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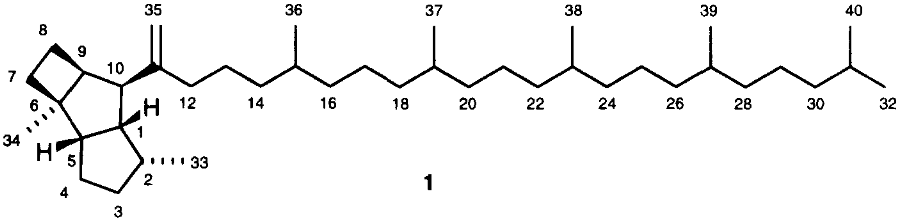
Poduran, an Unusual Tetraterpene from the Springtail *Podura aquatica*

Stefan Schulz[a]*, Christoph Messer[b], Konrad Dettner[b]

[a]Universität Hamburg, Institut für Organische Chemie, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany
[b]Universität Bayreuth, Lehrstuhl für Tierökologie II, D-95440 Bayreuth, Germany

Abstract: A new hydrocarbon tetraterpene, poduran (1), was isolated from the springtail *Podura aquatica*. It possesses a tricyclic head region and a tail of five isoprene units. The structure was elucidated by one- and twodimensional NMR experiments, mass spectrometric investigations as well as chemical transformations. © 1997 Elsevier Science Ltd.

During our investigations on the defensive chemistry of springtails (Collembola)[3] we investigated the widespread springtail *Podura aquatica*. By column chromatography, 0.5 to 1 mg of a hydrocarbon was isolated[1] which eluted earlier than straight chain alkanes from silica. Mass spectrometric investigations revealed its molecular weight to be 554 with a molecular formula of $C_{40}H_{74}$. A characteristic ion at m/z = 526 (M–28) showed the easy loss of ethene, probably from a cyclobutane ring.[2] One equivalent of hydrogen was taken up during microhydrogenation, thus showing the presence of one double bond and three rings in the molecule.



1

Figure 1. Poduran (**1**)

The structure of **1** was deduced from extensive NMR studies (^1H, ^{13}C, DEPT, H,H-COSY, HMQC, HMBC, H,H-NOESY). The proton connectivities of the tricyclic ring system for H1-H5 and H7-H10 were established from phase sensitive ^1H,^1H-DQF-COSY spectra. The position of the two quarternary carbons C6 and C11 could be elucidated by HMBC correlations. Individual assignment of the carbons of the oligoisopentyl side chain was possible up to C15 and again starting from C28 (see table). The remaining signals in the ^{13}C NMR spectrum were only partly resolved and could not be assigned individually. Only four sets of signals occur in this part of the molecule (CH_3, CH, CH_2–$(CH_2)_2$ and CH_2–CH). Their shift values and the corresponding ^1H NMR as well as HMBC data support a regular head to tail connection between the single isopentyl units. This is in accord with NMR data obtained from squalane and pristane.[4]

The relative configuration of the ring system was determined by NOESY experiments (see fig. 2 for key enhancements). The *cis-anti-cis* ring arrangement is supported by strong enhancements of H5/H7, H1/H5, and H1/H8. The oligoisopentyl chain is *cis* attached relative to the cyclobutane ring because of crosspeaks from H35a to H1 and H8, as well as from H35b to H33. This is supported by the large vicinal coupling constant $J_{1,10}$ = 10.5 Hz, showing an antiperiplanar arrangement of H1 and H10 in the rigid five-membered ring. In addition, a crosspeak at H3/H10 can be observed. The protons H1 and H2 are also *cis* configured, because of enhancements of H33 with H10 and H35b. The assignment of the relative configuration of the side chain was not possible. Nevertheless, the absence of peak splitting in the ^{13}C NMR spectrum proved the presence of only one diastereomer.[4]

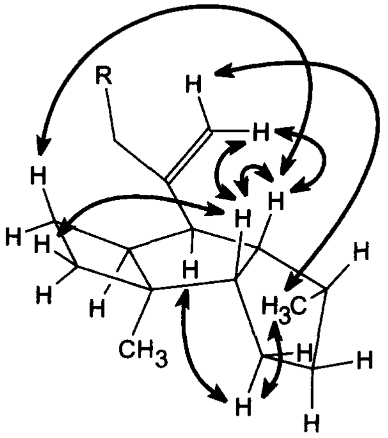
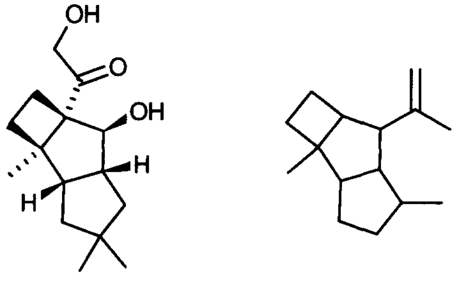


Figure 2. Key NOE enhancements in the tricyclic subunit of poduran (**1**)

The unusual tricyclo[6.2.0.0^{2,6}]decane system has so far only rarely been observed in nature. The mould metabolite Sulcatine G[5] (**2**) has a different substitution pattern than **1**, but the same *cis-anti-cis* arrangement of the rings. The sesquiterpene **3** was recently isolated from a marine sponge.[6] The only other springtail investigated chemically so far is *Tetrodontophora bielanensis*.[3,7,8] It also contains a tetraterpene, the open chain compound lycopane (2,6,10,14,19,23,27,31-octamethyldotriacontane).[8] To our knowledge, no other tetraterpene with a polycyclic head region and a regular oriented pentakisisopentyl chain has been reported from nature.

The investigation of the biosynthesis as well as the function of **1** for *Podura aquatica* is currently under way.



2 3

Figure 3. Sulcatine G (**2**) and the sesquiterpene **3**

Table. ^1H and ^{13}C NMR data[9] of poduran (1) in C_6D_6.[a]

position	δ_C (ppm)	δ_H (ppm)[b]		HMBC[c] correlations
1	50.2 (CH)	2.87		C2,C3,C4,C5,C10,C11
2	36.7 (CH)	2.24		C1,C3,C10,C33
3	33.7 (CH_2)	1.39	1.79	C1,C2,C4,C5
4	26.3 (CH_2)	1.36	1.49	C1,C2,C3,C5
5	58.0 (CH)	2.03		C1,C3,C4,C6,C9,C10
6	45.9 (C)			
7	33.4 (CH_2)	1.73		C5,C6,C8,C9,C34
8	15.2 (CH_2)	1.74	1.85	C6,C7,C9,C10,C11,C34
9	48.0 (CH)	2.43		C1,C7,C8,C10
10	47.1 (CH)	2.52		C1,C2,C8,C9,C11,C12,C35
11	149.5 (C)			
12	38.2 (CH_2)	1.97		C10,C11,C13,C14,C35
13	25.8 (CH_2)	1.48	1.60	C12,C14
14	37.3 (CH_2)	1.16	1.41	C12,C13,C15,C16,C36
15	33.2 (CH)	1.47		[d]
16, 18, 20, 22, 24, 26	37.9 (CH_2)	1.18	1.40	[d]
17, 21, 25	25.0 (CH_2)	1.32	1.46	[d]
19, 23, 27	33.2 (CH)	1.47		[d]
28	37.7 (CH_2)	1.15	1.35	[d]
29	25.3 (CH_2)	1.30	1.37	[d]
30	39.7 (CH_2)	1.17	1.39	[d]
31	28.3 (CH)	1.53		C29,C30,C32,C40
32, 40	22.8, 22.9 (CH_3)	0.92		C30,C31,C32,C40
33	18.3 (CH_3)	0.94		C1,C2,C3
34	23.7 (CH_3)	1.19		C5,C6,C7,C9
35	109.5 (CH_2)	4.97	5.07	C10,C11,C12
36, 37, 38, 39	20.0, 20.1 (CH_3)	0.95	0.96	[d]

[a] J (H/H) in Hz: 1/2 = 6.6, 1/5 = 6.6, 1/10 = 10.5, 1/33 = 0.5, 1/35a = 1.5, 2/3a = 7.2, 2/3b = 9, 2/33 = 6.8, 4a/5 = 9.5, 4b/5 = 8.5, 8a/9 = 4.2, 8b/9 = 10, 9/10 = 7.2, 10/35a = 1.5, 10/35b = 1.5, 12/35a = 3, 12/35b = 2

[b] First value proton a, second proton b.

[c] Oberserved enhancements between H-atoms and the indicated C-atoms.

[d] HMBC correlations are in accordance with a regular oligoisopentyl chain.

ACKNOWLEDGEMENTS

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REFERENCES AND NOTES

1. Isolation of **1**: Whole *Podura aquatica* springtails (5 g) were extracted with dichloromethane. The solvent was evaporated and the residue separated by chromatography on silica (5 g).
2. MS (70 eV): *m/z* = 554 (9), 526 (38), 472 (7), 203 (18), 189 (35), 176 (31), 161 (91), 148 (57), 135 (54), 121 (28), 119 (26), 107 (48), 95 (34), 93(36), 81 (60), 71 (57), 69 (29), 57 (100), 55 (53), 43 (68).
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9. NMR experiments were performed on a Bruker WM500 instrument at 500 MHz (^{1}H) and 125 MHz (^{13}C).

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