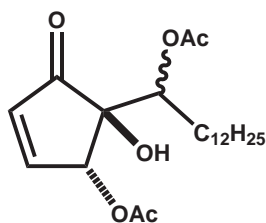


7. Charakterisierung

4,6-Di-*O*-acetylhygrophoron A¹² (31)



4,5-*trans*-4-Acetoxy-5-hydroxy-5-(1-acetoxytridecyl)-2-cyclopenten-1-on

farbloses Öl

isoliert aus *H. personii* Arnolds

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 7.462 *dd* (6.2/2.1) H-3, 6.441 *dd* (6.2/1.8) H-2, 5.721 *dd*(2.1/1.8) H-4, 5.017 *m* H-6, 3.247 *br s* 5-OH, 2.136 *s* 4-OAc, 1.996 *s* 6-OAc, 1.7 *m* H-7, 1.20 – 1.33 *m* H-8 – H-17, 0.888 *t* (7.0) H-18

¹³C-NMR (125 MHz, CDCl₃) δ ¹³C ppm: 202.3 C-1, 170.5 4-OAc, 169.9 6-OAc, 156.8 C-3, 134.4 C-2, 81.4 C-5, 79.7 C-4, 74.1 C-6, 28.7 C-7, 31.8, 29.63, 29.59, 29.57, 29.5, 29.4, 29.34, 29.28, 25.9, 22.6 C-8 – C-17, 20.9 4-OAc, 20.7 6-OAc, 14.1 C-18

ESI-FT-ICR-MS *m/z* 419.23986 ([M+Na]⁺, ber. für C₂₂H₃₆NaO₆⁺ 419.24041)

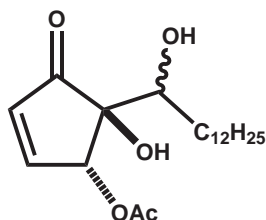
(+)-ESI-CID-MS (-13 eV) *m/z* (rel. int., %): 397 (13, [M+H]⁺), 379 (31, [M+H-H₂O]⁺), 337 (100, [M+H-HOAc]⁺), 319 (16, [M+H-HOAc-H₂O]⁺), 295 (30, [M+H-HOAc-CH₂CO]⁺), 277 (60, [M+H-2 HOAc]⁺), 259 (7, [M+H-2 HOAc-H₂O]⁺), 123 (30, [C₇H₇O₂]⁺), 111 (4, [C₆H₇O₂]⁺)

(-)-ESI-CID-MS (+20 eV) *m/z* (rel. int., %): 395 (2, [M-H]⁻), 353 (8, [M-H-CH₂CO]⁻), 335 (42, [M-H-HOAc]⁻), 307 (13, [M-H-HOAc-CO]⁻), 293 (100, [M-H-HOAc-CH₂CO]⁻), 291 (21, [M-H-HOAc-CO₂]⁻), 275 (14, [M-H-2 HOAc]⁻), 263 (8), 249 (6), 139 (2, [C₇H₇O₃]⁻), 95 (5), 59 (20)

[α]_D²³ +53.0° (MeOH; *c* 0.940)

$\nu_{\max}^{\text{film}} \text{ cm}^{-1}$	3470 (br, w), 2955 (m), 2924 (s), 2854 (s), 1746 (s), 1729 (s), 1653 (vw), 1595 (vw), 1465 (m), 1435 (w), 1372 (m), 1329 (vw), 1233 (s), 1192 (w), 1118 (w), 1100 (m), 1070 (m), 1035 (m), 912 (w), 828 (vw), 769 (vw), 719 (vw)
DC	LM 1: $R_f = 0.67$, LM 2: $R_f = 0.49$
Chirale HPLC	(Gradient 11) Säule: OD-H: $R_t = 12.2$ min, OB-H: $R_t = 12.9$ min, AS-H: $R_t = 14.1$ min, AD-H: $R_t = 12.5$ min.

4-*O*-Acetylhygrophoron A¹² (32)

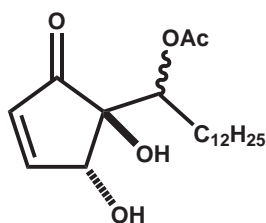


4,5-*trans*-4-Acetoxy-5-hydroxy-5-(1-hydroxytridecyl)-2-cyclopenten-1-on

farbloses Öl

isoliert aus *H. persoonii* Arnolds

¹ H-NMR	(500 MHz, CDCl ₃) δ ¹ H ppm: 7.561 <i>dd</i> (6.1/2.2) H-3, 6.437 <i>dd</i> (6.1/1.6) H-2, 5.801 <i>dd</i> (2.2/1.6) H-4, 3.725 <i>dt</i> (9.6/3.0) H-6, 3.185 <i>br s</i> 5-OH, 2.39 <i>br d</i> (3.0) 6-OH, 2.171 <i>s</i> 4-OAc, 1.7 <i>m</i> H-7, 1.20 – 1.33 <i>m</i> H-8 – H-17, 0.880 <i>t</i> (7.0) H-18
¹³ C-NMR	(125 MHz, CDCl ₃) δ ¹³ C ppm: 204.7 C-1, 170.2 4-OAc, 161.4 C-3, 134.9 C-2, 81.4 C-5, 79.3 C-4, 74.4 C-6, 32 – 22 C-7 – C-17, 20.8 4-OAc, 14.0 C-18
ESI-FT-ICR-MS	m/z 377.23084 ($[M+Na]^+$, ber. für C ₂₀ H ₃₄ NaO ₅ ⁺ 377.22984)
(+)-ESI-CID-MS	(-15 eV) m/z (rel. int., %): 355 (4, $[M+H]^+$), 295 (100, $[M+H-HOAc]^+$), 277 (14, $[M+H-HOAc-H_2O]^+$), 267 (8, $[M+H-HOAc-CO]^+$), 259 (7, $[M+H-HOAc-2H_2O]^+$), 249 (15, $[M+H-HOAc-H_2O-CO]^+$), 123 (4, $[C_7H_7O_2]^+$)
(-)-ESI-CID-MS	(+20 eV) m/z (rel. int., %): 353 (2, $[M-H]^-$), 293 (100, $[M-H-HOAc]^-$), 275 (4, $[M-H-H_2O-HOAc]^-$), 265 (15, $[M-H-HOAc-CO]^-$), 139 (4, $[C_7H_7O_3]^-$)
DC	LM 1: $R_f = 0.30$

6-*O*-Acetylhygrophoron A¹² (33)

4,5-*trans*-4,5-Dihydroxy-5-(1-acetoxytridecyl)-2-cyclopenten-1-on

farbloses Öl

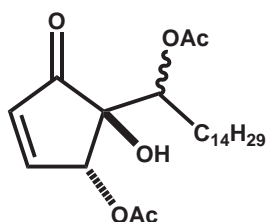
isoliert aus *H. persoonii* Arnolds

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 7.524 *dd* (6.1/2.0) H-3, 6.316 *dd* (6.1/1.8) H-2, 5.145 *dt* (10.4/2.9) H-6, 4.835 *ddd* (6.7/2.0/1.8) H-4, 3.012 *d* (6.7) 4-OH, 2.958 *s* 5-OH, 2.045 *s* 6-OAc, 1.7 *m* H-7, 1.20 – 1.33 *m* H-8 – H-17, 0.880 *t* (7.0) H-18

¹³C-NMR (125 MHz, CDCl₃) δ ¹³C ppm: 204.5 C-1, 171.2 6-OAc, 158.1 C-3, 132.5 C-2, 82.8 C-5, 78.8 C-4, 75.4 C-6, 32 – 22 C-7 – C-17, 21.1 6-OAc, 14.0 C-18

ESI-FT-ICR-MS *m/z* 377.22897 ([M+Na]⁺, ber. für C₂₀H₃₄NaO₅⁺ 377.22984)

DC LM 1: R_f = 0.30

4,6-Di-*O*-acetylhygrophoron A¹⁴ (34)

4,5-*trans*-4-Acetoxy-5-hydroxy-5-(1-acetoxypentadecyl)-2-cyclopenten-1-on

farbloses Öl

isoliert aus *H. persoonii* Arnolds

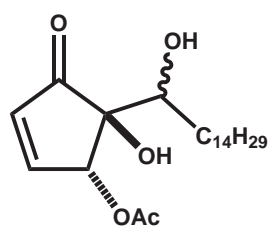
¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 7.462 *dd* (6.2/2.1) H-3, 6.441 *dd* (6.2/1.8) H-2, 5.721 *dd* (2.1/1.8) H-4, 5.017 *m* H-6, 3.247 *s* 5-OH, 2.136 *s* 4-OAc, 1.996 *s* 6-OAc, 1.7 *m* H-7, 1.20 – 1.33 *m* H-8 – H-19, 0.888 *t* (7.0) H-20

¹³C-NMR (125 MHz, CDCl₃) δ ¹³C ppm: 202.1 C-1, 170.7 4-OAc, 170.0 6-OAc, 156.8 C-3, 134.5 C-2, 81.6 C-5, 79.9 C-4, 74.1 C-6, 28.8 C-7, 32.0, 29.80, 29.79, 29.77, 29.76, 29.74, 29.69, 29.58, 29.51, 29.47, 26.1, 22.8 C-8 – C-19, 21.1 4-OAc, 20.9 6-OAc, 14.3 C-20

ESI-FT-ICR-MS *m/z* 447.27221 ([M+Na]⁺, ber. für C₂₄H₄₀NaO₆⁺ 447.27171)

(+)-ESI-CID-MS	(-13 eV) m/z (rel. int., %): 425 (12, [M+H] ⁺), 407 (23, [M+H-H ₂ O] ⁺), 365 (100, [M+H-HOAc] ⁺), 347 (15, [M+H-HOAc-H ₂ O] ⁺), 323 (38, [M+H-HOAc-CH ₂ CO] ⁺), 305 (83, [M+H-2 HOAc] ⁺), 287 (14, [M+H-2 HOAc-H ₂ O] ⁺), 277 (4), 259 (4), 123 (55, [C ₇ H ₇ O ₂] ⁺)
(-)-ESI-CID-MS	(+20 eV) m/z (rel. int., %): 423 (13, [M-H] ⁻), 405 (4, [M-H-H ₂ O] ⁻), 381 (8, [M-H-CH ₂ CO] ⁻), 363 (54, [M-H-HOAc] ⁻), 335 (5, [M-H-HOAc-CO] ⁻), 321 (100, [M-H-HOAc-CH ₂ CO] ⁻), 303 (7, [M-H-2 HOAc] ⁻), 205 (8), 59 (37)
ν_{\max}^{film} cm ⁻¹	3447 (br, w), 2950 (m), 2923 (s), 2852 (s), 1744 (s), 1727 (s), 1645 (vw), 1594 (vw), 1465 (m), 1437 (w), 1371 (m), 1330 (w), 1234 (s), 1119 (w), 1102 (m), 1041 (m), 910 (w), 826 (vw), 753 (vw), 713 (vw)
DC	LM 1: $R_f = 0.67$, LM 2: $R_f = 0.49$

4-*O*-Acetylhygrophoron A¹⁴ (35)

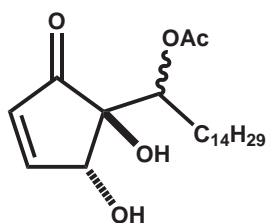


4,5-*trans*-4-Acetoxy-5-hydroxy-5-(1-hydroxypentadecyl)-2-cyclopenten-1-on

farbloses Öl

isoliert aus *H. persoonii* Arnolds

¹ H-NMR	(500 MHz, CDCl ₃) δ ¹ H ppm: 7.561 <i>dd</i> (6.1/2.2) H-3, 6.437 <i>dd</i> (6.1/1.6) H-2, 5.801 <i>dd</i> (2.2/1.6) H-4, 3.725 <i>dt</i> (9.6/3.0) H-6, 3.185 <i>s</i> 5-OH, 2.39 <i>br</i> 6-OH, 2.171 <i>s</i> 4-OAc, 1.7 <i>m</i> H-7, 1.20 -1.33 <i>m</i> H-8 – H-19, 0.880 <i>t</i> (7.0) H-20
ESI-FT-ICR-MS	m/z 405.26152 ([M+Na] ⁺ , ber. für C ₂₂ H ₃₈ NaO ₅ ⁺ 405.26115)
DC	LM 1: $R_f = 0.30$

6-*O*-Acetylhygrophoron A¹⁴ (36)

4,5-*trans*-4,5-Dihydroxy-5-(1-acetoxypentadecyl)-2-cyclopenten-1-on

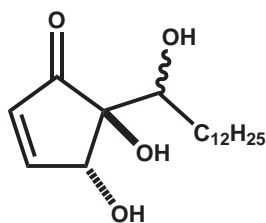
farbloses Öl

isoliert aus *H. persoonii* Arnolds

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 7.524 *dd* (6.1/2.0) H-3, 6.316 *dd* (6.1/1.8) H-2, 5.145 *dt* (10.4/2.9) H-6, 4.835 *ddd* (6.7/2.0/1.8) H-4, 3.012 *d* (6.7) 4-OH, 2.958 *s* 5-OH, 2.045 *s* 6-OAc, 1.7 *m* H-7, 1.20 -1.33 *m* H-8 – H-19, 0.880 *t* (7.0) H-20

ESI-FT-ICR-MS *m/z* 405.26152 ([M+Na]⁺, ber. für C₂₂H₃₈NaO₅⁺ 405.26115)

DC LM 1: R_f = 0.30

Hygrophoron A¹² (37)

4,5-*trans*-4,5-Dihydroxy-5-(1-hydroxytridecyl)-2-cyclopenten-1-on

farbloses Öl

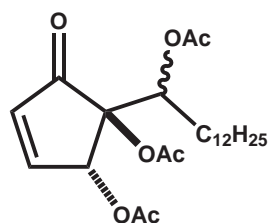
semisynthetisches Derivat von **31**

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 7.646 *dd* (6.1/2.0) H-3, 6.366 *dd* (6.1/1.6) H-2, 4.873 *dd* (2.0/1.6) H-4, 3.859 *m* H-6, 1.7 *m* H-7, 1.20 – 1.33 *m* H-8 – H-17, 0.880 *t* (7.0) H-18

¹³C-NMR (125 MHz, CDCl₃) δ ¹³C ppm: 205.7 C-1, 162.7 C-3, 133.1 C-2, 83.4 C-5, 79.5 C-4, 75.6 C-6, 32 – 22 C-7 – C-17, 14.0 C-18

ESI-FT-ICR-MS *m/z* 335.21881 ([M+Na]⁺, ber. für C₁₈H₃₂NaO₄⁺ 335.21928)

(–)-ESI-CID-MS (+20 eV) *m/z* (rel. int., %): 311 (7, [M–H][–]), 293 (21, [M–H–H₂O][–]), 265 (6, [M–H–H₂O–CO][–]), 255 (25, [M–H–C₃H₄O][–]), 251 (7), 249 (37, [M–H–CO₂][–]), 239 (15, [M–H–CO–CO₂][–]), 227 (44, [M–H–C₄H₄O₂][–]), 213 (100, [M–H–C₅H₆O₂][–]), 97 (21)

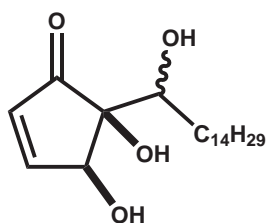
4,5,6-Tri-*O*-acetylhygrophoron A¹² (**39**)

4,5-*trans*-4,5-Diacetoxy-5-(1-hydroxytridecyl)-2-cyclopenten-1-on

farbloses Öl

semisynthetisches Derivat von **31**

¹ H-NMR	(500 MHz, CDCl ₃) δ ¹ H ppm: 7.347 <i>dd</i> (6.4/2.1) H-3, 6.489 <i>dd</i> (6.4/1.8) H-2, 6.244 <i>dd</i> (2.1/1.8) H-4, 5.176 <i>t</i> (6.5) H-6, 2.135 <i>s</i> 4-OAc, 2.123 <i>s</i> 5/6-OAc, 1.983 <i>s</i> 5/6-OAc, 1.7 <i>m</i> H-7, 1.20 – 1.33 <i>m</i> H-8 – H-17, 0.880 <i>t</i> (7.0) H-18
¹³ C-NMR	(125 MHz, CDCl ₃) δ ¹³ C ppm: 197.6 C-1, 154.8 C-3, 135.4 C-2, 170.2 4-OAc, 169.5 5/6-OAc, 169.4 5/6-OAc, 84.3 C-5, 75.6 C-4, 72.1 C-6, 28.8 C-7, 31.9, 29.63, 29.61, 29.59, 29.53, 29.45, 29.39, 29.32, 25.8, 22.7 C-8 – C-17, 20.9 OAc, 20.8 OAc, 20.6 OAc, 14.0 C-18
ESI-FT-ICR-MS	<i>m/z</i> 461.25013 ([M+Na] ⁺ , ber. für C ₂₄ H ₃₈ NaO ₇ ⁺ 461.25097)
(+)-ESI-CID-MS	(-13 eV) <i>m/z</i> (rel. int., %): 439 (1, [M+H] ⁺), 379 (54, [M+H-HOAc] ⁺), 337 (100, [M+H-HOAc-CH ₂ CO] ⁺), 319 (6, [M+H-2 HOAc] ⁺), 295 (70, [M+H-HOAc-2 CH ₂ CO] ⁺), 277 (25, [M+H-2 HOAc-CH ₂ CO] ⁺), 259 (7, [M+H-3 HOAc] ⁺), 231 (3), 123 (9, [C ₇ H ₇ O ₂] ⁺)
ν_{\max}^{film} cm ⁻¹	2955 (m), 2925 (s), 2854 (s), 1746 (s), 1731 (s), 1597 (vw), 1465 (w), 1434 (w), 1372 (m), 1355 (w), 1249 (s), 1225 (s), 1185 (w), 1155 (w), 1108 (w), 1073 (w), 1032 (m), 980 (w), 922 (w), 905 (w), 825 (w), 794 (w), 757 (w)
DC	LM 1: R _f = 0.75, LM 2: R _f = 0.62

Hygrophoron B¹⁴ (44)

4,5-*cis*-4,5-Dihydroxy-5-(1-hydroxypentadecyl)-2-cyclopenten-1-on

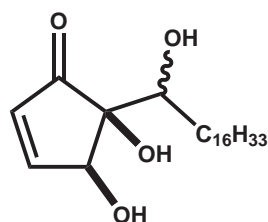
weißer Feststoff

isoliert aus *H. olivaceoalbus* (Fr.) Fr.

¹ H-NMR	(500 MHz, CDCl ₃) δ ¹ H ppm: 7.644 <i>dd</i> (6.0/2.3) H-3, 6.301 <i>dd</i> (6.0/1.3) H-2, 4.727 <i>dd</i> (2.3/1.3) H-4, 3.777 <i>br d</i> (10.1) H-6, 3.718 <i>br s</i> 6-OH, 3.073 <i>br s</i> 4-OH, 2.196 <i>br s</i> 5-OH, 1.7 <i>m</i> H-7, 1.20 – 1.33 <i>m</i> H-8 – H-19, 0.880 <i>t</i> (7.0) H-20
¹³ C-NMR	(125 MHz, CDCl ₃) δ ¹³ C ppm: 207.3 C-1, 163.5 C-3, 133.5 C-2, 75.8 C-5, 73.3 C-6, 71.4 C-4, 31.2 C-7, 31.9, 29.68, 29.67, 29.65, 29.64, 29.61, 29.56, 29.51, 29.41, 29.35, 26.1, 22.7 C-8 – C-19, 14.1 C-20
ESI-FT-ICR-MS	<i>m/z</i> 363.24825 ([M+Na] ⁺ , ber. für C ₂₀ H ₃₆ NaO ₄ ⁺ 363.25058)
ESI-QqTOF-MS	(CE +15 eV, DP +20 V) <i>m/z</i> (rel. int., %): 341.2686 (4) (C ₂₀ H ₃₇ O ₄ ⁺), 323.2581 (100) (ber. für C ₂₀ H ₃₅ O ₃ ⁺ : 323.2581), 305.2492 (82) (ber. für C ₂₀ H ₃₃ O ₂ ⁺ : 305.2475), 287.2364 (27) (ber. für C ₂₀ H ₃₁ O ⁺ : 287.2369), 277.2525 (13) (ber. für C ₁₉ H ₃₃ O ⁺ : 277.2526), 269.2281 (8) (ber. für C ₂₀ H ₂₉ ⁺ : 269.2264), 259.2405 (30) (ber. für C ₁₉ H ₃₁ ⁺ : 259.2420), 165.0931 (26) (ber. für C ₁₀ H ₁₃ O ₂ ⁺ : 165.0910), 151.0743 (27) (ber. für C ₉ H ₁₁ O ₂ ⁺ : 151.0754), 123.0435 (35) (ber. für C ₇ H ₇ O ₂ ⁺ : 123.0441), 111.0431 (10) (ber. für C ₆ H ₇ O ₂ ⁺ : 111.0441).
(+)-ESI-CID-MS	(-15 eV) <i>m/z</i> (rel. int., %): 341 (3, [M+H] ⁺), 323 (100, [M+H-H ₂ O] ⁺), 305 (73, [M+H-2 H ₂ O] ⁺), 287 (30, [M+H-3 H ₂ O] ⁺), 259 (21, [M+H-3 H ₂ O-CO] ⁺), 245 (15), 165 (16), 147 (15), 123 (16, [C ₇ H ₇ O ₂] ⁺), 111 (10, [C ₆ H ₇ O ₂] ⁺)
(-)-ESI-CID-MS	(+20 eV) <i>m/z</i> (rel. int., %): 339 (9, [M-H] ⁻), 321 (42, [M-H-H ₂ O] ⁻), 277 (60, [M-H-H ₂ O-CO ₂] ⁻), 241 (100, [M-H-C ₅ H ₆ O ₂] ⁻), 295 (7, M-H-CO ₂] ⁻), 293 (10, [M-H-H ₂ O-CO] ⁻), 283 (24, [M-H-C ₃ H ₄ O] ⁻), 279 (10), 267 (21, [M-H-H ₂ O-C ₃ H ₂ O] ⁻), 255 (23, [M-H-C ₄ H ₄ O ₂] ⁻), 113 (16), 97 (45), 83 (13)

$[\alpha]_D^{23}$	+10.5° (MeOH; <i>c</i> 0.640)
$\nu_{\max}^{\text{film}} \text{ cm}^{-1}$	3509 (m), 3445 (m), 3403 (m), 3372 (m), 2954 (m), 2916 (s), 2871 (m), 2849 (s), 1715 (s), 1696 (s), 1676 (w), 1653 (w), 1595 (w), 1470 (m), 1399 (w), 1355 (w), 1243 (w), 1214 (w), 1115 (m), 1102 (vw), 1078 (m), 1011 (w), 983 (w), 946 (w), 919 (vw), 900 (vw), 843 (m), 791 (w), 720 (w), 687 (w)
DC	LM 1: $R_f = 0.22$, LM 2: $R_f = 0.41$

Hygrophoron B¹⁶ (45)

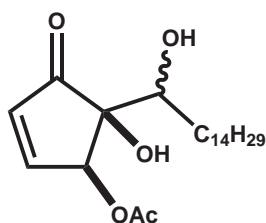


4,5-*cis*-4,5-Dihydroxy-5-(1-hydroxyheptadecyl)-2-cyclopenten-1-on

weißer Feststoff

isoliert aus *H. olivaceoalbus* (Fr.) Fr.

¹ H-NMR	(500 MHz, CDCl ₃) δ ¹ H ppm: 7.644 <i>dd</i> (6.0/2.3) H-3, 6.301 <i>dd</i> (6.0/1.3) H-2, 4.727 <i>dd</i> (2.3/1.3) H-4, 3.777 <i>br d</i> (10.1) H-6, 3.718 <i>br s</i> 6-OH, 3.073 <i>br s</i> 4-OH, 2.196 <i>br s</i> 5-OH, 1.7 <i>m</i> H-7, 1.2-1.4 <i>m</i> H-8 – H-21, 0.880 <i>t</i> (6.9) H-22
ESI-FT-ICR-MS	<i>m/z</i> 391.28259 ([M+Na] ⁺ , ber. für C ₂₂ H ₄₄ NaO ₄ ⁺ 391.28188)
(+)-ESI-CID-MS	(-15 eV) <i>m/z</i> (rel. int., %): 369 (7, [M+H] ⁺), 351 (100, [M+H-H ₂ O] ⁺), 333 (35, [M+H-2 H ₂ O] ⁺), 315 (31, [M+H-3 H ₂ O] ⁺), 287 (38, [M+H-3 H ₂ O-CO] ⁺), 259 (12), 241 (21), 147 (18), 123 (15, [C ₇ H ₇ O ₂] ⁺), 111 (20, [C ₆ H ₇ O ₂] ⁺)
(-)-ESI-CID-MS	(+20 eV) <i>m/z</i> (rel. int., %): 367 (24, [M-H] ⁻), 349 (48, [M-H-H ₂ O] ⁻), 305 (42, [M-H-H ₂ O-CO ₂] ⁻), 269 (100, [M-H-C ₅ H ₆ O ₂] ⁻), 323 (3, [M-H-CO ₂] ⁻), 321 (9, [M-H-H ₂ O-CO] ⁻), 311 (18, [M-H-C ₃ H ₄ O] ⁻), 295 (10, [M-H-H ₂ O-C ₃ H ₂ O] ⁻), 283 (24, [M-H-C ₄ H ₄ O ₂] ⁻), 113 (30), 97 (79), 95 (11), 83 (14)
DC	LM 1: $R_f = 0.22$, LM 2: $R_f = 0.41$

4-*O*-Acetylhygrophoron B¹⁴ (46)

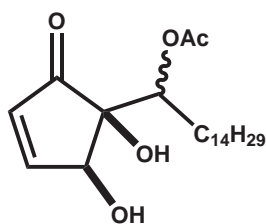
4,5-*cis*-4-Acetoxy-5-hydroxy-5-(1-hydroxypentadecyl)-2-cyclopenten-1-on

farbloses Öl

semisynthetisches Derivat von 44

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 7.588 *dd* (6.2/2.7) H-3, 6.438 *dd* (6.2/1.3) H-2, 5.722 *dd* (2.7/1.3) H-4, 3.818 *m* H-6, 2.156 *s* 4-OAc, 1.7 *m* H-7, 1.20 - 1.33 *m* H-8 - H-19, 0.880 *t* (7.0) H-20

ESI-FT-ICR-MS *m/z* 405.26155 ([M+Na]⁺, ber. für C₂₂H₃₈NaO₅⁺ 405.26115)

6-*O*-Acetylhygrophoron B¹⁴ (47)

4,5-*cis*-4,5-Dihydroxy-5-(1-acetoxypentadecyl)-2-cyclopenten-1-on

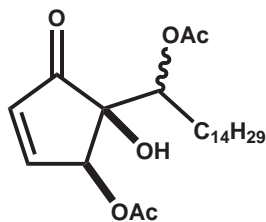
farbloses Öl

semisynthetisches Derivat von 44

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 7.640 *dd* (6.1/2.4) H-3, 6.300 *dd* (6.1/1.2) H-2, 5.177 *dd* (10.1/2.8) H-6, 4.793 *dd* (2.4/1.2) H-4, 2.000 *s* 6-OAc, 1.7 *m* H-7, 1.20 - 1.33 *m* H-8 - H-19, 0.880 *t* (7.0) H-20

¹³C-NMR (125 MHz, CDCl₃) δ ¹³C ppm: 205.9 C-1, 162.8 C-3, 132.9 C-2, 170.6 6-OAc, 76.1 C-5, 73.4 C-6, 71.5 C-4, 32 - 22 C-7 - C-19, 20.5 6-OAc, 14.0 C-20

ESI-FT-ICR-MS *m/z* 405.26155 ([M+Na]⁺, ber. für C₂₂H₃₈NaO₅⁺ 405.26115)

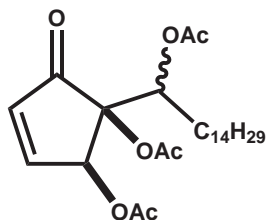
4,6-Di-*O*-acetylhygrophoron B¹⁴ (48)

4,5-*cis*-4-Acetoxy-5-hydroxy-5-(1-acetoxypentadecyl)-2-cyclopenten-1-on

farbloses Öl

semisynthetisches Derivat von 44

¹ H-NMR	(500 MHz, CDCl ₃) δ ¹ H ppm: 7.550 <i>dd</i> (6.2/2.8) H-3, 6.438 <i>dd</i> (6.2/1.2) H-2, 5.785 <i>dd</i> (2.8/1.2) H-4, 5.086 <i>dd</i> (9.7/3.6) H-4, 2.730 <i>s</i> 5-OH, 2.151 <i>s</i> 4-OH, 2.062 <i>s</i> 6-OH, 1.7 <i>m</i> H-7, 1.20 – 1.33 <i>m</i> H-8 – H-19, 0.880 <i>t</i> (7.0) H-20
¹³ C-NMR	(125 MHz, CDCl ₃) δ ¹³ C ppm: 204.2 C-1, 157.7 C-3, 135.4 C-2, 170.4 6-OAc, 169.8 4-OAc, 77.1 C-5, 73.8 C-6, 72.5 C-4, 32 – 22 C-7 – C-19, 20.71 OAc, 20.70 OAc, 14.0 C-20
ESI-FT-ICR-MS	<i>m/z</i> 447.27131 ([M+Na] ⁺ , ber. für C ₂₄ H ₄₀ NaO ₆ ⁺ 447.27171)
(+)-ESI-CID-MS	(-13 eV) <i>m/z</i> (rel. int., %): 425 (23, [M+H] ⁺), 407 (100, [M+H-H ₂ O] ⁺), 365 (73, [M+H-HOAc] ⁺), 323 (38, [M+H-HOAc-CH ₂ CO] ⁺), 305 (51, [M+H-2 HOAc] ⁺), 287 (11, [M+H-2 HOAc-H ₂ O] ⁺), 189 (7), 123 (24, [C ₇ H ₇ O ₂] ⁺), 111 (2, [C ₆ H ₇ O ₂] ⁺)
(-)-ESI-CID-MS	(+20 eV) <i>m/z</i> (rel. int., %): 423 (4, [M-H] ⁻), 405 (22, [M-H-H ₂ O] ⁻), 381 (13, [M-H-CH ₂ CO] ⁻), 363 (100, [M-H-HOAc] ⁻), 361 (2, [M-H-H ₂ O-CO ₂] ⁻), 351 (4, [M-H-H ₂ O-C ₃ H ₂ O] ⁻), 335 (19, [M-H-HOAc-CO] ⁻), 333 (12, [M-H-H ₂ O-CO-CO ₂] ⁻), 321 (73, [M-H-HOAc-CH ₂ CO] ⁻), 319 (15, [M-H-HOAc-CO ₂] ⁻), 303 (5, [M-H-2 HOAc] ⁻), 291 ([M-H-HOAc-CO-CO ₂] ⁻ , 35), 283 (11, [M-H-2 H ₂ O-HOAc-CO ₂] ⁻), 277 (18, [M-H-HOAc-CH ₂ CO-CO ₂] ⁻), 273 (25, [M-H-HOAc-H ₂ O-CO-CO ₂] ⁻), 197 (14), 181 (17), 139 (20, [C ₇ H ₇ O ₃] ⁻), 59 (48)
DC	LM 1: R _f = 0.57, LM 2: R _f = 0.52

4,5,6-Tri-*O*-acetylhygrophoron B¹⁴ (49)4,5-*cis*-4,5-Diacetoxy-(1-acetoxypentadecyl)-2-cyclopenten-1-on

farbloses Öl

semisynthetisches Derivat von 44

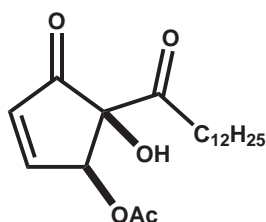
¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 7.432 *dd* (6.3/2.8) H-3, 6.470 *dd* (6.3/1.5) H-2, 5.967 *dd* (2.8/1.5) H-4, 5.227 *dd* (10.1/2.9) H-4, 2.102 *s* 4/5-OAc, 2.094 *s* 4/5-OAc, 2.002 *s* 6-OAc, 1.83 *m* H-7A, 1.69 *m* H-7B, 1.20 – 1.33 *m* H-8 – H-19, 0.880 *t* (7.0) H-20

¹³C-NMR (125 MHz, CDCl₃) δ ¹³C ppm: 200.4 C-1, 169.6 6-OAc, 169.2 4-OAc, 168.6 5-OAc, 154.7 C-3, 135.6 C-2, 79.1 C-6, 73.0 C-5, 70.7 C-4, 32 – 22 C-7 – C-19, 20.5 6-OAc, 20.3 4-OAc, 20.1 5-OAc, 14.0 C-20

ESI-FT-ICR-MS *m/z* 489.28213 ([M+Na]⁺, ber. für C₂₆H₄₂NaO₇⁺ 489.28227)

(+)-ESI-CID-MS (-13 eV) *m/z* (rel. int., %): 467 (2, [M+H]⁺), 407 (100, [M+H-HOAc]⁺), 365 (66, [M+H-HOAc-CH₂CO]⁺), 347 (3, [M+H-2 HOAc]⁺), 323 (9, [M+H-HOAc-2 CH₂CO]⁺), 305 (12, [M+H-2 HOAc-CH₂CO]⁺), 123 (3, [C₇H₇O₂]⁺)

ν_{\max}^{film} cm⁻¹ 5956 (m), 2922 (s), 2850 (s), 1760 (s), 1601 (w), 1468 (m), 1434 (m), 1371 (m), 1258 (s), 1122 (w), 1102 (w), 1047 (m), 1027 (m), 961 (w), 814 (w), 758 (w), 720 (w)

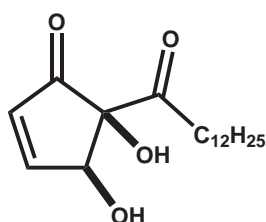
4-*O*-Acetylhygrophoron C¹² (50)*cis*-4-Acetoxy-5-hydroxy-5-tridecanoyl-2-cyclopenten-1-on

weißer Feststoff

isoliert aus *H. pustulatus* (Pers.) Fr.

$^1\text{H-NMR}$	(500 MHz, CDCl_3) δ ^1H ppm: 7.802 <i>dd</i> (6.0/2.6) H-3, 6.537 <i>dd</i> (6.0/1.6) H-2, 5.734 <i>dd</i> (2.6/1.6) H-4, 4.064 <i>s</i> 5-OH, 2.595 <i>ddd</i> (17.9/8.1/6.7) H-7A, 2.439 <i>ddd</i> (19.7/8.1/6.7) H-7B, 2.138 <i>s</i> 4-OAc, 1.619 <i>m</i> H-8, 1.20 – 1.33 <i>m</i> H-9 – H-17, 0.880 <i>t</i> (7.0) H-18
$^{13}\text{C-NMR}$	(125 MHz, CDCl_3) δ ^{13}C ppm: 205.3 C-6, 201.2 C-1, 170.1 4-OAc, 160.0 C-3, 135.4 C-2, 82.6 C-5, 73.6 C-4, 37.0 C-7, 31.9, 29.62, 29.60, 29.56, 29.4, 29.32, 29.30, 28.95, 23.0, 22.7 C-9 – C-17, 20.3 4-OAc, 14.1 C-18
ESI-FT-ICR-MS	m/z 387.19523 ($[\text{M}+\text{Cl}]^-$, ber. für $\text{C}_{20}\text{H}_{32}^{35}\text{ClO}_5^-$ 387.19438)
(+)-ESI-CID-MS	(-15 eV) m/z (rel. int., %): 353 (15, $[\text{M}+\text{H}]^+$), 335 (10, $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$), 311 (60, $[\text{M}+\text{H}-\text{CH}_2\text{CO}]^+$), 307 (100, $[\text{M}+\text{H}-\text{H}_2\text{O}-\text{CO}]^+$), 293 (52, $[\text{M}+\text{H}-\text{HOAc}]^+$), 275 (8, $[\text{M}+\text{H}-\text{HOAc}-\text{H}_2\text{O}]^+$), 265 (10, $[\text{M}+\text{H}-\text{HOAc}-\text{CO}]^+$), 197 (31, $[\text{C}_{13}\text{H}_{25}\text{O}]^+$), 139 (39, $[\text{C}_7\text{H}_7\text{O}_3]^+$), 123 (5, $[\text{C}_9\text{H}_{11}]^+$), 97 (4, $[\text{C}_5\text{H}_5\text{O}_2]^+$)
(-)-ESI-CID-MS	(+20 eV) m/z (rel. int., %): 351 (7, $[\text{M}-\text{H}]^-$), 333 (2, $[\text{M}-\text{H}-\text{H}_2\text{O}]^-$), 323 (3, $[\text{M}-\text{H}-\text{CO}]^-$), 309 (100, $[\text{M}-\text{H}-\text{CH}_2\text{CO}]^-$), 307 (3, $[\text{M}-\text{H}-\text{CO}_2]^-$), 291 (19, $[\text{M}-\text{H}-\text{HOAc}]^-$), 265 (36, $[\text{M}-\text{H}-\text{CH}_2\text{CO}-\text{CO}_2]^-$)
$\nu_{\text{max}}^{\text{film}} \text{ cm}^{-1}$	3360 (br, m), 3092 (vw), 3020 (vw), 2950 (m), 2918 (s), 2871 (m), 2850 (s), 1746 (s), 1725 (s), 1689 (s), 1593 (w), 1463 (m), 1404 (w), 1373 (m), 1344 (m), 1315 (w), 1272 (w), 1260 (w), 1227 (m), 1198 (m), 1154 (m), 1112 (w), 1093 (m), 1066 (m), 1046 (w), 955 (vw), 930 (vw), 915 (w), 900 (w), 882 (vw), 845 (w), 826 (vw), 795 (w), 756 (m), 746 (m), 729 (w), 717 (m)
DC	LM 1: $R_f = 0.60$, LM 2: $R_f = 0.58$

Hygrophoron C¹² (51)



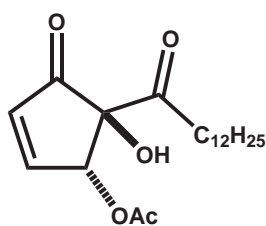
cis-4,5-Dihydroxy-5-tridecanoyl-2-cyclopenten-1-on

weißer Feststoff

isoliert aus *H. pustulatus* (Pers.) Fr.

$^1\text{H-NMR}$	(500 MHz, CDCl_3) δ ^1H ppm: 7.857 <i>dd</i> (6.0/2.4) H-3, 6.466 <i>dd</i> (6.0/1.3) H-2, 4.850 <i>ddd</i> (7.2/2.4/1.3) H-4, 4.646 <i>s</i> 5-OH, 3.046 <i>brd</i> (7.2) 4-OH, 2.452 <i>dt</i> (17.6/7.4) H-7A, 2.390 <i>dt</i> (17.6/7.3) H-7B, 1.612 <i>m</i> H-8, 1.22 – 1.32 <i>m</i> H-9 – H-17, 0.880 <i>t</i> (7.0) H-18
$^{13}\text{C-NMR}$	(125 MHz, CDCl_3) δ ^{13}C ppm: 205.7 C-6, 201.3 C-1, 164.8 C-3, 134.1 C-2, 82.4 C-5, 71.7 C-4, 37.1 C-7, 31.9, 29.61, 29.59, 29.5, 29.4, 29.33, 29.26, 29.0, 23.1, 22.7 C-9 – C-17, 14.1 C-18
ESI-FT-ICR-MS	m/z 345.18679 $[\text{M}+\text{Cl}]^-$, ber. für $\text{C}_{18}\text{H}_{30}^{35}\text{ClO}_4$ 345.18381)
70 eV-EIMS vom Methylboronat	m/z (rel. int., %): 334 ($[\text{M}]^+$, 4), 197 (58), 151 (12), 138 (51), 137 (100), 123 (11), 109 (21), 96 (37), 95 (44), 85 (26), 71 (46), 57 (67)
$\nu_{\text{max}}^{\text{film}}$ cm^{-1}	3416 (br, w), 2954 (m), 2922 (s), 2852 (s), 1728 (m), 1711 (m), 1465 (w), 1438 (w), 1399 (w), 1377 (w), 1341 (w), 1256 (w), 1226 (w), 1199 (w), 1173 (w), 1159 (w), 1111 (w), 1078 (w), 1018 (w), 758 (w), 720 (w)
DC	LM 1: $R_f = 0.31$, LM 2: $R_f = 0.48$

4-*O*-Acetylhygrophoron D¹² (52)



trans-4-Acetoxy-5-hydroxy-5-tridecanoyl-2-cyclopenten-1-on

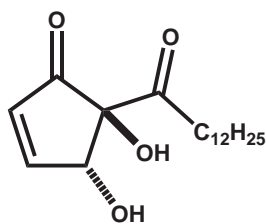
farbloses Öl

isoliert aus *H. latitabundus* Britz.

$^1\text{H-NMR}$	(500 MHz, CDCl_3) δ ^1H ppm: 7.701 <i>dd</i> (6.1/2.1) H-3, 6.591 <i>dd</i> (6.1/1.6) H-2, 5.827 <i>dd</i> (2.1/1.6) H-4, 4.622 <i>brs</i> 5-OH, 2.591 <i>ddd</i> (17.9/7.6/7.1) H-7A, 2.320 <i>ddd</i> (17.9/7.6/7.0) H-7B, 2.089 <i>s</i> 4-OAc, 1.566 <i>m</i> H-8, 1.24 – 1.26 <i>m</i> H-9 – H-17, 0.878 <i>t</i> (6.9) H-18
$^{13}\text{C-NMR}$	(125 MHz, CDCl_3) δ ^{13}C ppm: 202.7 C-6, 198.6 C-1, 169.5 4-OAc, 158.2 C-3, 136.0 C-2, 87.9 C-5, 80.4 C-4, 39.0 C-7, 32.0, 29.72, 29.70, 29.66, 29.50, 29.43, 29.42, 29.12, 23.3, 22.8 C-9 – C-17, 20.8 4-OAc, 14.3 C-18

ESI-FT-ICR-MS	m/z 375.21436 ($[M+Na]^+$, ber. für $C_{20}H_{32}NaO_5^+$ 375.21419)
(+)-ESI-CID-MS	(-15 eV) m/z (rel. int., %): 353 (13, $[M+H]^+$), 335 (3, $[M+H-H_2O]^+$), 311 (44, $[M+H-CH_2CO]^+$), 307 (8, $[M+H-H_2O-CO]^+$), 293 (42, $[M+H-HOAc]^+$), 265 (31, $[M+H-HOAc-CO]^+$), 197 (70, $[C_{13}H_{25}O]^+$), 139 (100, $[C_7H_7O_3]^+$), 97 (29)
(-)-ESI-CID-MS	(+20 eV) m/z (rel. int., %): 351 (33, $[M-H]^-$), 333 (36, $[M-H-H_2O]^-$), 323 (15, $[M-H-CO]^-$), 309 (26, $[M-H-CH_2CO]^-$), 307 (8, $[M-H-CO_2]^-$), 291 (35, $[M-H-HOAc]^-$), 265 (100, $[M-H-CH_2CO-CO_2]^-$), 263 (29, $[M-H-HOAc-CO]^-$), 305 (16, $[M-H-H_2O-CO]^-$), 289 (24), 279 (18), 239 (10), 139 (18, $[C_7H_7O_3]^-$), 113 (11)
$[\alpha]_D^{23}$	+111.7° (MeOH; c 0.470)
ν_{\max}^{film} cm^{-1}	3441 (br, m), 3081 (w), 2954 (m), 2923 (s), 2872 (m), 2853 (s), 1757 (s), 1746 (s), 1739 (s), 1731 (s), 1713 (s), 1591 (w), 1466 (m), 1401 (w), 1372 (m), 1349 (m), 1283 (w), 1224 (s), 1183 (w), 1143 (m), 1131 (m), 1093 (m), 1035 (m), 981 (w), 960 (w), 897 (w), 821 (w), 758 (w), 722 (w)
DC	LM 1: $R_f = 0.65$, LM 2: $R_f = 0.53$

Hygrophoron D¹² (53)



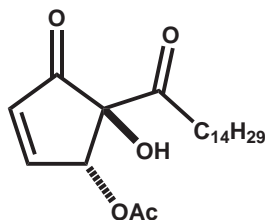
trans-4,5-Dihydroxy-5-tridecanoyl-2-cyclopenten-1-on

farbloses Öl

isoliert aus *H. latitabundus* Britz.

¹ H-NMR	(500 MHz, CDCl ₃) δ ¹ H ppm: 7.722 <i>dd</i> (6.1/2.0) H-3, 6.446 <i>dd</i> (6.1/1.7) H-2, 4.942 <i>dd</i> (2.0/1.7) H-4, 2.643 <i>ddd</i> (18.3/8.0/6.9) H-7A, 2.464 <i>ddd</i> (18.3/8.0/6.5) H-7B, 1.65 <i>m</i> H-8, 1.2 – 1.4 <i>m</i> H-9 – H-17, 0.880 <i>t</i> (7.0) H-18
¹³ C-NMR	(125 MHz, CDCl ₃) δ ¹³ C ppm: 205.8 C-6, 199.5 C-1, 162.7 C-3, 133.4 C-2, 91.5 C-5, 79.5 C-4, 39.2 C-7, 32.0, 29.74, 29.73, 29.68, 29.52, 29.45, 29.44, 29.0, 23.0, 22.8 C-8 – C-17, 14.1 C-18

ESI-FT-ICR-MS	m/z 333.20417 ($[M+Na]^+$, ber. für $C_{18}H_{30}NaO_4^+$ 333.20363)
(+)-ESI-CID-MS	(-15 eV) m/z (rel. int., %): 311 (76, $[M+H]^+$), 293 (83, $[M+H-H_2O]^+$), 265 (79, $[M+H-H_2O-CO]^+$), 215 (25, $[C_{13}H_{27}O_2]^+$), 197 (100, $[C_{13}H_{25}O]^+$), 123 (20, $[C_9H_{15}]^+$), 109 (19), 95 (38), 97 (40, $[C_5H_5O_2]^+$)
(-)-ESI-CID-MS	(+20 eV) m/z (rel. int., %): 309 (34, $[M-H]^-$), 291 (14, $[M-H-H_2O]^-$), 281 (49, $[M-H-CO]^-$), 265 (100, $[M-H-CO_2]^-$), 263 (56, $[M-H-H_2O-CO]^-$), 253 (30, $[M-H-2 CO]^-$), 247 (45, $[M-H-CO_2-H_2O]^-$), 237 (34, $[M-H-CO_2-CO]^-$), 235 (14), 113 (3)
ESI-QqTOF-MS	(CE -20 eV, DP -50 V) m/z (rel. int., %): 309.2071 (100) ($C_{18}H_{29}O_4^-$), 291.1967 (14) (ber. für $C_{18}H_{27}O_3^-$: 291.1966), 281.2107 (50) (ber. für $C_{17}H_{29}O_3^-$: 281.2122), 265.2179 (91) (ber. für $C_{17}H_{29}O_2^-$: 265.2173), 263.2032 (30) (ber. für $C_{17}H_{27}O_2^-$: 263.2017), 253.2164 (23) (ber. für $C_{16}H_{29}O_2^-$: 253.2173), 247.2096 (33) (ber. für $C_{17}H_{27}O^-$: 247.2067), 237.2224 (16) (ber. für $C_{16}H_{29}O^-$: 237.2224), 235.2072 (6) (ber. für $C_{16}H_{27}O^-$: 235.2067), 213.1879 (11) (ber. für $C_{13}H_{25}O_2^-$: 213.1860), 113.0254 (10) (ber. für $C_5H_5O_3^-$: 113.0244).
ESI-QqTOF-MS	(CE +20 eV, DP +50 V) m/z (rel. int., %): 311.2217 (100) ($C_{18}H_{31}O_4^+$), 293.2120 (21) (ber. für $C_{18}H_{29}O_3^+$: 293.2111), 265.2177 (19) (ber. für $C_{17}H_{29}O_2^+$: 265.2162), 251.2019 (4) (ber. für $C_{16}H_{27}O_2^+$: 251.2006), 215.1973 (5) (ber. für $C_{13}H_{27}O_2^+$: 215.2006), 197.1907 (60) (ber. für $C_{13}H_{25}O^+$: 197.1900), 139.0397 (62) (ber. für $C_7H_7O_3^+$: 139.0390), 123.1164 (18) (ber. für $C_9H_{15}^+$: 123.1168), 109.1022 (18) (ber. für $C_8H_{13}^+$: 109.1012), 97.0330 (6) (ber. für $C_5H_5O_2^+$: 97.0284), 95.0870 (13) (ber. für $C_7H_{11}^+$: 95.0855).
$\nu_{\max}^{\text{film}} \text{ cm}^{-1}$	3416 (br, m), 2952 (m), 2924 (s), 2853 (s), 1729 (s), 1712 (s), 1629 (w), 1464 (m), 1438 (w), 1406 (m), 1376 (m), 1236 (m), 1180 (m), 1149 (m), 1125 (m), 1080 (w), 1047 (w), 977 (w), 822 (vw), 722 (vw)
DC	LM 1: $R_f = 0.26$, LM 2: $R_f = 0.41$

4-*O*-Acetylhygrophoron D¹⁴ (54)

trans-4-Acetoxy-5-hydroxy-5-pentadecanoyl-2-cyclopenten-1-on

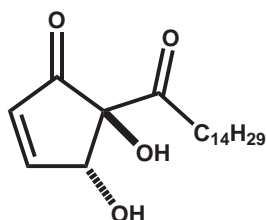
farbloses Öl

isoliert aus *H. latitabundus* Britz.

¹ H-NMR	(500 MHz, CDCl ₃) δ ¹ H ppm: 7.700 <i>dd</i> (6.2/2.1) H-3, 6.591 <i>dd</i> (6.2/1.7) H-2, 5.826 <i>dd</i> (2.1/1.7) H-4, 4.613 <i>s</i> 5-OH, 2.590 <i>ddd</i> (17.9/7.2/7.1) H-7A, 2.319 <i>ddd</i> (17.9/7.5/6.7) H-7B, 2.088 <i>s</i> 4-OAc, 1.619 <i>m</i> H-8, 1.20 – 1.33 <i>m</i> H-9 – H-19, 0.878 <i>t</i> (6.8) H-20
¹³ C-NMR	(125 MHz, CDCl ₃) δ ¹³ C ppm: 202.7 C-6, 198.6 C-1, 169.5 4-OAc, 158.2 C-3, 136.0 C-2, 88.0 C-5, 80.4 C-4, 39.0 C-7, 32.0, 29.78, 29.76, 29.74, 29.73, 29.47, 29.51, 29.45, 29.44, 29.13, 23.3, 22.8: C-8 – C-19, 20.8 4-OAc, 14.3 C-20
ESI-FT-ICR-MS	<i>m/z</i> 403.24474 ([M+Na] ⁺ , ber. für C ₂₂ H ₃₇ NaO ₅ ⁺ 403.24604)
(+)-ESI-CID-MS	(-15 eV) <i>m/z</i> (rel. int., %): 339 (56, [M+H] ⁺), 321 (100, [M+H-H ₂ O] ⁺), 293 (47, [M+H-H ₂ O-CO] ⁺), 243 (27, [C ₁₅ H ₃₁ O ₂] ⁺), 225 (85, [C ₁₅ H ₂₉ O] ⁺), 123 (14, [C ₉ H ₁₅] ⁺), 109 (12), 97 (21, [C ₅ H ₅ O ₂] ⁺), 95 (14)
(-)-ESI-CID-MS	(+20 eV) <i>m/z</i> (rel. int., %): 337 (54, [M-H] ⁻), 319 (14, [M-H-H ₂ O] ⁻), 309 (49, [M-H-CO] ⁻), 293 (100, [M-H-CO ₂] ⁻), 291 (46, [M-H-H ₂ O-CO] ⁻), 281 (22, [M-H-2CO] ⁻), 275 (40, [M-H-CO ₂ -H ₂ O] ⁻), 265 (24, [M-H-CO ₂ -CO] ⁻), 241 (10)
ESI-QqTOF-MS	(CE -20 eV, DP -50 V) <i>m/z</i> (rel. int., %): 337.2384 (100) (C ₂₀ H ₃₃ O ₄ ⁻), 319.2264 (10) (ber. für C ₂₀ H ₃₁ O ₃ ⁻ : 319.2279), 309.2432 (30) (ber. für C ₁₉ H ₃₃ O ₃ ⁻ : 309.2435), 293.2483 (62) (ber. für C ₁₉ H ₃₃ O ₂ ⁻ : 293.2486), 291.2350 (18) (ber. für C ₁₉ H ₃₁ O ₂ ⁻ : 291.2330), 281.2478 (13) (ber. für C ₁₈ H ₃₃ O ₂ ⁻ : 281.2486), 275.2387 (22) (ber. für C ₁₉ H ₃₁ O ⁻ : 275.2380), 265.2552 (8) (ber. für C ₁₈ H ₃₃ O ⁻ : 265.2537), 263.2407 (3) (ber. für C ₁₈ H ₃₁ O ⁻ : 263.2380), 241.2215 (6) (ber. für C ₁₅ H ₂₉ O ₂ ⁻ : 241.2173), 113.0256 (7) (ber. für C ₅ H ₅ O ₃ ⁻ : 113.0244).

ESI-QqTOF-MS	(CE +20 eV, DP +50 V) m/z (rel. int., %): 339.2530 (100) ($C_{20}H_{35}O_4^+$), 321.2445 (38) (ber. für $C_{20}H_{33}O_3^+$: 321.2424), 293.2495 (21) (ber. für $C_{19}H_{33}O_2^+$: 293.2475), 279.2326 (30) (ber. für $C_{18}H_{31}O_2^+$: 279.2319), 243.2326 (18) (ber. für $C_{15}H_{31}O_2^+$: 243.2319), 225.2231 (90) (ber. für $C_{15}H_{29}O^+$: 225.2213), 139.0401 (27) (ber. für $C_7H_7O_3^+$: 139.0390), 123.1176 (31) (ber. für $C_9H_{15}^+$: 123.1168), 109.1030 (30) (ber. für $C_8H_{13}^+$: 109.1012), 97.0310 (15) (ber. für $C_5H_5O_2^+$: 97.0284), 95.0880 (24) (ber. für $C_7H_{11}^+$: 95.0855).
$[\alpha]_D^{23}$	+98.7° (MeOH; c 0.475)
$\nu_{\max}^{\text{film}} \text{ cm}^{-1}$	3446 (br, m), 3080 (w), 2955 (m), 2923 (s), 2853 (s), 1734 (s), 1711 (s), 1591 (w), 1465 (m), 1400 (w), 1371 (m), 1326 (w), 1282 (w), 1225 (s), 1185 (w), 1131 (m), 1097 (m), 1086 (m), 1035 (m), 981 (w), 897 (w), 822 (w), 762 (vw); 721 (vw)
DC	LM 1: $R_f = 0.65$, LM 2: $R_f = 0.53$

Hygrophoron D¹⁴ (55)



trans-4,5-Dihydroxy-5-pentadecanoyl-2-cyclopenten-1-on

Reinheit ca. 50% (¹H-NMR)

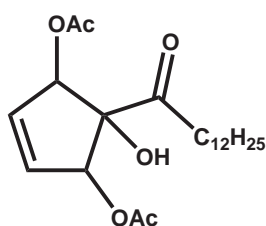
semisynthetisches Derivat von 54

¹ H-NMR	(400 MHz, CDCl ₃) δ ¹ H ppm: 7.736 <i>dd</i> (6.1/2.0) H-3, 6.455 <i>dd</i> (6.1/1.6) H-2, 4.953 <i>dd</i> (2.0/1.6)
ESI-FT-ICR-MS	m/z 361.23554 ($[M+Na]^+$, ber. für $C_{20}H_{34}NaO_4^+$ 361.23493)
(+)-ESI-CID-MS	(-15 eV) m/z (rel. int., %): 381 (2, $[M+H]^+$), 339 (20, $[M+H-CH_2CO]^+$), 321 (72, $[M+H-HOAc]^+$), 293 (17, $[M+H-HOAc-CO]^+$), 225 (58, $[C_{15}H_{29}O]^+$), 139 (100, $[C_7H_7O_3]^+$), 97 (11, $[C_5H_5O_2]^+$)

(-)-ESI-CID-MS (+20 eV) m/z (rel. int., %): 379 (48, [M-H]⁻), 361 (21, [M-H-H₂O]⁻), 351 (10, [M-H-CO]⁻), 337 (21, [M-H-CH₂CO]⁻), 335 (17, [M-H-CO₂]⁻), 319 (24, [M-H-HOAc]⁻), 293 (100, [M-H-CH₂CO-CO₂]⁻), 291 (24, [M-H-HOAc-CO]⁻), 317 (16), 307 (23), 139 (13, [C₇H₇O₃]⁻), 113 (8)

DC LM 1: $R_f = 0.28$, LM 2: $R_f = 0.46$

1,4-Di-*O*-acetylhygrophoron E¹² (56)



1-(2,5-Diacetoxy-1-hydroxy-cyclopent-3-enyl)-tridecan-1-on

farbloses Öl

isoliert aus *H. latitabundus* Britz.

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 6.190 *ddd* (6.1/1.9/1.1) H-3, 6.159 *ddd* (6.1/2.1/1.1) H-2, 5.724 *ddd* (2.0/1.9/1.1) H-4, 5.707 *ddd* (2.1/2.0/1.1) H-1, 4.003 *br s* 5-OH, 2.659 *ddd* (17.8/9.0/6.0) H-7A, 2.589 *ddd* (17.8/8.8/6.1) H-7B, 2.108 *s* 1-OAc, 2.018 *s* 4-OAc, 1.20 – 1.33 *m* H-8 – H-17, 0.881 *t* (7.0) H-18

¹³C-NMR (125 MHz, CDCl₃) δ ¹³C ppm: 207.7 C-6, 170.4 1-OAc, 169.7 4-OAc, 134.5 C-3, 133.8 C-2, 86.2 C-4, 83.6 C-5, 77.5 C-1, 38.3 C-7, 32.0, 29.75, 29.73, 29.71, 29.59, 29.57, 29.45, 29.37, 23.7, 22.8 C-8 – C-17, 21.0 4-OAc, 20.8 1-OAc, 14.3 C-18

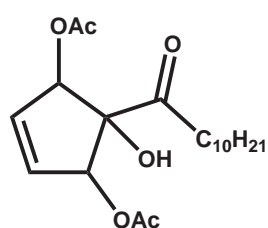
ESI-FT-ICR-MS m/z 419.24159 ([M+Na]⁺, ber. für C₂₂H₃₆NaO₆⁺ 419.24041)

(+)-ESI-CID-MS (-15 eV) m/z (rel. int., %): 397 (68, [M+H]⁺), 365 (10), 379 (13, [M+H-H₂O]⁺), 347 (8), 337 (30, [M+H-HOAc]⁺), 309 (11, [M+H-HOAc-CO]⁺), 295 (71, [M+H-HOAc-CO]⁺), 277 (15, [M+H-HOAc-CO-H₂O]⁺), 249 (18), 197 (100, [C₁₃H₂₅O]⁺), 97 (11, [C₅H₅O₂]⁺)

(-)-ESI-CID-MS (+20 eV) m/z (rel. int., %): 395 (8, [M-H]⁻), 335 (30, [M-H-HOAc]⁻), 317 (10, [M-H-HOAc-H₂O]⁻), 293 (71, [M-H-HOAc-CH₂CO]⁻), 265 (100, [M-H-HOAc-CH₂CO-CO]⁻), 237 (5), 59 (7)

$[\alpha]_D^{23}$	+80.3° (MeOH; <i>c</i> 0.395)
$\nu_{\max}^{\text{film}} \text{ cm}^{-1}$	3449 (br, m), 3073 (w), 2954 (m), 2924 (s), 2853 (s), 1744 (s), 1718 (s), 1465 (w), 1435 (w), 1372 (m), 1319 (vw), 1300 (vw), 1225 (s), 1154 (vw), 1114 (vw), 1024 (m), 967 (w), 915 (w), 831 (vw), 786 (vw), 721 (vw)
DC	LM 1: $R_f = 0.72$, LM 2: $R_f = 0.64$

1,4-Di-*O*-acetylhygrophoron E¹⁰ (57)



1-(2,5-Diacetoxy-1-hydroxy-cyclopent-3-enyl)-undecan-1-on

farbloses Öl

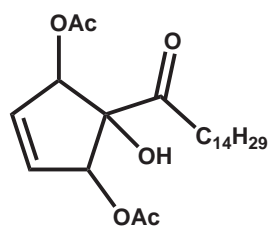
isoliert aus *H. latitabundus* Britz.

¹ H-NMR	(500 MHz, CDCl ₃) δ ¹ H ppm: 6.190 <i>ddd</i> (6.1/1.9/1.1) H-3, 6.159 <i>ddd</i> (6.1/2.1/1.1) H-2, 5.724 <i>ddd</i> (2.0/1.9/1.1) H-4, 5.707 <i>ddd</i> (2.1/2.0/1.1) H-1, 4.003 <i>brs</i> 5-OH, 2.659 <i>ddd</i> (17.8/9.0/6.0) H-7A, 2.589 <i>ddd</i> (17.8/8.8/6.1) H-7B, 2.108 <i>s</i> 1-OAc, 2.018 <i>s</i> 4-OAc, 1.20 – 1.33 <i>m</i> H-8 – H-15, 0.881 <i>t</i> (7.0) H-16
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ESI-FT-ICR-MS	<i>m/z</i> 391.21037 ([M+Na] ⁺ , ber. für C ₂₀ H ₃₂ NaO ₆ ⁺ 391.20911)
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DC	LM 1: $R_f = 0.72$, LM 2: $R_f = 0.64$
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1,4-Di-*O*-acetylhygrophoron E¹⁴ (58)



1-(2,5-Diacetoxy-1-hydroxy-cyclopent-3-enyl)-pentadecan-1-on

farbloses Öl

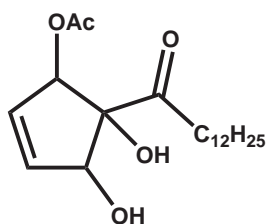
isoliert aus *H. latitabundus* Britz.

¹ H-NMR	(500 MHz, CDCl ₃) δ ¹ H ppm: 6.190 <i>ddd</i> (6.1/1.9/1.1) H-3, 6.159 <i>ddd</i> (6.1/2.1/1.1) H-2, 5.724 <i>ddd</i> (2.0/1.9/1.1) H-4, 5.707 <i>ddd</i> (2.1/2.0/1.1) H-1, 4.003 <i>brs</i> 5-OH, 2.659 <i>ddd</i> (17.8/9.0/6.0) H-7A, 2.589 <i>ddd</i> (17.8/8.8/6.1) H-7B, 2.108 <i>s</i> 1-OAc, 2.018 <i>s</i> 4-OAc, 1.20 – 1.33 <i>m</i> H-8 – H-19, 0.881 <i>t</i> (7.0) H-20
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ESI-FT-ICR-MS m/z 447.27530 ($[M+Na]^+$, ber. für $C_{24}H_{40}NaO_6^+$ 447.27171)

DC LM 1: $R_f = 0.72$, LM 2: $R_f = 0.64$

1-*O*-Acetylhygrophoron E¹² (59)



1-(2-Acetoxy-1,5-dihydroxy-cyclopent-3-enyl)-tridecan-1-on

farbloses Öl

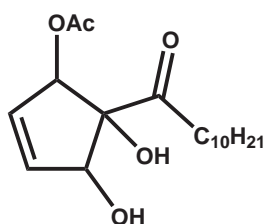
isoliert aus *H. latitabundus* Britz.

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 6.192 ddd (6.0/2.0/1.0) H-3, 6.058 ddd (6.0/2.2/1.2) H-2, 5.659 ddd (2.2/1.5/1.0) H-1, 4.932 ddd (2.0/1.4/1.4) H-4, 2.698 ddd (17.7/8.2/6.7) 7A, 2.541 ddd (17.7/8.2/6.6) 7B, 2.018 s 1-OAc, 1.20 – 1.33 m H-8 – H-17, 0.881 t (7.0) H-18

ESI-FT-ICR-MS m/z 377.23029 ($[M+Na]^+$, ber. für $C_{20}H_{34}NaO_5^+$ 377.22984)

DC LM 1: $R_f = 0.46$, LM 2: $R_f = 0.55$

1-*O*-Acetylhygrophoron E¹⁰ (60)



1-(2-Acetoxy-1,5-dihydroxy-cyclopent-3-enyl)-undecan-1-on

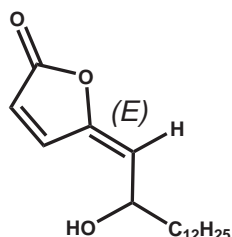
farbloses Öl

isoliert aus *H. latitabundus* Britz.

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 6.192 ddd (6.0/2.0/1.0) H-3, 6.058 ddd (6.0/2.2/1.2) H-2, 5.659 ddd (2.2/1.5/1.0) H-1, 4.932 ddd (2.0/1.4/1.4) H-4, 2.698 ddd (17.7/8.2/6.7) 7A, 2.541 ddd (17.7/8.2/6.6) 7B, 2.018 s 1-OAc, 1.20 – 1.33 m H-8 – H-15, 0.881 t (7.0) H-16

ESI-FT-ICR-MS m/z 349.20050 ($[M+Na]^+$, ber. für $C_{18}H_{30}NaO_5^+$ 349.19854)

DC LM 1: $R_f = 0.46$, LM 2: $R_f = 0.55$

Hygrophoron F¹² (40)(5*E*)-5-(2-Hydroxytetradexylidene)-furan-2(5*H*)-on

weißer Feststoff

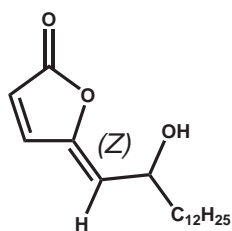
isoliert aus *H. latitabundus* Britz.

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 7.794 *dd* (5.6/0.8) H-3, 6.256 *dd* (5.6/1.8) H-2, 5.756 *ddd* (8.1/1.8/0.8) H-5, 4.52 *m* H-6, 1.7 *m* H-7, 1.2 – 1.4 *m* H-8 - H-17, 0.881 *t* (7.0) H-18

¹³C-NMR (125 MHz, CDCl₃) δ ¹³C ppm: 169.1 C-1, 150.3 C-4, 140.5 C-3, 121.0 C-2, 117.3 C-5, 68.3 C-6, 38.1 C-7, 32.0, 29.72, 29.71, 29.69, 29.62, 29.57, 29.5, 29.4, 25.3, 22.8 C-8 - C-17, 14.2 C-18

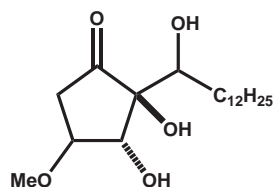
ESI-FT-ICR-MS *m/z* 317.20921 ([M+Na]⁺, ber. für C₁₈H₃₀NaO₃⁺ 317.20872)

ν_{\max}^{film} cm⁻¹ 3487 (m), 3396 (br, m), 3269 (br, m), 3133 (w), 3100 (w), 3074 (w), 2953 (m), 2918 (s), 2850 (s), 1785 (m), 1751 (s), 1718 (w), 1669 (w), 1554 (w), 1466 (w), 1372 (vw), 1297 (vw), 1237 (w), 1195 (vw), 1122 (w), 1077 (w), 1064 (w), 1035 (w), 1019 (w), 1008 (vw), 920 (w), 908 (w), 894 (w), 840 (vw), 816 (w), 757 (w), 711 (w)

Hygrophoron G¹² (41)(5*Z*)-5-(2-Hydroxytetradexylidene)-furan-2(5*H*)-onisoliert aus *H. persoonii* Arnolds

¹H-NMR (500 MHz, CDCl₃) δ ¹H ppm: 7.372 *dd* (5.5/0.4) H-3, 6.230 *dd* (5.5/0.7) H-2, 5.326 *ddd* (8.4/0.7/0.4) H-5, 4.793 *m* H-6, 1.7 *m* H-7, 1.2 – 1.4 *m* H-8 - H-17, 0.881 *t* (7.0) H-18

ESI-FT-ICR-MS *m/z* 317.21078 ([M+Na]⁺, ber. für C₁₈H₃₀NaO₃⁺ 317.20872)

2,3-Dihydroxy-2-(1-hydroxytridecyl)-4-methoxycyclopentanon (**38**)

2,3-Dihydroxy-2-(1-hydroxytridecyl)-4-methoxycyclopentanon

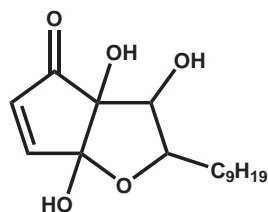
farbloses Öl

semisynthetisches Derivat von **31**

$^1\text{H-NMR}$ (500 MHz, CDCl_3) δ ^1H ppm: 4.073 *ddd* (8.8/5.3/4.5) H-4, 2.956 *ddd* (19.4/8.8/0.7) 5A, 2.360 *ddd* (19.4/4.5/0.7) 5B, 3.435 *s* 4-OMe, 4.224 *dd* (5.3/0.7) H-3, 3.916 *ddd* (10.2/4.3/1.6) H-6

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ ^{13}C ppm: 214.6 C-1, 83.0 C-2, 82.6 C-3, 80.5 C-4, 73.2 C-6, 57.6 4-OMe, 41.9 C-5, 31-22 C-7 – C17, 14.4 C-18

ESI-FT-ICR-MS m/z 367.24501 ($[\text{M}+\text{Na}]^+$, ber. für $\text{C}_{19}\text{H}_{36}\text{NaO}_5^+$ 367.24549)

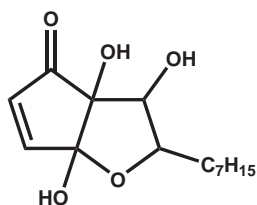
F-15784 (**86**)3,3a,6a-Trihydroxy-2-undecyl-2,3,3a,6a-tetrahydro-4H-cyclopenta[*b*]furan-4-onReinheit ca. 45% ($^1\text{H-NMR}$)nachgewiesen in *Rigidoporus lineatus* (Pers.) Ryvarden

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ^1H ppm: 7.573 *d* (6.2) H-3, 6.115 *d* (6.2) H-2

ESI-FT-ICR-MS m/z 321.16775 ($[\text{M}+\text{Na}]^+$, ber. für $\text{C}_{16}\text{H}_{26}\text{NaO}_5^+$ 321.16724)

(-)-ESI-CID-MS (+20 eV) m/z (rel. int., %): 297 (4, $[\text{M}-\text{H}]^-$), 111 (100, $[\text{C}_5\text{H}_3\text{O}_3]^-$)

Homologes von F-15784 (87)



2-Heptyl-3,3a,6a-trihydroxy-2,3,3a,6a-tetrahydro-4*H*-cyclopenta[*b*]furan-4-on

Reinheit ca. 45% ($^1\text{H-NMR}$)

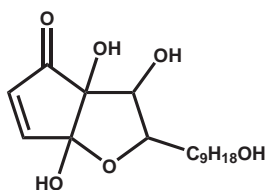
nachgewiesen in *Rigidoporus lineatus* (Pers.) Ryvardeen

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ^1H ppm: 7.573 *d* (6.2) H-3, 6.113 *d* (6.2) H-2

ESI-FT-ICR-MS m/z 293.13624 ($[\text{M}+\text{Na}]^+$, ber. für $\text{C}_{14}\text{H}_{22}\text{NaO}_5^+$ 293.13594)

(-)-ESI-CID-MS (+20 eV) m/z (rel. int., %): 269 (3, $[\text{M}-\text{H}]^-$), 111 (100, $[\text{C}_5\text{H}_3\text{O}_3]^-$)

Hydroxy-Derivat von F-15784 (88)



3,3a,6a-Trihydroxy-2-(9-hydroxynonyl)-2,3,3a,6a-tetrahydro-4*H*-cyclopenta[*b*]furan-4-on

Reinheit ca. 50% ($^1\text{H-NMR}$)

nachgewiesen in *Rigidoporus lineatus* (Pers.) Ryvardeen

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ^1H ppm: 7.566 *d* (6.2) H-3, 6.115 *d* (6.2) H-2

ESI-FT-ICR-MS m/z 337.16280 ($[\text{M}+\text{Na}]^+$, ber. für $\text{C}_{16}\text{H}_{26}\text{NaO}_6^+$ 337.16216)

(-)-ESI-CID-MS (+20 eV) m/z (rel. int., %): 313 (4, $[\text{M}-\text{H}]^-$), 111 (100, $[\text{C}_5\text{H}_3\text{O}_3]^-$)

