Fraction	M. P.	Analysis				
		Subst.(g)	N. (cc)	T	P (mm)	N (%) found
III	57	0.0607	3.75	18	762	7.18
IV	56	0.0940	5.85	16	758.4	7.26
n-butylalc. (literature)	56					7.25 (C ₁₁ H ₁₅ O ₂ N)

c. α -naphthylcarbamate of fract. III.

M. P. 70° (literature 72°).

(8) Yield of succinic acid: 3.5 g.

On the Alcoholic Fermentation of Amino-acids.

Part VII. Decomposition of *d-l*-valine by saké yeast.

By Masakazu YAMADA

(Received October 29, 1934)

If isoamyl alcohol is derived from leucine in the alcoholic fermentation, it is the most probable that isobutyl alcohol ought to come from valine, while in the author's previous experiment showed that alanine was the mother substance of the latter⁽¹⁾. So decomposition of valine by yeast must be examined again. F. Ehrlich obtained *l*-valine as the decomposition product by yeast from *d-l*-valine but did not discuss any volatile products.

The author's experiment showed that valine was a quite poor nitrogen nutriment for yeast and so decomposition was not smooth and complete. The fusel oil fraction obtained in the modified Hayduck solution with *d-l*-valine in place of asparagine did not contain any trace of isobutyl alcohol but consisted of an amyl alcohol which boiled at ca. 123~130°. The chemical position of the alcohol has not yet been decided. It must be careful that in this case quite enormous quantity of succinic acid was produced.

EXPERIMENTAL

- (1) *d-l*-valine was prepared from isobutyl alcohol (B. P. 107~8°).
- (2) Medium: Modified Hayduck solution with 0.32% of valine in place of asparagine.
- (3) In 30 L of medium 33.5 g as dry matter of saké yeast was inoculated. After 20 days, whole sugar was disappeared.
- (4) Fermentation products:

alcohol 4.2%, fusel oil 0.05%, total acid 0.2596%

yield of alcohol 1603 cc (ca 94%)

„ „ oil (B. P. above 100°) 11.1 g

„ „ yeast 40 g (together with the yeast added)

(5) Fractional distillation of the oil.

Fract.	B. P.	Yield (g)	Fract.	B. P.	Yield (g)
I	95~109°	0.1	VI	127.5~128.5	2.0
II	109~121	0.3	VII	128.5~129.5	3.1
III	121~123	0.4	VIII	129.5~130	1.5
IV	123~125	0.5	IX	130~130.5	1.0
V	125~127.5	1.5	X	residue	0.6

(6) Identification of the fractions.

The following derivatives of alcohol were prepared.

a. 3:5-dinitro-benzoate:—

Fraction	M. P.	Analysis				
		Subst (g)	N (cc)	T	P (mm)	N (%) found
V	61°					
VI	65	0.0353	3.10	15	772	10.01
VII	63	0.0448	3.80	15	765.7	10.03
VIII	64	0.0430	3.70	16	766.6	10.14
isobutyl ester	87					10.45
isoamyl ester	62					(C ₁₁ H ₁₂ O ₆ N ₂) 9.93 (C ₁₂ H ₁₄ O ₆ N ₂)

b. Phenyl carbamate:

Fraction	M. P.	Analysis				
		Subst. (g)	N (cc)	T	P (mm)	N (%) found
V	40°	0.0811	4.85	16	762.3	7.01
VI	40	0.0856	5.00	16	765.4	6.87
VII	41.5	0.0812	4.65	14	760.0	6.76
VIII	45	0.0688	4.00	14	765.0	6.90
IX	46					6.76
isoamyl ester	55					7.25 (C ₁₂ H ₁₇ O ₂ N)
isobutyl ester	80					7.25 (C ₁₁ H ₁₆ O ₂ N)

- c. α -naphthyl carbamate of Fract. VI. M. P. 61° (isoamylalc. 68°)
- (7) Optical rotation of mixture: Subst. Mixture of fract. III~VIII.
 $[\alpha]^{26.5^\circ} = -2.57^\circ$ $r = -2.22^\circ$ $l = 2.2$ dm $C = 39.21\%$ (alcohol solution)
- (8) Valine recovered from the residue: 77 g.
- (9) Succinic acid (M. P. 187°) obtained: 30.36 g.
 The acid may perhaps be formed from sugar alone.

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Part VIII. Decomposition of glutaminic acid and asparagine by saké yeast.

By Masakazu YAMADA

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In the series of the author's previous experiments, the mother substance of normal propyl alcohol as an ordinary constituent of fusel oil has not yet been found. On the one hand, *n*-propyl alcohol shows quite faint color reaction with vanilline- H_2SO_4 reagent and so the previous preliminary experiment with glutaminic acid or asparagine ought to be examined again. In those cases no remarkable production of fusel oil were perceived⁽¹⁾. F. Ehrlich supposed first that glutaminic acid was the mother substance of *n*-propyl alcohol, but he obtained succinic acid instead of the alcohol contrary to his expectation.

The author's experiment showed that glutaminic acid or asparagine was not the mother substance of *n*-propyl alcohol and gave very poor yield of fusel oil as the preliminary experiment had shown. The superior production of succinic acid was observed in the case of glutaminic acid.

EXPERIMENTAL

I. Decomposition of glutaminic acid by saké yeast.

- (1) Glutaminic acid: Ajino-moto (sodium-glutamate) was used.
- (2) Medium: Modified Hayduck solution with 0.5% of Na-glutamate in place of asparagine.
- (3) Fermentation: The details of experiments are the same as the case of leucine. 30 L of the fermentation liquid was distilled.