



*mellifera*). Dinitrophenyl (DNP) derivatives of long-chain bases were prepared as described elsewhere.<sup>5,6</sup> It should be added, that about half of the long-chain base hydrochlorides remained in the upper phase after partition of the hydrolysis products. The DNP-fraction from the lower phase was shown by gas chromatography after lead tetraacetate oxidation<sup>5</sup> to contain dodecenal (57%), tetradecenal (33%), and hexadecenal (3%). The DNP-derivative (I), producing dodecenal on oxidation, was isolated by reversed-phase chromatography.<sup>6</sup> Its infrared spectrum from chloroform solution had a *trans* double bond intensity (10.3  $\mu$ ) comparable to the 18-carbon homologue, indicating one double bond. An *erythro* configuration was assigned

by thin-layer chromatography, using the somewhat faster-moving *erythro* and *threo* isomers of the 16- and 18-carbon homologues as references. (I) was silylated<sup>7</sup> and subjected to mass spectrometry (Fig. 1), using an MS 902 instrument (AEI, Manchester) and a direct inlet system. A low intensity molecular ion at  $m/e$  553 is consistent with the formula given in Fig. 1. The base peak,  $m/e$  255, results from a cleavage between carbon atoms 2 and 3. 73 is the mass of a trimethylsilyl substituent. Other fragments are indicated at the formula.

To get conclusive evidence for the double bond position, (I) was methylated by reflux overnight in methyl iodide-silver oxide, followed by hydroxylation of the

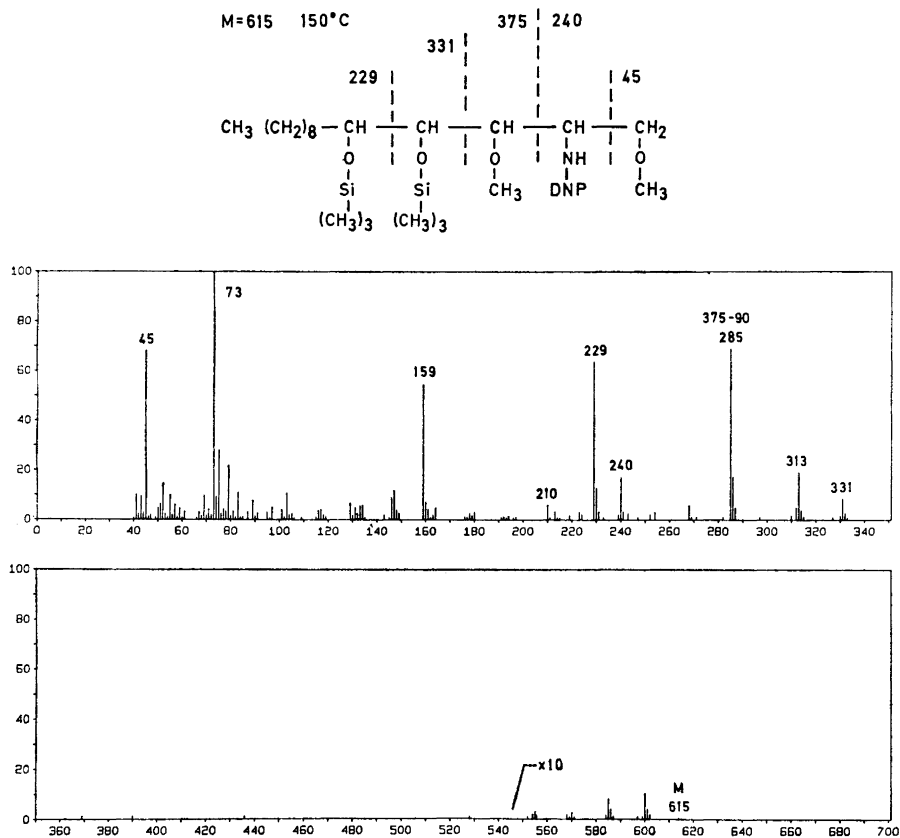


Fig. 2. Mass spectrum of *erythro*-1,3-dimethoxy-2-dinitrophenylamino-4,5-di-trimethylsilyloxy-tetradecane. Conditions were the same as those given in Fig. 1.

double bond with osmium tetroxide.<sup>8</sup> The mass spectrum of the silylated compound is shown in Fig. 2, and is analogous to the spectrum of the derivative of the 18-carbon homologue.<sup>9</sup> The allylic double bond (Fig. 2) is indicated by fragments at  $m/e$  229 and 331. The peak at  $m/e$  159 is the base peak from the 18-carbon derivative and is probably derived from a three carbon unit including carbon atoms 3 and 4 (original allylic portion). This peak is absent when the hydroxylated double bond is in a non-allylic position.<sup>9</sup> The peak at  $m/e$  313 is present with a similar intensity in the spectrum of the 18-carbon derivative and therefore probably originates from the polar portion. Other fragments are indicated in Fig. 2.

The present work is part of the project "Structure and Function of Membrane Lipids", supported by a grant from *The Tri-Centennial Fund of the Bank of Sweden*. The authors thank Karin Nilsson for important assistance, and Anders Lilja and Hakon Leffler for collecting the honey bees.

1. Morrison, W. R. *Biochim. Biophys. Acta* **176** (1969) 537.
2. Moscatelli, E. A. and Gilliland, K. M. *Lipids* **4** (1969) 244.
3. Panganamala, R. V., Geer, J. C. and Cornwell, D. G. *J. Lipid Res.* **10** (1969) 445.
4. Bieber, L. L., O'Connor, J. D. and Sweeley, C. C. *Biochim. Biophys. Acta* **187** (1969) 157.
5. Karlsson, K.-A. *Acta Chem. Scand.* **22** (1968) 3050.
6. Karlsson, K.-A. *Nature* **188** (1960) 312.
7. Karlsson, K.-A. *Acta Chem. Scand.* **19** (1965) 2425.
8. Niehaus, Jr., W. G. and Ryhage, R. *Anal. Chem.* **40** (1968) 1840.
9. Karlsson, K.-A. To be printed in Proceedings from a Symposium on Chemistry and Metabolism of Sphingolipids, held at Michigan State University, East Lansing, U.S.A., May 5 and 6, 1969.

Received November 15, 1969.

## Phase Relations in the System Ni-S-Se at 500°C

KJELL HAUGSTEN and ERLING RØST

*Kjemisk Institutt A, Universitetet i Oslo,  
Blindern, Oslo 3, Norway*

The phase relations at 500°C of the ternary system Ni-S-Se have been examined by X-rays and metallographic methods. The alloys were prepared by melting calculated amounts of the elements in evacuated silica tubes. The samples were then annealed for about a week at 500°C and quenched in water. 65 samples were synthesized for this investigation.

No isolated ternary phase was found at 500°C. However, in the phases existing in the binary systems, Ni-S and Ni-Se, complete mutual interchange of sulfur and selenium is possible.

In the phase  $Ni_3(S,Se)_2$ , with rhombohedral structure, the successive replacement of sulfur by selenium is accompanied by an increase of the lattice dimensions, linear to the S/Se-ratio; see Table 1a. The rhombohedral angle is less than 90° in the sulfur-rich and greater than 90° in the selenium-rich compounds. No variation from the stoichiometric composition  $Ni_3(S,Se)_2$  could be observed.

A phase  $Ni_6S_5$  with orthorhombic structure was first found by Lundqvist,<sup>1</sup> and later confirmed by others. According to different authors, this phase is stable between approximately 400 and 570°C. There are, however, some discrepancies concerning the composition of the phase. For instance, Kullerud and Yund<sup>2</sup> report the stoichiometry to be  $Ni_7S_6$ , whereas Rosenqvist<sup>3</sup> found a small homogeneity range including both the compositions  $Ni_6S_5$  and  $Ni_7S_6$ . A phase  $Ni_6Se_5$ , with orthorhombic crystal structure similar to that of the phase mentioned above, has been reported by Grønvold *et al.*<sup>4</sup>

In the present investigation samples of  $Ni_6S_5$  and  $Ni_7S_6$  contained two phases; one on either side of the orthorhombic phase, whereas a sample with composition  $Ni_{5.87}S_5$  appeared to contain this phase only. (The notation  $Ni_xS_5$  is used in this paper for reasons given below). No variation of the lattice constants of the orthorhombic phase could be observed in these samples and therefore variation of the Ni/S ratio is assumed to be negligible.