Phytochemistry, 1978, Vol 17, p 599. Pergamon Press. Printed in England.

THE STRUCTURE OF ALKALOID Y FROM *SCHEFFEROMITRA SUBAEQUALIS**

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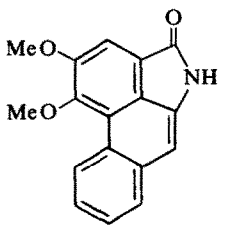
Key Word Index—*Schefferomitra subaequalis*; Anonaceae; alkaloid Y structure; phenanthrene derivative.

Abstract—Alkaloid Y has been shown by direct comparison of samples to be identical with Aristolactam BII, the lactam of 10-amino-3,4-dimethoxyphenanthrene-1-carboxylic acid.

In Part 1* of this series the isolation of alkaloid Y from the bark of *Schefferomitra subaequalis* (Scheff.) Diels was reported, and some spectral data were described, but neither the amount of material nor the spectral data available allowed us to propose even a tentative structure for it. It was apparent, however, that with a molecular formula $C_{17}H_{13}NO_3$ it is highly unsaturated, and the strong band at 1720 cm^{-1} in the IR spectrum had to be considered in conjunction with the bands at 3170 and 3450 cm^{-1}. The presence of signals in the proton NMR spectrum corresponding to six aromatic protons, two methoxyl groups and one NH or OH group accounted for all the hydrogen atoms present.



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Investigation of the high resolution mass spectrum of alkaloid Y, now available to us reveals a parent ion at 279.09009 ($CH_{17}H_{13}NO_3$ requ. 279.08954) and regular losses of Me, CO and HCN fragments only; peaks at *m/e* 82.5 and 96.5 are considered to be due to doubly charged ions of mass 165 and 193 respectively. Such fragmentation patterns point to an ionizable lactam moiety within an aromatic structure. The spectral properties of alkaloid Y are very similar to those reported [1] for Aristolactum BII (1), isolated from the roots of *Aristolochia argentina* (Aristolochiaceae). Direct comparison of samples confirmed their identity.

Acknowledgements—We thank Dr. H. A. Priestap for a sample of aristolactam BII.

* Part 2 in the series 'Alkaloids of *Schefferomitra subaequalis*'; for part 1 see Gellert, E. and Rudzats, R. (1972) *Australian J. Chem.* **25**, 2477.

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ZWEI NEUE ACYLPYRROLE AUS *KLEINIA KLEINIOIDES*

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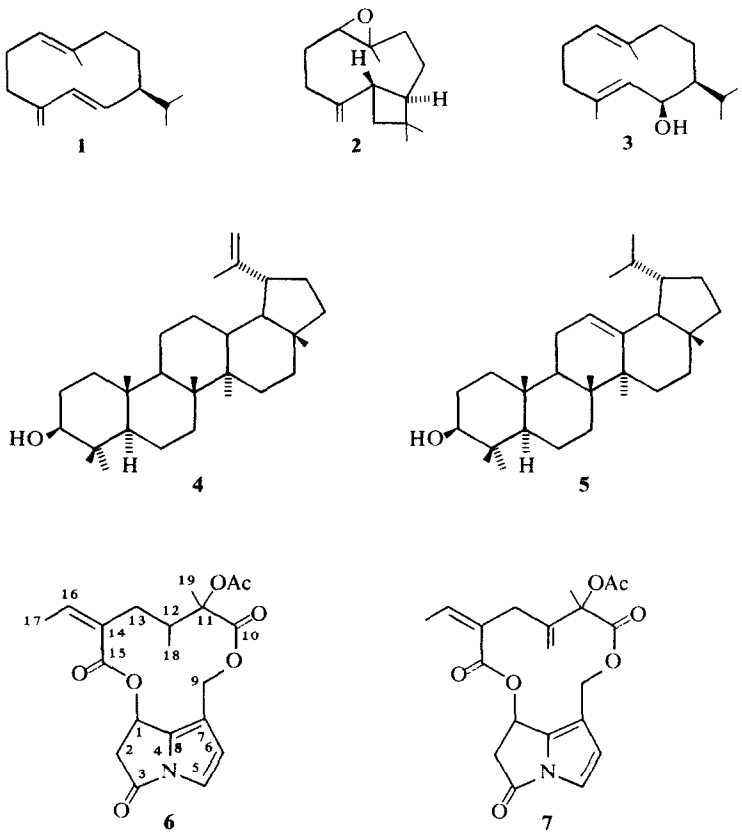
Key Word Index—*Kleinia kleinioides*; Senecioneae; Compositae; new acylpyrrole derivatives; senecio alkaloids.

Die oberirdischen Teile von *Kleinia kleinioides* (Sch. Bip.) M.R.F. Taylor, die früher zur Sektion *Kleinia* der Gattung *Senecio* gerechnet wurde, enthalten Germacren D (1), Caryophyllenoxid (2), das Hydroxygermacren 3, Lupeol (4), das Isomere 5 sowie zwei Acylpyrrole, die sich von Senecioalkaloiden ableiten.



Die spektroskopischen Daten letzterer Verbindungen entsprechen weitgehend denen der kürzlich aus *Senecio*-Arten isolierten Alkaloide [1]. Die eine Verbindung mit der Summenformel $C_{20}H_{23}O_7N$ muß ein Isomeres vom *Senaetnin* sein. Unterschiede bestehen neben geänderten Drehwerten und Schmelzpunkten bei den

Tabelle 1. ^{1}H-NMR-Daten von **6** und **7** (δ-Werte, $CDCl_3$, TMS als innerer Standard, 270 MHz)

	6	Senaetnin	**7**
1-H	*dd* 5.83	*dd* 5.84	*dd* 5.83
2-H	*dd* 3.64	*dd* 3.74	*dd* 3.54
2'-H	*dd* 3.01	*dd* 3.05	*dd* 2.97
5-H	*d* 7.12	*d* 7.11	*d* 7.10
6-H	*d* 6.46	*d* 6.57	*d* 6.51
9-H	*d* 5.37	*d* 5.54	*d* 5.22
9'-H	*d* 5.00	*d* 4.65	*d* 4.68
12-H	*m* 1.75	*dq* 2.13	—
13-H	*m* 1.75	*dd* 1.88	*dddd* 3.46
13'-H	*ddd* 2.70	*d(br)* 2.46	*dddd* 2.85
16-H	*dq* 5.98	*q(br)* 6.00	*ddq* 6.06
17-H	*dd* 1.88	*d* 1.96	*dd* 2.05
18-H	*d* 1.00	*d* 0.98	*d* 5.26
			dd 4.99
19-H	*s* 1.74	*s* 1.67	*s* 1.78
OAc	*s* 2.06	*s* 2.10	*s* 2.07

J(Hz): 1, 2 = 7; 1, 2' = 2; 2, 2' = 19; 5, 6 = 3; 9, 9' = 13; 12, 13 = 2, 12, 18 = 7; 13, 13' = 13; 13, 16 = 1.5; 16, 17 = 7; bei **7**: 13, 13' = 17.5; 13, 16 = 1.5; 13, 17 = 2; 13, 18 = 1; 13', 16 = 1.5; 13', 18 = 2 und 2.

den ^{1}H-NMR-Signalen hinsichtlich der Lage, so daß eine unterschiedliche Stereochemie zu vermuten ist, wobei als Zentren unterschiedlicher Isomerie nur die C-Atome 1, 11 und 12 in Betracht kommen. Aus Substanzmangel war jedoch eine Klärung der Stereochemie nicht möglich. Die zweite Substanz mit der Summenformel $C_{20}H_{21}O_7N$ unterscheidet sich von der ersten nur durch das Fehlen einer Methylgruppe, die durch eine Methylengruppe ersetzt ist. Es handelt sich demnach bei den beiden neuen Pyrrolderivaten um die Verbindungen **6** und **7**, wobei lediglich die Stereochemie ungeklärt ist. Wir möchten **6** *Isosenaetnin* und **7** 12,18-*Dehydroisosenaetnin* nennen. Weitere Untersuchungen müssen zeigen, welche chemotaxonomische Bedeutung diesen Verbindungen zukommt.

EXPERIMENTELLES

IR: Beckman IR 9, CCl_4; ^{1}H-NMR Bruker WH 270; MS: Varian Mat 711, 70 eV, Direkteinlaß; optische Rotation: Perkin–Elmer-Polarimeter, $CHCl_3$. Die lufttrockenen oberirdischen Teile (East African Herbar, Kenia) extrahierte man mit Et_2O–Petrol (1:2) und trennte den erhaltenen Extrakt grob durch SC (Si gel, Akt. -St. II) und anschliessend weiter durch DC (Si gel, GF 254). Als Laufmittel dienten Et_2O–Petrol-Gemische. Der Extrakt aus 100 g oberirdischen Teilen ergab 100 mg **1**, 3 mg **2**, 40 mg **3**, 200 mg **4**, 200 mg **5**, 20 mg **6**, (Et_2O–Petrol, 1:1) und 10 mg **7** (Et_2O–Petrol, 1:1).

Isosenaetnin (**6**). Farblose Kristalle aus Et_2O–Petrol, Schmp. 198.5°. IR: >C=O 1765, 1747, 1721 cm^{-1}. MS. M^+ *m/e* 389.147 (8%) (ber. für $C_{20}H_{23}O_7N$ 389.147), —AcOH 329

(4); $C_8H_7NO^+$ 133 (95) C_7H_7N 105 (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-34.8 \quad -34.8 \quad -39.0 \quad -58.0} \quad (c = 1.0)$$

Dehydroisosenaetnin (7). Farbloses, zähes Öl, IR: >C=O 1773, 1750, 1725 cm^{-1}. MS: M^+ *m/e* 387.131 (3%) (ber. für $C_{20}H_{21}O_7N$ 387.132); $C_8H_7NO^{7+}$ 133(100); $C_7H_7N^{7+}$ 105 (28).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-45.6 \quad -46.1 \quad -48.8 \quad -89.0^\circ} \quad (c = 0.5)$$

Anerkennung—Der Deutschen Forschungsgemeinschaft danken wir für die Förderung dieser Arbeit, dem East African Herbar, Kenia, für das Pflanzenmaterial.

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A NEW PIPERIDINE ALKALOID FROM *PIPER PEEPULOIDES*

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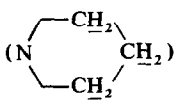
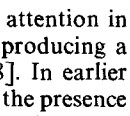
Key Word Index—*Piper peepuloides*; Piperaceae; 2-methoxy-4, 5-methylenedioxy cinnamoyl piperidine

The genus *Piper* has received considerable attention in recent years because of its reputation for producing a number of new chemical compounds, [1–8]. In earlier communications [1, 9, 10] we have reported the presence of a new pyrrolidine alkaloid, peepuloidin, from the leaves of *P. peepuloides* and from the fruits of the same plant a number of interesting compounds such as [+]-diaeudesmin, pipataline, 5-hydroxy,3',4',7-trimethoxyflavone, 5-hydroxy-4', 7-dimethoxyflavone, *N-iso*butyl dodeca-*trans*-2-*trans*-4-dienamide, *N-iso*butyldeca-*trans*-2-*trans*-4-dienamide and sesamin. We now wish to report the isolation and structure elucidation of a new piperidine alkaloid from the leaves of *P.peepuloides*, identified as 2-methoxy-4, 5-methylenedioxy cinnamoyl piperidine.

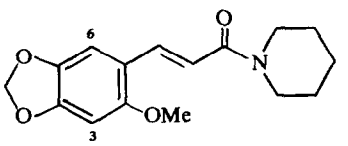
The petrol extract of the leaves on repeated column chromatography over neutral Al_2O_3 and repeated crystallisation furnished a white crystalline compound.

The compound analysed for $C_{16}H_{19}NO_4$, M^+-289.1318 (Cal. for $C_{16}H_{19}NO_4$, M^+289.1313); UV 333, 305 and 240 nm. The IR (KBr) spectrum of the compound showed characteristic bands for >C=O (1650 cm^{-1}) indicating the compound to be an amide and lack of an —NH stretching frequency demonstrated that it was a tertiary amide; C=C (1660 cm^{-1}) and methylenedioxy group) (1260, 1040, 930 cm^{-1}). The 60 MHz PMR ($CDCl_3$) spectrum of the compound showed a broad multiplet between δ1.0 and 1.9 which is attributed to 6 protons



a triplet and a multiplet at δ3.30 and 3.55 respectively accounts for 4 protons (); a singlet at 3.75 has been assigned to 3 protons (O—Me). A doublet at 5.85 (1H, J = 14 Hz), indicating a *trans* olefinic proton (α) adjacent to carbonyl; a singlet at 5.85 is due to two protons of methylenedioxy group. A doublet at 6.78 (J = 14 Hz) is assigned to one (β) olefinic proton, singlets at δ6.45 and 6.9 are attributed to C-3 and C-6 aromatic protons respectively. The MS is also in complete agreement with the proposed structure (**1**).

On hydrogenation (Pd/C) the compound quickly absorbed one mole of H_2 to give a waxy dihydro derivative (M^+-291). The $KMnO_4$ oxidation of the compound furnished an acid mp 147–147.5° (lit., [11] mp 148–149°). identified as 2-methoxy-4, 5-methylendioxy benzoic acid.



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EXPERIMENTAL

The air dried powdered leaves of *P. peepuloides* Roxb. (0.9 kg) were continuously extracted in a Soxhlet with petrol (bp 60–80°) for 75 hr. The extract was concd under red. pres. and the resultant viscous liquid was subjected to column chromatography over neutral Al_2O_3 and eluted with different solvents in order of increasing polarity. The fractions eluted with C_6H_6 gave a crude viscous liquid which on repeated column chromatography over