Phenarctin, a Fully Substituted Depside from *Nephroma arcticum*

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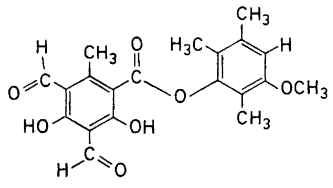
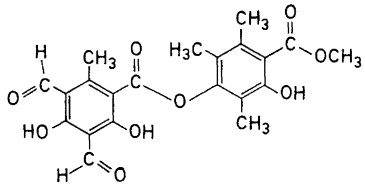
Recently Nuno, Kuwada and Kamiya reported on the structure of nephroarctin (I),[1] isolated from *Nephroma arcticum* (L.) Torss. The substance was obtained also in this laboratory, and the results of degradative and synthetic work, which were in progress when the note [1] was published, confirm the X-ray structure. In addition another compound, m.p. 167–168°, was obtained by chromatography on oxalic acid coated silica gel, for which the name phenarctin and the formula (II) are suggested.



I



II

The IR spectrum of phenarctin 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 $CDCl_3$ 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, OCH_3), 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 D_2O). The only important difference in the NMR. spectra of phenarctin and nephroarctin [1] is the signal at 10.93 in phenarctin, which is absent in that of nephroarctin, whilst the latter has a signal at 6.61, which is absent in the spectrum of phenarctin.

The mass spectrum of phenarctin showed M^+ 416.112 (calc. 414.111 for $C_{21}H_{20}O_9$) (12 % of base peak). In addition it contained the following major fragments: 210.089 (calc. 210.089 for $C_{11}H_{14}O_4$) (60 %) – 207.029 (calc. 207.029 for $C_{10}H_5O_5$) (75%) – 178.063 (calc. 178.063 for $C_{10}H_{10}O_3$) (100 %) – 166 (15 %) – 150.068 (calc. 150.068 for $C_9H_{10}O_2$) (70 %). A "metastable" fragment at 126.3 indicated a direct formation of *m/e* 150 from *m/e* 178. It was concluded that phenarctin might be a carboxylated derivative of nephroarctin. 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 Δ-value of +0.55 [$\Delta = \delta(CDCl_3) - \delta$(benzene)], too large for a methoxyl group flanked by two *ortho* substituents.[2] This Δ-value was compared with the corresponding shift of methyl 2-hydroxy-4-benzyloxy-3,5,6-trimethylbenzoate (Δ = +0.57) and with that of methyl 2-methoxy-4-benzyloxy-3,5,6-trimethylbenzoate, which had methoxyl signals at 3.88 and 3.74 in $CDCl_3$ and at 3.63 and 3.66 in benzene.

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

I thank Mr. Thorleif Anthonsen for drawing my attention to the usefulness of the solvent shift and for advice. The NMR spectra were recorded by Mrs. Ellen Hemmer on a Varian A-60 A spectrometer, and the mass spectral determinations were done by Mrs. Turid Sigmond and her staff of the Physics department with an AEI MS 902 machine.

1. Nuno, M., Kuwada, Y. and Kamiya, K. *Chem. Commun.* **1968** 78.
2. Anthonsen, T. *Acta Chem. Scand.* **22** (1968) 352.

Received November 15, 1969.