The Structure of Carotatoxin, a Natural Toxicant from Carrot

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IN a recent publication under the above title,[1] the rather improbable structure (I) was proposed for a toxic acetylenic compound isolated from *Daucus carota* L.

This structure was assigned on the basis of the spectra of the compound itself, the ultraviolet spectrum of a "dehydration" product of the alcohol (I) with toluene-*p*-sulphonic acid in benzene, and the chain lengths of the fatty acids (C_8 and C_7) obtained by alkaline permanganate oxidation of the alcohol (I).

A plant-screening programme has been in progress in this Department to detect the presence of short interrupted acetylenic chromophores which would elude detection by the conventional ultraviolet screening of crude plant extracts. The carrot, earlier found to be negative as a polyacetylene producer[2] was reinvestigated, the presence of a C_{17}-alcohol with an interrupted chromophore was detected and proved to be falcarinol (II), isolated by Bohlmann *et al.*,[3] from another Umbellifer, *Falcaria vulgaris* Bernh. On the basis of the spectra and some of the chemical data quoted for carotatoxin, the latter seemed to be identical with falcarinol.[4] This was proved by repeating the isolation procedure given for carotatoxin and by

oxidising the alcohol obtained with manganese dioxide to give falcarinone[2] (III).

The 'dehydration' of carotatoxin with toluene-*p*-sulphonic acid in benzene gave a mixture of compounds with very similar chromophores but differing polarities. One of them† is the primary alcohol (IV) obtained by aniontropic rearrangement; its ultraviolet absorption at 2840, 2680, and 2540 Å is characteristic for an ene-diyne chromophore, and was wrongly allocated[1] to a diene-diyne system. (the C_{10}-compound $CH_3{\cdot}[C{\equiv}C]_2{\cdot}[CH{=}CH]_2{\cdot}CH_3$ has λ_{max} 3080, 3010, 2915, 2760, 2335, and 2250 Å[5]).

The formation of the C_8-acid as the major oxidation product is more easily explained by the falcarinol (II) structure.

In the light of the above, the suggested structures for the fragments obtained by high-resolution mass spectrometry[1] must also be revised: *m/e* 159 is the base peak in falcarinol and corresponds to the base peak *m/e* 157 in the C_{18}-aldehyde[6] (V); it results from allylic cleavage on the saturated side of the molecule next to the *cis*-double bond.

$$CH_2{=}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}[C{\equiv}C]_2{\cdot}CH_2{\cdot}CH\overset{t}{=}CH{\cdot}[CH_2]_5{\cdot}CH_3 \quad (I)$$

$$CH_2{=}CH{\cdot}CH(OH){\cdot}[C{\equiv}C]_2{\cdot}CH_2{\cdot}CH\overset{c}{}CH{\cdot}[CH_2]_6{\cdot}CH_3 \quad (II)$$

$$CH_2{=}CH{\cdot}CO{\cdot}[C{\equiv}C]_2{\cdot}CH_2{\cdot}CH\overset{c}{=}CH{\cdot}[CH_2]_6{\cdot}CH_3 \quad (III)$$

$$HO{\cdot}CH_2{\cdot}CH{=}CH{\cdot}[C{\equiv}C]_2{\cdot}CH_2{\cdot}CH\overset{c}{=}CH{\cdot}[CH_2]_6{\cdot}CH_3 \quad (IV)$$

$$CH_2{=}CH{\cdot}CO{\cdot}[C{\equiv}C]_2{\cdot}CH_2{\cdot}CH\overset{c}{=}CH{\cdot}[CH_2]_7{\cdot}CHO \quad (V)$$

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† The nature of the other compounds involved will be discussed in a forthcoming publication.

[1] D. G. Crosby and N. Aharonson, *Tetrahedron*, 1967, **23**, 465.
[2] F. Bohlmann, Ch. Arndt, H. Bornowski, and K.-M. Kleine, *Chem. Ber.*, 1961, **94**, 958.
[3] F. Bohlmann, U. Niedballa, and K.-M. Rode, *Chem. Ber.*, 1966, **99**, 3552.
[4] Panaxynol, isolated from the Araliaceae *Panax ginseng* C. A. Meyer also turned out to be identical with falcarinol as shown by M. Takahashi and M. Yoshikura, *J. Pharm. Soc. Japan*, 1966, **86**, 1053.
[5] F. Bohlmann and P. Herbst, *Chem. Ber.*, 1958, **91**, 1631.
[6] Sir Ewart R. H. Jones, S. Safe, and V. Thaller, *J. Chem. Soc.* (*C*), 1966, 1220.