Lack of time and material prevented us from carrying the purification of the levo form further.

An attempt to separate the fumaroid form of the α-α'-dimethyladipic acid (m. 143°) into optical isomers by means of its brucine salt was unsuccessful. It is undoubtedly a "meso" form, optically inactive by internal compensation.

Summary.

By using magnesium amalgam for the preparation of magnesium ethylate and condensing ethylene bromide with malonic ester by means of the latter the yield of butanetetracarboxylic ester has been greatly improved and this compound is now rather easily accessible.

The *dl*,α,α'-dimethyladipic acid (m. 70°) has been resolved into its optical components, of which the dextro form has been obtained in a state of purity. It melts at 104–105° and has a rotation $(\alpha)_D^{28°} = +31.3°$ in a 10 per cent. alcoholic solution.

The levo form was only obtained in a relatively impure form, melting over a wide range and given a rotation $(\alpha)_D = -23.4°$.

The "meso" form of α,α'-dimethyladipic acid (m. 143°) gave no indication that it could be separated into optically active components by crystallization with brucine.

The separation of the racemic α-α'-dimethyladipic acid into its optically active components definitely disproves the view expressed by Lean[1] that the carbon atoms are so united in this and similar cases that optical isomerism is impossible. These acids exist in four forms in close analogy with the four tartaric acids and in strict accord with the theory. The synthesis of laurolene from α-α'-dimethyladipic acid will be described in a subsequent paper.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. III. OXIDATION PRODUCTS OF *l*- AND *d*-LAURÓLENE.[2]

BY WILLIAM A. NOYES AND C. G. DERICK.

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Levo-laurolene.

In a previous paper[3] it was shown that laurolene, when prepared from the nitroso derivative of aminolauronic anhydride by boiling with sodium hydroxide solution, always gave an optically negative hydrocarbon,

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[1] *Loc. cit.*

[2] Abstract of one part of a thesis presented by Mr. Derick to the Graduate School of the University of Illinois in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[3] Noyes and Derick, THIS JOURNAL, 31, 670.

C_8H_{14}. This work has been repeated and the hydrocarbon from different preparations gave $(\alpha)_D^{29°} = -15.72$ and $(\alpha)_D^{27°} = -18.13$. The value of the negative rotation changes with the method of preparation, as Crossley and Renouf[1] have previously shown. The higher value of the rotatory power was found when the hydrocarbon was distilled from its sodium hydroxide solution as rapidly as it was formed. It would seem that longer contact with the alkaline solution causes the racemization of a part of the laurolene.

This product upon oxidation gave the diketone mentioned in the first article. Contrary to the statement made at that time, the diketone does not easily condense. In fact it gives very constant boiling point determinations with no evidence of decomposition. The boiling point,[2] under 750 mm. pressure, is 204° (cor.). The optical activity was found to be $(\alpha)_D^{36.5°} = 0.53°$ while that of the previous preparation[3] was found to be $(\alpha)_D^{25°} = -8.47°$. Hence it is evident that the diketone, like the hydrocarbon, possesses an optical rotation which varies with the method of preparation.

The diketone forms an oily dioxime, which gave upon analysis:

Calculated for $C_8H_{16}N_2O_2$: N, 16.27; found: N, 15.45.

An oily monophenylhydrazone was obtained which gave upon analysis:

Calculated for $C_{14}H_{20}ON_2$: N, 12.07; found: N, 12.72.

Although these analyses were made with products which could not be carefully purified they are sufficiently accurate to show that the oxidation product of *l*-laurolene is a diketone.

In the case of the semicarbazone, more satisfactory results were obtained in the form of a white crystalline product melting at 194° (cor.) The substance separates very slowly from the solution in which it is prepared. It was not found possible to recrystallize it. The portion used for the melting point and analysis was washed thoroughly with warm water (about 60°) till free from chlorides. The analysis gave:

Calculated for $C_{10}H_{20}O_2N_6$:	C, 46.87	H, 7.82	N, 32.81
Found:	46.50	8.80	31.71

These analyses were made with very small amounts, since the yield of the disemicarbazone was very small and much time is required for the preparation. But the results prove beyond a doubt that the oxidation product of laurolene is a diketone.

Attempts to condense the diketone by heating alone and with sodium hydroxide were unsuccessful. Phosphorus pentoxide gave a very small yield of a product, boiling at 143°, which could not be further investigated.

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[1] Crossley and Renouf, *J. Chem. Soc.*, 89, 38.

[2] This was determined by Sivolobov's method, *Ber.*, 19, 795, as modified by Mulliken, "A Method for the Identification of Pure Organic Compounds," p. 222.

[3] Noyes and Derick, *Loc. cit.*

A diketone of the formula $C_8H_{14}O_2$ must necessarily be an open chain compound. This view of its structure receives strong confirmation from the synthesis of laurolene (see the following paper) and from the boiling point and specific gravity of isomeric diketones.

	Boiling point.	Specific gravity.	
2,3-Octanedione $CH_3(CH_2)_4COCOCH_3$	172–173°	732 mm.	.....[1]
3,4-Dimethyl-2,5-hexanedione, $CH_3COCH(CH_3)CH(CH_3)COCH_3$	210°	....	.....[2]
3-Methyl-2,4-heptanedione, $C_3H_7COCH(CH_3)COCH_3$	89–90°	20 mm.	0.955[3]
3-Methyl-2,6-heptanedione, $CH_3COCH(CH_3)CH_2CH_2COCH_3$	203–204°	750 mm.	0.988[4]

In general the specific gravities and boiling points increase as the carbonyl groups are further apart.

The presence of the acetyl group in the diketone was also demonstrated by the formation of bromoform when it is treated with sodium hypobromite. The diketone reduces a neutral solution of potassium permanganate instantly, as acetone does.

Dextro-laurolene.

In our previous article on laurolene, we stated that the direct decomposition of the hydrochloride of aminolauronic acid by means of sodium nitrite always gave an optically positive hydrocarbon, C_8H_{14}. Similar results have been obtained since the publication of the above article. The rotation of laurolene prepared in this manner being $(\alpha)_D^{26.2°} = +28.15°$. The rotation of the hydrocarbon varies, therefore, with the method of preparation as was found to be the case with the optically negative laurolene. The density of the optically positive laurolene was found to be $d_{4°}^{15°} = 0.8030$ and $d_{20°}^{20°} = 0.7991$. The boiling point was 120.3–121° at 750 mm. Thus levo- and dextro-laurolene possess the same composition, boiling points and density.

Oxidation of dextro-laurolene by the same method employed with levo-laurolene gave a diketone. It was also purified by fractional distillation with a Sprengel pump and distilled from 70–80° under ½ to 1 mm. pressure. The product gave upon analysis:

Calculated for $C_8H_{14}O_2$: C, 67.60 ; H, 9.86
Found: C, 66.53, 66.50, 67.9; H, 9.90, 10.15, 10.60.

The analysis of the diketone was very difficult. If burned in an open boat the results were uniformly too low, while if burned in a bulb with copper oxide it was exceedingly hard to burn the last traces of carbon. Extra long burning with some copper oxide in the bulb with the diketone gave the last analysis, which is within the limits of experimental error

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[1] Ponzio and Prandi, *J. prakt. Chem.*, (2) **58**, 402.

[2] Demétre Vladesco, *Bull. soc. chim.*, (3) **6**, 809.

[3] Bouveault and Bongert, *Ibid.*, **27**, 1087.

[4] Noyes and Derick, THIS JOURNAL, **31**, 672.

for carbon. The results show that a diketone is formed which boils at the same temperature as the diketone from levo-laurolene.

Several determinations of the optical activity of the diketone from dextro-laurolene, as above prepared, showed it to be optically inactive. Experiments were performed with the diketone in the pure form as well as in 20.5 per cent. ethereal and alcoholic solutions.

As in the case with diketone from levo-laurolene, the diketone from dextro-laurolene gave an oily oxime and phenylhydrazone.

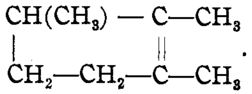
The semicarbazone was a white crystalline product which separated from water after long standing. It melted fairly sharply at 192° (cor.) and appeared to resolidify and again melt at 225° (cor.). A very recent preparation gave a semicarbazone which melted at 228° (cor.) with no evidence of a preliminary melting. The analysis of the product melting first at 192° gave:

Calculated for $C_{10}H_{20}O_2N_6$: N, 32.81. Found: N, 33.25

It is evident that the oxidation product of dextro-laurolene is a diketone identical with the diketone obtained from levo-laurolene. Therefore dextro- and levo-laurolene are mixtures of optical isomers, but the *d*- and *l*-forms occur in different proportions. In the levo-laurolene the *l*-form predominates while in the dextro-laurolene the *d*-form is in excess.

Structure of Laurolene.

The experiments described in this paper give further confirmation of the structure of laurolene first proposed by Eijkman[1] on the basis of refractometric studies and advocated by us in our previous paper.[2] They have shown, also, that both *d*- and *l*-laurolene give a diketone by oxidation and that the semicarbazones of the ketones from the two hydrocarbons are, apparently, identical, indicating that the two hydrocarbons differ only in configuration and are otherwise identical in structure. The formula established for laurolene is,



$$\begin{array}{l} CH(CH_3) - C-CH_3 \\ | \qquad\qquad\quad \| \\ CH_2-CH_2-C-CH_3 \end{array}.$$

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. IV. SYNTHESIS OF LAUROLENE.

BY WILLIAM A. NOYES AND L. P. KYRIAKIDES.

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Of the two hydrocarbons having the formula C_8H_{14}, the structure of isolaurolene has been established synthetically by Blanc.[3] Eijkman,[4]

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[1] *Chem. Weekblad*, 1906, No. 45; 1907, No. 4; *Chem. Zentr.*, 1907, II, 1208.

[2] THIS JOURNAL, 31, 671.

[3] *Bull. soc. chim.*, (3) 19, 703; *Compt. rend.*, 142, 1084.

[4] *Chem. weekblad.*, 1906, No. 45; 1907, No. 4; *Chem. Zentralbl.*, 1907, II, 1208.