**206.** *The Carbonyl Constituents of Eucalyptus Oils. Part I. The Occurrence of Cryptal.*

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An examination by Penfold (J., 1922, **121**, 266) showed that the " aromadendral " previously isolated from various eucalyptus oils by Smith (*J. Roy. Soc. New South Wales,* 1900, **34**, 286; *Pharm. J.,* 1905, **75**, 356, 382; *Trans. Roy. Soc. South Australia,* 1916, **40**, 485) was in fact a mixture of cuminal and phellandral, and occurring with it was the substance cryptal which had already been isolated on several occasions by Smith and his co-workers (Baker and Smith, " A Research on the Eucalypts and Their Essential Oils," 2nd edn., Sydney, 1920, pp. 61, 386, 387). Cryptal was regarded as an aldehyde isomeric with phellandral, and later Penfold and Simonsen (J., 1930, 403) considered it to be *l*-4-*iso*propyl-Δ^2-*cyclo*hexenal (I), since, when oxidised in acetone solution by potassium permanganate, it yielded *d*-α-*iso*propylglutaric acid (II) in practically quantitative yield.
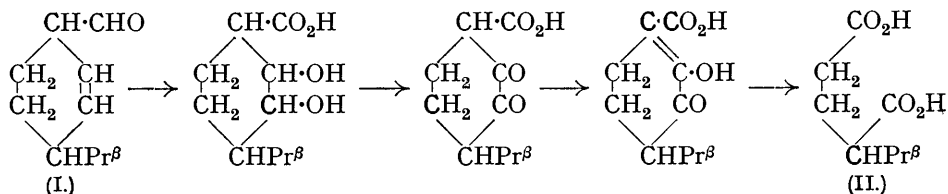
The constitution as a ten-carbon aldehyde was not in accord with analytical results we had obtained on examining some derivatives of the so-called cryptal from *E. cneorifolia,* but Cahn, Penfold, and Simonsen (J., 1931, 1366) showed that a sample of " cryptal " from this source, although agreeing excellently in physical properties with the sample of cryptal used in the previous work, was in fact the 9-carbon ketone *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one (III), since oxidation of the corresponding reduced ketone gave β-*iso*propyladipic acid (IV).
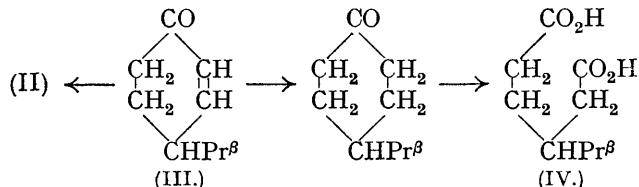
Our results entirely confirm this constitution, for the same oxidation product has been isolated from the reduced ketone, whereas the ketone itself yields α-*iso*propylglutaric acid. Further, the αβ-unsaturation is confirmed by the isolation of a characteristic hydrosulphide (Hooper, Macbeth, and Price, J., 1934, 1147). The occurrence of cryptal in eucalyptus oils would thus appear to be problematical, but Cahn, Penfold, and Simonsen (*loc. cit.*) were

of opinion that " there would appear to be no doubt of its separate existence and it is possible that it is only present during certain seasons." Apart from the fact that *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one yields the same oxidation product as that on which the structure of cryptal is based, two further significant observations were made in the original paper. In the first place attempts to oxidise cryptal to the corresponding acid were uniformly unsuccessful; and also the *oxime*, when heated with acetic anhydride, was not dehydrated to the nitrile and the reaction was thought to be proceeding abnormally. The absence of an aldehyde group is thus definitely suggested, and we have now examined the oxime derived from *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one. Its physical properties agree closely with those recorded for cryptal oxime, and, further, on treatment with acetic anhydride it yields a crystalline product identical with that obtained by Penfold and Simonsen from the alleged cryptal. This strengthens the view that 4-*iso*propyl-Δ^2-*cyclo*hexenal has not hitherto been isolated from eucalyptus oils. This opinion is further supported by the fact that our examination of the " cryptal " component of a number of oils has invariably shown the presence only of the ketone. This examination has included several samples of *E. polybractea* oil, samples of *E. hemiphloia* from two districts in Victoria, the " cryptal " from the oil of the same species in New South Wales, and numerous distillations of *E. cneorifolia*. A large-scale fractionation of the oil of the last class also failed to give any indication of the occurrence of the aldehyde mixed with the ketone fraction; and we have not succeeded in isolating a dimedon derivative. The results of the seasonal examination of *E. cneorifolia*, which has not disclosed any evidence of such a kind, will be communicated later.

EXPERIMENTAL.

Isolation of l-4-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one*.—Previous methods of separating the carbonyl constituents of eucalyptus oils consisted in treatment with sodium bisulphite solution, the phellandral and cuminal being combined as an insoluble derivative whilst the ketone was dissolved and recovered from the filtrate. A better procedure appears to be that adopted in the present work, in which the oil, or the fraction rich in carbonyl compounds, is shaken with neutral sodium sulphite solution (35% wt./wt. $Na_2SO_3,7H_2O$) to remove the ketone. If the oil is treated with more than five times its volume of neutral sulphite solution and the sodium hydroxide set free is periodically neutralised with sulphuric acid (10%), a satisfactory extraction of the ketone takes place and the process is completed in about an hour. The ketone is recovered from the solution by the addition of sodium hydroxide (40% solution) in the presence of ether. The original oil, after the removal of the ketone, is then shaken for 8—10 hours at laboratory temperature with twice its volume of saturated sodium bisulphite solution to recover the cuminal and phellandral, which are purified in the usual way. If the first extraction of the ketone is not complete, a further yield is obtained by the addition of sodium hydroxide to the bisulphite filtrate after removal of unabsorbed oil by ether.

In all cases the ketone was purified by re-treatment with neutral sulphite solution and fractional distillation. It was obtained as a clear liquid, α_D ranging from $-54.5°$ to $-80.4°$ in various samples and b. p. from 94°/5 mm., 104°/13 mm., to 110—112°/25 mm. It is thus not stereochemically pure (Galloway, Dewar, and Read, J., 1936, 1595). In its identification the following derivatives were employed : semicarbazone, m. p. 187—188° (Found : C, 61·6; H 8·9. Calc. : C, 61·5; H, 8·7%); *p*-nitrophenylhydrazone, m. p. 168—169° (Found : C, 65·9 H, 6·75. Calc. : C, 65·9; H, 6·9%); 2 : 4-dinitrophenylhydrazone, m. p. 138° (Hooper, Macbeth, and Price, *loc. cit.*) (Found : C, 56·7; H, 5·6. Calc. : C, 56·6; H, 5·7%); this derivative only gives the high m. p. recorded after some ten crystallisations from ethyl alcohol (compare Galloway, Dewar, and Read, *loc. cit.*, m. p. 129—130°); hydrosulphide, which is readily prepared by passing hydrogen sulphide into a solution of the ketone in absolute alcohol in the presence of anhydrous sodium carbonate; recrystallised from chloroform, m. p. 206—207° (Found : S, 10·2. Calc. : S, 10·3%) (Hooper, Macbeth, and Price, *loc. cit.*).

Oxime of l-4-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one*.—The ketone (35 g.) was refluxed for an hour with alcohol (350 g.) and hydroxylamine hydrochloride (20 g.) in the presence of anhydrous sodium acetate. After removal of the major part of the alcohol the *oxime* was distilled in steam, extracted in ether, dried (anhydrous sodium sulphate), recovered, and distilled under reduced pressure, yielding a thick clear oil (22 g.), b. p. 160—161°/33 mm., $n_D^{20°}$ 1·5160 (Found : C, 70·8; H, 9·9. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%).

A solution of the oxime in acetic anhydride (10 parts) containing anhydrous sodium acetate was refluxed for 2 hours, cooled, and poured into water. The dark brown oil obtained, after being washed in ether with sodium carbonate solution and dried (potassium carbonate), was distilled under reduced pressure. The fraction, b. p. 200—212°/26 mm., was a viscous oil which crystallised and after draining on a porous tile was obtained in long needles, m. p. 103°, from light petroleum (b. p. 60°). This is evidently identical with the product obtained by Cahn, Penfold, and Simonsen (*loc. cit.*) and is being further examined.

Reduction of 1-4-iso*Propyl*-Δ^2-cyclo*hexen*-1-*one*.—The catalytic reduction of the ketone by hydrogen in the presence of palladised charcoal (as described by Cahn, Penfold, and Simonsen, *loc. cit.*) was carried out on several occasions for its further identification in various oils. The amounts of hydrogen absorbed in the various experiments (1125—1173 c.c.) were nearly theoretical (1136 c.c.) for the amount of ketone treated (7 g.). The product, 4-*iso*propyl*cyclo*hexan-1-one, was identified by the semicarbazone, m. p. 188—189°, the *p*-nitrophenylhydrazone, m. p. 123—124°, and also the 2 : 4-dinitrophenylhydrazone, which crystallised at once when the ketone (1 g.) in alcohol (20 c.c.) was added to 2 : 4-dinitrophenylhydrazone (1 g.) in concentrated sulphuric acid (2 c.c.) and alcohol (15 c.c.) and on recrystallisation from alcohol formed orange-yellow plates, m. p. 119—120° (Found : C, 56·4; H, 6·15. Calc. for $C_{15}H_{20}O_4N_4$: C, 56·25; H, 6·25%) (compare Macbeth and Price, J., 1935, 151).

The oxidation of *l*-4-*iso*propyl*cyclo*hexan-1-one as described by Cahn, Penfold, and Simonsen (*loc. cit.*) yielded β-*iso*propyladipic acid, m. p. 83—84° (recrystallised from water).

Large-scale Distillations of E. cneorifolia.—As the main object of the work was a search for cryptal associated with the ketone, distillations of *E. cneorifolia* on a commercial scale were carried out under supervision at Kangaroo Island, South Australia, samples being examined at different stages of the distillation. Typical results are recorded in the table, and it is evident that the aldehydes distil without much variation until the final stage; the percentage is then about doubled. No cryptal was found in any of the fractions.

Time.	Oil in distillate, lb.	$d^{15\cdot5°}_{15\cdot5°}$.	Aldehydes, %.	Cineole, %.	Rotation of oil $(l = 1 \text{ dm.})$.
11.15 a.m.	—	—	—	—	—
11.25 ,,	3	0·9215	8·56	75·6	−3·14°
11.30 ,,	1·75	0·9224	9·07	74·2	−2·9
11.35 ,,	3·5	0·9227	8·62	73·5	−2·97
11.45 ,,	3·5	0·9237	9·75	72·8	−3·62
12.5 p.m.	3·5	0·9221	9·53	70·5	−4·14
12.30 ,,	2·25	0·9209	11·1	68·6	−4·27
2.30 ,,	4·5	0·9233	18·0	54·6	−7·74

The cineole content was determined by the B.P. *o*-cresol method, and the aldehydes were estimated by the neutralisation of $N/2$-alcoholic sodium hydroxide by the oil in the presence of 5% hydroxylamine hydrochloride solution, bromophenol-blue being used as indicator. The results were calculated in terms of $C_{10}H_{14}O$, as subsequent work showed that the aldehydes and ketone were present in approximate amounts in agreement with this formula. Each c.c. of alkali is thus equivalent to 0·075 g. of aldehyde (including the ketone).

Further large-scale work involved the steam distillation of three drums of commercial *E. cneorifolia* oil supplied by a Kangaroo Island distiller from leaf cut during the autumn months. The last fractions distilling from 134 gallons of oil in three separate experiments were combined and gave 6·5 gallons of oil, which was again fractionally steam-distilled. The first fraction (1 gallon) had α_D − 7·32°, $d^{15\cdot5°}_{15\cdot5°}$ 0·9301, cineole 67%; the second fraction (3 gallons) had α_D − 17·6°, $d^{15\cdot5°}_{15\cdot5°}$ 0·9427, cineole 40·8%, aldehydes 36%; and a third fraction (1·5 gallons) had $\alpha_D^{20°}$ − 35·01, $d^{15\cdot5°}_{15\cdot5°}$ 0·9622, cineole 22·6% and aldehydes 40%. After shaking with 5% sodium hydroxide solution and subsequent washing, portions of the fractions were treated by the method already outlined for the separation of the carbonyl compounds. Cuminal (semicarbazone, m. p. 210—211°; 2 : 4-dinitrophenylhydrazone, m. p. 238°) and *l*-phellandral [semicarbazone, m. p. 202—203°; *p*-nitrophenylhydrazone, m. p. 169—170° (Found : C, 66·8; H, 7·4. Calc. : C, 66·9; H, 7·3%); atmospheric oxidation to the corresponding carboxylic acid, m. p. 143·5—144·5°] were isolated. The latter was further characterised by its 2 : 4-dinitrophenylhydrazone, which separated on the addition of the aldehyde (1 g.) in alcohol (20 c.c.) to 2 : 4-dinitrophenylhydrazine (1 g.) in concentrated sulphuric acid (2 c.c.) and alcohol (15 c.c.). *Phellandral* 2 : 4-*dinitrophenylhydrazone* is sparingly soluble in alcohol, but easily soluble in chloroform. It is obtained on recrystallisation from alcohol–chloroform in deep orange needles,

m. p. 202—203° (Found : C, 57·6; H, 5·7. $C_{16}H_{20}O_4N_4$ requires C, 57·8; H, 6·0%). *l*-4-*iso*-Propyl-Δ^2-*cyclo*hexen-1-one also was isolated and identified by its derivatives; but cryptal was not found.

Eucalyptus polybractea. Two 4-gallon samples of the oil of *E. polybractea* from Victoria were examined. The oil from one-year old leaf had $d_{15\cdot5°}^{15\cdot5°}$ 0·9270, cineole 87·1%, alcohols 7·6%, and aldehydes 2·5%. Treatment in the usual way with sodium sulphite, followed by sodium bisulphite, led to the isolation of cuminal, *l*-phellandral, and *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one. The same products were obtained from the oil from two-year old leaf, which had $d_{15\cdot5°}^{15\cdot5°}$ 0·9279, cineole 91·0%, alcohols 2·9%, and aldehydes 2·6%. In neither case was any cryptal detected.

Eucalyptus hemiphloia. Two samples of the oil of this species from different districts in Victoria were examined. The first, from the Rushworth district, was obtained through the courtesy of the Inspector General of Forests, Mr. C. E. Lane Poole. It had α_D — 17·2°, ester value 25·9, alcohols 19·1%, cineole 16·9%, and aldehydes 19·4%. The ketone (37·5 g.) was isolated by the usual treatment and the proportion of ketone in the total aldehydes was some 36%. Cuminal and *l*-phellandral also were isolated; but no cryptal was found. For the second sample, from the Somerton district, we are indebted to Mr. S. G. Reilly of Messrs. J. Bosisto & Co., Richmond, Victoria. It had α_D — 21·8°, cineole 19·2%, and aldehydes 22·6% In this case also the ketone was isolated and identified, but cryptal was not detected.

Mr. A. R. Penfold kindly supplied a sample of " cryptal " from the oil of *E. hemiphloia* from New South Wales. It also was identified as *l*-4-*iso*propyl-Δ^2-*cyclo*hexen-1-one, giving the characteristic hydrosulphide and other derivatives.

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