Tetrahedron Letters No.47, pp. 4071-4074, 1970. Pergamon Press. Printed in Great Britain.

THE STRUCTURE AND CHEMICAL TRANSFORMATIONS OF XANTHOXIN

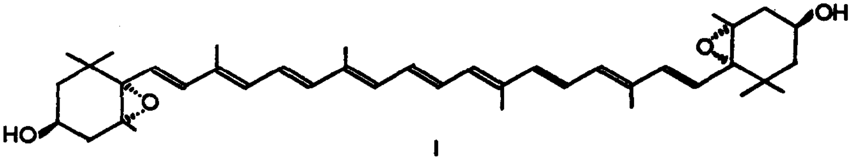
R.S. Burden and H.F. Taylor

A.R.C. Plant Growth Substance and Systemic Fungicide Unit

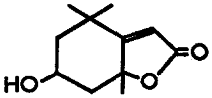
Wye College (University of London), Ashford, Kent

(Received in UK 7 September 1970; accepted for publication 10 September 1970)

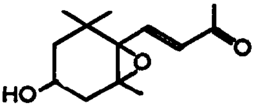
Photooxidation of violaxanthin (I) and related xanthophyll epoxides produces a number of substances one of which is highly inhibitory to the germination of seeds and the growth of plant tissues[1,2]. Compounds (II) and (III) were characterised as products of the photooxidation together with a potent growth inhibitor, now termed xanthoxin, for which the isomeric structures (IV) and (V) were tentatively suggested[3]. We now confirm that xanthoxin is a mixture of (IV) and (V) and report a chemical conversion to (+)-*trans*-abscisic



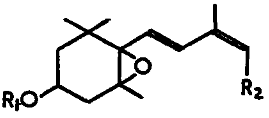
I

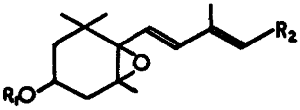


II



III





IV R_1 = H, R_2 = CHO

VI R_1 = CH_3CO, R_2 = CHO

IX R_1 = H, R_2 = CH_2OH

V R_1 = H, R_2 = CHO

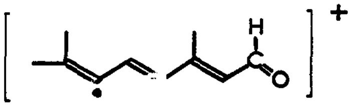
VII R_1 = CH_3CO, R_2 = CHO

X R_1 = H, R_2 = CH_2OH

acid (t-ABA) (XIV), a geometric isomer of the important plant growth inhibitor (+)-ABA (XIII).

In our early experiments the violaxanthin polyene chain was cleaved photolytically; more recently we have employed neutral zinc permanganate oxidation and obtained increased yields of xanthoxin. By this means the inhibitor was obtained as a t.l.c. homogeneous syrup which formed an orange 2,4-dinitrophenylhydrazone. Infra-red absorptions (in $CHCl_3$) were at 3420 cm^{-1} (hydroxyl) and at 1663, 1632 and 1600 cm^{-1} (conjugated dienal). The u.v. maximum (in MeOH) at 283 nm ($E^{1\%}_{1cm}$ = 720) was consistent with a βδ-disubstituted dienal chromophore. Aldol condensation with acetone on a spectral scale produced a new maximum at 320 nm.

Xanthoxin was readily acetylated to produce t.l.c. pure material of higher R_f with maxima 1725 and 1663 cm^{-1}. This could be resolved by g.l.c. into two components which gave almost identical mass spectra. In each case the molecular ion was present at $^m/e$ 292 with prominent fragment ions at $^m/e$ 263 (M - CHO) and at $^m/e$ 232 (M - CH_3CO_2H). The base peak at $^m/e$ 149 was attributed to the formation of the ion (VIII).



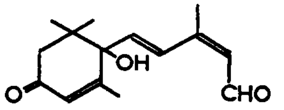
VIII

High resolution mass measurements confirmed these assignments.

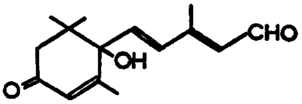
The close similarity of the two acetates suggested that the compounds were geometric isomers, probably (VI) and (VII). Support for this came from an examination of the sodium borohydride reduction product of xanthoxin which could be separated by t.l.c. into two diols with λmax 239 nm and 237 nm. From a comparison with model dienol chromophores[4], these were assigned the cis,trans (IX) and trans,trans (X) configuration respectively. Reoxidation with manganese dioxide gave (IV) and (V) with absorption maxima at 281.5 nm and 283.5 nm respectively. Exposure of a methanolic solution of either (IV) or (V) to sunlight led to the rapid formation of a 1 : 1 equilibrium mixture.

Chromium trioxide / pyridine treatment of the mixture of (IV) and (V) gave a new product with λmax 283 nm and 233 nm. It had νmax 3410 cm^{-1}

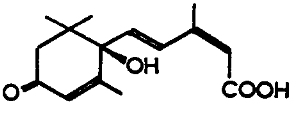
(hydroxyl) and 1665 cm^{-1} (unsaturated carbonyl) and was shown to be a mixture of abscisic aldehyde (XI) and trans-abscisic aldehyde (XII) by g.l.c. comparison with the authentic substances.



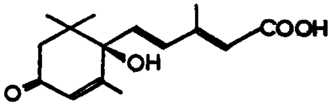
XI



XII

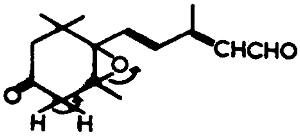


XIII



XIV

The formation of the abscisic aldehydes appears to involve oxidation of the ring hydroxyl followed by a base-catalysed β-elimination of the type indicated. An analogous process is the formation of isofucoxanthin from fucoxanthin[5].



Further oxidation of the mixture of (XI) and (XII) with alkaline silver oxide yielded trans-ABA (XIV). Little cis isomer was detected in the product as the 2,3-cis olefinic bond is isomerised under these conditions[6].

The formation of t-ABA from violaxanthin establishes an important stereochemical link between the two compounds. The absolute configurations of (+)-ABA and violaxanthin have been assigned by independent methods[7,8] as (XIII) and (I) respectively, and natural (+)-t-ABA, which has an almost identical O.R.D. curve, to (+)-ABA[9], is hence (XIV). The t-ABA produced from violaxanthin would be expected to be the enantiomer of this. However, its O.R.D. spectrum exhibited a well defined positive Cotton effect with extrema at 295 nm (ϕ+34000) and at 245 nm (ϕ-113000). It was hence identified as (+)-t-ABA.

This conversion indicates that the published absolute configurations of violaxanthin[8] and ABA[7] are at variance and that one of the proposed structures requires revision. Moreover, it raises the possibility that the xanthoxin isomers, which we have now shown to occur naturally[10], may be precursors of ABA and its trans isomer in plant tissues.

We thank Professor J.W. Cornforth, F.R.S. (Shell Research Laboratories, Sittingbourne, Kent) and Dr. P.G. Philpott (Hoffmann-La-Roche, Basel) for chemicals; and gratefully acknowledge the assistance of Dr. P.M. Scopes, Westfield College (O.R.D. measurements) and Mr. R. Self, Food Research Institute, Norwich (G.L.C. - Mass spectroscopy). Mr. R.P. Townsend is thanked for technical assistance and Professor R.L. Wain, F.R.S. for advice and encouragement.

References

[1] H.F. Taylor and T.A. Smith, Nature, 1967, 215, 1513.

[2] H.F. Taylor, Plant Growth Regulators, S.C.I. Monograph 31, p.22, 1968.

[3] H.F. Taylor and R.S. Burden, Phytochemistry, in the press.

[4] L. Crombie, S.H. Harper and R.J.D. Smith, J. Chem. Soc., 1957, 2754.

[5] J. Hora, T.P. Toube and B.C.L. Weedon, J. Chem. Soc.(C), 1970, 241.

[6] N.L. Wendler, H.L. Slates, N.R. Trenner and M. Tishler, J. Amer. Chem. Soc., 1951, 71, 719.

[7] J.W. Cornforth, W. Draber, B.V. Milborrow and G. Ryback, Chem. Communs., 1967, 114.

[8] L. Bartlett, W. Klyne, W.P. Mose, P.M. Scopes, G. Galasko, A.K. Mallams, B.C.L. Weedon, J. Szabolos and G. Toth, J. Chem. Soc.(C), 1969, 2527.

[9] B,V. Milborrow, J. exp. Bot., 1970, 21, 17.

[10] H.F. Taylor and R.S. Burden, Nature, 1970, 227, 302.