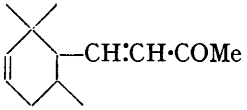
18. *Observations on the Absorption Spectra of Terpenoid Compounds. Part II. Irone.*

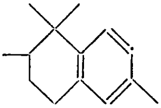
By A. E. Gillam and T. F. West.

The absorption spectrum of irone is recorded and it is pointed out that the nature of the curve definitely precludes the presence of a conjugated dienone system such as is present in β-ionone (cf. Kilby and Kipping, J., 1939, 435). On the other hand, the absorption data indicate the presence of a monosubstituted αβ-unsaturated ketone group and are consistent with the presence of the R·CH:CH·CR:O structure similar to that found in α-ionone. The absorption spectra of two irone samples from different sources are sufficiently different to indicate that the natural ketone is a mixture. A critical examination of the crude thiosemicarbazones derived from these two samples supports this view (cf. also Ruzicka and co-workers, *Helv. Chim. Acta*, 1933, **16**, 1143; 1940, **23**, 935, 959; Tiemann and Krueger, *Ber.*, 1893, **26**, 2675; 1895, **28**, 1757).

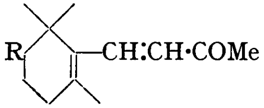
On the basis of analytical results and the examination of oxidation products Tiemann and Krueger (*locc. cit.*) assigned the structure (I) to the naturally occurring ketone *d*-irone, but the synthesis of a ketone possessing this formula claimed by Merling and his co-workers (*Annalen*, 1909, **366**, 119) has recently been disproved (Ruzicka, Seidel, and Schinz, *Helv. Chim. Acta*, 1933, **16**, 1143; 1940, **23**, 935), although Verley's synthesis (*Bull. Soc. chim.*, 1935, **2**, 1205) has apparently not been questioned. Ruzicka and his collaborators (1933, *loc. cit.*) concluded that irone has in fact the empirical formula $C_{14}H_{22}O$, and the structure (II) then advanced for its dehydration product, irene, was subsequently confirmed synthetically by Bogert and Apfelbaum (*J. Amer. Chem. Soc.*, 1938, **60**, 930). The structural formula of irone, however, remains obscure. For instance, Ruzicka *et al.* (1933, *loc. cit.*) concluded that the new formulation for irene corresponded to the structure (III; R = Me) for the ketone, but the production of ββγ-trimethylpimelic acid by ozonolysis was difficult to reconcile with this, and they suggested the possibility of (IV), with (III; R = Me) as an intermediate produced by pinacolin rearrangement of (IV) during the formation of irene.



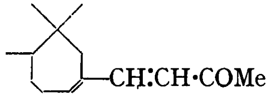
(I.)



(II.)

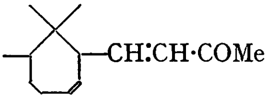


(III.)

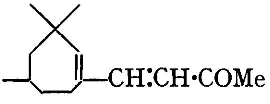


(IV.)

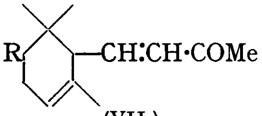
More recently Ruzicka, Schinz, and Seidel (*locc. cit.*, 1940) have stated that irone is undoubtedly a mixture of isomeric ketones, and (III; R = Me) and (VII) may exist together with (IV) or (V) in the natural ketone, the last two explaining the formation of ββγ-trimethylpimelic acid. Stoll and Scherrer (*Helv. Chim. Acta*, 1940, **23**, 941) reported that the properties of the synthetic ketone (VI) showed that " la présence d'un cycle heptanique ne suffit nullement à elle seule à produire l'odeur typique de l'irone," and Ruzicka and Schinz (*Helv. Chim. Acta*, 1940, **23**, 959) found that a synthetic ketone which was either 6-methyl-α-ionone (VII; R = Me) or 6-methyl-β-ionone (III; R = Me) did not simulate the properties of irone.



(V.)



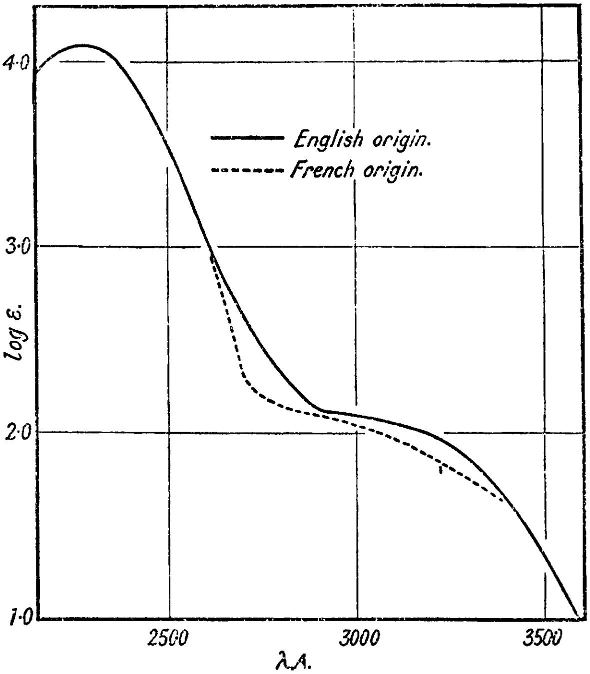
(VI.)



(VII.)

(VIII.) $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}COMe$

Since the absorption spectrum of a compound affords such a definite means of deciding between an αβ-unsaturated ketone and a dienone, it was decided to examine that of a sample of natural irone with a view to eliminate some of the postulated formulæ. Accordingly, a specimen of oil of orris obtained from a French source was purified by vacuum distillation, and the irone isolated through the compound with *p*-phenylhydrazinesulphonic acid, and when it was certain that the ketone had the required analytical constants, its absorption spectrum was determined. The results are shown in the figure and Table I. The first point that emerges is that the absorption curve is perfectly characteristic of an αβ-unsaturated ketone and this fact alone is sufficient to disprove the presence of a dienone structure, since we know that typical compounds of this type absorb at much longer wave-lengths [cf. β-ionone (III; R = H) and ψ-ionone (VIII) (Table I)].



Absorption spectrum of irone in ethyl alcohol.

From the observed absorption spectrum of irone, we can not only conclude that the active chromophoric group is C:C·C:O and not C:C·C:C·C:O, but using Woodward's generalisation (*J. Amer. Chem. Soc.*, **1941**, **63**, 1123), we can infer that only one of the three hydrogen atoms capable of being attached to the ethylene linkage is replaced by other groups, *i.e.*, that the chromophore is either CHR:CH·CR:O or $CH_2{:}CR{\cdot}CR{:}O$. Evans and Gillam (J., 1941, 815) have shown that α-substituted αβ-unsaturated ketones exhibit an absorption maximum situated at shorter wave-lengths than in the case of the corresponding β-substituted compounds. Hence, irone must be a β-substituted, αβ-unsaturated ketone. If any further evidence were needed, we have the fact that the short-wave absorption band of α-ionone (VII; R = H) is located at the same wave-length as that of irone (Burawoy, J., **1941**, 20; Evans and Gillam, *loc. cit.*) and α-ionone is accepted as being a β-substituted, αβ-unsaturated ketone having what must be a closely similar structure to that of irone.

TABLE I.

Compound.	*K*-Band.†		*R*-Band.†	
	λmax..	εmax..	λmax..	εmax..
Irone (French)	2280	12,200	near 3080	108
Irone (English)	2280	12,500	near 3050	117
α-Ionone	2285 *	14,300	?	—
β-Ionone	2935 *	8,700	none	—
ψ-Ionone	2910 *	21,800	none	—

* Burawoy, J., 1941, 20. † See Burawoy, J., 1939, 1177.

In order to obviate the possibility of erroneous inferences based on the examination of a single specimen, we obtained a second sample of irone from a different source (English orris oil). Its constants and purity were carefully checked, and the absorption spectrum examined. This specimen exhibited the same type of absorption spectrum as the first, with the short-wave band situated at identically the same wave-length (2280 A.), thus confirming the previous finding. The curves are shown in the figure, but it will be noticed that, although both show a maximum at 2280 A., the general shape of the long-wave part of the curve differs in the two cases. Since these curves are each the mean of two independent determinations, we believe the slight differences to be real and that they are consistent with the specimens being mixtures of somewhat variable composition.

Ruzicka, Seidel, and Schinz (1933, *loc. cit.*) found m. p. 175° for the *p*-bromophenylhydrazone prepared from irone of German origin, whereas the thiosemicarbazone melted to a turbid liquid at 110—120° and became clear and free from bubbles at 130°. They confirmed the m. p. of 181° recorded by Chuit for the irone thiosemicarbazone prepared by him (*Rev. Gén. Chim.*, 1903, **6**, 433).

The sample of irone which we obtained from orris oil of French origin, yielded a *p*-bromophenylhydrazone, m. p. 174° (Gillam and West, *Nature*, 1941, **148**, 114), and a thiosemicarbazone which could be separated into two components : (*a*) m. p. 184—185°, and (*b*) melting turbid between 107—115° and becoming clear at 130°. The irone isolated from the orris oil distilled in England had similar constants and gave a *p*-bromophenylhydrazone, m. p. 175°, and two thiosemicarbazones, (*c*) m. p. 185°, and (*d*) m. p. 107—110°, clear at 131°. The nitrogen content of our thiosemicarbazones corresponded with those reported for equivalent derivatives by the authors mentioned, but the proportion of ketone yielding the higher-melting thiosemicarbazone was considerably higher in the oil of French origin. It may be significant that Ruzicka *et al.* (1933, 1940, *locc. cit.*) have stated that the ketone is undoubtedly a mixture of isomerides, the composition of which may depend on the province of origin of the orris root and the method of manufacturing the oil, but the nitrogen content of our pairs of thiosemicarbazones pointed strongly to the presence of ketones possessing different empirical formulæ (Table II). The absorption data for these compounds, which will be more conveniently considered in another communication, support this hypothesis. The yield of the characteristic *p*-bromophenylhydrazones was low, and it was unfortunately not possible to purify the residue obtained from the mother-liquors.

TABLE II.

Details of Irone Thiosemicarbazones.

Authors.	Source of oil.	M. p.	N, % (found).*
Chuit[1]	German	181°	15·85
Ruzicka, Seidel, and Schinz[2]	German	110—120°, clear at 130°	14·73
Gillam and West	French	(*a*) 184—185°	15·7
		(*b*) 107—115°, clear at 130°	14·5
Gillam and West	English	(*c*) 185°	15·2
		(*d*) 107—112°, clear at 131°	14·75

[1] *Loc. cit.* [2] *Loc. cit.*, 1933.

* Calc. for $C_{16}H_{27}N_3S$: N, 14·3%. Calc. for $C_{15}H_{25}N_3S$: N, 15·05%. Calc. for $C_{14}H_{23}N_3S$: N, 15·85%.

EXPERIMENTAL.

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

(*a*) Commercial concrete oil of orris (112 g.) of French origin was distilled under reduced pressure, leaving a residue (95 g.), which was discarded, and suitable fractions redistilled. Two fractions, (i) (9 g.) having b. p. 108—120°/2 mm., $\alpha_D + 23·9°$, $n_D^{19°}$ 1·4803, $d_{15°}^{21°}$ 0·879, and (ii) (3·5 g.), b. p. 125—150°/2 mm., $\alpha_D + 13·7°$, $n_D^{18°}$ 1·4700, $d_{15°}^{21°}$ 0·885, were bulked and treated with *p*-phenylhydrazinesulphonic acid according to the method used by Schmidt (*Z. angew. Chem.*, 1900, **1**, 191; see also Ruzicka, Seidel, and Schinz, *Helv. Chim. Acta*, 1933, **16**, 1143) for the isolation of the ionones. After removal of the uncombined constituents (6·75 g.) by ten extractions with ether (Schmidt, *loc. cit.*), the aqueous solution was treated with phthalic anhydride, and the liberated ketone distilled in steam. The oil extracted from the distillate with ether was twice carefully distilled under reduced pressure, whereupon the main fraction (4·5 g.) had b. p. 106—108°/2 mm., $\alpha_D + 37·5°$, $n_D^{17°}$ 1·5017, $d_{15°}^{20°}$ 0·912 (Found : C, 81·2; H, 10·6. Calc. for $C_{13}H_{20}O$: C, 81·2; H, 10·4%. Calc. for $C_{14}H_{22}O$: C, 81·5; H, 10·7%).

The ketone (0·8 g.) yielded a *p*-bromophenylhydrazone which was recrystallised twice from methyl alcohol to give white crystals (0·1 g.), m. p. 174° (sintering at 165°) when rapidly heated (Found : N, 7·5. Calc. for $C_{20}H_{27}N_2Br$: N, 7·5%. Calc. for $C_{19}H_{25}N_2Br$: N, 7·75%).

Irone (2 g.) and thiosemicarbazide (1·4 g.) were treated as described by Ruzicka, Seidel, and Schinz (*Helv. Chim. Acta*, 1933, **16**, 1150). The crude thiosemicarbazone (2·05 g.) (which softened at 100°, lost shape at 108°, and finally became clear at 145°) was dissolved in warm methyl alcohol (15 ml.), and the solution kept at 0° overnight. The crystals (0·7 g.) which separated melted at 178°, and after twice recrystallising from methyl alcohol had m. p. 184—185° (Found : N, 15·7, 15·7%). Water (1 ml.) was added to the filtrate and an oil separated on standing. This oil was washed with dilute methyl alcohol, and after drying for two days in a vacuum desiccator, the product (1·1 g.) melted at 105° (sintering at 60°). This was dissolved in *cyclo*hexane–benzene (4 : 1) (charcoal) and the solution allowed to concentrate, and after a repetition of this process the small blunt crystals obtained (0·2 g.) became turbid at 107°, ran to the bottom of the tube at 115°, and became clear and free from bubbles at 130° (Found: N, 14·5%).

(*b*) Concrete oil of orris (83 g.), prepared in England by steam-distillation from orris root, was distilled under reduced pressure, and the appropriate fraction treated as in (*a*) above. The irone (3·5 g.) regenerated from the compound with *p*-phenylhydrazinesulphonic acid and distilled had b. p. 116—118°/3 mm., $\alpha_D + 46·6°$, $n_D^{21°}$ 1·5015, $d_{15°}^{25°}$ 0·915.

The ketone (0·5 g.) yielded a *p*-bromophenylhydrazone which, after recrystallising from methyl alcohol, was obtained as small white crystals (0·1 g.) having m. p. 175° (sintering at 161°) unchanged by further recrystallisation (Found: N, 7·5. Calc. for $C_{20}H_{27}N_2Br$: N, 7·5%).

Irone (1·5 g.), treated with thiosemicarbazide (1·05 g.) as in (*a*) above, gave a crude thiosemicarbazone (1·6 g.) which softened at 101°, lost shape at 107°, and became clear at 135°. This was dissolved in hot methyl alcohol (12 ml.) and after standing at 0° overnight the crystals which separated (0·2 g.) had m. p. 180° (sintering at 176°) which after recrystallisation from methyl alcohol was raised to 185°, unaltered on admixture with the higher-melting thiosemicarbazone from (*a*) above (Found: N, 15·2, 15·2%). After separation of the crystals, the methyl alcohol was allowed to evaporate at room temperature, and the product dried in a vacuum desiccator over paraffin wax. The solid (1·2 g.) softened at 57°, lost shape at 84°, and finally melted at 100°. After twice recrystallising from *cyclo*hexane–benzene, the white crystals (0·3 g.) began to melt at 107°, ran to the bottom of the tube at 112°, and became clear at 131° (Found: N, 14·9, 14·6%). When mixed with the corresponding product from (*a*) above, this thiosemicarbazone began to melt at 107° and became finally free from bubbles at 132°.

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

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