87. Observations on the Absorption Spectra of Terpenoid Compounds. Part IV. Five-atom-ring Unsaturated Ketones.

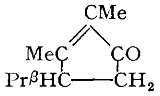
By A. E. GILLAM and T. F. WEST.

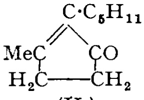
Absorption data are recorded for the five-atom-ring compounds dihydrojasmone and tetrahydropyrethrolone and their semicarbazones. The data on the first two compounds are not in accord with Woodward's generalisation (*J. Amer. Chem. Soc.*, 1941, **63**, 1123) covering the absorption spectra of *αβ*-unsaturated ketones. These results and the anomalous case of *iso*thujone previously reported (Gillam and West, J., 1941, 811) are therefore best explained by the specific effect due to the five-atom-ring environment as compared with C=C—C=O compounds in acyclic and six-atom-ring systems. On the other hand the seven-atom-ring compound *β*-dihydroeucarvone (V) (Gillam and West, preceding paper) falls into line with the six-atom-ring and acyclic compounds.

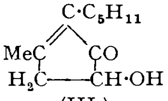
It has been shown that the absorption spectra of αβ-unsaturated ketones fall regularly into three classes depending on whether the C=C—C=O chromophore has one, two, or three non-absorbing substituents (Woodward, *loc. cit.*); for instance, trisubstituted αβ-unsaturated ketones absorb maximally at 2540 ± 50 A. Exceptionally, it has been found (Gillam and West, *loc. cit.*, 1941) that *iso*thujone (I) prepared by the isomerisation of thujone with sulphuric acid shows maximum absorption at 2370 A. (ε = 13,500), whereas the lævorotatory form prepared from sabinol by hydrogenation and subsequent oxidation (Short and Read, J., 1939, 1043) shows an even greater divergence (ε = 6180 at 2310 A.).

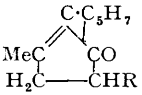
More recently Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 76) has reconsidered the data on trisubstituted αβ-unsaturated ketones and finds that the best average position of the band is at 2470 ± 50 A. when there is no exocyclic double bond and at 2520 ± 50 A. with one exocyclic ethylene linkage.

In view of the anomalous position of *iso*thujone, we have examined two other five-atom-ring unsaturated ketones in order to determine whether this molecular environment normally produces a hypsochromic effect on the location of the *K*-band in the absorption spectrum, and if so, whether there is any constancy in the effect.

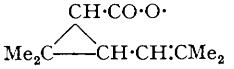

(I.)
*iso*Thujone.


(II.)
Dihydrojasmone.

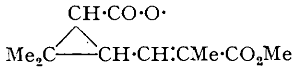

(III.)
Tetrahydropyrethrolone.

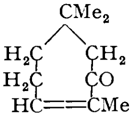

(IV.)

Pyrethrin-I, R =



Pyrethrin-II, R =




(V.)
β-Dihydroeucarvone.

Dihydrojasmone was prepared by the catalytic reduction of a mixture of pyrethrins-I and -II (IV), described by LaForge and Haller (*J. Org. Chem.*, 1937, **2**, 49), and the ketone regenerated from the semicarbazone of appropriate melting point. Two samples of tetrahydropyrethrolone, (*a*) and (*b*), were examined; they were obtained (*a*) by the reduction of pyrethrolone (IV, R = OH) semicarbazone obtained from a semicarbazone predominantly derived from pyrethrin-I, and (*b*) from pure pyrethrin-II semicarbazone.

The absorption spectra of the five-atom ring ketones and their semicarbazones are shown in the following table.

Absorption data for solutions in alcohol.

	K-Band.		*R*-Band.	
	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
*iso*Thujone (I) [1]	2375	12,000	(3100)	80
l-2 : 3-Dimethyl-4-*iso*propyl-Δ^2-*cyclo*pentenone [1,2]	2310	6,180	3100	35
Dihydrojasmone (II)	2370	12,200	3040	55
Tetrahydropyrethrolone (III) (*a*)	2320	11,540	3120	64
Tetrahydropyrethrolone (III) (*b*)	2320	12,700	not determined	
*iso*Thujone semicarbazone [1]	2670	24,800	absent	
Dihydrojasmone semicarbazone	2665	20,400		
Tetrahydropyrethrolone semicarbazone (*a*), *ex* pyrethrin-I	2650	22,500		
Tetrahydropyrethrolone semicarbazone (*b*), *ex* pyrethrin-II	2650	21,770		

[1] Gillam and West, J., 1941, 811.

[2] The low value of both $\lambda_{max.}$ and $\varepsilon_{max.}$ here may be due to the specimen's not being pure.

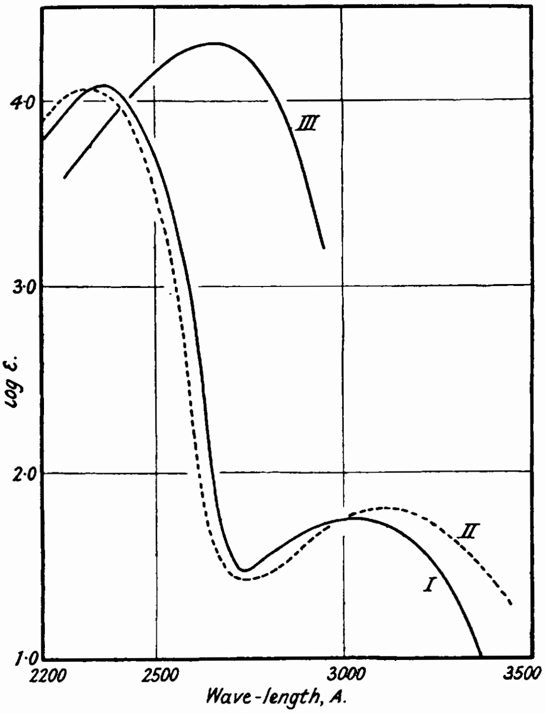
Woodward's amended average value of 2470 ± 50 A. being taken for trisubstituted six-atom-ring and acyclic αβ-unsaturated ketones, the deviations of the three five-atom-ring ketones from this value are as follows (for alcoholic solutions) :

	$\lambda_{max.}$, A., obs.	Deviation for five-atom-ring environment, A.
*iso*Thujone	2375	− 95
Dihydrojasmone	2370	−100
Tetrahydropyrethrolone	2320	−150
Mean	2355 ± 35	

The mean value for these compounds thus differs from that obtained on analogous six-atom-ring and acyclic compounds by approximately −110 A., and this decrement can be used as an amendment to Woodward's rule when a five-atom-ring system is suspected or known to be present. In this connection it has already been noted that *cyclo*pentadiene is anomalous among other dienes (Booker, Evans, and Gillam, J., 1940, 1453) in that it absorbs maximally at 2385 A. (Scheibe, *Ber.*, 1926, **59**, 1333), whereas the corresponding six-atom-ring diene, $\Delta^{1:3}$-*cyclo*hexadiene (cf. Allsopp, *Proc. Roy. Soc.*, 1934, *A*, **143**, 618), absorbs at 2560 A., *i.e.*, a difference of −175 A.

It is now highly probable that the explanation of the abnormally short wave-length of the maximum in the absorption spectrum of *iso*thujone previously reported (see above) lies in the effect of the five-atom-ring environment on the position of the absorption band. The alternative suggestion that the accepted structure (I) was open to doubt must now be withdrawn.

The hypsochromic effect of the five-atom-ring structure being thus evident in at least three compounds, it is interesting to notice that the only authentic αβ-unsaturated ketone in a seven-atom ring (β-dihydroeucarvone) for which the location of the *K*-band has been recorded (Gillam and West, preceding paper) is quite typical of similar acyclic and six-atom-ring compounds, having $\lambda_{\text{max.}}$ 2395 A.



Absorption spectra of alcoholic solutions of :

I. *Dihydrojasmone.*
II. *Tetrahydropyrethrolone.*
III. *Dihydrojasmone semicarbazone.*

EXPERIMENTAL.

(Carbon and hydrogen determinations are by Drs. Weiler and Strauss, Oxford.)

Dihydrojasmone.—A concentrated extract of pyrethrum (7·83 g.), prepared essentially as described by LaForge and Haller (*J. Amer. Chem. Soc.*, 1935, **57**, 1893) and containing, by the Wilcoxon method, pyrethrin-I 55·7%, pyrethrin-II 7·3%, was reduced in alcoholic solution in the presence of a platinum oxide catalyst and absorbed 1547 ml. hydrogen at N.T.P. The mixture of dihydrojasmone and hexahydropyrethrone was then isolated (2·1 g.) and converted into the semicarbazone as described by Haller and LaForge (*loc. cit.*, 1937). The dihydrojasmone semicarbazone (0·62 g.) obtained by fractional crystallisation from alcohol had m. p. 165° (sintering at 160°), and after two recrystallisations from benzene, m. p. 175—176°. It showed maximum absorption at 2665 A. ($\varepsilon = 20{,}400$). The dihydrojasmone regenerated by steam distillation in the presence of potassium bisulphate (Staudinger and Ruzicka, *Helv. Chim. Acta*, 1924, **7**, 245) had b. p. 75—76°/1 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4800, and showed maximum absorption at 2370 A. ($\varepsilon = 12{,}200$) and at 3040 A. ($\varepsilon = 55$) (Found : C, 79·4; H, 11·0. Calc. for $C_{11}H_{18}O$: C, 79·5; H, 10·8%).

Tetrahydropyrethrolone.—The preparation of pyrethrolone semicarbazone will be considered elsewhere. A sample (3·5 g.), m. p. 210—211° (decomp.), obtained from practically pure pyrethrin-I semicarbazone, m. p. 113° (sintering at 103°), by treatment with a solution of sodium methoxide, was dissolved in ethyl acetate–methyl alcohol and hydrogenated in the presence of a platinum oxide catalyst (Haller and LaForge, *J. Org. Chem.*, 1936, **1**, 50) ; 682 ml. of hydrogen (N.T.P.) were absorbed. The crude tetrahydropyrethrolone semicarbazone (3·2 g.) had m. p. 178—180°, raised to 193—194° by three recrystallisations from acetone (Found : C, 60·0; H, 8·8. Calc. for $C_{12}H_{21}O_2N_3$: C, 60·25; H, 8·8%). It showed maximum absorption at 2650 A. ($\varepsilon = 22{,}500$). The tetrahydropyrethrolone regenerated in the presence of cold potassium bisulphate solution (LaForge and Haller, *J. Amer. Chem. Soc.*, 1936, **58**, 1779) had b. p. 135°/1 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4930, $[\alpha]_{\mathrm{D}}$ +11·5° (*c*, 2·777 in alcohol) and showed maximum absorption at 2320 A. ($\varepsilon = 11{,}540$) and at 3120 A. ($\varepsilon = 64$) (Found : C, 73·0; H, 9·8. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 9·9%).

Pyrethrolone semicarbazone (1·93 g.), m. p. 212—213° (decomp.), obtained *via* pyrethrin-II semicarbazone, m.p. 164—165°, and treated as described above, absorbed 379 ml. of hydrogen at N.T.P. The crude tetrahydro-compound (1·98 g.) melted at 176° and after three recrystallisations had m. p. 196° and showed maximum absorption at 2650 A. ($\varepsilon = 21{,}770$) (Found : C, 60·0; H, 8·7%). The ketone regenerated from this sample had b. p. 142—143°/1·5 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4911, $[\alpha]_{\mathrm{D}}$ + 17·7° (*c*, 0·935 in alcohol) and displayed maximum absorption at 2320 A. ($\varepsilon = 12{,}700$) (Found : C, 72·1; H, 9·8%).

Absorption-spectra determinations were carried out in purified ethyl alcohol by means of a Hilger E_3 quartz spectrograph and a Spekker photometer.

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