The Crystal Structures of $Na_4Fe(CN)_6.10H_2O$ and $Na_4Mn(CN)_6.10H_2O$

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The crystal structures of the isomorphous compounds $Na_4Fe(CN)_6.10H_2O$ and $Na_4Mn(CN)_6.10H_2O$ have been determined by single crystal methods.

Crystals of $Na_4Mn(CN)_6.10H_2O$ were prepared from $MnCO_3$ and NaCN according to the method of Brauer,[1] whereas those of $Na_4Fe(CN)_6.10H_2O$ were obtained commercially. It proved to be difficult to obtain crystals suitable for single crystal X-ray work, especially in the case of $Na_4Fe(CN)_6.10H_2O$. X-Ray data for $Na_4Fe(CN)_6.10H_2O$ were recorded with a single crystal diffractometer (Philips Pailred), using Mo$K\alpha$-radiation, while equi-inclination Weissenberg methods with Cu$K\alpha$-radiation were employed for $Na_4Mn(CN)_6.10H_2O$.

Both compounds are monoclinic with the unit cell dimensions $a = 9.8$ Å, $b = 11.4$ Å, $c = 9.0$ Å, and $\beta = 97.5°$. The cell parameters have not yet been refined. The space group is $P2_1/n$, and there are two formula units per unit cell. Preliminary parameters were deduced by means of three-dimensional Patterson and electron density calculations (Table 1). Isotropic least squares refinement yielded R-factors of 0.14 and 0.09 for $Na_4Fe(CN)_6.10H_2O$ and $Na_4Mn(CN)_6.10H_2O$, respectively.

The corresponding atomic parameters are listed in Table 1. Further refinement of the structures based on more extensive data is in progress.

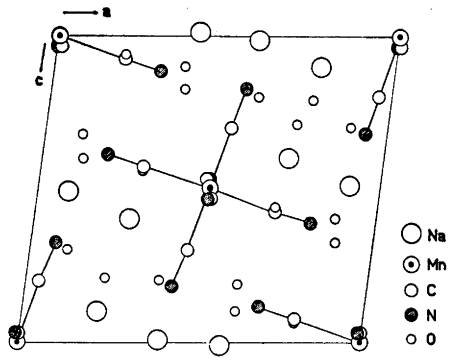

Fig. 1. Projection of the structure of $Na_4Mn(CN)_6.10H_2O$ along the b-axis.

The structure of $Na_4Mn(CN)_6.10H_2O$ is built up of sodium ions, complex $Mn(CN)_6^{4-}$ ions and water molecules, the complex ions being linked through water molecules by means of hydrogen bonds.

A projection of the unit cell of $Na_4Mn(CN)_6.10H_2O$ along the b-axis is

Table 1. Atomic parameters for $Na_4Me(CN)_6.10H_2O$, Me being Fe or Mn. Space group $P2_1/n$. The Me atoms occupy two-fold positions, while the remaining atoms occupy four-fold positions

Atom	x Fe	x Mn	y Fe	y Mn	z Fe	z Mn	B Fe	B Mn Å^{-2}
Me	0.000	0.000	0.000	0.000	0.000	0.000	0.02	2.56
Na(1)	0.091	0.093	0.139	0.142	0.508	0.509	2.37	3.98
Na(2)	0.712	0.716	0.127	0.128	0.398	0.402	2.06	3.47
C(1)	0.295	0.304	0.514	0.509	0.421	0.433	1.05	2.63
C(2)	0.489	0.495	0.335	0.327	0.475	0.471	3.35	2.66
C(3)	0.552	0.540	0.519	0.515	0.297	0.302	2.38	2.70
N(1)	0.183	0.187	0.526	0.519	0.376	0.392	1.45	3.06
N(2)	0.489	0.503	0.230	0.228	0.462	0.474	2.72	3.36
N(3)	0.429	0.431	0.471	0.471	0.824	0.822	3.15	2.89
O(1)	0.306	0.302	0.038	0.037	0.446	0.443	0.07	3.24
O(2)	0.099	0.106	0.488	0.487	0.696	0.700	4.04	5.07
O(3)	0.266	0.266	0.224	0.218	0.709	0.713	1.47	4.73
O(4)	0.118	0.113	0.272	0.271	0.310	0.319	3.89	6.16
O(5)	0.391	0.382	0.281	0.277	0.105	0.097	2.19	4.12

Table 2. Interatomic distances within the complex ion $Me(CN)_6^{4-}$, Me being Fe or Mn.

Bond	d (Å), Fe	d (Å), Mn
Me–C(1)	2.04	1.93
Me–C(2)	1.90	2.00
Me–C(3)	1.98	1.89
C(1)–N(1)	1.12	1.16
C(2)–N(2)	1.21	1.13
C(3)–N(3)	1.14	1.20

shown in Fig. 1, and approximate interatomic distances within the complex ions are listed in Table 2.

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Constitutents of Umbelliferous Plants

XVIII.* Terpenoids and Coumarins of the Root of *Ligusticum seguieri* Koch

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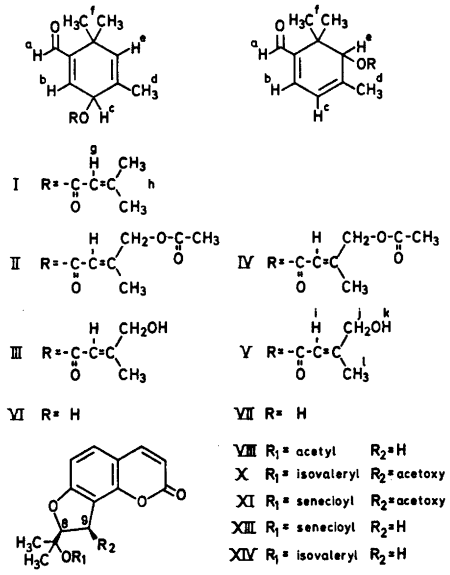
The root of *Ligusticum seguieri* Koch, in addition to several coumarins, has afforded a number of esters (I–V), derived from the terpene alcohols (VI) and (VII). Esters of these alcohols have recently been shown to occur in several umbellifers.[1–3] An important feature of their chemistry is their rapid cleavage by treatment with mineral acids. In addition to the carboxylic acid liberated in this reaction, mainly 2,3,4-trimethylbenzaldehyde is formed by rearrangement of the terpenoid skeleton.

The terpene esters (II), (III), and (IV) are known from other umbelliferous plants,[1,3] whereas (I) and (V) appeared to be new. The structures 1,1,5-trimethyl-2-formyl-4-(3-methyl-2-butenoyloxy)-cyclohexadiene-(2,5) (I) and 1,1,5-trimethyl-2-formyl-6-((*E*)-3-hydroxymethyl-2-butenoyloxy)-cyclohexadiene-(2,4) (V) for these compounds were deduced from the results of their acid cleavage and from comparisons of their UV-, IR-, ^1H NMR-, and mass spectra with those of their congeners.

Samples of esters of (VI) and, in particular, esters of (VII), show severe deterioration during storage. Contrary to esters of (VII), esters of (VI) show no fall in



optical activity, when regained from partly deteriorated samples by chromatography. Nevertheless compound (II), obtained from *Ligusticum seguieri*, was optically less pure than that obtained earlier from

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