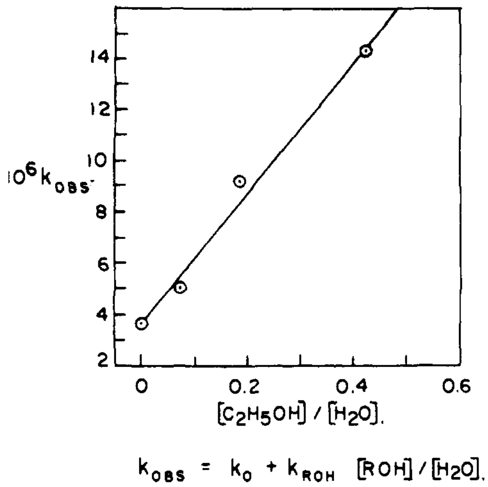
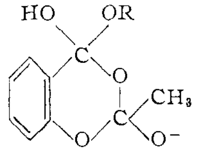


Fig. 6.—Plot of the observed rate constant for *p*H-independent hydrolysis of aspirin anion at 25° against the molar ratio of ethanol to water. The postulated dependence of this plot is the equation $k_{obs} = k_0 + k_{ROH}[ROH]/[H_2O]$.

If it is assumed that water and alcohol compete for aspirin anion ion II to form a reacting cyclic intermediate such as



IV

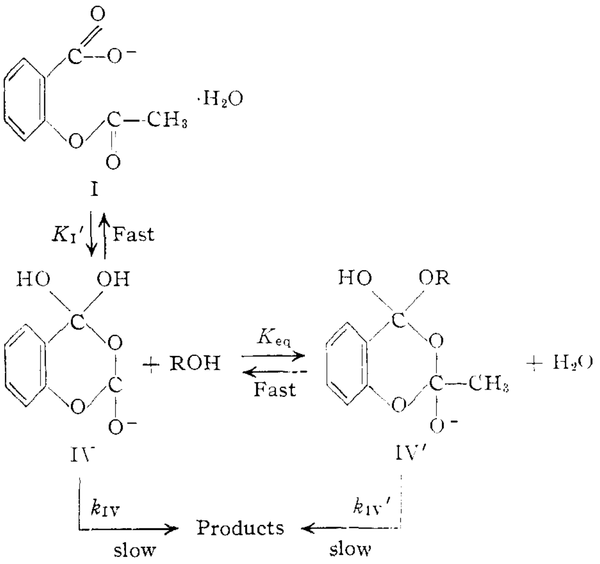
where R is H– or C_2H_5–, then

$$k_{obs} = k_a[H_2O] + k_b[ROH] \qquad (9)$$

However, the data of Table VII do not follow equation 9. At best, a linear representation is valid only for $[C_2H_5OH] > 3.33$ and

$$k_{obs} = 1.43 \times 10^{-6}[C_2H_5OH];\ k_a = 0 \qquad (10)$$

A possible explanation that best fits the data is that the cyclic intermediate in the hydrolysis of an aspirin anion II is formed stoichiometrically as the hydrate IV and $[IV] = K_{I'}[I']$ in a non-rate-determining step. Subsequently, the alcoholate equilibrates with the hydrate and the further steps to products are rate determining



On the basis of this mechanism, the rate expression can be formulated.

$$\begin{aligned} k_{obs}[I'] &= k_{IV}[IV] + k_{IV'}[IV'] \\ &= k_{IV}[IV] + k_{IV'}K_{eq}[IV][ROH]/[H_2O] \\ &= k_{IV}K_{I'}[I'] + k_{IV'}K_{eq}K_{I'}[I'][ROH]/[H_2O] \qquad (11) \end{aligned}$$

Thus

$$k_{obs} = k_0 + k_{ROH}[ROH]/[H_2O] \qquad (12)$$

Equation 11 best fits the data which are plotted accordingly in Fig. 6. The resultant quantitative equation is

$$k_{obs} = 3.65 \times 10^{-6} + 25.5 \times 10^{-6}[C_2H_5OH]/[H_2O] \quad (13)$$

Acknowledgment.—The author is greatly indebted to Miss Kathryn G. Stimson for excellent technical assistance and to Mr. Maxton Murray for the supply of the esters.

KALAMAZOO, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

The Effect of Various Solvents on the Carbonyl Absorption Spectrum of Glycidic Esters

BY HORTON H. MORRIS[1] AND RAYMOND H. YOUNG, JR.

RECEIVED JANUARY 7, 1957

The infrared spectra of a number of glycidic esters show two well-defined absorption bands of approximately equal intensity in the 1800–1700 cm.$^{-1}$ carbonyl stretching region instead of the one to be expected. Of greater interest is the fact that, although the spectra of solutions of the esters in non-hydrogen bonding solvents show the two absorption bands in the carbonyl region, the two bands disappear and are replaced by a single band when the esters are dissolved in a solvent capable of forming hydrogen bonds with the ester. Possible explanations of these effects are advanced.

We have determined the infrared spectra of a number of previously reported[2] glycidic esters and have found that, without exception, the esters give two well-defined absorption bands of almost equal intensity in the 1800–1700 cm.$^{-1}$ carbonyl stretching region instead of the one expected band. The average position of the centers of the two bands for the esters studied are 1729 and 1753 cm.$^{-1}$.

Of even greater interest is the fact that the two bands disappear and are replaced by a single, rather broad band centering at about 1737 cm.$^{-1}$ when the

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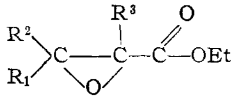
(1) Southern Clays, Inc., Gordon, Ga.

(2) H. H. Morris and R. H. Young, Jr., THIS JOURNAL, **77**, 6678 (1955) and previous papers.

TABLE I



CARBONYL FREQUENCIES OF $R^1R^2C(-O-)C(R^3)-C(=O)-OEt$ IN CCl_4 AND IN $CHCl_3$

				CCl_4 solution							$CHCl_3$ solution		
No.	R_1	R_2	R_3	$\bar{\nu}_1$	$\bar{\nu}_2$	$\Delta\bar{\nu}$	$\epsilon_{\bar{\nu}_1}$	$\epsilon_{\bar{\nu}_2}$	$\frac{\epsilon_{\bar{\nu}_1}+\epsilon_{\bar{\nu}_2}}{2}$	A_{CCl_4}	$\bar{\nu}_3$	$\epsilon_{\bar{\nu}_3}$	A_{CHCl_3}
I	CH_3	CH_3	C_2H_5	1726	1748	22	246	231	239	13.2	1740	262	14.2
II	CH_3	CH_3	C_3H_7	1729	1756	27	292	258	275	18.4	1737	252	19.2
III	CH_3	CH_3	C_4H_9	1726	1752	26	273	221	247	16.1	1732	232	13.6
IV	CH_3	CH_3	C_5H_{11}	1729	1752	23	288	254	271	14.8	1736	251	16.5
V	CH_3	CH_3	C_6H_{13}	1727	1756	29	283	238	261	14.9	1737	251	13.6
VI	CH_3	CH_3	C_7H_{15}	1730	1753	23	286	242	264	15.5	1740	266	16.7
VII	CH_3	CH_3	C_8H_{17}	1727	1752	25	268	225	247	15.7	1735	254	17.4
VIII	CH_3	CH_3	C_9H_{19}	1729	1753	24	300	217	259	17.1	1730	278	18.4
IX	$-(CH_2)_5-$		CH_3	1729	1756	27	285	269	277	14.1	1740	304	14.2
X	$-(CH_2)_5-$		C_2H_5	1734	1760	26	238	216	227	13.9	1740	260	13.8
XI	$-(CH_2)_5-$		C_3H_7	1728	1751	23	292	218	255	17.5	1734	259	19.9
XII	$-(CH_2)_5-$		C_4H_9	1730	1756	26	317[b]	281[b]	299[b]	24.1[b]	1738	264[b]	26.6[b]
XIII	$-(CH_2)_5-$		C_5H_{11}	1727	1752	25	259	223	241	11.9	1739	260	14.5
XIV	$-(CH_2)_5-$		C_7H_{15}	1728	1754	26	249	202	226	14.4	1738	251	16.0
XV	$-(CH_2)_5-$		C_8H_{17}	1727	1755	28	268	201	235	14.3	1737	224	15.1
XVI	$-(CH_2)_5-$		$C_{10}H_{21}$	1726	1750	24	312	182	247	20.5	1732	235	17.8
XVII	C_6H_5	CH_3	CH_3	1726	1752	26	298	231	265	16.9	1739	261	15.5
XVIII	C_6H_5	H	CH_3	1732	1751	19	287	209	248	17.0	1741	268	17.2
XIX	C_6H_5	H	H	1736	1753	17	237	275	256	15.4	1739	293	15.1
Average values[a]				1729 ± 2	1753 ± 2	24.5 ± 2	276 ± 18	228 ± 19	252 ± 13	15.6 ± 1.5	1737 ± 3	259 ± 15	16.0 ± 1.6

[a] Average values calcd. from $\frac{\text{(observations)}}{\text{no. of observations}}$; average error $= \frac{\text{(absolute value of deviation).}}{\text{no. of observations}}$ [b] These values were excluded from calculation of averages.

esters are dissolved in a solvent capable of forming hydrogen bonds, while the spectra of the esters in a variety of non-hydrogen bonding solvents all show the two clearly defined absorption bands. Thus the two bands are present when the esters are dissolved in carbon tetrachloride, carbon disulfide, benzene, cyclohexane, 2-nitropropane, *n*-propyl mercaptan or dimethylaniline; but are replaced by a single band (often fairly broad) when solvents such as chloroform, *n*-butyl alcohol, aniline, methanol or *m*-cresol are used. In those solvents capable of hydrogen bonding with the ester there is a gradual shift of band center position to lower frequencies with increasing hydrogen bonding ability.

It is also of interest that the area under the curves of the esters in CCl_4 solution is found to be approximately equal to the area under the curve of chloroform solutions of the esters. The average value of the extinction coefficient, determined by taking one-half the sum of the extinction coefficients of each of the two bands observed in carbon tetrachloride solution, is approximately equal to that of the single band obtained when the esters are dissolved in chloroform. Thus the average molar extinction coefficient for the two bands in carbon tetrachloride solutions of the esters is 252, while the molar extinction coefficient for the single band given by the esters in chloroform solution is 259.

Table I lists the esters studied and gives the positions of the bands in the carbonyl region when the esters are dissolved in carbon tetrachloride ($\bar{\nu}_1$, $\bar{\nu}_2$) and when they are dissolved in chloroform ($\bar{\nu}_3$). No change in position or intensity of any other band in the spectra with change of solvent has been observed. Table I also gives the difference in frequency ($\Delta\bar{\nu}$) between the two bands, the molar extinction coefficients ($\epsilon_{\bar{\nu}_1}$, $\epsilon_{\bar{\nu}_2}$, $\epsilon_{\bar{\nu}_3}$) as determined for each band, the average molar extinction coefficient for the two bands observed in carbon tetrachloride solutions $((\epsilon_{\bar{\nu}_1} + \epsilon_{\bar{\nu}_2})/2)$ and the areas under the curves (A_{CCl_4}, A_{CHCl_3}) as determined between 1800 and 1600 cm.$^{-1}$ by means of a planimeter. Average values are given at the bottom of each column.

Figure 1 shows the appearance of the bands in the carbonyl region of ethyl α-*n*-propyl-β,β-dimethylglycidate dissolved in various solvents. The curves have been displaced upward for clarity.

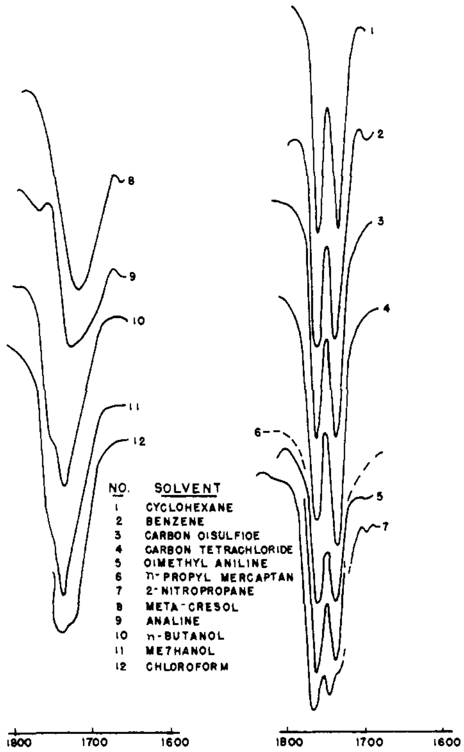
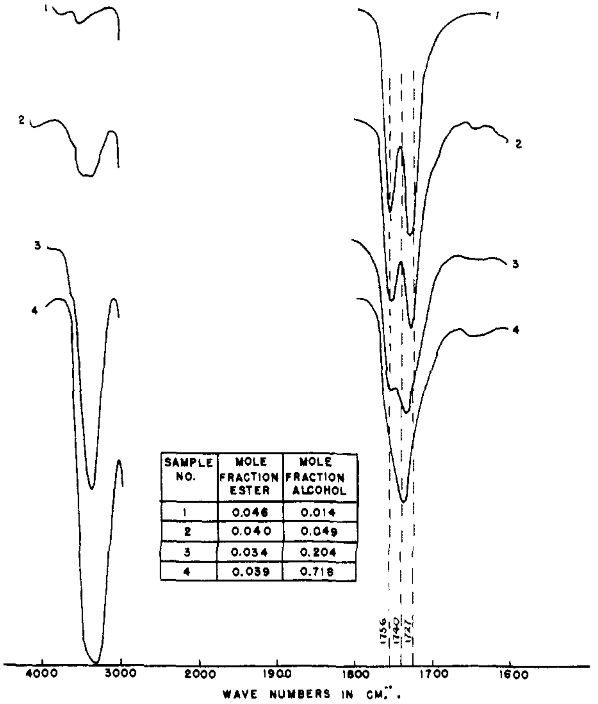
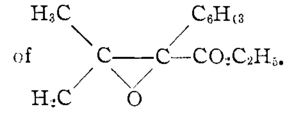


Fig. 1.—Ethyl α-*n*-propyl β,β-dimethylglycidate in various solvents.



SAMPLE NO.	MOLE FRACTION ESTER	MOLE FRACTION ALCOHOL
1	0.046	0.014
2	0.040	0.049
3	0.034	0.204
4	0.039	0.718

Fig. 2.—The effect of the addition of *n*-butyl alcohol to a CCl_4 solution of



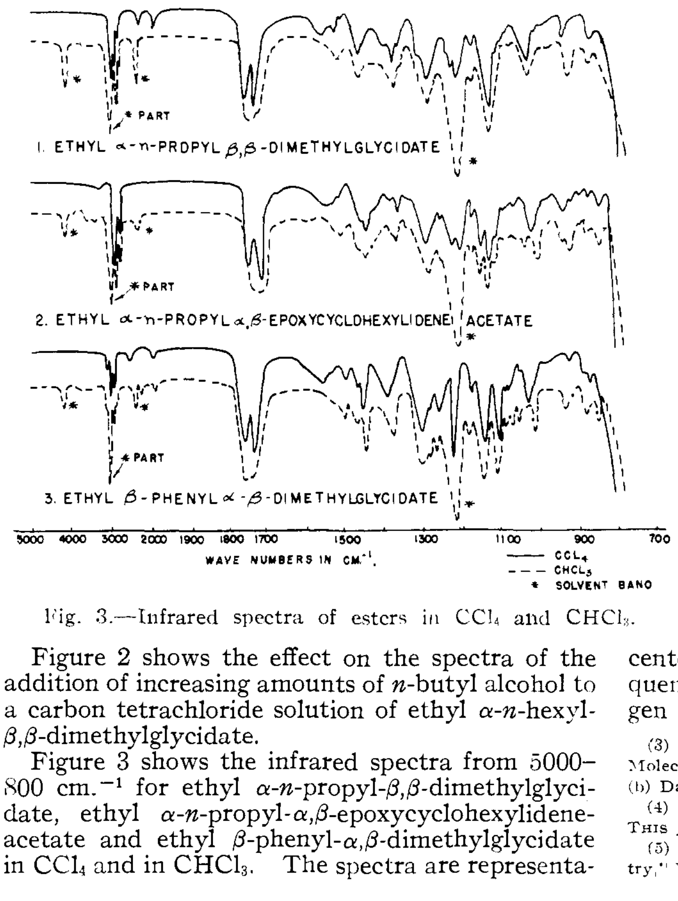


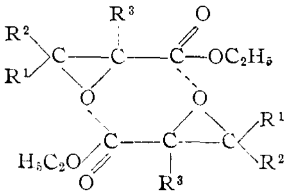
Fig. 3.—Infrared spectra of esters in CCl_4 and $CHCl_3$.

Figure 2 shows the effect on the spectra of the addition of increasing amounts of *n*-butyl alcohol to a carbon tetrachloride solution of ethyl α-*n*-hexyl-β,β-dimethylglycidate.

Figure 3 shows the infrared spectra from 5000–800 cm.$^{-1}$ for ethyl α-*n*-propyl-β,β-dimethylglycidate, ethyl α-*n*-propyl-α,β-epoxycyclohexylideneacetate and ethyl β-phenyl-α,β-dimethylglycidate in CCl_4 and in $CHCl_3$. The spectra are representative of the types of glycidic esters herein discussed and the spectra of other members of the three homologous series differ only slightly from those shown.

Discussion

It may be possible to explain these observations by assuming dimer formation and hence a coupling between the characteristic stretching vibrations of the two ester carbonyl bonds to cause a frequency splitting, thus giving rise to a pair of absorption bands on either side of the unperturbed frequency. It seems reasonable to assume that two molecules of the ester could orient through dipole–dipole interaction as indicated in the diagram below to form bonds which are strong enough to allow coupling of the two ester carbonyl vibrations.



That the bonding is between the carbon of the ester carbonyl group and the oxygen of the oxirane ring may be indicated by the distance between the two absorption bands (average 24.5 cm.$^{-1}$) observed in CCl_4 solutions of the esters, since the split is a measure of the efficiency of the coupling.[3a] Davison[3b] has shown that in diacyl peroxides (two atoms separating the two carbonyl groups) the split between the two observed carbonyl absorption bands is about 25 cm.$^{-1}$, while anhydrides[4] show a similar pair of absorption bands with a split of about 65 cm.$^{-1}$ resulting from the shorter coupling link.

That the interaction does not involve a linear polymerization and is between two molecules only may be indicated by the fact that no change in the appearance of the two absorption bands occurs upon dilution—an effect to be expected with the type of bonding shown in the diagram, but not to be expected if the bonding were linear.[5]

Intensity measurements and determination of the area under the curves for the esters in CCl_4 and in $CHCl_3$ may also support the dimer picture. The data would seem to indicate that only the ester carbonyl stretching vibration is involved and that a splitting is occurring in non-hydrogen bonding solvents, rather than the juxtaposition of absorption bands caused by two different types of carbonyl vibrations.

The disappearance of the two absorption bands and the appearance of a single band centering approximately at the unperturbed frequency when a solvent capable of forming hydrogen bonds with the ester is added may be an indi-

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(3) (a) Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 199; (b) Davison, *J. Chem. Soc.*, 2456 (1951).

(4) Thompson, *ibid.*, 328 (1948); E. J. Modest and J. Szmuszkovicz, THIS JOURNAL, **72**, 577 (1950).

(5) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. V, Longmans, Green and Co., Ltd., London, 1954, p. 384.

cation of the relative strength of the bonds involved in dimer formation.

That the frequency of the single band formed in hydrogen-bonding solvents appears to move toward lower frequencies with increasing hydrogen bonding ability of the solvent and that the appearance of the single band in hydrogen bonding solvents is concentration dependent (see Fig. 2) indicates a dissolution of the dimer and the formation of two molecules of the ester, each associated through hydrogen bonding with a solvent molecule.

The bonding which results in dimer formation, as postulated, must be very weak since molecular weight determinations by freezing point depression, as determined in benzene or cyclohexane, give the normal value for a monomeric unit.

It is of interest to note that Schotte[6] has recently recorded the infrared spectra of the diastereomers of $HO_2CCHEtCHMeCO_2H$, m.p. 177–178° (I) and 100–101° (II) and of $HO_2CCHEtCH_2CHMeCO_2H$, m.p. 104.5–5.5 (III) and 83.5–84.5° (IV), and has noted that II and III show a split peak for the carbonyl stretching frequency. He assumed these to have the racemoid configuration. I and IV showed no such split and were presumed to be the mesoid isomers.

Since the esters herein reported are all racemic mixtures, it may be that the proposed dimer is a racemic pair. Molecular models of such a racemic pair and of a pair having a single configuration indicate that the racemic pair may allow a closer approach of the ring oxygens to the carbonyl carbons because of less interference by the alkyl substituents.

The observations might be interpreted in a different way by assuming that two rotational isomers are present in which the carbonyl oxygen is on the same side of the molecule as the ring oxygen in one case and away from the ring oxygen in the other. Since this would represent an equilibrium mixture and since the extinction coefficients of the two observed bands are approximately equal in every case, the unlikely assumption must be made that equal numbers of molecules exist in each of the states for each of the esters. Since resonance splitting does seem to be indicated, we believe that dimer formation offers a better explanation of the data than the assumption of rotational isomerism.

Experimental

The infrared spectra were measured with a Baird Associates model 4–55 recording infrared spectrometer employing sodium chloride optics. The same 0.029-mm. cell was used for all determinations. No reference cell was used. The accuracy of the wave length measurement is estimated to be ±5 cm.$^{-1}$ in the region discussed. Polystyrene bands at 1602.5 and 1594.7 cm.$^{-1}$ were recorded on each spectrum for calibration purposes.

Compounds XV, XVI, XVIII and XIX may contain small amounts of impurities. The other esters are considered to be quite pure (see reference 2).

Acknowledgment.—We wish to express our great appreciation for the financial aid and encouragement given us through a Cottrell grant from Research Corporation.

ORONO, MAINE

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[6] L. Schotte, *Arkiv. Kemi*, **9**, 397 (1956).

[CONTRIBUTION FROM THE FISHERY TECHNOLOGICAL LABORATORY[1]]

Liquid–Solid Countercurrent Distribution of Fatty Acids with Urea

BY W. N. SUMERWELL

RECEIVED FEBRUARY 7, 1957

The reaction of fatty acids with urea to form inclusion adducts has been used as the basis of a liquid–solid countercurrent distribution method for separating mixtures of fatty acids. The fatty acids and urea, dissolved in an appropriate solvent, served as the moving liquid phase while the precipitated reaction products served as the stationary solid phase. The character of the distribution curve obtained for a given mixture of fatty acids depends on the differences in the distribution coefficients for the individual fatty acids when they are distributed between solid inclusion adducts and organic solvent. The method was found to be effective in the separation of mixtures of fatty acids such as arachidic, stearic, palmitic and oleic acid as well as in the separation of a mixture of the *cis–trans* isomers, oleic and elaidic acids. The method also was applied to a mixture of highly unsaturated salmon egg oil fatty acids (iodine value 350). The results indicate that urea distribution may be a valuable tool in the separation of such unstable compounds.

Introduction

Studies on the formation of urea inclusion adducts as a means of fractionating marine oil fatty acids and their derivatives were begun in this Laboratory several years ago. A preliminary report of this work has been published.[2] The present paper describes the development of a liquid–solid countercurrent distribution procedure based on the differential binding of fatty acids by urea and its application to some synthetic and natural mixtures of fatty acids.

Subsequent to Craig's description of his two-phase liquid–liquid countercurrent distribution technique[3] and its use in the separation of organic compounds, he published a report on a liquid–solid countercurrent system.[4] By this technique, he distributed chrysene and anthracene between cyclohexane and alumina. He defined a coefficient *A* as the ratio of the weight of solute dissolved in the liquid phase to the weight of solute adsorbed on the solid phase. The position of the maximum concentration of a compound in the distribution system was then calculated by substituting the value of *A*

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[1] A laboratory of the Branch of Commercial Fisheries, U. S. Fish and Wildlife Service, Seattle, Washington.

[2] C. Domart, D. T. Miyauchi and W. N. Sumerwell, *J. Am. Oil Chemists' Soc.*, **32**, 481 (1955).

[3] L. C. Craig, *J. Biol. Chem.*, **155**, 519 (1944).

[4] L. C. Craig, C. Golumbic, H. Mighton and E. Titus, *Science*, **103**, 587 (1946).