Reaktionen von Trichlormethansulfenylchlorid mit Stickstoffverbindungen

VI. 1-Trichlormethansulfenyl-L-prolinanhydrid *

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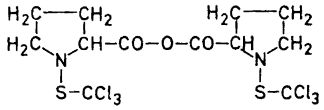
Im Rahmen unseres Studiums der Reaktionen einfacher Stickstoffverbindungen mit Trichlormethansulfenylchlorid setzten wir unter anderem auch L-Prolin und L-4-Hydroxyprolin mit CCl_3SCl um. Während L-4-Hydroxyprolin in Benzol (in Gegenwart von Triäthylamin) bei Zimmertemperatur nicht mit Trichlormethansulfenylchlorid reagiert, erhält man aus L-Prolin und Trichlormethansulfenylchlorid unter diesen Bedingungen 1-Trichlormethansulfenyl-L-prolinanhydrid *I* in 35 % Rohausbeute.



I

I schmilzt bei 106,5–108,5° und wurde elementaranalytisch, polarimetrisch ($[\alpha]_{589}^{25} = -174°$, $[\alpha]_{365}^{25} = -583°$, $CHCl_3$, $c = 2{,}819$), infrarotspektroskopisch (in KBr, Anhydridschwingungen bei 1750 und 1820 cm^{-1}), NMR-spektroskopisch ([in $CDCl_3$ ($Si(CH_3)_4$], breite Multiplette bei 1,7–2,7 δ, 3,4–4,1 δ und 4,4–4,8 δ, Integralverhältnis 4:2:1) sowie massenspektrometrisch (*m/e* 508: $[C_{12}H_{14}Cl_6N_2O_3S_2]^+$, M^+; *m/e* 391: $[C_{11}H_{14}Cl_3N_2O_3S_2]^+$; *m/e* 263: $[C_6H_8Cl_3NO_2S]^+$; *m/e* 218: $[C_5H_7Cl_3NS]^+$; *m/e* 136: $[C_4H_7ClNS]^+$; *m/e* 101: $[C_4H_7NS]^+$) charakterisiert. Unseres Wissens ist *I* das erste bekannte Derivat des acyclischen Prolinanhydrids.

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1-Trichlormethansulfenyl-L-prolinanhydrid I. 2,30 g (0,02 Mol) L-Prolin wurden mit 100 ml trockenem Benzol und 5,6 ml (0,04 Mol) Triäthylamin aufgeschlemmt und unter Rühren langsam mit 4,4 ml (0,04 Mol) Trichlormethansulfenylchlorid versetzt. Nach anfänglicher schwacher Wärmeentwicklung trat eine rötliche Färbung auf, die im Laufe von 2 Stunden weiteren Rührens nach gelb umschlug. Der Ansatz wurde über Nacht stehen gelassen, danach vom Niederschlag abfiltriert und das Filtrat eingeengt. Der Rückstand wurde in Acetonitril gelöst und daraus durch Abkühlen rohes *I* ausgefällt. Nach Digerieren mit Wasser und Trocknen betrug die Rohausbeute an *I*, F: 101–105°, 1,8 g (35 %). Eine analysenreine Probe schmolz nach dreimaligem Umkristallisieren aus Acetonitril bei 106,5–108,5°. (Gef. C 28,15; H 2,80; Cl 41,63; N 5,47; S 12,67. Ber. für $C_{12}H_{14}Cl_6N_2O_3S_2$: C 28,20; H 2,76; Cl 41,63; N 5,48; S 12,55).

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The Trisaccharide Fraction of the Bulbs of some Liliaceous Species

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In a previous paper [1] we have described the analytical separation by thin-layer chromatography of the naturally occurring fructosyl-sucroses: 1^F-β-D-fructofuranosyl-sucrose (1^F-kestose), 6^F-β-D-fructofuranosyl-sucrose (6^F-kestose), and 6^G-β-D-fructofuranosyl-sucrose (6^G-kestose or neokestose). The method was used to examine the trisaccharides of the bulbs of three plant species belonging to the Amaryllidaceae. They proved to contain[1] a mixture of 1^F-kestose and 6^G-kestose. This compo-

sition of the trisaccharide fractions was confirmed by methylation analysis on a semi micro-scale.

The present communication records the results of an analysis by the same methods of the trisaccharide fraction of three species belonging to the Liliaceae: *Tulipa silvestris* L., *Tulipa clusiana*, and *Ornithogalum nutans* L. Bulbs of commercial origine were used. They also contained oligofructosides of higher degree of polymerization (tetra, penta) in amounts equal to those of the trisaccharides. It is seen from Table 1 that

Table 1. Separation of kestoses by thin-layer chromatography on silica-gel.[a]

	1^F-kestose	6^F-kestose	6^G-kestose
R_F values of reference substances	0.39	0.44	0.48
Analysis of the trisaccharide fraction of:			
Tulipa silvestris L.	++	−	(+)
Tulipa clusiana	++	−	(+)
Ornithogalum nutans L.	+	−	++

[a] Solvent system: butanol saturated with water-methanol, 100:60.

Tulipa silvestris and *Tulipa clusiana* appeared to contain mainly 1^F-kestose together with traces of 6^G-kestose, whereas *Ornithogalum nutans* had a trisaccharide fraction composed of 1^F-kestose and 6^G-kestose, the latter predominating. The molecular proportion between fructose and glucose in the hydrolysate of the unfractionated trisaccharide mixture from each of the three species was determined by quantitative paper chromatography [2] and found to be 1.5:1.0 after acid hydrolysis, and 1.8:1.0 after hydrolysis with invertase.

Methylation analysis of the unseparated trisaccharide fractions gave results which are in agreement with the chromatographic analysis shown in Table 1. *Tulipa clusiana* gave approximately equimolecular proportions of 1,3,4,6-tetra-*O*-methyl-fructose, 2,3,4,6-tetra-*O*-methyl-glucose, and 3,4,6-tri-*O*-methyl-fructose, which is consistent with the result that the trisaccharide fraction of this species appeared to contain mainly 1^F-kestose. The trisaccharide fraction of the other tulip species examined (*T. silvestris*) gave similar results by methylation analysis, the only difference being that the tetra-*O*-methyl-fructose appeared to be present in a sligthly higher quantity. Additional spots originating from the observed trace amounts of 6^G-kestose were, however, not detected. The trisaccharide fraction of *Ornithogalum nutans* gave in agreement with its composition (Table 1) by methylation analysis the following sugar derivatives: 1,3,4,6-tetra-*O*-methyl-fructose (predominating), 2,3,4,6-tetra-*O*-methyl-glucose, 3,4,6-tri-O-methyl-fructose, and 2,3,4-tri-O-methyl-glucose. 1,3,4-Tri-*O*-methyl-fructose (corresponding to 6^F-kestose), which by the thin-layer chromatographic technique employed [1] separates clearly from the 3,4,6-isomer, was not detectable in any of the materials examined. It is concluded that the third isomeric kestose, 6^F-kestose, is absent in the plant material examined. The two other kestoses are present although their relative proportion is not the same in *Ornithogalum nutans* as in the *Tulipa* species (Table 1). As already mentioned we have found the same two kestoses in bulbs of species belonging to the Amaryllidaceae,[1] and Bacon [3,4] has characterized these two kestoses in *Allium* species (Liliaceae).

Knowledge of the composition of the trisaccharide fraction of all these fructan-containing bulbs is of interest to further work, now in progress, on the constitution of higher oligosaccharides and polysaccharides (fructans) extracted from the same material.

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