I. Referring to a publication by H. Adkins, the authors establish a comparison between the catalytic activity of nickel and that of copper chromite. In conclusion, they add: "these seem to be the only known examples . . . of the attack of an ester group in the presence of a nickel catalyst," an attack which is, on the contrary, normal in the presence of copper chromite.

However, in 1935 my collaborator, S. Sabetay, and I showed that over nickel alone as a catalyst, the high pressure hydrogenation of certain essential oils brought about a lowering of the index of saponification and an elevation of the index of acetylation; in other words, there was some transformation of the ester function to the alcohol function, catalytically, by a true Bouveault–Blanc reaction.[2]

We have confirmed these preliminary results by the hydrogenation of pure esters. Ethyl laurate and butyl stearate have furnished the corresponding alcohols, lauryl and stearyl, free from impurity, with yields up to 62%. We think that we were the first to have realized the direct conversion of esters to alcohols under the action of nickel alone as a catalyst.

II. Since it is coumarin which constituted the principal object of the article by de Benneville and Connor, we recall at this time that the preparation of dihydrocoumarin is very easily carried out over Raney nickel.[3]

The hydrogenation begins at about 40° and becomes very rapid in the neighborhood of 80°. At the end of an hour a charge of 1300 g. is converted to a product which distills entirely at 145° (13 mm.) and freezes at 24°; that is to say, the product is free from impurity and the yield quantitative. Simultaneous recording of temperature and pressure on the same graph, using the apparatus which we have devised, permits the operation to be followed in detail.

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RECEIVED JUNE 26, 1940

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[2] (a) Palfray and Sabetay, *Chemie et Industrie, numero special* (Congrès de Bruxelles), 1935, p. 746; (b) *Bull. soc. chim.*, **3**, 682 (1936); (c) **5**, 1424 (1938).

[3] A more complete account may be found in two of our articles; one, chiefly technical, Palfray, *Science et Industrie*, **284** (bis), 53 (1937); the other, chiefly chemical, *Bull. soc. chim.*, in press, to appear in the April–June issue.

[4] All attempts to communicate with Professor Palfray have been in vain and we have not, therefore, been able either to submit to him Dr. Connor's reply or to secure his approval of the translation of his own manuscript.—THE EDITOR.

THE BEHAVIOR OF ESTERS OVER RANEY NICKEL

Sir:

The statement from our paper[1] quoted above was intended to apply to results with Raney nickel and the nickel on kieselguhr catalysts described by Adkins.[2,3] We are sorry if our failure to make clear this limitation has seemed to detract from the work of Palfray and Sabetay. The results of these workers indicate that their method differs considerably from the one we used. Over their catalyst they obtained alcohols from esters, while we have observed that ethyl β-cyclohexylpropionate and cyclohexyl *n*-butyrate were unchanged[4] after treatment at 250° over Raney nickel at pressures of 100–150 atmospheres. Furthermore, they report the formation of hydrocarbons having the same number of carbon atoms as the alcohols, while under the conditions we used, primary alcohols may be converted to hydrocarbons with one less carbon atom.[5] It was these indications of differences in conditions which led us to omit the citation of the work of Palfray and Sabetay, and we are glad to acknowledge their contributions using nickel alone as a catalyst. Their work has been cited in our subsequent papers.[4,6]

We should also like to call attention to the hydrogenation[7] of ethyl laurate over another type of nickel catalyst. This constitutes, so far as we are aware, the earliest report of hydrogenation of the ester group over a catalyst containing nickel.

The formation of dihydrocoumarin by the catalytic hydrogenation of coumarin is in line with the usual behavior of α,β-unsaturated esters and it had been carried out previously.[8] We did not regard our result as novel or original but reported the isolation of dihydrocoumarin to show that it was the precursor of the other hydrogenation products.

We should like to make clear the fact that, in

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[1] De Benneville and Connor, THIS JOURNAL, **62**, 283 (1940).

[2] Adkins, "Reactions of Hydrogen, etc.," University of Wisconsin Press, Madison, Wis., 1937.

[3] Our original statement suggested that other functional groups might alter the ease of hydrogenation of the ester group. This was based on the report of Raney and Adkins [THIS JOURNAL, **61**, 1107 (1939)] that a hydroxymethylpyrrolidine was formed by the hydrogenation of 2-carbethoxypyrrole over Raney nickel. Ovakimian, Kuna and Levene [THIS JOURNAL, **62**, 677 (1940)] have since found that other α-amino esters behave similarly.

[4] McClellan and Connor, THIS JOURNAL, **63**, 484 (1941). However, this paper reports the formation of glycols from substituted coumarins and of alcohols from esters of phenols over Raney nickel.

[5] Wojcik and Adkins, *ibid.*, **55**, 1293 (1933).

[6] De Benneville and Connor, *ibid.*, **62**, 3067 (1940).

[7] Folkers and Adkins, *ibid.*, **53**, 1097 (1931).

[8] Adkins, private communication (1937); Späth and Galinowsky, *Ber.*, **70B**, 235 (1937); Palfray and Sabetay, *Bull. soc. chim.*, **5**, 1424 (1938).

our first paper[1] on this subject, we did *not* describe the formation of alcohols from esters over Raney nickel.[9] While we plan to continue our work with coumarin and other lactones, the investigations already mentioned[4,6] conclude our interest in the behavior of simple esters over Raney nickel and we now have no plans for extending this phase of the work.

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[9] The communication of Ovakimian, Kuna and Levene[3] indicates a misunderstanding of this point.

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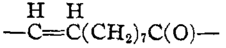
RECEIVED NOVEMBER 3, 1941

UNSATURATED FAT OXIDASE: SPECIFICITY, OCCURRENCE AND INDUCED OXIDATIONS

Sir:

An oxidase found in soybeans converts unsaturated fats into peroxides.[1-6] Carotenoid pigments or vitamin A present in the fat are oxidized by unstable intermediate products, not by direct enzymatic action nor by the relatively stable fat peroxides.[3-8]

This enzyme (soy beans ground with 5 parts of water and centrifuged) has now been found to oxidize directly only those compounds containing the  $-\overset{H}{C}=\overset{H}{C}(CH_2)_7C(O)-$ group with *cis* configuration. For example, oleic, ricinoleic, linoleic and linolenic acids and their esters absorbed oxygen rapidly. Under the same conditions, oleyl alcohol, elaidic and erucic acids (in decalin) and a variety of other unsaturated compounds were not oxidized (many of these compounds were generously donated by Dr. George Burr and by Dr. C. R. Noller).

The unsaturated fat oxidase has been detected in seeds of various legumes: *Acacia melanoxyln*, alfalfa, scarlet runner bean, white clover, *Laburnum anagyroides*, *Lupinus albus*,[2] *L. Benthamii*, *L. Greyi*, *L. nanus*, garden peas (green and dry), purple vetch (green and dry). It was not detectable in seeds of castor bean, almond, maize, cucumber, flax or sunflower, nor in etiolated barley seedlings in which rapid oxidations of the carotenoids are also known to occur.[9]

Many factors influence the oxidation of organic substances induced by concomitant enzymatic oxidation of fats. Easily autoöxidizable carotenoids (as eschscholtzxanthin)[10] were decolorized more rapidly than stabler pigments (as zeaxanthin).[9] In highly unsaturated fatty compounds (ethyl linolenate), the oxidation of carotenoids was much slower than that of the same pigments dissolved in olive oil, an indication of competition between the fat and the carotenoid for the oxidizing agent.

Chlorophylls *a* and *b* were oxidized to colorless substances by the system of fat, enzyme and oxygen. *p*-Phenylenediamine (but not the *o* or *p* isomer) was oxidized to a blue pigment, a reaction similar to that produced by the cytochrome complex. Dihydroxyphenylalanine (dopa) was oxidized to the black pigment melanin, a reaction also catalyzed by the highly specific dopa oxidase. Ascorbic acid was oxidized at a slow rate. In the absence of fats or if heated enzyme preparations were used, none of these induced oxidations took place.

Polyphenols exhibited remarkable effects upon the enzymatic oxidation of fats and upon the induced oxidation of other substances. Hydroquinone, pyrogallol and catechol (10 mg. per 2–3 ml. of enzyme solution) prevented the absorption of oxygen by unsaturated fats and thus prevented the induced oxidation of other substances. Phloroglucinol and resorcinol, by contrast, did not inhibit absorption of oxygen by the fat or decolorization of carotenoids. They did, however, prevent oxidation of *p*-phenylenediamine to the blue pigment. Formation of this blue pigment resulted from reaction between the amine and the fat peroxides. This reaction was inhibited by all the polyphenols, most of which were oxidized at a slow rate.

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[1] André and Hou, *Compt. rend.*, **194**, 645 (1932); **195**, 172 (1932).

[2] Craig, *J. Biol. Chem.*, **114**, 727 (1936).

[3] Haas and Bohn, *Chem. Abs.*, **28**, 4137 (1936).

[4] Tauber, THIS JOURNAL, **62**, 2251 (1940).

[5] Sumner and Dounce, *Enzymologia*, **7**, 130 (1939).

[6] Sumner and Sumner, *J. Biol. Chem.*, **134**, 531 (1940).

[7] Süllmann, *Helv. Chim. Acta*, **24**, 465, 646 (1941).

[8] Fry, Schultz and Light, *Ind. Eng. Chem.*, **28**, 1254 (1936).

[9] Strain, "Leaf Xanthophylls," Carnegie Institution of Washington Publ. No. 490 (1938).

[10] Strain, *J. Biol. Chem.*, **123**, 425 (1938).