

CONCLUSIONS

1. Several derivatives of 2-methyl-pentanol-2-one-4 have been prepared and some of their physical properties noted.

2. Efforts to form the amine of 2-meth-

yl-2-chloro-pentanone-4 have thus far been unsuccessful.

3. Some preliminary work on the introduction of sulfur into 2-methyl-pentanol-2-one-4 has been completed.

REFERENCES

(1) Miller, C. E., and Cain, R. A., *JOUR. A. PH. A.*, 26 (1937) 308.

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(3) Solzberg, P. L., and Supniewski, J. V., "Or-

ganic Syntheses, Collective Volume I," John Wiley & Sons, Inc., New York, N. Y., 1932, p. 114.

(4) Cumming, Hooper and Wheeler, "Systematic Organic Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1931, Chaps. 20, 21.

Ketone Alcohols*.[†]

II. Derivatives of the Polymerization of Pentanone-3

By Kathryn C. Odney and Clifton E. Miller[‡]

Certain derivatives of 2-methyl-pentanol-2-one-4 have been prepared (1). The pharmacological action shown by one of these derivatives made it seem worth while to prepare higher homologues, confining our efforts to the even-numbered carbon atom compounds, with the intention of determining the effect of length of carbon chain on the pharmacological action of ketone alcohols. The authors present a report of the work completed thus far on the polymerization of pentanone-3 to form 3-ethyl-octanol-3-one-6.

EXPERIMENTAL

The pentanone-3 employed in this investigation was prepared by the following methods: oxidation of diethyl carbinol by the use of Beckman's oxidizing mixture, employing variable amounts of benzene as a carrying agent; consistently small yields were obtained following this procedure, therefore method two consisting of the dry distillation of calcium propionate was employed with favorable results.

The polymerization of pentanone-3 was accomplished by placing 200 cc. of pure ketone in a 500-cc.

three-neck flask fitted with a Soxhlet extractor containing a thimble of barium hydroxide, a thermometer for recording internal temperature and a device for removal of samples. It was found advantageous to place two long water-cooled condensers above the Soxhlet extractor to minimize the amount of loss by volatilization. Heating, with a flask temperature of 110–115° C., was continued for a period of 100 hrs. during which time the mixture became dark in color and samples were withdrawn at varying intervals for refractive index determinations. The results are summarized in the following table. All readings were made at 20° C.

TABLE I

Hours of Heating	Average Reading	Hours of Heating	Average Reading
0	1.3929	50	1.3947
5	1.3937	60	1.3948
15	1.3937	70	1.3943
20	1.3940	80	1.3951
30	1.3940	90	1.3943
40	1.3940	100	1.3948

It was apparent from the results obtained that a complete polymerization did not occur and this is in accord with the published results of Voitila (2) who found incomplete polymerization of methyl-ethyl ketone under similar conditions. A possible explanation of the oscillation in readings may be that when the samples were withdrawn from time to time the ratio between the polymerized and unpolymerized products was not always the same.

After completing this heating period, the product was allowed to cool to room temperature and filtered.

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The filtrate was distilled in vacuum and the portion boiling at 24°C./27 mm. collected. A total of 55 Gm., representing a yield of 34%, was obtained. This product which was colorless and very volatile had a boiling point of 98°C. when determined by micro methods

This volatile liquid yielded a phenylurethane melting at 232–233°C.; an α -naphthylurethane melting at 217°C.; and a dinitro-osazone consisting of bright yellowish orange crystals melting at 148°C. No color was observed on the addition of a small amount of this product to anhydrous copper sulfate. Schiff's reagent gave a negative reaction.

Because of its extreme volatility, only an approximate specific gravity was determined between the range of 0.84–0.86 at 15°C. The product rapidly decolorized a solution of bromine in chloroform leading us to suspect the presence of an unsaturated structure. Several iodine determinations were carried out with values ranging from 91 to 139. This variance may be attributed, possibly, to the extreme volatility of the liquid.

CONCLUSIONS

1. Preliminary studies of the polymerization of pentanone-3, using barium hydroxide as the condensing agent have been made.

2. The principal product formed appeared to be an unsaturated aliphatic alcohol of low molecular weight.

3. The failure to isolate the desired 3-ethyl-octanol-3-one-6 is being investigated.

REFERENCES

1. Miller, C. E., and Cain, R. A., *JOUR. A. PH. A.*, 26 (1937), 308.
- (2) Voitila, Tauno, *Chem. Abstr.*, 31 (1937), 2582.

The Phytochemistry of Helonias

I. Preliminary Examination of the Drug*

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Chamaelirium luteum (L.) A. Gray, is a perennial, diœcious herb of the lily family found growing in low grounds from New England to Georgia and westward. It is known by such synonyms as False Unicorn, Blazing Star, Starwort, Devil's Bit and Helonias, the last named being the title by which the dried rhizome and roots are recognized by the National Formulary. The drug has long been recognized by the Homeopathic Pharmacopœia of the United States, and it was used as a remedy by the American Indians (1, 2, 3).

Moser (3) has reported on the pharmacognosy of the drug, but chemical investigation is apparently limited to the work of Greene and Kruskal¹. Greene (4, 5) reported

the presence of a saponaceous glycoside, reducing sugar, tannic acid and a small quantity of a white substance which he did not characterize but believed to be a fatty acid. He further showed that the glycoside was hydrolyzed when heated with 2% hydrochloric acid, the products of the hydrolysis being a reducing sugar and a white, resinous substance which he named chamæliretin. Ultimate analyses carried out by Kruskal (6) indicated that the empirical formula of the glycoside may be represented as $C_{18}H_{32}O_9$ or $C_{36}H_{62}O_{18}$.

Helonias has been used as a sialagogue, emetic and uterine tonic. In connection with the latter use it is of interest to note that Pilcher (7) has shown that the drug has no action on the excised uterus of the guinea pig.

EXPERIMENTAL

PRELIMINARY EXAMINATION

The moisture content, determined by heating at 100°C. to constant weight, was found to be 10.8%. Using the U. S. P. methods, the total ash was found to be 4.33% and acid-insoluble ash was 1.58%. No

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¹ In a paper published subsequent to the completion of this paper, Marker [*J. Am. Chem. Soc.*, 64 (1942), 1238] showed that diosgenin could be isolated from *Chamaelirium luteum*.