# NOTES

## Isolation and Identification of the Organic Nitrogenous and Non-Nitrogenous Compounds Occurring in the Alaska Pea. II. The Isolation of Pyrrolidone-carboxylic Acid, Tyrosine, and Diamino Acids from the Non-Proteins of the Alaska Pea

BY S. L. JODIDI

Previously the presence of citric acid[1] in Alaska pea was reported. Work on phenylalanine and cystine was undertaken because they were never reported to occur among the non-proteins of the pea. Phenylalanine is known to be hard to isolate. However, when heated with potassium dichromate plus sulfuric acid it develops the odor of an aldehyde which oxidizes to benzoic acid. This reaction which was used for elaborating a quantitative method for the estimation of phenylalanine as benzoic acid[2] was applied to the work on that amino acid.

Four hundred grams of meal prepared from Alaska peas of sizes 2, 3 and 4 was treated twice with ether to remove fat, lecithin and pigments. The defatted meal was extracted with 92% alcohol, and the filtered extract evaporated *in vacuo* to dryness. The residue was oxidized by boiling with Beckmann's mixture (20% of potassium dichromate + 17% of sulfuric acid) for five to six hours. The oxidation liquid was extracted with ether in a continuous extractor[3] and the ethereal layer filtered into anhydrous sodium sulfate. The dehydrated filtered ether solution left on evaporation crystals whose aqueous solution showed acid reaction. Recrystallized from alcohol they melted at 182°. Benzoic acid melts at 120–121°, pyrrolidonecarboxylic acid at 182–183°.

*Anal.* Silver salt. Calcd. for $C_5H_6NO_3Ag$: Ag, 45.76. Found: Ag, 45.67.

The acid reaction, melting point and silver salt agree with the properties of pyrrolidonecarboxylic acid. Its origin is undoubtedly due to glutamine[4] present in peas.

For isolation of cystine, 500 g. of pea meal was extracted with water, the extract evaporated in a vacuum to dryness, and the residue treated with absolute alcohol to remove citric acid, fats, lecithin, etc. The undissolved portion was dissolved in water, purified with basic lead acetate, the filtrate treated with hydrogen sulfide, and the filtrate from lead sulfide concentrated *in vacuo*. The concentrate was treated repeatedly with mercuric sulfate in a 5% sulfuric acid solution. The mercuric sulfate precipitates obtained were suspended in water, decomposed with hydrogen sulfide, the filtrate from mercuric sulfide neutralized with potassium hydroxide solution, treated with bone black and the filtrate concentrated in a vacuum. The concentrated solution yielded in a vacuum desiccator crystals which failed to yield with alkali and lead acetate the cystine reaction, but they gave the Millon and Mörner reactions characteristic of tyrosine, and the pyrrole and diazo reactions, showing the presence of histidine.

To obtain arginine, the filtrate from the mercuric sulfate precipitates was treated with hydrogen sulfide, the filtrate from the mercuric sulfide acidified with sulfuric acid and treated with flavianic acid. There was thus obtained 2.25 g. of arginine flavianate.

*Anal.* Calcd. for $C_{16}H_{20}N_6SO_{10}$: N, 17.22; S, 6.57. Found: N, 17.31; S, 6.75.

The filtrate from arginine flavianate which probably contained lysine was lost by accident.

**Summary.**—Pyrrolidone-carboxylic acid, the isolation of which from peas is reported here for the first time, appears to owe its origin to glutamine occurring in that legume. The presence of histidine was demonstrated by the diazo and pyrrole reactions. The quantity of arginine obtained was equal to 0.7% of the oven-dried peas, while tyrosine was identified by Millon and Mörner reactions.

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WASHINGTON, D. C.
RECEIVED MARCH 6, 1935

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[1] Jodidi, THIS JOURNAL, 55, 4663 (1933).

[2] Kollmann, *Biochem. Z.*, 194, 1 (1928).

[3] Palkin, Murray and Watkins, *Ind. Eng. Chem.*, 17, 612 (1925).

[4] Schulze und Winterstein, *Z. physiol. Chem.*, 65, 431 (1910).

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## The Preparation of Mercury Diisobutyl

BY ADOLF MÜLLER

As has been long known, ethyl iodide[1] and ethyl bromide[2] react readily with sodium amalgam to form the mercury diethyl. H. F. Lewis and E. Chamberlin[3] found, however, that isobutyl iodide yielded 50–55% of the mercury compound, whereas isobutyl bromide yielded only traces under the same conditions.

I have succeeded in preparing in several experiments mercury diisobutyl from the bromide under conditions very similar to the modified procedure of A. Müller and A. Sauerwald for preparing mercury diethyl.[4] However, the yield of the ethyl compound was about 44% and that of the isobutyl compound 27%.

The proportions used were one mole of diisobutyl bromide, 0.15 mole of ethyl acetate, 1.5 to 2 moles of sodium contained in 0.5 to 1% amalgam.

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[1] Frankland and Duppa, *J. Chem. Soc.*, 16, 418 (1863); *Ann.*, 130, 109 (1864).

[2] Chapman, *J. Chem. Soc.*, 19, 150 (1866); *Ann.*, 139, 128 (1866).

[3] Lewis and Chamberlin, THIS JOURNAL, 51, 291 (1929).

[4] A. Müller and A. Sauerwald, *Monatsh.*, 48, 738 (1927).

The mixture is shaken vigorously for at least ten hours. For 5 kg. of mercury a 5-liter heavy-walled bottle connected with an air condenser (the heat of the reaction is small) was used. The contents of the bottle were transferred to a separatory funnel with the aid of water, the lowest layer consisting of mercury withdrawn, and then the gray precipitate (oil emulsified with mercury), the water and oil remaining in the funnel. The precipitate was steam distilled and the resulting oil united with the portion in the separatory funnel. After washing with dilute sodium hydroxide, water, and drying with calcium chloride, the oil was fractionally distilled under diminished pressure, b. p. 85° at 11 mm.

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RECEIVED APRIL 6, 1935

# COMMUNICATIONS TO THE EDITOR

## LOCATION OF ACTIVITY IN MIXED CATALYSTS

*Sir:*

We have investigated the case where each component of a mixed catalyst promotes its proper reaction, acting on a single substance; from the standpoint of the multiplet theory this is effected as a result of specific orientation. The catalysts used were of the Zelinsky and Kommarewsky type [*Ber.*, **57,** 668 (1924)], $Ni:Al_2O_3 = 1:1$, prepared in different conditions of precipitation from nitrates, sulfates and chlorides. The parallel dehydrogenation and dehydration of isoamyl alcohol, together with carbon monoxide elimination from valeraldehyde formed, were kinetically studied in an apparatus described previously [Balandin, *Z. physik. Chem.*, **B19,** 453 (1932)]. A complete analysis of the gases evolved was made. The data fitted the Arrhenius equation. With different preparations of the catalyst the energies of activation $Q$ varied in the range from 8850 to 22,400, from 17,950 to 45,100 and from 14,500 to 33,100 cal./mole for the dehydrogenation, dehydration and the aldehyde decomposition processes, respectively. The ratio of $Q$'s for different processes with the same catalyst preparation was determined. It is most remarkable that for different preparations this ratio remains constant within experimental errors.

| Catalyst No. | 1 | 2 | 5 | 6 | 7 | 8 | Av. |
|---|---|---|---|---|---|---|---|
| $Q_{H_2}/Q_{H_2O}$ | (0.32) | 0.50 | 0.61 | 0.50 | 0.59 | 0.57 | 0.51 |
| $Q_{H_2}/Q_{CO}$ | .62 | .67 | .64 | .59 | .71 | .90 | .69 |
| $Q_{H_2O}/Q_{CO}$ | 1.20 | 1.36 | 1.05 | 1.20 | 1.20 | 1.58 | 1.26 |

The logarithmic relation between $k_0$ and $Q$ in $k = k_0 \exp(-Q/RT)$, found previously [Balandin, *loc. cit.*] for catalytic dehydrogenation processes, holds true with practically the same coefficient $Q/\log k_0$ as before. The same relation is found for the dehydration process, $Q/\log k_0$ being here about 2 times larger.

The dehydration proceeds on the surface of nickel and the dehydration on that of alumina. Geometrically these surfaces are situated separately. But the energies of activation characterizing the processes are related one to another. Hence, the places where both reactions occur must geometrically be connected, and this can happen only at the nickel–alumina interfaces. Thus, one can conclude that the reaction on a mixed catalyst is located on its component interfaces.

In the systems considered there are two solid phases and one gaseous phase. Three phases can join together only by lines (or points) but not by surfaces. As the logarithmic relation shows, these active lines possess a varying activity. This property is the same as that of surfaces and crystal edges in the theory of H. S. Taylor [*J. Phys. Chem.*, **30,** 145 (1926); *Acta Ph. Ch. U. R. S. S.*, **1,** 397 (1935)]; however, these lines are not edges, since the micro-crystals but seldom join together by edges. These boundary lines resemble those of the Schwab and Pietsch topochemical theory [*Z. physik. Chem.*, **B1,** 385 (1928)], but are endowed with a varying activity in the sense of the theory of Taylor (*loc. cit.*) and Constable [*Proc. Roy. Soc.* (London), **A108,** 355 (1925)]. This new fact has to be taken into account in the theory of catalytic action.

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RECEIVED MARCH 29, 1935