Biosynthesis of Dioscorine

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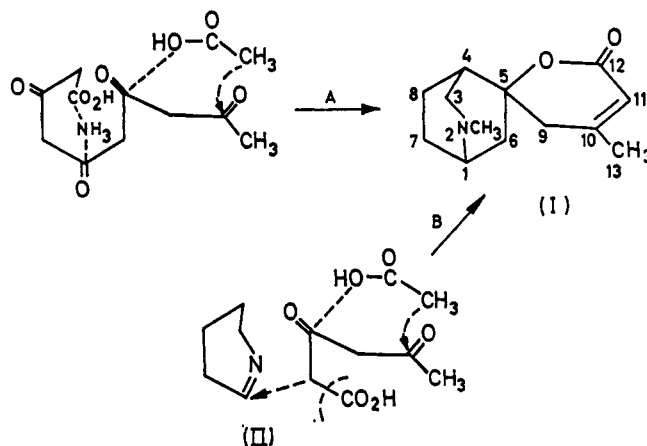(Department of Chemistry, Clemson University, Clemson, South Carolina 29631)

Summary The administration of [1-^{14}C]acetate to Dioscorea hispida plants resulted in the formation of radioactive dioscorine (0·2% incorporation), the pattern of labelling being consistent with the hypothesis that this alkaloid is formed from four acetate units and a piperidine moiety which may be derived from lysine.

DIOSCORINE (I) is the major alkaloid of the tropical yam, Dioscorea hispida, Dennstedt, and its structure has been established by extensive degradations[1] and synthesis.[2] It was suggested[3] that this alkaloid is derived from a branched polyacetyl chain formed from six acetate units as illustrated in the Scheme (Route A).

This hypothesis has been tested by spraying† the leaves of D. hispida plants with an aqueous solution of sodium [1-^{14}C]acetate (1 mCi, 41 mg). After 14 days the whole plants were extracted[4] yielding dioscorine (100 mg), purified as its picrate, having a specific activity of 1·01 × 10^7 d.p.m./mmole (0·2% incorporation). The radioactive dioscorine was degraded systematically in duplicate, and the following percentage distribution of activity determined: C-5 (30 ± 1), C-10 (29 ± 2), C-11 (<1), C-12 (28 ± 1), and C-13 (0·2). The carbons of the isoquinuclidine nucleus, excepting C-5, contained less than 6% of the total activity of the alkaloid.

It was thus established that approximately one third of the activity of the alkaloid was located on carbons 5, 10, and 12, a result which is not consistent with our hypothesis,[3]

which would require one sixth of the activity at each of these carbons. We therefore now suggest that dioscorine is formed from a branched 8-carbon unit, derived from four acetate units, and a piperidine moiety such as (II), which could be derived from lysine (Route B).

SCHEME

† The administration of sodium [1-^{14}C]acetate to the stems of the plant by the wick feeding method, or by direct injection into the tubers (where the alkaloid is found) failed to yield radioactive dioscorine.

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Electron-diffraction Investigation of the Molecular Structures of Adamantane

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Summary Assuming T_d–$\bar{4}3m$ symmetry adamantane is found by electron diffraction to have essentially tetrahedral bond angles; the C–C bond length is 1·540(2) Å and the C–H bond length 1·112(4) Å.

ADAMANTANE is of considerable theoretical interest because of the similarity of its carbon skeleton to the atomic arrangement of diamond. We have reinvestigated its structure in the gas phase by electron diffraction and have

obtained results in excellent agreement with those from the earlier study[1] but considerably more precise. In addition, mean amplitudes of vibration of the more important atomic pairs have been evaluated.

The structure was refined by least-squares based upon intensity curves[2] assuming T_d–$\overline{4}3m$ symmetry and equal lengths for the two types of C–H bonds. The phases and scattering amplitudes were taken from ref. 3. The results of the refinement lead us to select the following values of the principal distances, amplitudes of vibration, and bond angles as a fair representation of the structure (distances and amplitudes in Å, angles are in degrees; 2σ values are given in parentheses including estimates of systematic error; subscripts denote secondary and tertiary atoms):

r(C–H) = 1·112 (0·004), r(C–C) = 1·540 (0·002), $\angle C_tC_sC_t$ = 108·8 (1·0), $\angle C_sC_tC_s$ = 109·8 (0·5), $\angle$HCH = 116·9 (6·0), l(C–H) = 0·061 (0·004), l(C–C) = 0·052 (0·002), $l(C_s\cdot C_s)$ = 0·066 (0·006), and $l(C_t\cdot C_t)$ = 0·078 (0·018). The carbon–carbon distance is felt to be especially well determined because it was found to be independent of starting model and refinement conditions. The skeletal bond angle values were found to be strongly correlated both with each other and with the amplitudes associated with distances $C_s\cdot C_s$ and $C_t\cdot C_t$, so that the difference between them is probably insignificant.

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