

Table 1. Content of reducing sugars (mg glucose/g dry weight) after irradiation and storage at different water contents.

Water content %	Analysis after	Seeds irradiated with, r		
		0	$5 \times 10^5$	$10 \times 10^5$
7.5	15 hours	1.46	1.53	1.46
	4 weeks	1.51	1.61	1.64
17	15 hours	1.15	1.33	1.21
	4 weeks	1.92	2.21	2.05
17*	2 weeks	1.98	2.55	—

\* Experiment not simultaneous with those above.

crease of the water content first caused a fall in reducing sugars, possibly a consequence of the increased respiration<sup>3,4</sup>. During 2–4 weeks storage, at unchanged water content, the value increases, possibly becoming slightly higher at the higher water content.

Irradiation with  $5 \times 10^5$  r increases the content of reducing sugars, especially at the higher water content. ( $10 \times 10^5$  r gives a somewhat lesser chemical change. After treatment with this high dose, a fraction of the seeds do not germinate; and death of seeds might therefore be responsible for any disturbed values.) As this increase is already observed immediately after irradiation, it is probably not an effect of a changed metabolic rate (e. g., decrease of respiration rate<sup>9</sup>). It might be ascribed to a radiation induced disintegration of, e. g., starch. If this is so, intermediates originating from cellular constituents other than carbohydrates and water, obviously play a role, as the disintegration of starch, irradiated at 8–23 % H<sub>2</sub>O, was only measurable as viscosity decrease.

It can be concluded that irradiation causes a greater chemical change in sugars when the seeds have a higher moisture content, and consequently are protected against biological damage. The significance of this result, for the interpretation of the mechanism of action of radiations, will be discussed elsewhere<sup>10</sup>.

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## The States <sup>1</sup>I of Trivalent Praseodymium and Thulium

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The identification by Spedding<sup>1</sup> of the states of Pr<sup>3+</sup> has for many years been assumed to be complete. But the proposal of Ellis<sup>2</sup> that the band in the orange is due to a transition to <sup>1</sup>D<sub>2</sub>, rather than to <sup>1</sup>I<sub>6</sub>, was recently supported by the crystal field studies of Hellwege<sup>3</sup>. The Condon-Shortley theory<sup>4</sup> was applied to this f<sup>3</sup>-system by Trefftz<sup>5</sup>. This author calculated the electrostatic interaction parameters  $F_2$ ,  $F_4$ , and  $F_6$  for a hydrogen-like 4f-wave function with an effective charge  $Z_0 = 9.48$  (this seems very reasonable, because the ionization energy of Ce<sup>3+</sup> corresponds to  $Z_0 = 6.56$ ). However, the value of  $F_6$  calculated by Trefftz is 64 times too small due to a misinterpretation of Condon and Shortley's decimal point as a multiplication operator. This led Trefftz to accept Spedding's very small value of  $F_6$ .

In the author's opinion<sup>6</sup>,  $F_6$  is not necessarily negligible<sup>7-9</sup>. The position of <sup>1</sup>D<sub>2</sub>, relatively to <sup>3</sup>P<sub>2</sub>, can easily be accounted for by the set of ratios<sup>6</sup>  $F_4 = 0.2 F_2$ , and  $F_6 =$

\* Note added in proof: Judd<sup>15</sup> has recently drawn the same conclusion from Eu<sup>3+</sup>. The present author must here correct the highest value among the three diagonal elements of energy of the <sup>5</sup>D-states to  $9E^1 - 11E^3$  rather than  $9E^1 + \frac{143}{7} E^3$ , given in Ref. 8, p. 19.

0.02  $F_2$  just as well as by Trefftz's values,  $F_4 = 0.138 F_2$  and  $F_6 = 0.0152 F_2$  (if  $F_2$  multiplied by 64). Also Racah's values<sup>9</sup> for  $\text{Th}^{++}$  suggest a similar decrease in the  $F^k$  integrals:  $F_4 = 0.19 F_2$  and  $F_6 = 0.018 F_2$ . Both Trefftz's revised and the other proposals give  $^1I$  at nearly the same place as the triplet  $^3P$ . Thus, it will probably be masked by the three strong bands in the blue. Broer, Gorter and Hoogschagen, in their investigation of band intensities<sup>10</sup>, could not explain the anomalously high intensity of the  $^1I$ -band of  $\text{Pr}^{+3}$ . Hellwege's identification of the band as  $^1D_2$  removes this difficulty, and one must consider the  $^1I$  as not yet observed. The triplet character<sup>10</sup> expressed in squares of the wave function will only be of the magnitude<sup>1</sup>.

$$[S = 1] = \frac{6 \zeta^2}{(^1I_6 - ^3H_6)^2}$$

Since  $\zeta = 400 \text{ cm}^{-1}$  and the distance  $^1I_6 - ^3H_6$  between the two perturbing levels is  $\sim 15\,000 \text{ cm}^{-1}$ , the quantity  $[S = 1]$  will only be  $\sim 0.005$ . Even if the molar extinction coefficient  $\epsilon_0$  of the band  $^3H_4 - ^1I_6$  were 20 for the pure triplet transition, the actual  $\epsilon_0$  would only be 0.1. Nevertheless, this should be observable. The author has tried in vain in the wavelength range 550–270  $\mu\text{m}$  for 0.2  $M$   $\text{Pr}(\text{ClO}_4)_3$  in 5 cm cells. However, the spectrum does show a conspicuous broadening towards shorter wavelengths of the band  $^3P_1$ , but no definite conclusion can be drawn.

According to Pauli's equivalence theorem of holes,  $f^{12}$  in  $\text{Tm}^{+3}$  and  $f^2$  in  $\text{Pr}^{+3}$  have the same set of terms. The band at 350  $\mu\text{m}$  of  $\text{Tm}^{+3}$ , supposed to be due to

$^3H_4 - ^1I_6$ , is cited above<sup>10</sup> as the only other known example of anomalously high intensity. But an aqueous solution of thulium(III) perchlorate in 1  $M$   $\text{HClO}_4$  shows this band as not having any larger oscillator strength  $P$  (which is proportional to the area of the band as a function of wave number<sup>10</sup>) than the other bands, while Hoogschagen, Scholte and Kruyer<sup>11</sup> give  $P \sim 30 \cdot 10^{-6}$ , contrary to usual lanthanide bands with  $P \sim 10^{-6}$ . The materials used by these authors seem to contain strongly ultraviolet-absorbing impurities (iron?) as was true in the case of their holmium<sup>11</sup>. Measurements on a Cary spectrophotometer of 0.1  $M$   $\text{Tm}(\text{ClO}_4)_3$  in 2 cm cells give the following maximum values  $\epsilon_0$  and oscillator strengths  $P$  (uncertainty  $\sim 20\%$ ):

Maxima observed	$\epsilon_0$	$P$	$P$ (Ref. 11)
780 $\mu\text{m}$	1.0	$1.9 \cdot 10^{-6}$	$1.98 \cdot 10^{-6}$
695,682,655	0.9; 1.5; 0.3	3.0	3.18
462	0.4	0.4	$\sim 0.45$
358,355	0.8; 0.8	2.4	$\sim 30$
290,284	0.1; 0.2	0.4	
276,274	0.1; 0.2	0.3	
263,260	1.4; 1.2	5	

Qualitative agreement is found with the measurements by Rodden<sup>12</sup> for wavelengths over 350  $\mu\text{m}$ . Besides the bands of the table, weak and narrow bands at 520, 378 and 255  $\mu\text{m}$  (with  $\epsilon_0 \sim 0.1$ ) may be ascribed to an impurity of  $\sim 3\%$  erbium, whose strong bands occur at these wavelengths<sup>8</sup>. Below 300  $\mu\text{m}$  the background rises appreciably, and below 230  $\mu\text{m}$  a steep absorption limit appears. The latter

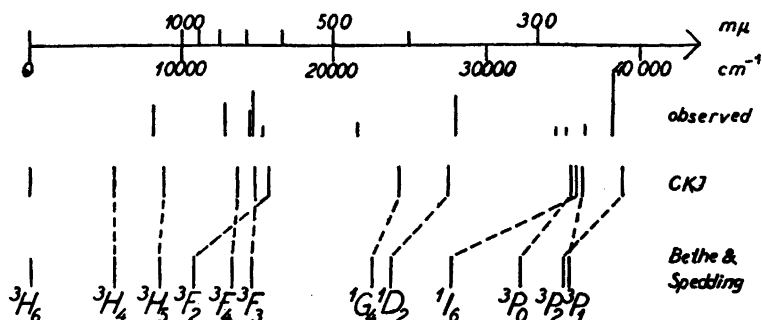


Fig. 1. Observed bands of  $\text{Tm}^{+3}$  (except that at 8100  $\text{cm}^{-1}$ ) represented by peaks proportional to the oscillator strength  $P$ . Calculated positions with intermediate coupling from the parameters, given in the text.

is not due to  $\text{ClO}_4^-$  and is perhaps due to  $4f^{13}-4f^{13}5d$  transitions in  $\text{Tm}^{+3}$ . The three band groups in the range 290–260  $m\mu$  are equivalent to those found by Gobrecht<sup>13</sup> in solid  $\text{Tm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ . The multiplet  $^3P$  is somewhat perturbed, the most intense band group 263–260  $m\mu$  presumably being due to  $^3H_4-^3P_2$ .

Since  $[S = 1] = 0.02$  for  $^1I_6$  in  $\text{Tm}^{+3}$ , the transition to this state is still of unusually high probability, if it corresponds to the 358–355  $m\mu$  band group. This is not certain, since the strong intermixing of the states with  $J = 4$ , viz.  $^3H_4$ ,  $^3F_4$  and  $^1G_4$ , may distribute two of the states to 685 and 355  $m\mu$ . Bethe and Spedding<sup>1,14</sup> choose the set of parameters  $F_2 = 308 \text{ cm}^{-1}$ ,  $F_4 = 71 \text{ cm}^{-1}$ , and  $F_6 = 0.86 \text{ cm}^{-1}$  by extrapolation from  $\text{La}^{+3}$ . If the possibility  $^6 F_2 = 450 \text{ cm}^{-1}$ ,  $F_4 = 90 \text{ cm}^{-1}$ , and  $F_6 = 9 \text{ cm}^{-1}$  is applied to  $\text{Tm}^{+3}$  with  $\zeta = -1400 \text{ cm}^{-1}$ , the identifications are changed somewhat. Fig. 1 gives the two sets of calculated wave numbers and the observed. But the question cannot be settled, before  $J$  can be determined from crystal field studies. The low intensity of the band at 462  $m\mu$  might support the identification with  $^1D_2$ .

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## isoThiocyanates XI.

### 4-Methylthiobutyl isoThiocyanate, a New Naturally Occurring Mustard Oil

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In a previous communication of this series<sup>1</sup> it was observed that seeds of *Eruca sativa* Mill. contain a volatile mustard oil which is paperchromatographically different from the known, naturally occurring isothiocyanates. We now wish to report on the identity of this mustard oil as 4-methylthiobutyl isothiocyanate (I), a compound first synthesized by Schmid and Karrer<sup>2</sup>.



I



II R = H

III R =  $\text{CH}_2\text{C}_6\text{H}_5$

From a larger seed sample, made available to us during the summer of 1954, we isolated the thiourea derivative (II) of the volatile isothiocyanate. The chemical structure was established by analysis and by comparison with a synthetic specimen of (II). Mixed melting point, paper chromatography in various solvents and infrared spectra left no doubt as to the identity of the two preparations.

In Nature (I) occurs as a yet uncharacterized glycoside for which we suggest the name *glucoerucin*. Its presence is disclosed upon paper chromatography according to Schultz and Gmelin<sup>3</sup>. These authors noticed in seeds of *Eruca sativa*

\* Part of the present work was carried out during a visit by one of us (A.K.) to the Department of Physiological Chemistry of the University of Lund, Sweden.