

## Note on the Crystal Structures of $\text{Nb}_{11}\text{O}_{27}$ , $\text{Nb}_{25}\text{O}_{62}$ and $H\text{-Nb}_2\text{O}_5$

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The system  $\text{NbO}_x$  ( $2.0 < x < 2.5$ ) has been investigated at the above Departments since 1959. Some previously unknown phases have been reported, namely two forms of  $\text{Nb}_{12}\text{O}_{29}$ ,<sup>1,2,4</sup>  $\text{Nb}_{11}\text{O}_{27}$ ,<sup>1,3</sup> and  $\text{NbO}_{2.48}$ ,<sup>1,3</sup> the latter being supposed to have the formula  $\text{Nb}_{25}\text{O}_{62}$ , and to be isostructural with  $\text{TiNb}_{24}\text{O}_{62}$ .<sup>5</sup> Gatehouse and Wadsley have suggested that  $\text{Nb}_{11}\text{O}_{27}$ <sup>6</sup> is a member of the homologous series  $\text{Nb}_{2n+1}\text{O}_{6n-2}$  with  $n = 7$ . Further crystal structure studies using single crystal and powder methods have now been performed in order to ascertain the validity of the structures proposed for  $\text{Nb}_{11}\text{O}_{27}$  and  $\text{Nb}_{25}\text{O}_{62}$ . Single crystal photographs of  $\text{Nb}_{11}\text{O}_{27}$  were also compared with photographs of the high temperature form of  $\text{Nb}_2\text{O}_5$ ,<sup>6</sup> which is the member of the above series having  $n = 9$ .

In the investigation of  $\text{Nb}_{11}\text{O}_{27}$  and  $\text{Nb}_{25}\text{O}_{62}$ ,  $\text{NbO}_x$  samples prepared in a way described earlier<sup>1</sup> were used. Two samples of  $H\text{-Nb}_2\text{O}_5$  containing very beautiful crystals well suited to single crystal work, were most kindly placed at the authors' disposal by Drs. Gruehn and Mertin at the University of Münster. Weissenberg photographs  $h0l-h2l$  were taken using  $\text{CuK}\alpha$  radiation, and the intensities of the reflections were estimated visually. Calculations of structure factors, Fourier syntheses, and least squares refinements were performed on a SAAB D 21 computer using programmes written by Abrahamsson *et al.*<sup>7</sup>

For  $\text{Nb}_{25}\text{O}_{62}$ , structure factors were calculated using the parameters of  $\text{TiNb}_{24}\text{O}_{62}$ ,<sup>5</sup> and these showed fair agreement with the observed structure factors ( $R = 20\%$ ). After a few cycles of least squares refinement the  $R$  value dropped to 15%. This agreement between observed and calculated structure factors was taken as evidence that  $\text{Nb}_{25}\text{O}_{62}$  is structurally closely

related to  $\text{TiNb}_{24}\text{O}_{62}$  and that the two phases are probably isostructural.

During the examination of the Weissenberg photographs of  $\text{Nb}_{11}\text{O}_{27}$  some previously unobserved, very weak reflexions, leading to a doubling of the  $c$ -axis, were noted, the following cell dimensions thus being obtained:

$$a = 17.86 \text{ \AA}, b = 3.822 \text{ \AA}, c = 31.50 \text{ \AA}, \\ \beta = 102.11^\circ.$$

The systematically absent reflexions were:

$$h0l \text{ with } l = \text{odd}$$

which is in accordance with space groups No. 13,  $P2_1/c$ , and No. 7,  $Pc$ . Atomic parameters for the Gatehouse-Wadsley structure for  $\text{Nb}_{11}\text{O}_{27}$  (space group No. 3,  $P2_1$ ) were derived graphically from the structure of  $H\text{-Nb}_2\text{O}_5$ ,<sup>6</sup> and structure factors were calculated which showed satisfactory agreement with the observed structure factors, reflexions with odd  $l$  being excluded. A least squares refinement performed using the structure factors corresponding to reflexions with even  $l$  only lowered the  $R$  value for these reflexions from about 30% to 13.8%. This makes it probable that the structure proposed by Gatehouse and Wadsley for  $\text{Nb}_{11}\text{O}_{27}$  is very closely related to the real one. The doubling of an axis in structures of this type has been discussed previously<sup>4</sup> in terms of small deviations in the  $y$  direction for some of the atomic positions.

In order to investigate whether crystals of  $H\text{-Nb}_2\text{O}_5$  give reflexions analogous to the weak ones with odd  $l$  described above for  $\text{Nb}_{11}\text{O}_{27}$ , new Weissenberg photographs  $h0l-h2l$  were taken with  $\text{CuK}\alpha$  radiation, using a large single crystal (about 0.3 mm) and an exposure time of 72 h. In the  $h1l$  and  $h2l$  photographs a number of weak reflexions were found which necessitated a doubling of both the  $a$  and  $c$  axes. If, however, new axial directions were chosen by making the transformation 101/010/001, the cell dimensions of  $H\text{-Nb}_2\text{O}_5$  became

$$a = 20.37 \text{ \AA}, b = 3.822 \text{ \AA}, c = 38.70 \text{ \AA}, \\ \beta = 115.69^\circ$$

The presence of these reflexions thus led to a doubling of the cell content only. Pictures of idealized structures of  $H\text{-Nb}_2\text{O}_5$  and  $\text{Nb}_{11}\text{O}_{27}$  have been published by Gatehouse and Wadsley<sup>6</sup> the axes of which must, however, be transformed to agree with the dimensions given above.

Attempts to explain the doubling of the cell contents of the two compounds in terms of placing every second "tetrahedral"

niobium atom in  $y = 1/4$  and the remainder of these atoms in  $y = 3/4$  have not been successful.

Further refinement of these structures is now in progress.

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### (—)-Torreyol ("δ-Cadinol")\*

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Torreyol, a dextrorotatory sesquiterpene alcohol,<sup>1-3</sup> was first isolated in 1922 from the leaves of *Torreya nucifera* Sieb et Zucc. (Taxaceae).<sup>1</sup> Several compounds, e.g. "(+)-δ-cadinol"<sup>4</sup> and "sesquigoyol",<sup>5,6</sup> occurring in some pines,<sup>4-6</sup> have been shown to be identical with (+)-torreyol.

"Albicaulol" from *Pinus albicaulis* Engelm.<sup>7</sup> is identical<sup>3,6</sup> with (—)-torreyol. It has been isolated from other pine species,<sup>8-10</sup> as well as from many other conifers<sup>11,17</sup> and it has been described under various synonyms, such as "pilgerol"<sup>12</sup> and "δ-cadinol".<sup>13</sup> It also occurs in an angiosperm, *Cedrela odorata*, Meliaceae

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("cedrelanol")<sup>14</sup> and in a cryptogam, the alga *Dictyopteris divaricata* (Phaeophyta) ("brown alga cadinol").<sup>15</sup> Lambertol from *Pinus lambertiana* Dougl. is probably either (+)- or (—)-torreyol.<sup>8</sup>

In view of its priority, we suggest the name torreyol be retained and used instead of the many synonyms.

Different structures, (2),<sup>13</sup> (3),<sup>16</sup> (4),<sup>17</sup> and (5),<sup>14</sup> have been proposed for torreyol, but none of them appeared to us to be definitely ascertained. (—)-Torreyol has now been found to be represented by formula (1).

On treatment with hydrogen chloride torreyol gave a mixture, as shown by its IR spectrum,<sup>18</sup> of cadinene dihydrochloride and muurolene dihydrochloride, indicating *cis* ring junction in the alcohol. Under the same conditions, cadinenes and cadinols (*trans* ring junction) do not give any muurolene dihydrochloride. Torreyol was proved to be a muurolol in the following way.

(—)-Torreyol was refluxed with an equivalent amount of brosyl chloride in pyridine for 4 h. Without removal of the solvent, the reaction mixture was filtered through basic alumina. Elution with light petroleum gave a mixture of olefins, which, according to GLC (conditions and retention data, see Ref. 9), consisted of three components: an unidentified hydrocarbon (almost same

