Recoveries were only 10% less than the calculated values.

Other composite milk samples have been used for biological assay by the Bourquin-Sherman[6] method, shown[7] to measure the flavin factor. The rats, kept for the customary eight-week period, produced satisfactory composite growth curves. Estimates of the lactoflavin or vitamin G content of the samples were made from the composite growth curves of the rats, compared with the reference curve of rats fed the standard lactoflavin, shown in the table.

Five biological estimates checked the rapid chemical determinations with a maximum difference of 25% as indicated.

Supplements Milk	No. rats	Daily portion, ml.	Av. gain for 8 weeks, g.	Estimated flavin per ml. milk, γ	Flavin per ml. milk Fluoray lamp, γ	Diff. from biological value per ml. γ	%
A	10	3	43	2.2	2.30	+0.10	+ 4
B	10	3	40	2.0	1.76	− .24	−12
C	10	3	46	2.3	2.20	− .10	− 5
D	10	3	54	2.6	2.55	− .05	− 2
E	10	3	50	2.5	1.88	− .62	−25
Lactoflavin		γ		Animals for reference curve			
	9	5.0	33				
None	25	..	±0	Negative control animals			

Effort is being made to apply this rapid method to colostrum, shown by biological work in our laboratory to be higher in lactoflavin content than ordinary milk. Certain characteristics of the colostrum, due to physical or chemical properties, present difficulties not yet overcome.

KANSAS AGRICULTURAL EXPT. STA.
MANHATTAN, KANSAS
RECEIVED APRIL 20, 1937

---

[6] Bourquin-Sherman, THIS JOURNAL, **53**, 3501 (1931).

[7] Booher, Blodgett and Page, *J. Biol. Chem.*, **107**, 599 (1934); Bisbey and Sherman, *ibid.*, **112**, 415 (1935).

COMMUNICATIONS TO THE EDITOR

THE THERMAL DECOMPOSITION OF α-TOCOPHEROL

Sir:

Last year, H. M. Evans, O. H. Emerson and G. A. Emerson [*J. Biol. Chem.*, **113**, 319 (1936)] reported the isolation from wheat germ oil and later from cottonseed oil [*Science*, **83**, 421 (1936)] of alcohols having the biological properties of vitamin E. These substances were named "tocopherols" and appear to be isomers with the empirical formula $C_{29}H_{57}O_2$, and to be chemically closely related. Structurally, it is known that the compounds contain a hydroxyl group which accounts for one of the oxygen atoms.

I have recently investigated α-tocopherol, the most active of these substances, using material prepared from cottonseed oil, and wish to report certain observations on the behavior of this compound at higher temperatures which seem to permit deductions to be drawn regarding the constitution of α-tocopherol.

When α-tocopherol is heated decomposition sets in at 350° and a crystalline sublimate is obtained as well as an oily distillate. The crystalline material is very readily obtained in the pure state and its investigation led to a formula $C_{10}H_{14}O_2$. A literature search revealed its close resemblance to durohydroquinone and the identity was established by direct comparison with a sample of this compound kindly furnished through the courtesy of Professor Lee Irvin Smith of the University of Minnesota. Both the diacetyl derivative and the quinone were also prepared and compared by mixed melting point determinations with the corresponding derivatives of the known durohydroquinone.

ANALYSES AND MELTING POINTS

Compound		Diphenol	Diacetate	Quinone
M. p., °C.		230	201	111
Formula		$C_{10}H_{14}O_2$	$C_{14}H_{18}O_4$	$C_{10}H_{12}O_2$
Calcd.	C, %	72.28	67.18	73.14
	H, %	8.40	7.25	7.36
Found	C, %	72.29 72.32	67.12	73.42
	H, %	8.54 8.46	7.21	7.41

The above findings seem to be best explained by assigning the structure of a mono-ether of durohydroquinone to α-tocopherol. The ultraviolet spectrum of α-tocopherol is very similar to that of hydroquinone as has been pointed out to me by Dr. Oliver H. Emerson. Its insolubility in alkalies and its high reducing power, as well as the lack of reducing properties in its esters are also in good agreement with such an assumption.

My present efforts are mainly directed to an elucidation of the alkyl portion of α-tocopherol. On completion of these investigations I intend to publish the details of the above experiments. I wish to express my appreciation of the assistance of Professor H. M. Evans and Dr. Oliver H. Emerson of the University of California who kindly advised me on the production of α-tocopherol and who assayed various concentrates during its preparation.

RESEARCH LABORATORIES
MERCK & COMPANY, INC.
RAHWAY, N. J.
E. FERNHOLZ

RECEIVED MAY 20, 1937

CIS-TRANS ISOMERIZATION BY BROMINE ATOMS

Sir:

An investigation to ascertain whether halogens and halogen acids add "*cis*" or "*trans*" to maleinoid (*cis*) or fumaroid (*trans*) forms of unsaturated substances has been under way in this Laboratory for some time. It is evident that for a complete understanding of this problem it is necessary to know the effectiveness of the addition reagent causing the transformation of the "maleinoid" and the "fumaroid" form. Yet, while numerous observations on the rearrangement in solution of the "maleinoid" to the "fumaroid" form are available, no critical study has been made of the inter-relationship of the reagents responsible for the transformation, and no comprehensive hypothesis has been advanced which would correlate these diverse observations.

We have found that in the dark, in two hours, carefully purified isostilbene, dissolved in benzene, is not isomerized to stilbene by hydrogen bromide when the reactants are mixed either in air or in a highly evacuated tube, or in the presence of antioxidants (*e. g.*, hydroquinone, catechol, thiophenol). However, the addition of a peroxidic substance (*e. g.*, benzoyl peroxide, ascaridole) to the reaction mixture caused complete isomerization to stilbene in a few minutes. The time required for complete conversion varied with the amount of the peroxide used, but even minute traces of peroxides caused complete conversion in thirty minutes.

In direct sunlight or in artificial light, isostilbene, dissolved in benzene, is transformed to stilbene by hydrogen bromide in about five minutes. Here evacuation of the reaction vessel had a pronounced effect in that twenty minutes was required for complete isomerization. Most striking, however, is the effect of antioxidants. Thus, hydroquinone, ethyl mercaptan, etc., completely prevent the transformation of isostilbene to stilbene by hydrogen bromide in the light, either in the presence or absence of air.

Furthermore, no isomerization of isostilbene to stilbene was observed under any of the above conditions (antioxidant or peroxidic, in the light or in the dark) with hydrogen chloride. Neither has a mixture of bromine and hydrogen bromide caused isomerization in the dark. The halogens are well known to cause isomerization in the light.

The above experiments lead us to believe that bromine atoms[1] are the active catalysts in this transformation. They would be produced by the action of oxygen or a peroxide, or by light, on hydrogen bromide. Once produced, they convert isostilbene to stilbene by a chain reaction. The ineffectiveness of hydrogen chloride in causing isomerization is thus readily explainable on the basis of its relative stability toward oxygen.

Several investigators[2] have observed that alkali metals and traces of certain organo-alkali compounds cause similar isomerizations. We are, therefore, engaged in an extensive study to evaluate the part played by atoms in such conversions, and the role of other agencies.

(1) The hypothesis that bromine atoms are responsible for the "peroxide effect" in the addition of hydrogen bromide to unsaturated molecules is proposed in an article by M. S. Kharasch, H. Englemann and F. R. Mayo, in the *Journal of Organic Chemistry*, in press.

(2) Meerwein and Weber, *Ber.*, **58**, 1266 (1925); Schlenk and Bergmann, *Ann.*, **463**, 107-117 (1928); Ziegler and Wollschitt, *ibid.*, **479**, 129-131 (1930).

JONES CHEMICAL LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
M. S. KHARASCH
J. V. MANSFIELD
F. R. MAYO

RECEIVED MAY 18, 1937

PHOTODECOMPOSITION OF CHLORINE DIOXIDE IN CARBON TETRACHLORIDE SOLUTION

Sir:

We have investigated recently the bromine sensitized photodecomposition of chlorine dioxide in carbon tetrachloride solution and find that appreciable amounts of Cl_2O_6 are formed during the reaction. A reinvestigation of the unsensitized decomposition of chlorine dioxide in carbon tetrachloride solution using $\lambda = 3650$ Å. showed that