Tabelle 1. <sup>1</sup>H-NMR-Daten von **6–8** und 16 (270 MHz,  $CDCl_3$ ,  $\delta$ -Werte)

	6	7	8	16
3-H	d 5.61	d 5.51	d 5.68	d 4.35
4-H	d 6.27	d 6.30	d 6.32	
5-H	s 7.11	s 7.73	d 7.43	s 7.82
7-H		-	d 7.26	_
8-H	s 6.38	s 6.35		s 6.40
9-H	_	_		q(br) 5.05
10-H	d 4.79	d 4.64	s 2.52	d 1.51
11,12-H	s 1.46	s 1.44	s 1.49	s 1.64
OCH,		s 3.86	_	s 3.90
ОН	11.86		s 7.75	d 3.79

J(Hz): 3,4 = 9.5; 6/7: 10, OH = 4; 8: 5,7 = 2; 16: 9,10 = 7; 3, OH = 2.5.

acetophenon-Derivate eher für die nächste Subtribus Helianthinae typisch sind, wo ebenfalls Kaurensäure-Derivate häufig vorkommen.

### **EXPERIMENTELLES**

IR: Beckman IR 9 (CCl<sub>4</sub>): <sup>1</sup>H-NMR. Bruker WH 270, CDCl<sub>3</sub>: MS: Varian MAT 711, 70 eV, Direkteinlaß. Die lufttrockenen zerkleinerten Pflanzenteile (Herbar Nr. RMK 7347) extrahierte man mit Et<sub>2</sub>O-Petrol 1:2 und trennte die erhaltenen Extrakte zunächt durch SC (Si gel, Akt.-St. II) und weiter durch mehrfache DC (Si gel, GF 254). 350 g Wurzeln ergaben Spuren von 1, 280 mg 2, 700 mg 12 und 14 (ca 2:1). 50 mg 13, 2 mg 3, 2 mg 4, 3 mg 5, 10 mg 8 (Et<sub>2</sub>O-Petrol 1:1), 35 mg 7 (Et<sub>2</sub>O-Petrol 1:1), 30 mg 6 (Et<sub>2</sub>O), 60 mg 9, 3 mg 10, 7 mg 11, 15 mg 15, 5 mg 16 (Et<sub>2</sub>O) und 3 mg 17. 65 g oberirdische Teile lieferten 20 mg 12, 15 mg 13, 4 mg 9 und 1 mg 5.

2-Hydroxy-7-methoxy-6-(1-hydroxyethyl)-2,3-dimethyl-chroman-4-on (16). Farbloses Öl, IR: OH 3610, 3480 (brückengebunden); PhCO 1685, 1612, 1575 cm<sup>-1</sup>. UV (Et<sub>2</sub>O) max: 314, 271 nm. MS:  $M^+$  m/e 266.115 (28%) (ber. für  $C_{14}H_{18}O_5$  266.115);  $-CH_3$  251 (33);  $-(H_3C)_2C=COH$  195 (100).

$$[\alpha]_{24^{\circ}}^{\lambda} = \frac{589}{-49} \frac{578}{-51} \frac{546}{-62} \frac{436}{-156^{\circ}} (c = 0.21).$$

 $3\alpha$ ,7-Dihydroxy-5,4-dimethoxyflavan (17): Farbloses Öl, MS: M<sup>+</sup> m/e 302.115 (32 %) (C<sub>17</sub>H<sub>18</sub>O<sub>5</sub>).

Desacetyl-ripariochromen B (6): Farbloses Öl, IR (CHCl<sub>3</sub>): OH 3490; C=O (brückengebunden) 1640; C=C 1610; Aromat 1580 cm<sup>-1</sup> UV (Et<sub>2</sub>O) max: 340, 257 nm. MS: M<sup>+</sup> m/e 234.089 (42 °<sub>o</sub>) (C<sub>13</sub>H<sub>14</sub>O<sub>4</sub>); -CH<sub>3</sub> 219 (100); -OH 217 (22); -CH<sub>2</sub>OH 203 (75); 219 -H<sub>2</sub>O 201 (81).

7-(0)-Methyl-desacetylripariochromen B (7): Farblose Kristalle aus Et<sub>2</sub>O-Petrol, Schmp. 138°. IR: OH 3560; PhCO 1680, 1600; C=C 1630 cm<sup>-1</sup>. UV (Et<sub>2</sub>O) max · 330, 255 nm. MS. M<sup>+</sup> m/e 248.105 (28%) (C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>); -··CH<sub>3</sub> 233 (40), -··CH<sub>2</sub>OH 217 (100).

8-Hydroxy-6-acetyl-2,2-dimethylchromen (8): Farblose Kristalle aus Et<sub>2</sub>O-Petrol, Schmp. 132°. IR: OH 3470; Ph 1655, 1605, 1560 cm<sup>-1</sup>. UV (Et<sub>2</sub>O) max: 255, 247 nm. MS. M<sup>+</sup> m/e 218.094 (27%) (C<sub>13</sub>H<sub>14</sub>O<sub>3</sub>); -- CH<sub>3</sub> 203 (100).

Anerkennung—Herrn Dr. R. M. King, Smithsonian Institution, Washington, danken wir für das Pflanzenmaterial, der Deutschen Forschungsgemeinschaft für die Förderung dieser Arbeit.

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Phytochemistry, 1978, Vol. 17, pp. 1678-1679 C Pergamon Press Ltd. Printed in England

0031 -9422/78/0901-1678 \$02 00/0

# NOVEL 7-PHENYLHEPTAN-3-ONES FROM THE FUNGUS PHELLINUS TREMULAE

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## (Received 27 February 1978)

Key Word Index—*Phellinus tremulae*; Hymenochaetaceae; fungitoxic excretion; oxidized phenylheptanes; new  $\beta$ -ketol 5-hydroxy-7-phenylheptan-3-one; synthesis; 7-phenylheptan-3-one; 7-phenylheptan-3-ol.

Work in this Institute [1] has shown that a fungitoxic product can be isolated from decayed wood of European aspen (*Populus tremula L.*) infected by the widespread and economically important wood-rotting fungus *Phellinus tremulae* (Bond.) Bond. et Borisov. The product was obtained by extraction of the wood with acetone, followed by partition of the extracted material between water and petrol (b.p. 40-60°), and short-path distillation of the petrol residue at 0.5 Torr and 100°. The distillate, a

laevorotatory yellow oil with a woody smell, had an antibiotic effect on certain saprophytic fungi usually found on aspen [1]. This effect may contribute to the solitary occurrence of *P. tremulae* in the stems of aspen [1, 2].

The IR spectrum of the distillate was quite different from the triglyceride spectrum of the non-toxic distillation residue, with strong absorption bands indicating the presence of hydroxyl ( $3450 \text{ cm}^{-1}$ ), carbonyl ( $1710 \text{ cm}^{-1}$ ) and phenyl ( $750 \text{ and } 700 \text{ cm}^{-1}$ ) groups. Gas chromato-

grams (silicone columns OV-1 or SE-30 at 150°, FID) were simple: two peaks dominated, the first clearly complex. Mass spectra suggested that the major component was the  $\beta$ -ketol 5-hydroxy-7-phenylheptan-3-one (1), an unstable compound giving rise to variable amounts of 3-phenylpropanal when analysed by GC-MS. The ketol was preceded by 7-phenylheptan-3-one (2), the corresponding alcohol (3), and an enone later shown to be the conjugated trans isomer 7-phenyl-4t-hepten-3-one (4), perhaps an artefact formed by dehydration of the  $\beta$ -ketol (1).

Ph(CH<sub>2</sub>)<sub>2</sub>CHOHCH<sub>2</sub>COEt Ph(CH<sub>2</sub>)<sub>4</sub>COEt  
1 2  
Ph(CH<sub>2</sub>)<sub>4</sub>CHOHEt Ph(CH<sub>2</sub>)<sub>2</sub>CH
$$\stackrel{\ell}{=}$$
CHCOEt  
3 4

Trimethylsilylation (by means of BSTFA) increased the GLC retention times of 1 and 3, and the mass spectra of the TMSi derivatives supported the tentative structures. When the distillate was shaken with P<sub>2</sub>O<sub>5</sub> suspended in petrol, the ketol GC peak disappeared completely and the enone peak increased. Permanganate oxidation of the dehydrated product in acetone for a few minutes at room temprature [3] produced 3-phenylpropanoic acid, identified by its mass spectrum.

The tentative structures (1-4) were confirmed by the mass spectra and GC retention times of synthetic compounds.

The ketol (1), a new compound, was synthesized in racemic form and about 70 % yield from the commercial products 3-phenylpropanal (hydrocinnamaldehyde) and ethyl 3-oxopentanoate, by a Schöpf aldol condensation [4]. Purified by vacuum distillation followed by crystallization from petrol at  $-25^\circ$ , it was obtained as colourless needles with a GC purity >99%; mp 21-22°;  $n_D^{25}$ 1.5120,  $n_D^{15}$  1.5158 (undercooled); IR (neat):  $v_{O-H}$ 3450 cm<sup>-1</sup>,  $v_{C=0}$  1710 cm<sup>-1</sup>; characteristic positive ions produced by MS (via GLC) at 70 eV: m/e 91 (100%), M-18 = 188 (3-20%), 159/116 (10%), 134 (20%), 105(15%); at 15 eV: 134 (100%), 92 (60%); TMSi ether at 70 eV: 57/91 (100%), M-15 = 263 (5%), 188/117 (30%), 173 (8 %), 159/131 (20 %), 129 (40 %).

The ketone (2) is known as a synthetic product [5, 6], and was kindly provided by Prof. H. Reinheckel [6] as a colourless liquid with a fruity smell. The alcohol (3) is also known as a synthetic product [5, 7]. We prepared it from the synthetic ketone (2) by reduction with  $LiAlH_4$ .

The enone (4), a new compound, was prepared in about 75% yield by dehydration of the synthetic ketol (1) with P,O, in boiling petrol for 1 hr. After vacuum distillation it was obtained as a colourless, mobile, strong-smelling liquid with IR bands characteristic of a conjugated *trans*-enone [8–10] (neat:  $v_{C=0}$  1700s and 1675*v*s cm<sup>-1</sup>,  $v_{C=C}$  1630s cm<sup>-1</sup>,  $\gamma_{H-CC}$  –H 980*m* cm<sup>-1</sup>); checked by PMR (100 MHz, CCL<sub>4</sub>)!  $\delta$  6.00 and 6.72 (1H/1H, *dt*, *J* = 16 Hz, C-4/5). GC-MS indicated 97% 4-trans isomer identical with the enone from the wood distillate. MS(GC) 70 eV: m/e 91 (100%), M = 188 (2%), M-29 = 159 (20%),M-57 = 131 (7%), 116 (15%), 79.5 (0.1)%. Two small GC

peaks before the 4t-peak seem to be due to the 4c-enone and (in the middle) the 5t-enone.

These compounds (1-4) could not be found in healthy wood, but they were produced in sterilized wood inoculated with P. tremulae, and were also excreted into a synthetic nutrient solution (for composition see [11]). Their relative proportions were about the same in naturally infected wood and in the synthetic medium, indicating that they are produced by the fungus independent of the wood. The amount of distilled product from 100 g of dried, naturally infected wood was roughly 100 mg, about the same as from 1 l. of medium from an 8-week-old culture. n-Heptylbenzenes with oxidized side-chains have been isolated before from higher plants. They contain either acetylenic bonds [12, 13] or unsaturated lactone rings [14-16]. A compound of the latter type, but phenolic, has been isolated from Phellinus igniarius [17] and from P. pomaceus [18].

From P. tremulae a product consisting of nearly 50% of methyl benzoate, with some 10% each of benzyl alcohol, methyl salicylate and linalool, has been isolated by steam distillation [19]. These compounds are probably minor components concentrated by the isolation procedure.

Acknowledgements-We are indebted to Prof. Göran Bergson and Prof. Sixten Abrahamsson for permission to use their Departments' IR and GC-MS equipment, to Dr Kjell Olsson and Mr Rolf Andersson for PMR spectra, and to Prof. H. Reinheckel for samples. The work was supported by grants from the Swedish Natural Science Research Council.

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