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.

DEPARTMENT OF PHYSICS
IOWA STATE COLLEGE
AMES, IOWA

T. G. NORTHROP
R. L. NUTTER
R. L. SINSHEIMER

RECEIVED JULY 24, 1953

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 C^{14}-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 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 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.

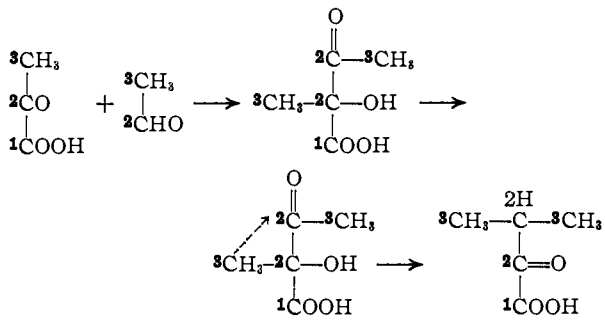
DISTRIBUTION OF LABELED CARBONS IN VALINE CARBON

Values are specific activities in cpm of $BaCO_3$, corrected for equal initial activities of substrates.

Valine carbon number[a]	Precursors: Acetate CH_3–	Acetate –COOH	Glycine $-CH_2-$	Glycine –COOH	Lactate –CHOH–	Lactate –COOH	Glucose-1-C^{14} –CHO
1	105	170	30	575	45	905	25
2	155	−3	365	−4	750	−5	45
3	150	0	310	0	700	} 5[b]	50
4,4′	155	0	335	0	20	}	358

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

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.



LANKENAU HOSPITAL RESEARCH INSTITUTE
AND INSTITUTE FOR CANCER RESEARCH
PHILADELPHIA 11, PA.

MURRAY STRASSMAN[6]
ALICE J. THOMAS
SIDNEY WEINHOUSE

RECEIVED AUGUST 14, 1953

REARRANGEMENT OF THE STEROID C/D RINGS. SYNTHESIS OF AN 11-KETO-$\Delta^{13(17a)}$-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; $\lambda_{max.}^{CH_3OH}$ 226 mμ (4.1), was submitted to a Bamford–Stevens rearrangement[1] 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°; $[\alpha]^{23}D$ −52.6 ($CHCl_3$). 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) 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).

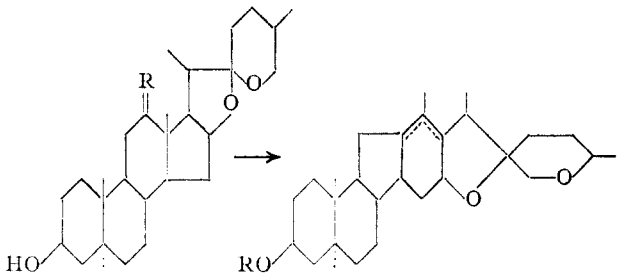
(4) T. P. Singer and J. Pensky, *Biochim. et Biophys. Acta*, **9**, 316 (1952).

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

(6) Postdoctoral Fellow of the National Institutes of Health, Department of Health, Education and Welfare.

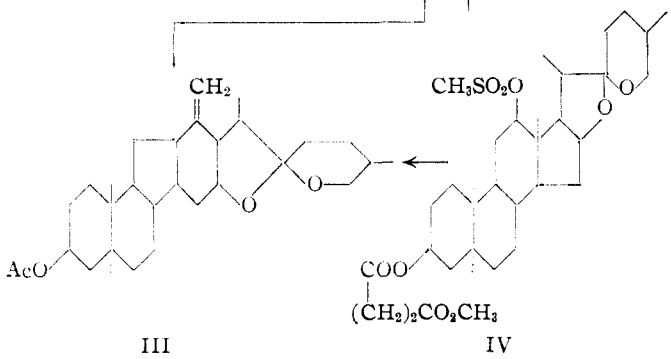
(1) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

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

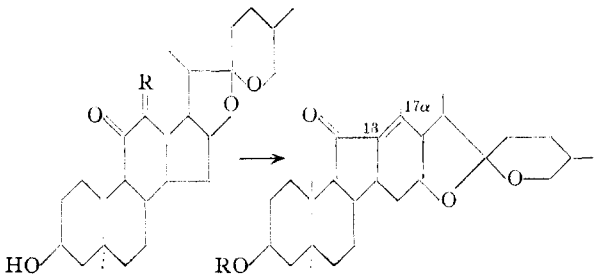


I, R, O =
Ia, R, $C_7H_7SO_2NHN$ =

II, R, H
IIa, R, CH_3CO



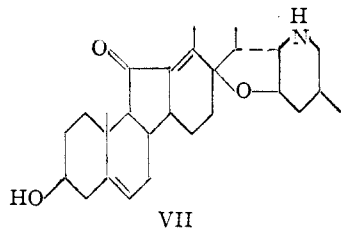
III IV



V, R, O =
Va, R, $C_7H_7SO_2NHN$ =

VI, R, H
VIa, R, CH_3CO

exhibited no absorption in the double bond region of the infrared and was smoothly converted with



VII

osmium tetroxide to a triol which on treatment with acetic anhydride in pyridine at room temperature gave only a monoacetate derivative m.p. 215–18°; $[\alpha]^{25}D$ −39.3° ($CHCl_3$). Found: C, 71.00; H, 9.45.

In a similar manner 11-ketohecogenin (V)[3] was converted to its toluene *p*-sulfonylhydrazone derivative (Va), m.p. 156–158° (dec.); $\lambda\lambda_{max.}^{CH_3OH}$ 228 mμ (3.90), 275 mμ (3.82). Found: N, 4.84. The latter rearranged on treatment with potassium hydroxide in refluxing ethylene glycol to give the 11-keto-$\Delta^{13(17a)}$-C-*nor*/D-*homo*-sapogenin (VI) m.p. 190–192°; $[\alpha]^{24}D$ −78.4° ($CHCl_3$); $\lambda\lambda_{max.}^{CH_3OH}$ ultraviolet 255 mμ (4.17), 350 mμ (2.88); $\lambda\lambda_{max.}^{CHCl_3}$ infrared 5.85 μ, 6.1 μ (more intense). Found: C, 75.54; H, 9.62. *Acetate:* (VIa) m.p. 178.5–179.5°; $[\alpha]^{24}D$ −80.7° ($CHCl_3$); $\lambda\lambda_{max.}^{CH_3OH}$ 225 mμ (4.18), 350 mμ (2.87). Found: C, 73.74; H, 8.92.

The spectral characteristics of VI are essentially the same as those of jervine (VII).[4] Of particular note is the unique reversal in intensity of the C=O and C=C bands in the infrared spectra of both VI and jervine.

(3) C. Djerassi, H. Ringold and G. Rosenkranz, *ibid.*, **73**, 1513 (1951).

(4) J. Fried, O. Wintersteiner, M. Moore, B. M. Iselin and A. Klingsberg, *ibid.*, **73**, 2970 (1951).

RESEARCH LABORATORIES
MERCK & CO., INC.
RAHWAY, N. J.

CLAUDE F. HISKEY
RALPH HIRSCHMANN
N. L. WENDLER

RECEIVED SEPTEMBER 14, 1953

BOOK REVIEWS

Computing Methods and the Phase Problem in X-Ray Crystal Analysis. Report of a Conference Held at The Pennsylvania State College, April 6–8, 1950. By RAY PEPINSKY (Editor). The X-Ray Crystal Analysis Laboratory, Department of Physics, The Pennsylvania State College, State College, Pa. 1952. xvii + 390 pp. 21.5 × 27.5 cm. Price, $7.50.

The conference report presented in this volume is the result of a meeting of about fifty specialists in the field of crystal structure determination from X-ray diffraction data, which was organized by Professor Ray Pepinsky at the Pennsylvania State College under the joint sponsorship of the Rockefeller Foundation and the Office of Naval Research. It was the intent of the conference and the resulting report to review the current status of the problem posed by the lack of experimental information on the phases of the X-ray beams scattered by a given crystal and also of the progress in computing methods applicable to crystal structure determination. This intent has been very successfully fulfilled, and this collected review is a basic contribution to the literature of that field.

The report consists essentially of four parts. The first is a group of ten papers dealing with the basic mathematical problems involved in the application of Fourier transformations in the analysis of the experimental intensity data. Following an introduction by R. Pepinsky and a general statement of the problem by J. M. Bijvoet, papers by C. A. Beevers and A. L. Patterson discuss the structural information which can be obtained from the "Patterson" synthesis using $|F|^2$ coefficients. M. J. Buerger then presents an-