effect, a value which stands in approximate theoretical agreement with the 2.92 ± 0.07% result for the related C^{13} effect according to a recent study.[8] Since the isotope effect ratio 2 is a clear prediction of the absolute rate theory, we have attempted to establish more firmly whether the malonic acid case does deviate by redetermining the C^{13} and C^{14} intramolecular isotope effects, employing only mass spectrometric measurements. The results given below are preliminary.

Labeled malonic acid was synthesized *via* the cyanide-cyanoacetate route employed previously.[6] The crude malonic acid was purified on a silicic acid column, using the *n*-butanol-chloroform solvent system[9]; after preliminary concentration, the product was freed of solvents by sublimation *in vacuo* at 95–100°. This material was diluted to the desired isotopic composition (about 1% C^{14}, total carbon basis) with Eastman Kodak Co. White Label acid which had been subjected to the same manipulations. The mixture was recrystallized from acetone–benzene, resublimed, then stored at room temperature in a vacuum desiccator. The batch decomposition, combustion and degradation techniques employed have been described in detail elsewhere[8]; all samples of carbon dioxide submitted for mass analysis were equilibrated first with standard water to eliminate the effect of variation in O^{18} content.

TABLE I

MOLE FRACTIONS FROM ION CURRENT RATIOS × 10^6

	CO_2 evolved	Acetic acid combustion	Methyl carbon of acetic acid
	10420	10684	10661
C^{13}	10416	10675	10657
	10424	10681	
	16313	8543	
C^{14}	16290	8581	
	16299	8645	

In Table I are given the C^{13} and C^{14} mole fractions obtained from three runs in which yields were nearly quantitative; the results for carboxyl carbon of acetic acid were erratic, however. From the data shown we calculate for the C^{14} effect 5.45 ± 0.46%, for the C^{13} effect 2.85 ± 0.09%; the ratio of these is 1.91 ± 0.17. Since the two heavy isotopes are present in approximately the same concentration in the carboxyl carbon atoms, the results obtained for C^{13} depend upon those for C^{14}; accordingly, agreement of the present C^{13} figure with that obtained previously by the same techniques applied to unlabeled starting material[8] increases our confidence in the C^{14} result. We believe that these results indicate strongly that the malonic acid case can no longer be considered deviant from the predictions of the absolute rate theory.

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RECEIVED SEPTEMBER 10, 1954

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(8) P. E. Yankwich and A. L. Promislow, THIS JOURNAL, **76**, 4648 (1954).

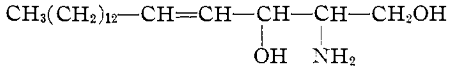
(9) C. S. Marvel and R. D. Rands, *ibid.*, **72**, 2642 (1950).

THE SYNTHESIS OF SPHINGOSINE

Sir:

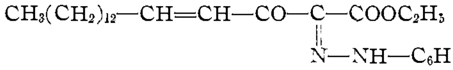
The structure of sphingosine (I) was conclusively established by Carter and his co-workers.[1] Evidence for the *trans* configuration of the double bond has been presented recently by other investigators.[2,3] We wish to announce the synthesis of *trans*-DL-*erythro*-1,3-dihydroxy-2-amino-4-octadecene (I).

Ethyl α-(*trans*-2-hexadecenoyl)-acetoacetate (II) (m.p. 33–34°) was obtained in a 75% yield from the acid chloride and ethyl acetoacetate. *Anal.* Calcd. for $C_{22}H_{38}O_4$: C, 72.1; H, 10.4. Found: C, 72.2; H, 10.6. The Japp–Klingemann reaction[4] of (II) with benzenediazonium chloride afforded a 60–70% yield of the α-phenylazo ester (III), m.p. 39–41°. *Anal.* Calcd. for $C_{26}H_{40}N_2O_3$: C, 72.8; H, 9.3; N, 6.5. Found: C, 72.9; H, 9.5; N, 6.2.



$$CH_3(CH_2)_{12}—CH{=}CH—\underset{\displaystyle OH}{\underset{|}{CH}}—\underset{\displaystyle NH_2}{\underset{|}{CH}}—CH_2OH$$

(I)



$$CH_3(CH_2)_{12}—CH{=}CH—CO—\underset{\displaystyle N—NH—C_6H_5}{\underset{\|}{C}}—COOC_2H_5$$

(III)

Reductive acetylation with zinc in acetic acid gave a quantitative yield of the corresponding α-acetamido ester, m.p. 62–63°. *Anal.* Calcd. for $C_{22}H_{39}NO_4$: C, 69.3; H, 10.2; N, 3.6. Found: C, 69.8; H, 10.6; N, 4.0.

Selective reduction of the β-oxo group was effected with sodium borohydride under mild conditions. The two diastereoisomeric carbinols could be separated by crystallization. One of them (m.p. 64–65°) was obtained in a pure state. *Anal.* Calcd. for $C_{22}H_{41}NO_4$: C, 68.9; H, 10.7; N, 3.6. Found: C, 68.9; H, 10.8; N, 3.6.

Saponification of the pure isomer with diluted hydrochloric acid yielded ethyl 2-amino-3-hydroxy-4-octadecenoate hydrochloride, m.p. 110–112°. *Anal.* Calcd. for $C_{20}H_{40}NO_3Cl$: C, 63.4; H, 10.7; N, 3.7; Cl, 9.4. Found: C, 63.5; H, 10.8; N, 4.0; Cl, 9.6.

Direct treatment of the hydrochloride with an excess of lithium aluminum hydride gave the desired 1,3-dihydroxy-2-amino-4-octadecene (I). The *erythro* configuration of this base was proven by its hydrogenation to the corresponding dihydrosphingosine.

The triacetyl derivative of (I) melted sharply at 90–91° after one crystallization from methanol. *Anal.* Calcd. for $C_{24}H_{43}NO_5$: C, 67.7; H, 10.1; N, 3.3. Found: C, 67.9; H, 10.3; N, 3.6.

The presence of an allylic system involving the carbon atoms 3, 4 and 5 was demonstrated by hydrogenolysis of the secondary acetoxy group (1). When the triacetyl derivative was shaken with platinum oxide and hydrogen, approximately 50–60% of the theoretical amount of acetic acid was produced.

The infrared spectrum of the triacetyl compound showed the characteristic *trans*-peak[2] near 10.3μ.

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(1) H. E. Carter, F. G. Glick, W. P. Norris and G. E. Phillips, *J. Biol. Chem.*, **170**, 285 (1947).

(2) K. Mislow, THIS JOURNAL, **74**, 5155 (1952).

(3) G. Fodor, *Nature*, **171**, 651 (1953).

(4) R. Japp and F. Klingemann, *Ber.*, **20**, 2942, 3284, 3398 (1887).

Further peaks were observed at 9.53, 7.3, 6.82, 6.65, 5.99, 5.76, 3.4 and 2.9μ. These data are in good agreement with the infrared analysis of the triacetyl derivative of natural sphingosine recently reported by Mislow.[2]

As a preliminary study of this route we carried out the above sequence of reactions on ethyl palmitoylacetoacetate and obtained the expected dihydrosphingosine in good over-all yield. A synthesis of the latter involving α-phenylhydrazono-β-oxo-stearic acid has been realized previously.[5]

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RECEIVED SEPTEMBER 2, 1954

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(5) Crosby, Thesis, University of Illinois, 1948.

BOOK REVIEWS

Flow Properties of Disperse Systems. Volume V of Deformation and Flow Series. Edited by J. J. HERMANS, Professor of Physical Chemistry, University, Leiden. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1953. xi + 445 pp. 16.5 × 23.5 cm. Price, $9.90.

This volume comprises reviews on a variety of topics, by a number of authors, all of European origin. It therefore reflects the state of rheological thought in Europe, and while invaluable for this presentation perhaps does less than justice to work in this field done in this hemisphere. The disperse systems discussed include all types from coarse suspensions to macromolecular solutions such as the proteins. R. Roscoe in a short section has given a lucid account of most of the phenomena such as dilatancy, thixotropy and rheopexy encountered in suspensions. E. G. Richardson describes the flow characteristics of emulsions and also contributes a section on liquid sprays, a subject which received much study during the war years. The chapters on smoke and atomization of liquids written by H. L. Green of the British Chemical Defence Experimental Establishment likewise have military application and give the present state of theoretical knowledge in these subjects. The theory of dilute solutions is covered in sections by Ch. Sadron and J. J. Hermans, the former dealing with impenetrable rigid particles while the latter gives the statistical approach to the rheological behavior of flexible, long-chain molecules. J. J. Hermans has contributed also a chapter on gels, their swelling and elastic behavior, which, while valuable in itself, seems somewhat out of place in this volume. The behavior of foams is described by R. Matalon, while Mrs. B. S. Neumann treats the interesting but little understood flow phenomena encountered with powders of finely divided materials such as clay, flour and cement.

This is a well documented book, carefully written and would seem to be an essential for any worker in the field.

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(1) Deceased September 10, 1954.

Progress in the Chemistry of Fats and Other Lipids. Edited by R. T. HOLMAN, Associate Professor of Physiological Chemistry, Hormel Institute of Minnesota, W. O. LUNDBERG, Director, Hormel Institute of Minnesota and T. MALKIN, Reader in Organic Chemistry, University of Bristol. Academic Press, Inc., Publishers, 125 E. 23rd Street, New York 10, N. Y. 1954. vii + 347 pp. 16 × 24.5 cm. Price, $9.80.

Although the structure of fats had been known long before the structure of proteins or carbohydrates was elucidated, it is only recently that there has been an upsurge of interest in lipid substances. This interest is reflected in the increasing number of current books on this subject. The second series of "Progress in the Chemistry of Fats and Other Lipids" presents a review of the recent work in the whole range of fat chemistry and biochemistry. The editors are to be complimented on the diversity and scope of the areas covered, which include the following topics: The Polymorphism of Glycerides by T. Malkin, 50 pp., Autoxidation of Fats and Related Substances by Ralph T. Holman, 48 pp., Nutritional Significance of the Fats by Harry J. Deuel, Jr., 94 pp., The Surface Properties of Fatty Acids and Allied Substances by D. G. Dervichian, 50 pp., Urea Inclusion Compounds of Fatty Acids by H. Schlenk, 25 pp., Infrared Absorption Spectroscopy in Fats and Oils by D. H. Wheeler, 24 pp., and Countercurrent Fractionation of Lipids by H. J. Dutton, 34 pp.

The practice of assigning a particular subject to a specialist in the field is continued in Volume 2. Thus, Malkin presents a strong argument for existence of four solid forms of triglyceride rather than the three proposed by Lutton. It is unfortunate that Lutton's views were not mentioned in greater detail. It also seemed to this reviewer that since Holman's views on the autoxidation of fat differ from those of Hilditch, a brief review of Hilditch's theories might have been included. Deuel's chapter on the Nutritional Significance of Fats is very well done, the presentation is balanced by the inclusion of both sides of controversial issues. The wide scope of material is well classified and well written. The last four chapters provide valuable reference material—the chapter on Urea Inclusion Compounds seemed particularly timely.

The physical aspects of this volume are, indeed, satisfactory. The book is attractively and durably bound, with the title in gold print. The printed text is clear and easily readable. Only one error in spelling was noted. Each chapter contained many helpful sub-titles. I felt that a table of contents at the beginning of each chapter would have been desirable.

Volume II of Progress in the Chemistry of Fats and Other Lipids is certainly to be recommended to all scientists interested in the chemistry and biochemistry of lipids.

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Cell Chemistry, In Honor of Otto Warburg. Edited by DEAN BURK, Foreign Member, Max Planck Institute for Cell Physiology, Berlin-Dahlem (Germany), and Head of Cytochemistry Section, National Institutes of Health, United States Public Health Service, Bethesda, Md. (U.S.A.). Elsevier Press, 402 Lovett Blvd., Houston, Texas. 1953. 362 pp. 17.5 × 25.5 cm. Price, $7.50.

This is a "Festband" in the German tradition. It was published originally as Volume XII, Numbers 1 and 2 of the journal, *Biochimia et Biophysica Acta*, 1953. Its title is perhaps more descriptive of Warburg's activity than it is of the contents of the book, being as it is a collection of thirty-seven articles and having as its only unification some contact with Warburg, either as a teacher or scientist.

The subject matter of these essays, although primarily biochemical in nature, varies all the way from straight organic and physical chemistry through a major collection of biochemical contributions into cellular physiology and