they melted at 227° and agreed in all other characteristics with the alkaloid obtained from the valves.

This procedure was much more satisfactory than the immiscible-solvent method used in isolating the alkaloid from the valves. It was carried out more quickly, was less wasteful, and yielded a crude alkaloid that was more easily purified. It should be especially useful in the isolation of alkaloids that are quite soluble in water and that are not reduced by hydrogen sulfide.

Summary

A new alkaloid has been isolated from *Lupinus spathulatus*, a plant that occurs in Utah and Colorado. The new base has been named spathulatine and has been assigned the formula $C_{33}H_{64}O_5N_4$. The properties of the free alkaloid and the preparation of its mercuric iodide compound which may serve as a microchemical test are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

THE CONDENSATION OF NORMAL BUTYRALDEHYDE WITH METHYLETHYL KETONE

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As *n*-butyl alcohol has become a common article of commerce, the hitherto difficultly obtainable *n*-butyraldehyde is now readily prepared in quantity. It, seemed, therefore, worth while to investigate the use of *n*-butyraldehyde as a starting material in various syntheses.

This paper describes the condensation of *n*-butyraldehyde with methylethyl ketone, and the preparation of various derivatives of the condensation products.

Weizmann[1] has shown that *n*-butyraldehyde reacts with acetone under the influence of solid sodium hydroxide to give the aldol, which loses water on distillation, yielding *n*-butylidene acetone. The aldol is not described. *n*-Butyraldehyde reacts with methylethyl ketone under the influence of solid or alcoholic potassium hydroxide in a similar manner, yielding 4-hydroxy-3-methyl-2-heptanone, $C_3H_7CHOH.CH(CH_3)CO.CH_3$. A small quantity of low-boiling substances is formed at the same time, consisting principally of the unsaturated ketone resulting from the dehydration of the aldol, although a small amount of α-ethyl-α-hexenal and some lower-boiling substances are also obtained. Similar lower-boiling substances were also found among the products of the condensation of *n*-butyraldehyde with acetone.[1] Practically no high-boiling, tarry products were obtained, the residue consisting of only a few cubic centimeters of material.

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[1] Weizmann and Garrard, *J. Chem. Soc.*, **117**, 334 (1920).

As methylethyl ketone can react with the aldehyde in either of two ways, the aldol could be either $C_3H_7.CHOH.CH_2.CO.C_2H_5$ or $C_3H_7.CHOH.CH(CH_3)CO.CH_3$. That the latter is actually the compound obtained is readily shown by the series of reactions: Aldol $\xrightarrow{\text{dehydration}}$ Unsaturated Ketone $\xrightarrow{\text{hydrogenation}}$ Saturated Ketone. The saturated ketone thus obtained is identical with that obtained by the hydrolysis of ethyl *n*-butylmethyl-aceto-acetate and therefore is $C_4H_9.CH(CH_3)CO.CH_3$. The unsaturated ketone is therefore $C_3H_7CH{=}C(CH_3)CO.CH_3$, and the aldol $C_3H_7.CHOH.CH(CH_3)CO.CH_3$.

As this condensation furnishes a convenient source of certain derivatives of 3-methylheptane, several of these were prepared and characterized. Among those prepared was 3-methyl-2-heptanol, which is obtained by the reduction of both the unsaturated ketone and the saturated ketone. While the latter is reduced almost exclusively to the secondary alcohol, the former gives also a small quantity of a high-boiling substance, probably resulting from the union of two molecules of the unsaturated ketone. The compound was not further investigated.

The condensation of *n*-butyraldehyde with other ketones, and of other aldehydes with methylethyl ketone, is being investigated, and will be described in a later communication.

Experimental Part

4-Hydroxy-3-methyl-2-heptanone, $C_3H_7.CHOH.CH(CH_3)CO.CH_3$.—Seventy-two g. of *n*-butyraldehyde is added drop by drop with constant stirring to a mixture of 220 g. of methylethyl ketone and 50 cc. of *N* alcoholic potassium hydroxide. Slightly more than the calculated quantity of tartaric acid solution is then added and the potassium acid tartrate filtered off. As much as possible of the excess of methylethyl ketone is distilled on the water-bath and the residue fractionated under diminished pressure. After the remainder of the methylethyl ketone is removed, two fractions are obtained, a small quantity boiling at about 85° (20 mm.) and the main fraction boiling at 105–112° (16 mm.). The latter on redistillation boils constantly at 110° (16 mm.) and consists of the desired aldol. It forms a colorless, not unpleasant-smelling liquid, with a consistency about that of concd. sulfuric acid; n_D^{20}, 1.442; d_4^{20}, 0.9238; M_D(obs.) 41.26; M_D(calc.) 40.68; yield, 60 g., or 45%.

Anal. Subs., 0.2112, 0.2180: CO_2, 0.5110, 0.5286; H_2O, 0.2114, 0.2196. Calc. for $C_8H_{16}O_2$: C, 66.67; H, 11.1. Found: C, 66.0, 66.1; H, 11.1, 11.2.

3-Methyl-Δ^3-2-heptenone (*n*-Butylidene-methylethyl Ketone), $C_3H_7.CH{=}C(CH_3)CO.CH_3$.—This forms the major portion of the low-boiling fraction obtained in carrying out the condensation, but is more readily obtained in pure form by dehydrations of the aldol. One g. of iodine is added to 144 g. of the aldol and the mixture slowly heated. Water begins to separate almost immediately and distils, carrying with it a little of the unsaturated ketone. As soon as the water is all gone, the temperature rapidly rises to 170° and the main portion of the ketone distils between 170° and 175°. The oily part of the distillate is shaken with a little very dilute sodium bisulfite solution, dried with calcium chloride and distilled under diminished pressure; b. p., 68–69° (15 mm.). The ketone forms a colorless, mobile liquid with a characteristic odor, pleasant at first but soon becoming very disagreeable. It boils at 170–176° (760 mm.) leaving a small residue, probably due to slight decomposition; n_D^{10}, 1.451; d_4^{10}, 0.8613; M_D(obs.) 39.40; M_D(calc.) 38.69 (plus exaltation for mesityl oxide = 39.55).

Even after very careful purification, ultimate analysis gave low results, as the following typical example shows. Similar results were obtained by Weizmann and Garrard,[2] with *n*-butylidene acetone and by Franke and Kohn,[3] with *iso*butylidene acetone.

Anal. Subs., 0.2500: CO_2, 0.6860; H_2O, 0.2500. Calc. for $C_8H_{14}O$: C, 76.18; H, 11.11. Found: C, 74.83; H, 11.11.

Semicarbazone.—A solution of equimolecular quantities of the ketone, semicarbazide hydrochloride and sodium acetate in aqueous alcohol is allowed to stand for several hours, and then diluted with water. The semicarbazone is filtered off and recrystallized from aqueous alcohol; m. p., 164°.

Anal. Subs., 0.1794, 0.1493. N_2, 38.0 cc. (31°, 750 mm., over 50% KOH), 29.8 cc. (27°, 750 mm., over 50% KOH). Calc. for $C_9H_{17}ON_3$: N, 23.0. Found: 23.0, 22.8.

Oxime.—A solution of equimolecular quantities of the ketone, hydroxylamine hydrochloride and sodium carbonate in aqueous alcohol is allowed to stand for 24 hours. Most of the alcohol is then distilled, the residue extracted with ether, the ether solution washed with water and finally dried with sodium sulfate. After removal of the ether the residue is distilled, when the oxime is obtained as a colorless oil; b. p., 119–120° (20 mm.).

Anal. Subs., 0.4157: N_2, 37 cc. (26°, 760 mm., over 50% KOH). Calc. for $C_8H_{15}ON$: H, 9.93. Found: 10.16.

3-Methyl-2-heptanone, $C_4H_9.CH(CH)_3COCH_3$.—The unsaturated ketone is smoothly reduced to the saturated ketone when its vapor and hydrogen are passed over nickel at 180°. The methyl-heptanone is a colorless, mobile liquid with a pleasant, fruity odor; b. p., 162° (760 mm.); n_D^{20}, 1.415; d_4^{20}, 0.8175; M_D(obs.) 39.22; M_D(calc.) 39.15.

Anal. Subs., 0.2084: CO_2, 0.5696; H_2O, 0.2380. Calc. for $C_8H_{16}O$: C, 75.00; H, 12.50. Found: C, 74.55; H, 12.80.

Semicarbazone.—Equimolecular quantities of the ketone, semicarbazide hydrochloride and sodium acetate are dissolved in a small quantity of aqueous alcohol and the mixture is allowed to stand several days. Water is then added and the semicarbazone filtered off and crystallized from dil. methanol, from which it separates in shiny plates; m. p., 82°.

Anal. Subs., 0.1540: N_2, 31 cc. (23°, 760 mm., over 50% KOH). Calc. for $C_9H_{19}ON_3$: N, 22.7. Found: 23.2.

3-Methyl-2-heptanone is also obtained by the oxidation of 3-methyl-2-heptanol. Twenty-six g. of 3-methyl-2-heptanol is added drop by drop, with constant stirring, to a mixture of 25 g. of sodium dichromate, 150 cc. of water, and 45 g. of concd. sulfuric acid, while the temperature is kept below 50°. The stirring is continued for several hours. The ketone is then taken up in ether and the ether solution dried with calcium chloride. After removal of the ether the residue is fractionated; yield, 17 g., or 68%.

3-Methyl-2-heptanol, $C_4H_9.CH(CH_3)CHOH.CH_3$.—A solution of 64 g. of 3-methyl-2-heptanone in 300 cc. of ether is added to a suspension of 100 g. of sodium bicarbonate in 300 cc. of water. Forty g. of sodium is then added in small portions, while the solution is kept cool, and shaken well before each addition. The ether layer is

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[2] Ref. 1, p. 335.

[3] Franke and Kohn, *Monatsh.*, **20**, 876 (1899).

removed and dried with sodium sulfate. After removal of the ether, the residue is distilled, when the desired alcohol is obtained as a colorless liquid with a characteristic odor resembling that of methyl-*n*-hexyl carbinol; b. p., 172–173° (760 mm.); n_D^{13}, 1.436; d_4^{13}, 0.8272; M_D (obs.) 41.10; M_D(calc.) 40.67; yield 50 g., or 77%.

Anal. Subs., 0.2336: CO_2, 0.6298; H_2O, 0.2772. Calc. for $C_8H_{18}O$: C, 73.85; H, 13.85. Found: C, 73.53; H, 13.2.

This methyl-heptanol is also obtained by the reduction of the unsaturated ketone.

Sixty-three g. of *n*-butylidene-methylethyl ketone is reduced in the same manner with 65 g. of sodium. After removal of the ether, the residue is fractionated, yielding the methyl-heptanol boiling at 172–173° (760 mm.) and a small quantity of material boiling at 168–175° (27 mm.); n_D^{15}, 1.4745; d_4^{15}, 0.9185. This was not further investigated; yield of methyl-heptanol, 35 g., or 54%.

ACETATE.—Twenty-six g. of 3-methyl-2-heptanol is added to 50 g. of acetic anhydride, followed by one drop of concd. sulfuric acid, and the mixture is warmed on the water-bath for 30 minutes. The whole is then poured into an excess of water, the ester taken up in ether, the ether solution washed with water, then with dil. sodium carbonate solution, then with water again and finally dried with calcium chloride. After removal of the ether the residue is distilled, yielding the ester as a colorless, very fragrant oil boiling at 185°; n_D^{21}, 1.418; d_4^{21}, 0.8545; M_D(obs.) 50.75; M_D(calc.) 50.03.

Anal. Subs., 0.2006: CO_2, 0.5088; H_2O, 0.2085. Calc. for $C_{10}H_{20}O_2$: C, 69.78; H, 11.63. Found: C, 69.20; H, 11.30.

Ethyl *n*-Butylmethyl-aceto-acetate, $C_4H_9(CH_3)C(CO.CH_3)CO.OC_2H_5$.—One hundred g. of ethyl *n*-butyl-aceto-acetate[4] is added to a solution of 13 g. of sodium in 250 cc. of absolute alcohol, the mixture cooled, 80 g. of methyl iodide added, and the whole refluxed for six hours on the steam-bath. Most of the alcohol is distilled and the residue then diluted with water and extracted with ether. The ether solution is washed with 200 cc. of 5% potassium hydroxide solution to remove any unchanged ethyl *n*-butyl-aceto-acetate, and then dried with sodium sulfate. After removal of the ether, the ester is distilled, and that portion boiling between 118° and 122° (10 mm.) is collected. The ester is a colorless liquid with a pleasant odor; b. p., 120–121° (10 mm.); n_D^{20}, 1.4320; d_4^{20}, 0.9460; M_D(obs.) 54.80; M_D(calc.) 54.66; yield, 80 g.

Anal. Subs., 0.2340: CO_2, 0.5670; H_2O, 0.2064. Calc. for $C_{11}H_{20}O_3$: C, 66.00; H, 10.00. Found: C, 66.02; H, 9.80.

3-Methyl-2-heptanone from Ethyl *n*-Butylmethyl-aceto-acetate.—Sixty-two g. of ethyl *n*-butylmethyl-aceto-acetate is boiled under a reflux condenser for 14 hours with 400 cc. of 10% aqueous potassium hydroxide. The mixture is then distilled with steam, when the ketone passes over with the water as a colorless oil. This is dried with calcium chloride, distilled, and the portion boiling between 159° and 164° collected. The ketone is in every way identical with that obtained by hydrogenation of the *n*-butylidene-methylethyl ketone, and the two semicarbazones melt, separately and mixed, at 82°.

Summary

1. 4-Hydroxy-3-methyl-2-heptanone and 3-methyl-Δ^3-2-heptenone have been prepared by the condensation of *n*-butyraldehyde with methylethyl ketone.

2. Certain derivatives of 3-methyl-heptane have been prepared and described.

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[4] Tafel and Jürgens, *Ber.*, **42**, 2555 (1909).