necessary for production of the radicals (also *cf.* (ii)). However, the reddish-brown colour described above (v) seems in some way to be connected with the ninhydrin radicals, but it is not clear if the coloured substances is identical with the radicals or not. Evidently, both of them are destroyed by molecular oxygen.

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The Absolute Configuration of Cleomin *

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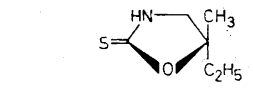
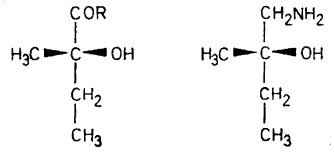
Glucocleomin is a thioglucoside occurring in *Cleome spinosa* Jacq. and other species of the family Capparidaceae.[1] Upon enzymic hydrolysis, glucocleomin produces cleomin, previously identified in this laboratory as (−)-5-ethyl-5-methyl-2-oxazolidinethione.[1] We now report that cleomin possesses the absolute configuration depicted in (I).

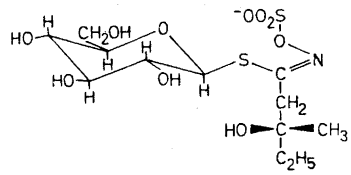
On reaction with liquid ammonia at 100° for 42 h, levorotatory methyl 2-hydroxy-2-methylbutyrate, to which we recently assigned the (*R*)-configuration (II, R = OCH_3),[2] was converted into (*R*)-2-hydroxy-2-methylbutyramide (II, R = NH_2), m.p. 55° (stable) or 46° (dimorphism), $[\alpha]_D^{22}$ + 18.8° (*c* 4.2, 96 % ethanol). (Found: C 51.25; H 9.54; N 11.93. Calc. for $C_5H_{11}NO_2$: C 51.26; H 9.47; N 11.96). By reduction with lithium aluminium hydride in ether, the



I



II III



IV

amide was transformed into (*R*)-1-amino-2-methyl-2-butanol (III) which was isolated as the dextrorotatory neutral oxalate, m.p. 204° (decomp.), $[\alpha]_D^{23}$ + 3.5° (*c* 2.4, H_2O). (Found: C 48.53; H 9.58; N 9.52. Calc. for $C_{12}H_{28}N_2O_6$: C 48.63; H 9.52; N 9.46). On critical comparison with the previously synthesized specimen of the oxalate, that was formerly transformed into cleomin,[1] the two preparations proved to be identical, * except for their optical rotations which were equal in magnitude within the experimental error *but opposite in sign*. Consequently, the naturally derived, levorotatory cleomin possesses the (*S*)-configuration (I).

2-Oxazolidinethiones arise from spontaneous cyclization of 2-hydroxy-substituted isothiocyanates, which are initial products of the enzymic hydrolysis of the corresponding glucosidic progenitors (*cf.* Ref.[3]). Consequently, glucocleomin possesses the absolute configuration shown in (IV).

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* Part XLVII of a series of papers on isothiocyanates (part XLVI: *Acta Chem. Scand.* **16** (1962) 2065).

* The previously reported [1] m.p. 192° for the levorotatory oxalate appears to be too low. When determined under the present conditions (oil bath, capillary tube, rate 2°/min), the same sample now decomposed at 204°.

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Long-range Proton Spin Couplings in Thieno[3,2-b] thiophene

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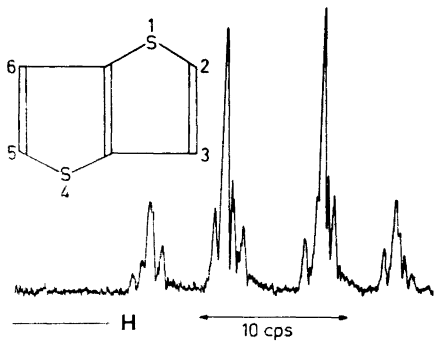

Fig. 1.

In connection with the investigation of the ring-closure of some α-[thienylthio] substituted acids [1], the NMR-spectrum of thieno[3,2-b] thiophene has been studied. At low resolution it appears as an AB spectrum, but at higher resolution additional fine structure is seen revealing the presence of cross-ring couplings giving an A_2B_2 pattern [2]. A complete analysis of the spectrum gave the following coupling constants; $J = +5.30$ cps, $J' = -0.20$ cps, $J_A = +1.50$ cps and $J_B = +0.75$ cps.

$J = J_{23} = J_{56}$ is of the same order as in thiophene [3] and is arbitrarily chosen positive. $J' = J_{26} = J_{35}$ is over five bonds and is small ,while J_A and J_B are over five and six bonds and are unexpectedly large. Out of the A_2B_2 analysis it is impossible to determine which diagonal coupling is J_A and which J_B. J_{36} is over five bonds while J_{25} is over six bonds which might lead to the conclusion that J_{36} is the largest. The recent suggestion [4] of largest coupling through the "straightest zig-zag path" also supports this assignment. Results obtained for a structurally similar compound, N-benzylthieno [3,2-b]pyrrole [5], however supports the opposite assignment. There [5] it was found that the cross-ring coupling over six bonds between the α-hydrogens is the largest (1.3 cps), more than twice the corresponding β coupling (0.5 cps). Any cross-ring couplings between the α and β hydrogens were not observable.

In analysing the A_2B_2 spectrum it is possible to take advantage of the fact that the rough shape of the spectrum is that of an AB quartet showing that the cross-ring couplings are much smaller than the AB coupling. In A_2B_2 spectra the energy levels can be calculated in closed form except for the S_0 levels which are obtained from a 4×4 matrix [2]. Now, instead of choosing the base functions of this submatrix as the products of the base functions for A_2 and B_2 of appropriate symmetry, it is in the present case suitable to choose as base functions the products of the AB eigenfunctions of correct symmetry. This leads to the approximate diagonalization of this submatrix making the off-diagonal elements small compared with the corresponding diagonal element differences. For sufficiently small off-diagonal elements, that is small J', J_A and J_B, it would thus be accurate enough to use only first order perturbation theory. With this treatment all expressions for the transition frequencies and intensities are given in closed form. Aslo for not too large off-diagonal elements, it may suffice to go to second order perturbation theory.

Five parameters, the relative shift ($\nu_0\delta$) and four coupling constants had to be determined by comparison of calculated spectra with the observed one. Good values of $\nu_0\delta$ and the largest coupling J were immediately obtainable by disregarding the fine structure and treating the spectrum as an AB case. The three remaining couplings were then simultaneously varied and promising assignments closer investigated. The method of Dischler and Maier [6] was also used to test calculated assignments, and several were found to fulfill the criteria given by these authors. However only the one here reported gave a calculated spectrum in agreement with the measured one. This assignment was also checked by exact diagonalization.