Calculated for $C_{17}H_{22}O_2N_2$, 10.85 per cent. N; found, 10.83 per cent. N.

IV. β-Acetyl β-Benzoylpropionic Ethyl Ester, $C_6H_5COCH(COCH_3)CH_2COOC_2H_5$.—Ten grams of benzoyl acetone were dissolved in anhydrous benzene, to this were added 1.43 grams sodium and the reaction completed by heating on the water bath. The benzene was removed by distillation and the sodium benzoyl acetone treated with 12.2 grams bromacetic ethyl ester. The mixture was heated on the water bath for four hours, at the end of which period there is no longer the characteristic odor of the bromacetic ester. The mixture resulting was treated with water. This solution gave an alkaline reaction. It was extracted with ether and the ethereal extract dried over calcium chloride. The ether was removed and the substance remaining boiled at 194° at 44 mm. An analysis gave:

Calculated for $C_{14}H_{16}O_4$:	C, 67.74; H, 6.45.
Found:	C, 67.50; H, 6.39.

Pyrazole of β-acetyl-β-benzoylpropionic Acid.—One molecule of the ester is treated with an excess of phenylhydrazine in alcoholic solution. The mixture is heated for eight hours on the water bath, and the alcohol removed by distillation. The residue crystallized in large white cubes which were slightly impure, and melted at 101–106°. If this substance be permitted to stand, it gradually loses water and passes into the pyrazole, a red liquid which boils at 270° at 47 mm. The white crystalline substance is undoubtedly the mono-phenylhydrazone, but is so unstable as to render an analysis unsatisfactory. The pyrazole gave 9.80 per cent. N; calculated for the acid $C_{18}H_{16}O_2N_2$, 9.59 per cent.; for the ester $C_{20}H_{20}O_2N_2$, 8.75 per cent.

V. α-Methyl β-acetyl-β-benzoylpropionic Ethyl Ester, $C_6H_5COCH(COCH_3)CH(CH_3)COOC_2H_5$.—In the preparation of this substance sodium benzoylacetone and α-brompropionic ethyl ester are mixed in molecular quantities and the method employed is analogous to the one given under IV above. It boils at 205° at 69 mm. The pyrazole is prepared by heating a mixture of phenylhydrazine and the ester, without the use of a solvent. This pyrazole boils at 250°–3° at 55 mm. An analysis gave 9.80 per cent. N; calculated for the acid $C_{19}H_{18}O_2N_2$, 9.15 per cent.

VI. α-Ethyl β-Acetyl-β-benzoylpropionic Ethyl Ester, $C_6H_5COCH(COCH_3)CH(C_2H_5)COOC_2H_5$.—This ester is prepared by the action of α-brombutyric ethyl ester on sodium benzoylacetone. It boils at 198° at 37 mm. Its pyrazole boils at 250°–3° at 46 mm. The analysis gave 9.06 per cent. N; calculated for the acid $C_{20}H_{20}O_2N_2$, 8.75 per cent.

This work is being continued in this laboratory. Mr. Guy A. Reddick carried out the experimental work with acetylacetone, and Mr. Gail J. Fink that with benzoylacetone.

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

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES.[1]

II. LAUROLENE.

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

Received May 3, 1909

Two fairly well-defined hydrocarbons, C_8H_{14}, derived from camphor are known. Laurolene, which boils at 120–122°, has been obtained by

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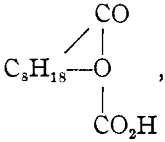
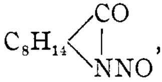
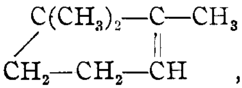
[1] For the first paper, see THIS JOURNAL, 31, 278.

the slow distillation of camphanic acid,  $C_8H_{18}\text{—}O(\text{—}CO)\text{—}CO_2H$,[1] either alone or in a slow current of carbon dioxide, by the distillation of allocampholytic acid[2] (γ-lauronolic acid), by distilling calcium camphanate,[3] by decomposing amino lauronic acid with nitrous acid,[4] and by boiling the nitroso derivative of aminolauronic anhydride,  $C_8H_{14}\left\langle\begin{matrix}CO\\ |\\ NNO\end{matrix}\right.$, with a solution of sodium hydroxide.[5] The hydrocarbon obtained by Wreden[6] by heating camphoric acid in sealed tubes with concentrated hydrochloric acid or hydriodic acid seems to have been in part tetrahydrometaxylene or hexahydrometaxylene but very probably contained laurolene as well.

Laurolene has usually been obtained in an optically active form, but the rotation has been found to vary from +22.9° (Zelinsky) to —29.2° (Walker and Henderson). We have found for the hydrocarbon formed by treating aminolauronic acid hydrochloride with nitrous acid, $[\alpha]_D = +23.6°$ at 15° and +22.8° at 23°. For the laurolene formed by warming the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide, we have found $[\alpha]_D = —14.5°$ at 20° with a preparation which had stood for a year but which had been recently fractioned. Another recent preparation gave —14.7° at 35°. A portion recovered after partial oxidation gave —11.1°. The other hydrocarbon, isolaurolene, has been prepared by distilling copper camphorate,[7] from sulphocamphylic acid,[8] and from β-campholytic acid.[9]

The structure of isolaurolene as 1, 1, 2 - trimethyl-Δ^2-cyclopentene,  $C(CH_3)_2\text{—}C\text{—}CH_3$ / $CH_2\text{—}CH_2\text{—}CH$, has been fully established by Blanc, both by means of its oxidation products and by synthesis.[10]

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[1] Wreden, *Ann.*, **163**, 336. Aschan, *Ann.*, 290, 187. Zelinsky, *Ann.*, **319**, 311. Crossley and Renouf, *J. Chem. Soc.*, **89**, 27.

[2] Walker and Henderson, *J. Chem. Soc.*, **69**, 749. It would seem from the description that only a part of the acid decomposed and that the portion which did not decompose differed from that which did.

[3] Rupe and Maull, *Ber.*, **26**, 1202.

[4] Noyes, *Am. Chem. J.*, **17**, 432. Tiemann, *Ber.*, **33**, 2949.

[5] Noyes and Taveau, *Am. Chem. J.*, **32**, 288; **35**, 379.

[6] *Ann.*, **187**, 168.

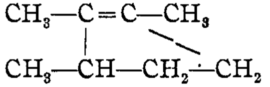
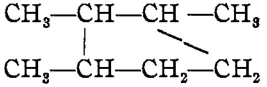
[7] Moitessier, *Jahresber.*, 1866, 410.

[8] Damsky, *Ber.*, 20, 2959. Koenigs and Meyer, *Ibid.*, **27**, 3470.

[9] Blanc, *Bull. soc. chim.* [3], **19**, 700. Crossly and Renouf, *J. Chem. Soc.*, **89**, 29.

[10] *Bull. soc. chim.* [3], **19**, 703. *Compt. rend.*, **142**, 1084.

Walker and Henderson,[1] Aschan,[2] and Crossly and Renouf[3] have oxidized laurolene in various ways, but each has failed to secure any definite oxidation products other than acetic and oxalic acids. Zelinsky, on the basis of the reduction products, has expressed the opinion[4] that laurolene and isolaurolene are both bicyclic derivatives of gemdimethylcyclohexane. Their conduct toward permanganate is in poor accord with such a structure, however, and Crossly and Renouf have shown[5] that dihydrolaurolene and dihydroisolaurolene are different compounds, instead of being identical as Zelinsky supposed. Crossly and Renouf have also shown that dihydrolaurolene is not gemdimethylcyclohexane by the synthesis of the latter compound, which is different from dihydrolaurolene and which gives ββ-dimethyl adipic acid by oxidation, while dihydrolaurolene gives only oxalic acid.[6]

On the basis of refractometric studies, Eijkman[7] has proposed the formulas  and  for laurolene and dihydrolaurolene. As will be seen below, our experiments have given strong evidence in favor of these formulas.

Experimental.

The laurolene used was prepared partly by the direct treatment of aminolauronic hydrochloride with sodium nitrite (yield 10 per cent.) and partly by boiling the nitroso compound of aminolauronic anhydride with 10 per cent. sodium hydroxide (yield, 28 per cent. of the nitroso derivative taken, or 53 per cent. of the theoretical). The hydrocarbon prepared by the first method was dextrorotatory, $[\alpha]_D = +22.8°$ at 23°, and had a sp. gr., d 15°/4° = 0.8030. That prepared by the second method was levorotatory, $[\alpha]_D = -14.5°$ at 20°, and had a sp. gr., d 15°/4° = 0.8043.

Calculated for C_8H_{14}: C, 87.27; H, 12.72
Found: C, 87.14; H, 12.77

In the first attempts at oxidation, the hydrocarbon (dextrorotatory, from aminolauronic acid) was treated, as usual, with a cold, dilute solution of potassium permanganate and the alkaline solution, after filtering from the oxides of manganese, was concentrated and examined for organic acids with no satisfactory results. In a second experiment, after completing the oxidation as usual, the oxides of manganese were dissolved with the aid of sulphuric acid and acid sodium sulphite, when a neutral oil was found suspended in the solution. This was taken up with ether and after the removal of the latter, was distilled under diminished pressure with water vapor. The first portions, which contained unchanged laurolene were rejected, while later portions were dried and analyzed.

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[1] *J. Chem. Soc.*, **69**, 754.

[2] *Ann.*, **290**, 192.

[3] *J. Chem. Soc.*, **89**, 39.

[4] *Ann.*, **319**, 320.

[5] *J. Chem. Soc.*, **89**, 28.

[6] *Loc. cit.*, p. 41.

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

Calculated for $C_8H_{14}O_2$: C, 67.60 ; H, 9.68.
Found: C, 70.48, 71.43; H, 10.41, 10.54.
Calculated for $C_8H_{12}O$: C, 77.42 ; H, 12.90.

The sp. gr. of this product was $d_4^{15} = 0.9561$.

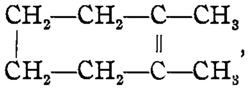
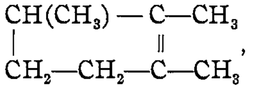
As the product gave no test for an aldehyde with fuchsine and sulphurous acid, these results indicated that the primary product of the oxidation was a diketone which had condensed in part to an unsaturated cylic monoketone. In order to secure the diketone in pure condition, the oxidation was repeated as follows: Five grams of the hydrocarbon (levorotary from aminolauronic anhydride) were mixed with 50 g. of ice and 200 cc. of a 2 per cent. solution of potassium permanganate (10 per cent. excess) were dropped in slowly while the mixture was shaken and cooled with ice water. When the reduction of the permanganate was complete, the ketone and unchanged hydrocarbon were extracted by ether directly from the mixture containing the oxides of manganese, the ether being distilled away and used over as far as possible to avoid loss by volatilization. The residue obtained was taken up with a little ether, thoroughly dried with sodium sulphate and distilled in the vacuum obtained with a Sprengel pump, the distillate being condensed in a bulb surrounded with a mixture of ether and solid carbon dioxide. The unchanged hydrocarbon distilled over first at ordinary temperatures, while the diketone came over at about 60° under a pressure of 5–10 mm. The larger portion of the diketone was an oil which solidified only at a very low temperature. Toward the end of the distillation there was obtained, however, a small amount of a solid which melted at 68° (corr.) and which proved, on analysis, to be of the same composition as the oil. Whether the solid is simply the pure ketone or whether it is the racemic form while the oil is partly the optically active form we have not been able to determine. The fact that the hydrocarbon used had a rotatory power of only —14.5° makes it quite probable that it consisted, in part, of the racemic form, since the positive hydrocarbon has a rotatory power of +23° at least (see above). On the other hand, the oil probably contained a small amount of the condensed monoketone $C_8H_{12}O$, which might easily prevent the solidification of the main portion of the diketone. The analyses gave:

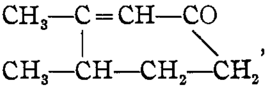
Calculated for $C_8H_{14}O_2$: C, 67.60 ; H, 9.86.
Found: C, 66.98, 66.91; H, 9.90, 9.73.
C, 67.47, 67.00; H, 10.23, 10.50.

The last analysis was made with the solid compound.

The ketone is optically active. In 32.5 per cent. solution in ether $[\alpha]_D =$ —8.5 at 25°. The *oxime* and *hydrazone* were obtained only as oils. The semicarbazone is solid but we have not succeeded, thus far, in obtaining it pure, the per cent. of nitrogen found in different preparations being 28.98, 28.50, 29.50, 33.25, 26.47. Calculated for $C_8H_{14}(NNHCONH_2)_2$, 32.81; for $C_8H_{14}ONNHCONH_2$, 21.10; for $C_8H_{12}NNHCONH_2$, 23.20. The compound was difficultly soluble in water and alcohol and could not be crystallized satisfactorily from any solvent tried.

The specific gravity of the ketone from oxidation of the negative laurolene was $d_{15}^{15} = 0.9888$ and $d_{20}^{20} = 0.9881$ for two different preparations. The compound gave no reaction for an aldehyde group with fuchsine solution decolorized with sulphurous acid.

The facts which have been given, establish pretty clearly that the compound obtained by the oxidation of laurolene is a diketone. If this is the case, from its formula it must be an open-chain compound and the only formulas for laurolene, consistent with the formation of such a ketone, are those in which two doubly united carbon atoms bear two methyl groups. If we consider, further, the formulas of aminolauronic and of camphoric acids, the two possible formulas for laurolene are 1,2-dimethyl-Δ^1-cyclohexene,  $\begin{array}{l} CH_2-CH_2-C-CH_3 \\ | \qquad\qquad\qquad \| \\ CH_2-CH_2-C-CH_3 \end{array}$, and 1,2,3-trimethyl-$\Delta^1$-cyclopentene,  $\begin{array}{l} CH(CH_3)-C-CH_3 \\ | \qquad\qquad\qquad \| \\ CH_2-CH_2-C-CH_3 \end{array}$, as proposed by Eijkman. The first of these and also the 2,6-octanedione, which it would give by oxidation, are necessarily inactive as neither contains an asymmetric carbon atom. As both laurolene and the diketone are optically active, Eijkman's formula seems to be altogether probable.

On heating, the diketone appears to condense with loss of water, probably to form a cyclic ketone, either 3,4-dimethyl-Δ^2-cyclohexenone,  $\begin{array}{l} CH_3-C=CH-CO \\ \quad | \qquad\qquad \diagdown \\ CH_3-CH-CH_2-CH_2 \end{array}$, 3,6-dimethyl-$\Delta^2$-cyclohexenone, or 1,3-acetylmethyl-Δ^2-cyclopentene. It seems quite possible that this condensation product is identical with laurenone of Tiemann and Tigges.[1] The work will be continued and a discussion of the mechanism of the rearrangements which give laurolene is reserved for a later communication.

URBANA, ILLINOIS.

[FROM THE LABORATORY OF ANIMAL PHYSIOLOGY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

FACTORS WHICH INFLUENCE THE CREATININE DETERMINATION.[2]

BY F. C. COOK.

Received March 31, 1909.

During the past five years, since the Folin[3] colorimetric method for the estimation of creatinine has been available, a great amount of work involving this method has been performed. The determination of creatinine now holds an important place in Nitrogen Metabolism experiments, and in all investigations on the chemistry of meat products. The author applied this method to beef extracts and similar products during the winter of 1905, and obtained fairly satisfactory results for total creatinine. The determination of the original creatinine in meat products has not appeared to be entirely satisfactory, and the factors which influence this determination have not been studied.

The object of this investigation was to obtain some additional information on the various factors which influence the determination of crea-

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[1] *Ber.*, 33, 2950.

[2] Published by permission of the Secretary of Agriculture.

[3] *Z. physiol. Chem.*, 41, 223 (1904).