

l'ATP est maximum lorsque le rapport $\mu\text{moles MgCl}_2/\mu\text{moles ATP}$ est égal à 1/3. Par ailleurs, la vitesse d'hydrolyse du pyrophosphate devient également maximum lorsque le rapport $\mu\text{moles MgCl}_2/\mu\text{moles PP}$ est égal à 1/3, mais elle reste maximum lorsque la valeur de ce rapport augmente.

Tab. II. Influence du PCMB sur l'hydrolyse de l'ATP et du pyrophosphate

Exp.	Contenu en chlorophylle des chloroplastes mg	PCMB $\times 10^{-4} M$	Glutathion $\times 10^{-4} M$	P_i libéré à partir d'ATP μmole	P_i libéré à partir de pyrophosphate μmole
1	3,5	0	—	0,82	0,62
		1	—	0,44	0,60
		10	—	0,15	0,61
2	3,2	0	0	0,68	
		5	0	0,18	
		5	10	0,53	

Conditions: voir Matériel et méthodes. – Expérience 1: Volume total 600 μl , Incubation 18 min à 30°. Expérience 2: Volume total 500 μl , Incubation 16 min à 30°.

Tab. III. Effet du «vieillessement» des chloroplastes sur l'hydrolyse de l'ATP et du pyrophosphate

Temps de «vieillessement» à 30° min	P_i libéré à partir d'ATP μmole	P_i libéré à partir de pyrophosphate μmole
0	0,66	0,44
30	0,43	0,49
120	0,35	0,41

Conditions: voir Matériel et méthodes. – Contenu en chlorophylle des chloroplastes 3,3 mg. Volume total 400 μl . Incubation 15 min à 30°.

Über die Herkunft der Isovaleriansäure im Magnamycin¹

Im Magnamycin² ist die 4-Hydroxylgruppe der Mycarose mit Isovaleriansäure (I) verestert. Auch in den Antimycinen kommt I als Esterkomponente vor³. Wie unsere früheren Untersuchungen zur Biogenese des Magnamycins zeigten, werden Acetat, Propionat und *d*-Glucose nicht in die Isovaleriansäure eingebaut⁴. Es war daher zu vermuten, dass I durch Abbau des Leucins gebildet wird⁵. Um dies zu prüfen, wurde einem normalen Fermentationsansatz⁶ (250 ccm) von *S. halstedii* L-Leucin-[U-¹⁴C] (5 μC = 0,11 mg, Radiochemical Centre Amersham) zugesetzt und nach 2 Tagen das nach Trägerzusatz (200 mg) isolierte Magnamycin bis zur konstanten spezifischen Aktivität gereinigt (Einbaurate 0,16%) und abgebaut⁴. Die Aktivitätsverteilung zeigt Tabelle I.

Beim direkten Übergang von L-Leucin-[U-¹⁴C] in Isovaleriansäure sollte man auch in der Säure eine Gleichverteilung der Aktivität erwarten. Dies ist der Fall, wie sich durch Kuhn-Roth Oxydation von I zeigen lässt (Tabelle II)⁷.

Effet du PCMB: Le PCMB inhibe l'hydrolyse de l'ATP, mais non celle du pyrophosphate. L'activité ATPasique inhibée par le PCMB est régénérée par le glutathion (Tableau II).

Effet du «vieillessement» des chloroplastes: Après «vieillessement» des chloroplastes (séjour de la suspension de chloroplastes à 30° en absence de substrat), l'hydrolyse de l'ATP est notablement ralentie tandis que celle du pyrophosphate n'est pas modifiée (Tableau III).

L'ensemble de ces résultats permet de différencier dans les chloroplastes de feuilles d'épinards l'activité de l'ATPase de celle de la pyrophosphatase et indique qu'à pH 7,6 l'hydrolyse de l'ATP est due probablement en grande partie à une ATPase spécifique. Cette ATPase sensible aux ions Mg^{2+} et mise en évidence dans les chloroplastes maintenus à l'obscurité est insensible à des effecteurs positifs de la photophosphorylation: FMN, PMS, vit. K_3 ; elle semble donc différente de l'ATPase stimulée par la lumière, par le PMS ou le FMN^{11,12}. Ses relations avec le système plurienzymatique qui catalyse la photophosphorylation restent à préciser.

Summary. ATP hydrolysis and inorganic pyrophosphate hydrolysis in chloroplasts of spinach leaves are characterized by a different pH optimum, a different sensitivity to magnesium ions, to *p*-chloromercuribenzoate and to ageing. It is concluded that ATP and inorganic pyrophosphate are likely hydrolyzed by two different enzymes in chloroplasts.

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Tab. I. Aktivitätsverteilung im Magnamycin mit L-Leucin-[U-¹⁴C] als Vorstufe. Messungen im Proportionalzählrohr mit Antikoinzidenzanlage. Messfehler $\pm 2\%$

	ipm/mMol	% Aktivität
Magnamycin	6080	100
Carimbose	820	14
Mycarose	470	8
Isovaleriansäure ^a	4740	79

^a als *p*-Bromphenacyl ester.

¹ IX. Mitt. Zur Biogenese der Makrolide. VIII. Mitt. W. HOFHEINZ, H. GRISEBACH und H. FRIEBOLIN, Tetrahedron, im Druck.

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⁷ Die Arbeit wurde durch die Deutsche Forschungsgemeinschaft und den Fonds der Chemischen Industrie unterstützt.

Tab. II. Kuhn-Roth-Abbau der Isovaleriansäure. Messfehler $\pm 2\%$

	ipm/mMol	% Aktivität gefunden	erwartet
Isovaleriansäure	4740	100	
Essigsäure*	1810	38	40

* als *p*-Nitrobenzylester.

Flavonoid Sophorosides

Sophorose (glucosyl(1 $\rightarrow$ 2)- β -glucose) was first isolated¹ from the unripe pods of *Sophora japonica*, in which it occurs combined with kampferol as the 3-sophoroside. It was later found as the disaccharide unit of stevioside, a very sweet glycoside occurring in the leaves of *Stevia rebaudiana*². Its structure has been confirmed by at least two syntheses^{3,4} but no other reports of its natural occurrence have appeared⁵. Recent studies of the sugars attached to the anthocyanins and flavones isolated from many plant sources now show that sophorose is commonly associated in nature with these pigments.

In the anthocyanin series, five pigments containing sophorose have been found. They are the 3-sophorosides and the 5-glucoside 3-sophorosides of pelargonidin and cyanidin and the 7-glucoside 3-sophoroside of pelargonidin. One or other of these pigments has been identified in the following plants: *Brassica oleracea*, var. *rubra* (leaves), five species of *Papaver* (petals), *Phaseolus multiflorus* (flowers), *Raphanus sativus* (roots), *Tropaeolum majus* (petals) and three species of *Watsonia* (petals). The occurrence of cyanidin 3-sophoroside in *Papaver rhoeas* requires special mention, because this pigment (called mecocyanin) was originally thought to be the 3-gentiobioside⁶ and a preliminary reinvestigation⁷ suggested that it might be the 3-cellobioside. More detailed studies, involving electrophoretic and chromatographic comparison of its sugar with all the eight known glucosyl-glucoses, now show that it is the 3-sophoroside. It should also be mentioned that the cyanidin pigment occurring in acylated form in red cabbage, now identified as the 5-glucoside 3-sophoroside, was earlier reported to be a 3-triglucoside⁸. Sophorose was isolated from these pigments in excellent yield by oxidizing away the anthocyanidins to which it was attached with H_2O_2 , as first described by KARRER⁹ and later modified by CHANDLER and HARPER¹⁰. Details of structural studies on the anthocyanidin sophorosides will be described elsewhere¹¹.

In the flavone series, at least ten pigments containing sophorose are now known. Two of these, the 3-sophorosides of kampferol and quercetin, appear to occur widely. Thus, the kampferol and quercetin 3-diglucosides recently reported^{12,13} to occur in the petals of nineteen wild potato species have now been identified as the 3-sophorosides. Also, the 3-di- and 3-triglucoside, 7-rhamnosides of kampferol present in potato seeds yield sophorose on hydrolysis or on oxidation. Further, it is likely on genetic grounds¹⁴ that the 3-glucosylrhamnosyl-glucosides of kampferol and quercetin, occurring in potato flowers with the 3-sophorosides, contain a β 1 $\rightarrow$ 2 link; the trisaccharide attached to these two pigments may be formulated as glucosyl(1 $\rightarrow$ 2)- β -rhamnosyl-(1 $\rightarrow$ 6)- α -glucose. This formula takes into account the fact

Summary. *L*-Leucine is the precursor of the isovaleric acid in magnamycin, as could be demonstrated with *L*-Leucine-[U-¹⁴].

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that rutinose, a constituent of the trisaccharide, has recently been found to have an α - rather than a β -linkage¹⁴. Again, the quercetin 3-diglucoside 7-glucoside found at the same time^{12,13} in another solanaceous plant, the cultivated *Petunia*, is now shown to be the 3-sophoroside 7-glucoside. Independent confirmation of this conclusion is provided by BIRKOFER and KAISER¹⁵, who have just isolated this pigment, the corresponding kampferol derivative and the two related sophorosides from the same plant. Quercetin 3-sophoroside 7-glucoside also occurs (acylated with caffeic acid) in the flowers of *Helleborus foetidus* (fam. Ranunculaceae).

Kampferol and quercetin 3-sophorosides have also been detected in the leaves of *Pisum* (both wild and cultivated)¹⁶ and in the petals of most wild and garden roses. In the case of *Pisum*, it is clear that the 3-triglucosides, which accompany the 3-sophorosides and which occur in acylated form, contain one, if not two, β 1 $\rightarrow$ 2 linkages. These acylated triglucosides have been studied in some detail by other workers^{17,18} because of their inhibitory effect on indoleacetic acid oxidase. The kampferol and quercetin 'monoglucosides' reported to occur in the variety 'Alaska'¹⁸ must, from their R_f-values and from our own studies, be 3-sophorosides or 3-triglucosides. Another related pigment occurs characteristically in the field pea, *Pisum arvense*; it is an acylated kampferol 3-galactosylsophoroside. In *Rosa*, the 3-sophorosides have been detected in 14 out of 25 species examined; they occur here in association with the corresponding 3- and 4'-glucosides.

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