

soluble in water. The analysis shows it to be 2-thio-4-ethylidene hydantoin. Nitrogen (Kjeldahl).

Calc. for $C_6H_8ON_2S$: N = 19.72%. Found: N = 19.57%.

PITTSBURGH, PA.

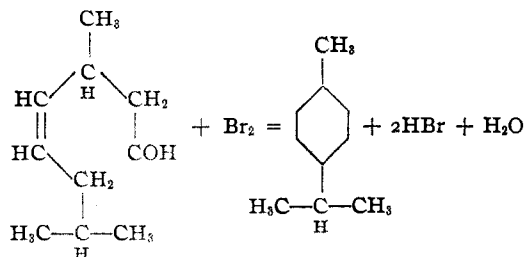
[CONTRIBUTION FROM THE LABORATORY OF THE DODGE & OLCOTT Co.]

ISOPULEGOL PHOSPHONIC ACID.

By FRANCIS D. DODGE.

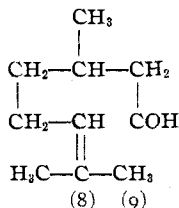
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The characteristic constituent of the essential oil of citronella is an aldehyde, having the composition $C_{10}H_{18}O$, and known as citronellal aldehyde, or citronellal. In an investigation of this oil, in 1889,¹ the writer found that this aldehyde was an aliphatic or open-chain compound, singly unsaturated, and hence homologous with acrolein. This was one of the first examples of open-chain compounds closely related to the terpene series, and the first clue to its structure was afforded by the conversion into *p*-cymene, an aromatic hydrocarbon frequently found as the final transformation product of many terpene derivatives. To explain this reaction, the following formula was suggested:



which would appear to locate the relative positions of the methyl and isopropyl groups, but leaves the position of the unsaturation undetermined. The location of the double bond was deduced from the apparent formation of iso-valerianic acid on oxidation. Semmler² also reported this acid as an oxidation product of the aldehyde, but this was found later to be erroneous.

In 1896, citronellal was made the subject of an investigation by Tiemann



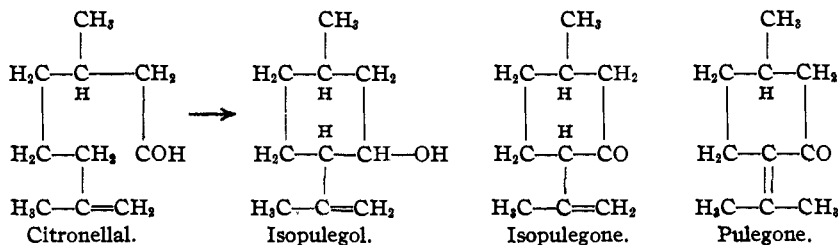
¹ *Am. Chem. J.*, 11, 456 (1889).

² *Ber.*, 24, 201 (1891).

and Schmidt.¹ By careful progressive oxidation, they obtained methyl adipic acid and acetone, which result pointed to the above formula.

There are, however, reasons for believing the double bond to be (8)-(9), and that a rearrangement occurs during the oxidation.

The conversion of citronellal into a cyclic isomer was also accomplished by Tiemann and Schmidt, and its relation to the menthol group was thus established, the structure of isopulegone being subsequently cleared up by Harries and Roeder.²



Among the products of the action of phosphoric anhydride on citronellal, the writer found a crystalline acid, containing phosphorus.³ This compound, called provisionally "citronellal phosphoric acid," but which now might more properly be termed "isopulegol phosphonic acid," has the composition, $\text{C}_{10}\text{H}_{19}\text{PO}_4$, and is formed when phosphoric anhydride acts on citronellal, in presence of a little water, as, *e. g.*, in moist ether solution:



The most favorable conditions for the reaction have not yet been determined, the yield being at best about 25% of the theoretical.

This compound is a strong monobasic acid, yielding a series of well-defined salts, which are, in general, remarkably crystalline. It is difficultly soluble in water, but easily in alcohol and chloroform, and melts at 181-182°. From alcohol, the acid crystallizes in large, transparent plates, which were examined by the writer, in 1891, in the laboratory of Prof. Rosenbusch, at Heidelberg.

System: Mono-symmetric.

$$a : b : c :: 1.9828 : 1 : 1.9745. \quad \beta = 57^\circ 50'.$$

$$\text{Planes: } (001) \text{ oP, } (100) \infty \bar{\text{P}}\infty, (011) \infty \text{ P.}$$

The crystals are tabular, (001) being the principal plane. A plane of the orthodoma zone was observed on only one crystal. The substance however, possesses a well-defined cleavage according to this plane, from which the value of the axis *a* was calculated. No twinning was observed.

$$\begin{array}{l}
 \text{Angles: } (001) : (100) \quad 57^\circ 50' \\
 \quad \quad (001) : (011) \quad 59^\circ 6' 30'' \\
 \quad \quad (100) : (10\bar{1}) \quad 60^\circ 52' \\
 \quad \quad (011) : (01\bar{1}) \quad 61^\circ 49' \text{ (calc.)}
 \end{array}$$

¹ *Ber.*, 29, 904 (1896).

² *Ibid.*, 32, 3357 (1899).

³ *Am. Chem. J.*, 12, 553 (1890).

The cleavage according to the basis is perfect, large sections of any desired thickness being readily obtained. There is also a well-defined cleavage according to (101) but none in the clinodomal zone. The plane of the optic axes is perpendicular to the plane of symmetry, and inclined to the basis. Double refraction, strong, negative. Horizontal dispersion, weak. The angle of the optic axes is small.

Salts.—The potassium salt is easily obtained, in large, transparent plates:

1.000 g. pure acid, titrated with 0.5 *N* KOH, required 8.55 cc. (calc. for $C_{10}H_{18}PO_4$, 8.55 cc.). The solution was allowed to crystallize in desiccator, and the product recrystallized, and dried in air. 1.147 g. at 100° lost 0.1976 g., or 17.2% (calc. for $KC_{10}H_{18}PO_4 \cdot 3H_2O$: 16.56%). The anhydrous salt yielded on ignition 43.44% KPO_3 ; calc. 43.38%.

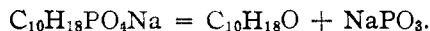
Attempts to prepare a di-potassium salt were unsuccessful. The sodium salt also crystallizes in large plates, much resembling those of the acid. The alkaline salts are remarkably stable; no decomposition was noticed on long boiling of the aqueous solutions.

The magnesium salt is readily soluble in water, and the crystals are like the sodium salt; the calcium salt is less soluble, but crystallizes well from hot water. The silver salt is at first a curdy precipitate, which soon becomes crystalline, and under the microscope exhibits characteristic forms.

At the time of discovery, very little could be inferred as to the structure of this acid. The formula proposed was merely empirical. The reaction appeared to be peculiar to citronellal, yet the stability and general properties of the acid made it improbable that it could be considered a true member of the citronellal series.

In 1894, Marsh and Gardner¹ described two crystalline acids, obtained from camphene by reaction with phosphorus pentachloride, and subsequent hydrolysis: an α acid, $C_{10}H_{17}PO_3 \cdot \frac{1}{2}H_2O$ (m. p. about 160°), and a β acid, $C_{10}H_{17}PO_3$ (m. p. about 167°). These acids showed some resemblance to the compound from citronellal, yet were evidently different bodies, and their structure is still unexplained.

Tiemann's discovery of the isopulegol reaction, however, suggested the possibility that the acid might be really a derivative of isopulegol, or a similar cyclic nucleus, and a study of the decomposition of the sodium salt on heating showed that this was probably the case.



This decomposition proceeds smoothly, and at a comparatively low temperature. For example, 9 g. of the dry sodium salt, in a small distilling flask, were heated cautiously until white fumes appeared. After cooling, 5 g. water were added, and the mixture distilled to dryness. The residue was again heated to fumes, distilled with water, etc., until no more oil was obtained. The product, after redistillation with water,

¹ *J. Chem. Soc.*, 65, I, 35 (1894).

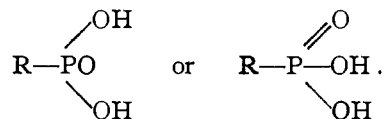
was a light colorless oil, with an odor resembling menthone. It was readily soluble in 70% alcohol, and by quantitative acetylation and saponification, showed an alcohol content of 92.5% $C_{10}H_{18}O$.

Chromic acid solution reacts immediately with the alcohol, and the oxidation product has the characteristic odor of pulegone. 1 g. treated with the calculated amount of chromic acid in 25 cc. of water, yielded, on steam distillation, 0.5 g. oil, which gave a well-crystallized semicarbazone, melting at about 171° . (Tiemann obtained from isopulegone a mixture of semi-carbazones, melting at 173° .)

The alcoholic product of the decomposition of the sodium salt is then most probably isopulegol, and the formation of the acid from citronellal is due to a ring-condensation analogous to that occurring with acetic anhydride.

As to the structure of the acid, the following points may be considered:

1. The acid is not hydrolyzed by hot alcoholic potassium hydroxide, nor by hot dilute sulfuric acid. Hence the PO_3 group is directly connected to carbon, and the compound must be regarded as a phosphonic acid,



Normal phosphonic acids are, however, dibasic, while the acid in question is sharply monobasic, and a di-potassium salt could not be prepared. It is to be noted that the camphene phosphonic acids of Marsh and Gardner¹ appear also to be monobasic.

2. The ready formation of isopulegol would lead to the assumption of a secondary hydroxyl group in the acid. Boiling acetic anhydride, however, leaves the acid unaltered; chromic acid and cold dilute permanganate are also without action, so that the presence of hydroxyl (except possibly in tertiary combination) seems improbable. Nor could any indications of a ketonic group be obtained: no oxime, or phenylhydrazone could be prepared from the acid. Moreover, if a CO group were present, menthone, or an isomeric ketone should result from the decomposition of the alkaline salt.

3. Isopulegol behaves as an unsaturated secondary alcohol, but the phosphonic acid appears to be a saturated compound. A solution of the sodium salt does not decolorize bromine water in the cold, nor, as already mentioned, does it reduce a weak permanganate solution. On heating with bromine water, a slow reaction occurs, and some of the acid crystallizes out unchanged.

The position of the phosphonic group is, of course, unknown, and the data available will hardly warrant further conjectures as to the molecu-

¹ *Loc. cit.*

lar design of this acid. It is evident, however, that isopulegol phosphonic acid is a peculiarly characteristic derivative of citronellal. The rearrangement of the open-chain aldehyde to a cyclic secondary alcohol is unique and the fact that no other aldehyde so far examined has yielded an analogous compound, is easily explained.

It appeared, then, not improbable that this reaction might be utilized for the detection of citronellal in oils in the presence of other aldehydes, especially as so far no very satisfactory method has been suggested.

For example, we find, as frequently occurring constituents of various essential oils, three closely related aldehydes:

1. Decylic aldehyde	$C_{10}H_{20}O$ (saturated)	(normal chain) (?)
2. Citronellal	$C_{10}H_{18}O$ (unsaturated)	(terpene chain)
3. Citral	$C_{10}H_{16}O$ (doubly unsaturated)	(terpene chain)

The first has been found in the oils of orange, citronella, and ginger; the second, in the oils of citronella, eucalyptus, and lemon; the third, in oils of lemon, orange, lemongrass, verbena, etc.

The separation of these aldehydes can be accomplished by utilizing their varying behavior with bisulfite solution. The saturated decylic aldehyde forms a normal compound, $Ald.NaHSO_3$, slightly soluble, and decomposed by sodium carbonate. Citronellal also yields the normal $Ald.NaHSO_3$, with similar properties, but, on warming with excess of bisulfite, or in dilute acid solution, a sulfonate is formed, which is not decomposed by sodium carbonate or hydroxide. Citral forms at least three compounds: in cold, acid solution, $Ald.NaHSO_3$, unstable, decomposed by sodium carbonate; in cold, strongly alkaline solution, $Ald.2NaHSO_3$, very soluble, decomposed by cold hydroxide, not by carbonate; in warm acid solution, $Ald.2NaHSO_3$, not decomposed by carbonate nor hydroxide.

Hence, if we treat a mixture of the aldehydes (or an oil containing them) with a solution of sodium sulfite, containing some bicarbonate (to neutralize the alkali liberated), citral dissolves, and can be recovered, in good yield from the solution, by treatment with cold, strong sodium hydroxide. From the portion insoluble in neutral sulfite, decylal and citronellal can then be precipitated by slightly acid bisulfite, in the cold. If the solution is heated, citronellal redissolves slowly and permanently, while the normal bisulfite compound of the saturated aldehyde generally crystallizes from the solution on cooling. From the crystals, decylic aldehyde can be obtained by careful treatment with bicarbonate.¹

In this way, citral and decylic aldehyde can generally be isolated and identified without much difficulty, but citronellal cannot be recovered from the solution, and the positive detection of the latter in the presence of a saturated aldehyde appears impracticable.

¹ Dodge, *8th Congr. Appl. Chem.*, 6, 77 (1912).

The occurrence of citronellal in oil of lemon has been reported by various observers. Doebner,¹ applying his general aldehyde reaction with pyroracemic acid and β -naphthylamine, obtained a mixture of crystalline naphthocinchoninic acids, which could be separated into the citral derivative, melting at 197° , and the citronellal derivative, melting at 225° , the latter in larger amount. Tiemann² fractionated the oil, and from the high-boiling sections, by the sulfite method, could isolate a small amount of aldehyde, identified as citronellal by the naphthocinchoninic acid. The amount present was estimated at 0.4% (or about $1/10$ of the citral). Schimmel and Co.³ consider the average aldehyde content of the oil to be: citral, 4.8%; citronellal, 1.2%. Burgess,⁴ however, was unable to confirm the presence of citronellal, but found a small amount of a lower saturated aldehyde, apparently octoic aldehyde. von Soden and Rojahn,⁵ from 10 kg. of oil, obtained besides citral, 10–15 g. of a mixture of aldehydes, apparently octoic and nonoic aldehydes and citronellal.

It appears possible that the relatively large amount of citronellal found by Doebner may be due to a confusion with the lower aldehydes, the presence of which was at that time unsuspected. Or, on the other hand, there may be a considerable loss of citronellal involved in the sulfite separation used by Tiemann, and von Soden and Rojahn.

In the hope of obtaining further information on this point, the phosphoric reaction described above was tried on the natural oil of lemon, and also on the commercial concentrated oil, containing 45–50% aldehydes, but in neither case could the formation of the isopulegol phosphonic acid be detected, and the conclusion appears warranted that the citronellal content of oil of lemon is quantitatively insignificant.

Summary.

The writer has made a further examination of the crystalline acid, containing phosphorus, resulting from the reaction of phosphoric anhydride on citronellal.

The compound is very stable, and yields a series of well-crystallized salts. By dry distillation of the sodium salt, a volatile alcohol was obtained, apparently identical with the isopulegol of Tiemann, a cyclic isomer of citronellal. The acid is then most probably a phosphonic acid of isopulegol, and hence a very characteristic derivative of citronellal.

Attempts to demonstrate the presence of citronellal in oil of lemon, by means of this reaction, were unsuccessful.

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¹ *Arch. Pharm.*, **232**, 688 (1894).

² *Ber.*, **32**, 822 (1899).

³ S. & Co., *Ber.*, **1900**, Oct. 25.

⁴ *J. Chem. Soc.*, **79**, 171 (1901).

⁵ *Ber.*, **34**, 2809 (1901).