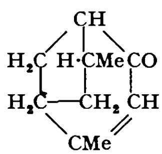
25. *Observations on the Absorption Spectra of Terpenoid Compounds. Part V. Umbellulone.*

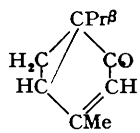
By A. E. Gillam and T. F. West.

Umbellulone and certain of its derivatives have been prepared from oil of Californian laurel such that their physical and analytical constants were identical with those of the previously described ketone. The absorption spectra of the ketone and its semicarbazone are found to be quite different from those expected of a simple $\alpha\beta$-unsaturated ketone. Since a carbonyl group in conjugation with a *cyclo*propane ring produces a measure of hyperconjugation as in carone, it is concluded that the abnormal absorption spectrum of umbellulone is due to the unusual chromophoric group consisting of a *cyclo*propane ring in crossed conjugation with a carbonyl group and an ethylene linkage.

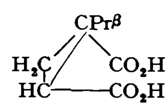
In earlier papers in this series the absorption spectra of various terpenes and related compounds have been studied with a view to obtain information that would throw light on their molecular structures (Part IV, J., 1942, 486). The subject of the present investigation—umbellulone—was first isolated from the leaves of the Californian laurel (*Umbellularia Californica*, Nuttall) by Power and Lees (J., 1904, **85**, 629) and shown to be a ketone, $C_{10}H_{14}O$. Largely on the basis of an examination of oxidation products Tutin (J., 1907, **91**, 271, 275; 1908, **93**, 252) suggested structure (I), but Semmler (*Ber.*, 1907, **40**, 5017; *loc. cit.*) preferred structure (II). Rydon's synthesis of umbellularic acid (III) (J., 1936, 829; cf. Phillips, Ramage, and Simonsen, *ibid.*, p. 828), which was shown by direct comparison to be identical with the oxidation product obtained by Tutin, was the first synthetic evidence for the presence of the *cyclo*propane ring postulated by Semmler. Later,



(I.)



(II.)



(III.)

Weinhaus and Todenhöfer (*Schimmel Berichte, Jubiläumes Ausgabe*, 1929, 285) showed that umbellulone can be separated from other constituents of laurel oil by treatment with neutral sodium sulphite and regenerated from the sulphite compound by treatment with alkali.

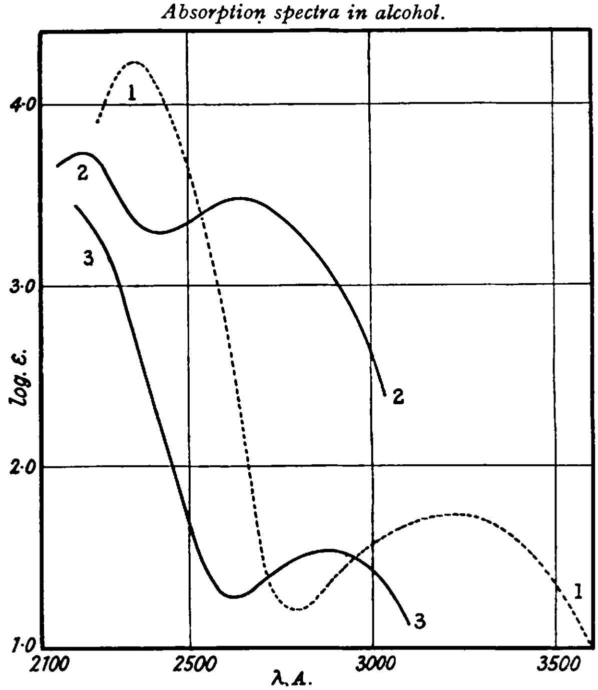
We have now subjected Californian laurel oil to fractional distillation under reduced pressure to obtain umbellulone having the appropriate constants, and then carried out the reaction with semicarbazide as described by Semmler but only obtained low yields of the semicarbazido-semicarbazone (about 50%). Small quantities of the monosemicarbazone were also obtained and (following Semmler) were separated by means of its sparing solubility in hot water.

Experiments to ascertain whether the yield of semicarbazido-semicarbazone or, better still, that of monosemicarbazone could be increased did not produce very marked improvement at first. However, it was discovered, fortuitously, that if the first crop of semicarbazones is removed together with the excess of alcohol, and the residual oil is left in contact with the aqueous reagents for some 8—10 weeks, considerably more of the monosemicarbazone is produced. By regeneration of the ketones from both the normal and the semicarbazido-semicarbazone, it has been possible to establish their identity and so confirm that the same ketone is the parent of both types of derivative.

From the foregoing it is clear that umbellulone contains a *cyclo*propane ring, an ethylene linkage, and a keto-group in a molecule $C_{10}H_{14}O$. Having obtained the absorption spectrum of the compound (Fig. 1 and Table), we sought to determine whether the >C=O and >C=C< groups are conjugated or not.

Fig. 1.

Absorption spectra in alcohol.



1, *Piperitone*. 2, *Umbellulone*. 3, *Carone*.

This is easily decided from the light-absorption data, since the isolated carbonyl group in a chromophorically simple molecule usually gives rise to an absorption band *near* 2800 A. having ε of the order of <100, whereas in an $\alpha\beta$-unsaturated carbonyl compound this band is displaced to the neighbourhood of 3000—3200 A. and a new band of much greater intensity appears between 2200 and 2500 A. (ε, order 6000—14,000). The intensity

Spectrographic Data on Umbellulone and Related Compounds.

	$\lambda_{max.}$	$\varepsilon_{max.}$		$\lambda_{max.}$	$\varepsilon_{max.}$
Umbellulone *	{ 2200 2650	5,000 2,900	Carone semicarbazone	2365	13,500
Piperitone	{ 2355 3210	17,780 54	Piperitone thiosemicarbazone	{ 2450 3020	13,470 32,200
Carone	{ <2200 2880	>2,680 34	*Carone thiosemicarbazone*	{ 2360 2790	9,000 23,000
Umbellulone semicarbazone	2860	14,000	*Umbellulone thiosemicarbazido-thiosemicarbazone* *	{ 2425 2785	18,400 24,600
Piperitone semicarbazone	2660	19,300	Umbellulone semicarbazido-semicarbazone	2363	16,000

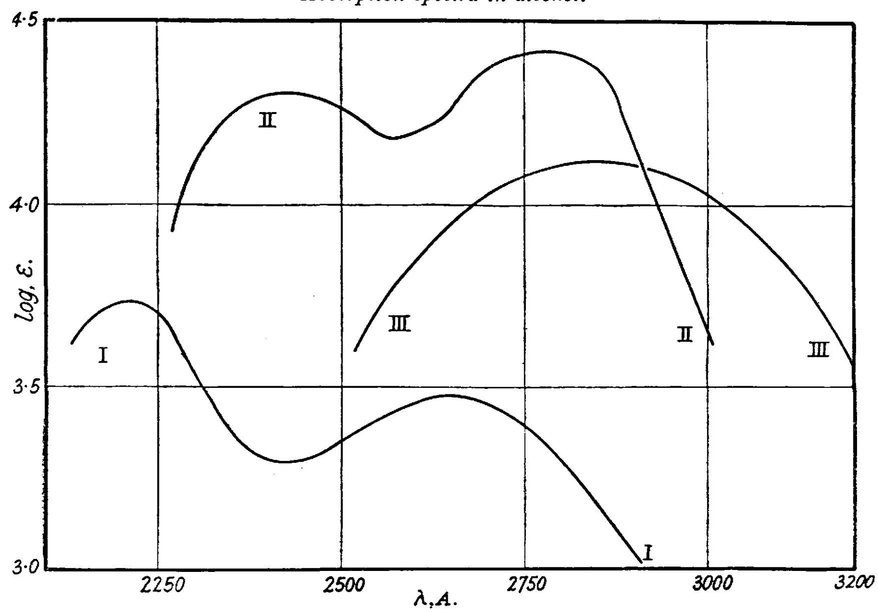
* Mean values on independent preparations.

of absorption in umbellulone is thus too high to be explained by an isolated carbonyl group and is consistent with some form of conjugated system.

From the postulated structure of umbellulone (II) we see that the most likely absorbing entity is the >C=C–C=O grouping. The light-absorption data for compounds of this type have been collected by Woodward

FIG. 2.

Absorption spectra in alcohol.

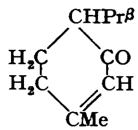


I, *Umbellulone.*
II, *Umbellulone thiosemicarbazido-thiosemicarbazone.*
III, *Umbellulone semicarbazone.*

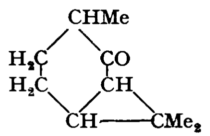
(*J. Amer. Chem. Soc.*, 1941, **63**, 1123) and extended by Evans and Gillam (J., 1941, 815) and are found to be very regular in type, falling within certain narrow limits as to location of the more intense absorption band (2200—2590 A. according as there is less or more substitution). The only disturbing factor which is relevant here arises when the chromophore is situated in a five-atom ring, for if so there is a displacement of the main band to shorter wave-lengths, usually in the range 2100—2400 A. (Gillam and West, J., 1942, 486). αβ-Unsaturated ketones are also further characterised by the light absorption of their semicarbazones, the intensity maximum of which usually lies between 2600 and 2740 A., with $\varepsilon \approx 20,000$ (Evans and Gillam, J., 1943, 565). Examination of the absorption spectra data on umbellulone and derivatives (Figs. and Table) shows that these spectra are quite different from those of any other αβ-unsaturated ketones yet examined. The points of difference are as follows: (*a*) Umbellulone exhibits *two* absorption bands of fairly high intensity in contrast to one band of high intensity and one of very low intensity in normal αβ-unsaturated ketones; (*b*) the band of shorter wave-length in the absorption spectrum of umbellulone is situated at a lower wave-length than that of any but the simplest of unsubstituted αβ-unsaturated ketones, and the other band lies at a longer wave-length than that of any other αβ-unsaturated ketone yet recorded; (*c*) the intensities of the umbellulone bands (order $\varepsilon = 5000$ and 3000 respectively) are unusually low for *K*-bands (usual value of ε in αβ-unsaturated ketones = 6000—14,000); (*d*) the location of the absorption band of umbellulone semicarbazone is also displaced to longer wave-lengths (λ max. = 2860 A., instead of order 2700 A.).

The nearest normal analogue of umbellulone is piperitone (IV) and the absorption spectrum of this unsaturated ketone is shown for comparison in Fig. 1.

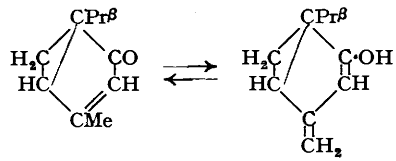
The anomalous nature of the observed absorption spectra of umbellulone and its derivatives might possibly be explained in one of three ways as follows : (*a*) the substance is a mixture of two absorbing entities or even tautomeric forms in equilibrium; (*b*) the proposed formula is not the correct one; or (*c*) the peculiar molecular environment of a *cyclo*propane ring fused to a *cyclo*pentane ring and in crossed conjugation with an ethylene linkage and a carbonyl group modifies the light absorption normally expected of an αβ-unsaturated ketone



(IV.) Piperitone.



(V.) Carone.



(VI.) (VII.)

so that it is different from anything yet encountered. The mixture hypothesis has been tested, but we have been unable to produce any signs of separation into two components either by rigorous fractional distillation or by chromatographic separation on alumina. Moreover, the umbellulone prepared by us and earlier workers has identically the same physical constants. The possibility of a tautomeric system of two components each having a different chromophoric system is difficult to support by postulation of suitable isomerides. The failure to obtain appreciable amounts of formaldehyde on ozonolysis appeared to preclude the possibility of tautomerism of the type (VI) $\rightleftharpoons$ (VII). Furthermore it was not possible to isolate the enolic form or to prepare an enol acetate.

Although umbellulone itself has not been synthesised, the chemical evidence seems to justify the formula (II) previously put forward for the compound, so the explanation of the anomalous light-absorption data must lie in the unusual nature of the molecular structure. The only unknown quantity likely to affect the absorption spectra is the three-atom ring in conjugation with a carbonyl group and fused to a five-atom ring—a most unusual molecular environment. It has recently been shown that when a saturated three-atom ring is conjugated with a carbonyl group or an ethylene linkage a species of conjugated system is produced which affects the absorption spectrum in the sense of producing what Mulliken (*J. Chem. Physics*, 1939, **7**, 339) calls "hyperconjugation." Attention has recently been directed to this effect in carone (V) (Klotz, *J. Amer. Chem. Soc.*, 1944, **66**, 88), where the absorption spectrum approaches that of an αβ-unsaturated ketone. Our own absorption data on this compound are in the table.

If, in the accepted umbellulone formula (II), we look upon the *cyclo*propane ring as a chromophoric group, the chromophore consists of an ethylene linkage and a *cyclo*propane ring in crossed conjugation with a carbonyl group, a system for which there appears to be no suitable model substance available. Until such model substances of known structure are available, we can only conclude that the unexpected absorption spectrum of umbellulone is associated with this unusual unsymmetrical chromophoric make-up of crossed conjugation and hyperconjugation.

EXPERIMENTAL.

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

Preparation of Umbellulone Semicarbazido-semicarbazone and Monosemicarbazone.—Californian laurel oil (50 g.), having $d_{15\cdot5^\circ}^{15\cdot5^\circ}$ 0·984, α_D − 25·9°, ester value 5·8, was fractionated through an 8-bulb column to give umbellulone (19·3 g.) having b. p. 87—90°/4 mm., $d_{15\cdot5^\circ}^{15\cdot5^\circ}$ 0·950, $n_D^{20^\circ}$ 1·4832, α_D − 35·8°, λ max. 2165 A., ε = 2500. A number of experiments were carried out upon this fraction, using sodium acetate and pyridine with semicarbazide hydrochloride. In a typical experiment umbellulone (14 g.), dissolved in alcohol (70 ml.), was added to a solution of semicarbazide hydrochloride (10·75 g.) and pyridine (35 ml.) in water (10 ml.). After standing for 24 hours at the ordinary temperature and at 0° for 3 days, the crystalline deposit (8·2 g.) had m. p. 195—196° (decomp.) (A). The bulk of the alcohol was removed in a vacuum, and the product refrigerated overnight to give a second crop of crystals (1 g.), m. p. 185—220° (B). The filtrate was kept at room temperature for 2 months, a layer of red oily material occluding some crystalline material separating at the surface. Ether (20 ml.) was added, and the insoluble material removed by filtration (1·6 g., m. p. 218—223°) (C). The oil was extracted with ether, the ethereal solution washed with water, and the ether removed to give 4 g. of unchanged oil. Crops A and B (9·2 g.) were heated rapidly to boiling with water (400 ml.), and the solution filtered from insoluble material (0·6 g.) (D). Then C and D were bulked and boiled with 50 ml. of water and filtered. The filtrate was added to the 400 ml. filtrate. The water-insoluble material (1·92 g.) had m. p. 224° (indefinite, decomp.). This was recrystallised from methyl alcohol (120 ml.) to give a first crop (1·6 g.), m. p. 228—231° (decomp.). This was recrystallised from 90% w/v aqueous methyl alcohol (120 ml.) to give 1·41 g., m. p. 231—232° (decomp.). After three further recrystallisations from aqueous methyl alcohol the umbellulone semicarbazone (1·12 g.) had m. p. 238—239° (decomp.) (rapid heating, 240—242°) unchanged by further recrystallisation; λ max. 2885 A., ε 13,000 (Found : C, 63·7; H, 8·2. Calc. for $C_{11}H_{17}ON_3$: C, 63·8; H, 8·2%). The first crop from the water-soluble portion (7·7 g.) had m. p. 209° (decomp.). Recrystallised from water (300 ml.) the product (6·4 g.) had m. p. 211° (decomp.). This was recrystallised from ethyl alcohol (650 ml.) to give 6·0 g., m. p. 205—206° (decomp.), which when recrystallised from water (300 ml.) gave umbellulone semicarbazido-semicarbazone (3·9 g.), m. p. 215—216° (decomp.), λ max. 2360 A., ε 16,600 (Found : C, 50·95; H, 7·8. Calc. for $C_{12}H_{22}O_2N_6$: C, 51·1; H, 7·7%). The 4 g. of recovered unreacted oil was poured off from the small quantity of solid which was precipitated on standing and steam distilled with oxalic acid (2·5 g.), the oil being recovered from the steam distillate by ether extraction, and distilled under reduced pressure to give 2·8 g. (leaving a residue of 0·5 g.), b. p. 63—76°/2 mm., $n_D^{20^\circ}$ 1·4829, $d_{15^\circ}^{20^\circ}$ 0·9372, $[\alpha]_D$ − 26·25° (*c*, 12 in alcohol); λλ max. 2200 A., ε 3100; 2675 A., ε 1450. This recovered oil (2·6 g.) in alcohol (22 ml.) was added to a solution of semicarbazide hydrochloride (3·7 g.) in water (3·7 ml.) and pyridine (13 ml.). The mixture was kept at room temperature, then diluted with water (41 ml.) and kept at 0° for 3 weeks. The semicarbazone which separated (1·26 g.) had m. p. 193—236°. The alcohol was removed from the filtrate under reduced pressure, the residue diluted with water (250 ml.), and thoroughly extracted with ether. The ethereal solution was washed until neutral with brine, and the ether removed. The residue was treated with water, oxalic acid (0·8 g.) added, and the oil distilled in steam. The oil (0·7 g.) recovered from the distillate by extraction with light petroleum was distilled to give 0·65 g., b. p. 56—70°/1·5 mm., $n_D^{20°}$ 1·4849, $[\alpha]_D^{20°}$ — 20·8° (in alcohol), $d_{15·5°}^{15·5°}$ 0·944, λλ max. 2200 and 2690 A., ε 1713 and 687 respectively.

Regeneration of Umbellulone.—(i) Umbellulone monosemicarbazone (1·1 g.) was steam distilled in the presence of phthalic anhydride and water (10 ml.). The umbellulone extracted from the distillate with ether and purified by distillation (0·3 g.) had b. p. 69°/3 mm., $n_D^{20°}$ 1·4846, $d_{20°}^{20°}$ 0·950, $[\alpha]_D$ — 36° (*c*, 1 in alcohol), λλ max. 2200 A., ε 4920; 2650 A., ε 2850. (ii) Umbellulone semicarbazido-semicarbazone (7·8 g.), m. p. 216—217°, was steam distilled with oxalic acid (15·6 g.) and water (30 ml.) to give by ether extraction umbellulone (3·25 g.), b. p. 72°/3 mm., $n_D^{20°}$ 1·4847, $d_{15°}^{15°}$ 0·9518, α_D — 37° (Found: C, 80·2; H, 9·8. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·3%); λλ max. 2200 A., ε 5070; 2650 A., ε 2900.

Umbellulone Thiosemicarbazido-thiosemicarbazone.—Umbellulone (0·7 g.) was added to a solution of thiosemicarbazide (0·43 g.) in 70% aqueous ethyl alcohol (14 ml.). Two drops of hydrochloric acid were added, and the solution boiled under reflux for 15 mins. After being kept at room temperature overnight and then at 0° for 24 hours, the white powdery crystals (0·19 g.) which separated had m. p. 203—204°. This product was recrystallised twice from absolute alcohol to give *umbellulone thiosemicarbazido-thiosemicarbazone* (70 mg.), m. p. 210—211° (Found: C, 46·1, 45·8; H, 7·4, 7·1. $C_{11}H_{17}N_3S$ reqpires C, 59·2; H, 7·6%. $C_{12}H_{22}N_6S_2$ requires C, 46·0; H, 7·0%); λλ max. 2785 A., ε 26,200; 2425 A., ε 19,800. After separation of the first crop above (m. p. 203—204°), the alcohol was removed at room temperature in a current of air until oily droplets separated at the surface. The mixture was then kept at 0° for 6 weeks, and a solid collected. This was triturated with methyl alcohol (40 ml.), and the mixture kept at 0° for 3 days. By filtration, 0·34 g. of white powdery material was obtained, m. p. 198—199°. This was twice recrystallised from *iso*propyl alcohol (50 and 40 ml.) to give 0·19 g., m. p. 209° unchanged (Found: N, 25·8. Calc. for $C_{11}H_{17}N_3S$: N, 18·8%. Calc. for $C_{12}H_{22}N_6S_2$: N, 26·75%); λλ max. 2425 A., ε 17,000; 2785 A., ε 23,000.

Ozonolysis.—This was carried out in four separate lots, the yields being bulked for working up. Umbellulone regenerated from the semicarbazido-semicarbazone (1 g.) in carbon tetrachloride (30 ml.) was subjected to a slow stream of ozonised oxygen (6 hours) and then treated with ice to decompose the ozonide (24 hours) and shaken with separate lots of water, these being finally bulked and divided into two portions, A and B, A being one-eighth of the whole sample (= 0·5 g. of umbellulone). This was extracted with water exhaustively, treated with dimedon (1·2 g.) in saturated aqueous solution, and left for 40 hours. The silky, needle-like precipitate (30·2 mg.) was filtered off and recrystallised, m. p. 190° (corr.); the pure dimedon derivative of formaldehyde had m. p. 189° (corr.), mixed m. p. 186° (corr.). The yield of formaldehyde was 0·62 g. per 100 g. of umbellulone.

Portion B, seven-eighths of the whole sample (= 3·5 g. of umbellulone), was treated as follows. The aqueous liquors were made neutral by adding N/10-sodium hydroxide (300 ml.), and the volume reduced to 100 ml. by distillation under reduced pressure. Then N/10-sulphuric acid (300 ml.) was added, and the product extracted with ether. The ether was removed, giving an oil, which was fractionated: (i) b. p. 108—110° (0·265 g.), which yielded an anilide, m. p. 101—102°, not depressed on admixture with the anilide, m. p. 103—104°, prepared directly from propionic acid; (ii) b. p. 150—220° (0·351 g.), and (iii) b. p. 220—250° (0·314 g.), were not identified. In another ozonolysis experiment the combined carbon tetrachloride and aqueous extracts were transferred to alcohol, and the absorption spectrum examined. The selective absorption was found to have disappeared and the low intensity of the general absorption indicated that the umbellulone had been effectively decomposed.

Carone and its Semicarbazone and Thiosemicarbazone.—*d*-Carone, having b. p. 95—97°/10 mm., $n_D^{20°}$ 1·4953, α_D +58·75°, $d_{15·5°}^{15·5°}$ 0·952, obtained by fractionation from English dill oil, was converted essentially as described by Klotz (*J. Amer. Chem. Soc.*, 1944, **66**, 91) into carone, having b. p. 80—82°/7 mm., $n_D^{20°}$ 1·4765, $d_{15·5°}^{15·5°}$ 0·954, $[\alpha]_D$ + 154·6°, λ max. <2200 A., ε >2680. The semicarbazone after recrystallisation from aqueous methyl alcohol had m. p. 170—172°, λ max. 2365 A., ε 13,500.

Attempts to regenerate carone were unsuccessful; for instance, the oil obtained by steam distillation in the presence of oxalic acid had b. p. 63—64°/1·5 mm., $n_D^{20°}$ 1·4785, $[\alpha]_D$ + 39·5° (*c*, 8 in alcohol), λ max. 2345 A., ε 5200. The λ max. and ε values showed that a change had occurred during regeneration resulting in the formation of an αβ-unsaturated ketone (probably monocyclic). This ketone did not yield a crystalline semicarbazone, and as the observation was irrelevant to the present work it was not further investigated.

Carone thiosemicarbazone was prepared as follows. Carone (0·4 g.) in alcohol (22 ml.) was added with stirring to a cold solution of thiosemicarbazide (0·28 g.) in water (14 ml.), to which one drop of 10% hydrochloric acid had been added. After standing for 20 hours at room temperature, the mixture was refrigerated for 12 hours. Then water was added slowly until no further crystalline material separated. The white, waxy crystals (0·13 g.) had m. p. 125° (sintering at 118°), raised by one recrystallisation from aqueous (70%) methyl alcohol (5 ml.) to 131—132° (Found: N, 19·7. $C_{11}H_{19}N_3S$ requires N, 18·7%); λλ max. 2360 A., ε 9000; 2790 A., ε 23,000.

Determinations of absorption spectra were made in ethyl-alcoholic solution on a Hilger E_3 quartz spectrograph in conjunction with a Spekker photometer.

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