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Studies on the Chemistry of Lichens

27* The Absolute Configuration of Rangiformic Acid

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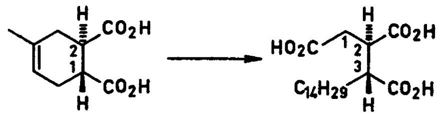
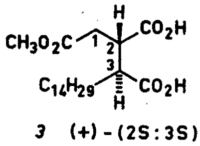
The absolute configuration of (−)-norrangiformic acid, 1, (2R:3R)-heptadecanetricarboxylic acid (*2*) has been determined by a stereospecific synthesis from 4-methyl-4-cyclohexen-(1R:2R)-dicarboxylic acid (*1*). The antipode, (+)-norrangiformic acid, has been obtained by mild hydrolysis of naturally occurring (+)-rangiformic acid which is therefore methyl dihydrogen 1, (2S:3S)-heptadecanetricarboxylate (*3*). The position of the ester group is still uncertain.

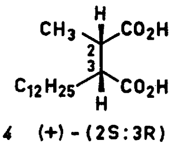
It is interesting to note that rangiformic acid and the structurally related roccellic acid (*4*) have opposite configurations at position 3, which is presumably the position where oxaloacetate and the appropriate alkanoyl coenzyme A are coupled during the biosynthesis of the compounds (*3*) and (*4*).



1 (-)-(1R:2R) *2* (-)-(2R:3R)



3 (+)-(2S:3S)



4 (+)-(2S:3R)

Experimental. *(−)-4-Methyl-4-cyclohexene-(1R:2R)-dicarboxylic acid (1)* was obtained by repeated crystallizations from water of the brucine salt of *trans*-4-methyl-4-cyclohexene-1,2-dicarboxylic acid (compare Ref. 1). On acidification of an aqueous solution of the salt, followed by extraction with ethyl acetate and evaporation of the solvent, a low yield of the acid (*1*) was obtained (5 %), partial melting at 139−140°, followed by recrystallisation and melting at 146−149°, $[\alpha]_D^{25}$ −150 ± 5° (lit.[1] m.p. 152−164°, $[\alpha]_D^{25}$ + 160 ± 1° for the enantiomer).

(−)-(3R:4R)-Dimethoxycarbonyl-6-oxoheptanoic acid. The dimethylester of (*1*) was prepared by methylation with diazomethane, $[\alpha]_D^{25}$ −150 ± 5° (neat), and then ozonised. The ozonides were decomposed with "activated zinc powder"[2] and the product recrystallised from light petroleum-ether 1:1 at −20° to give (−)-(3R:4R)-dimethoxycarbonyl-6-oxoheptanoic acid, m.p. 76−79°, $[\alpha]_D^{25}$ −70 ±5° (*c* 0.97, chloroform). (Found: C 50.6; H 6.2. Calc. for $C_{11}H_{16}O_7$: C 50.8; H 6.2).

(+)-2-Oxo-(4R:5R)-nonadecanedicarboxylic acid was prepared in a similar manner to the inactive compound[2] by electrolytic coupling of (−)-3,4-dimethoxycarbonyl-6-oxoheptanoic acid and myristic acid, followed by hydrolysis. M.p. 119−123°, $[\alpha]_D^{25}$ + 52 ± 5° (*c* 1.0, ethanol). (Found: C 67.6; H 10.1. Calc. for $C_{21}H_{38}O_5$: C 68.1; H 10.3).

(−)-1,(2R:3R)-Heptadecanetricarboxylic acid (2) was prepared by hypobromite oxidation of (+)-2-oxo-4,5-nonadecanedicarboxylic acid,[2] followed by chromatography on ethanol washed silica (using light petroleum-ether as eluent) and recrystallisation from ethyl acetate.

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M.p. 116–122°, $[\alpha]_D^{25}$ −11 ± 1° (*c* 0.59, ethanol). (+)-Norrangiformic acid obtained from rangiformic acid by hydrolysis had m.p. 114–122° (lit.[3] m.p. 118°, $[\alpha]_D^{25}$ + 12.9). The IR-spectra of the two samples were superimposable. Surprisingly, the melting point of the natural (+)-norrangiformic acid was not raised on mixing with the synthetic (−) sample (compare Ref. 2). It is possible that an increase is difficult to observe due to the unusually large melting range of the acids, which is presumably caused by anhydride formation. (Found: C 64.8; H 9.6. Calc. for $C_{20}H_{36}O_6$: C 64.5; H 9.7).

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Thortveitite-Type Structure of $Mn_2V_2O_7$

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Several diphosphates and other $A_2B_2O_7$ compounds with thortveitite structure have been reported during recent years.[1] The main structural problem as regards the thortveitite, $Sc_2Si_2O_7$, is whether there exists a linear Si-O-Si bonding. This matter has been discussed by Cruickshank *et al.*[2] The thortveitite structure has now been found in dimanganesedivanadate $Mn_2V_2O_7$. This compound was first reported by Brisi[3] among other vanadates in the system Mn-V-O. The interplanar distances given by Brisi are in accordance with those found by the present authors.

The dimanganesedivanadate was synthesized by two different methods. The products gave identical powder patterns. If a sample was prepared from the oxides and vanadium in the stoichiometric composition of $MnVO_4$ — the preparation of which was the original purpose — and heated at 800°C the loss of weight corresponded exactly to one eighth of the oxygen contents. If, instead, oxides in the stoichiometric composition of $Mn_2V_2O_7$ were mixed and heated there was no loss of weight.

The cell dimensions calculated from Guinier powder photographs were refined by a least squares method program written by Werner.[4] Strictly monochromatized $CuK\alpha_1$ radiation was used. The dimensions are

$$\begin{aligned} a &= 6.710 \pm 0.002 \text{ Å} \\ b &= 8.726 \pm 0.002 \text{ Å} \\ c &= 4.970 \pm 0.001 \text{ Å} \\ \beta &= 103.57 \pm 0.01° \end{aligned}$$

The unit cell contains 2 formula units (observed and calculated density values of 3.79 g/cm³ and 3.80 g/cm³, respectively). The crystals are black and inclined towards twinning.

Single crystal data were collected with a Weissenberg camera using $CuK\alpha$ radiation. The multiple film technique was applied. The intensities of the layers $hk0-hk3$ were estimated visually. The scale factors between the layers were calculated by comparing the measured intensities with those obtained from a zero layer photograph recorded around another axis. No absorption correction was made, a fact which has obviously affected the temperature factors which came out slightly negative (see Table 1).

At an early stage of the structure determination it was apparent that the structure was of the thortveitite type and thus there was a choice between the three space groups $C2/m$, $C2$, and Cm.

As an attempt to determine the space group unequivocally, refinements were carried out using the least squares method. In Table 1 the resulting distances within the V_2O_7 group and the V–O–V angle are given. The oxygen shared by the two VO_4-tetrahedra is assigned index 11.