{\cdot}9453$ at 20°/20°; α_D $-21°55'$ in a 1-dcm. tube.

Two thousand grams of this oil were freed from acids and phenols by shaking with potassium hydroxide, after which the washed and dried oil was submitted to a prolonged fractional distillation, and the following fractions were eventually collected. Below 190°, 190—200°, 200—215°, 215—225°, 225—235°, 235—245°, 245°+.

The fraction 215—225° weighed 580 grams; it had α_D $-34°4'$ in a 1-dcm. tube, and a specific gravity of 0·9600 at 15°/15°. On treatment with semicarbazide, it gave from 50—60 per cent. of the theoretical yield of semicarbazidodihydroumbellulonesemicarbazone (m. p. 216°), and evidently represented fairly pure umbellulone. Except where otherwise stated, this fraction boiling from 215—225° was the "umbellulone" used throughout this investigation.

Oxidation of Umbellulone with Potassium Permanganate.

One hundred and twenty grams of umbellulone were shaken into an emulsion with 1500 c.c. of water and the mixture cooled by the introduction of powdered ice. A 4 per cent. solution of potassium permanganate was then gradually added, with vigorous shaking, until the pink colour produced was only slowly discharged.

In this manner, it was found that an amount of permanganate equivalent to rather less than four atomic proportions of oxygen was required. After removing the manganese dioxide, the liquid was concentrated, and a small amount of non-volatile, neutral products removed by shaking with ether; the aqueous liquid was then made strongly acid by the addition of sulphuric acid, the precipitated acids extracted with ether, and the ethereal solution washed and dried. On removing the ether, an oil was obtained which was found to be entirely soluble in cold sodium carbonate solution.

Formation of the Unsaturated Lactone, $C_9H_{12}O_2$.

The acids obtained by the oxidation of the umbellulone were then slowly distilled under 20 mm. pressure, when the portion of the distillate which passed over below 180° formed a fairly mobile liquid, whilst that which boiled above this temperature was a very viscous, brown syrup. The whole of the distillate was dissolved in ether, the ethereal liquid shaken several times with sodium carbonate solution, washed, dried, and the ether removed. The residue was a pale yellow, mobile oil having a pleasant odour; when distilled under atmospheric pressure, it nearly all (35 grams) passed over between 217° and 220°, and was evidently identical with the lactone obtained by Lees (*loc. cit.*).

0·1647 gave 0·4356 CO_2 and 0·1192 H_2O. C = 70·96; H = 7·91.
$C_9H_{12}O_2$ requires C = 71·05; H = 7·88 per cent.

This lactone was found to have the following constants: b. p. 129—133°/50 mm. and 99—100°/15 mm.; $d = 1·0197$ at 20°/20°; a_D (without solvent) $-53°4'$ in a 25 mm. tube, whence $[a]_D$ $-210·58°$.

It is unsaturated, since it instantly decolorises a solution of bromine in chloroform, and, as it is readily oxidised by cold potassium permanganate, it is evident that the ethylenic linking contained in it must have been produced during the distillation of the products of oxidation.

Hydrolysis of the Lactone, $C_9H_{12}O_2$, *and Formation of a Saturated Keto-acid*, $C_9H_{14}O_3$.

Five grams of the lactone were dissolved in an excess of alcoholic potassium hydroxide and the mixture boiled for a few minutes. This liquid was then poured into water and acidified with sulphuric acid, after which it was extracted with ether and the ethereal solution washed, dried, and evaporated, when an almost colourless, viscous liquid was obtained.

This substance distilled at 193—195°/50 mm., and was a saturated compound, since it did not decolorise a dilute solution of bromine in chloroform.

0·1544 gave 0·3579 CO_2 and 0·1173 H_2O. C = 63·22 ; H = 8·44.

$C_9H_{14}O_3$ requires C = 63·52 ; H = 8·23 per cent.

The empirical formula of this acid, $C_9H_{14}O_3$, agrees with that of the hydroxy-acid which would have been expected to be produced by the hydrolysis of the lactone, $C_9H_{12}O_2$, but it is evident that it cannot be this compound, as it is saturated, whereas the lactone from which it is derived is unsaturated.

On treatment with hydroxylamine, this acid readily yields a crystalline oxime melting at 169—170°; it is therefore a keto-acid, and was, in fact, found to be identical with the umbellulonic acid subsequently described, from which it will be seen that the lactone is derived.

Examination of the Acids formed by the Oxidation of Umbellulone.

The acids which had been removed from the ethereal solution of the lactone by shaking it with sodium carbonate were liberated by the addition of sulphuric acid and extracted with ether. On removing the ether, a brown liquid was obtained, which consisted of a mixture of acids, and it was observed that when this was distilled under 20 mm. pressure it yielded a further quantity of lactone. This mixture of acids was dissolved in absolute ethyl alcohol, and esterified by passing dry hydrogen chloride through the boiling liquid for three hours. The esters were then precipitated by the addition of water and extracted with ether, the ethereal liquid freed from acids by shaking with sodium carbonate solution, washed, and dried. On removing the ether, a nearly colourless liquid was obtained, which was distilled under 20 mm. pressure, and the following fractions collected: 125—135°, 135—165°, 165—176°.

Isolation of Umbellulonic Acid.—The fraction 125—135° was the largest, and had a pleasant odour. It was distilled under the ordinary pressure, when the greater portion passed over as an almost colourless liquid at 237—241°, the temperature being most constant at 238—239°.

0·1326 gave 0·3236 CO_2 and 0·1085 H_2O. C = 66·56 ; H = 9·09.
0·1326 ,, 0·3237 CO_2 ,, 0·1086 H_2O. C = 66·58 ; H = 9·10.

$C_{11}H_{18}O_3$ requires C = 66·66 ; H = 9·09 per cent.

This ester was then hydrolysed and the acid extracted with ether in the usual manner. After removal of the ether, a nearly colourless, viscous liquid was obtained, which, after standing for some time, became solid. When crystallised from light petroleum, it separated in colourless prisms melting sharply at 102°.

0·1031 gave 0·2412 CO_2 and 0·0770 H_2O. C = 63·80 ; H = 8·29.

$C_9H_{14}O_3$ requires C = 63·53 ; H = 8·23 per cent.

This compound has been designated *umbellulonic acid.*

Umbellulonic acid dissolves sparingly in cold, but more readily in hot water. It is moderately soluble in ether and light petroleum, from which it can be crystallised, and is extremely soluble in the other ordinary organic solvents. A determination of its optical rotatory power gave the following result:

0·5343 dissolved in 25 c.c. of chloroform gave a_D $+16°8'$ in a 2-dcm. tube, whence $[a]_D$ $+377·6°$.

The fact that umbellulonic acid is a keto-acid is shown by the following experiment: half a gram of the acid was dissolved in an excess of potassium hydroxide and 0·3 gram of hydroxylamine hydrochloride added. After allowing the mixture to stand overnight, it was acidified with sulphuric acid, when a substance was precipitated which rapidly became solid. This, when recrystallised from ethyl acetate, was obtained in the form of minute, colourless prisms, which melted with decomposition at 169—170°. This substance was evidently the oxime of umbellulonic acid, and was identical in all respects with the oxime of the keto-acid obtained by the hydrolysis of the lactone.

0·1118 gave 0·2388 CO_2 and 0·0843 H_2O. C = 58·25; H = 8·37.
$C_9H_{14}O_2{:}NOH$ requires C = 58·37; H = 8·11 per cent.

As umbellulonic acid is the principal constituent of the mixture of acids obtained by the oxidation of umbellulone, and is also obtained by the hydrolysis of the lactone which is formed on distillation of this mixture, it would appear probable that this acid is the parent substance of the lactone; or, in other words, that the unsaturated lactone is formed by the elimination of water from the enolic modification of unbellulonic acid. If this supposition is correct, it would be expected that umbellulonic acid on distillation would pass to some extent into the lactone, and this was found to be the case.

Conversion of Umbellulonic Acid into the Lactone.—About 15 grams of umbellulonic acid were slowly distilled under 50 mm. pressure, when it was observed that some water was eliminated. The distillate was again distilled, then dissolved in ether, and the ethereal liquid, after being freed from acid by repeatedly shaking with sodium carbonate solution, was washed and dried. On evaporating the ether, a few grams of a mobile oil having the odour of the lactone were obtained. This was distilled under the ordinary pressure, when a liquid boiling from 218—221° was obtained, which was found to be identical with the lactone formed on distillation of the original mixture of acids prepared by the oxidation of umbellulone.

0·1236 gave 0·3222 CO_2 and 0·0919 H_2O. C = 71·09; H = 8·26.
$C_9H_{12}O_2$ requires C = 71·05; H = 7·89 per cent.

The proportion of the lactone thus obtained from the pure keto-acid was not so great as that given by the distillation of the original mixture of acids. It would therefore appear that the greater yield of lactone initially obtained is due to the influence of the other acids with which the umbellulonic acid is associated when first produced; these other acids having a higher boiling point, and some of them apparently giving rise to anhydrides. The correctness of this explanation is evident from the fact that these acids, when free from umbellulonic acid, yield no lactone on distillation, but, if again mixed with the keto-acid and distilled under suitable conditions, as much as 40—50 per cent. of the latter is converted into the lactone.

Examination of the Acids of Higher Boiling Point.—The fraction of esters boiling at 135—165°, prepared from the oxidation acids as previously described, was only small in amount. It evidently consisted of a mixture of substances, as it was found impossible to obtain from it any ester of constant boiling point.

The fraction of esters boiling at 165—176° was larger than the preceding one. It was fractionally distilled under 20 mm. pressure, when the greater portion passed over between 173° and 176°, principally at 174°, as a pale yellow oil having a very faint odour. On analysing this liquid, results were obtained which were not in agreement with any possible formula, and it therefore appeared to be a mixture of substances, although it distilled at such a constant temperature. It was hydrolysed by boiling with alcoholic potassium hydroxide, and the acids extracted with ether in the usual manner. On evaporating the ether, a rather viscid, brown oil was obtained, which, on standing for some weeks, became partially crystalline; it was spread on a porous tile and allowed to drain. The solid thus obtained was dissolved in benzene, the solution filtered, concentrated, and allowed to cool. The crystalline substance which separated was removed by filtration, well washed with benzene, and recrystallised from a large volume of this solvent, when it was obtained in nearly colourless, needle-shaped crystals melting at 164°. It was finally recrystallised from water, in which it is nearly insoluble in the cold, and was then obtained in large, colourless, needle-shaped crystals, which melted at 165° and sublimed without undergoing change.

0·1035 gave 0·2527 CO_2 and 0·0624 H_2O. C = 66·59; H = 6·70.
0·1132 „ 0·2774 CO_2 and 0·0700 H_2O. C = 66·83; H = 6·87.
$C_{10}H_{12}O_3$ requires C = 66·66; H = 6·66 per cent.

This acid cannot be derived from umbellulone; it is a saturated compound, and would therefore appear to be a benzene derivative. So far as can be ascertained, it is not identical with any compound hitherto described, and its formation would seem to indicate the presence in the essential oil of Californian Laurel of a substance which has not been identified.

The benzene mother liquors from this acid yielded a quantity of a-homopiperonylic acid, which was undoubtedy derived from the safrole contained in the original oil (Power and Lees, *loc. cit.*). Although other acids were certainly present in this mixture, and also in that obtained from the fraction of esters boiling at 135—165°/20 mm., they could not be separated. By the oxidation of umbellulone under the conditions employed, no derivative other than umbellulonic acid could therefore be isolated.

Oxidation of Pure Umbellulone.—Thirty grams of the umbellulone fraction were treated with semicarbazide, the resulting semicarbazido-semicarbazone washed with ether until free from adhering oil, then decomposed with dilute sulphuric acid, and the regenerated umbellulone isolated. This was subsequently oxidised with potassium permanganate under the same conditions as were employed when oxidising the umbellulone fraction of the oil. The resulting acids yielded some lactone on distillation, and, when converted into their ethyl esters, gave ethyl umbellulonate and a comparatively small proportion of a mixture of esters which distilled from 135—172°. Umbellulonic acid, therefore, is not the only product of the oxidation of umbellulone.

Oxidation of the Lactone. Formation of Umbellularic Acid.—Thirty grams of the pure lactone were shaken into an emulsion with 600 c.c. of water, and a 4 per cent. solution of potassium permanganate gradually added with constant shaking, the mixture being kept cool by immersion in cold water. When an amount of permanganate equivalent to four atomic proportions of oxygen had been added, the pink colour was no longer discharged. A moderate excess of the oxidising agent was then added, and the mixture allowed to stand for some hours, when apparently no more potassium permanganate became decolorised. The excess was then removed by means of sulphurous acid, and the precipitated manganese dioxide was separated by filtration. The liquid was subsequently concentrated to a small bulk, acidified with sulphuric acid, and repeatedly extracted with ether; the ethereal liquid was then washed, dried, and the ether removed. The residue was an almost colourless syrup, which, after standing for a few hours, became entirely crystalline.

When fractionally crystallised from benzene, this acid was found to be homogeneous, as all the fractions yielded colourless prisms which melted sharply at 120—121°.

0·1062 gave 0·2176 CO_2 and 0·0661 H_2O. C = 55·88; H = 6·91.

$C_8H_{12}O_4$ requires C = 55·81; H = 6·98 per cent.

0·5111 dissolved in 25 c.c. of chloroform had a_D $-3°40'$ in a 2-dcm. tube, hence $[a]_D$ $-89·7°$.

This acid has been designated *umbellularic acid*, and, for reasons which have been fully discussed in the introductory portion of this paper, it is probably 1-methylpentamethylene 3 : 5-dicarboxylic acid.

Umbellularic acid is moderately soluble in benzene and almost insoluble in light petroleum, but dissolves with great readiness in the other ordinary organic solvents. When crystallised from water, in which it is moderately soluble, it separates in needle-shaped crystals, which melt at 85° and contain one molecule of water of crystallisation.

0·6586 of the acid which had been crystallised from water and dried in the air, when heated for two hours at 100°, suffered a decrease in weight equivalent to 10·1 per cent.; one molecule of water requires a loss of 9·4 per cent. On further heating, it continued slowly to decrease in weight, owing to sublimation. The hydrated acid was analysed:

0·0975 gave 0·1760 CO_2 and 0·0635 H_2O. C = 50·16 ; H = 7·37.
$C_8H_{12}O_4,H_2O$ requires C = 50·52 ; H = 7·37 per cent.

When umbellularic acid is heated to about 150°, water is eliminated, with the formation of the anhydride.

Umbellularic anhydride is a colourless liquid, which distils at 167—169°/50 mm., and on boiling it with water umbellularic acid is regenerated.

0·1342 gave 0·3061 CO_2 and 0·0800 H_2O. C = 62·21 ; H = 6·62.
$C_8H_{10}O_3$ requires C = 62·34 ; H = 6·49 per cent.

The umbellularic acid was esterified by boiling it with an excess of absolute ethyl alcohol containing a small proportion of sulphuric acid, but only a relatively small yield of ester could be obtained.

Diethyl umbellularate is a colourless liquid, possessing a fruity odour, and distils at 158—160°/50 mm.

0·1335 gave 0·3077 CO_2 and 0·1078 H_2O. C = 62·86 ; H = 8·97.
$C_{12}H_{20}O_4$ requires C = 63·16 ; H = 8·77 per cent.

Umbellularic acid is a very stable substance. It is not appreciably oxidised by potassium permanganate at 60°, and is recovered unchanged after boiling for ten hours with eight times its weight of a mixture of three parts of fuming nitric acid and one part of water. After boiling for five hours with undiluted fuming nitric acid, besides unchanged umbellularic acid, only a trace of oxalic acid could be identified. It is unaltered by heating with concentrated hydrochloric acid at 190° for five hours. An attempt was made to prepare a bromoumbellularic acid by heating together the dry acid, red phosphorus, and bromine in the requisite proportions, but after the formation of the acid bromide was complete only a very slight action occurred. The mixture was heated on the water-bath for two hours, then treated with ethyl alcohol, and the resulting esters freed from bromine. On distillation, these esters were found to boil between 90° and 180°/20 mm., but the greater portion passed over at the boiling point of ethyl umbellularate, and only contained a trace of bromine. It was therefore not found possible to obtain a bromoumbellularic acid from the amount of material available.

Bromination of Pure Umbellulone.

Forty grams of the umbellulone fraction were treated with semicarbazide, and the resulting semicarbazido-semicarbazone washed with ether until free from adhering oil, after which it melted at 216° and was evidently pure. It was then decomposed with dilute sulphuric acid and the regenerated umbellulone isolated. This was then dissolved in chloroform and treated with bromine in the manner described by Lees (*loc. cit.*). The resulting dibromide was then distilled under 20 mm. pressure, when it yielded products identical with those obtained by Lees by the bromination of the umbellulone, namely: a limpid liquid boiling below 130°/20 mm.; a heavy, pale yellow oil (b. p. 140—145°/20 mm.) having a very pungent odour; and the solid dibromodihydroumbellulone (m. p. 119°).

The liquid boiling at 140—145°/20 mm. was analysed:

0·1482 gave 0·2826 CO_2 and 0·0775 H_2O. C = 52·00; H = 5·81.

$C_{10}H_{13}OBr$ requires C = 52·40; H = 5·68 per cent.

This unsaturated monobromoumbellulone was treated with hydrogen bromide under varying conditions, but it was found impossible to cause it to combine with the latter. When reduced with zinc dust and acetic acid, it yielded the saturated ketone, $C_{10}H_{16}O$, obtained in a similar manner by Lees (*loc. cit.*), but its semicarbazone was found to have the melting point of 177°, and not 171—172°, as stated by him. This ketone has been designated *a-dihydroumbellulone.*

The fraction boiling below 130° was distilled under the ordinary pressure, and afterwards over metallic sodium, when it was finally obtained as a colourless liquid boiling at 176—177° and having the odour of cymene.

0·1233 gave 0·4052 CO_2 and 0·1156 H_2O. C = 89·60; H = 10·42.

$C_{10}H_{14}$ requires C = 89·55; H = 10·45 per cent.

Eighty grams of umbellulone were brominated in order to obtain a further quantity of this hydrocarbon, and about 8 c.c. of it were thus obtained. Five grams of this were oxidised by boiling for a week with a mixture of 47 grams of potassium bichromate, 65 grams of sulphuric acid, and 200 c.c. of water. The white, insoluble precipitate which had been formed was then removed by filtration, dissolved in ammonia, the solution filtered, and the acid reprecipitated by the addition of hydrochloric acid. This precipitate was collected, well washed with hot water, and dried, after which, when heated, it sublimed without melting.

0·1108 gave 0·2340 CO_2 and 0·0375 H_2O. $C = 57·60$; $H = 3·76$.
$C_8H_6O_4$ requires $C = 57·83$; $H = 3·61$ per cent.

This substance was evidently terephthalic acid, as it gave a dimethyl ester which melted sharply at 140°. The hydrocarbon from which this acid was obtained is therefore *p*-cymene.

All the compounds obtained by Lees (*loc. cit.*) by the bromination of the umbellulone, namely, a hydrocarbon, $C_{10}H_{14}$, monobromoumbellulone, $C_{10}H_{13}OBr$, and dibromodihydroumbellulone, $C_{10}H_{14}OBr_2$, were therefore derived from the umbellulone itself, and not from any impurity contained in the fraction of oil employed.

Reduction of Umbellulone.

Twenty-five grams of umbellulone were dissolved in 100 c.c. of absolute alcohol, and 18 grams of sodium in small pieces were gradually introduced. The liquid was not cooled, but allowed to boil vigorously. When all the sodium had dissolved, the mixture was distilled in steam, and the oil contained in the distillate isolated by extracting with ether. After removal of the ether, the residual oil was found to be highly unsaturated, as it instantly decolorised a solution of bromine in chloroform. The reduction was therefore repeated, and the oil isolated in a similar manner, but it was found to be still unsaturated. It was then distilled under the ordinary pressure, when the greater portion of it was obtained as a colourless liquid, boiling at 208—210°, and having a pleasant, somewhat camphoraceous odour. This liquid was unsaturated, and on analysis gave results which indicated it to be a mixture of compounds of the formulæ $C_{10}H_{16}O$ and $C_{10}H_{18}O$ respectively.

β-Dihydroumbellulone.—Fifteen grams of the liquid boiling at 208—210° were oxidised with a mixture of 20 grams of potassium bichromate, 17 grams of sulphuric acid, and 100 c.c. of water. After heating for about three-quarters of an hour, the bichromate had become completely reduced, and the mixture was then distilled in steam. The distillate was extracted with ether, and, on removing the latter, about 6 grams of a pale yellow oil were obtained. When this was distilled under the ordinary pressure, it passed over between 204° and 209° as an almost colourless liquid, and had an odour closely resembling that of pulegone.

0·1398 gave 0·4032 CO_2 and 0·1337 H_2O. C = 78·66; H = 10·63.
$C_{10}H_{16}O$ requires C = 78·95; H = 10·53 per cent.

This substance was unsaturated, as it instantly decolorised a dilute solution of bromine in chloroform. It is isomeric with the *a*-dihydroumbellulone obtained by the reduction of monobromoumbellulone, and is therefore *β-dihydroumbellulone*. As only 6 grams of this ketone, $C_{10}H_{16}O$, had been obtained by oxidising 15 grams of the mixture of alcohols, $C_{10}H_{16}O$ and $C_{10}H_{18}O$, it is evident that the former alcohol must have been completely destroyed.

The oxime of β-dihydroumbellulone was prepared in the usual manner, and found to be a liquid boiling at about 130° under 25 mm. pressure. The semicarbazone of this ketone was first obtained as a liquid, but after standing for some time it became crystalline. It was recrystallised from a mixture of ethyl acetate and light petroleum, after which it melted at 155—156°.

0·1008 gave 0·2330 CO_2 and 0·0838 H_2O. C = 63·04; H = 9·24.
$C_{11}H_{19}ON_3$ requires C = 63·16; H = 9·09 per cent.

Tetrahydroumbellulone, $C_{10}H_{18}O$.

In order that tetrahydroumbellulone might be compared with the known ketones of the formula $C_{10}H_{18}O$, it was prepared by oxidising "tetrahydroumbellulol" (compare Lees, *loc. cit.*) in the usual manner.

This ketone is a colourless liquid, boiling at 197—198°, and has a pleasant, somewhat camphoraceous odour.

0·1185 gave 0·3371 CO_2 and 0·1235 H_2O. C = 77·58; H = 11·58.
$C_{10}H_{18}O$ requires C = 77·92; H = 11·69 per cent.

The semicarbazone was prepared from it, and crystallised once from alcohol, when it was obtained in colourless prisms melting at 148°.

0·1161 gave 0·2662 CO_2 and 0·1060 H_2O. C = 62·53; H = 10·14.
$C_{11}H_{21}ON_3$ requires C = 62·56; H = 9·95 per cent.

On fractional crystallisation, this was found to be a mixture of isomeric semicarbazones, as substances of the melting point 171° and 150° respectively were obtained from it.

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