concentration and an accompanying decrease in the ferrous iron concentration and increase in the ferric iron concentration. Following these adjustments the system approached a steady state in which the benzoyl peroxide concentration continued to decline at a slow rate while the ferrous and ferric iron concentrations became constant. This behavior can be readily interpreted in terms of the proposed "Redox" cycle. For given concentrations of benzoyl peroxide and sorbose, the rates of the various reactions will depend primarily upon the concentrations of the ferrous and ferric iron. But since the reaction which produces ferrous iron consumes ferric iron, and vice versa, it is obvious that the reaction system will approach a steady state in which the rates of the benzoyl peroxide–ferrous iron and the sorbose–ferric iron reactions become equal and the concentrations of the ferrous and ferric iron become constant.

Summary

A mechanism is proposed for the reduction activation of polymerizations in emulsion systems. It is found that ferrous iron, solubilized in the oil phase as the stearate, promotes the decomposition of benzoyl peroxide into free radicals which are capable of initiating polymerization. In this process the ferrous iron is oxidized to the ferric form which is subsequently transferred to the aqueous phase where it exists as a pyrophosphate complex. The ferric iron is then reduced by an appropriate water soluble reducing agent such as sorbose. The reduced ferrous iron is ultimately transferred back to the oil phase to resume the cycle.

Sodium stearate is used as an emulsifying agent, but it does more than promote emulsification since it also renders the iron salts oil soluble. Omitting any of the reagents mentioned above or replacing the soap by a cationic emulsifying agent which is incapable of solubilizing the iron in oil, disrupts the smooth operation of the cycle. The net result of the entire cycle is the reduction of organic peroxides into free radicals and acid ions by a reducing sugar with iron serving as the effective intermediary.

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[CONTRIBUTION FROM GELATIN PRODUCTS DIV., R. P. SCHERER CORP.]

Absorption Spectra of Steroid–Antimony Trichloride Reaction Products[1]

BY ALEXANDER MUELLER

It has been reported by numerous workers that sterols give color reactions with various reagents.[2] The employment of antimony trichloride has been shown to give a greater specificity for quantitative determinations.[3] Examinations in this laboratory[4,5] have revealed that the spectra of the colors developed with the widely used antimony trichloride reagent are highly characteristic and have reasonably high extinction coefficients with magnitudes at specific wave length maxima directly related to the structure of the steroid molecule. Measurements on thirty-four steroids, mostly cholesterol derivatives, to confine the study to a homologous series, are reported in this communication. The interrelationships between molecular groupings and resulting spectra are summarized and the applicability of the measurements in characterization of molecular structure is indicated.

Experimental

A 1-ml. aliquot of the steroid[6] solution in purified chloroform was pipetted into a 25-ml., glass-stoppered cylinder, 10 ml. of antimony trichloride reagent[7] added, and the reaction mixture thoroughly shaken. The solution is poured into one pair of matched 10-mm. corex cells while the second or reference cell is filled with 1 ml. of chloroform and 10 ml. of antimony trichloride reagent. The absorption spectra were determined with a Beckman spectrophotometer, Model DU, using an incandescent lamp as the source of illumination and varying the slit width to accord with the region of the spectrum examined.

Throughout the measurements, reaction periods were determined with a stopwatch and optimum concentrations of steroid solutions were ascertained as the result of adjustments in preliminary trials. For additional manipulative details see reference.[5] From the optical densities determined for the solutions at the respective time intervals and wave length maxima, corresponding extinction coefficients, $E(1\%, 1\text{ cm.})$, were calculated. The values are summarized in the accompanying table and graphs.

Discussion

The compounds in Table I are arranged according to the following order: (1) saturated hydrocarbons with one or more substituents (excepting hydrogen) on Rings I and II; (2) one double bond with no substituents on Rings I and II; (3) one double bond with one substituent (such as hydroxy, keto, ester or halogen) on Rings I and II; (4) one double bond with two substituents on Ring I or II; (5) two double bonds with no substituents on Ring I or II; (6) two double bonds with one substituent on Ring I or II; (7) unclassified (calciferol and sex hormones).

Comparing the magnitude of absorption intensities of the various antimony trichloride reaction products, calciferol (Fig. 8), with an exo-

(1) Presented in part before the Division of Organic Chemistry, American Chemical Society, Chicago, Illinois, September 9 to 13, 1946.

(2) Sobotka "The Chemistry of the Steroids," The Williams and Wilkins Co., Baltimore, 1938) has reviewed applications of the qualitative aspects.

(3) G. Pincus, *Endocrinology*, **32**, 176 (1943).

(4) A. Mueller, *Ind. Eng. Chem. Anal Ed.*, **18**, 214 (1946).

(5) F. W. Lamb, A. Mueller and G. W. Beach, *ibid.*, **18**, 187 (1946).

(6) The compounds examined were prepared in the Fine Chemicals Division of the R. P. Scherer Corp., and the purity verified by elemental analysis, melting point, optical rotation and ultraviolet absorption spectra.

(7) The solvent and reagent were prepared according to D. T. Ewing, G. V. Kingsley, R. A. Brown and A. D. Emmett, *Ind. Eng. Chem. Anal. Ed.*, **15**, 301 (1943).

TABLE I

ABSORPTION PROPERTIES OF VARIOUS STEROID–ANTIMONY TRICHLORIDE REACTION PRODUCTS

Compound	$\lambda_{max.}$, mμ	E (1%, 1 cm.)	Time	Remarks
Cholestanone	320	2.0	19 hr.	Slight maximum; continues to rise
Coprostanone	320	24.3	44 hr.	Maxima develop very slowly, and are not sharp
	415	6.0	20 hr.	
	510	3.0	44 hr.	
7-Keto-cholestanyl acetate	355	11.4	1 hr.	Stable from 60 to 80 minutes
6-Keto-cholestanyl acetate	320	1.8	2 hr.	Very low absorption
		3.2	24 hr.	
5,6-Dibromide cholestanyl acetate	322	45.0	2 hr.	All maxima continue to rise
	397	13.0	2 hr.	
	490	6.0	2 hr.	Absorption similar to cholesteryl-α-oxide acetate (see Fig. 7)
Δ^4-Cholestene	320	5.0	30 min.	Absorption increases slowly
	322	36.3	24 hr.	
	424	19.5	30 min.	At 24 hr. 424 mμ max. has shifted to 450 mμ, and new max. is present at 525 mμ
	450	15.0	24 hr.	
	525	17.7	24 hr.	
Δ^5-Cholestene	322	7.0	30 min.	Absorption increases slowly
	316	45.0	20 hr.	
	420	24.0	30 min.	Both maxima are shifted at 20 hr.
	430	33.0	20 hr.	
Cholesterol	322	135.0	90 min.	Figure 1 (yellow color)
	360	103.0	25 min.	
	420	88.0	40 min.	
	505	90.0	120 min.	
Δ^4-Cholestenol-7 (pseudo-cholesterol)	322	147.0	90 min.	Similar to cholesterol
	360	106.0	25 min.	
	420	45.0	40 min.	
	505	36.0	120 min.	
Cholesteryl acetate	322	107.0	90 min.	Similar to cholesterol
	360	74.0	25 min.	
	420	69.0	40 min.	
	505	55.0	120 min.	
Cholesteryl benzoate	322	95.0	90 min.	Similar to cholesterol
	360	68.0	20 min.	
	420	70.0	20 min.	
	505	60.0	120 min.	
Cholesteryl chloride	322	95.0	90 min.	Similar to cholesterol except reaction rate. E (1%, 1 cm.) values continue to rise
	360	49.0	35 min.	
	420	35.0	35 min.	
	505	87.0	90 min.	
Cholesteryl methyl ether	322	114.6	90 min.	Similar to cholesterol except time reaction rate
	360	69.4	40 min.	
	420	63.6	60 min.	
	505	82.2	120 min.	
i-Cholestanyl-6-methyl ether	322	108.0	90 min.	Similar to cholesterol except time reaction rate
	360	50.0	60 min.	
	420	46.0	120 min.	
	505	80.0	90 min.	
Cholesteryl-α-oxide acetate	322	68.0	18 hr.	Figure 7. Maxima continue to rise
	397	53.0	18 hr.	
	480	28.0	18 hr.	
Cholestenone	318	61.0	35 min.	Figure 4. Stable, then rises and shifts to 320 mμ, continues to rise
	320	88.0	4 hr.	
	320	116.0	24 hr.	
	375	68.0	24 hr.	First observed at 24 hours
	530	25.0	4 hr.	Maximum rises, then drops, then rises again
	530	22.0	6 hr.	
	530	40.0	24 hr.	Maximum shifts to 520 mμ at 24 hr.
	650	7.0	4 hr.	
		12.0	6 hr.	Broad maximum, rises slowly shifts to 658, mμ
		15.0	24 hr.	
β-Sitosterol	322	109.0	105 min.	Similar to cholesterol except time reaction rate
	360	87.0	30 min.	
	420	98.0	45 min.	
	505	83.0	120 min.	
Stigmasteryl acetate	322	48.0	30 min.	Similar to cholesterol except a marked change in time reaction rate and appearance of new maxima at 24 hours (green color)
	360	72.0	20 min.	
	420	114.0	50 min.	
	505	67.0	120 min.	
	640	30.0	24 hr.	
	720	23.0	24 hr.	
7-Keto-cholesterol	355	533.0	50 min.	Figure 3
	460	22.0	2 hr.	
	690	24.0	2 hr.	
7-Keto-cholesteryl acetate	355	593.0	50 min.	Similar to 7-keto-cholesterol
	457	29.6	2 hr.	
	695	25.6	2 hr.	
7-Keto-cholesteryl benzoate	355	450.0	50 min.	Similar to 7-keto-cholesterol except no 460 mμ maximum
	685	36.0	90 min.	
7-Hydroxy-cholesteryl benzoate	590	159.0	1 min.	In usual $SbCl_3$ concentration
	590	132.0	1 min.	In one-half usual $SbCl_3$ concentration
	460	132.0	1 min.	In one-half usual $SbCl_3$ concentration
Cholesteryl dibenzoate	590	138.0	1 min.	Figure 5. Similar to 7-hydroxycholesteryl benzoate (blue color)
	460	125.0	1 min.	
	590	181.0	5 min.	In one-half usual $SbCl_3$ concentration
Δ^3, Δ^5-Cholesterilene	322	127.0	3 hr.	Figure 6
	360	141.0	5 min.	
	420	268.0	3 min.	
	500	100.0	3 hr.	
7-Keto-cholesterilene	355	655.0	1 min.	Stable from 1 to 25 minutes
	450	11.0	2 hr.	Similar to 7-keto-cholesterol (see Fig. 3)
6-Bromo-7-ketocholesterilene	320	225.0	1 min.	Stable from 1 to 60 minutes (introduction of bromine changes entire character of absorption curve)
	388	30.0	60 min.	
	700	26.0	5 hr.	
	700	68.0	22 hr.	
7-Dehydro-cholesterol	322	320.0	8 min.	Figure 2. The 322 mμ max. is stable from 4 to 10 min., then drops slowly
	520	7.0	8 min.	
Ergosterol	322	63.0	5 min.	Figure 2. The 393 mμ max. is stable from 5 to 10 min., then drops slowly
	393	250.0	5 min.	
	505	12.4	5 min.	
Androsterone	320	110.0	48 hr.	Figure 9. Absorption rises very slowly
	388	100.0	48 hr.	
	455	22.0	48 hr.	
	485	8.0	48 hr.	
	570	16.0	48 hr.	
	620	16.0	48 hr.	
Dehydro-iso-androsterone	320	26.0	1 hr.	Figure 10
	388	142.0	6 hr.	
	416	75.0	1 hr.	
	510	86.0	6 hr.	
	580	64.0	6 hr.	
	615	65.0	6 hr.	
Δ^5-Androstene-diol-(3β,17α)	365	70.0	50 min.	Figure 12
	418	171.0	50 min.	
	500	36.0	50 min.	
Testosterone	320	83.0	5 min.	Figure 12
	320	108.0	2.5 hr.	
	355	98.0	2.5 hr.	
	355	59.0	2.5 hr.	
Estrone	420	440.0	44 hr.	Figure 11
	510	95.0	44 hr.	
Calciferol	500	1800.0	3 min.	Figure 8

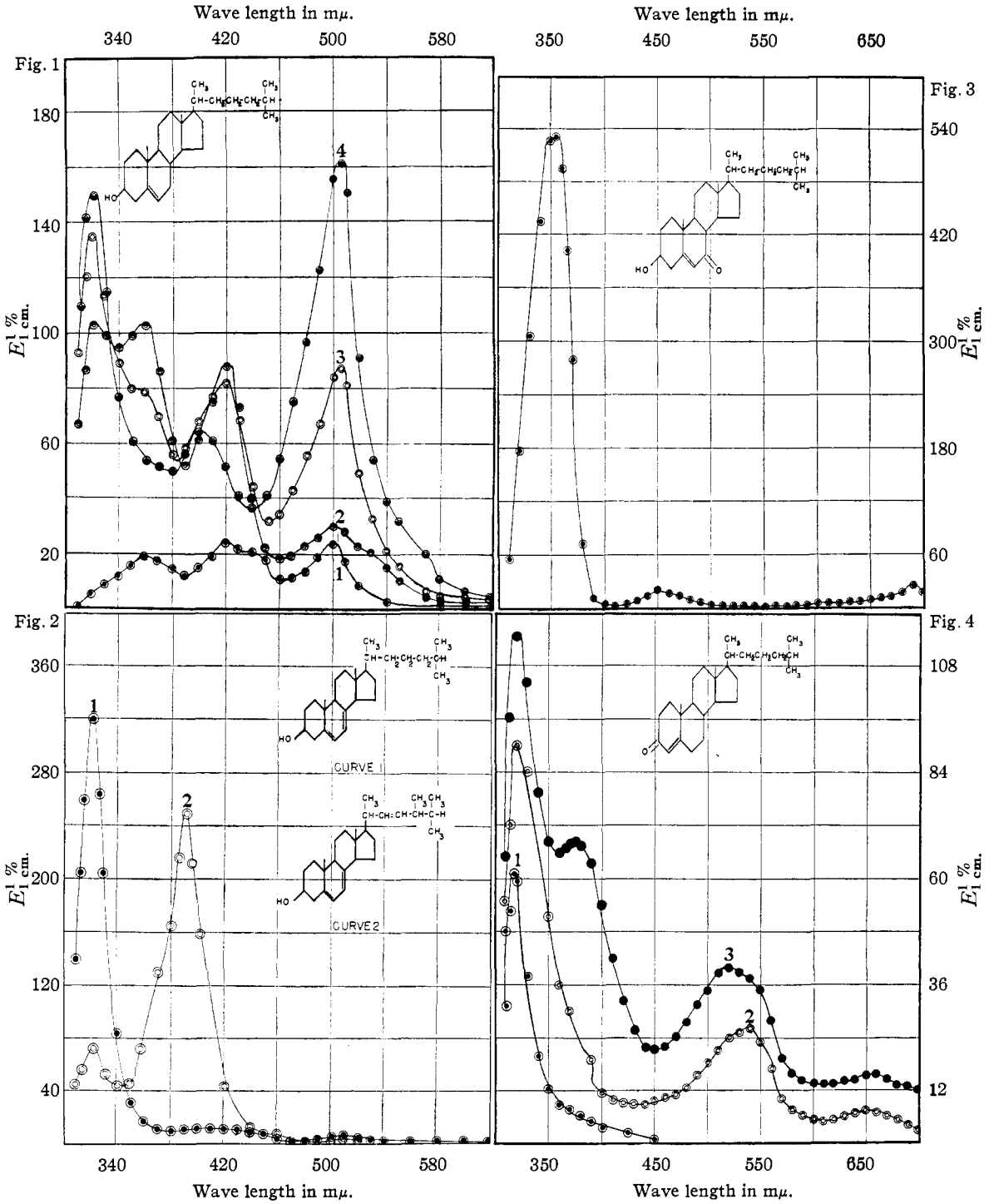

Fig. 1.—Absorption curves of cholesterol–antimony trichloride reaction products: 1, curve at five to fifteen minutes; 2, at thirty to forty minutes; 3, at ninety to one hundred minutes; 4, at twenty-four hours.

Fig. 2.—Absorption curves of 7-dehydrocholesterol and ergosterol–antimony trichloride reaction products: 1, 7-dehydrocholesterol at five to fifteen minutes; 2, ergosterol at one to ten minutes.

Fig. 3.—Absorption curve of 7-keto-cholesterol–antimony trichloride reaction product: (curve between 300–400 mμ at forty to fifty minutes, between 400–700 mμ at ninety to one hundred minutes).

Fig. 4.—Absorption curves of cholestenone–antimony trichloride reaction products: 1, curve at thirty to forty minutes; 2, at three and one-half to four hours; 3, at twenty-four hours.

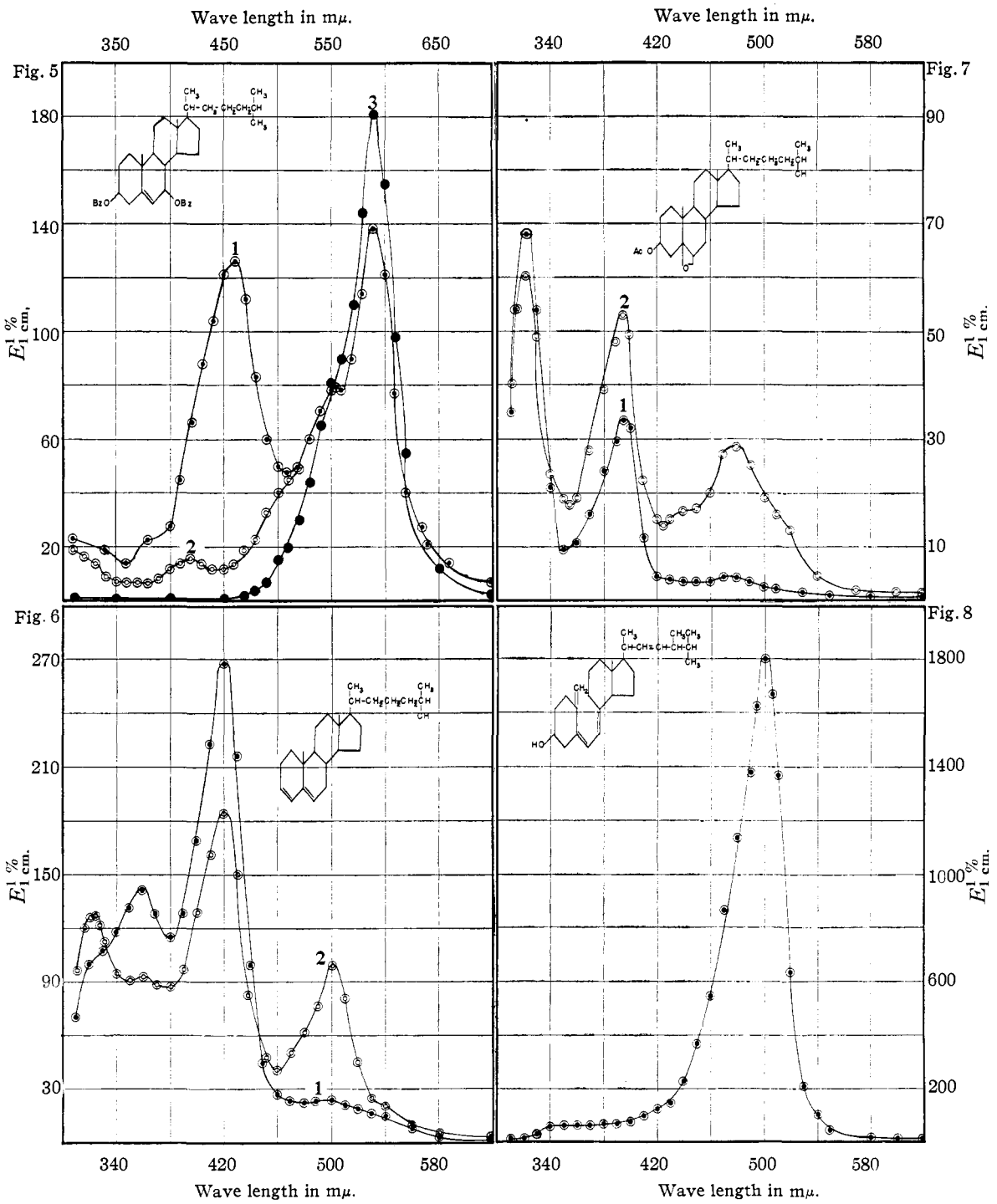

Fig. 5.—Absorption curves of cholesteryl dibenzoate–antimony trichloride reaction products: 1, curve at one to ten minutes; 2, at fifteen to twenty minutes (from 520–700 mμ, it is identical with curve 1); 3, at one to ten minutes with one-half the usual antimony trichloride concentration.

Fig. 6.—Absorption curves of Δ^3,Δ^5-cholesterilene–antimony trichloride reaction products: 1, curve at one to ten minutes; 2, at three hours.

Fig. 7.—Absorption curves of cholesteryl α-oxide acetate–antimony trichloride reaction products: 1, curve at twenty to thirty minutes; 2, at eighteen hours.

Fig. 8.—Absorption curve of calciferol–antimony trichloride reaction product; curve at one to five minutes.

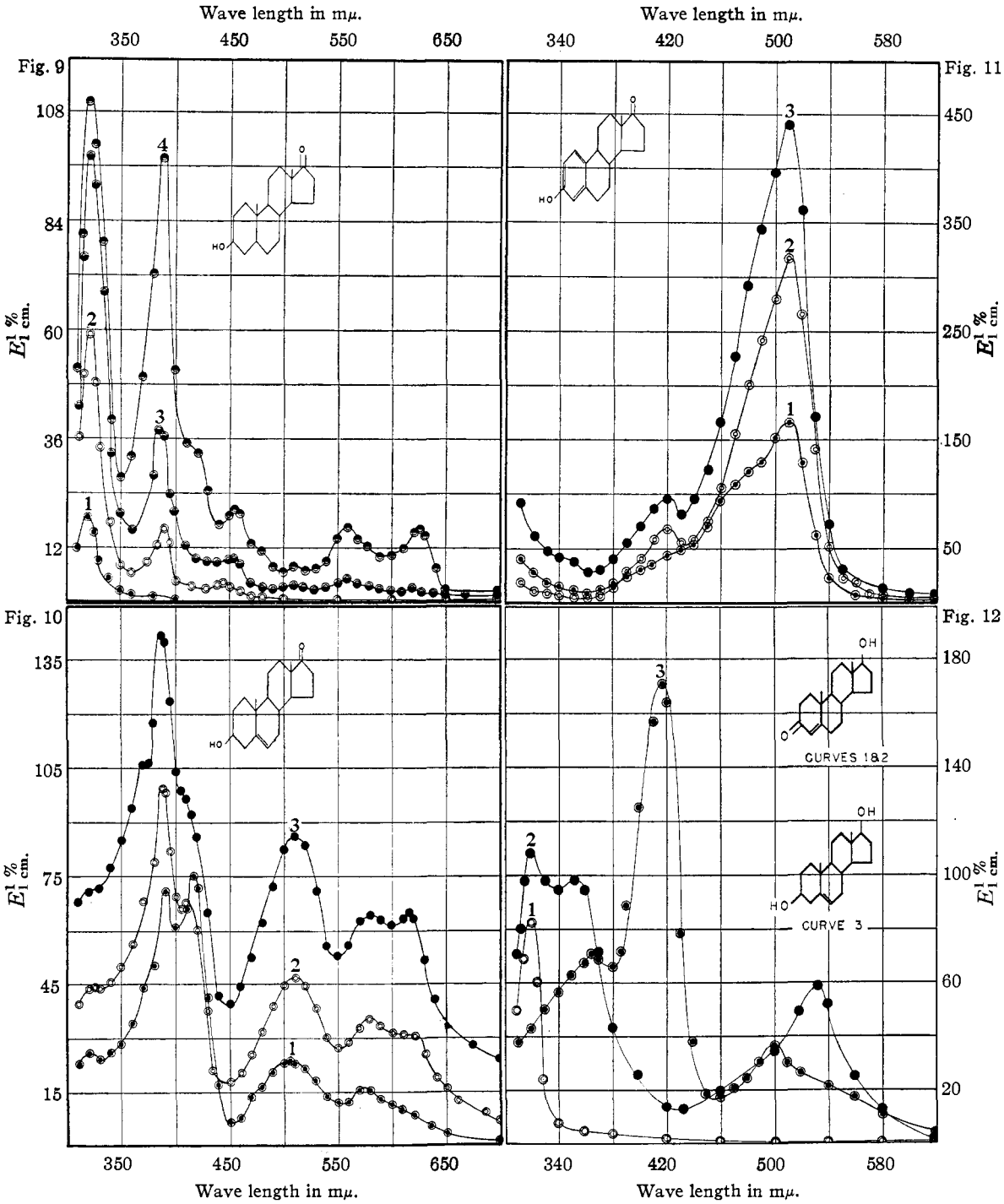

Fig. 9.—Absorption curves of androsterone–antimony trichloride reaction products: 1, curve at one hour; 2, curve at six hours; 3, curve at twenty-four hours; 4, at forty-eight hours.

Fig. 10.—Absorption curves of dehydro-isoandrosterone–antimony trichloride reaction products: 1, curve at one hour; 2, at two hours; 3, at six hours.

Fig. 11.—Absorption curves of estrone–antimony trichloride reaction products: 1, curve at twenty hours; 2, curve at twenty-seven hours; 3, curve at forty-four hours.

Fig. 12.—Absorption curves of testosterone– and Δ^5-androstenediol-(3β,17α)–antimony trichloride reaction products: 1, testosterone at one to five minutes; 2, testosterone at two to two and one-half hours; 3, Δ^5-androstenediol-(3β,17α) at fifty to sixty minutes.

cyclic, triply conjugated system, has the highest value. On the other hand, estrone (Fig. 11) with an endocyclic, triply conjugated system in Ring I has a contrastingly low absorption intensity. In general, the type of linkages which produces the highest absorption are the conjugated double bond, and the double bond in conjugation to a keto, hydroxy, or other polar grouping. Compounds having both endocyclic and exocyclic unsaturation produce high extinction coefficients (see 7-keto-cholesterilene, and 7-keto-cholesterol (Fig. 3)). The influence of exocyclic changes have little effect in the absence of endocyclic unsaturation, while endocyclic unsaturation in the absence of exocyclic groupings produces a spectrum of rather high intensity (see cholesterilene, Fig. 6). Generally, in a conjugated double bond system wherein there is one center of electronic interaction a single narrow absorption band is exhibited while a system having two or more locations of electron concentration exhibits more than one maximum. Comparing the antimony trichloride spectra of 7-dehydrocholesterol and ergosterol (Fig. 3) the difference apparently is due to the side chain double bond of ergosterol. 7-Dehydrocholesterol gives a single strong maximum, due to the single conjugated system in Ring II, while ergosterol with electronic interaction between the side chain and Ring II give two prominent bands. Conversely, calciferol (Fig. 8) with a double bond in the side chain gives a single absorption maximum. Possibly there is no interaction between the semicyclic, triply conjugated system in Ring II and the side chain double bond of calciferol. An interesting analogy exists in the comparison of the ultraviolet absorption of ergosterol and calciferol.[8]

(8) H. Dannenberg, *Abhandl. preuss. Acad. Wiss., Math. naturw. Klasse*, No. 21 (1939).

The nature of antimony trichloride reaction on a sterol was assumed (in the initial stages of this work) to be one of dehydration with subsequent shifting of double bonds, and possible introduction of an additional double bond. Preliminary experiments on the isolated reaction products of cholesterol, however, seem to indicate a cyclization product, probably forming a dicyclopentanoperhydrophenanthrene entity. A continuation of studies on this phase, as well as systematic investigations of a series are necessary before definite conclusions may be drawn.

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Summary

The absorption spectra data of the antimony trichloride reaction products of thirty-four steroids are presented. Absorption curves are shown for fourteen representative compounds in the region from 310 to 700 mμ. The data indicate that the spectra are characteristic for specific molecular groupings or combination of groupings in the molecule. Generalizations of the influence of various groupings in the steroid molecule on the resulting spectra are summarized. The analysis of the data obtained from the spectra would indicate that the latter are particularly helpful in following the progress or change in a molecule during synthesis, degradation, or in its quantitative analysis for purity and concentration.

DETROIT, MICHIGAN RECEIVED FEBRUARY 24, 1948

[CONTRIBUTION FROM MASSACHUSETTS INSTITUTE OF TECHNOLOGY, AND HARVARD UNIVERSITY]

The Microwave Spectra of CH_3NCS and CH_3SCN[1]

BY C. I. BEARD[2] AND B. P. DAILEY[3]

Introduction

The use of microwave absorption spectroscopy in determining the structure of linear and symmetric top molecules is now well established. The application to asymmetric molecules, although of much importance in broadening the scope of the techniques, has been very slow because of the complexity of the spectra which are observed. These complexities arise not only from the pattern (or lack of one) of rotational energy levels for the asymmetric rotor, but from nuclear quadrupole coupling, rotational-vibrational interaction, internal free or hindered rotation, and from experimental difficulties in observing spectra in the microwave region. All of these complications, except the last, are potential sources of useful information provided an analysis can be carried out. The natural procedure would seem to be to select molecules for study, to begin with, which would exhibit only one or two of these complications. As an example sulfur dioxide,[4] for whose spectrum a preliminary analysis has appeared, has no quad-

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(4) B. P. Dailey, S. Golden and E. B. Wilson, Jr., *Phys. Rev.*, **72**, 871 (1947).