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5-(3-HYDROXYPROPYL)-2-(3',4'-METHYLENEDIOXYPHENYL)BENZOFURAN: A NEW BENZOFURAN FROM STYRAX OBASSIA SIEB. ET ZUCC.

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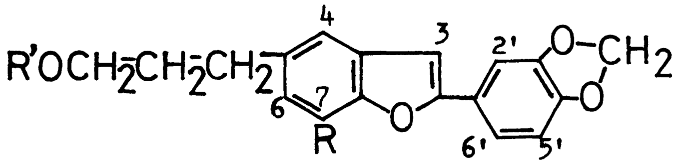
A new benzofuran derivative was isolated from the seed-oil of Styrax obassia Sieb. et Zucc., and the structure was determined as 5-(3-hydroxypropyl)-2-(3',4'-methylenedioxyphenyl)benzofuran.

In the course of chemical investigation of constituents of the Styrax family,1) we have isolated a new benzofuran from Styrax obassia Sieb. et Zucc. We report here the evidence leading to the structure of 5-(3-hydroxypropyl)-2-(3',4'-methylenedioxyphenyl)benzofuran (Ia) for this substance.



I R=H
a R'=H
b R'=Ac

II R=OMe
a R'=H
b R'=Ac

The seed-oil was extracted with ether, saponified with 10 % KOH-EtOH and the resulted unsaponifiable fraction was submitted to separation by preparative SiO_2 TLC using a mixture of solvents C_6H_6 : EtOAc (10:1, v/v) as eluent.

Two fluorecent compounds under UV lamp (2650 Å) were isolated. The major constituent (Rf 0.11, Ca. 65%) was identified as egonol (IIa), mp 113-115° (lit.2a) 117.5-118°) by direct comparison with authentic sample and its acetate (IIb), mp 103-105° (lit.2b) 107°). The NMR data of the isolated egonol agreed very closely with those of Hopkins3).

The molecular formula of $C_{18}H_{16}O_4$ (M^+ at m/e 296) was given for another compound (Ia) (Rf 0.15, Ca. 25 %), a colorless crystal, mp 118-119^o (methanol).

The IR spectrum revealed the presence of hydroxy group (ν_{max}^{KBr} 3380 cm^{-1}), aliphatic CH_2 group (ν_{max} 2950), unsaturated ring (ν_{max} 1600), substituted furan ring (ν_{max}1480), cyclic ether (furan ring)(ν_{max}1230) and methylenedioxy (ν_{max}930).

The UV spectrum showed absorption at λ_{max}^{EtOH} 218, 319.5 and 333 nm (ε 159000, 17300 and 13800, respectively). Egonol gave the typical redpurple color by warming after spraying conc. H_2SO_4 but Ia did not and showed blue color by warming after spraying ethanolic $FeCl_3$ and conc. H_2SO_4.

The NMR spectrum of Ia in $CDCl_3$ showed the following characteristic peaks, assigned to the substituent and side-chain protons; δ, 5.97 (s, 2H ; $-OCH_2-O-$), 3.66 (t, 2H, J=6.3 Hz ; $-CH_2-OH$), 2.78 (q, 2H, J=7.5 Hz ; $-CH_2$-arom., coupled with adjacent methylene protons), 1.91 (m, 2H ; J=6.3 Hz, J=1.1 Hz ; coupled with second oder splitting), and 1.57, [s, 1H ; aliphatic OH (disappeared with D_2O)].
The peaks attributed to ring protons represented a total of seven protons, including one proton on the furan ring. The assignments of the peaks were made by comparing the spectra of Ia and its acetate (Ib) with those of egonol$^{3)}$ (Table 1) .

Table 1. NMR data for the ring protons of Ia, Ib and egonol (IIa)

Proton	Ia	Ib	IIa$^{3)}$ (chemical shift, δ)
$H_{6'}$	7.33	7.35	7.36
$H_{2'}$	7.25	7.27	7.28
H_4	7.30	7.33	6.92
$H_{5'}$	6.84	6.85	6.82
H_3	6.76	6.78	6.73
H_6	7.04	7.04	6.61
H_7	7.39	7.37	-

Coupling constant (Hz)

	Ia	Ib	IIa$^{3)}$
$J_{5',6'}$	8.0	8.0	8.9
$J_{2',6'}$	1.5	1.5	1.8
$J_{4,6}$	1.5	1.5	1.5
$J_{6,7}$	8.0	8.0	-

J values of Ia and Ib were determined from their NMR spectra in $CDCl_3$ using $Eu(DPM)_3$ as shift reagent.

The chemical shift values of H_4 and H_6 of Ia agree well with the calculated values considering the effect of methoxyl group of benzene nucleus[4].
Treatment of Ia with acetic anhydride yielded the acetate (Ib), mp 97.8°, M^+ 338 ; ν_{max}^{KBr} 1740 (acetate CO), λ_{max}^{EtOH}215.5, 318.5 and 332.5 nm (ε, 30500, 29100 and 24500, respectively). The NMR spectrum of Ib showed a downfield shift (0.45 ppm) of the signal of the γ-methylene protons in the side chain. These data together with the strong peak at M-60 observed in the mass spectrum suggest that Ib is 5-(3-acetoxypropyl)-2-(3',4'-methylenedioxyphenyl)benzofuran.

Hydrogen peroxide oxidation of Ib, followed by basic hydrolysis,[5] gave piperonylic acid and a salicylic acid derivative. The latter gave yellow color with $K_2S_2O_8$-$AgNO_3$ reagent[6]. This means para position of the phenolic OH is not free.
The NMR spectrum of it showed the following peaks and these data support 5-(3-Hydroxy propyl)salicylic acid ; δ, 2.64 (q, 2H, J= 7.5 Hz : $-CH_2$-arom), 2.20 (m, 2H, J= 6.3 Hz, J=1.1 Hz, $-CH_2-$), 3.60 (t, 2H, J=6.3 Hz : $-CH_2-OH$), 4.80 (b, 1H, aliphatic OH, disappeared with D_2O), 6.86 (d, 1H, C_3-H, J=8.8 Hz), 7.61 (dd, 1H, C_4-H J=8.8, 2.0 Hz), 7.64 (d, 1H, C_6-H, J=2.0 Hz), 7.66 (b, 1H, aromatic OH, disappeared with D_2O). The IR spectrum showed the carboxyl group of it (ν_{max} 1700). These results indicated that Ia was related to egonol and that it differed only in the lack of methoxyl group on C_7.

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REFERENCES

1) H.Okada, J.Pharm.Soc.Japan., 657 (1915).
2) a) S.Kawai and T.Miyoshi, Ber., 71 B, 1457 (1938).
   b) S.Kawai and M.Suga, Ber., 71 B, 2071 (1938).
   c) S.Kawai and F.Yoshimura, Ber., 71 B, 2415 (1938); S.Kawai and N.Sugiyama, ibid., 71 B, 2421 (1938); S.Kawai and K.Yamagami, ibid., 71 B, 2438 (1938); S.Kawai and N.Sugiyama, Proc.Japan.Acad., 14, 348 (1938); S.Kawai and N.Sugiyama, Ber.,72, 367 (1939); S.Kawai, T.Nakamura and N.Sugiyama,ibid., 72, 1146 (1939).
3) C.Y.Hopkins, D.F.Ewing M.J.Chsholm, Can.J.Chem., 45, 1425 (1967).
4) H.Spiesecke, and W.G.Schneider, J.Chem.Phys., 35, 731 (1961).
5) R.Segal, I.Milo-goldzweig, S.Sokoloff and D.V.Zaitschek, J.Chem.Soc.(C),2402(1967).
6) S.Solway and A.Santoro, Anal.Chem., 27, 798 (1955).

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