

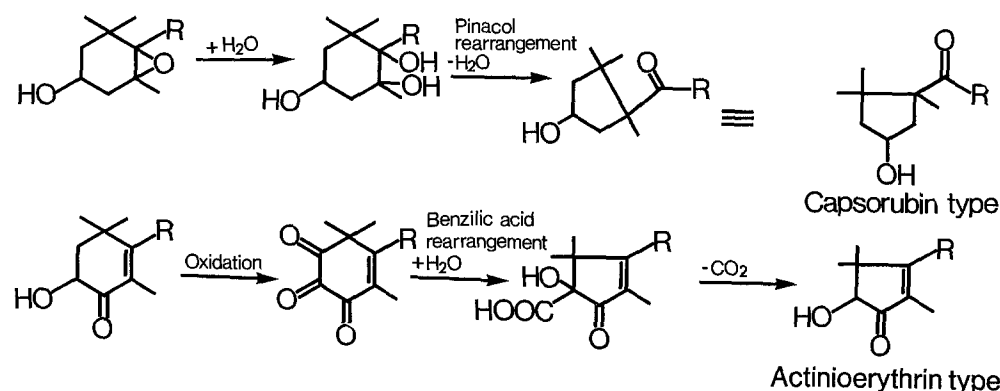


Fig. 20. Postulated biosynthesis of 5-ring type carotenoid end groups^{52,55}.

Concerning the formation of carotenoids with 5-ring end groups, KARRER⁵⁵ assumed that in the case of the capsorubin end group a pinacol rearrangement of an intermediary α -glycol was responsible for the *in vivo* synthesis from violaxanthin (Figure 20). We suspect that actinoerythrin is formed *in vivo* from a hypothetical 6-ring triketone by ring contraction (benzilic acid rearrangement) and subsequent decarboxylation. Small amounts of astaxanthin diesters occur together with actinoerythrin in *A. equina*⁵².

The last example is typical. So many of the present problems in carotenoid chemistry are somehow linked to PAUL KARRER's work. Every carotenoid chemist has the greatest respect and admiration for his contribution to a field that is continuing to develop on a solid fundament of his work.

Zusammenfassung. Nach einleitender kurzer Würdigung der Höhepunkte der KARRER'schen Carotinoid-

Forschung wird zunächst ein knapper Überblick über den gegenwärtigen Stand der Carotinoid-Forschung gegeben. Die jetzige Kenntnis von Biosynthese und Funktion der Carotinoid-Pigmente wird kurz und die organisch-chemischen Aspekte werden etwas ausführlicher erläutert, und zwar Strukturaufklärung einschliesslich neuer Trennmethoden, unentbehrliche spektroskopische Methoden und neue Reaktionen zur Herstellung von Derivaten sowie schliesslich die Totalsynthese.

Anschliessend werden einige ausgewählte Beispiele der Nachlese KARRER'scher Beiträge behandelt, nämlich Probleme, die von KARRER aufgegriffen wurden oder auf andere Weise mit KARRER's Arbeit verbunden sind und später im Laboratorium der Autorin weiter verfolgt wurden. Beispiele von Carotinoiden aus photosynthetischen Bakterien, C₅₀-Carotinoiden, glycosidischen Carotinoiden und Nor-carotinoiden mit Ringverengung werden diskutiert.

SPECIALIA

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Shock Effects on Plants: Oxygen Evolution of Elodea

A fast-rising pressure pulse, produced as an air blast in a shock tube, inhibited photosynthesis in *Elodea* 27% after a 20 ψ (pounds per square inch) exposure, 44% after a 40 ψ exposure, and 74% after a 50 ψ exposure (1.21, 2.81, and 3.02 kg/cm² respectively).

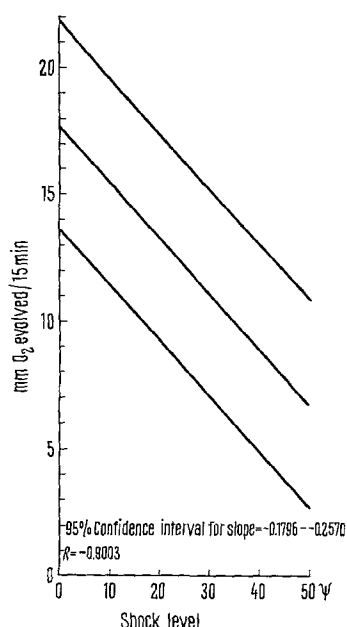
The present work stems from an interest in the possibilities for using plants as experimental bio-indicators of underground shock¹⁻³. The shock used, defined as a fast-rising pressure pulse of air lasting several seconds, was produced by specially built shock tubes³. Since the efficiency of photosynthesis is a good indicator of the oxygen concentration in the immediate atmosphere of

the plants^{4,5}, oxygen evolution in *Elodea* was measured for 3 shock levels, namely 20, 40 and 50 pounds per square inch (ψ ; 1.21, 2.41 and 3.02 kg/cm² respectively).

Materials and methods. An air loader, previously described⁶, was used for developing air blasts. The pressure duration for each shock level was approximately 4 sec. Photosynthetic rates were estimated by means of an Audus microburette which measured the amount of oxygen that was produced⁷. Healthy, green, unfractured plants of *Elodea* were used for both control and test plants. Plants that were fractured by the shock stimulus were discarded. The plants to be shocked were wrapped

in a single layer of wet cheesecloth and carefully placed in a loose circle following the inner circumference of the test chamber of the shock tube in order to reduce fracturing of the plants during their brief exposure to shock. Plants fractured readily at the 50 ψ shock level, thus limiting the number of plants that were studied at this shock level. The plants, which displaced from 4–6 ml of water, were cut from their stem bases to a length of 7 inches, and were placed in a weak nutrient solution that contained 0.5% sodium bicarbonate. The intensity of light from an incandescent source was saturating (150–190 ft-c), and the temperature was maintained at 21.5–22 °C.

Results and discussion. Shock inhibited oxygen evolution in *Elodea* 27% after a 20 ψ exposure, 44% after 40 ψ , and 74% after 50 ψ . The inhibitory effect of shock measured in plants shocked at 40 ψ persisted for at least 5 h after shock. This finding is in contrast to those for photosynthetic response under prolonged partial pressures, which is known to be rapidly produced and completely reversible when the plant is restored to ambient atmospheric conditions⁸.



Regression of oxygen evolution on shock level showing the 95% confidence belts.

The results of the multiple regression analysis, shown in the Figure, indicate that oxygen evolution was significantly reduced by shock treatment, and that the inhibitory effect of shock on photosynthetic response is apparently graded and more pronounced at higher shock levels. The large correlation coefficient (R) indicates a strong relationship between shock and photosynthetic response and suggests that measurements of this response could be used for detecting underground explosions if the explosions produced a significant air pressure wave. Accordingly, assays of samples from an appropriately designed grid could serve to locate the epicenter at the explosion and also provide estimates of the magnitude of the pressure source⁹.

Résumé. Une augmentation rapide de la pression, produit comme une rafale d'air dans un tube de choc réduit chez *Elodea* la photosynthèse à 27% après une exposition de 20 ψ , à 44% après une exposition de 40 ψ , et à 74% après une exposition de 50 ψ (1,21, 2,41, et 3,02 kg/cm² respectivement).

SYLVIA A. MURRAY

1522 Willow Street, Alameda (California 94501, USA),
12 January 1970.

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- ⁹ Acknowledgements. This study has been conducted under the direction of Professor CURTIS L. NEWCOMBE, Director of the Frederic Burk Foundation Research Center, San Francisco State College and supported by the U.S. Department of the Interior, Geological Survey, under Contract No. 14-08-0001-10926. Thanks are also expressed to Dr. HANSFORD T. SHACKLETTE of the Geological for making this study possible and for his helpful suggestions.

Desazetylierung von Cardenoliden mit der Zinkazetatmethode¹

Die Verwendung von Zinkazetat zur Desazetylierung von Lignanglukosiden wurde von KUHN und v. WARTBURG² beschrieben. Die Autoren erwähnten dabei, dass sich Digitoxin-tetraacetat und Proscillaridin A-triacetat ebenfalls auf diese Weise entazetylieren liessen. Nachfolgend wird über die Anwendung der Methode bei azetylierten Cardenoliden berichtet, die sich mit den gebräuchlichen alkalischen Reagenzien (KHCO₃, NaOH, Bariummethylat) nur mit ziemlich unbefriedigenden Resultaten desazetylieren lassen. (Unvollständige Verseifung, sehr langsame Reaktion, Bildung von Isoverbindungen, Verharzungen.)

Als Beispiele seien hier folgende Desazetylierungen angeführt:

1. Digitalinum verum-hexaacetat (I) → Digitalinum verum (II)
2. Lanatosid B → Desacetyl-lanatosid B (= Purpureaglykosid B)
3. k-Strophanthosid-heptaacetat → k-Strophanthosid

¹ 56. Mitteilung über Herzglykoside. 55. Mitt. s. *Helv. chim. Acta* 51, 1317 (1968).

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