X-Ray Structure Determination of Gardmultine. A Bis-indole Alkaloid Isolated from *Gardneria Multiflora* Makino

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The structure of gardmultine, $C_{45}H_{54}N_4O_{10}$, isolated from *Gardneria multiflora* Makino, has been determined by single crystal *X*-ray analysis. The orthorhombic crystals belong to the space group $P2_12_12_1$ with a = 8.625(1), b = 20.791(2), c = 24.494(3) Å and Z = 4. The phase problem was solved by direct methods making use of the technique of negative quartet frequencies to determine the starting set of MULTAN, and refined to a final R value of 0.053 for 3 238 observed diffractometer data taken with Cu-K_α radiation. Gardmultine is a novel bis-indole alkaloid, comprising gardneramine and chitosenine linked by a spiro-five-membered ring.

GARDMULTINE, $C_{45}H_{54}N_4O_{10}$ is a novel bis-indole alkaloid which has been isolated from *Gardneria multiflora* Makino together with a number of structurally related compounds.[1] Sakai *et al.* proposed structure (1) on the basis of its chemical and spectroscopic properties.[2] We now report the results of a complete *X*-ray crystallographic analysis which confirmed the proposed structure of gardmultine.

EXPERIMENTAL

Crystallographic Measurements.—The crystals, grown from chloroform–methanol, were found to be suitable for the *X*-ray analysis, but since they gradually lose solvent of crystallization to form a white powder, for all crystallographic measurements, crystals were cut to size under methanol and sealed inside thin-walled glass capillaries. Three standard reflections were measured at intervals of every 50 reflections and no significant deterioration of the crystals was observed during the data collection. The basic experimental data and data collection methods are as follows. Cu-K_α radiation, graphite monochromator, λ = 1.5418 Å. $C_{45}H_{54}N_4O_{10}$, M_r = 810.94, asymmetric unit $C_{45}H_{54}N_4O_{10}\cdot CH_3OH$, asymmetric unit weight, 842.98. Orthorhombic prisms elongated along b. Crystal size, *ca.* 0.2 × 0.2 × 0.3 mm. Space group $P2_12_12_1$ (No. 19). Cell dimensions were from least-square refinement of $\pm\theta$ data. a = 8.625(1), b = 20.791(2), c = 24.494(3) Å, U = 4 392.3 Å^3, Z = 4. D_m not measured because of rapid loss of solvent. Diffractometer, Enraf–Nonius CAD-4, 2θ–ω scan, maximum sin θ/λ = 0.616 Å^{-1}. Reflections, 3 639 (observed): 401 ($F_o < 1\sigma$). Lorentz and polarization factor corrections were applied to the *X*-ray data but no absorption corrections were used. (Azimuth scans of several reflections showed no significant variations.) Function minimized $\Sigma\omega\Delta^2$, weighting given in ref. 3; refinement was full-matrix least-squares (partitioned), R (observed reflections only, with statistical weights) 0.053. The temperature factor used had the form $\exp -2\pi^2\sum_i\sum_j(U_{ij}h_ih_ja_i^*a_j^*)$.

Determination of the Structure.—Many attempts were made to solve the structure using the standard symbolic addition procedure [4] and also symbolic addition with limited sets of triplets indicated as most probable by the calculation of structure invariants,[5,6] but no interpretable *E*-maps were obtained. Multisolution approaches using the MULTAN system [7] with up to 256 solutions were also tried, but again none of the solutions with the best figure of merit showed recognizable molecular fragments. At this point we tested the solution by the use of negative quartet discrimination (NQEST),[8] using 255 potentially negative quartets, but no significant discrimination was observed. Finally the structure was successfully solved by the technique [9] which used the reflections occurring most often in the negative quartets as a starting set in the multisolution approach. Among the 128 solutions, three solutions were found to be essentially identical from which practically all the skeletal atoms of the molecule were located.

Refinement by least-squares techniques followed by difference maps resulted in the location of the missing heavier atoms and of all hydrogen atoms except for those of the solvent and the C(18g) through C(25g) side chain. The structure was refined by the full-matrix least-squares techniques, although because of the size of the molecule, partitioning was necessary. For the final cycles of refinement anisotropic temperature factors were utilized for heavier atoms and isotropic parameters for hydrogen atoms. The positional parameters of hydrogen atoms located from difference syntheses were refined and co-ordinates of missing hydrogen atoms were calculated, but not refined.

At the final stage of the refinement it was found that the apparent thermal parameters of side-chain atoms [C(18g) through C(25g)] were surprisingly high and a difference Fourier synthesis calculated from the all expected atoms indicated the presence of *ca.* 0.3 eÅ^{-3} residual density near C(18g). Mass spectroscopy of the crystals indicated the presence of 5—10% of the demethoxy-compound. The contamination is not unlikely since the packing does not appear strongly controlled by the side-chain [C(18g)–C(25g)]. Since the demethoxy-compound has the reverse (*z*) configuration,† its side-chain atoms could not occupy exactly the same sites as the main compound and thus might explain the residual peak. Given the small amount of the contaminant, it did not seem worthwhile to try elaborate models but the problem was partially accounted for by giving C(18g), O(5g), and C(25g) a population parameter of 0.90.

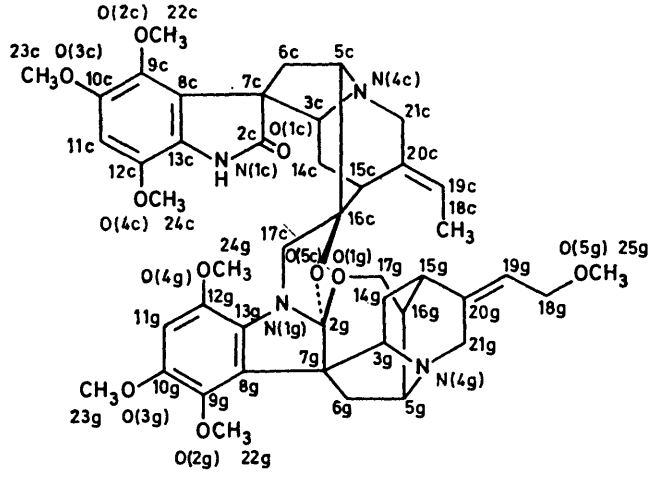
In view of the above problem, we did not attempt to determine the absolute configuration by *X*-ray methods, but based on the known stereochemistry of gardneramine,[10] the absolute stereochemistry is that shown in the Figures.

† After the *X*-ray analysis of gardmultine was completed, Sakai *et al.*[14] succeeded in the separation of these bis-indole alkaloids and the structure of the demethoxy-compound was established as (2) by chemical and spectroscopic methods.

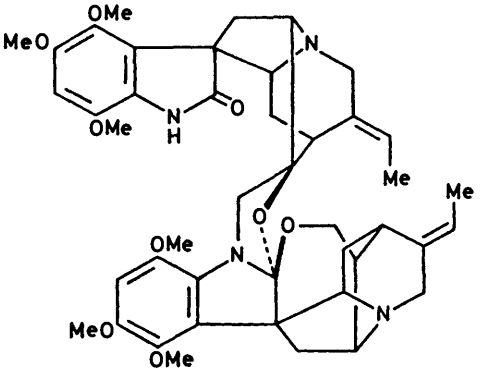
Scattering factors for carbon, oxygen, and nitrogen were taken from the International Tables for *X*-Ray Crystallography,[11] and those for hydrogen from Stewart *et al.*[12] Programs used in this investigation were MULTAN,[7] XRAY 72,[13] and local programs for negative quartets and data reduction.

RESULTS AND DISCUSSION

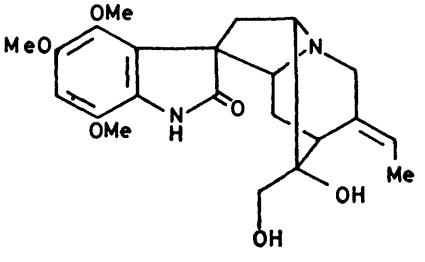
Description of the Structure.—The present *X*-ray analysis confirms the previously assigned molecular structure of gardmultine (1) on the basis of chemical and spectroscopic evidence.[14] Gardmultine (1) is composed of two units; an oxoindole half, chitosenine (3) and an indolenine half, gardneramine (4), linked by a spiro-five-membered ring with a loss of one mole of water. Figure 1 shows the chemical structures of gardmultine (1), chitosenine (3), gardneramine (4), and demethoxygardmultine (2). The atom numbering scheme of gardmultine adopted in this publication is also shown in Figure 1 and the suffix c refers to chitosenine unit and g to gardneramine unit of the molecule. Figure 2 shows a perspective drawing of the gardmultine molecule produced by ORTEP.[15] Tables 2 and 3 show bond lengths and angles calculated from the co-ordinates given in Table 2. These values generally agree well with anticipated values except for bond lengths involving C(18g) through C(25g) which have e.s.d.s of 0.01 Å. The apparent shortening of bond lengths can be explained by the apparent large temperature factors. Corresponding bond lengths of the units are very similar. The smaller value of the bond length between C(2c)–N(1c) (1.353 Å) in the chitosenine unit as compared with 1.454 Å of the



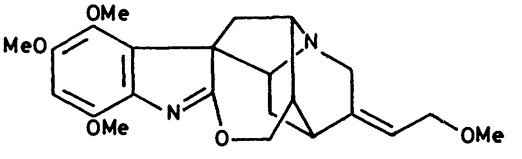
(1) Gardmultine



(2) Demethoxygardmultine



(3) Chitosenine



(4) Gardneramine

FIGURE 1 Structural formulae. For clarity parentheses have been omitted around the carbon-atom crystallographic numbers in formula (1)

TABLE 1

Positional (× 10 000) parameters for the heavier atoms

Atom	*x/a*	*y/b*	*z/c*
N(1c)	15 577(4)	10 100(1)	5 373(1)
O(1c)	13 078(3)	9 841(1)	5 125(1)
C(2c)	14 343(5)	10 101(2)	5 032(1)
O(2c)	16 556(3)	11 685(1)	4 067(1)
C(3c)	15 304(5)	9 971(1)	4 060(1)
O(3c)	19 153(4)	12 072(1)	4 581(1)
N(4c)	15 329(3)	10 412(1)	3 592(1)
O(4c)	18 330(3)	10 404(1)	5 950(1)
C(5c)	13 737(5)	10 670(1)	3 605(1)
O(5c)	12 413(3)	10 297(1)	2 776(1)
C(6c)	13 502(5)	10 824(2)	4 218(1)
C(7c)	14 817(4)	10 468(1)	4 514(1)
C(8c)	16 247(5)	10 837(1)	4 714(1)
C(9c)	17 078(5)	11 335(2)	4 509(1)
C(10c)	18 401(5)	11 545(2)	4 791(1)

TABLE 1 (*continued*)

TABLE 1 (*continued*)

Atom	*x/a*	*y/b*	*z/c*
C(11c)	18 873(6)	11 235(2)	5 264(1)
C(12c)	18 004(5)	10 733(2)	5 476(1)
C(13c)	16 670(5)	10 559(2)	5 202(1)
C(14c)	14 106(5)	9 428(2)	3 971(1)
C(15c)	13 400(5)	9 500(1)	3 399(1)
C(16c)	12 605(4)	10 159(1)	3 359(1)
C(17c)	10 906(5)	10 170(2)	3 575(1)
C(18c)	14 117(9)	8 430(3)	2 551(2)
C(19c)	15 056(5)	9 014(2)	2 657(1)
C(20c)	14 727(4)	9 487(1)	3 001(1)
C(21c)	15 700(5)	10 083(2)	3 073(1)
C(22c)	17 520(8)	11 662(3)	3 586(2)
C(23c)	20 429(10)	12 314(3)	4 882(3)
C(24c)	19 820(7)	10 500(4)	6 181(2)
N(1g)	9 937(3)	10 136(1)	3 078(1)
O(1g)	10 720(3)	11 146(1)	2 775(1)
C(2g)	10 845(4)	10 491(1)	2 679(1)
O(2g)	10 064(4)	9 049(1)	1 381(1)
C(3g)	8 834(5)	10 538(2)	1 856(1)
O(3g)	9 193(5)	7 874(1)	1 888(1)
N(4g)	9 352(4)	10 734(1)	1 298(1)
O(4g)	8 848(3)	8 987(1)	3 613(1)
C(5g)	10 914(6)	10 997(1)	1 432(1)

TABLE 1 (*continued*)

Atom	*x/a*	*y/b*	*z/c*
O(5g)	6 185(16)	12 830(4)	577(3)
C(6g)	11 605(5)	10 400(2)	1 684(1)
C(7g)	10 357(4)	10 236(1)	2 107(1)
C(8g)	10 035(4)	9 545(1)	2 266(1)
C(9g)	9 830(5)	9 002(1)	1 943(1)
C(10g)	9 329(6)	8 439(1)	2 183(1)
C(11g)	9 014(6)	8 412(2)	2 742(1)
C(12g)	9 206(5)	8 958(2)	3 068(1)
C(13g)	9 746(4)	9 519(1)	2 825(1)
C(14g)	8 153(6)	11 129(2)	2 137(1)
C(15g)	9 004(6)	11 724(2)	1 909(1)
C(16g)	10 738(6)	11 583(2)	1 838(1)
C(17g)	11 572(7)	11 526(2)	2 384(1)
C(18g)	7 235(21)	12 521(5)	610(4)
C(19g)	7 847(11)	12 403(3)	1 171(2)
C(20g)	8 353(7)	11 838(2)	1 354(1)
C(21g)	8 312(7)	11 214(2)	1 041(1)
C(22g)	11 300(8)	8 670(3)	1 169(2)
C(23g)	7 874(11)	7 859(3)	1 543(2)
C(24g)	8 035(9)	8 442(2)	3 842(2)
C(25g)	5 734(19)	13 045(5)	62(4)
C(met)	10 239(13)	14 206(6)	10 020(3)
O(met)	9 315(9)	14 107(3)	9 535(3)

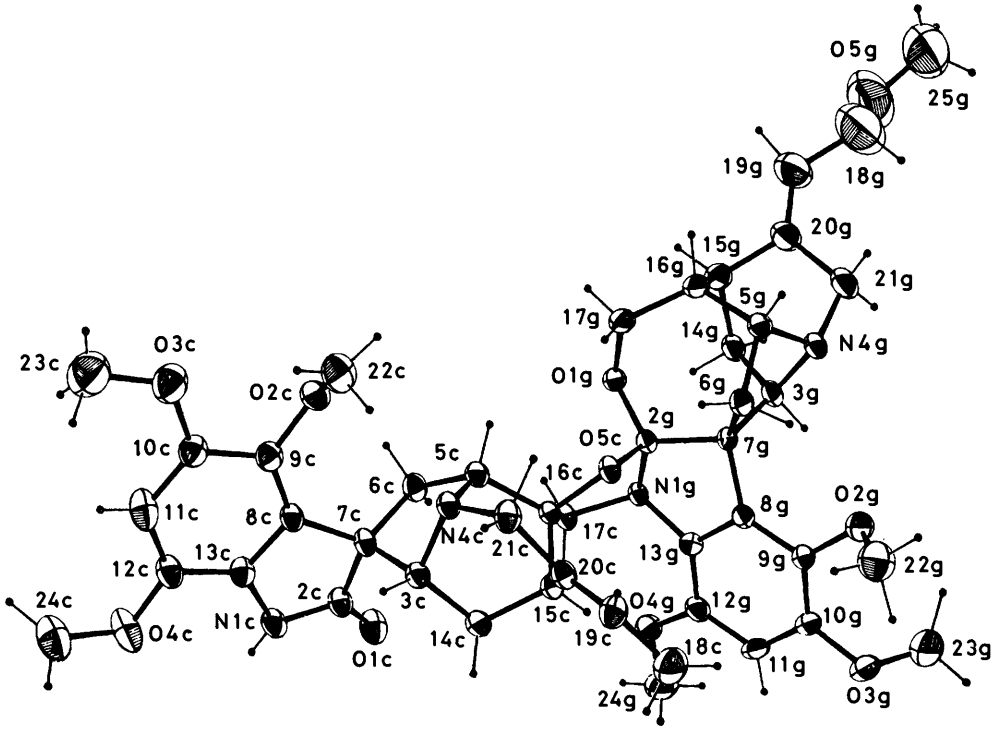


FIGURE 2 The molecular structure of gardmultine in its crystal conformation. 40% Probability ellipsoids are shown for heavier atoms but those of the hydrogens are arbitrary

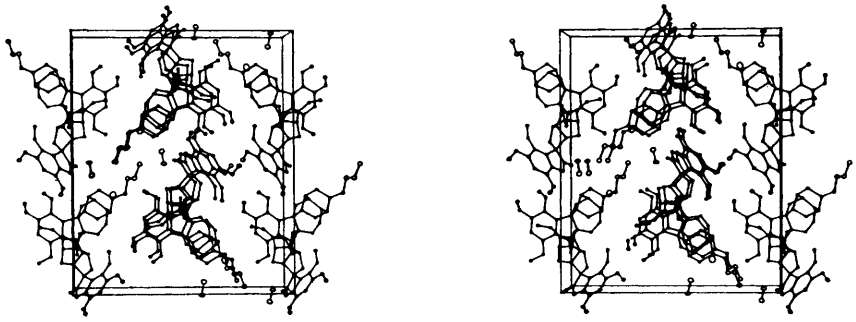


FIGURE 3 Packing diagram. The direction of projection is *a*

TABLE 2

Bond lengths

N(1c)–C(2c)	1.353(5)	N(1g)–C(2g)	1.454(4)
N(1c)–C(13c)	1.405(5)	N(1g)–C(13g)	1.434(3)
O(1c)–C(2c)	1.239(5)	O(1g)–C(2g)	1.386(3)
C(2c)–C(7c)	1.536(4)	O(1g)–C(17g)	1.443(5)
O(2c)–C(9c)	1.380(4)	C(2g)–C(7g)	1.556(4)
O(2c)–C(22c)	1.443(6)	O(2g)–C(9g)	1.395(4)
C(3c)–N(4c)	1.468(3)	O(2g)–C(22g)	1.424(7)
C(3c)–C(7c)	1.575(3)	C(3g)–N(4g)	1.495(4)
C(3c)–C(14c)	1.546(5)	C(3g)–C(7g)	1.580(5)
O(3c)–C(10c)	1.373(5)	C(3g)–C(14g)	1.526(6)
O(3c)–C(23c)	1 417(9)	O(3g)–C(10g)	1 384(3)
N(4c)–C(5c)	1.474(5)	O(3g)–C(23g)	1.417(9)
N(4c)–C(21c)	1.479(4)	N(4g)–C(5g)	1.491(6)
O(4c)–C(12c)	1.377(4)	N(4g)–C(21g)	1.482(5)
O(4c)–C(24c)	1.418(7)	O(4g)–C(12g)	1.372(4)
C(5c)–C(6c)	1.549(4)	O(4g)–C(24g)	1.446(6)
C(5c)–C(16c)	1.564(4)	C(5g)–C(6g)	1.509(5)
O(5c)–C(16c)	1.466(4)	C(5g)–C(16g)	1.580(4)
O(5c)–C(2g)	1.431(4)	O(5g)–C(18g)	1.113(20)
C(6c)–C(7c)	1.536(5)	O(5g)–C(25g)	1.394(13)
C(7c)–C(8c)	1.533(5)	C(6g)–C(7g)	1.532(5)
C(8c)–C(9c)	1.356(5)	C(7g)–C(8g)	1.514(3)
C(8c)–C(13c)	1.377(4)	C(8g)–C(9g)	1.390(3)
C(9c)–C(10c)	1.403(6)	C(8g)–C(13g)	1.393(4)
C(10c)–C(11c)	1.387(4)	C(9g)–C(10g)	1.379(4)
C(11c)–C(12c)	1.386(6)	C(10g)–C(11g)	1.397(4)
C(12c)–C(13c)	1.380(6)	C(11g)–C(12g)	1.398(5)
C(14c)–C(15c)	1.535(4)	C(12g)–C(13g)	1.390(5)
C(15c)–C(16c)	1.535(4)	C(14g)–C(15g)	1.543(6)
C(15c)–C(20c)	1.504(5)	C(15g)–C(16g)	1.534(7)
C(16c)–C(17c)	1.558(5)	C(15g)–C(20g)	1.490(5)
C(17c)–N(1g)	1.478(4)	C(16g)–C(17g)	1.523(5)
C(18c)–C(19c)	1.482(8)	C(18g)–C(19g)	1.492(13)
C(19c)–C(20c)	1.326(4)	C(19g)–C(20g)	1.331(8)
C(20c)–C(21c)	1.507(5)	C(20g)–C(21g)	1.507(5)

TABLE 3

Bond angles for the heavier atoms. E.s.d.s in parentheses

C(2c)–N(1c)–C(13c)	110.0(3)
N(1c)–C(2c)–C(7c)	107.5(3)
C(9c)–O(2c)–C(22c)	115.8(3)
N(4c)–C(3c)–C(14c)	110.8(2)
C(10c)–O(3c)–C(23c)	117.1(4)
C(3c)–N(4c)–C(21c)	112.7(2)
C(12c)–O(4c)–C(24c)	116.8(3)
N(4c)–C(5c)–C(16c)	109.0(2)
C(16c)–O(5c)–C(2g)	108.9(2)
C(2c)–C(7c)–C(3c)	109.2(2)
C(2c)–C(7c)–C(8c)	101.5(2)
C(3c)–C(7c)–C(8c)	109.8(3)
C(7c)–C(8c)–C(9c)	133.6(3)
C(9c)–C(8c)–C(13c)	120.1(3)
O(2c)–C(9c)–C(10c)	119.2(3)
O(3c)–C(10c)–C(9c)	116.6(3)
C(9c)–C(10c)–C(11c)	120.3(4)
O(4c)–C(12c)–C(11c)	125.4(3)
C(11c)–C(12c)–C(13c)	117.8(3)
N(1c)–C(13c)–C(12c)	126.3(3)
C(3c)–C(14c)–C(15c)	108.8(3)
C(14c)–C(15c)–C(20c)	106.7(3)
C(5c)–C(16c)–O(5c)	108.2(2)
C(5c)–C(16c)–C(17c)	116.5(2)
O(5c)–C(16c)–C(17c)	102.8(2)
C(16c)–C(17c)–N(1g)	104.6(2)
C(15c)–C(20c)–C(19c)	126.0(3)
C(19c)–C(20c)–C(21c)	124.4(3)
C(17c)–N(1g)–C(2g)	103.0(2)
C(2g)–N(1g)–C(13g)	103.0(2)
O(5c)–C(2g)–N(1g)	104.7(2)
O(5c)–C(2g)–C(7g)	108.0(2)
N(1g)–C(2g)–C(7g)	106.7(2)
C(9g)–O(2g)–C(22g)	115.4(3)
N(4g)–C(3g)–C(14g)	107.9(3)
C(10g)–O(3g)–C(23g)	113.4(4)
C(3g)–N(4g)–C(21g)	113.0(3)

TABLE 3 (*continued*)

C(12g)–O(4g)–C(24g)	116.9(3)
N(4g)–C(5g)–C(16g)	109.6(3)
C(18g)–O(5g)–C(25g)	118.5(11)
C(2g)–C(7g)–C(3g)	116.1(2)
C(2g)–C(7g)–C(8g)	98.1(2)
C(3g)–C(7g)–C(8g)	108.9(3)
C(7g)–C(8g)–C(9g)	130.4(2)
C(9g)–C(8g)–C(13g)	120.4(2)
O(2g)–C(9g)–C(10g)	121.7(2)
O(3g)–C(10g)–C(9g)	121.6(2)
C(9g)–C(10g)–C(11g)	120.8(3)
O(4g)–C(12g)–C(11g)	124.4(3)
C(11g)–C(12g)–C(13g)	118.5(2)
N(1g)–C(13g)–C(12g)	127.2(2)
C(3g)–C(14g)–C(15g)	107.4(3)
C(14g)–C(15g)–C(20g)	106.2(4)
C(5g)–C(16g)–C(15g)	108.2(3)
C(15g)–C(16g)–C(17g)	112.1(3)
O(5g)–C(18g)–C(19g)	116.7(10)
C(15g)–(20g)–C(19g)	124.8(4)
C(19g)–C(20g)–C(21g)	125.5(4)
N(1c)–C(2c)–O(1c)	125.4(3)
O(1c)–C(2c)–C(7c)	127.1(3)
N(4c)–C(3c)–C(7c)	98.4(2)
C(7c)–C(3c)–C(14c)	113.6(3)
C(3c)–N(4c)–C(5c)	101.3(2)
C(5c)–N(4c)–C(21c)	112.9(2)
N(4c)–C(5c)–C(6c)	102.6(3)
C(6c)–C(5c)–C(16c)	115.6(3)
C(5c)–C(6c)–C(7c)	105.2(3)
C(2c)–C(7c)–C(6c)	115.6(3)
C(3c)–C(7c)–C(6c)	100.4(2)
C(6c)–C(7c)–C(8c)	120.2(2)
C(7c)–C(8c)–C(13c)	106.3(3)
O(2c)–C(9c)–C(8c)	121.4(3)
C(8c)–C(9c)–C(10c)	119.0(3)
O(3c)–C(10c)–C(11c)	123.0(4)
C(10c)–C(11c)–C(12c)	120.3(4)
O(4c)–C(12c)–C(13c)	116.8(3)
N(1c)–C(13c)–C(8c)	111.5(3)
C(8c)–C(13c)–C(12c)	122.2(4)
C(14c)–C(15c)–C(16c)	108.8(2)
C(16c)–C(15c)–C(20c)	108.3(2)
C(5c)–C(16c)–C(15c)	107.6(3)
O(5c)–C(16c)–C(15c)	106.7(2)
C(15c)–C(16c)–C(17c)	114.3(2)
C(18c)–C(19c)–C(20c)	127.0(4)
C(15c)–C(20c)–C(21c)	109.5(2)
N(4c)–C(21c)–C(20c)	111.1(3)
C(17c)–N(1g)–C(13g)	117.6(2)
C(2g)–O(1g)–C(17g)	112.7(3)
O(5c)–C(2g)–O(1g)	108.8(2)
N(1g)–C(2g)–O(1g)	110.1(2)
O(1g)–C(2g)–C(7g)	117.8(2)
N(4g)–C(3g)–C(7g)	102.5(3)
C(7g)–C(3g)–C(14g)	117.7(3)
C(3g)–N(4g)–C(5g)	99.7(2)
C(5g)–N(4g)–C(21g)	113.2(3)
N(4g)–C(5g)–C(6g)	98.4(2)
C(6g)–C(5g)–C(16g)	114.5(2)
C(5g)–C(6g)–C(7g)	100.5(3)
C(2g)–C(7g)–C(6g)	110.1(3)
C(3g)–C(7g)–C(6g)	103.4(2)
C(6g)–C(7g)–C(8g)	120.9(3)
C(7g)–C(8g)–C(13g)	108.8(2)
O(2g)–C(9g)–C(8g)	119.1(2)
C(8g)–C(9g)–C(10g)	119.1(2)
O(3g)–C(10g)–C(11g)	117.5(3)
C(10g)–C(11g)–C(12g)	120.3(3)
O(4g)–C(12g)–C(13g)	117.1(3)
N(1g)–C(13g)–C(8g)	111.7(2)
C(8g)–C(13g)–C(12g)	120.9(2)
C(14g)–C(15g)–C(16g)	110.6(3)
C(16g)–C(15g)–C(20g)	107.1(3)
C(5g)–C(16g)–C(17g)	116.6(3)
O(1g)–C(17g)–C(16g)	112.6(4)
C(18g)–C(19g)–C(20g)	124.8(6)
C(15g)–C(20g)–C(21g)	109.6(3)
N(4g)–C(21g)–C(20g)	110.4(3)

gardneramine unit could be caused by the extension of the resonance structure of the aromatic ring to the lone pair of the nitrogen atom and carbonyl group. Observed and calculated structure factors together with the thermal parameters form part of a Supplementary publication; the positional parameters for the hydrogen atoms also form part of SUP. No. 23261 (25 pages).*

Crystal Structure.—The molecular packing diagram viewed along the *a* axis is shown in Figure 3. The molecules appear to be held together in the crystal by van der Waals contacts and no intermolecular distances are significantly shorter than normal values. There are large columnar holes near the centre of the unit cell. The holes are partially filled by the methanol molecules which are linked to O(1c) by a hydrogen bond (2.689 Å). The instability of the crystals might be caused by the loosely bound nature of the methanol molecules which can easily be lost in the air. One of the methoxy-groups and the methoxymethyl group in the side-chain of the gardneramine unit protrude into the hole, but they are not tightly bound each other. The absence of the strong contacts in this region might give rise to co-crystallization with demethoxygardmultine (2) in which the methoxymethyl group of gardmultine (1) is replaced by a methyl group. The difference of these groups in the side-chain does not seem to play a crucial role in the construction of the crystal structure.

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* For details of the Supplementary publications Scheme, see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

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