

scattering determinations of molecular weights, the molecular weights of DNA as determined by Smith and Sheffer, Katz, and Doty and Bunce would seem to be too high by 37%. It should be pointed out that Tennent and Vilbrandt did not specify the wave length light used in their refractive measurements; hence direct comparison of their value of 0.160 with the above value of 0.201 should not be made.

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VALINE BIOSYNTHESIS IN *TORULOPSIS UTILIS*¹

Sir:

Results are reported herein which indicate that the carbon chain of lactic acid is a direct precursor of the valine carbon skeleton. The materials for this investigation were specimens of labeled valine isolated, by slight modifications of the method of Moore and Stein,² from hydrolysates of yeast grown in the presence of C¹⁴-labeled tracer substances. Growth of the cells and other experimental details have been described previously.³ Submission of the valines to a degradation procedure for radioactivity assay of each of the four different valine carbons gave the results shown in the table. Glycine, acetate, and lactate carboxyl

DISTRIBUTION OF LABELED CARBONS IN VALINE CARBON

Values are specific activities in cpm of BaCO₃, corrected for equal initial activities of substrates.

Valine carbon number ^a	Precursors					Glucose-1-C ¹⁴ -CHO	
	Acetate CH ₃ -COOH	Glycine -CH ₂ -COOH	Lactate -CHOH-COOH				
1	105	170	30	575	45	905	25
2	155	-3	365	-4	750	-5	45
3	150	0	310	0	700		50
4,4'	155	0	335	0	20		358

^a Numbering begins with valine carboxyl carbon. ^b Acetone not further degraded.

carbons appeared only in the valine carboxyl; glycine and acetate α -carbons appeared approximately equally in all of the valine non-carboxyl carbons; and the lactate α -carbon appeared equally and nearly exclusively in carbons 2 and 3 of valine. The relatively low incorporation of acetate and glycine carbons precluded these substances, as well as citric acid cycle components, as direct precursors of valine. However, the relatively high incorporation of lactate carbons suggested that lactate or pyruvate may be the direct source of carbons for valine biosynthesis, and that acetate and glycine carbons were incorporated in valine *via* their prior conversion to pyruvate. The observed distribution of activity is in accord with the conversion of glycine to pyruvate *via* serine, and of acetate to pyruvate *via* the citric acid cycle and oxalacetate. If this postulation is correct, it follows that the methyl carbon of pyruvate should be the precursor

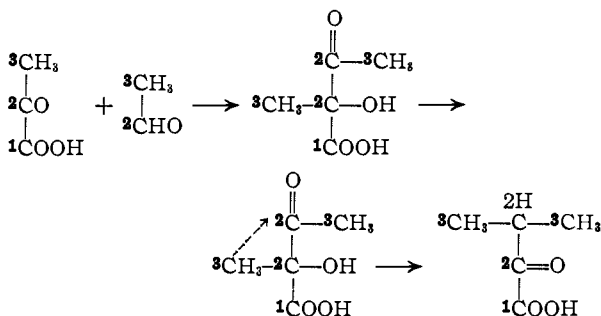
(1) Aided by grants from the Atomic Energy Commission, contract No. AT(30-1)777; the American Cancer Society; and the National Cancer Institute of the Department of Health, Education and Welfare.

(2) S. Moore and W. H. Stein, *J. Biol. Chem.*, **192**, 663 (1951).

(3) M. Strassman and S. Weinhouse, *THIS JOURNAL*, **74**, 1726 (1952).

of the valine methyl carbons. Indirect proof that carbon 3 of pyruvate can provide the carbon for the valine methyl carbons was obtained in the last experiment in the table in which it was found that carbon 1 of glucose, presumably *via* 3-labeled pyruvate, appeared preponderantly in the methyl carbons of valine.

In speculating on the mechanism of this conversion, the equal incorporation of lactate carbon 2 into valine carbons 2 and 3 suggests a direct coupling of 2 lactate α -carbons. The only conceivable biological reaction of similar type is the condensation of pyruvate and acetaldehyde to yield acetolactic acid.⁴ From the structure of this substance it is not unreasonable to assume that migration of a methyl group might occur, as in the pinacol or related rearrangements, to yield β, β' -dimethylpyruvic acid, a logical precursor of valine. Some precedent for the biological occurrence of methyl group migration has recently been provided by Woodward and Bloch.⁵ This pathway is under further investigation.



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(4) T. P. Singer and J. Pensky, *Biochim. et Biophys. Acta*, **9**, 316 (1952).

(5) R. B. Woodward and K. Bloch, *THIS JOURNAL*, **75**, 2023 (1953).

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REARRANGEMENT OF THE STEROID C/D RINGS. SYNTHESIS OF AN 11-KETO- $\Delta^{13(17\alpha)}$ -C-NOR/D-HOMO-STEROID

Sir:

Hecogenin (I) in the form of its toluene *p*-sulfonylhydrazone derivative (Ia), m.p. 259-60° (dec.); found: S, 5.39; $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 226 m μ (4.1), was submitted to a Bamford-Stevens rearrangement¹ with sodium in ethylene glycol to yield the C-nor/D-homo-sapogenin (II) m.p. ca. 110°; found: C, 77.95; H, 10.00. Acetate (IIa) m.p. 142-144°; $[\alpha]_{\text{D}}^{23}$ -52.6 (CHCl₃). Found: C, 76.03; H, 9.72. II was found to be identical with a companion olefin isolated together with III from the solvolytic rearrangement of the rockogenin derivative (IV)²; II was also formed in good yield from III on treatment of the latter with formic acid at room temperature. The endocyclic olefin (II)

(1) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(2) R. Hirschmann, C. S. Snoddy, Jr., and N. L. Wendler, *THIS JOURNAL*, **74**, 2693 (1952).