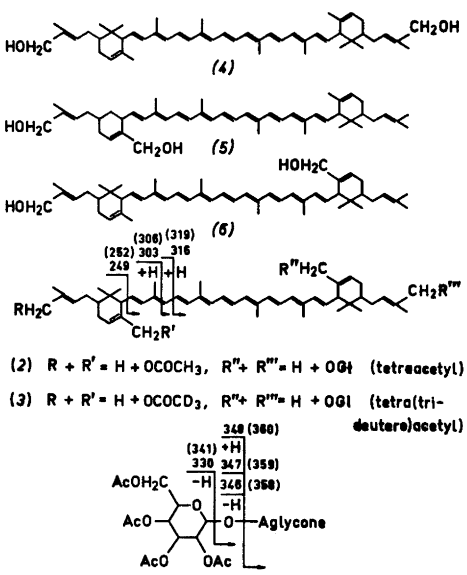

Scheme 2

Scheme 2. Structures of decaprenoxanthin (*4*), sarcinaxanthin (*5* or *6*) and mass spectrometric fragmentations assigned to the acetylated D-glucoside (*2*, *3*). Bracketed values refer to *3*. Arrows point in the direction of the fragment bearing the charge.

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1. Liaaen-Jensen, S. *J. Pure Appl. Chem.* **17** (1970). *In press.*
2. Francis, G. W., Hertzberg, S., Andersen, K. and Liaaen-Jensen, S. *Phytochem.* **9** (1970) 629.
3. Arpin, N., Norgård, S., Francis, G. W. and Liaaen-Jensen, S. *Acta Chem. Scand. To be published.*
4. Enzell, C. R., Francis, G. W. and Liaaen-Jensen, S. *Acta Chem. Scand.* **22** (1968) 1054.
5. Biemann, K., DeJongh, D. C. and Schnoes, H. K. *J. Am. Chem. Soc.* **85** (1963) 1763.
6. Aasen, A. J., Francis, G. W. and Liaaen-Jensen, S. *Acta Chem. Scand.* **23** (1969) 2605.
7. Hertzberg, S. and Liaaen-Jensen, S. *Phytochem.* **8** (1969) 1281.
8. Jensen, A. *Norw. Inst. Seaweed Research*, Report No. 9, 1965.
9. Stahl, E. *Dünnschichtschromatographie*, Springer, Berlin 1962.
10. Hertzberg, S. and Liaaen-Jensen, S. *Phytochem.* **8** (1969) 1259.
11. Richterich, R. *Klinische Chemie, Theorie und Praxis*, Basel 1965, pp. 191–194.
12. Enzell, C. R., Francis, G. W. and Liaaen-Jensen, S. *Acta Chem. Scand.* **23** (1969) 727.
13. Liaaen-Jensen, S., Weeks, O. B., Strang, R. H. C. and Thirkell, D. *Nature* **214** (1967) 379.
14. Thirkell, D., Strang, R. H. C. and Chapman, I. R. *J. Gen. Microbiol.* **49** (1967) 157.
15. Liaaen-Jensen, S., Hertzberg, S., Weeks, O. B. and Schwieter, U. *Acta Chem. Scand.* **22** (1968) 1171.
16. Schwieter, U. and Liaaen-Jensen, S. *Acta Chem. Scand.* **23** (1969) 1057.
17. Weeks, O. B., Andrewes, A. G., Brown, B. O. and Weedon, B. C. L. *Nature* **224** (1969) 879.
18. Arpin, N., Francis, G. W. and Liaaen-Jensen, S. *Unpublished data.*

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A Low Temperature, Closed Vacuum System Distillation Technique

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Volatile compounds from tobacco and other natural products are frequently of considerable interest, but the isolation of these are usually difficult as they often occur in low concentrations mixed with large amounts of non-volatile material. The early technique of steam distillation has the disadvantage that artefacts are readily formed, while modern and milder chromatographic methods such as gel permeation chromatography are of restricted applicability due to the limited capacity of the gel. Ordinary vacuum distillation, which involves continuous pumping, often leads to substantial loss of volatile compounds,

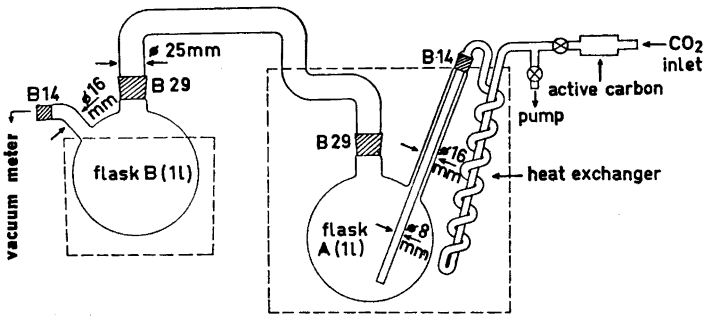

Fig. 1.

while increasing the pressure frequently requires temperatures giving decomposition products. We have therefore investigated a low-temperature distillation technique, which is a modification of an earlier method,[1] using carbon dioxide as carrier gas and excluding continuous pumping.

Apparatus and procedure. The distillation apparatus used is shown in Fig. 1. Carbon dioxide of high purity (>99.99 % CO_2) is passed through a filter of active carbon and a heat exchanger into flask A and finally condensed in flask B, which is kept at about −180° by means of a liquid nitrogen bath. The pressure, which is measured with the aid of a vacuum meter attached to flask B, is mainly regulated by the carbon dioxide flow. This flow also provides a means of stirring the material in flask A.

Before starting the distillation, the air is removed from the system to prevent condensation of oxygen. The operation is performed in the following manner: (1) The extract, preferably pre-saturated with carbon dioxide, is transferred into flask A. (2) Flask A is connected to the system and cooled in a carbon dioxide/acetone bath. (3) The system is evacuated (1 mm Hg) and filled with carbon dioxide until a pressure of 700 mm Hg is attained. This procedure is repeated four times. (4) The carbon dioxide/acetone bath is removed and flask B is cooled with liquid nitrogen; the resulting pressure is about 0.1 mm Hg. Carbon dioxide is led *via* the active carbon filter and the heat exchanger into flask A, which is slowly heated to the desired temperature in a thermostated bath. The tube connecting flasks A and B is kept at the same temperature by means of a heating tape. (5) The distillation is interrupted when on removal of the heating tape no condensation is observed. (6) The cooling and heating baths are removed. When the pressure of the system has increased somewhat, carbon dioxide is introduced until room pressure is attained. The receiver is disconnected and the solidified carbon dioxide is allowed to evaporate leaving the distillate in flask B.

Results. The distillation system was tested with a synthetic mixture (2.5 g) of equal amounts of n-alkanes ranging from C_6 to C_{28} to evaluate the yield and the degree of overlap in the distillate and the residue. The distillation was performed for 30 min at 50° using 100 g of carbon dioxide. The distillate and residue were analysed by gas chromatography (2 m × 1/8″ column with 2 % OV 17 on Chromosorb G, programmed from 25° to 280° with 6°/min). The stylized chromatograms (peak area measured by triangulation) are given in Fig. 2.

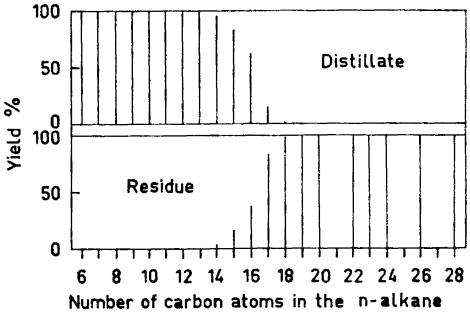

Fig. 2.

It follows from Fig. 2 that the yields, even of the low boiling alkanes, are better than 99 %. Any appreciable amount of

overlap is observed only in the C_{14} to C_{17} range. Since the distillation temperature determines the position of this range, the method is flexible and readily applied to a number of problems in flavour and natural product chemistry. It has been used with success in our laboratory for more than a year on various fractions from tobacco and tobacco additives of natural origin.

1. Honkanen, E. and Karvonen, P. *Acta Chem. Scand.* **20** (1966) 2626.

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The Crystal Structure of 2-(5′-Phenyl-1′,2′-dithiole-3′-ylidene)-6-(5″-*t*-butyl-1″,2″-dithiole-3″-ylidene)-cyclohexanethione. An Extended No-bond Resonance System Comprising Five Sulphur Atoms

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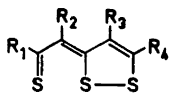
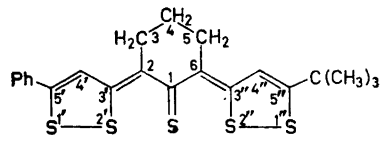
In thiathiophthenes (I) the sulphur-sulphur distance has been found in the



(I)

region single bond — van der Waals distance.[1–5] The nature of this type of bonding has been described in terms of one-bond, no-bond resonance. To see if this no-bond resonance can be extended to include more than three sulphur atoms, a series of X-ray crystallographic structure determinations of compounds containing linear four- and five-sulphur systems has been initiated. So far, structure reports on two linear four-sulphur compounds have been published.[6,7] In this communication, the first structure determination of a linear five-sulphur compound is reported.

The compound (II) was synthesized by Lozac'h and Stavaux.[8] It crystallizes from



(II)

dimethyl sulphoxide as extremely thin platelets. The crystals tend to be split, and have high mosaic spread. Several other crystallization procedures were tried, but did not give crystals of better quality.

The crystals belong to the monoclinic class, space group $P2_1/c$. Cell dimensions were derived from least-squares treatment of the 2θ settings for 12 reflections measured on a four-circle computer-controlled diffractometer: $a=20.009(9)$ Å, $b=8.066(6)$ Å, $c=13.457(7)$ Å, $\beta=103.07(2)°$. The crystal used for data collection had dimensions 0.15 mm × 0.15 mm × 0.01 mm. 1972 unique reflections within a sphere limited at $\sin\theta/\lambda=0.48$ were measured on the diffractometer using niobium-filtered Mo$K\alpha$ radiation ($\lambda=0.71069$ Å). Only 570 of these reflections had net counts significantly above the background. This extraordinary low number of observed reflections is a consequence of the small size of the crystal and the high mosaic spread.

The structure was solved by sharpened Patterson synthesis and refined by full-matrix least-squares to an R of 0.105. The sulphur atoms were refined anisotropically, while the carbon atoms were given isotropic thermal parameters. The hydrogen atoms have not been located. Standard deviations in S—S, S—C, and C—C bond lengths are 0.02 Å, 0.04—0.06 Å, and 0.06—0.10 Å, respectively.

71 of the reflections that had been coded unobserved, were calculated greater than the threshold value of $4\sigma_F$. These reflections were included with their threshold values in the final refinement together with the observed reflections.

The final coordinates from the least-squares refinement are listed in Table 1, and the molecular dimensions are shown in Fig. 1. Each of the four sulphur-sulphur