Summary. After their biosynthesis alkaloids usually have no physiological and only in rare cases an ecological function. The advantage of the alkaloidal character, therefore, is very small or dubious. Thus, we occasionally find in the same genus species or races which are free of alkaloids beside others containing these compounds. Also microorganisms and animals can form alkaloids. In all cases they appear to be excretes or end- or by-products of the basic metabolism. Only in relatively rare cases, N-free substances, as e.g. steroids, are transformed by additional incorporation of ammonia (probably via glutamine) to alkaloids. Mostly alkaloids arise from proteinogenous amino acids which enter these compounds not only with the greater part of their C-skeleton, but also with their amino-N. Thus the quinolizidines are formed by only 2 or 3 molecules of lysine splitting off the carboxyl group and a part of the amino groups. In a similar way benzylisoquinolines are built up. For their formation additional methyl groups are added or used for a further ring-closure, and stable systems are produced by phenolic oxydations and couplings. While in the Papaveraceae 2 molecules of tyrosine or phenylalanine act as precursors, in the Amaryllidaceae 1 molecule of tyrosine and 1 molecule of phenylalanine are needed for alkaloidal synthesis. In a single plant we occasionally find reaction chains from simple to more and more complicated alkaloids, and the last members of such series may be already degradation products. Some rare reactions, as e.g. the transformation of thebaine to codeine and morphine, may even be performed by plant tissue devoid of alkaloid, which under natural conditions never practises this capacity. Certain enzymes of alkaloidal synthesis are probably quite widespread. The N-heterocyclic systems become complicated by the participation of additional N-free building stones. Among these, active isoprene and monoterpenes play a very important role. The tryptamine-monoterpene alkaloids are distinguished by an enormous variability. More than 500 different structures are known and in one species up to 50 of them have been found. Thus, nature works with simple building-stones, producing, however, a great variability which is observed occasionally very specifically in related plant groups and some time quite 'unsystematically' widespread, although in principle developed in a similar way.

SPECIALIA

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Synthesis of $Ca_3Y_2Ge_3O_{12}$

Calcium yttrium germanate has been synthesized in the past by dry solid state methods[1]. In the present work, it was also prepared by hydrothermal techniques.

Spectrographically pure starting materials ($CaCO_3$, Y_2O_3, and GeO_2) were mixed in appropriate proportions and fired in a cold-seal bomb at 850 °C and 15,000 ψ for

Observed and calculated interplanar spacings (d) of calcium yttrium germanate, $Ca_3Y_2Ge_3O_{12}$

hkl	d_{obs}	d_{calc}	I_{obs}	hkl	d_{obs}	d_{calc}	I_{obs}
211	5.28	5.23	7	664	1.363	1.365	13
220	4.55	4.53	10	10.4.0	1.1880	1.1888	16
321	3.43	3.42	10	10.4.2	1.1666	1.1688	17
400	3.21	3.20	73	880	1.1299	1.1317	11
420	2.86	2.86	90	12.0.0	1.0659	1.0670	6
332	2.73	2.73	20	12.2.0	1.0511	1.0525	3
422	2.61	2.61	100	11.5.2	1.0466	1.0455	17
510	2.50	2.51	7	12.6.0	0.9542	0.9544	6
611	2.06	2.08	1	12.6.2	0.9433	0.9439	7
620	2.02	2.02	14	888	0.9244	0.9240	2
631	1.883	1.888	2	14.1.1	0.9100	0.9099	<1
444	1.844	1.848	5	14.2.0	0.9052	0.9054	1
640	1.773	1.776	41	12.8.0	0.8877	0.8878	4
642	1.708	1.711	91	14.4.0	0.8795	0.8794	6
732	1.622	1.626	3	14.4.2	0.8708	0.8712	28
800	1.598	1.601	21	12.10.0	0.8197	0.8197	8
822	1.507	1.509	1	14.6.4	0.8129	0.8131	16
752	1.444	1.450	<1	15.5.2	0.8034	0.8034	<1
840	1.430	1.432	13	16.0.0	0.8003	0.8003	2
842	1.393	1.397	21	16.2.2	0.7881	0.7881	1
921	1.378	1.381	2	16.4.0	0.7764	0.7764	30

several days. It was found that a single phase, well-crystallized material was produced using this technique, whereas some unreacted material was present in the dry fired materials.

$Ca_3Y_2Ge_3O_{12}$ has the garnet structure. The X-ray diffraction powder pattern is given in the Table. The cell size, determined from this pattern is 12.804 ± 0.002 Å. The index of refraction is 1.805 ± 0.003[2].

Zusammenfassung. $Ca_3Y_2Ge_3O_{12}$ wurde in chemisch homogener Form auf hydrothermalem Weg hergestellt. Es besitzt eine Garnet-Struktur mit dem Gitterparameter $a_o = 12{,}804$ Å.

THELMA ISAACS

Westinghouse Research Laboratories, Pittsburgh (Pennsylvania 15235, USA), 4 November 1968.

[1] B. V. MILL, Soviet Phys. Dokl. *10*, 1015 (1966).

[2] Appreciation is expressed to G. HARKNESS for her help in the synthesis of this compound.

Sur la pyrolyse d'α-acétoxy cétones. Pyrolyse du tétraacétyl-7,12,15,32 nor-16 glaucanol

Dans le cadre de l'étude des substances amères des Simarubacées, nous nous sommes proposés de réaliser une corrélation expérimentale entre les constituants caractéristiques de *Simaruba glauca*[1] et ceux de *Samadera indica*[2]. Dans ce but, nous envisagions de préparer un dérivé commun de la glaucarubine I (1a) et de la samaderine II (2). A cet effet, il s'agissait de transformer la glaucarubine I en dérivé VI.

L'aldéhyde formiate III (1b), produit de dégradation de la glaucarubine, traité par le diborane, conduit au tétrol IVa qui, par acétylation, fournit le composé IVb, $C_{27}H_{34}O_9$, que nous appelons tétraacétyl-7,12,15,32 nor-16 glaucanol. Les spectres de RMN des composés IVa et IVb montrent l'absence de fonction aldéhydique alors que la présence de la cétone en C-11 est confirmée par l'effet Cotton notable du composé IVb en dichroïsme circulaire (D.C.) ($\Delta\varepsilon_{283} = -0{,}05$, $\Delta\varepsilon_{314} = +0{,}52$, $\Delta\varepsilon_{325} = +0{,}36$).

Nous pensions préparer le composé VI par réduction du triacétate V que l'on devait obtenir par pyrolyse du tétraacétate IVb, mettant en jeu une élimination *cis* du groupement acétoxy α-axial en C-7.

Or, la décomposition thermique du tétraacétate IVb conduit à un mélange complexe duquel nous isolons, en plus de tétraacétate de départ IVb, un composé non cristallisé homogène en chromatographie sur couche mince.

Les propriétés physiques de ce dernier ne sont pas compatibles avec la structure du composé éthylénique V attendu mais suggère la formule VII. En effet:

(a) Alors que le tétraacétate IVb révèle en D.C. un effet Cotton, le dichrogramme du produit de pyrolyse en est dépourvu.

(b) La mesure de masse de ce composé indique qu'il possède la formule brute $C_{24}H_{30}O_6$ (Calc. pour $C_{24}H_{30}O_6$: 414,2042; Tr.: 414,2042). Ce poids moléculaire est inférieur à celui du composé IVb (p.m. = 502) de 88 unités

[1] J. POLONSKY, C. FOUQUEY et A. GAUDEMER, Bull. Soc. chim. Fr. 1827, 1818 (1964).

[2] J. ZYLBER et J. POLONSKY, Bull. Soc. chim. Fr. 2016 (1964).