Chlorophyll b to Chlorophyll a Conversion Precedes Chlorophyll Degradation in *Hordeum vulgare* L.

Patrick Folly and Norbert Engel
University of Fribourg, Institute of Organic Chemistry
CH-1700 Fribourg, Switzerland

www.unifr.ch

Introduction

In 1985 the first chlorophyll (CH) catabolites were isolated from green plants, the Chlorophyta, Chlorella protothecoides, and the Spermatophyta, Hordeum vulgare. Their constitutional formulas revealed them to be closely related. Both are likely pigment-like linear 19-formylbilinones which result from an oxygenic cleavage of the chlorophyll macrocycle. CH b (2) occurs as an accessory pigment in the light harvesting systems of higher plants and green algae. The latter comprises up to 20% of the total CHs. While both CH a and CH b catabolites (3 and 5) are recorded as red pigments into the culture medium of the green algae, *C. protothecoides*, only the catabolites originating from CH a have been isolated so far from higher plants.

Chlorophyll degradation in presence of heavy water (Quantification)

Recently it has been convincingly demonstrated that in higher plants CH b is converted to CH a as a part of a CH a inter-conversion cycle which permits plants to adjust to changing light conditions. The aim of this investigation was to prove that in higher plants CH b is converted to CH a prior to degradation.

For this purpose de-greening of excised green primary leaves of barley (*Hordeum vulgare*) was induced by permanent darkness in the presence of heavy water (80 atom% D). The resulting CH a catabolite CH b present in the plant extract was subjected to chemical degradation by chromic acid. The key maleimide fragment, 3-(2-hydroxyethyl)-4-methyl-maleimide (B) that originated from the CH catabolite was isolated. High resolution 1H, 13C-NMR and mass spectrometry unequivocally demonstrated that a fraction of the maleimide fragment consisted of a non-deuterated methyl group.

Experimental

Green leaves

H. vulgare (barley)

Bleaching using D2O

Yellow leaves

Filtrate

Chemical degradation

Maleimide mixture

Silica gel chromatography

Conclusions

1) CH b is converted into CH a prior to degradation.

2) Quantification of the degradation process showed that the initial ratio of CH a : CH b in the green plant was preserved to about 65:35 in the catabolite composition isolated from yellowing leaves.

3) The incorporation of only one deuterium atom indicates the involvement of two distinguishable redox enzymes during the conversion.

4) Of the three maleimide fragments 6, 7 and 8 isolated from the degradation mixture, only the CH b

Mechanical suggestion

References and acknowledgements


We thank the Swiss National Science Foundation and the Stipendienfonds der Basler Chemischen Industrie.