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Studies on the Chemistry of Lichens

27* The Absolute Configuration of Rangiformic Acid

BJÖRN AKERMARK

Department of Organic Chemistry, Royal Institute of Technology, Stockholm, Sweden

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 roccelic 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).

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°, [α]_D^{25} +150 ± 5° (lit.1 m.p. 152–164°, [α]_D^{25} +160 ± 1° for the enantiomer).

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

(+)-2-Oxo-(4R:5R)-nonadecanedicarboxylic acid was prepared in a similar manner to the inactive compound by electrolytic coupling of (-)-3,4-dimethoxy carbonyl-6-oxoheptanionic acid and myristic acid, followed by hydrolysis. M.p. 119–123°, [α]_D^{25} +52 ± 5° (c 1.0, ethanol). (Found: C 76.7; H 10.1. Calc. for C_{19}H_{28}O_{4}: C 68.1; H 10.3).

(-)-1,(2R:3R)-Heptadecanetricarboxylic acid (2) was prepared by hypobromite oxidation of (+)-2-oxo-4,5-nonadecanedicarboxylic acid, 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°, [α]D 48° –11 ± 1° (c 0.59, ethanol), (+)-Norrangeforic acid obtained from rangeforic acid by hydrolysis had m.p. 114–122° (lit 3 m.p. 118°, [α]D 48° + 12.9). The IR-spectra of the two samples were superimposable. Surprisingly, the melting point of the natural (+)-norrangeforic 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_{34}O_{6}: C 64.5; H 9.7).

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Thortveitite-Type Structure of Mn$_2$V$_2$O$_7$

EBBA DORM and BENGT-OLOV MARINDER

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

Several diphosphates and other $A_2B_2O_7$ compounds with thortveitite structure have been reported during recent years. The main structural problem as regards the thortveitite, Sc$_2$Si$_2$O$_7$, is whether there exists a linear Si-O-Si bonding. This matter has been discussed by Cruickshank et al. The thortveitite structure has now been found in dimanganesedivanadate Mn$_3$V$_4$O$_{11}$.

This compound was first reported by Brisi 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$_3$V$_4$O$_{11}$ 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. Strictly monochromatized CuK$_{α}$ radiation was used. The dimensions are

\[
\begin{align*}
\alpha &= 6.710 \pm 0.002 \text{ Å} \\
b &= 8.728 \pm 0.002 \text{ Å} \\
c &= 4.970 \pm 0.001 \text{ Å} \\
\beta &= 103.57 \pm 0.01^\circ
\end{align*}
\]

The unit cell contains 2 formula units (observed and calculated density values of 3.79 g/cm$^3$ and 3.80 g/cm$^3$, respectively). The crystals are black and inclined towards twinning.

Single crystal data were collected with a Weissenberg camera using CuK$_{α}$ 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 VO$_4$ group and the V–O–V angle are given. The oxygen shared by the two VO$_4$-tetrahedra is assigned index 11.

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