Phenarctic, a Fully Substituted Depside from *Nephroma arcticum*

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Recently Nuno, Kuwada and Kamiya reported on the structure of nephroarctic (I), isolated from *Nephroma arcticum* (L.) Torss. The substance was obtained also in this laboratory, and the results of degradative and synthetic work, which were in progress when the note was published, confirm the X-ray structure. In addition another compound, m.p. 167–168°, was obtained by chromatography on oxalic acid coated silica gel, for which the name phenarctic and the formula (II) are suggested.

![Diagram of compounds I and II](image)

The IR spectrum of phenarctic in KBr had a sharp band at 1750 (depside CO), and a broad band with a peak at 1630 and a shoulder at 1655 cm⁻¹ (hydrogen bonded CO). The UV spectrum in ethanol showed maxima at 254 nm (ε 31 000), 283 (29 000), 313.5 (29 500) and 376.5 (10 500) and minima at 235.5 (22 000), 271 (28 500), 299 (26 500) and 359 (10 000). The NMR spectrum in CDCl₃ exhibited singlets at δ 2.14 (6 H), 2.43 (3 H) and 2.70 (3 H), all aromatic methyl groups, at 3.95 (3 H, OCH₃), 10.13 (1 H), 10.29 (1 H) (two aldehyde-H), 10.93 (1 H), 13.42 (1 H) and 13.78 (1 H) (three hydrogen bonded phenolic OH, slowly exchanged in D₂O). The only important difference in the NMR spectra of phenarctic and nephroarctic is the signal at 10.93 in phenarctic, which is absent in that of nephroarctic, whilst the latter has a signal at 6.61, which is absent in the spectrum of phenarctic.

The mass spectrum of phenarctic showed M⁺ 416.112 (calc. 414.111 for C₂₁H₂₅O₄) (12 % of base peak). In addition it contained the following major fragments: 210.089 (calc. 210.089 for C₁₁H₁₂O₄) (60 %) → 207.029 (calc. 207.029 for C₁₀H₁₀O₃) (75 %) → 178.063 (calc. 178.063 for C₈H₁₄O₃) (100 %) → 166 (15 %) → 150.068 (calc. 150.068 for C₇H₁₄O₂) (70 %). A “insta-stable” fragment at 126.3 indicated a direct formation of m/e 150 from m/e 178. It was concluded that phenarctic might be a carboxylated derivative of nephroarctic. This raised the question whether the methoxyl signal in the NMR spectrum would be due to a methyl ester or an aromatic methyl ether. It was answered by the solvent induced shift of the methoxyl signal. In benzene solution this signal was found at 3.40, corresponding to a large A-value of +0.55 [A = δ(CDCl₃) – δ(benzene)], too large for a methoxyl group flanked by two ortho substituents. This A-value was compared with the corresponding shift of methyl 2-hydroxy-4-benzoxymethyl-3,5,6-trimethylbenzoate (A = +0.57) and with that of methyl 2-methoxy-4-benzoxymethyl-3,5,6-trimethylbenzoate, which had methoxyl signals at 3.88 and 3.74 in CDCl₃ and at 3.63 and 3.66 in benzene.

A full account of the work will be submitted for publication in this journal.

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