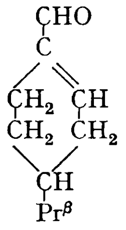
265. *Reactions of αβ-Unsaturated Cyclic Aldehydes and Ketones. Part II. Absorption Spectra of Typical Compounds and their Dihydro-derivatives.*

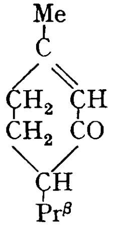
By R. G. COOKE and A. KILLEN MACBETH.

Quantitative measurements of the absorption spectra of a series of αβ-unsaturated cyclic carbonyl compounds show that the substances have two maxima of absorption, one of comparatively low intensity in the region 3120—3190 A., the other of high intensity in the region 2260—2355 A. The former is due to the carbonyl group influenced by the double bond, $C{=}C{\cdot}\overset{*}{CO}$, and the latter to the ethenoid linkage influenced by carbonyl, $C\overset{*}{=}C{\cdot}CO$. In the case of phellandral with its conjugated aldehyde group, the intensity of the $C{=}C{\cdot}\overset{*}{CO}$ band is 8—11 times greater than is observed in the ketones examined.

The absorption spectra of cuminal and cuminic acid are respectively in good agreement with the data of typical aromatic aldehydes and acids.

Although much attention has already been directed to the study of the absorption spectra of aldehydes and ketones, it was considered of interest to examine the maxima of αβ-unsaturated cyclic compounds and their saturated analogues. Work in progress on the eucalyptus oils made phellandral, piperitone, and cryptone * available; and the corresponding dihydro-derivatives may be obtained by catalytic reduction. This series was supplemented by carvone and carvomenthone; and data recorded for carvenone (Lowry and Lishmund, J., 1935, 1313) and pulegone (Lowry, Simpson, and Allsopp, *Proc. Roy. Soc.*, 1937, *A*, **163**, 483) are referred to, as these materials were not available. The relative positions of the ethenoid linkage and the carbonyl group in the substances under discussion are seen in the accompanying formulæ.


Phellandral.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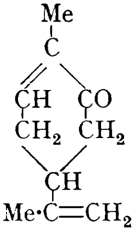
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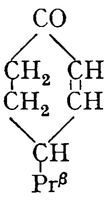
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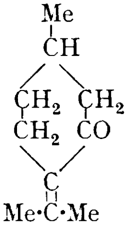
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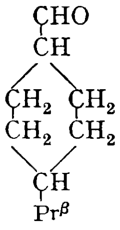
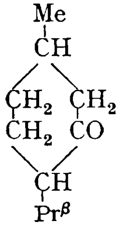
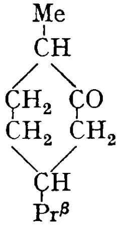
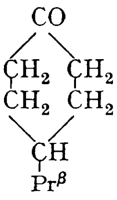
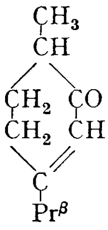

Dihydrophellandral.


Menthone.


Carvomenthone.


Dihydrocryptone.


Carvenone.

Of the materials used in the work, attention need only be directed to phellandral and its dihydro-derivative. The former was obtained by repeated crystallisation of a semicarbazone prepared from a carefully fractionated sample of the aldehyde, followed by regeneration of phellandral; this had [α] —160·2°, which is considerably higher than any value we have been able to trace in the literature. The dihydrophellandral was conveniently prepared by catalytic hydrogenation of phellandral using palladised charcoal; its physical properties are recorded in the experimental part, but its fuller characterisation will be described in another context.

The absorption spectra of the aldehydes and ketones are shown in Figs. 1—4, and the locations of the maxima observed with their intensities are set out in Table I, together with data previously recorded.

The simple ketone, acetone, has a well-defined band which Lowry and Lishmund (*loc. cit.*) located at 2775 A. with a molecular extinction coefficient of 13·0. Ley and Arends (*Z. physikal. Chem.*, 1931, **12**, *B*, 32) gave the position of the maximum as 2750 A., and showed the presence of a second band at 1870 A., which is outside the region ordinarily examined. In the saturated cyclic ketones one may therefore expect two maxima of

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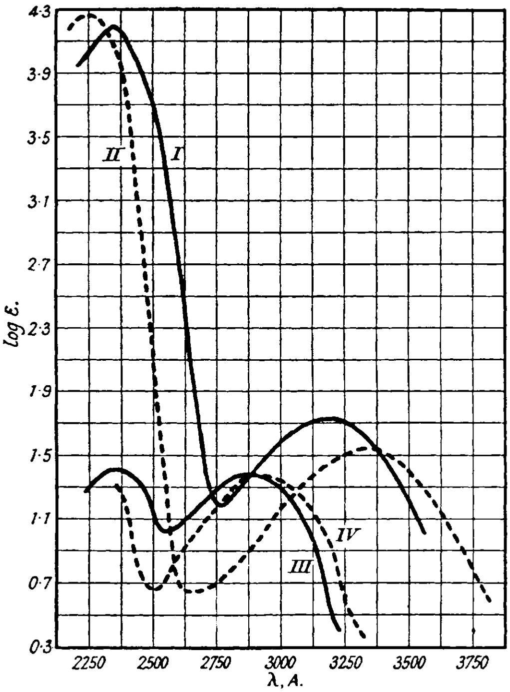
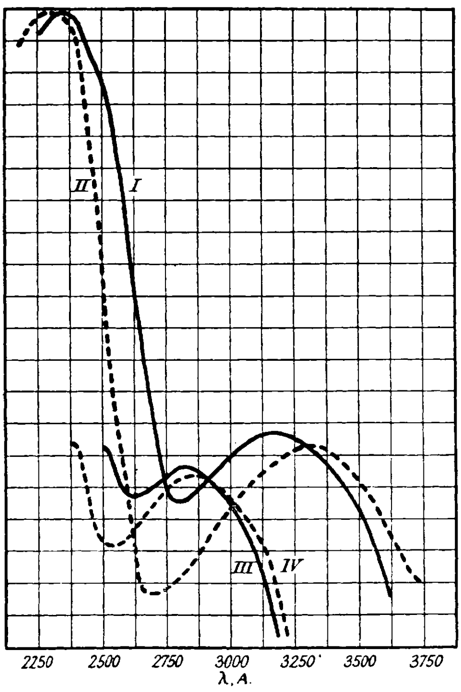
* The name *cryptone* is, for convenience of reference, now applied to 4-*iso*propyl-Δ^2-*cyclo*hexen-1-one, formerly erroneously called cryptal.

FIG. 1.



I. *Piperitone in alcohol* ————
II. *Piperitone in hexane* – – – – –
III. *Menthone in alcohol* ————
IV. *Menthone in hexane* – – – – –

FIG. 2.



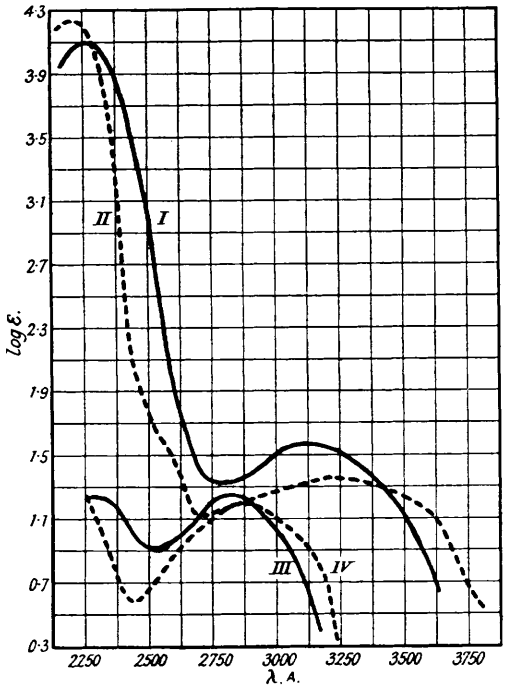
I. *Carvone in alcohol* ————
II. *Carvone in hexane* – – – – – – – –
III. *Carvomenthone in alcohol* ————
IV. *Carvomenthone in hexane* – – – – –

TABLE I.

Substance.	In alcohol. $\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.	log ε.	In hexane. $\lambda_{max.}$, A.	log ε.	$\lambda_{max.}$, A.	log ε.
(a) *Unsaturated.*								
Piperitone	2353	4·20	3190	1·73	2253	4·25	3330	1·54
Carvone	2353	4·28	3175	1·62	2295	4·28	3318	1·56
Cryptone	2263	4·10	3140	1·56	2201	4·22	3216	1·36
Phellandral	2285	4·27	3125	2·62	indefinite		3080	2·41
Pulegone	2450	3·71	3240	1·6	(Lowry, Simpson, and Allsopp)			
Carvenone	—	—	3119	1·69	(Lowry and Lishmund)			
(b) *Saturated.*								
Menthone	2356	1·40	2869	1·38	—	—	2924	1·37
Carvomenthone	—	—	2834	1·43	—	—	2861	1·37
Dihydrocryptone	*ca.* 2280	1·26	2830	1·24	—	—	2878	1·20
Dihydrophellandral	2565	1·86	*2875*	1·30	2505	1·82	*2875*	1·34
Mesityl oxide	2348	4·15	3135	1·86	(Ley and Wingchen)			
Citral	2352	4·61	3220	1·99	(Bielecki and Henri)			

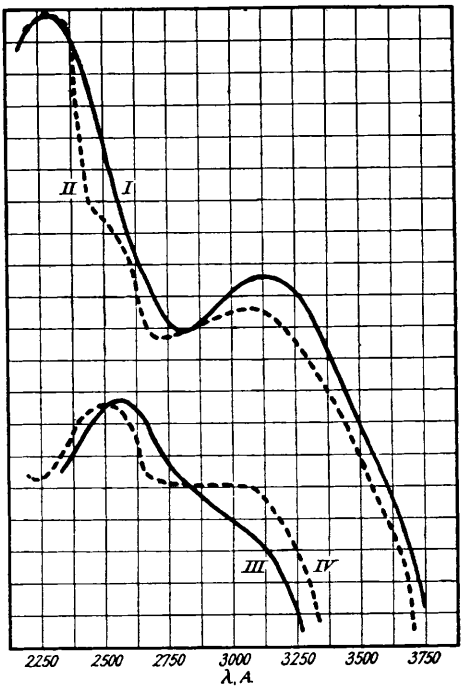
comparatively low intensity, with a possible modification in their location. The band of shorter wave-length may thus be brought within the region ordinarily examined. Reference to the graphs and the records in Table I will show that this is realised in the case of the saturated cyclic ketones, a maximum in alcoholic solution in the region 2830—2875 A. being found in every case. A second band of shorter wave-length is also found in the case of menthone and dihydrophellandral and is clearly indicated in the case of dihydrocryptone; but in the case of carvomenthone it was too ill-defined to warrant any readings being taken. The results now recorded for the band of longer wave-length of menthone and carvomenthone are in good agreement with those of Lowry and Lishmund

FIG. 3.



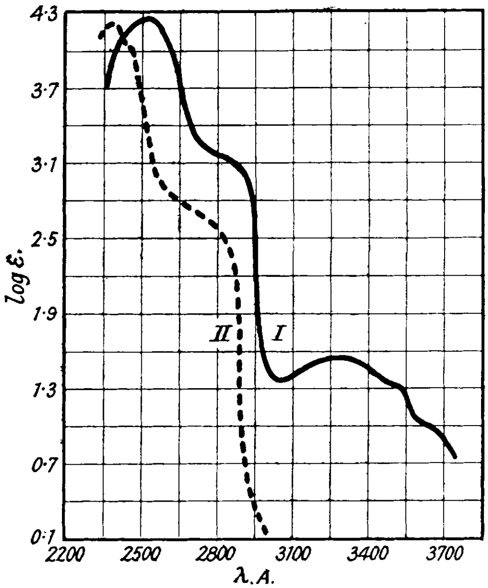
I. *Cryptone in alcohol* ———————
II. *Cryptone in hexane* – – – – – – – – –
III. *Dihydrocryptone in alcohol* ————
IV. *Dihydrocryptone in hexane* – – – – –

FIG. 4.



I. *Phellandral in alcohol* ———————
II. *Phellandral in hexane* – – – – – – – – –
III. *Dihydrophellandral in alcohol* ————
IV. *Dihydrophellandral in hexane* – – – – –

FIG. 5.



Cuminaldehyde in hexane ————
Cuminic acid in alcohol – – – – – –

(*loc. cit.*); and Marchlewski and Wyrobek (*Bull. Acad. polonaise*, 1929, *A*, 93) have recorded two maxima of equal intensity at 2350 and 2890 A. for menthone.

In the open-chain αβ-unsaturated ketone, mesityl oxide, two maxima are also recorded (Ley and Wingchen, *Ber.*, 1934, **67**, 501), but whilst one of these, at 3135 A., is of low intensity (log ε, 1·86), the other, at 2348 A., has a high extinction coefficient (log ε, 4·15). Morton, Hassan, and Calloway (J., 1934, 897) reviewed the behaviour of a large number of substances containing both an ethenoid linkage and a carbonyl group, and concluded that the different energy levels characteristic of the carbonyl group are approximately the same as those characterising the ethenoid linkage, but in the case of an electron under the joint control of both carbon and oxygen the molecular extinction is low, whereas if the electron responsible for the band forms part of the C═C linkage, the molecular extinction coefficient will be of the order 10^3—10^5. In the case of mesityl oxide, the band of longer wave-length is therefore associated with the carbonyl group influenced by its conjugation with the ethenoid linkage, and conveniently represented by $\mathrm{C{=}C{\cdot}\overset{*}{CO}}$; whereas the band of high intensity is attributed to the ethenoid linkage influenced by the carbonyl group, $\mathrm{C\overset{*}{=}C{\cdot}CO}$.

In piperitone, phellandral, cryptone, and carvone the results are closely parallel to those recorded for mesityl oxide and may be attributed to the same centres of electronic vibration. Pulegone, which has recently been examined by Lowry, Simpson, and Allsopp (*loc. cit.*), also shows two bands similarly located and of corresponding intensities. The piperitone results for the band of longer wave-length are also in agreement with those previously recorded (Lowry and Lishmund, *loc. cit.*; Walker and Read, J., 1934, 240). Attention may here be directed to the maxima found for phellandral. Although these are similarly located to those shown by the ketones, the intensity of the $\mathrm{C{=}C{\cdot}\overset{*}{CO}}$ band is markedly greater. This is doubtless a feature of the conjugated aldehyde group, and some support for this view is found on comparing mesityl oxide and citral (Bielecki and Henri, *Ber.*, 1914, **47**, 1715), the latter having a log ε value of approximately 2 compared with log ε of 1·86 in the former ($\mathrm{C{=}C{\cdot}\overset{*}{CO}}$ band). A further point in which the aldehyde group differs from the keto-compounds is found in the absorption of the saturated derivatives. In dihydrophellandral the two bands are found much closer together, one being well-defined and of higher intensity than usual, and the other appearing as a marked inflexion. In the cyclic saturated ketones, however, the bands, where measurement has been possible, are of like intensity and do not show the same displacement.

The spectra of cuminaldehyde and cuminic acid were also examined, although not related to the main work. The results (Table II) show that these agree with data already established for typical simple aromatic compounds.

TABLE II.

Acid.	$\lambda_{\max.}$, A.	log ε.	$\lambda_{\max.}$, A.	log ε.
Benzoic	2270	4·15	—	—
o-Toluic	2290	4·09	2750	3·34
m-Toluic	2310	4·13	2788	3·20
p-Toluic	2360	4·18	No clear maximum	
Cuminic	2380	4·20	*2700*	2·72

	$\lambda_{\max.}$, A.	log ε.	$\lambda_{\max.}$, A.	log ε.	$\lambda_{\max.}$, A.	log ε.
Acetophenone	2415	4·21	2785	3·06	3200	1·73
Benzaldehyde	2440	4·21	2805	3·21	3280	1·31
Cuminal	2520	4·26	*2800*	3·16	3280	1·54

EXPERIMENTAL.

Phellandral.—A sample of phellandral, $[\alpha]_D^{20^\circ}$ − 140·8°, isolated from the oil of *E. cneorifolia* was converted into the semicarbazone which, after repeated crystallisation from alcohol, was obtained as small needles, m. p. 204—205°. The purified semicarbazone (20 g.) was added to sulphuric acid (250 c.c., 10%) and steam-distilled in a current of nitrogen. The distillate was extracted with ether, the extract dried, the solvent removed, and the phellandral distilled under reduced pressure, all operations being carried out as far as practicable in the presence of nitrogen. The purified material (8 g.) had b. p. 75°/1·5 mm.; $n_D^{20^\circ}$ 1·4897; $\alpha_D^{20^\circ}$ − 151·3°

(homogeneous, 1 dm.). The last value, which corresponds to a specific rotation of − 160·2°, is much higher than the values hitherto recorded for the aldehyde.

Dihydrophellandral.—This was prepared by the catalytic reduction of phellandral. The aldehyde (50 g., $[\alpha]_D$ − 140·8°), when dissolved in absolute alcohol (450 c.c.) containing palladised charcoal (6 g.), readily absorbed approximately 7500 c.c. of hydrogen at 16° and 765 mm. After filtration and removal of the solvent, the residual oil when fractionated gave a yield of some 87% of the saturated (inactive) aldehyde, b. p. 68—69°/3 mm.; $n_D^{20°}$ 1·4608. Part of the product was converted into the semicarbazone, which on repeated recrystallisation from alcohol had m. p. 172—173°. The purified semicarbazone (17 g.) when mixed with sulphuric acid (200 c.c., 10%) and steam-distilled gave, when worked up as described above, the pure saturated aldehyde (8 g.) having b. p. 61·5°/1·5 mm., $n_D^{20°}$ 1·4572.

Cryptone.—The ketone isolated from the oil of *E. cneorifolia* (Berry, Macbeth, and Swanson, J., 1937, 987) was subjected to further purification by repeated crystallisation of the semicarbazone from ethyl alcohol (m. p. 188°) and regeneration of the ketone as described above. The product so obtained had $\alpha_D^{20°}$ − 42·7° (homogeneous, 1 dm.), indicating that partial racemisation had occurred during the process (cf. Galloway, Dewar, and Read, J., 1936, 1595). This behaviour is in marked contrast to that of phellandral recorded above. The regenerated ketone had b. p. 63—64°/1·3 mm.

Dihydrocryptone, prepared by the catalytic hydrogenation of the above ketone (Cahn, Penfold, and Simonsen, J., 1931, 1366; Berry, Macbeth, and Swanson, *loc. cit.*), was converted into the semicarbazone, which was repeatedly crystallised (m. p. 188—189°). The regenerated saturated ketone had b. p. 55°/1·2 mm., $n_D^{22·5°}$ 1·4560, and was inactive.

Carvone.—A carefully fractionated sample of carvone was further purified by conversion into the hydrosulphide (see J., 1934, 1147), from which the ketone was regenerated by the action of alcoholic potassium hydroxide followed by steam-distillation. The regenerated carvone had b. p. 71°/1·3 mm., $n_D^{25°}$ 1·4970, $\alpha_D^{18°}$ + 54·6°.

Carvomenthone was obtained in satisfactory yield by the catalytic hydrogenation of carvone (42 g.) in absolute alcohol (350 c.c.) in the presence of palladised charcoal (6 g.). The amount of hydrogen absorbed was approximately 13·5 l. at 17° and 750 mm. The first 8 l. of hydrogen were rapidly taken up, but thereafter the reaction was slow and was only completed after the lapse of some 8 hours. After filtration, drying with sodium sulphate, and removal of the alcohol, the residual oil when distilled gave a main fraction (28 g.), b. p. 87—89°/9 mm., and had $n_D^{20°}$ 1·4568, α_D − 13° (homogeneous, 1 dm.) (cf. Read and Johnson, J., 1934, 229). After conversion into the semicarbazone and regeneration of the ketone, the spectroscopic sample was obtained having b. p. 58·5°/1·2 mm., $n_D^{26°}$ 1·4523, $\alpha_D^{18°}$ − 15°.

Piperitone.—A sample of piperitone from the oil of *E. dives* was purified through the semicarbazone (Read and Smith, J., 1922, **121**, 1867; Walker and Read, J., 1934, 239). The purified ketone had b. p. 71°/1·3 mm., $n_D^{26°}$ 1·4820.

Menthone.—A commercial specimen (Fraenkel and Landau) of menthone after fractionation was converted into the semicarbazone, and the ketone regenerated and distilled under reduced pressure. The main fraction collected had b. p. 52·5°/1·4 mm., $n_D^{28°}$ 1·4475.

Cuminal.—An inactive sample of cuminal from *E. cneorifolia* oil was further purified for spectrophotometric work in order to ensure absence of cuminic acid. The process involved the formation of the bisulphite compound, the regeneration of the aldehyde, and its careful fractionation in an atmosphere of nitrogen. The specimen had b. p. 89°/6 mm., $n_D^{20°}$ 1·5301, $d_{15·5°}^{15·5°}$ 0·9825, and was inactive.

Cuminic Acid.—The acid was prepared by atmospheric oxidation of pure cuminal in the light of the mercury lamp. The crude product was extracted from ethereal solution by sodium carbonate, and the acid recovered on acidification of the extract was recrystallised three times from methyl alcohol.

We are indebted to the Commonwealth Government for a Federal Research Grant which enabled one of us (R. G. C.) to take part in the work. We also thank Dr. F. L. Winzor for carrying out some of the catalytic reductions.

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[*Received, August 5th,* 1938.]