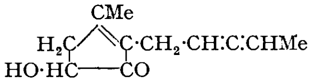
18. *Absorption Spectra and the Structure of Pyrethrins I and II. Part II.*

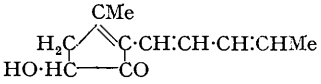
By A. E. Gillam and T. F. West.

The evidence of absorption spectra on the structure of the unsaturated pentadienyl side chain of pyrethrolone and the pyrethrins is summarised together with new data on pyrethrolone enol semicarbazone. The light-absorption evidence on the latter compound amply confirms the conclusion previously reached (Part I), that the side chain contains a conjugated system of double bonds and not a cumulated one (cf. LaForge and Acree, *J. Org. Chem.*, 1942, **7**, 418).

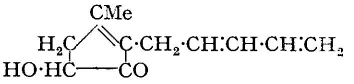
The original structures assigned to pyrethrins I and II by Staudinger and Ruzicka (*Helv. Chim. Acta*, 1924, **7**, 177) have been substantially confirmed by the work of LaForge and his collaborators, who have shown it to be necessary to replace the *cyclo*pentanolone structure of the pyrethrolone fragment by a *cyclo*pentenolone structure (LaForge and Haller, *J. Amer. Chem. Soc.*, 1936, **38**, 1777), the location of the double bonds in the pentadienyl side chain still remaining doubtful (cf. Part I, J., 1942, 671). The most probable structure for the pyrethrolone fragment then appeared to be either (I) or (II).



(I.)



(II.)



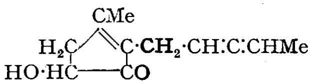
(III.)

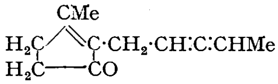
In Part I (*loc. cit.*) we reported an examination of the absorption spectra of pyrethrins I and II, pyrethrolone, and tetrahydropyrethrolone, as well as various derivatives, with a view to obtain evidence on the molecular structures of these compounds and especially the nature of the unsaturation in the side chain. It was concluded that the light-absorption of pyrethrolone (and of the pyrethrins) was due to a summation of the separate contributions of two *isolated* chromophores, the one a conjugated diene and the other an αβ-unsaturated ketone. The evidence of absorption spectra ruled out the possibility of the presence of a crossed-conjugated trienone system as in (II), and the alternative structure (III), which is one of the formulations that would be consistent with the absorption-spectra data, does not fit with the observation that on ozonolysis pyrethrolone yields acetaldehyde (Staudinger and Ruzicka, *loc. cit.*; LaForge and Haller, *J. Org. Chem.*, 1938, **2**, 546). If it be assumed that there is no movement of the terminal ethylene linkage, the ozonolysis evidence favours the arrangement of the two terminal carbon atoms in (II) and not that in (III).

Since it is not possible to fit a terminal $CH_3{\cdot}CH{:}$, a conjugated diene, and an αβ-unsaturated ketone grouping into these formulæ as they stand without giving a crossed-conjugated trienone system which is contra-indicated by the light-absorption data, we have been forced to consider alternative locations in the molecule for the $-C{=}C-C{=}O$ grouping (cf. Part I).

While Part I was being prepared, LaForge and Acree (*J. Org. Chem.*, 1942, **7**, 418) independently reviewed the evidence on the nature of the side chain in pyrethrolone but, with only the light-absorption data on pyrethrone (the deoxy-derivative of pyrethrolone) and 1-*cyclo*hexylpenta-2 : 3-diene available in addition to the rather indirect chemical evidence, they concluded that pyrethrone was an αβ-unsaturated ketone having a side chain containing two cumulated double bonds (V). These authors found that pyrethrone showed maximum absorption at 2350 A. with log $\varepsilon = 4{\cdot}2$, and considered that the position of the maximum excluded a formula in which a conjugated system of double bonds in the side chain is in conjunction with the carbonyl group and a double bond of the ring system. Since 1-*cyclo*hexylpenta-2 : 3-diene showed practically no absorption above 2500 A. and only slight absorption below, it was considered that a cumulated side chain was the most probable, the presence of a 3-membered ring beng excluded on chemical evidence. It was then concluded that formula (IV) " may therefore be accepted as representing the correct structure of pyrethrolone."

(IV.)

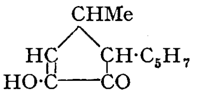




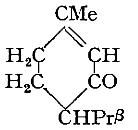
(V.)

Although we think the spectroscopic evidence in Part I leaves no doubt as to the *conjugated* nature of the unsaturation in the side chain, we summarise below the data from which we infer that the two double bonds are conjugated and not cumulated, and bring forward further direct supporting evidence. (*a*) When the two ethylene linkages in pyrethrolone are removed by hydrogenation, the resulting tetrahydro-compound exhibits an absorption spectrum typical of that of an αβ-unsaturated ketone in a five-atom ring environment (Gillam and West, J., 1942, 487, 671). (*b*) The subtraction curve between pyrethrolone and tetrahydropyrethrolone gives $\lambda_{max.}$ 2275 A. with $\varepsilon = 18{,}600$ for the diene component (Gillam and West, *loc. cit.*). (*c*) The subtraction curve between the semicarbazones of these two compounds gives $\lambda_{max.}$ 2245 A., $\varepsilon = 17{,}200$, for the diene component (*idem, ibid.*). These observed locations of the diene absorption band are closely in accord with the calculated value of λ 2270 A. for an unsymmetrical disubstituted diene of the type $CHR{:}CH{\cdot}CH{:}CHMe$ (cf. Woodward, *J. Amer. Chem. Soc.*, 1942, **64**, 72).

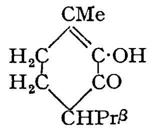
We have now found, however, that in pyrethrolone enol it is possible to demonstrate the presence of two separate chromophores by a third independent but more direct method. Structure (VI) was suggested for pyrethrolone enol by Staudinger and Ruzicka (*loc. cit., p.* 212), and the compound has been examined by Halle and LaForge (*J. Org. Chem.*, 1938, **3**, 543). Now the presence of a hydroxyl group on the $>\mathrm{C{:}C{-}}\overset{|}{\mathrm{C}}\mathrm{{:}O}$ chromophore causes a displacement of the corresponding absorption band to longer wave-lengths but has no effect on that due to the diene component. This displacement to longer wave-lengths is shown, *e.g.*, in piperitone (VII) and diosphenol (VIII), the former showing maximum absorption at 2350 A. and the latter at 2740 A. In pyrethrolone enol the two bands are still close enough together to overlap slightly, but if the semicarbazone of pyrethrolone enol be prepared the C═C—C═O band only should suffer yet another displacement to longer wave-lengths, the diene band being again unaffected. Thus the absorption of pyrethrolone enol semicarbazone might be expected to show two well-separated absorption bands due respectively to the conjugated diene and the twice-modified αβ-unsaturated ketone grouping. These bands are shown in the figure and lie at 2260 A. and 3090 A., the value for the diene component (2260 A.) agreeing very well with that obtained previously (Gillam and West, *loc. cit.*) and with the value calculated by Woodward's method.



(VI.)

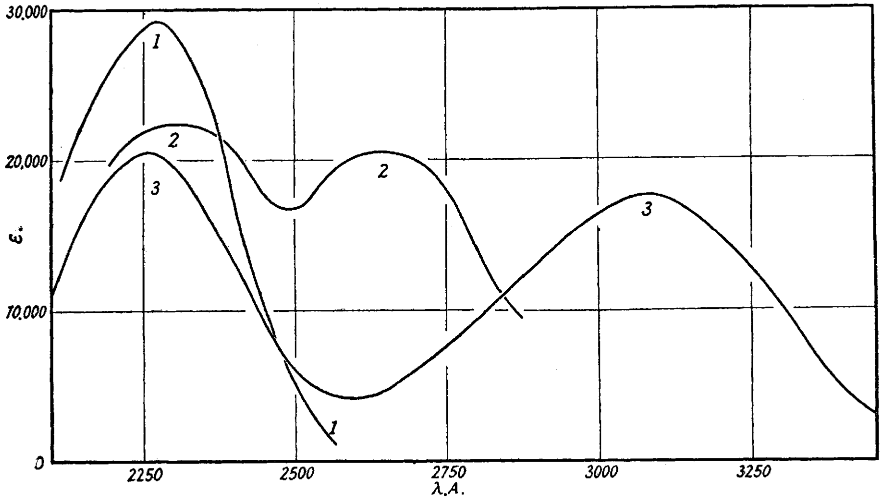


Piperitone (VII.)



Diosphenol (VIII.)

Absorption spectra in ethyl-alcoholic solution.



1. *Pyrethrolone.* The maxima of the bands due to the diene and to the C═C—C═O chromophore are so close together as to give a smooth summation curve.
2. *Pyrethrolone semicarbazone.* The diene band remains fixed but the modified C═C—C═O band has been displaced up the spectrum and is seen as a nearly separated band.
3. *Pyrethrolone enol semicarbazone.* The diene band remains as before but the still further modified C═C—C═O band is displaced sufficiently far to longer wave-lengths to be seen as a clearly separated band.

A more detailed examination of the application of the Ponndorf–Meerwein reduction method to pyrethrolone and its methyl ether has shown that these compounds are either converted into high-boiling derivatives or recovered substantially unchanged. There is little doubt that the absorption shown by the reduction products of pyrethrolone methyl ether examined by Gillam and West (*loc. cit.*) was, in fact, due to unchanged material, and the fact that the position of maximum absorption was situated at nearly the same wave-length but at a reduced intensity must be ignored.

EXPERIMENTAL.

(Analyses are by Drs. Weiler and Strauss, Oxford.)

Pyrethrolone Enol.—Pyrethrolone (6·2 g.) was heated under reflux for 20 hours with a solution of sodium (0·95 g.) in aqueous methyl alcohol (90% w/v) (86 ml.), water (300 ml.) added, and the bulk of the methyl alcohol removed by distillation under reduced pressure (Staudinger and Ruzicka, *loc. cit.*, p. 220; Haller and LaForge, *loc. cit.*, 1938). The aqueous solution was repeatedly extracted with ether, only 0·2 g. of unchanged pyrethrolone being recovered. The solution was acidified with dilute sulphuric acid, and the liberated oil extracted with ether. The crude enol mixture (5·8 g.) was distilled, and suitable fractions redistilled to give pyrethrolone enol (0·56 g.), b. p. 102°/1 mm., $n_D^{24^\circ}$ 1·5100 (Found: C, 74·0; H, 7·9. Calc. for $C_{11}H_{14}O_2$: C, 74·15; H, 7·9%). It showed maximum absorption at 2440 A. (ε = 12,600). The data obtained for further samples of pyrethrolone enol prepared by similar methods from various samples of pyrethrolone are given on p. 51.

			Found.			
Sample.	B. p./1 mm.	n_D.	C, %.	H, %.	$\lambda_{max.}$ (A.).	$\varepsilon_{max.}$.
80/3	102—102·5°	1·5128 (25°)	74·0	8·0	2450	13,600
97/3	105—106	1·5132 (21°)	74·2	7·8	2435	15,000
27/4	102—103	1·5115 (19°)	73·9	8·3	2430	12,300

Semicarbazone. Pyrethrolone enol, b. p. 102°/2 mm., $n_D^{24°}$ 1·5100, (0·32 g.) in alcohol (3·2 ml.) was added to a solution of semicarbazide hydrochloride (0·48 g.) in water (0·65 ml.) and pyridine (0·65 ml.) (Haller and LaForge, *loc. cit.*, 1938). The semicarbazone separated almost immediately, but the solution was kept overnight and diluted with water (10 ml.) before the crystals were collected (0·41 g.); m. p. 250—252°. After recrystallisation from glacial acetic acid (8 ml.), the first crop (0·22 g.) had m. p. 255—256° (Found: C, 60·8; H, 7·1. Calc. for $C_{12}H_{17}O_2N_3$: C, 61·3; H, 7·2%). It showed maximum absorption at 2265 A., ε = 17,600, and at 3085 A., ε = 20,300. A sample of the semicarbazone, m. p. 255°, prepared from a second sample of pyrethrolone enol showed maximum absorption at 2260 A. (ε = 14,700) and at 3090 A. (ε = 20,600). A third sample, m. p. 255—256°, showed maximum absorption at 2270 A. (ε = 12,000) and at 3085 A. (ε = 16,500).

Attempts to Prepare Reduction Products by Ponndorf's Method.—Pyrethrolone enol (0·2 g.) was treated with aluminium *iso*propoxide (76 mg.) in dry *iso*propyl alcohol (0·7 ml.), the constant-volume distillation being continued for 4 hours. The solution was steam-distilled, and the light petroleum extract of the distillate, washed and dried, yielded on distillation substantially unchanged enol (42 mg.), b. p. 93°/1 mm., $n_D^{21°}$ 1·4880 (Found: C., 72·4; H, 8·4%). Maximum absorption at 2445 A. (ε = 13,700).

Pyrethrolone (3·4 g.), b. p. 147°/0·5 mm., was treated with aluminium *iso*propoxide (1·3 g.) in *iso*propyl alcohol (11 ml.), the constant-volume distillation being continued for 6 hours. After steam distillation only a trace of oil was obtained from the distillate, but from the residue 2·7 g. of unchanged pyrethrolone were recovered (this oil treated in the usual way with semicarbazide hydrochloride gave 2·6 g. of recrystallised semicarbazone, m. p. 208—210°, unchanged by admixture with authentic pyrethrolone semicarbazone).

Pyrethrolone methyl ether, b. p. 116—118°/2 mm., $n_D^{20°}$ 1·5097 (5·1 g.) (Found: OMe, 16·0. Calc. for $C_{12}H_{16}O_2$: OMe, 16·1%), was treated with aluminium *iso*propoxide (1·96 g.) and *iso*propyl alcohol (17 ml.), the constant-volume distillation being continued for 5 hours. The reaction mixture was steam distilled, but the oil (5·0 g.) extracted from the distillate was unchanged ($n_D^{20°}$ 1·5110). Accordingly, this product was subjected to a second 6-hour treatment with the aluminium *iso*propoxide solution; the oil then recovered (4·5 g.) had b. p. 111—113°/3 mm., $n_D^{20°}$ 1·5107, $\lambda_{max.}$ 2265 A., ε = 22,300 (Found: C, 75·0; H, 9·0%). Its identity as pyrethrolone methyl ether was confirmed by its conversion into a semicarbazone, m. p. 180—181°, unchanged by admixture with the semicarbazone prepared from the original pyretholone methyl ether.

Determinations of absorption spectra were made in alcoholic solution on a Hilger E_3 quartz spectrograph in conjunction with a Spekker photometer, standard methods being used.

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