mole of acetyl bromide, the ratio remaining constant for 22 hours. This result corresponds to a product containing 0.64 mole of ethyl acetate per mole of acetic acid and differs sufficiently from the value of this ratio which was observed by Farkas, *et al.*,[2] to eliminate acetyl bromide as a possible intermediate in the oxidation reaction.

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The Synthesis of 2-Ethylhexanol-1-C^{14} and Esters[1]

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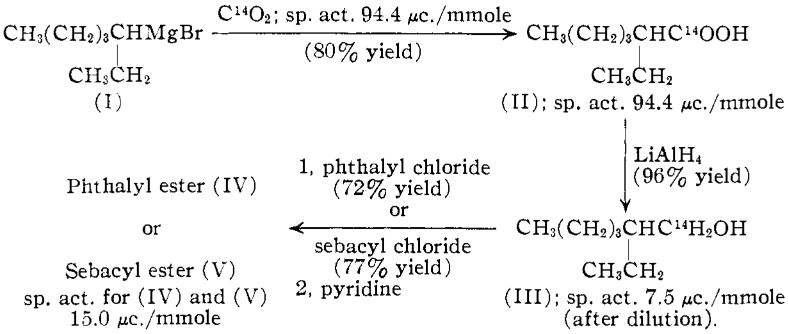
The sebacyl and phthalyl esters of 2-ethylhexanol-1-C^{14} were required at this Laboratory for the evaluation of primary plasticizers and synthetic lubricants using radioisotope-tracer techniques. These syntheses were accomplished by the radiocarbonation of 3-heptylmagnesium bromide (I), using a method similar to that of Dauben, Reid and Yankwich,[2] followed by lithium aluminum hydride reduction of the resulting 2-ethylcaproic acid-1-C^{14} (II). The 2-ethylhexanol-1-C^{14} (III) produced was esterified by the acid chloride–pyridine technique.



The alcohol and esters so obtained were identical in physical properties (including infrared spectra) with the pure unlabeled compounds.[3]

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[1] The opinions or assertions herein are those of the authors, and are not to be construed as reflecting the views of the Navy Department or the Naval Service at large.

[2] (a) W. G. Dauben, J. C. Reid and P. E. Yankwich, *Anal. Chem.*, **19**, 828 (1947); (b) M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. E. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 178.

[3] The full experimental details of the preparations described in this paper have been deposited as Document number 4229 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm, payable to Chief, Photoduplication Service, Library of Congress.

Pungents. Fatty Acid Amides[1]

BY LEONARD M. RICE, CHARLES H. GROGAN, BERNARD H. ARMBRECHT AND E. EMMET REID

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Pungent principles or irritants have been discussed in recent reviews.[2,3] Although most of the pungents are amides, this is not always the case, as for example, gingerone and gingerol. In amides such as piperidine and chavicine the amine moiety is piperidine; in capsicin it is vanillylamine.

Staudinger, *et al.*,[4] studied the relationship of various acids with different amines with respect to pungency. They concluded that the amide linkage was necessary, since a salt did not give the same action. They prepared various amides of piperidine using fatty acids. With the lower or higher members of the fatty acid series they did not observe any peppers. Asano, *et al.*,[5] have expanded this work and found that the piperidides of the fatty acids were most pungent at pelargonic acid and that this pungency decreased in going up or down the series. It is interesting that furylvaleric piperidide has a strong taste. This acid, if split enzymatically, would approximate the C_9 length. Mitter and Ray[6] have found that with the acylated isobutylamines the highest degree of activity lies with the unsaturated fatty acids, 2-heptenoic and 2-nonenoic. Also when employing vanillylamine they found that the fatty acid moiety gave maximal pungency at the C_9-acid.

As part of our continuing study of various amides, we have found that the morpholides of fatty acids containing from seven to twelve carbon atoms are strong pungents. We have found in this series of morpholides that the greatest activity is produced when the fatty acid moiety is octanoic, nonanoic or decanoic. When the acid portion of the amide was either increased or decreased in length the activity was diminished. It was of interest to study the amine moiety in the most potent acid range in order to find out how essential the morpholine portion might be. When pelargonic acid was used, which exhibited maximum pungency in the morpholine series, and the heterocyclic part of the molecule was contracted to pyrrolidine or expanded to hexamethylenimine, the products obtained were almost devoid of pungency. In a like manner when diethylamine, dipropylamine or ethylpropylamine was substituted for morpholine, the resulting amides had very little pungency. It thus appears that the morpholides occupy a unique place in pungency not previously recognized. Indeed, the

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[1] Supported by a grant from the Geschickter Fund for Medical Research, Inc.

[2] M. B. Jacobs, *Am. Perfumer*, **48**, #7, 60 (1946).

[3] S. Takata, *Koryo*, #4, 6 (1948).

[4] (a) H. Staudinger and H. Schneider, *Ber.*, **56**, 699 (1923); (b) H. Staudinger and F. Muller, *ibid.*, **56**, 711 (1923).

[5] (a) M. Asano and F. Nakatomi, *J. Pharm. Soc. Japan*, **53**, 174 (1933); *C. A.*, **27**, 2672, 2703 (1933); (b) M. Asano and T. Kanematsu, *J. Pharm. Soc. Japan*, **531**, 375 (1926); *C. A.*, **20**, 2844 (1926).

[6] P. C. Mitter and S. C. Ray, *J. Indian Chem. Soc.*, **14**, 421 (1937).