329. *Studies in the Polyene Series. Part III.*

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Cyclisation of the semicarbazone, m. p. 160°, of citrylidenecrotonaldehyde *a* with phosphoric acid by the method described in the preceding paper gives an *aldehyde*, m. p. 60—61°, $\lambda_{\text{max.}}$3210 A., probably 5 : 5 : 9-trimethyl-5 : 6 : 7 : 8 : 9 : 10-hexahydro-1-naphthaldehyde, characterised by a *semicarbazone*, m. p. 169—171°, $\lambda_{\text{max.}}$3230 A., and a 2 : 4-*dinitrophenylhydrazone*, m. p. 186°. The corresponding *alcohol* is an extremely viscous oil exhibiting an absorption maximum at 2680 A. and giving a blue-violet colour with chloroformic antimony trichloride. The semicarbazone, m. p. 206°, of citrylidenecrotonaldehyde *b* similarly yields an *aldehyde*, also probably dicyclic, m. p. 56·5—60·5°, $\lambda_{\text{max.}}$2350 A., giving a *semicarbazone*, m. p. 221—222°, $\lambda_{\text{max.}}$2680 A., and a 2 : 4-

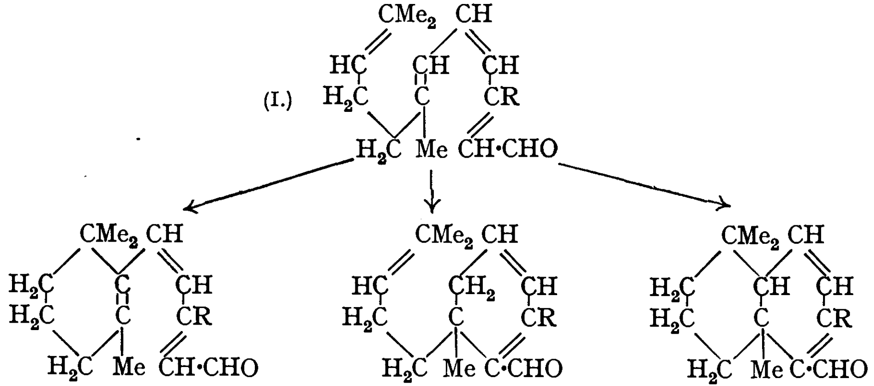
dinitrophenylhydrazone, m. p. 253—254°. The corresponding *alcohol* shows no selective absorption in the ultra-violet region.

The two isomeric semicarbazones, from the condensation product of citral with β-methylcrotonaldehyde (Part I; this vol., p. 1549), behave in exactly the same manner. ψ-Ionylideneacetaldehyde *a* semicarbazone, m. p. 178—179°, gives an aldehyde, $\lambda_{max.}$3160 A. (*semicarbazone*, m. p. 188—189°, $\lambda_{max.}$3250 A.), probably 2 : 5 : 5 : 9-tetramethyl-5 : 6 : 7 : 8 : 9 : 10-hexahydro-1-naphthaldehyde. The corresponding alcohol ($\lambda_{max.}$2720 A.) gives an intense blue colour ($\lambda_{max.}$ 6070 A.) with chloroformic antimony trichloride. ψ-Ionylideneacetaldehyde *b* semicarbazone, m. p. 112°, yields an aldehyde, $\lambda_{max.}$2400 A. (*semicarbazone*, m. p. 214—215°, $\lambda_{max.}$2650 A.).

It has been shown (preceding paper) that cyclisation of citrylideneacetaldehyde semicarbazone with cold concentrated phosphoric acid gives β-*cyclo*citrylideneacetaldehyde, and this reaction has been extended to the acyclic semicarbazones obtained from the condensation products of citral with crotonaldehyde and β-methylcrotonaldehyde (see Part I, *loc. cit.*). Cyclisation of the semicarbazone of citrylidenecrotonaldehyde *a* gave a steam-volatile *aldehyde*, m. p. 60—61°, exhibiting a well-defined absorption maximum at 3210 A. (Table I) (*semicarbazone*, m. p. 169—171°, $\lambda_{max.}$3230 A.; 2 : 4-*dinitrophenylhydrazone*, m. p. 186°). Reduction with aluminium *iso*propoxide gave the corresponding *alcohol* as a viscous oil characterised by a single absorption band at 2680 A.

Although the above method had proved very effective in the cases of ψ-ionone and citrylideneacetaldehyde, it was clear that in extending its application to citrylidenecrotonaldehyde *a* it was necessary to take into consideration the possibility that the cyclisation might take an alternative route owing to the greater chain-length. Thus in addition to the desired aldehyde (II; R = H), (III; R = H) and (IV; R = H) could also theoretically be formed. Of these, (III; R = H) was immediately disposed of, since ozonolysis failed to give acetone. Regarding (II; R = H) and (IV; R = H), no distinction could be made between them on spectrographic grounds, since two conjugated double bonds in a six-membered ring are spectroscopically equivalent to three in a chain (cf. Batty *et al.*, J., 1937, 758; Fieser and Campbell, *J. Amer. Chem. Soc.*, 1938, **60**, 159).

Ozonolysis of the aldehyde gave a keto-dicarboxylic acid, $C_{12}H_{18}O_5$, isolated as its *semicarbazone*, m. p. 163°. The failure to obtain geronic acid definitely eliminates (II; R = H) and therefore the above result indicates a structure of type (IV; R = H). Conclusive proof of the dicyclic nature of the aldehyde was supplied by quantitative microhydrogenation of the semicarbazone, which indicated three double bonds in contrast to the five found for the corresponding acyclic compound (J., 1937, 755).


(I.)

(II.) (III.) (IV.)

Cyclisation of ψ-*Ionylideneacetaldehyde* a *Semicarbazone.*—The aldehyde obtained on cyclisation as above was a pale yellow oil ($\lambda_{max.}$3160 A.) which could not be induced to crystallise (*semicarbazone*, m. p. 188—189°, $\lambda_{max.}$3250 A.). Quantitative microhydrogenation of the semicarbazone established its dicyclic nature, this being confirmed by the fact that neither acetone nor geronic acid could be detected on ozonolysis. Reduction of the aldehyde with aluminium *iso*propoxide yielded the corresponding alcohol as a viscous oil giving an intense blue colour with chloroformic antimony trichloride ($\lambda_{max.}$6070 A.). From the close similarity to the product obtained by cyclisation of citrylidenecrotonaldehyde *a*, the aldehyde would appear to be most probably 2 : 5 : 5 : 9-tetramethyl-5 : 6 : 7 : 8 : 9 : 10-hexahydro-1-naphthaldehyde (IV; R = Me).

Cyclisation of Citrylidenecrotonaldehyde b *Semicarbazone.*—The *aldehyde* obtained on cyclisation as described above crystallised in prisms, m. p. 56·5—60·5°, and was characterised by a *semicarbazone*, m. p. 221—222°, and a 2 : 4-*dinitrophenylhydrazone*, m. p. 253—254°. In contrast to the products obtained by cyclisation of the semicarbazones of citrylidenecrotonaldehyde *a* and ψ-ionylideneacetaldehyde *a*, the absorption maxima of the aldehyde (2350 A.) and its semicarbazone (2680 A.) establish that the former contains only one double bond in conjugation with the carbonyl group. This was confirmed by the fact that the *alcohol* obtained on reduction with aluminium *iso*propoxide showed only general absorption in the ultra-violet region. Quantitative microhydrogenation of the semicarbazone showed the presence of three ethylenic linkages, from which it follows, on the grounds stated above, that the aldehyde must be dicyclic and possibly (V; R = H).

FIG. 1.

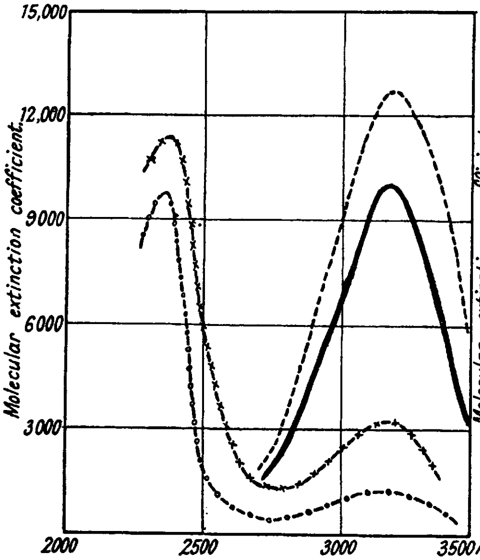
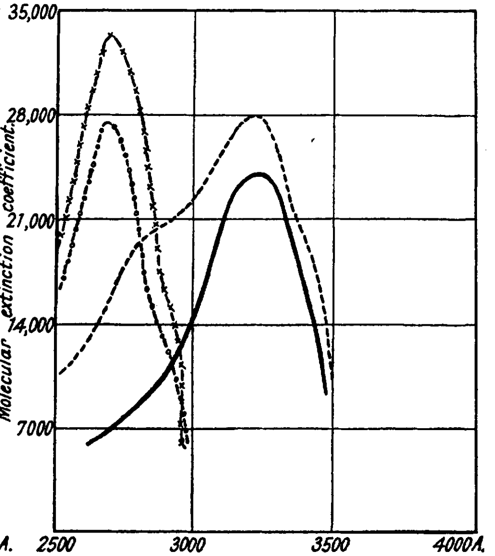
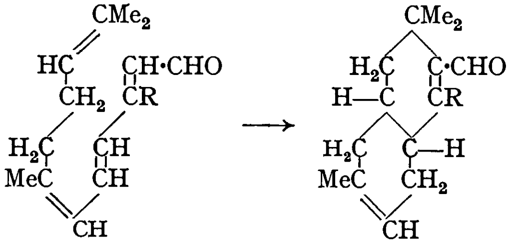


FIG. 2.



Solvent, alcohol.



(V.)

Cyclisation of ψ-Ionylideneacetaldehyde b *Semicarbazone.*—The results obtained on cyclisation of this semicarbazone are exactly analogous to those with citrylidenecrotonaldehyde *b* semicarbazone, the product being an aldehyde characterised by an absorption maximum at 2400 A. (*semicarbazone,* m. p. 214—215°) and probably possessing the structure (V; R = Me).

TABLE I.

Compound.	$\lambda_{max.}$, A.	$\epsilon_{max.}$	Semicarbazone. $\lambda_{max.}$, A.	Semicarbazone. $\epsilon_{max.}$
(i) Citrylidenecrotonaldehyde *a*	3140	12,490	3255	27,100
(ii) Dicyclic aldehyde from (i)	3210	13,260	3230	28,000
(iii) Citrylidenecrotonaldehyde *b*	3160	12,800	3255	24,400
(iv) Dicyclic aldehyde from (iii)	2350	14,000	2680	33,300
(v) ψ-Ionylideneacetaldehyde *a*	3150	14,700	3250	33,000
(vi) Dicyclic aldehyde from (v)	3160	10,900	3250	24,000
(vii) ψ-Ionylideneacetaldehyde *b*	3150	11,000	3240	24,400
(viii) Dicyclic aldehyde from (vii)	2400	8,000	2670	27,500
(ix) Alcohol corresponding to (i)	2680	12,000	—	—
(x) ,, ,, (ii)	2680	10,000	—	—
(xi) ,, ,, (v)	2650	11,000	—	—
(xii) ,, (vi)	2720	9,000	—	—

Solvent, alcohol.

The above results would appear to indicate that citrylidenecrotonaldehyde *a* is derived from the *trans*-form of citral (*i.e.*, citral *a* or geranial), whereas aldehyde *b*, which yields (V), is related to the *cis*-isomer (citral *b* or neral). This suggestion finds support in the fact that the ratio of the two isomers formed in the condensation by the neutral piperidine–acetic acid catalyst is *a* : *b* = 5 : 1 (J., 1937, 755), which is in agreement with the observation of Tiemann and Kerschbaum (*Ber.*, 1900, **33**, 877) that commercial citral consists largely of the *trans*-form. Further, the absence of citrylidenecrotonaldehyde *b* when the mild conditions of the sodamide condensation are used (Part I, *loc. cit.*) is exactly analogous to the finding of Tiemann and Kerschbaum that citral *a* condenses with cyanoacetic acid in dilute alkali solution much more readily than citral *b*.

EXPERIMENTAL.

Cyclisation of Citrylidenecrotonaldehyde a *Semicarbazone.*—The semicarbazone (10 g.) was added during ½ hour to phosphoric acid (100 c.c., *d* 1·75) with stirring at room temperature; it dissolved after 1 hour and the solution was then poured into ice-water. The crude product was distilled with steam in the presence of phthalic anhydride (25 g.) in a current of nitrogen, the volatile product crystallising in the distillate. Ether extraction and working up in the normal manner gave the cyclic *aldehyde* (5·1 g.), which crystallised from light petroleum in rhombic plates, m. p. 60—61° (Found : C, 82·3; H, 9·9. $C_{14}H_{20}O$ requires C, 82·4; H, 9·9%). The *semicarbazone* separated from methyl alcohol in needles, m. p. 114°, containing one molecule of methyl alcohol of crystallisation (Found : C, 65·5; H, 9·3. $C_{15}H_{23}ON_3,CH_3{\cdot}OH$ requires C, 65·5; H, 9·3%). Recrystallisation from ether–light petroleum gave pale yellow micro-needles, m. p. 169—171° (Found : C, 68·9; H, 8·7; N, 16·0. $C_{15}H_{23}ON_3$ requires C, 69·0; H, 8·8; N, 16·1%). The 2 : 4-*dinitrophenylhydrazone,* prepared by heating the aldehyde with the reagent in 95% acetic acid, crystallised from alcohol–ethyl acetate in red needles, m. p. 186° (Found : C, 62·2; H, 6·3; N, 14·4. $C_{20}H_{24}O_4N_4$ requires C, 62·5; H, 6·3; N, 14·6%).

Reduction of Cyclised Citrylidenecrotonaldehyde a.—The above aldehyde (3 g.) and aluminium *iso*propoxide (10 g.) were dissolved in dry *iso*propyl alcohol (50 c.c.) and heated at 110—120°, the solvent being distilled slowly and fresh *iso*propyl alcohol being added at such a rate as to keep the volume approximately constant. When acetone was no longer detectable in the distillate, the residue was dissolved in ether and washed successively with dilute sulphuric acid, sodium bicarbonate solution, and water. After drying over sodium sulphate and removal of solvent the crude alcohol was refluxed for 1 hour with Girard reagent P (2·5 g.) and glacial acetic acid (2·5 g.) in absolute alcohol (25 c.c.). The solution was cooled, diluted with water, and extracted with ether after neutralisation of 90% of the acetic acid with sodium bicarbonate. The residue obtained on removal of solvent from the ethereal solution was distilled in steam, yielding the *alcohol* (2 g.) as a pale yellow, viscous oil giving a blue-violet colour with chloroformic antimony trichloride, with absorption bands at 6410, 5800 and 5030 A. (Found : C, 81·7; H, 10·5. $C_{14}H_{22}O$ requires C, 81·5; H, 10·7%). Quantitative microhydrogenation :

9·912 mg. absorbed 3·969 c.c. at 755 mm. and 18° (solvent, acetic acid) equivalent to three double bonds. This apparently anomalous result is explained by the fact that the hydrogenation product is not the anticipated saturated alcohol but the corresponding hydrocarbon, as shown by the fact that no aldehyde was produced on oxidation with chromic acid (cf. the hydrogenation of farnesol to farnesane : Fischer, *Annalen*, 1928, **464**, 88).

Ozonolysis of Cyclised Citrylidenecrotonaldehyde a.—A solution of the aldehyde (3 g.) in dry carbon tetrachloride (35 c.c.) was treated at 0° with a slow stream of ozonised oxygen for 18 hours and after addition of glacial acetic acid (150 c.c.) the ozonolysis was continued for a further 6 hours. Water (150 c.c.) was then added and, after 24 hours' standing at room temperature, decomposition of the ozonide was completed by refluxing for 3 hours. The material obtained on evaporation to dryness was dissolved in ether, and the acid products extracted by washing with dilute sodium bicarbonate solution. The alkaline extract was acidified with dilute sulphuric acid and extracted with ether; after removal of solvent the resultant acid was dissolved in warm water (15 c.c.) and filtered. The semicarbazone was prepared by addition of a solution of semicarbazide hydrochloride (1·5 g.) and potassium acetate (1·5 g.) in water (5 c.c.) to the above filtrate, the oil which immediately separated solidifying at 0° after 24 hours. Crystallisation from ethyl acetate gave the *semicarbazone* as colourless micro-needles, m. p. 163°, which on admixture with geronic acid semicarbazone, m. p. 164°, showed a depression of more than 20° (Found : C, 51·6; H, 6·6; N, 13·7. $C_{13}H_{21}O_5N_3$ requires C, 52·2; H, 7·0; N, 14·0%). Ozonolysis as above for only 6 hours gave an identical product.

Cyclisation of ψ-Ionylideneacetaldehyde a *Semicarbazone.*—The semicarbazone (4 g.), cyclised as described above for citrylidenecrotonaldehyde, gave the cyclic aldehyde as a pale yellow oil (3 g.). The *semicarbazone* crystallised from methyl alcohol in needles, m. p. 189° (Found : C, 70·0; H, 8·7; N, 14·9. $C_{16}H_{25}ON_3$ requires C, 69·8; H, 9·2; N, 15·3%). Quantitative microhydrogenation : 2·05 mg. absorbed 0·50 c.c. at 760 mm. and 0°, equivalent to three double bonds. No geronic acid was obtained on ozonolysis of the aldehyde. Reduction of the aldehyde with aluminium *iso*propoxide as described above yielded the alcohol as a pale yellow oil, $\lambda_{max.}$2720 A.

Cyclisation of Citrylidenecrotonaldehyde b *Semicarbazone.*—Cyclisation as above gave a solid *aldehyde*, which crystallised from light petroleum in prisms, m. p. 56·5—60·5° (Found : C, 82·3; H, 9·5. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%). The *semicarbazone* separated from methyl alcohol as a micro-crystalline solid, m. p. 221—222° (Found : C, 69·0; H, 9·0; N, 15·8. $C_{15}H_{23}ON_3$ requires C, 69·0; H, 8·8; N, 16·1%). The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in red needles, m. p. 253—254° (Found : N, 14·8. $C_{20}H_{24}O_4N_4$ requires N, 14·6%). Reduction of the aldehyde with aluminium *iso*propoxide gave the *alcohol* as a pale yellow oil showing no selective absorption in the ultra-violet (Found : C, 81·3; H, 11·0. $C_{14}H_{22}O$ requires C, 81·5; H, 10·7%). Quantitative microhydrogenation : 4·501 mg. absorbed 1·50 c.c. at 757 mm. and 17·5°, equivalent to three double bonds. As with the alcohol from the cyclisation product of citrylidenecrotonaldehyde *a*, reduction gave the saturated hydrocarbon and not the anticipated alcohol.

Cyclisation of ψ-Ionylideneacetaldehyde b *Semicarbazone.*—The cyclic aldehyde, obtained in the usual manner, was a pale yellow oil; its *semicarbazone* crystallised from methyl alcohol in flat needles, m. p. 214—215° (Found : C, 69·8; H, 9·1; N, 15·3. $C_{16}H_{25}ON_3$ requires C, 69·8; H, 9·2; N, 15·3%). Quantitative microhydrogenation : 2·24 mg. absorbed 0·5615 c.c. at 762 mm. and 19°, equivalent to three double bonds.

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