therefore logical to assume that in this snail the pattern of enzyme production changes on ageing. Whether this affects the food preference, or whether it is only a part of the entire physiological process, leading to a change in feeding habita, is still an unsolved problem.

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Department of Zoology and Entomology, University of Hawaii (U.S.A.), September 16, 1959.

Zusammenfassung

Junge Individuen von *Achatina fulica* Bowdich fressen mit Vorliebe Pflanzenteile, ältere Individuen sind omnivor. Die Enzymaktivitäten der grossen Mitteldarmdrüse wurden untersucht: bei jungen Tieren wird etwas mehr Amylase als bei älteren Individuen, bei älteren Tieren deutlich mehr Protease als bei jüngeren Individuen produziert. Zwischen Enzymproduktion und Futterwahl besteht also eine Korrelation, doch ist ihre kausale Beziehung noch nicht geklärt.

Alkaloid Studies XXIII[1]

Isolation of Four New Aspidosperma Alkaloids: Cylindrocarpine, Refractine, Pyrifoline, and Pyrifolidine

The recent interest[2] in alkaloids of the genus *Aspidosperma* prompts us to record in preliminary form some of the results of a systematic survey of Brazilian *Aspidosperma* species which is now in progress in our laboratories.

Our results with *A. olivaceum* Muell.-Arg. do not differ from those already published recently[3], while the only

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[1] Paper XXII, J. S. E. Holker, M. Cais, F. A. Hochstein and C. Djerassi, J. org. Chem. *24*, 314 (1959).

[2] For leading references see: J. Schmutz and H. Lehner, Helv. chim. Acta *42*, 874 (1959). – P. C. Ferreira, G. B. Marini-Bettolo, and J. Schmutz, Exper. *15*, 179 (1959). – M. A. Ondetti and V. Deulofeu, Tetrahedron Letters No. 7, 1 (1959).

[3] J. Schmutz and F. Hunziker, Pharm. Acta Helv. *33*, 341 (1958).

Table

	Cylindrocarpine		Refractine		Pyrifoline		Pyrifolidine		
Formula	$C_{29}H_{32}N_2O_4$		$C_{22}H_{26}N_2O_4$		$C_{23}H_{30}N_2O_3$		$C_{22}H_{30}N_2O_3$	$C_{23}H_{32}N_2O_3$	
Analysis	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Calc.	Found
C	73·70	73·72	69·09	69·34	72·22	72·24	71·32	71·84	71·70
H	6·83	6·86	6·85	6·88	7·91	7·91	8·16	8·39	8·27
N	5,93	5·73	7·32	7·33	7·32	7·43	7·56	7·29	7·50
O	13·54	13·77	—	—	12·55	12·64	12·96	12·48	12·79
2 OCH_3	13·13	13·06	16·23	16·16	16·25	16·07	16·76	16·14	16·77
N-acetyl	—	—	11·25	11·65	11·25	11·15	11·62	11·20	11·25
Mol-weight [a]	—	—	382·5	378	382·5	373	370·5	384·5	374
M. p.	168–169° C		157·5–159° C		141·5–143·5° C		147·5–150° C		
[α][b]	–181°		–23·5°		+102°		+90°		
pKa[c]	5·9		6·64		6·40		6·85		
Ultraviolett absorption spectrum[d]	λmax mμ	log ε	λmax mμ	log ε	λmax mμ	log ε	λmax mμ		log ε
	216 248 285	4·53 4·05 4·31	216 260 286–289 inflection	4·43 4·12 3·44–3·45	217 261 286–288 inflection	4·41 4·04 3·63	223 252 286		4·50 3·94 3·32
	λmin	log ε	λmin	log ε	λmin	log ε	λmin		log ε
	237 254	4·02 4·04	237	3·78	238	3·73	243 279		3·91 3·31
Infraredabsorption spectrum [e]	λmax μ		λmax μ		λmax μ		λmax μ		
	5·79 6·06 6·23		5·74 6·00 6·27		6·10 6·23 6·29		6·05 6·14		

[a] Perchloric acid titration; [b] All rotations in chloroform; [c] Potential titration in 66% dimethylformamide; [d] In ethanol; [e] In chloroform

pure alkaloid encountered by us in *A. pyricollum* Muell.-Arg. proved to be ulein[4], as demonstrated by direct comparison with a specimen kindly provided by Dr. J. Schmutz. The following three species yielded several new alkaloids, of which four have been isolated in pure form. The empirical formulas given below are consistent with the analytical data, but they should only be considered as tentative ($\pm CH_2$) until more extensive degradative work has been completed.

Aspidosperma cylindrocarpon Muell.-Arg. furnished *cylindrocarpine* (Table) after purification through the crystalline perchlorate and regeneration of the alkaloid. All oxygen functions are accounted for by a N-cinnamoyl-7-methoxy-dihydroindole grouping and one carbomethoxy function. Their presence was established by acid hydrolysis (yielding cinnamic acid), by hydrogenation to dihydrocylindrocarpine (yielding dihydrocinnamic acid), whose ultraviolet absorption spectrum was practically superimposable upon that of aspidospermine[5], and by alkaline hydrolysis of dihydrocylindrocarpine to the amino acid dihydrocylindrocarpic acid, which could be remethylated with diazomethane to dihydrocylindrocarpine.

Aspidosperma refractum Mart. extract gave after chromatography of the weakly basic fraction *refractine* (Table). The extreme similarity of the ultraviolet absorption spectrum with that of aspidospermine coupled with the N-acetylanalysis indicates the presence[5] of a N-acetyl-7-methoxy-dihydroindole moiety, while the infrared band at 5·74 μ, the methoxyl analysis and the saponification results show that the other two oxygen atoms form part of a carbomethoxy group.

Aspidosperma pyrifolium Mart. furnished the two alkaloids *pyrifoline* and *pyrifolidine* which were separated by fractional crystallization of the perchlorates from the non-phenolic alkaloid fraction. The analytical, spectral and infrared data of pyrifoline indicate the presence of a N-acetyl-7-methoxy-dihydroindole chromophore and of an aliphatically bound methoxyl function.

Work is now under way in our laboratories on the structure elucidation of these alkaloids as well as on the isolation of additional alkaloids from the above-mentioned *Aspidosperma* species.

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Zusammenfassung

Die Isolierung von vier neuen *Aspidosperma*-Alkaloiden ergab *Cylindrocarpin* (erstes N-Cinnamoyl-dihydroindolderivat) sowie *Refractin*, *Pyrifolin* und *Pyrifolidin* (alles N-Acetyl-dihydroindole), die alle vier eine Methoxylgruppe im Dihydroindolsystem besitzen.

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[4] J. Schmutz, F. Hunziker, and R. Hirt, Helv. chim. Acta *40*, 1189 (1957). – G. Büchi and E. W. Warnhoff, J. Am. Chem. Soc. *81*, 4433 (1959).

[5] The presence of a N-acetyl-7-methoxy-dihydroindole chromophore in aspidospermine was demonstrated by J. R. Chalmers, H. T. Openshaw, and G. F. Smith, J. chem. Soc. *1957*, 1115.

[6] Postdoctorate research fellow 1958–1959 (Wayne State University); 1959–1960 (Stanford University).

Triterpene Acids from *Commiphora glandulosa* Schinz[1]

The chemistry of the genus *Commiphora* Jacq. (= *Balsamodendron* Kunth), natural order Burseraceae, has not been extensively studied; earlier references are given by Wehmer[2]. Myrrh, usually obtained from *C. abyssinica* (Berg) Engl., *C. molmol* Engl. and *C. opobalsamum* (L.) Engl., has been found to consist of volatile oils, mostly mono- and sesquiterpenes, gums, and unidentified resins, but the presence of triterpenes has never been suggested[3], and it was therefore of interest to find that the resin of *C. glandulosa* Schinz[4], a tree growing in the arid parts of Southern Africa, is a rich source of triterpene acids, both free and combined as glycosides. From two samples of resin collected for us by Dr. I. B. Pole Evans at different times from the same tree, we found that the free acids were present in roughly the same proportions, but that the glycosides in one case yielded mainly 'aglycone E' and in the other 'aglyconec' (see below for nomenclature).

The resin of *C. glandulosa* is soluble in cold ether to an extent of about 50%. The free acids (about 25% of original resin) were isolated from the ethereal solution through the barium salts, then methylated with diazomethane, and the methyl esters separated on a column of neutral alumina (activity III, according to Brockmann[5]). Extraction of the residual resin with ether or methanol at reflux temperature yielded the crude crystalline glycosides (about 10% of original resin).

Five methyl esters could be separated by this method; these will be designated methyl commate A, B, C, D, E, following the order in which they were eluted, graded solvents from ether-chloroform (1:1) through chloroform to chloroform-methanol (9:1) being used. Esters A, B, and C were purified by recrystallization from methanol and E was recrystallized from chloroform. Ester D could not be freed from C using methanol as a solvent, but recrystallization from methylene chloride, in which C dissolves readily, gave an apparently homogeneous product.

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[1] We are indebted to Dr. H. Hürlimann for supplying the botanical information in this paper.

[2] C. Wehmer, *Die Pflanzenstoffe*, 2. Aufl., II (Jena 1931), p. 647.

[3] Triterpenes are well known from other genera of the order Burseraceae, e.g. *Canarium* (Elemi resin), *Boswellia* etc.

[4] *C. glandulosa* belongs to the group of *C. pyracanthoides* Engl. s. lat., as pointed out by J. P. M. Brenan, Kew Bull. *1953*, 104. This author regards *C. lugardae* N. E. Br., *C. seineri* Engl. and *C. berberidifolia* Engl. as synonyms of *C. glandulosa*. The species seems to be distributed over a wide area of Southern Africa, from Mozambique through the Rhodesias to Bechuanaland, Transvaal, and South-West Africa. – It is noteworthy that we found the resins of *C. roxburghii* (Stocks) Engl. (= *C. mukul*) and of *C. viminea* Burtt-Davy, a species still somewhat related to *C. pyracanthoides* (Brenan), to be completely devoid of triterpene acids both free and combined as glycosides.

[5] H. Brockmann and H. Schodder, Ber. dtsch. chem. Ges. *74*, 73 (1941).