

Framework structures formed from parallel four- and eight-membered rings.

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Summary. Feldspars, paracelsian and danburite, harmotome and phillipsite have aluminosilicate frameworks that consist of three out of the seventeen simplest ways of cross-linking chains of the feldspar type. The four-membered rings that form the feldspar type of chain are parallel and have two adjacent tetrahedra pointing one way and the other two the other way. Chains are produced by sharing oxygen atoms of oppositely-pointing tetrahedra of parallel four-membered rings. Cross-linking of chains produces frameworks containing parallel eight-membered rings. If alternate tetrahedra in the rings point the same way, a new type of chain is produced, and there are four simple ways of joining these chains together to make a framework. If all four tetrahedra in a ring point the same way, only one structure can be developed, which has been proposed already by Barrer *et al.* for the zeolite Na-P1 and other members of the harmotome family. If three tetrahedra in the ring point the same way, very many simple structures can be constructed, and the seven simplest of these are described. It is suggested from comparison of cell dimensions that gismondine and, perhaps, yugawaralite may belong to this series of hypothetical structures. It is also suggested that some of the complexity and confusion in the harmotome group of zeolites may arise from hitherto unrecognized members of this hypothetical group. Major angular distortions from the ideal shape occur for the naturally-occurring silicates belonging to these structural groups.

ONE of the notable achievements in the early days of structure analysis was the determination of the aluminosilicate framework of feldspars by W. H. Taylor in 1933. W. L. Bragg showed that danburite, $\text{CaB}_2\text{Si}_2\text{O}_8$, contained the same double zigzag of linked tetrahedra as is found in feldspars, but with the chains cross-linked in a different way. Later it was found that paracelsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$; Smith, 1953) and hurlbutite ($\text{CaBe}_2\text{P}_2\text{O}_8$; Bakakin and Belov, 1960) were isostructural with danburite. Recently Sadanaga, Marumo, and Takéuchi (1961) have found that the zeolite harmotome contains a framework that consists of a third way of linking together the double zigzag chains, and Steinfink (1961) has independently reported the same type of framework for phillipsite. At a conference on zeolites arranged by Dr. D. W. Breck of the Linde Company, we suggested that there may be further ways of cross-linking chains, and that one or more zeolites whose structures were

currently unknown might correspond to these additional variants. Such has proved to be true, for a total of seventeen simple variants are possible, and these may contain the structures of gismondine and yugawaralite. A new type of chain based on the linkage of opposite instead of adjacent tetrahedra of parallel four-membered rings has been postulated, and the four simplest structures developed. If all tetrahedra of each ring point the same way, joining of rings produces 'cubes' instead of chains: cross-linking of such cubes leads to the structure that Barrer, Bultitude, and Kerr (1959) have proposed for synthetic zeolite Na-P1, and perhaps for the natural zeolite, garronite (Walker, 1962), and other synthetic members of the harmotome group. If three tetrahedra of each ring point the same way, a chain is produced, and such chains can be cross-linked to produce many different frameworks. Two of these structures are possible for gismondine.

Structures based on the UDD ring: In order to classify and describe these structures, a convenient and informative symbolism must be developed. Fortunately this is easy, for the ideal shape of the zigzag chains in feldspars is simple. If a ring of four tetrahedra is taken (fig. 1), with two adjacent tetrahedra pointing upwards and the other two downwards, a chain can be formed by taking further rings and superimposing them so that the upwards-pointing tetrahedra of one chain are joined to the downwards-pointing tetrahedra of the next chain by shared oxygen atoms. The resulting chain has the shape of a double crankshaft that may be represented by writing the symbols *U* and *D* at the corners of a square to represent the upwards- and downwards-pointing tetrahedra of any one ring in the chain. Projecting outwards from each chain are oxygen atoms, which can be shared with other chains to form a framework structure. In the feldspar, paracelsian, and harmotome structures, cross-linking of the chains produces eight-membered rings (fig. 2) in the planes normal to the chains. It will be noticed that in these three structures the only fundamental difference is in the sequences of tetrahedra around the eight-membered rings, and it is natural to inquire how many different sequences are possible. Because each chain can be rotated through 90° and re-integrated into the framework, it is clear that an infinite number of patterns are possible. However, only the simplest patterns will be chemically stable and consequently there is little chance that a very complex pattern will occur. In this paper we shall develop all the patterns whose repeat distances in the plane normal to the chain are less than 15 Å: this limits the number of configurations to 17. It will be seen from fig. 2 that the rings are distorted from the ideal

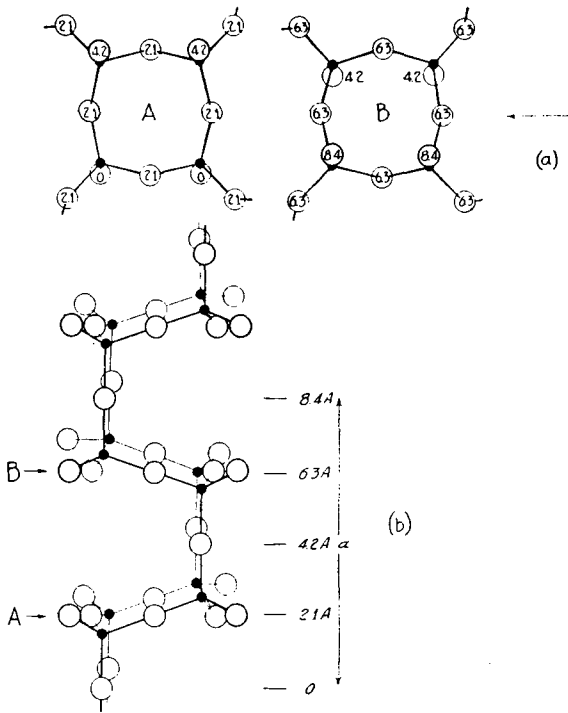


FIG. 1. The double-crankshaft chain formed by linking chains of tetrahedra of the *UDD* type. (a) Plans of rings A and B, which when joined together give the chain shown in perspective in (b). Copied from fig. 128 of 'The Atomic Structure of Minerals', by W. L. Bragg, Cornell University Press.

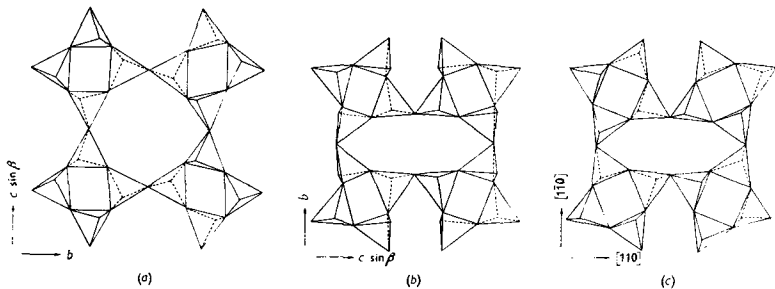


FIG. 2. Projections of the feldspar (centre), paracelsian (right), and harmotome structures (left) down the *UDD* chains. Note the considerable distortion of the eight-membered rings of feldspar and paracelsian. (After R. Sadanaga, F. Marumo, and Y. Takéuchi, *Acta Cryst.*, 1961, vol. 14, p. 1153.)

positions, especially those of feldspar and paracelsian: in our derivation of the hypothetical structures we shall assume an ideal configuration.

Table I contains a shorthand description of the seventeen structures. Because the chains are non-polar, there is no fundamental structural change if the direction of each tetrahedron is reversed: indeed, the structure has merely been turned over. Consequently in describing the

TABLE I. Sequences of tetrahedra in eight-membered rings formed by linking chains of *UUDD* type. In the two columns of structures, the first (Adj.) refers to the appropriate structure when the first symbol of the sequence applies to tetrahedra belonging to adjacent 4-rings, the second (Sa.) when it applies to tetrahedra of the same 4-ring. For further explanations see text.

Sequence.	Designation of structure having this sequence.		Sequence.	Designation of structure having this sequence.	
	Adj.	Sa.		Adj.	Sa.
CCCCCCC	A	A	CCSCSSS	J	K
CCCCCSC	B	B	CCCSCSS	K	L
CCCCSCS	C	D	CCSCSSC	F	F
CCCSCCS	E	E	CCCSCSS	E	M
CCSCCCS	paracelsian feldspar		SSSCSSC	N	feldspar
CCCSSSS	F	F	SSSSCSC	M	M
CCSSCCS	G	G	SSSSCSC	harmotome	D
CSCSCSC	A	H	SSSSSSC	I	I
CCSCSCS	I	B	SSSSSSS	H	H

sequence of tetrahedra around an eight-membered ring it is better to record whether adjacent tetrahedra have changed (*C*) or the same (*S*) directions than to record whether the tetrahedra point upwards or downwards. Thus the sequence in the eight-membered rings of paracelsian goes *CSCSCSCS*. Of the eight symbols for each ring there must be an even number of each kind, otherwise the ring would not close. There are 18 ways of arranging the symbols to satisfy this condition (table I). In addition there are two different ways in which the four-membered rings can be attached to an eight-membered ring, for the first symbol of the sequence can apply either to two tetrahedra of adjacent four-membered rings or to two tetrahedra of the same four-membered ring. Thus there are 36 possible eight-membered and related four-membered rings to be considered. Because 9 combinations do not change when a different origin is chosen, there are actually only 27 different types. If we restrict the repeat distance in the plane normal to the chain as described earlier, we can enumerate the possible structures by drawing out a 3 × 3 array of eight-membered rings with the linking four-membered rings, and placing the same sequence of symbols on each of the eight-membered

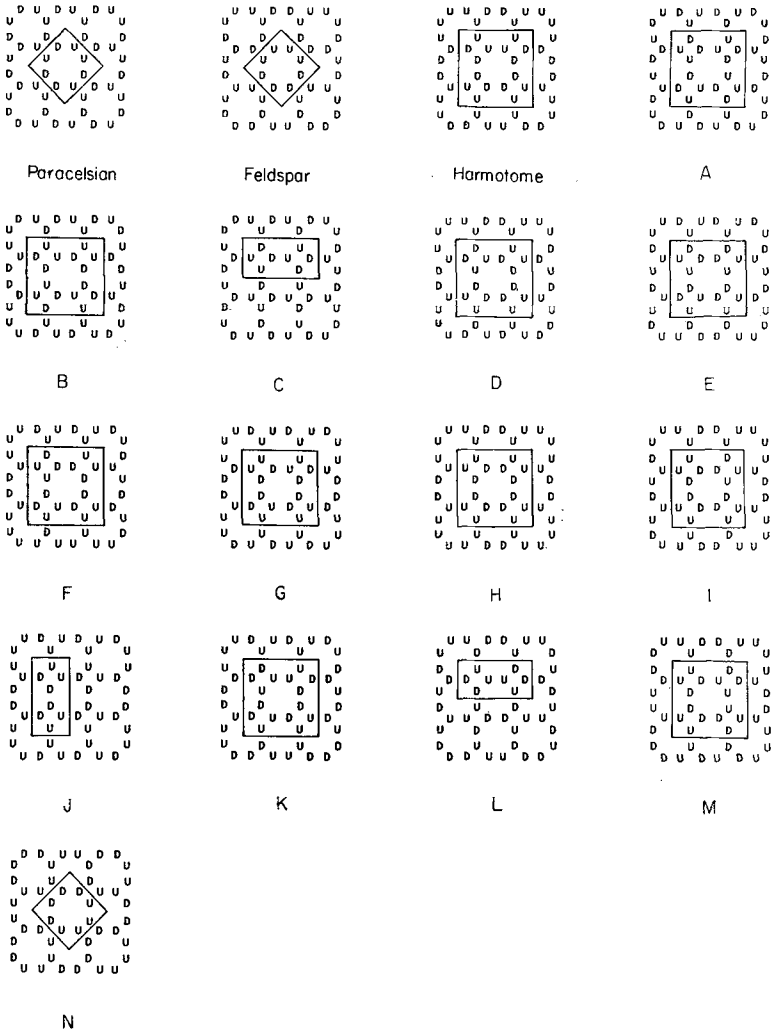


FIG. 3. The seventeen simplest ways of linking together *UDD* chains. The smallest unit cell of the ideal structure is shown by the rectangle.

rings at the four corners (fig. 3). Then the orientations of the tetrahedra in the other rings are already determined by using the condition that the sequence in the four-membered rings goes *UDD*. If the pattern is repeated so that every alternate ring in each row or column is identical,

a structure whose unit cell repeats at a distance of $6 \times 2.65 \times \sin 60^\circ = 13.8 \text{ \AA}$ in the layer perpendicular to the chains has been produced (assuming a regular tetrahedron of edge 2.65 \AA and an ideal chain and ring shape). For several of the 17 possible structures it is found

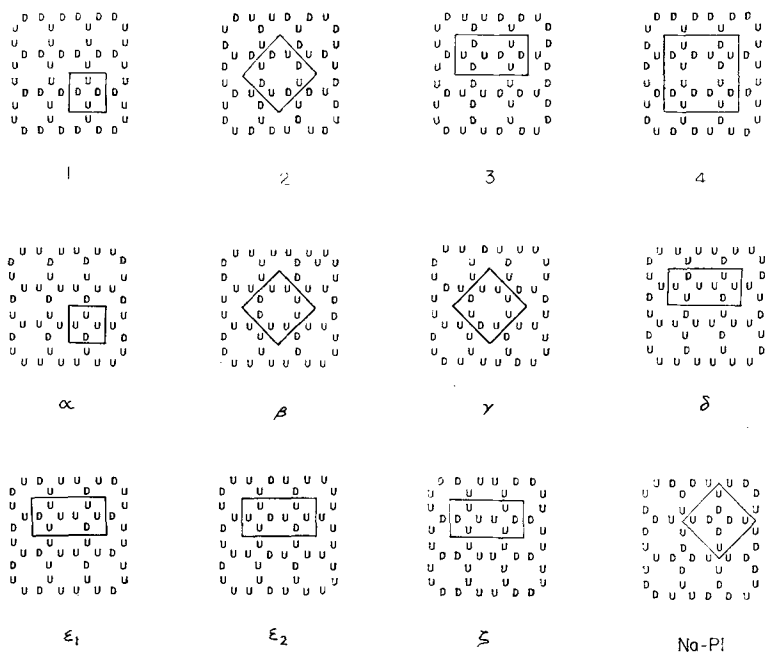


FIG. 4. The four simplest ways of linking together UDUD chains, the structure of Na-P1 formed from UUUU rings, and the seven simplest ways of linking together UUUD chains.

that the true repeat distance is less than 13.8 \AA because a smaller unit cell can be obtained (fig. 3). Thus for feldspar, paracelsian, and *N* a smaller cell can be taken at 45° , giving a repeat of $13.8/\sqrt{2} = 9.8 \text{ \AA}$, while *C*, *J*, and *L* have a reduced cell with one edge halved to give a repeat distance of 6.9 \AA . Examination of fig. 3 shows that seven of the structures contain only one type of eight-membered ring (paracelsian, harmotome, *C*, *G*, *J*, *L*, *N*) while the other ten contain two types. Thus there are 17 ways of linking together UUDD chains subject to the above-mentioned restriction.

Structures based on UDUD, UUUU, and UUUD rings: Using the same conditions as in the last section, four structures can be developed

from rings in which opposite instead of adjacent tetrahedra point the same way (the *UDUD* sequence). These are illustrated in fig. 4, where it may be seen that type 1 has a small cell with axes 6.9×6.9 , type 2 has a cell at 45° with repeat distances 9.8×9.8 , type 3 has a cell with 6.9×13.8 , and type 4 has the full 13.8×13.8 Å unit cell.

The sequence *UUUU* does not permit the formation of chains, for addition of the next ring gives a closed arrangement with each tetrahedron at the corners of a cube. However, a framework can be obtained by sharing the oxygen atoms that project horizontally. The resulting structure (fig. 4) has already been postulated by Barrer, Bultitude, and Kerr (1959) for the artificial zeolite Na-P1 and gives horizontal axes of 9.8×9.8 Å.

The sequence *UUUD* permits the formation of chains, which may be cross-linked to form frameworks. The number of possible structures is infinite if no restriction is placed on the volume of the repeat unit, and is still very large even when restrictions are applied. Fig. 4 shows the seven simplest: α has a 6.9×6.9 Å unit cell; β and γ have 9.8×9.8 Å unit cells; δ , ϵ_1 , ϵ_2 , and ζ have 6.9×13.8 Å unit cells (where ϵ_1 and ϵ_2 are enantiomorphic).

Distortions in the frameworks: Examination of fig. 2 shows that there are serious distortions of the frameworks of feldspar, paracelsian, and harmotome from the ideal configurations. In the two anhydrous minerals the chains have rotated and twisted so much that the large channels in the ideal structure have shrunk enough to permit sodium, barium, or potassium ions to bond with oxygen atoms from both sides of the channel. On the contrary, in harmotome the chains have twisted in such a way that the channels become even wider than those in the ideal framework, permitting occupancy by twelve water molecules in each unit cell. The distortion of the framework changes the symmetry in these minerals so much that there appears to be little resemblance between the space-groups of the ideal and actual structures.

The amounts of the distortion can be seen from the following comparisons: Smith (1954) has shown that the (Si,Al)-O distance varies linearly from Si-O = 1.60 Å to Al-O = 1.78 Å. (Some small modifications in these values have proved to be necessary: Bailey and Smith; to be published.) The repeat distance down an ideal chain is related to the (Si,Al)-O distance by the factor 4×1.3333 and varies from 8.53 to 9.49 Å as the Al/(Al+Si) ratio goes from 0 to 1. Similarly, the repeat distances in the layers for the largest unit cells in fig. 3 are related to the (Si,Al)-O distance by the factor 6×1.4142 and vary from

13.58 to 15.10 Å as the aluminium content increases from 0 to 100 %. In paracelsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$, the ideal structure has dimensions $9.86 \times 9.86 \times 9.01$ Å, to be compared with actual values of $9.08 \times 9.58 \times 8.58$ Å. In sanidine (KAlSi_3O_8) and albite ($\text{NaAlSi}_3\text{O}_8$) the ideal structure has dimensions $13.96 \times 13.96 \times 8.77$ Å (large cell) to be compared with actual values of $12.95 \times 13.1 \times 8.44$ Å for sanidine and $12.79 \times 12.9 \times 8.15$ Å for albite (the first of the actual values is for [010], the second for the axis [102], and the third for [100]). In harmotome, $\text{Ba}_2\text{Al}_4\text{Si}_{12}\text{O}_{32} \cdot 12\text{H}_2\text{O}$, the ideal values of $13.96 \times 13.96 \times 8.77$ must be compared with observed values of $14.14 \times 14.3 \times 9.87$ Å (the first value is for [010], the second for the axis [201], and the third for [100]). A further comparison can be made between Na-P1 and the ideal structure of fig. 4. Na-P1 is cubic with $a = 10.0$ Å, to be compared with the structure in fig. 4 which is tetragonal with $a = 9.69$ Å, $c = 8.84$ Å (for an Al/Si ratio of 1/2). By rotation of the tetrahedra, the bigger unit cell with higher, cubic, symmetry can be obtained. Actually other members of the zeolite-P family appear to be tetragonal (e.g. Na-P2 and Ca-exchanged Na-P1) and these may have a structure intermediate between the 'ideal' configuration and the cubic arrangement.

In summary, it is quite obvious that changes of dimensions as great as 10 % can occur between the ideal and the actual structures. It appears that the anhydrous minerals will have reduced cell dimensions, while the hydrous minerals (zeolites) will have increased cell dimensions.

Other possible members of this group of silicates: The second aim of this paper is to suggest trial structures for zeolites and other silicate minerals. Unfortunately the serious distortions of actual structures from the ideal shape make this difficult and uncertain, but two zeolites, gismondine and yugawaralite, look like possible candidates.

Gismondine is monoclinic, $P2_1/c$, with $a = 10.02$, $b = 10.62$, $c = 9.84$ Å, $\beta = 92^\circ 25'$, and $Z = 4$ (Fischer and Kuzel, 1958). An ideal structure corresponding to the Al/Si ratio of 1 in the gismondine formula, $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$, would have cell dimensions $9.86 \times 9.86 \times 9.01$ Å and cell contents $Z = 4$. These dimensions average 6 % smaller than those of gismondine but the distortion of Na-P1 shows that such a change is possible. Examination of the list of possible structures shows eight possibilities, three of which have already been assigned to paracelsian, feldspar, and Na-P1, but five of which, N , 2 , β , γ , and δ , are still unassigned. It is possible that gismondine has the same type of framework as one of the first three, but it seems more likely that one of the last five structures is the correct one. The *UDUD* chain is not so flexible

as the *UUUD* or *UUDD* chains, and because a large distortion from the ideal arrangement is possible, the structure 2 is thought to be unlikely. At the time of writing, Dr. Fischer is engaged on a structure determination of gismondine and it is hoped that confirmation or rejection of these ideas will soon be available.

Yugawaralite, $\text{CaAl}_2\text{Si}_5\text{O}_{14}\cdot 3\text{H}_2\text{O}$, is monoclinic with $a = 13.26$, $b = 13.65$, $c = 9.73$ Å, and $\beta = 111^\circ 30'$ (Sakurai and Hayashi, 1952). For this Al/Si ratio corresponding cell dimensions for an ideal structure would be $14.01 \times 14.01 \times 8.80$ Å, which values are not too far away from the observed values of yugawaralite. However, unlike gismondine, where both the postulated structure and the chemical analysis yield the same number of Si + Al atoms per unit cell, the cell content of yugawaralite from the chemical analysis (8Al + 20Si) does not provide enough tetrahedra to meet the 32 required for a structure with a *UUDD* related type of ring. If further work shows that there are really 32 (Al + Si) atoms in the unit cell, then it would be worth while trying to find a structure for yugawaralite from the ones listed in this paper. Examination of the figures in this paper shows that there are twelve structural types with *UDUD* or *UUDD* chains and many more with *UUUD* chains that have this size of unit cell and would need to be considered, and it is also possible that distortion of a smaller unit cell might lead to a larger cell, as occurs, for example, with feldspar.

The studies of Barrer, Bultitude, and Kerr (1959) and others have revealed great complexity in the harmotome group of zeolites. Identification of the fine-grained synthetic products was made by X-ray powder methods. Because all types of structures based on the *UUDD* and related chains should give similar powder patterns, it is possible that some of the complexity may arise because of the existence of several unrecognized members in this structural family. Growth of large synthetic crystals is usually rather difficult, and consequently it is doubtful if identification based on the more certain single-crystal X-ray methods will be carried out in the near future. Nevertheless, it is possible that uncertainties in this group of zeolites will not be resolved until such techniques are applied.

To conclude this section, an example is given of a mineral with cell dimensions similar to those for a structure with *UDUD* chains or one with *UUUD* chains but whose structure is quite different. Keatite, SiO_2 , is tetragonal with $a = 7.46$ and $c = 8.61$ Å. These cell dimensions fit fairly well with the ideal values for structure 1 with *UDUD* chains and structure α with *UUUD* chains: $a = 6.79$, $c = 8.53$ Å. Neverthe-

less, there is no resemblance between keatite and either of these two structures, for keatite has spirals of tetrahedra cross-linked to give rings with five and six tetrahedra, in contrast to the four- and eight-membered rings of the latter. It seems likely that banalsite, $\text{BaNa}_2(\text{Al}_2\text{Si}_2\text{O}_8)_2$, $a = 8.52$, $b = 9.99$, $c = 16.76 \text{ \AA}$, *Iba* or *Ibam* (Campbell Smith, Bannister, and Hey, 1944), does not belong to the *UUDD*, *UDUD*, or *UUUD* series even though two of its cell dimensions are possible in the hypothetical series.

Conclusion: An interesting consequence of this study is the possibility that there may be zeolites with the feldspar or paracelsian frameworks. Earlier in this paper it was shown that paracelsian and feldspar have collapsed frameworks, whereas harmotome has an expanded framework providing room for water molecules. It is thus possible that feldspar and paracelsian have zeolitic equivalents and, as mentioned earlier, gismondine might be such a material. Search for such equivalents should be made in the products of mixes of appropriate composition treated hydrothermally at temperatures in the range 100–400° C.

It is suggested that further studies of this type, in which known structural units are assembled in different patterns, should be of value, both to aid in the classification of zeolites and to help in the construction of trial structures. Indeed, it may prove to be just as important for an understanding of the forces in silicate and other structures to know that a possible structure does not occur in nature as it is to know that it does occur. Recognition that structures belong to a certain group is not always easy because of the distortions that occur: such distortions probably arise so that the Si–O–Si bond angles can be near 140°, the value commonly found in silicates (Liebau, 1961).

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Note added in proof: Dr. K. Fischer (priv. comm.) has found that gismondine has the structure labelled N.
