Sesquiterpenoids. Part IV. The Constitution of Carissone.*

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Dehydration of carissone under mild basic conditions, followed by conversion into the 2 : 4-dinitrophenylhydrazone in the usual way, gives β-cyperone 2 : 4-dinitrophenylhydrazone. Analogous dehydration of carissone 2 : 4-dinitrophenylhydrazone itself affords the α-cyperone derivative. On the basis of these observations the constitution (II) of carissone can be taken as established.

The isolation of an αβ-unsaturated ketone, carissone, $C_{15}H_{24}O_2$, from the roots of *Carissa lanceolata* (R. Brown) was reported recently by Mohr, Schindler, and Reichstein (*Helv. Chim. Acta*, 1954, **37**, 462). The infra-red spectrum of the compound revealed the presence of a hydroxyl group which, since it was stable to chromic acid, must be tertiary. The ultra-violet absorption spectrum ($\lambda_{max.}$ 250 mμ, ε 15,000) and the rotation ($[\alpha]_D$ +137° in $CHCl_3$) are reminiscent of those recorded (for summary see Simonsen and Barton, " The Terpenes," Vol. III, Cambridge Univ. Press, 1952) for α-cyperone (I) and it seemed to us that carissone might well be represented by the expression (II). Through the great kindness of Professor T. Reichstein, to whom we express our best thanks, in making available an adequate supply of carissone, it has been possible to adduce further evidence which has confirmed the correctness of our hypothesis.

Dehydration of carissone with phosphorus oxychloride in pyridine solution afforded an oil which, on conversion into the 2 : 4-dinitrophenylhydrazone in the usual way and

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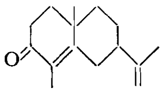
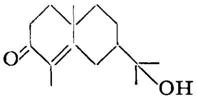
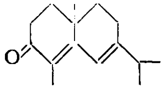
* Part III, *J.*, 1953, 3124.

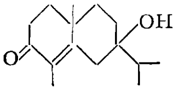
careful chromatography of the product over alumina, gave the 2 : 4-dinitrophenylhydrazone of β-cyperone (III) (Bradfield, Gillam, Hegde, and Simonsen, *J.*, 1936, 667; Bradfield, Pritchard, and Simonsen, *J.*, 1937, 760; Adamson, McQuillin, Robinson, and Simonsen, *J.*, 1937, 1576; McQuillin, *J.*, 1951, 717) identical in all respects with a purified authentic specimen.* This identity establishes the carbon skeleton of carissone and the position of the unsaturated ketone grouping, and leaves undecided only the point of attachment of the tertiary hydroxyl group. This tertiary hydroxyl group could be secured as in (IV) or, allowing for the ready acid-catalysed migration (Simonsen *et al.*, *locc. cit.*) of the ethylenic linkage in α-cyperone (I) to give β-cyperone (III), as in (II). The stability of carissone to aqueous-methanolic sodium hydroxide (Mohr, Schindler, and Reichstein, *loc. cit.*) contraindicates (IV). Furthermore, treatment of the 2 : 4-dinitrophenylhydrazone of α-cyperone (I) with acid of the concentration normally used in the preparation of 2 : 4-dinitrophenylhydrazones led to smooth conversion into the 2 : 4-dinitrophenylhydrazone of β-cyperone (III).


(I)



(II)


(III)



(IV)

Decisive evidence in favour of structure (II) was obtained by transforming carissone into its 2 : 4-dinitrophenylhydrazone and dehydrating this with phosphorus oxychloride in pyridine solution (mild basic conditions). Careful chromatography of the product afforded α-cyperone 2 : 4-dinitrophenylhydrazone, identical in all respects with a purified authentic specimen.

EXPERIMENTAL

Ultra-violet absorption spectra were determined in $CHCl_3$ with the Unicam S.P. 500 Spectrophotometer. $[\alpha]_D$ are in $CHCl_3$.

α- and β-Cyperone 2 : 4-Dinitrophenylhydrazones.—Authentic α-cyperone 2 : 4-dinitrophenylhydrazone was carefully chromatographed over alumina, and the fractions of $\lambda_{max.}$ 395 mμ were combined. Recrystallised from chloroform–*iso*propyl ether, the pure material had m. p. 188—190°, $[\alpha]_D$ +414° (*c*, 0·0124), $\lambda_{max.}$ 395 mμ (ε 29,000). Authentic β-cyperone 2 : 4-dinitrophenylhydrazone, purified by chromatography and crystallisation from chloroform-ethanol, had m. p. 229—230°, $[\alpha]_D$ +831° (*c*, 0·0052), $\lambda_{max.}$ 415 mμ (ε 34,000).

Isomerisation of α- to β-Cyperone 2 : 4-Dinitrophenylhydrazone.—A solution of α-cyperone 2 : 4-dinitrophenylhydrazone (150 mg.) in ethanol (10 ml.). water (3 ml.), and concentrated sulphuric acid (3 ml.) was refluxed for 1 hr. Crystallisation of the product from chloroform–ethanol gave β-cyperone 2 : 4-dinitrophenylhydrazone (93 mg.), m. p. 230—232°, $[\alpha]_D$ +896° (*c*, 0·0053), $\lambda_{max.}$ 415 mμ (ε 34,000), undepressed in m. p. on admixture with the comparable material described above.

Dehydration of Carissone.—A solution of carissone (207 mg.) in anhydrous pyridine (5 ml.) and redistilled phosphorus oxychloride (1 ml.) was heated on the steam-bath for 1 hr. The oily product was treated with 2 : 4-dinitrophenylhydrazine (200 mg.) in ethanol (10 ml.), water (3 ml.), and concentrated sulphuric acid (2 ml.) under reflux. Chromatography of the product over alumina and elution with benzene gave dark red leaflets (120 mg.), m. p. 209—215°. Crystallisation from chloroform–ethanol afforded β-cyperone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 230—232°, $[\alpha]_D$ +882° (*c*, 0·0046), $\lambda_{max.}$ 415 mμ (ε 31,500).

Carissone 2 : 4-Dinitrophenylhydrazone.—Carissone (108 mg.) was converted into the 2 : 4-dinitrophenylhydrazone in the usual way. Chromatography over alumina and elution with ether–benzene (1 : 3), followed by crystallisation from chloroform–methanol, gave the pure 2 : 4-*dinitrophenylhydrazone* (125 mg.), m. p. 174—175°, $[\alpha]_D$ +538° (*c*, 0·0139), $\lambda_{max.}$ 392 mμ (ε 26,000) (Found : N, 13·3. $C_{21}H_{28}O_5N_4$ requires N, 13·45%).

Dehydration of Carissone 2 : 4-Dinitrophenylhydrazone.—A solution of this hydrazone (460 mg.) in anhydrous pyridine (5 ml.) and redistilled phosphorus oxychloride (1 ml.) was heated

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on the steam-bath for 1 hr. Chromatography of the product over alumina, elution with benzene–light petroleum (b. p. 40—60°) (1 : 3), and collection only of fractions with $\lambda_{max.}$ 395 mμ gave, after recrystallisation from chloroform–*iso*propyl ether, α-cyperone 2 : 4-dinitrophenylhydrazone (93 mg.), m. p. and mixed m. p. 188—190°, $[\alpha]_D$ +422° (*c*, 0·013), $\lambda_{max.}$ 395 mμ (ε 30,000).

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