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THE STRUCTURE OF ARENOL AND HOMOARENOL, α-PYRONE DERIVATIVES FROM HELICHRYSUM ARENARIUM (L.) MOENCH

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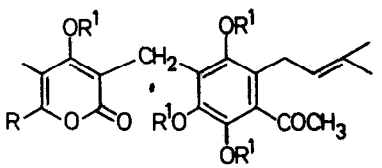
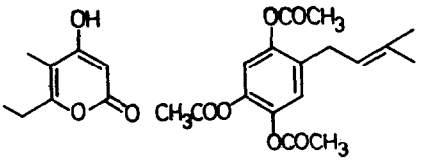
Some time ago, we have reported isolation of the yellow pigment, m.p. 192-194°, analyzing $C_{21}H_{24}O_7$, from flowers of the species Helichrysum arenarium (L.) MOENCH[1]. This report deals with the structure of this pigment.

High resolution mass spectrometry revealed the pigment as a mixture of two compounds, $C_{21}H_{24}O_7$ and $C_{22}H_{26}O_7$, though it was not possible to separate the two closely related homologs.

We propose the name arenol and the structural formula I of 3-[2,3,6-trihydroxy-4-acetyl-5-(3,3-dimethylallyl)benzyl]-4-hydroxy-5,6-dimethyl-2H-pyran-2-one for the lower homolog, and the name homoarenol and the structural formula II of 3-[2,3,6-trihydroxy-4-acetyl-5-(3,3-dimethylallyl)benzyl]-4-hydroxy-5-methyl-6-ethyl-2H-pyran-2-one for the higher homolog.





I R=CH_3; R^1=H *III* R=CH_3; R^1=$COCH_3$

II R=C_2H_5; R^1=H *IV* R=C_2H_5; R^1=$COCH_3$

V *VI*

The mixture of arenol (I) and homoarenol (II) was optically inactive, ν_{max} 1662,1618,1558,1432,1360,1310,1218,1168,1152,1120,1076 and broad chelate band 2600-3600 cm^{-1} [2b]. NMR spectrum[2c]: 1.18 (3H,t,J=7.4 Hz, $\underline{CH_3}CH_2$), 2.54 (2H,q,J=7.4 Hz $CH_3\underline{CH_2}$), 2.65 (3H,s, aromatic CH_3CO), 2.21, 1.93, 1.83, 1.79 (4 x sp^2 CH_3), 5.20 (1H,mt,sp^2 H), 3.15 (2H,d,J=7 Hz), 3.63 (2H,s), 9.89 (1H,br s, exchangeable, phenolic OH). Decoupling revealed the 3,3-dimethylallyl group.

Hydrogenation gave a dihydro derivative m.p. 152-154°C, as a mixture of $C_{21}H_{26}O_7$ and $C_{22}H_{28}O_7$ (MS). NMR: 0.95 (6H,d,J=6 Hz, isopropyl CH_3); no sp^2 protons. These findings are explained by the hydrogenation of the side chain double bond.

Acid catalysed cyclisation afforded a product m.p. 202-204°C, $C_{21}H_{24}O_7$ and $C_{22}H_{26}O_7$ (MS), NMR: 1.47 (6H,s), no allylic CH_2, no sp^2 protons. The spectra suggest the reaction of the dimethylallyl group with an ortho-located hydroxyl group and the formation of a 2,2-dimethyldihydropyran ring.

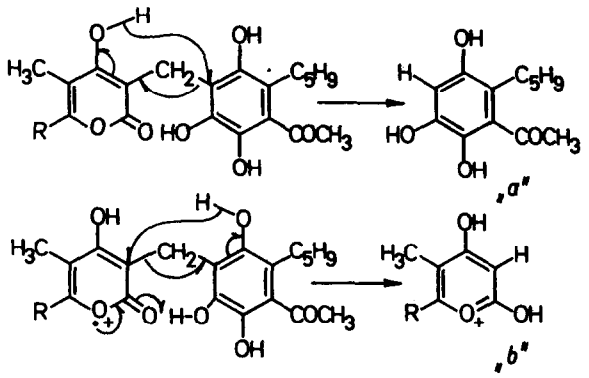
Arenol and homoarenol were separated as acetyl derivatives: Arenol tetraacetate (III), m.p. 166-168°C, M 556, m/e 514,472,430 and 388 (successive loss of four ketene molecules), λ_{max} 303 nm (3.93), ν_{max} 1773,1749,1711,1648, 1574,1426,1368,1168,1088,1079,1050 cm^{-1}, NMR: 2.40 (3H,s, aromatic CH_3CO), 2.17, 2.21 (6H), 2.25 (4 x AcO), 1.73, 2.22, 1.67 (6H) (4 x sp^2 CH_3), 3.56 (2H,s), 3.09 (2H,d,J=6.5 Hz, allylic CH_2), 4.94 (1H,mt,sp^2 H).

Homoarenol tetraacetate (IV), m.p. 130-132°C, M 570, m/e 528,486,444 and 402, λ_{max} 304 nm (3.78), ν_{max} 1773,1750,1711,1648,1574,1428,1368,1190,1168, 1099,1076,1050 cm^{-1}. NMR: 2.40 (3H,s, aromatic CH_3CO), 2.18, 2.21, 2.22, 2.25 (4 x AcO) 1.21 (3H,t,J=7.8 Hz, $\underline{CH_3}CH_2$), 2.48 (2H,q,J=7.8 Hz, $CH_3\underline{CH_2}$), 1.74, 1.67 (6H) (3 x sp^2 CH_3), 3.56 (2H,s), 3.10 (2H,d,J=6.4 Hz, allylic CH_2), 4.94 (1H mt,sp^2H). The long range coupling between the methyl at 1.74 and CH_2 protons of ethyl group suggest that both groups are located in the same ring (probably at the ortho-position). The NMR spectra of III and IV are very similar, except for the methyl and ethyl substituents. The chemical shift values of these groups indicate that this position is affected by an electronegative atom or group.

Treatment of homoarenol tetraacetate (IV) with potassium hydroxide yielded two main compounds V and VI; the latter was isolated as an acetyl derivative. The compound V, m.p. 160-163°C, $C_8H_{10}O_3$ (MS) showed typical α-pyrone UV spectrum λ_{max} 287 nm (3.84)[3], ν_{max} 1652,1612,1550,1488,1352,1246,1110,1055 cm^{-1} and broad chelate band with submax. at 2600,2780 and 3400 cm^{-1}. NMR: 1.94 (3H,s,sp^2 CH_3), 1.20 (3H,t,J=7.5 Hz, $\underline{CH_3}CH_2$), 2.58 (2H,q,J=7.5 Hz, $CH_3\underline{CH_2}$), 5.67 (1H,s,sp^2 H). V was assigned the structure of 4-hydroxy-5-methyl-6-

-ethyl-2H-pyran-2-one. The high resolution mass spectrum is in full accordance with the structure proposed. The spectrum contains peaks M-15, M-28 (a doublet in which M-CO strongly predominates over M-C_2H_4), M-29 (a doublet of the M-C_2H_5 and M-CHO fragments in approx. ratio 7:1), m/e 112 (M-C_2H_2O, very likely elimination of C_2 and C_3 with their substituents), m/e 111 (expulsion of a methyl from M-CO : m^x/e 75.3), and m/e 84 (carbon monooxide elimination from M-C_2H_2O, m^x/e 63.1). The compound VI, M = 320, m/e 194 (loss of 3 ketene units) and 139 (loss of C_4H_7 fragment from the ion of mass 194, m^x/e 99.6), λ_{max} 1765,1612,1584,1474,1422,1362,1180,1110,1038 and 1018 cm^{-1}. NMR: 2.24, 2.27 (6H) (3 x AcO), 6.83 (1H,s, aromatic H), 7.35 (1H,s, aromatic H), 1.67, 1.72 (2 x sp^2 CH_3), 3.17 (2H,d,J=6 Hz, allylic CH_2), 5.03 (1H,mt, sp^2 H). The nonequivalence of the aromatic protons and lack of any detectable coupling between them indicate their mutual para-position. The structure of the compound VI, however, is unexpected from the biogenetic point of view.

The remaining CH_2 group therefore represents a bridge joining both rings, so that the structures I and II are assigned to arenol and homoarenol, respectively.



Scheme 1

(R = CH_3 or C_2H_5)

The methylene bridge and the structures I and II for arenol and homoarenol are in full accordance with their mass spectral behaviour. The high resolution mass spectrum of the mixture of both compounds contains the peaks of the following fragments: M-C_4H_7 (m/e 333 and 347). M-C_5H_8 (m/e 320 and 334). The fragment $C_{13}H_{16}O_4$ of nominal mass 236 (238 at the hydrogenated product) may be formulated as "a" (scheme 1). It loses C_4H_7 radical (m^x/e 138.9), its

satellite of mass 235 ("a-H") eliminates a molecule of propene (m^x/e 158.5). The ions $C_7H_9O_3$, "b" (R=CH_3; nominal mass 141) and $C_8H_{11}O_3$, "b" (R=C_2H_5; nominal mass 155) contain the lactone moiety: the lower homologous fragment is observed in the mass spectrum of pure arenol tetraacetate, the higher one in the spectrum of the homoarenol tetraacetate. The fragmentation mechanism and the considered migration of the phenolic hydrogens given in the scheme 1 are supported by the mass spectrum of arenol-homoarenol mixture equilibrated with ethanol-O-d.

The alternative structure with interchanged acetoxyl group and the pyrone moiety may be excluded on the grounds of the measurements of the hydrogen bonding. IR spectrum of the mixture I and II in CCl_4 solution (0,0018 mol/l) showed a broad chelate band with submax. at 2630,2750,2175,3350 and 3590 cm^{-1}, which proved the presence of intramolecular hydrogen bonded OH and lack of free OH. The same measurement of the product with a 2,2-dimethyldihydropyran ring in CCl_4 solution (0,0006 mol/l) showed broad chelate band with submax. at 2675,2735 and 3240 cm^{-1} (hydrogen bonded OH) and a band 3618 cm^{-1} due to free OH. These observations favoured the structure I and II, since the alternative structure should show free OH even in the natural mixture.

The occurence of arenol and homoarenol in a Helichrysum species is of special interest in connection with the recently reported presence of two derivatives 4-hydroxy-5-methyl-6-ethyl-2H-pyran-2-one in closely related species[4].

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