INTERCONVERSION OF ARYLPROPANOIDS IN THE ESSENTIAL OIL OF *CROTON AFF. ZEHNTNERI*

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There are several types of plants that have essential oils which contain arylpropanoids as major constituents. Well known examples are species in the Lauraceae (e.g. *Cinnamomum zeylanicum*), Myrtaceae (e.g. *Pseudocaryophillus jaccoudii*), and Umbelliferae (e.g. *Foeniculum vulgare*) families (1–3). The simultaneous occurrence of allyl and propenylbenzenes is known but constitutes an exception rather than the general rule. These observations are relevant because there is agreement among investigators that cinnamic acid is the precursor of arylpropanoids. However, they are divided on the manner of biosynthetic formation of the structural entities, allyl and propenylbenzenes (4–7). Two independent routes are usually accepted, although direct conversion of the allyl to the propenyl group was postulated to occur in plants which have the necessary isomerase (3). The unusual co-occurrence of allyl and propenyl benzenes in the essential oil of *C. aff. zehntneri* (Euphorbiaceae) (8) prompted us to analyze the effect of light and storage time on the volatile constituents of this species and, therefore, perhaps to shed further light on this problem.

MATERIAL AND METHODS

Experiments *in planta* (on ground plant material) were done with bark of one specimen of *C. aff. zehntneri* which was collected

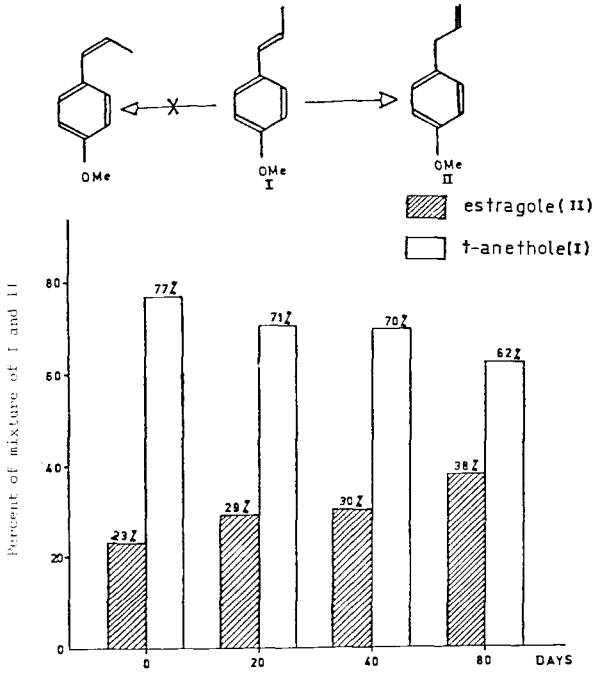

FIG. 1. Light induced modification in the essential oil *in planta*.

in the state of Ceará in Brazil. The *in vitro* experiment was carried out on the essential oil isolated from the same material.

Samples of finely ground dried bark were exposed to sunlight in transparent plastic bags. Aliquots (100 g) withdrawn after 20, 40 and 80 days of sunlight exposure were steam distilled and analyzed by gc/ms. Identifications were done by ms and comparison with authentic samples. Fig. 1 presents the variation of arylpropanoids *in planta* after 80 days of sunlight exposure.

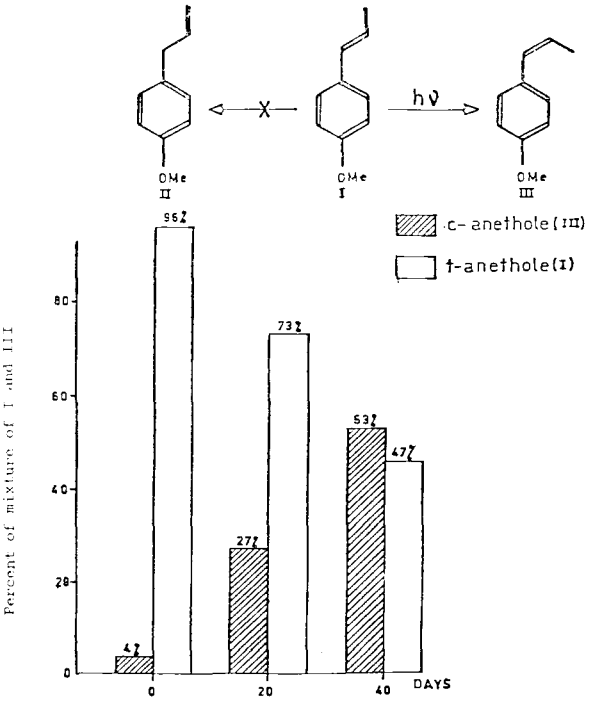

FIG. 2. Light induced modification in the essential oil *in vitro*.

Similar results were obtained with *in planta* material kept protected from sunlight in the same period of time. Simultaneously, a sample of essential oil (2 ml) was sealed in a transparent pyrex glass vial and exposed to sunlight. Gc/ms was performed after 10, 20 and 40 days; fig. 2 presents the transformations occurring in this *in vitro* experiment. Pure *trans*-anethole as well as estragole were submitted to the same conditions used for the isolated essential oil. In the first case, there was isomerization to *cis*-anethole, whereas no transformation was detected with estragole after 40 days of sunlight.

RESULTS AND DISCUSSION

While *in vitro* experiments produced the normal light-induced transformation of *trans* to *cis*-anethole, in the *in planta* experiments there was no formation of *cis*-anethole. Instead an interconversion of anethole to estragole was observed, and it was independent of light. The first of these observations is crucial to the essential oil industry. Since *cis*-anethole is highly toxic (9), it is important to keep the oil protected from light after extraction to prevent conversion to *cis*. The second fact indicates that anethole isomerization does not occur *in planta*, and the unexpected interconversion of *trans*-anethole to estragole gives some support to the direct route for biosynthetic formation of allyl and propenylbenzenes in this species.

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