

6. *Studies in the Light Absorption of Organic Compounds. Part IX.*
Unsaturated Carbonyl Compounds and Semicarbazones.

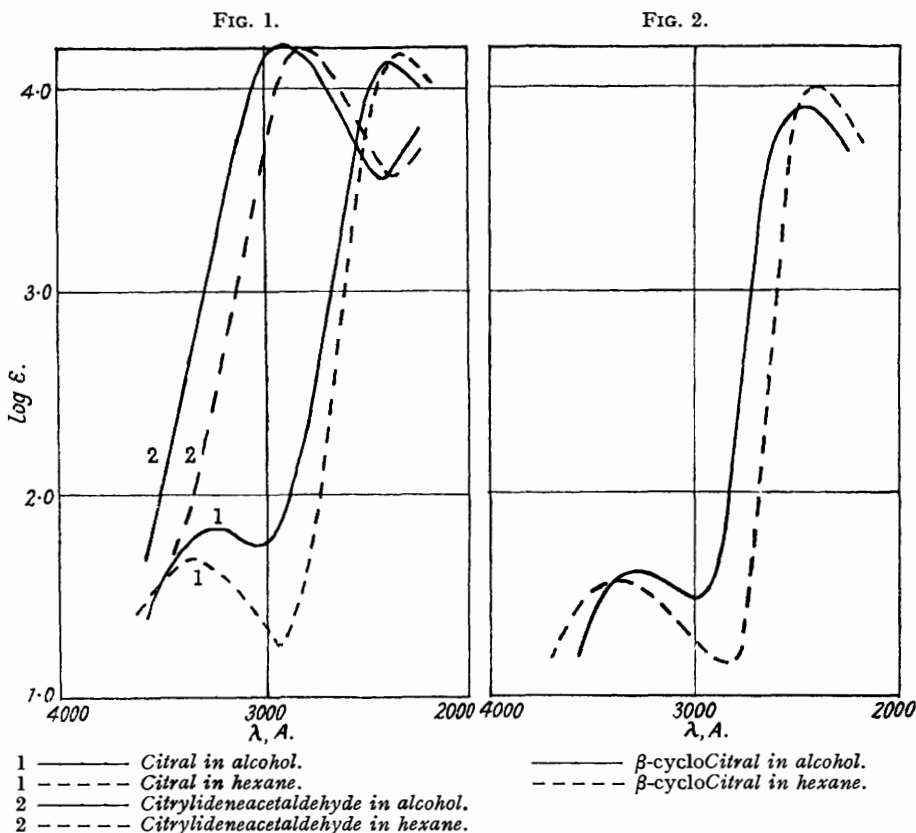
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The absorption spectra of numerous aldehydes and ketones and their semicarbazones are discussed.

DURING attempts to determine the structure of vitamin-A and to synthesise it (Heilbron *et al.*, J., 1937, 755; 1939, 1554, 1556), it was necessary to rely on spectroscopic data for confirmation of purely chemical evidence regarding the structures of many of the compounds synthesised and their purity. The absorption spectra of a series of related compounds were therefore investigated in order to obtain relevant data, and the absorption

maxima and molecular extinction coefficients of these compounds are recorded in the table. The plots of λ against $\log \epsilon$ are supplementary to those of Heilbron *et al.* (*loc. cit.*). The determinations were carried out with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, a tungsten-steel high-tension spark being employed as the source of light.

Citral (I, $n = 0$) and β -cyclocitral (II), like all $\alpha\beta$ -unsaturated carbonyl compounds, exhibit two absorption bands, one of low intensity due to the carbonyl group and the other of high intensity due to the conjugated system present (Figs. 1 and 2). Comparison of the spectra in hexane and alcohol shows that in hexane the latter band is displaced to shorter and the former band to longer wave-lengths, thus confirming their attribution to the two different types of chromophoric groups appearing in organic compounds, *viz.*, (i) unsaturated atoms of free radicals, and all multiple linkages (*R*-chromophores, *R*-bands); (ii) conjugated

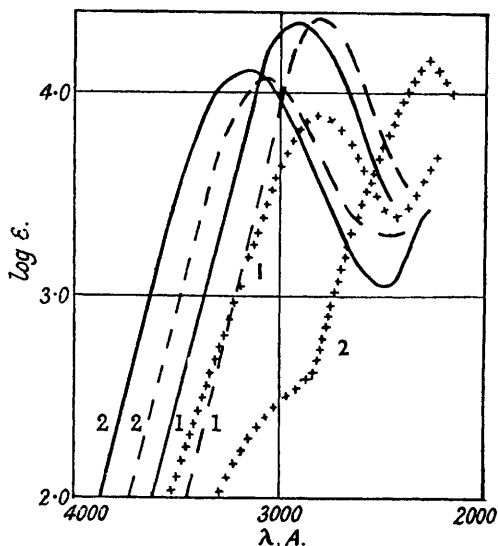


systems (*K*-chromophores, *K*-bands) (Burawoy, *Ber.*, 1930, **63**, 3155; 1931, **64**, 467; J., 1937, 1865; 1939, 1177).

The spectra of citrylideneacetaldehyde (I, $n = 1$), ψ -ionone (III), β -ionone (IV), and citrylideneacetaldehyde (I, $n = 2$) (Figs. 1 and 3) show that: (i) The intensive bands are displaced to longer wave-lengths with increasing length of the chromophoric conjugated system, but contrary to usual experience, the extinction coefficient of (I, $n = 2$) is smaller than those of both (I, $n = 0$) and (I, $n = 1$). The low-intensity band due to the carbonyl group is no longer detectable, since the additional ethenoid linkages, being only indirectly connected with this group, have only a small effect on this band; which is consequently superimposed by the high-intensity band. (ii) Ring closure is accompanied by a decrease in the intensity of the bands, but their relative positions remain unchanged. The intensity of the *K*-band of α -ionone (V), however, is of the same order as those of the open-chain compounds, since here, in contrast to β -cyclocitral and β -ionone, the double bond in the ring is not part of the chromophoric conjugated system.

In addition to the free carbonyl compounds, their semicarbazones have also been examined. Acetonesemicarbazone shows rising absorption (Menschik *et al.*, *Annalen*,

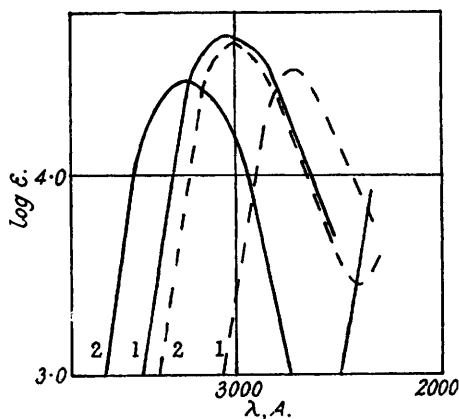
FIG. 3.



- 1 ——— ψ -Ionone in alcohol.
 1 - - - - ψ -Ionone in hexane.
 1 + + + + β -Ionone in hexane.
 2 ——— Citrylideneacetaldehyde in alcohol.
 2 - - - - Citrylideneacetaldehyde in hexane.
 2 + + + + α -Citrylideneacetaldehyde in alcohol.

1932, 495, 225), clearly indicating an intensive band in the spectral region of 2200 Å : this is doubtless due to the presence of a conjugated system consisting of the C=N group and the (substituted) amino-group -C=N-NH- (cf. Burawoy, *loc. cit.* ; *J. pr. Chem.*, 1932, 135, 145).

FIG. 4.



- 1 - - - - Citralsemicarbazone-a and -b.
 1 ——— Citrylideneacetaldehydesemicarbazone in alcohol.
 2 - - - - ψ -Iononesemicarbazone.
 2 ——— α -Citrylideneacetaldehydesemicarbazone.

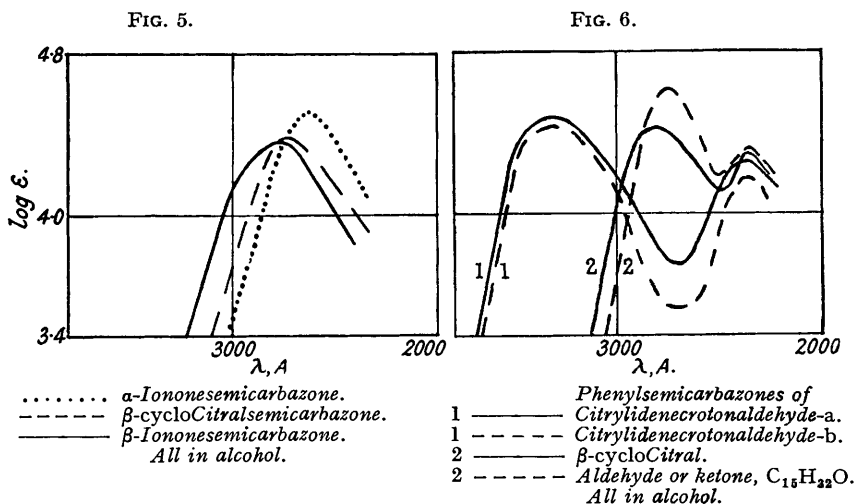
In the spectra of the semicarbazones of citral-*a* and -*b* (VI, $n = 0$), citrylideneacetaldehyde (VI, $n = 1$), ψ -ionone (VII), and citrylideneacetaldehyde-*a* (VI, $n = 2$) (cf. Fig. 4), the intensive band of acetonesemicarbazone is displaced to longer wave-lengths with

increasing length of the chromophoric conjugated system. The intensity in the case of (VI, $n = 2$) is smaller than those of the other semicarbazones, as was also found for the carbonyl compounds themselves.

	Compound.*	$\lambda_{\max.}$, A.	$\epsilon_{\max.}$	Remarks.
(i)	Citral	3240	65	} From sodium bisulphite derivative
		2380	13,500	
(ii)	† „	3360	48	
		2325	14,700	
(iii)	Citrylideneacetaldehyde	2900	15,960	} From semicarbazone,
(iv)	† „	2800	15,470	
(v)	Citrylideneacetaldehyde	3140	12,490	} From semicarbazone,
(vi)	† „	3070	11,550	
(vii)	ψ -Ionone	2910	21,800	} From semicarbazone,
(viii)	† „	2820	22,800	
(ix)	β -cycloCitral	3280	43	} From semicarbazone,
		2445	8,300	
(x)	† „	3380	38	
		2410	10,100	
(xi)	β -Ionone	2935	8,700	} From semicarbazone,
(xii)	† „	2805	7,700	
(xiii)	α -Ionone	2285	14,300	From oxime, m. p. 89°
	Semicarbazone of			
(xiv)	Citral- <i>a</i>	2720	31,350	M. p. 164°
(xv)	Citral- <i>b</i>	2720	31,350	M. p. 171
(xvi)	Citrylideneacetaldehyde	3045	47,200	M. p. 167
(xvii)	ψ -Ionone	2995	45,400	M. p. 142
(xviii)	Citrylideneacetaldehyde- <i>a</i>	3255	27,100	M. p. 160
(xix)	β -cycloCitral	2720	23,800	M. p. 167
(xx)	β -Ionone	2765	23,300	M. p. 148
(xxi)	α -Ionone	2635	31,600	M. p. 139
	Phenylsemicarbazone of			
(xxii)	Citrylideneacetaldehyde- <i>a</i>	3320	28,700	M. p. 134
		2370	19,150	
(xxiii)	Citrylideneacetaldehyde- <i>b</i>	3320	26,900	M. p. 173
		2365	15,400	
(xxiv)	β -cycloCitral	2805	26,600	
		2365	19,800	
(xxv)	Aldehyde or ketone, C ₁₅ H ₂₂ O	2765	40,600	M. p. 182—183
		2365	21,100	

* The solvent was alcohol, except for the solutions marked †, for which it was hexane.

β -cycloCitralsemicarbazone (VIII), like its acyclic isomer, absorbs at 2720 A., but, as with the free carbonyl compounds, the former has a lower intensity (Fig. 5). It is, therefore,



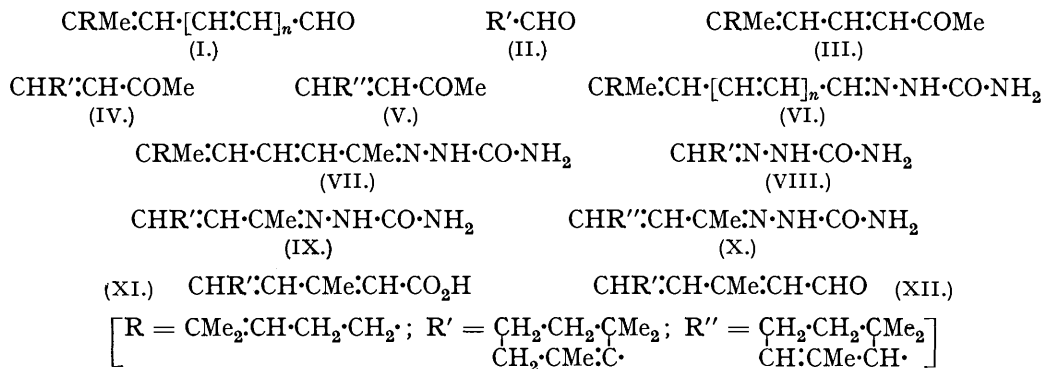
surprising that β -iononesemicarbazone (IX) exhibits a well-defined absorption band at 2765 A. (Fig. 5) instead of in the region of 3000 A. Not only does it absorb at a much

shorter wave-length than ψ -iononesemicarbazone (VII), but comparison with β -cyclocitralsemicarbazone (VIII) shows that the introduction of the additional ethenoid linkage has only a very slight effect on the position of the band. This phenomenon is the more remarkable, since the positions of the bands for both β -cyclocitral (2445 A.) and β -ionone (2935 A.) are normal. The suggestion that β -iononesemicarbazone does not possess the supposed structure is not justified, for two reasons: (i) Pure β -ionone is readily recovered from it by distillation with steam in the presence of phthalic anhydride (the only way of obtaining pure β -ionone, the commercial products containing only 40—50%); (ii) quantitative microhydrogenation by Jackson and Jones's method (J., 1936, 895) establishes the presence of three double bonds (actually 2.99) as compared with two (actually 2.08) in the case of β -cyclocitralsemicarbazone (4.66 mg. of β -iononesemicarbazone in decalin require 1.345 c.c. of hydrogen at 756.5 mm. and 19.7°; 5.38 mg. of β -cyclocitral semicarbazone in acetic acid require 1.290 c.c. of hydrogen at 763.5 mm. and 21.9°). It is probable that this anomaly is due to the effect of the steric hindrance of the methyl group on the light absorption (cf. Ley *et al.*, *Ber.*, 1921, **54**, 364; 1923, **56**, 771).

α -Iononesemicarbazone (X) exhibits a band at 2635 A. (Fig. 5), the intensity of which is of the same order as for the open-chain compounds, ring closure, as in the case of α -ionone itself, apparently having little effect.

The phenylsemicarbazones of β -cyclocitral and of both the isomeric citrylideneacetaldehydes have also been examined (Fig. 6). The phenyl group displaces the absorption bands to longer wave-lengths (60—80 A.), besides showing an additional band in the shorter ultra-violet; this is due to the chromophoric group $C_6H_5 \cdot NH \cdot CO$, for it also appears in the spectrum of acetanilide.

Heilbron *et al.* (J., 1935, 584) described the preparation of a substance $C_{15}H_{32}O$ by dry distillation of the barium salt of β -ionylideneacetic acid (XI) with barium formate under reduced pressure. This was at first thought to be β -ionylideneacetaldehyde (XII), but examination of its absorption spectrum and of that of its phenylsemicarbazone showed that it could not have this structure, containing three ethenoid linkages in conjugation with a carbonyl group, for the phenylsemicarbazone exhibits a well-defined band at 2765 A. (Fig. 6), indicating that it is derived from an $\alpha\beta$ -unsaturated aldehyde or ketone. This discovery was of importance, for the substance is an intermediate in the synthesis of vitamin-A.



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