

## A Reference List of Organic Structures whose Absolute Configurations have been determined by X-Ray Fluorescence

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DETERMINATIONS of absolute configurations by Bijvoet's X-ray fluorescence technique<sup>1</sup> are now appearing frequently in the press, but in rather scattered journals. Most are for organic substances, so the following list has been compiled, and groups them under five headings for the convenience of organic chemists. There are 54 entries, more than half of which have appeared in the last three years. They are confined to determinations based on X-ray fluorescence, the fluorescing atom and the radiation being quoted. The list is believed to be comprehensive up to the end of 1965, but we would be grateful if users or crystallographers would advise us of errors or omissions. If the list

is found useful we propose to issue supplements and corrigenda, and an attempt will be made in later lists to include assignments involving internal comparisons with reference centres<sup>2,3</sup> if the latter are quite reliable.

It is gratifying to note that more and more authors are determining the absolute configuration whenever possible, but attention is drawn in an accompanying Communication<sup>4</sup> to the possibility of resurrecting old structure determinations from the literature and getting their absolute configurations with comparatively little effort. We hope the list will indicate to crystallographers areas where reference compounds are still needed.

<sup>1</sup> J. M. Bijvoet, *Endeavour*, 1955, **14**, 71.

<sup>2</sup> A. McL. Mathieson, *Acta Cryst.*, 1956, **9**, 317.

<sup>3</sup> R. Hine and D. Rogers, *Chem. and Ind.*, 1956, 1428.

<sup>4</sup> F. H. Allen and D. Rogers, preceding Communication.

## (1) Simple Molecules and Amino-Acids.

Compound	Fluorescent atom	Radiation used	Reference
L-Aspartic acid as cobaltous salt	Co	Cu	T. Doyne, R. Pepinsky, and T. Watanabe, <i>Acta Cryst.</i> , 1957, <b>10</b> , 438.
D-(+)-Barium uridine-5'-phosphate	Ba and P	Cu	E. Shefter and K. N. Trueblood, <i>Acta Cryst.</i> , 1965, <b>18</b> , 1067.
Biotin as bis- <i>p</i> -bromoanilide of CO <sub>2</sub> -biotin	Br	Cu	J. Trotter and J. A. Hamilton, <i>Biochemistry</i> , 1966, <b>5</b> , 713.
Hirsutic acid as <i>p</i> -bromophenacyl ester	Br	Cu	F. W. Comer and J. Trotter, <i>J. Chem. Soc. (B)</i> , 1966, 11.
D-Isocitric acid as (1) Rb salt (2) K salt	Rb K	Mo Cr, Cu	A. L. Patterson, C. K. Johnson, D. Van der Helm, and J. A. Minkin, <i>J. Amer. Chem. Soc.</i> , 1962, <b>84</b> , 309.
D(-)-Isoleucine as hydrated hydrobromide	Br	Cu	J. Trommel and J. M. Bijvoet, <i>Acta Cryst.</i> , 1954, <b>7</b> , 703.
L-Lysine as hydrochloride dihydrate	Cl	Cu	S. Raman, <i>Z. Krist.</i> , 1959, <b>111</b> , 301.
D-Methadone as hydrobromide	Br	Cu	A. W. Hanson and F. R. Ahmed, <i>Acta Cryst.</i> , 1958, <b>11</b> , 724.
(+)-Benzylmethylphenylpropylphosphonium bromide	Br	Mo	A. F. Peerdemann, J. P. C. Holst, L. Horner, and H. Winkler, <i>Tetrahedron Letters</i> , 1965, 811.
(+)-Methylsuccinic acid	See Section 5 under Ergoflavin.		
(-)-Methyl- $\alpha$ -naphthylphenylsilane	Si	Co, Cu	T. Ashida, R. Pepinsky, and Y. Okaya, <i>Acta Cryst.</i> , 1963, <b>16</b> , (supplement), A48, abstract 5.8.
Tartaric acid as (1) Na, Rb salt	Rb	Zr	A. F. Peerdemann, A. J. Van Bommel, and J. M. Bijvoet, <i>Proc., k. ned. Akad. Wetenschap</i> , 1951, <b>B54</b> , 16.
(2) Rb, H salt	Rb	Zr	A. J. Van Bommel, and J. M. Bijvoet, <i>Acta Cryst.</i> , 1958, <b>11</b> , 61.
L-Tyrosine as hydrochloride	Cl	Cu	R. Parasarathy, <i>Acta Cryst.</i> , 1962, <b>15</b> , 41.

## (2) Terpenoids.

(+)-3-Bromocamphor	Br	Mo	M. G. Northolt and J. H. Palm, <i>Rec. Trav. chim.</i> , 1966, <b>85</b> , 143.
	Br	Cu	F. H. Allen and D. Rogers, preceding Communication.
(+)-Camphor as oxime hydrobromide	Br	Cu	H. A. J. Oonk, Ph.D. Thesis, Utrecht, 1965.
Cascarillin as deacetylcascarillin acetal iodoacetate	I	Cu	C. E. McEachan, A. T. McPhail, and G. A. Sim, <i>J. Chem. Soc. (B)</i> , 1966, 633.
Clerodin as bromolactone	Br	Cu	I. C. Paul, G. A. Sim, T. A. Hamor, and J. M. Robertson, <i>J. Chem. Soc.</i> , 1962, 4133.
Davallol as iodoacetate	I	Cu	Yow-Cam Oh and E. N. Maslen, <i>Acta Cryst.</i> , 1966, <b>20</b> , 852.
Enmein as acetyl-bromoacetyl dihydro-compound	Br	Cu	M. Natsume and Y. Iitaka, <i>Acta Cryst.</i> , 1966, <b>20</b> , 197.
Ophiobolin as bromomethoxy-derivative	Br	Cu	S. Nozoe, M. Morisaki, K. Tsuda, Y. Iitaka, S. Tamura, K. Ishibashi, and M. Shirasaka, <i>J. Amer. Chem. Soc.</i> , 1965, <b>87</b> , 4968.
Picrotoxinin as $\alpha_1$ -bromo-compound	Br	Cu	B. M. Craven, <i>Acta Cryst.</i> , 1962, <b>15</b> , 387.
Simarolide as <i>m</i> -iodobenzoate and 4-iodo-3-nitrobenzoate (both needed)	I	Cu	W. A. C. Brown and G. A. Sim, <i>Proc. Chem. Soc.</i> , 1964, 293.
Swietenine as <i>p</i> -iodobenzoate of destigloylswietenine	I	Cu	A. T. McPhail and G. A. Sim, <i>Tetrahedron Letters</i> , 1964, 2599; <i>J. Chem. Soc. (B)</i> , 1966, 318.
Bromoisotenulin	Br	Cu	D. Rogers and Mazhar-ul-Haque, <i>Proc. Chem. Soc.</i> , 1963, 92.
$\alpha$ -Bromoisotutin	Br	Cu	B. M. Craven, <i>Acta Cryst.</i> , 1964, <b>17</b> , 396.

Compound	Fluorescent atom	Radiation used	Reference
Verrucaric acid as <i>p</i> -iodobenzoate	I	Cu	A. T. McPhail and G. A. Sim, <i>Chem. Comm.</i> , 1965, 350.
<b>(3) Alkaloids.</b>			
Aspidospermine as <i>N</i> (a)-acetyl-7-ethyl-5-desethylaspidospermine <i>N</i> (b)-methiodide	I	Cu	A. Camerman, N. Camerman, and J. Trotter, <i>Acta Cryst.</i> , 1965, <b>19</b> , 314.
(+)-Demethanolaconinone as hydriodide trihydrate	I	Cu	M. Przybylska, <i>Acta Cryst.</i> , 1961, <b>14</b> , 429.
Bulbocapnine as methiodide	I	Cu	T. Ashida, R. Pepinsky, and Y. Okaya, <i>Acta Cryst.</i> , 1963, <b>16</b> , (supplement) A48, abstract 5.8.
Cleavamine as methiodide	I	Cu	N. Camerman and J. Trotter, <i>Acta Cryst.</i> , 1964, <b>17</b> , 384.
Codeine as hydrobromide dihydrate	Br	Cu	G. Kartha, F. R. Ahmed, and W. H. Barnes, <i>Acta Cryst.</i> , 1962, <b>15</b> , 326.
Cucurbitine as perchlorate	Cl	Cu	Hai-Fu Fan and Cheng-Chung Lin, <i>Wu Li Hsueh Pao</i> , 1965, <b>21</b> , 253.
Echitamine as iodide	I	Cu	H. Manohar and S. Ramaseshan, <i>Tetrahedron Letters</i> , 1961, 814.
Ephedrine as hydrochloride	Cl	Cu	G. N. Ramachandran and S. Raman, <i>Current Sci.</i> , 1956, <b>25</b> , 348.
Erythroidine as hydrobromide of dihydro-compound	Br	Cu	A. W. Hanson, <i>Proc. Chem. Soc.</i> , 1963, 52.
Galanthamine as methiodide	I	Cu	D. Rogers and D. J. Williams, <i>Proc. Chem. Soc.</i> , 1964, 357.
Gelsemicine as hydriodide of <i>N</i> -methyl compound	I	Cu	M. Przybylska, <i>Acta Cryst.</i> , 1962, <b>15</b> , 326.
Gliotoxin (also establishes sporidesmin in conjunction with circular dichroism data)	S	Cu	A. F. Beecham, J. Fridrichsons, and A. McL. Mathieson, <i>Tetrahedron Letters</i> , 1966, 3131.
(+)-Hetisine as hydrobromide	Br	Cu	M. Przybylska, <i>Acta Cryst.</i> , 1963, <b>16</b> , 871.
Himbacine as hydrobromide	Br	Cu	J. Fridrichsons and A. McL. Mathieson, <i>Acta Cryst.</i> , 1962, <b>15</b> , 119.
Jacobine as bromohydrin	Br	Cu	J. Fridrichsons, A. McL. Mathieson, and D. J. Sutor, <i>Acta Cryst.</i> , 1963, <b>16</b> , 1075.
Leurocristine (vincristine) as methiodide (also establishes vincalcekoblastine)	I	Cu	J. W. Moncrieff and W. N. Lipscomb, <i>J. Amer. Chem. Soc.</i> , 1965, <b>87</b> , 4963.
Lucidusculine as hydriodide	I	Cu	A. Yoshino and Y. Iitaka, <i>Acta Cryst.</i> , 1966, <b>21</b> , 57.
(+)-Des(oxymethylene)lycoctonine as hydriodide monohydrate	I	Cu	M. Przybylska and L. Marion, <i>Canad. J. Chem.</i> , 1959, <b>37</b> , 1843.
Methyl melaleucate iodoacetate	I	Cu	S. R. Hall and E. N. Maslen, <i>Acta Cryst.</i> , 1965, <b>18</b> , 265.
Securine as hydrobromide dihydrate	Br	Cu	S. Imado, M. Shiro, and Z. Horii, <i>Chem. and Ind.</i> , 1964, 1691.
Strychnine as hydrobromide	Br	Cu	A. F. Peerdemann, <i>Acta Cryst.</i> , 1956, <b>9</b> , 824.
Thelepogine as methiodide	I	Cu	J. Fridrichsons and A. McL. Mathieson, <i>Acta Cryst.</i> , 1963, <b>16</b> , 206.
<b>(4) Steroids.</b>			
Lanostane as 3 $\beta$ -acetoxy-7 $\alpha$ ,11 $\alpha$ -dibromolanostane 8 $\alpha$ ,9 $\alpha$ -epoxide	Br	Cu	J. K. Fawcett and J. Trotter, <i>J. Chem. Soc. (B)</i> , 1966, 174.
<b>(5) Miscellaneous large molecules and mould metabolites.</b>			
Duclauxin as monobromo-compound	Br	Cu	Y. Ogihara, Y. Iitaka, and S. Shibata, <i>Tetrahedron Letters</i> , 1965, 1289.

<i>Compound</i>	<i>Fluorescent atom</i>	<i>Radiation used</i>	<i>Reference</i>
Ergoflavin as tetra- <i>O</i> -methyl di- <i>p</i> -iodobenzoate [also establishes (+)-methylsuccinic acid]	I	Cu	A. T. McPhail, G. A. Sim, J. D. M. Asher, J. M. Robertson, and J. V. Silverton, <i>J. Chem. Soc. (B)</i> , 1966, 18.
Factor VIa, $C_{46}H_{66}O_9N_{11}Co, 11H_2O$	Co	Cu	D. Dale, D. C. Hodgkin, and K. Venkatesan. In: "Crystallography and Crystal Imperfection," (ed. G. N. Ramachandran), Academic Press, London, 1963.
Ferrichrome "A", $C_{41}H_{58}N_9O_{20}Fe, 4H_2O$	Fe	Cu	A. Zalkin, J. D. Forrester, and D. H. Templeton, <i>Science</i> , 1964, <b>146</b> , 261.
Dibromoleucodrin	Br	Cu	R. D. Diamand and D. Rogers, <i>Proc. Chem. Soc.</i> , 1964, 63.

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