

$$\frac{SX}{SY} = \frac{(r_S + r_R) \cos 180^\circ - \theta + \sqrt{(r_X + r_R)^2 - (r_S + r_R)^2 \sin^2 180^\circ} - 0}{(r_S + r_R) \cos \theta + \sqrt{(r_Y + r_R)^2 - (r_S + r_R)^2 \sin^2 \theta}}$$

is constant.

If θ is assumed as 90° at the transition stage, the expression reduces to

$$\frac{(r_X + r_R)^2 - (r_S + r_R)^2}{(r_Y + r_R)^2 - (r_S + r_R)^2} \text{ or } \frac{r_X^2 + m r_X - n}{r_Y^2 + m r_Y - n},$$

where $m = 2r_R$ and $n = r_S(r_S - 2r_R)$.

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¹ Wilkins, Brown and Stevens, *J. Chem. Soc.*, 163 (1950).

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An Unusual Distribution of the Lanthanons

AN analysis of the lanthanon (rare earth) fraction from davidite, a uranium-iron-titanium oxide complex from the Radium Hill area of South Australia, has revealed an unusual variation in the abundance of the lanthanons. The accompanying table compares (a) the percentage abundance found for davidite, with (b) that given by Goldschmidt and Thomassen¹ for some uranium-titanium-niobium-tantalum complex oxide minerals, and (c) xenotime. Also included in the table are Goldschmidt's values (d) for the average terrestrial abundance of the lanthanons, this abundance differing from that found for monazite mainly in exhibiting a slightly smaller proportion of the lighter (cerium group) lanthanons.

The mineral complex, which has been fully described by Mawson², is substantially primary in nature. The samples used contained approximately two per cent of lanthanon oxides in addition to silica, vanadium, aluminium and other minor components. Fourteen per cent of the total oxalate precipitate consisted of yttria.

Two analyses were carried out with material from different parts of the main ore-body, and almost identical results were obtained. In the first experiment the lanthanons, after complete extraction from the sample, were recovered by oxalate precipitation. In the second experiment, any scandium present, which might otherwise have been reported as yttria, was removed by ether extraction from a thiocyanate solution as recommended by Fischer and Bock³. Iron in this second experiment was removed beforehand by ether extraction from a hydrochloric-acid solution.

Where possible, the lanthanons were determined spectrophotometrically, using extinction coefficients previously reported⁴⁻⁶. Cerium was determined titrimetrically. A preliminary division into light and

heavy groups by controlled double-sulphate fractionation was made. Lanthana and yttria were determined by difference after allowing for gadolinia, terbium and lutetia. The yttria content of the heavy group was checked by average atomic weight determinations.

By showing enrichment towards both ends of the series, the observed distribution lacks any resemblance to the distributions reported by Goldschmidt and Thomassen. If it be accepted that fractionation of the lanthanon ions from a magma proceeds serially, it is difficult to interpret the above distribution unless more than one mineral species is present. Unfortunately, the complex is too fine-grained to permit a test of this hypothesis. The usefulness of the material as a source of lanthanum, erbium and ytterbium is evident.

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² Mawson, D., *Trans. Roy. Soc. South Australia*, **68**, 334 (1944).

³ Fischer, W., and Bock, R., *Z. anorg. Chem.*, **249**, 146 (1942).

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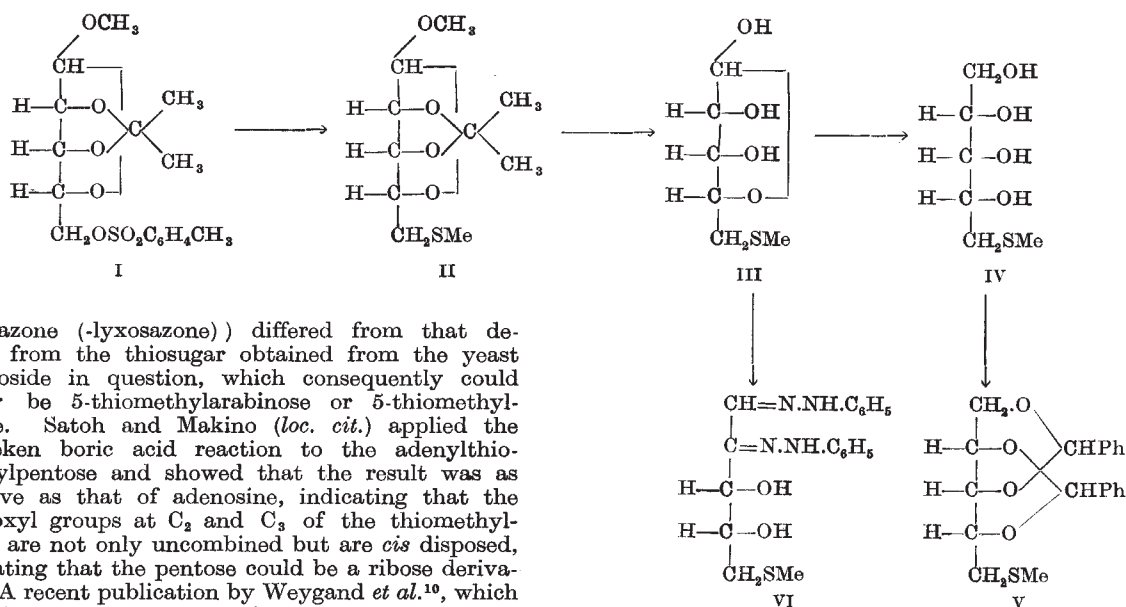
Synthesis of 5-Thiomethylribose

THERE has been isolated from yeast¹, crude oryzanin² and impure cozymase³ an unusual nucleoside which on acid hydrolysis yields adenine and a thiomethyl-sugar. Falconer and Gulland⁴ claim to have demonstrated that the thiomethyl-sugar and adenine are combined at the 9-position of the base. The thiomethyl-sugar has been the subject of several investigations; thus Suzuki *et al.*^{5,6} and Levene and Sobotka⁶ have shown that the thiomethyl group is retained during osazone formation, thereby excluding positions 1 and 2 of the sugar as the sites where it is combined. The thiomethyl-sugar could be readily reduced to a thiomethylpentitol, which on oxidation with lead tetra-acetate yielded 0.9 mol. of formaldehyde⁷, indicating that position 3 in the sugar cannot be the combining position of the thiomethyl group. Satoh and Makino⁸ adduced further evidence which excluded also the C₄ of the pentose as the site of the thiomethyl substituent. Previously, Wendt⁹, using titration data obtained by the Willstätter-Schüdel method, had shown that the thiomethyl-sugar obtained by acidic hydrolysis of the nucleoside was an aldose. Hence all the available evidence indicated that the derivative was a 5-thiomethylpentose.

Raymond⁹ synthesized 5-thiomethylxylose and proved that its osazone (that is, 5-thiomethyl-

	La	Ce	Pr	Nd	Sm	Eu†	Gd†	Tb†	Dy†	Ho†	Er	Tm†	Yb	Lu
a	48	29	1.3	1.7	2.2	0.9	1.2*	0.6*	0.9	0.9	6.5	0.6	6.1	0.6*
b	0.5	3	0.9	5.4	9	0	12	2	29	3.6	18	2	12	3
c	0	0	0	2	4	0	14	3	16	4	25	3	25	5
d	7	31	5	18	7	0.2	7	1	7	1	6	1	7	1.5

* Interpolated values. † Maximum values.



xylosazone (-lyxosazone)) differed from that derived from the thiosugar obtained from the yeast nucleoside in question, which consequently could either be 5-thiomethylarabinose or 5-thiomethylribose. Satoh and Makino (*loc. cit.*) applied the Boeseken boric acid reaction to the adenylylthiomethylpentose and showed that the result was as positive as that of adenosine, indicating that the hydroxyl groups at C₂ and C₃ of the thiomethylsugar are not only uncombined but are *cis* disposed, indicating that the pentose could be a ribose derivative. A recent publication by Weygand *et al.*¹⁰, which describes the preparation of 5-thiomethylarabinose, prompts us to report the synthesis of 5-thiomethylribose and derivatives thereof, the properties of which seem to be identical with those obtained by Suzuki *et al.*⁵ for the thiomethylpentose derived from the yeast nucleoside.

2:3-Isopropylidene 5-toluene-*p*-sulphonyl methyl-D-ribofuranoside (I) was prepared by the method of Levene and Stiller¹¹. This was heated in a sealed tube at 100° for 4 hr. with sodium thiomethoxide in acetone (cf. Raymond⁹) and gave 2:3-isopropylidene 5-thiomethyl methyl-D-ribofuranoside (II) in 62 per cent yield as a colourless mobile liquid. Raymond⁹ was unable to obtain 5-thiomethylribose derivatives by this method. When II was hydrolysed by being heated with *N*-sulphuric acid for 2 hr. at 80°, it afforded 5-thiomethylribose (III). Identical reactions to those carried out by Suzuki *et al.* with the thiomethylpentose obtained from yeast were effected with 5-thiomethylribose. Thus III was reduced with 3 per cent sodium amalgam and afforded 5-thiomethylribitol (IV) in 47 per cent yield. 5-Thiomethylribitol (IV) was shaken with benzaldehyde and concentrated hydrochloric acid and afforded a dibenzylidene derivative (possible structure as in V). III in solution in aqueous-ethanol was heated for 2 hr. at 100° with a solution of phenylhydrazine in glacial acetic acid and yielded 5-thiomethylribose phenylosazone (VI). Physical constants of the compounds IV, V, VI were identical with those reported by Suzuki *et al.*⁵ for the corresponding derivatives prepared from the yeast nucleoside, and it is considered that this establishes the identity of the thiomethylpentose in the latter as a ribose derivative.

The available evidence indicates that the adenylylthiomethylpentose being studied is 9-(5'-thiomethylribofuranosyl) adenine.

A full account of this work, including experimental details, will be published elsewhere. We thank Prof. M. Stacey for his interest, and Dr. T. F. Macrae and Dr. F. Bergel for generous gifts of D-ribose. One of us (L. F. J. P.) thanks Glaxo Laboratories, Ltd., for financial assistance.

Note added in proof. Since this letter was submitted for publication, independent workers (Satoh, K., and Makino, K., *Nature*, 167, 238 (1951); Baddi-

ley, J., Trauth, O., and Weygand, F., *Nature*, 167, 359 (1951)) have provided evidence, obtained by chromatographic and synthetic studies, which proves conclusively that the adenine thiomethyl pentoside derived from yeast is 5'-methylthio 9-β-D-ribofuranosido adenine.

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Curare-like Activity of some *bis*-Choline Derivatives

BOVET *et al.*¹ examined the curarizing properties of a large number of *bis*-quaternary ammonium salts. More recently, they have found that in the group of *bis*-choline esters of aliphatic dicarboxylic acids, the succinyl esters provide the most powerful members of the series².

It is known that in the choline derivatives the so-called muscarinic, nicotinic and curare-like properties vary independently of each other³. In an attempt to find substances having a pure curare-like action, we have prepared the succinyl esters of methyl-, phenyl- and benzyl-choline.

The products have been obtained by the action of succinyl chloride on the dialkylaminoalkanol in xylene solution. These *bis*-dialkylaminoalkylsuccinates have been transformed into quaternary ammonium salts by reaction with alkyl iodide in acetone solution. The formulae and the melting points of these