

(546), -0.3° (436), (c 0.67, CHCl_3).

Ozonolysis of norsolanadione. Norsolanadione (1, 30 mg) dissolved in CH_2Cl_2 (15 ml) and pyridine (0.1 ml) was treated with excess ozone at -65°C . Zinc powder (500 mg) and acetic acid (2 ml) were added and the mixture stirred 35 min during which the temperature was slowly raised to 20°C . The solution was decanted, the reaction vessel with its residue was washed with CH_2Cl_2 , and the combined solutions washed four times with water. Removal of the solvent left a slightly yellow oil which was chromatographed on silica gel furnishing pure (2*S*)-5-oxo-2-isopropylhexanal (3, 10 mg). NMR, IR, and mass spectra were indistinguishable from those of (2*S*)-5-oxo-2-isopropylhexanal (3) prepared previously by ozonolysis of solanone. $[\alpha]_{\text{D}}^{20} + 47.8^\circ$ (589 nm), $+ 50.7^\circ$ (578), $+ 61.4^\circ$ (546), $+ 146.6^\circ$ (436), $+ 400.8^\circ$ (365), (c 0.73, CHCl_3); lit.¹⁶ $[\alpha]_{\text{D}}^{20} + 43.7^\circ$ (589 nm), $+ 45.9^\circ$ (578), $+ 55.6^\circ$ (546), $+ 133.3^\circ$ (436), $+ 364.8^\circ$ (365) (c 0.54, CHCl_3).

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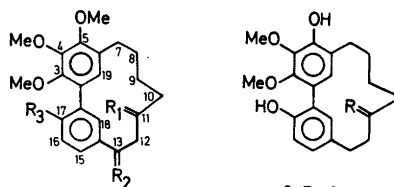
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Porson, a New [7,0]-Metacyclophane from *Myrica gale* L.

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We have continued¹ our studies of the phenolic constituents of *Myrica gale* L. From an ethyl acetate extract of the stems we have isolated after partition between methanol/water and petroleum ether and repeated column and thin layer chromatography a crystalline phenolic ketone, porson (1) [m.p. $186-187^\circ\text{C}$, $\nu_{\text{max}}(\text{CHCl}_3)$ 1713 cm^{-1} , $\lambda_{\text{max}}(\text{MeOH})$ 248 (11 200), 293 (6300) nm, calc. for $\text{C}_{22}\text{H}_{20}\text{O}_6$ 386.1728 as found]. Porson was recognized as a [7,0]-metacyclophane by comparison of its spectroscopic data with two related compounds, myricanone (2) and myricanol (3) previously isolated from *Myrica nagi*.²



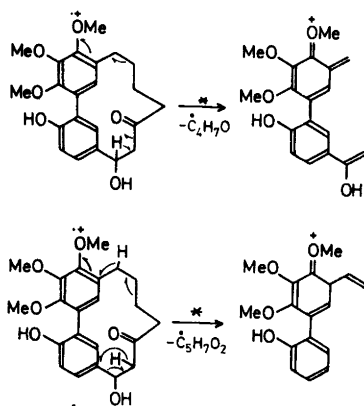
- | | | | |
|---|--------------------------|---------------------------|-------------------------|
| 1 | $\text{R}_1=\text{O}$ | $\text{R}_2=\text{H,OH}$ | $\text{R}_3=\text{OH}$ |
| 4 | $\text{R}_1=\text{O}$ | $\text{R}_2=\text{H,OAc}$ | $\text{R}_3=\text{OAc}$ |
| 5 | $\text{R}_1=\text{O}$ | $\text{R}_2=\text{O}$ | $\text{R}_3=\text{OH}$ |
| 6 | $\text{R}_1=\text{H,OH}$ | $\text{R}_2=\text{O}$ | $\text{R}_3=\text{OH}$ |

- | | |
|---|------------------------|
| 2 | $\text{R}=\text{O}$ |
| 3 | $\text{R}=\text{H,OH}$ |

The most prominent features of the NMR spectrum of 1 are the presence of resonances due to three methoxy groups (δ 3.83, 3.91 and 3.95) and the signals of four aromatic protons [δ 6.46 (s, H-19), ABX pattern: 6.65 ($J \approx 2$ Hz, H-18), 6.88 ($J \approx 8$ Hz, H-16), 7.02 ($J \approx 2$ and 8 Hz, H-15)]. Two hydroxy resonances are also visible; one phenolic (δ 7.82) and one due to a secondary aliphatic hydroxy group ($\delta \sim 3$), the carbonyl proton being located at δ 4.35 as a doublet of doublets ($J = 2$ and 6 Hz). The relative low field resonance of this proton is indicative of its position at C-13, close to the aromatic nucleus. Irradiation at δ 4.35 collapses a multiplet at δ 2.95 and *vice versa* thus indicating the resonance position of the C-12 methylene group. In the same region of the spectrum (δ 2.5–3.0) is also located the resonances of four more protons, probably 2H-7 and 2H-10. Moreover, the resonance position of the H-12

protons indicates that their neighbour is the keto group. Consequently the keto group must be located at C-11. The resonances of the remaining four hydrogens in the seven membered carbon chain (2H-8 and 2H-9) are located between δ 1.5 and 2.0.

The mass spectrum of porson has a very large molecular ion peak, more than ten times the second most abundant peak. However, characteristic peaks due to cleavages in the seven-membered carbon chain are also of diagnostic value. Thus peaks at m/e 315 (6 %) and m/e 287 (7 %) may be explained as indicated in Scheme 1.



Scheme 1.

On acetylation porson yields a diacetate (4) (m.p. 168–169 °C, $\nu_{\max}(\text{CHCl}_3)$ 1765, 1740, 1715 cm^{-1}). The most significant features of its NMR spectrum are the appearance of the resonances of two acetoxy groups (δ 2.09, 2.23), the downfield shift of the methine proton at C-13 (δ 5.30) and an upfield shift of one of the methoxy resonances (δ 3.63). This upfield shift accords with one reported for one of the OCH₃ groups in myricanone diacetate² and it seems reasonable that the phenolic hydroxy group (C-17) and one of the methoxy groups (C-3) have a similar relative position in the two compounds.

The sterically hindered position of the phenolic hydroxy group is probably also the reason for its unwillingness to be methylated with diazomethane. Oxidation of porson with Jones reagent furnished an oily diketone (5).

The IR spectrum (CHCl₃) of this diketone reveals the presence of one aliphatic (1715 cm^{-1}) and one aromatically conjugated (1695 cm^{-1}) keto group. Due to the conjugation the band at 1615 has also gained considerably in intensity. This β -diketone does not seem to be enolized to any extent. Enolization is probably unfavourable due to steric reasons. In the NMR spectrum of 5 the resonance of the methine proton is absent.

When the secondary hydroxy group of porson (1) is acetylated or oxidized, there are only minor changes in the chemical shift of the methoxy groups. This indicates that the secondary hydroxy group is located at C-13 and not at C-7.

Oppenauer oxydation of porson (acetone/Al *tert*-butoxide) yielded 10 % of an isomeric ketol (6) in which the keto group is conjugated to the aromatic nucleus ($\nu_{\max}(\text{CHCl}_3)$ 1695, 1615 cm^{-1}).

The chemical and spectroscopic properties of porson supports the constitution 1. However, conclusive evidence for its correctness has not yet been provided. X-Ray studies of porson are under way.

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