Benzofuran Derivatives from *Lasthenia glabrata* Lindl.

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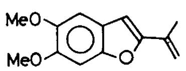
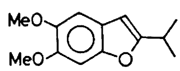
In 1956 one of us (A.R.A.) isolated from the overground parts of *Lasthenia glabrata* Lindl. (Compositae, tribus VI Helenieae) an aromatic compound (*1*), m.p. 70.5 – 71°C, further characterized as a dihydroderivative (*2*), m.p. 23 – 24°C.

Osmium tetroxide oxidation of *1* furnished a glycol (*3*), m.p. 122.5 – 125.5°C, which after further oxidation with lead tetraacetate yielded a ketone (*4*).

The physical and spectroscopic properties of the naturally occurring compound (*1*) agree well with the properties reported for 5,6-dimethoxy-2-isopropenylbenzofuran isolated from the roots of *Ligularia stenocephala* Matzum. et Koidz. (Compositae, tribus VIII Senecioneae) [1] and our ketone (*4*) seems to be identical with synthetic 5,6-dimethoxy-2-acetylbenzofuran.[1]



1



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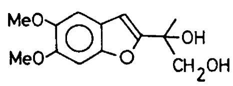

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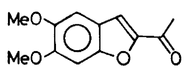

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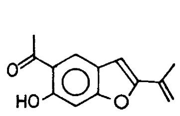

5

Moreover, the NMR and MS data (see experimental) of the glycol (*3*) are in excellent agreement with the suggested structure.

From the overground parts of *Lasthenia glabrata* we have also isolated small amounts of euparin (*5*), m.p. 120°C, identical (NMR, MS, TLC) with an authentic sample from *Abrotanella* species.[2]

Experimental. 8 kg Overground part of *Lasthenia glabrata* Lindl. was steam distilled to yield 2.96 g of oil which was chromatographed on neutral alumina (grade II – III). From the fraction eluted with 50 % benzene in light petroleum 275 mg crude product was obtained which on recrystallization from light petroleum gave colourless needles, m.p. 70.5 – 71°C (Ref. 1, 72.5 – 73°C). λ_{max} (hexane) 279 (15 800), 289 (15 400), 318 (26 800) and 330 (20 300) nm (Ref. 1 (MeOH) 324 (sh), 314, 287, 278 and 215 nm (log ε 4.13, 4.21, 4.00, 4.02 and 4.18)); IR (CCl_4) 1630, 1555, 1490, 1470, and 1441 cm^{-1} (Ref. 1 (nujol) 1612, 1550 and 890 cm^{-1}). (Found: C 71.2; H 6.62. Calc. for $C_{13}H_{14}O_3$: C 71.5; H 6.46.)

The fraction eluted with MeOH, after evaporation gave a yellow solid which was crystallized from ether. Yellow prisms, m.p. 118 – 119°C, were identical (IR, UV, NMR, TLC) with an authentic sample of euparin (*5*).

Hydrogenation of *1* yielded a dihydro compound (*2*), m.p. 23 – 24°C, purified on sublimation. λ_{max} (hexane) 296 (8550) and 302 (8200) nm; IR (CCl_4) 1626, 1490, 1470, and 1446 cm^{-1}.

Osmium tetroxide oxidation of 1. To *1* (50 mg), dissolved in dry ether (0.5 ml), was added OsO_4 (55 mg) in dry ether (0.5 ml) and a few drops of pyridine. The mixture was left overnight, then filtered and the residue dissolved in methylene chloride. The osmate ester was reduced with mannitol solution (25 ml 1 % KOH, 10 % mannitol in water) to yield crude glycol (*3*) (55 mg), m.p. 116 – 120°C, raised to 122.5 – 125.5°C on recrystallization from ethanol.

λ_{max} (ether) 296 (6960) and 302 (6610) nm. IR (KBr) 3500, 3400, 1630, 1490, 1470, and 1450 cm^{-1}, MW 252.0996, calc. for $C_{13}H_{16}O_5$ 252.0998. NMR 6.10 (6 H s), 2.95, 3.01, 3.38 (all 1 H s) and 6.2 (2 H s).

Oxidation of the glycol (3) *with lead tetraacetate.* To *3* (42 mg) dissolved in acetic acid (10 ml) was added a 0.0625 M solution (1.5 ml) of $Pb(OAc)_4$ in acetic acid. After being left overnight, the solution was treated with H_2S, PbS filtered off and the filtrate evaporated to dryness *in vacuo*. Three times recrystallization from ether/light petroleum yielded slightly yellow crystals (14 mg) of *4*, m.p. 115.5 – 117.5°C (Ref. 1, 118.5°C). λ_{max} (ether) 264 (4900), 295 (12 400) and 333 (24 700) nm (Ref. 1 (MeOH) 339, 298 (sh), 263, and 222 (sh) nm (log ε 4.37, 4.15, 3.81, and 4.18)); IR ($CHCl_3$)

1676, 1632, 1553, 1495, 1470, and 1447 cm^{-1} (Ref. 1 (nujol) 1673 cm^{-1}). (Found: C 64.2; H 5.34. Calc. for $C_{12}H_{12}O_4$: C 65.5; H 5.48.)

1. Murae, T., Tanahashi, Y. and Takahashi, T. *Tetrahedron* **24** (1968) 2177.
2. Anthonsen, T. and Chantharasakul, S. *Acta Chem. Scand.* **25** (1971) 1925.

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Gel Filtration of Lignin Model Compounds

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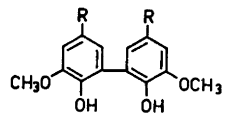
Gel filtration has been found to be useful in lignin degradation studies (see, *e.g.*, Refs. 1 and 2). It was found to be of importance to use a suitable combination of gel material and eluent in experiments with lignin degradation products. In order to get a basis for the selection of a system for the gel filtration, we have subjected a number of lignin model compounds, ranging from 124 to 512 in molecular weight, to gel filtration under different conditions. In the selection of model compounds a maximum of structural variation has been pursued.

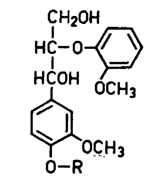
For the system Sephadex (G-series)/water the elution properties of a solute are described by a distribution coefficient, K_d, defined as the volume fraction of the water imbibed in the gel particles, which is available to the soluce.[3] In the present communication a similar parameter, K_d', has been used to compare results obtained in different systems. K_d' is defined as $(V_e-V_p)/(V_a-V_p)$, where V_e = the elution volume of the solute; V_p = the elution volume of a polymer such as Björkman lignin or India Ink (V_p corresponds approximately to the void volume of the column); V_a = the elution volume of acetone. In the systems investigated V_a-V_p was found to roughly correspond to the volume of eluent imbibed by the gel particles.

Results obtained on Sephadex G-25 with water as eluent are given in Table 1. Apparently the compounds examined are not eluted in the order of molecular size and furthermore the elution is delayed (all K_d'-values are >1). These phenomena have been observed previously on gel filtration of aromatic compounds under these conditions and have been attributed to a preferential adsorption to the gel matrix.[5]

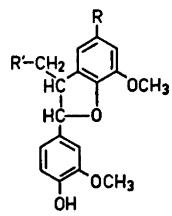
By the use of dioxane-water (1:1) as eluent adsorption effects were greatly diminished or eliminated (Table 1). Irregularities observed, *e.g.* the relatively high



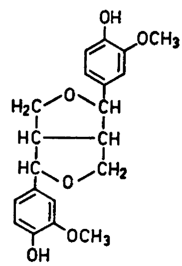
III R=CH2OH
V R=CH2-CH=CH2



IV R=H
VIII R=CH3



VI R=CH2CH2CH3 R'=H
X R=CH=CHCH2OH R'=OH



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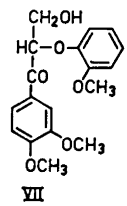
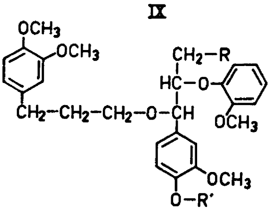


VII



XI R=R'=H
XII R=OH R'=CH3

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