Die katalytischen Eigenschaften einiger Zucker in homogener Lösung

Die von uns in den letzten Jahren bearbeitete homogene Lösungskatalyse in Redoxsystemen hat mehrfach praktische Anwendung gefunden[1]. So konnten verschiedene Penicilline[2] als Redoxkatalysatoren geprüft und zu ihrer Unterscheidung eine Schnellmethode auf dieser Grundlage ausgearbeitet werden. Gute Dienste leisteten dabei bestimmte Promotorionen, die die peroxydatische Entfärbung einer Indigocarminlösung wirksam förderten. Letztere Testlösung gehört zu den empfindlichsten Substraten dieser Art und wurde auch diesmal zur Prüfung der katalytischen Eigenschaften einiger Zucker verwendet. Fe^{3+} erwies sich in Spurenmengen als ausgezeichneter Aktivator, während sich das sonst bevorzugte[3] Co^{2+} hier indifferent verhielt. Man versetzt 25 mg Zucker in 25 cm^3 Wasser bei 37° mit 1 cm^3 $Fe(NO_3)_3$-Lösung bestimmter Konzentration, sodann mit 25 cm^3 H_2O_2 (1,2prozentig) und schliesslich mit 10 cm^3 Indigocarminlösung (= 3,3 mg Farbstoff) und bestimmt nach gutem Durchmischen die Entfärbungszeit bei 37°.

Peroxydatische Indigocarminentfärbung bei 37° in Gegenwart einiger Zucker und bei Zusatz der nachstehenden Ionen. Angegeben ist die Entfärbungszeit in min

Zucker/ Metallion	Fe^{3+} 0,1 mg	Fe^{3+} 0,01 mg	Co^{2+} 1 mg	–
Glukose	4	19	26	27
Fruktose	–	16	–	48
Laktose	–	12	–	22
Maltose	–	11	–	32
Saccharose	–	14	–	23
–	40	520	570	580

Sämtliche untersuchten Hexosen sowie auch die betr. Bisaccharide sind gute peroxydatische Katalysatoren, deren Wirkung sogar noch durch 0,01 mg Fe^{3+} bedeutend verstärkt wird (siehe Tabelle). Die beste Wirkung zeigen Laktose und Saccharose, die verhältnismässig schwächste die Fruktose. Dass die Zucker tatsächlich Katalysatoren sind, wird daraus wahrscheinlich, dass man in derselben Versuchsprobe bei gleichbleibender Zuckermenge immer neue Portionen von Indigocarmin entfärben kann, wobei nicht die Masse des Katalysators, sondern die Zahl seiner aktiven Zentren dabei ausschlaggebend ist. Man wird daher annehmen dürfen, dass gewisse OH-Gruppen der Zucker als Wirkgruppen fungieren, an welchen nach Deformierung der H_2O_2-Molekel und Bildung von HO- und HO_2-Radikalen die katalytische Reaktion ausgetragen wird. Der Mechanismus wurde bereits in anderem Zusammenhang ausführlicher besprochen[4].

Summary. Different sugars catalyze the peroxydatic decoloration of indigocarmine. Trace amounts of Fe^{3+}-ions accelerate this reaction.

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The Occurrence of Arachidonic and Related Acids in Plants[1]

In contrast to the accepted view that arachidonic acid is restricted to animals and unicellular photosynthetic organisms, but does not occur in higher forms of plant life[2–4], we have found it as a constituent of the lipids of mosses and ferns at a significant percentage. Arachidonic acid is associated in these materials with other polyenoic acids which are characteristic for animal lipids. The discovery of this group of acids in plants warranted verification by detailed study.

Arachidonic acid was found in several ferns, including *Onoclea sensibilis*, *Osmunda claytoniana*, *Adiantum pedatum* and *Matteucia struthiopteris*, when the fatty esters were prepared from lipids of these materials and subjected to gas-liquid chromatography (GLC). Besides establishing the presence of arachidonate by GLC retention times[5], the identity as 5,8,11,14-eicosatetraenoate was verified for *Adiantum p.* after collecting 5 mg of the substance from the pertinent peak of GLC. The ester was subjected to hydrogenation-GLC which verified the predicted chain length and to ozonization-hydrogenation-GLC which established the expected end fragments of the unsaturated ester.

The fatty acids of several individual mosses contained between 10% and 35% arachidonic acid. For a larger scale preparation, about 1 kg of mixed mosses consisting mainly of *Brachythecium* and *Mnium* were harvested,

[1] This work has been supported by a research grant from the National Institutes of Health (USPHS AM-05165) and by The Hormel Foundation.
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Fatty acids of mosses

Component[a]	*Polytrichum juniperinum*	*Hedwigia ciliata*	*Hylocomium splendens*	*Sphagnum*	*Brachythecium* + *Mnium*		
					Analysis	Isolated	Structure[b]
	%	%	%	%	%	mg	
C14	5.8	1.4	0.6	1.1	0.1		
C16	9.9	10.0	9.3	14.5	12.1	120	
C16:1	1.2	1.1	1.4	7.8	2.5	30	8% Δ7 31% Δ7 61% Δ11
C16:3	–	–	–	3.1	2.6	2	Δ7, 10, 13
C18	2.0	2.1	2.4	1.9	tr		
C18:1	7.5	9.6	8.5	11.8	2.8	28	65% Δ9 35% Δ11
C18:2	11.6	15.0	17.9	16.2	14.4	92	Δ9, 12
C18:3	12.9	24.4	20.6	31.4	14.7	88	3% Δ6, 9, 12 97% Δ9, 12, 15
C18:4	–	tr.	–	–	tr.	2	Δ6, 9, 12, 15
C20	9.9	2.4	1.0	tr.	0.3		
C20:1	–	–	–	tr.	0.3		
C20:2	–	–	–	–	tr.		
C20:3	–	tr.	–	tr.	tr.	10	78% Δ 8, 11, 14 22% Δ11, 14, 17
C20:4	9.3	14.9	13.2	9.6	33.8	175	Δ5, 8, 11, 14
C20:5	–	–	10.2	–	5.6	36	Δ5, 8, 11, 14, 17
C22	16.2	9.7	4.1	2.1	1.7		
C24	13.4	8.3	5.0	–	2.3		

[a] Small amounts of saturated and unsaturated short and odd-numbered chain acids have been found but are not listed. [b] The data refer to esters isolated from mixed mosses as described in the text.

washed free of soil and extracted with $CHCl_3$-MeOH in a Waring Blendor. The lipids were saponified by refluxing under N_2 for several hours with KOH in aqueous ethanol. After removal of the unsaponifiables, the fatty acids were esterified with diazomethane and freed from polar pigments on a silicic acid column. The yield of purified esters was 1.3 g. Liquid-liquid chromatography[6] followed by GLC[7] afforded separation of this material and yielded sufficient individual esters or isomeric mixtures for further expansion of the analytical data. Chain lengths and number of double bonds were indicated by retention times in the chromatographic separations. The chain lengths were verified with the isolated esters by hydrogenation-GLC; the unsaturation of eicosapentaenoate, eicosatetraenoate and octadecatrienoate was ascertained by ultraviolet absorption after alkaline isomerization[8]. UV-spectra before isomerization showed less than 5% conjugation in C20:5 and no conjugation in the other esters. Infrared spectra indicated 15% and less than 5% *trans* double bond in the respective esters. Double bonds other than *cis* and methylene-interrupted are not prominent and may rather be artefacts. The position of double bonds in all isolated esters was determined by ozonization-hydrogenation-GLC which identified both the aldehyde and aldehyde ester fragments. The Table lists the composition of fatty esters from individual mosses, together with the results of the preparative separation and the structures.

Analyses of numerous other plants, particularly the green parts, from several botanical divisions did not reveal the presence of arachidonic acid. Mosses and ferns are rather unique in having this acid as a major component.

Tetraenoic and other polyunsaturated C_{20} acids have been found in Ginkgo[9] and have also been detected in other plants in our search for arachidonic acid. They have a Δ^5 double bond, but the rest of the unsaturated system is set apart from it by more than one methylene group. Acids of the same type have been studied from several botanical sources[10–12]. Since the isolated double bond is never found in position 7, it appears that chain elongation is precluded once Δ^5 has been introduced. Similarly, elongation products of the Δ^5 acids (arachidonic and C20:5) in mosses and ferns have not been found. This is in contrast to the conversions of arachidonic acid which are characteristic for animals[13].

Zusammenfassung. Im Gegensatz zu der allgemeinen Auffassung, dass Arachidonsäure nur in Tieren und den niedrigsten Formen des Pflanzenreiches vorkomme, konnte diese Säure in mehreren Arten Farn und Moos nachgewiesen und identifiziert werden. Die relative Menge der Arachidonsäure beträgt in den bisherigen Beispielen zwischen 10 und 35% der Fettsäurekomponenten.

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