CONSTITUENTS OF THE ZINGIBERACEAE
CRYSTAL STRUCTURE OF (±)-BOESENBERGIN B
(±)-E-1-[5'-HYDROXY-7'-METHOXY-2'-METHYL-2'-(-4''-METHYLPENT-3''-ENYL)-2'H-1-BENZOPYRAN-6'-YL]-3-PHENYLPROP-2-EN-1-ONE

CHULABHORN MAHIDOL[a], PITTAYA TUNTIWACHWUTTIKUL[b], CHAVENG PAKAWATCHAI[c,d], VINCENT A. PATRICK[c], VICHAI REUTRAKUL[e], BRIAN W. SKELTON[c] AND ALLAN H. WHITE[c]

[a]*Chulabhorn Research Institute, Mahidol University, Bangkok 10400, Thailand.*
[b]*Department of Chemistry, Silpakorn University, Nakorn Pathom, Thailand.*
[c]*Department of Physical and Inorganic Chemistry, University of Western Australia, Nedland, W.A. 6009, Australia.*
[d]*Present address : Department of Chemistry, Prince of Songkla University, Haad-Yai, Thailand.*
[e]*Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand.*

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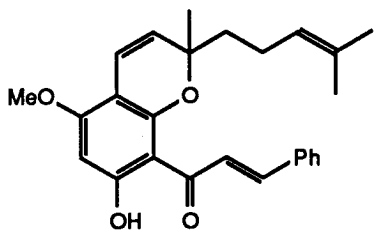
ABSTRACT

A single-crystal low temperature X-ray structure determination of the title compound, $C_{26}H_{28}O_4$, confirms the stoichiometry, connectivity and stereochemistry recently assigned spectroscopically. Crystals are orthorhombic, Pbca, *a = 23.65(2), b = 17.58(1), c =* 10.319(6)Å, *Z* = 8 ; the structure was refined to a residual of 0.074 for 485 "observed" independent reflections.

INTRODUCTION

The yellow rhizomes of a variey of *Boesenbergia pandurata* Schl. (Syn. *Kaemferia pandurata* Roxb.), which belongs to the family Zingiberaceae, have yielded the isomeric chromene derivatives boesenbergin A (**1**) and boesenbergin B (**2**).



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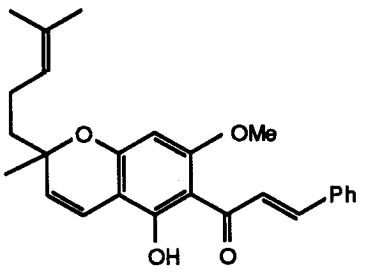

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The structures of **1** and **2** were deduced from their spectroscopic properties [1,2] supported in the case of boesenbergin A (**1**) by a single crystal X-ray structure.

Both **1** and **2** have been synthesized from the corresponding dihydroxy-methoxy chalcones by means of the Crombie reaction.[1,2] In the case of **1**, due to the symmetrical substitution pattern of the starting material, the synthesis is unambiguous, but this is not so in the case of boesenbergin B. Although we had no grounds to doubt the structure of boesenbergin B we considered that it would be prudent to determine the X-ray crystal structure of this substance. This has now been achieved, albeit with some difficulty, and has confirmed the structure (**2**) for boesenbergin B.

CRYSTALLOGRAPHY

Crystal data $C_{26}H_{28}O_4$, M = 404.5, Orthorhombic, space group *Pbca* (D_{15}^{2h}, No. 61), a = 23.65(2), b = 17.58(1), c = 10.319(6) Å, U = 4291(4) Å^3. $D_c(Z = 8)$ = 1.25 g.cm.$^{-3}$ $F(000)$ = 1728. Monochromatic Mo K_α radiation, λ = 0.7106 Å, μ_{Mo} = 0.88 cm.$^{-1}$ Specimen : 0.15×0.15×0.07 mm (no absorption correction). $T \sim$ 120 K.

Structure determination An initial attempt was made to determine the structure using data measured at room temperature ; although the structure was solved successfully, a combination of factors such as small crystal size, weakly diffracting specimen, etc., resulted in only a very small quantity of observable data. Recourse to the use of a low temperature data collection facility resulted in a doubling of the available data, and we report the structure, only still of marginal quality, but sufficing to define connectivity determined under these conditions. A unique data set was measured to $2\theta_{max} = 40°$ using a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode. 1870 Independent reflections were measured : 485 with $I > 3\sigma(I)$ and 682 with $I > 2\sigma(I)$ were considered 'observed' respectively for two independent refinement models. Atom coordinates and isotropic thermal parameters were refined in a full matrix least squares refinement for the non-hydrogen atoms after solution of the structure by direct method; $(x, y, z, U_{iso})_H$ were included at estimated values. At convergence, residuals on F were (R, R') 0.074, 0.057 for the 3σ (I) data, and 0.10, 0.062 for the 2σ (I) data ; atom parameters recorded below are for the latter. Reflection weights were $\sigma^2(F)^{-1}$. Neutral complex scattering factors were used; [3] computation used the XTAL 83 program system[4] implemented on a Perkin-Elmer 3240 computer by S.R. Hall. Results are given in the Figure and Tables. Material deposited* comprises structure factor amplitudes and hydrogen atom parameters. Crystallographic and systematic numbering schemes are as follows :

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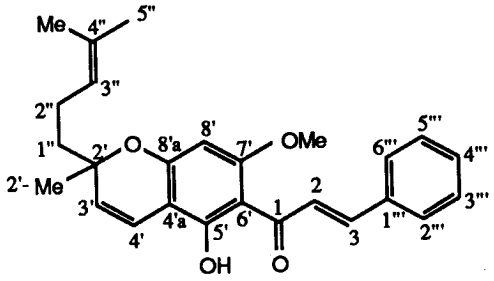
* Copies available on application to the Editor.



SYSTEMATIC NUMBERING

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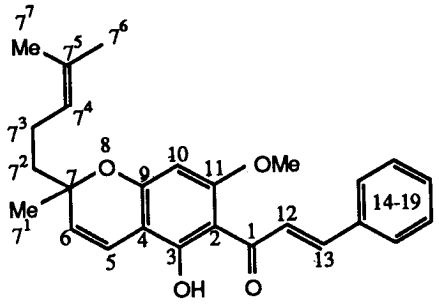

CRYSTALLOGRAPHIC NUMBERING

STRUCTURAL COMMENTARY

Single-crystal X-ray structure determination is consistent with the assignment of stoichiometry, connectivity and stereochemistry proposed in ref.,[2] given as **2** above. A nuclear Overhauser enhancement (n.O.e) experiment on boesenbergin B showed a 3.0% increase in integrated intensity of the H2 signal upon irradiation of the methoxy group. This result is in accord with the solid state conformation, with the C1 carbonyl group fixed by the strong hydrogen bond from the hydroxyl group. The n.O.e from 4″-Me to H3′ (1.5%) indicates, as in the solid state, that the homoprenyl side chain prefers to be folded back towards the chromene ring. The skeleton of the molecular core is substantially planar, substituent atom deviations from the C(2-4,9-11) plane (X^2 2.7) being C(1,5,6,7,111,12,13)O(1,3,8,11) 0.08, -0.10, 0.01, 0.35, -0.06, 0.23, 0.16, -0.04, -0.03, -0.05, 0.01 Å.

Interplanar contacts between molecules related by *(x, ½ − y, ½+z)* are many (Table 4), suggestive of charge transfer interactions (see Fig. 2 also).

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TABLE 1 Non-hydrogen atom parameters

Atom	*x*	*y*	*z*	$10^3\ \mu\ \text{Å}^2$
C(1)	0.3244(10)	0.341(1)	0.447(2)	37(7)
O(1)	0.3267(6)	0.4089(7)	0.482(1)	33(4)
C(2)	0.3564(8)	0.282(1)	0.520(1)	16(7)
C(3)	0.3938(10)	0.306(1)	0.620(2)	25(7)
O(3)	0.4003(6)	0.3808(7)	0.650(1)	31(4)
C(4)	0.4277(8)	0.256(1)	0.689(2)	15(6)
C(5)	0.4633(9)	0.280(1)	0.792(2)	41(8)
C(6)	0.4975(9)	0.229(1)	0.848(2)	33(7)
C(7)	0.5037(9)	0.147(1)	0.800(2)	21(6)
C(71)	0.5058(9)	0.089(1)	0.908(2)	45(8)
C(72)	0.5519(8)	0.144(1)	0.709(2)	26(7)
C(73)	0.5607(9)	0.068(1)	0.641(2)	36(7)
C(74)	0.6134(9)	0.070(1)	0.557(2)	28(6)
C(75)	0.6218(8)	0.066(1)	0.432(2)	18(6)
C(76)	0.6762(9)	0.069(1)	0.365(2)	32(7)
C(77)	0.5727(9)	0.065(1)	0.340(2)	50(8)
O(8)	0.4509(6)	0.1256(8)	0.726(1)	43(5)
C(9)	0.4223(9)	0.179(1)	0.659(1)	24(7)
C(10)	0.3845(9)	0.153(1)	0.568(2)	24(6)
C(11)	0.3522(9)	0.202(1)	0.502(2)	26(7)
O(11)	0.3156(6)	0.1782(7)	0.407(1)	25(4)
C(111)	0.3091(9)	0.097(1)	0.385(2)	40(7)
C(12)	0.2888(9)	0.322(1)	0.337(2)	34(7)
C(13)	0.2567(9)	0.372(1)	0.280(2)	23(6)
C(14)	0.2198(8)	0.357(1)	0.168(2)	34(7)
C(15)	0.1951(8)	0.418(1)	0.101(2)	23(6)
C(16)	0.1590(9)	0.404(1)	-0.008(2)	38(7)
C(17)	0.1487(9)	0.332(1)	-0.043(2)	37(7)
C(18)	0.1713(10)	0.269(1)	0.020(2)	38(7)
C(19)	0.2060(9)	0.284(1)	0.128(2)	35(7)

TABLE 2 Non-hydrogen interatomic distances (Å)

Atoms	Distance
C(1)-O(1)	1.25(3)
C(1)-C(2)	1.49(3)
C(1)-C(12)	1.45(3)
C(2)-C(3)	1.42(3)
C(2)-C(11)	1.42(3)
C(3)-O(3)	1.36(2)
C(3)-C(4)	1.37(3)
C(4)-C(5)	1.42(3)
C(4)-C(9)	1.41(3)
C(5)-C(6)	1.33(3)
C(6)-C(7)	1.53(3)
C(7)-C(71)	1.51(3)
C(7)-C(72)	1.48(3)
C(7)-O(8)	1.51(3)
O(8)-C(9)	1.35(3)
C(9)-C(10)	1.38(3)
C(10)-C-(11)	1.34(3)
C(11)-O(11)	1.38(3)
O(11)-C(111)	1.45(2)
C(12)-C(13)	1.31(3)
C(13)-C(14)	1.47(3)
C(14)-C(15)	1.40(3)
C(15)-C(16)	1.43(3)
C(16)-C(17)	1.34(3)
C(17)-C(18)	1.40(3)
C(18)-C(19)	1.41(3)
C(14)-C(19)	1.39(3)
C(72)-C(73)	1.53(3)
C(73)-C(74)	1.52(3)
C(74)-C(75)	1.31(3)
C(75)-C(76)	1.46(3)
C(75)-C(77)	1.50(3)

O(1) ...O(3) is 2.50(2) Å.

TABLE 3 Non-hydrogen interatomic angles (degrees)

Atoms	Angle
C(2)-C(1)-O(1)	120(2)
C(2)-C(1)-C(12)	122(2)
O(1)-C(1)-C(12)	118(2)
C(1)-C(2)-C(3)	119(2)
C(1)-C(2)-C(11)	126(2)
C(3)-C(2)-C(11)	116(2)
C(2)-C(3)-C(4)	123(2)
C(2)-C(3)-O(3)	121(2)
C(4)-C(3)-O(3)	116(2)
C(3)-C(4)-C(5)	123(2)
C(3)-C(4)-C(9)	117(2)
C(5)-C(4)-C(9)	120(2)
C(4)-C(5)-C(6)	120(2)
C(5)-C(6)-C(7)	123(2)
C(6)-C(7)-O(8)	109(2)
C(6)-C(7)-C(71)	114(2)
C(6)-C(7)-C(72)	108(2)
O(8)-C(7)-C(71)	103(2)
O(8)-C(7)-C(72)	108(2)
C(71)-C(7)-C(72)	115(2)
C(7)-O(8)-C(9)	120(2)
C(4)-C(9)-O(8)	121(2)
C(4)-C(9)-C(10)	122(2)
O(8)-C(9)-C(10)	117(2)
C(9)-C(10)-C(11)	121(2)
C(2)-C(11)-C(10)	122(2)
C(2)-C(11)-O(11)	117(2)
C(10)-C(11)-O(11)	121(2)
C(11)-O(11)-C(111)	119(2)
C(1)-C(12)-C(13)	122(2)
C(12)-C(13)-C(14)	126(2)
C(13)-C(14)-C(15)	121(2)
C(13)-C(14)-C(19)	122(2)
C(15)-C(14)-C(19)	117(2)
C(14)-C(15)-C(16)	121(2)
C(15)-C(16)-C(17)	119(2)
C(16)-C(17)-C(18)	124(2)
C(17)-C(18)-C(19)	116(2)

Atoms	Angle
C(14)-C(19)-C(18)	123(2)
C(7)-C(72)-C(73)	115(2)
C(72)-C(73)-C(74)	110(2)
C(73)-C(74)-C(75)	133(2)
C(74)-C(75)-C(76)	127(2)
C(74)-C(75)-C(77)	120(2)
C(76)-C(75)-C(77)	113(2)

TABLE 4 Intermolecular overlap contacts, < 3.6 Å
The second atom is generated by the operation $(x, \frac{1}{2}-y, \frac{1}{2}+z)$

MOLECULE 1	MOLECULE 2	DISTANCE (Å)
O(3)	C(111)	3.28(3)
C(5)	C(11)	3.42(3)
O(3)	O(11)	3.48(2)
C(3)	O(11)	3.50(3)
C(15)	C(111)	3.50(3)
C(19)	O(3)	3.52(3)
O(3)	C(71)	3.57(2)
C(14)	O(11)	3.58(3)
C(5)	C(10)	3.60(3)
C(10)	C(12)	3.61(3)
C(2)	C(5)	3.62(3)

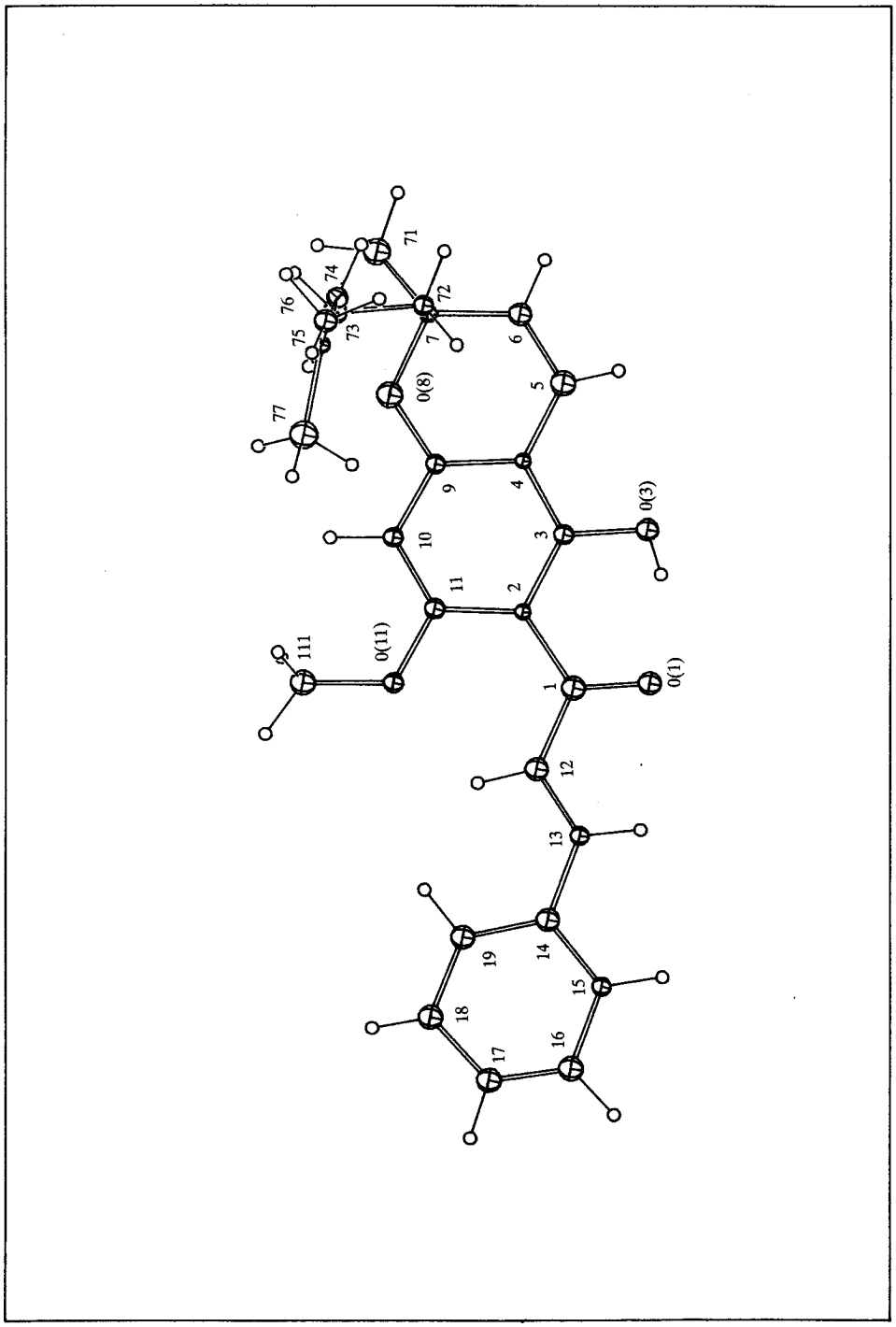

Fig. 1 A single molecule of **2**; non-hydrogen atom numbering is shown with isotropic thermal motion amplitudes shown at the 20% probability level. Hydrogen atoms have an arbitrary radius of 0.1 Å.

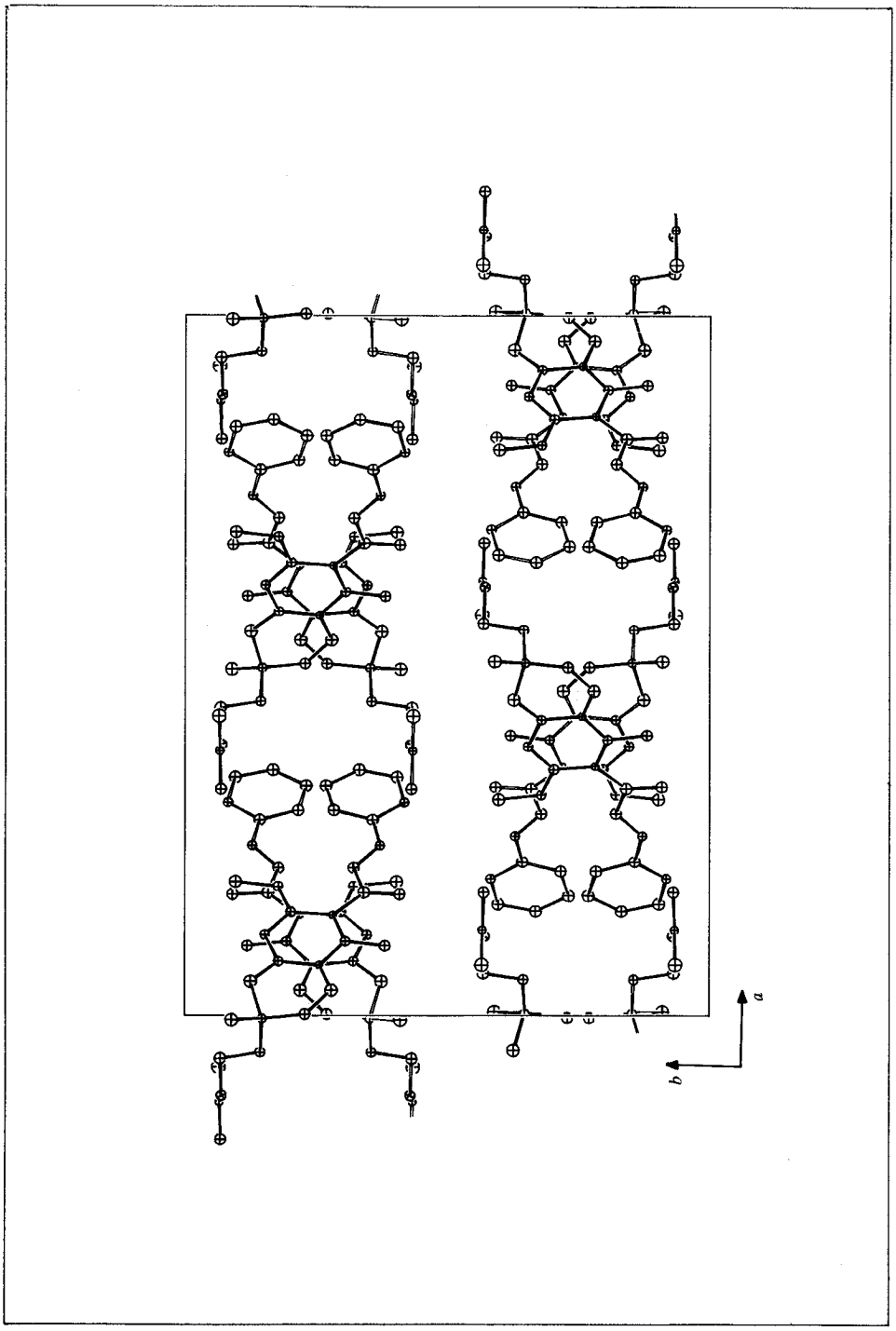

Fig. 2 Unit cell contents projected down *c*.

TABLE SUP-1 Hydrogen atom parameters

Atom	*x*	*y*	*z*	$10^3\ \mu Å^2$
H(5)	0.467(−)	0.328(−)	0.832(−)	51(−)
H(6)	0.520(−)	0.242(−)	0.925(−)	47(−)
H(71a)	0.541(−)	0.098(−)	0.965(−)	68(−)
H(71b)	0.476(−)	0.091(−)	0.969(−)	68(−)
H(71c)	0.511(−)	0.035(−)	0.886(−)	68(−)
H(72a)	0.550(−)	0.182(−)	0.643(−)	25(−)
H(72b)	0.589(−)	0.155(−)	0.754(−)	25(−)
H(73a)	0.563(−)	0.024(−)	0.704(−)	47(−)
H(73b)	0.527(−)	0.053(−)	0.588(−)	47(−)
H(74)	0.647(−)	0.083(−)	0.608(−)	38(−)
H(76a)	0.696(−)	0.113(−)	0.390(−)	62(−)
H(76b)	0.698(−)	0.025(−)	0.401(−)	62(−)
H(76c)	0.684(−)	0.063(−)	0.274(−)	62(−)
H(77a)	0.546(−)	0.025(−)	0.356(−)	76(−)
H(77b)	0.549(−)	0.113(−)	0.347(−)	76(−)
H(77c)	0.575(−)	0.063(−)	0.242(−)	76(−)
H(10)	0.380(−)	0.097(−)	0.553(−)	27(−)
H(111a)	0.344(−)	0.071(−)	0.364(−)	66(−)
H(111b)	0.295(−)	0.071(−)	0.463(−)	66(−)
H(111c)	0.283(−)	0.072(−)	0.318(−)	66(−)
H(12)	0.283(−)	0.271(−)	0.297(−)	48(−)
H(13)	0.260(−)	0.426(−)	0.310(−)	35(−)
H(15)	0.202(−)	0.471(−)	0.129(−)	37(−)
H(16)	0.141(−)	0.451(−)	-0.052(−)	52(−)
H(17)	0.126(−)	0.326(−)	-0.125(−)	51(−)
H(18)	0.161(−)	0.218(−)	-0.004(−)	52(−)
H(19)	0.223(−)	0.241(−)	0.178(−)	47(−)
H(3)	0.387(−)	0.401(−)	0.588(−)	39(−)

Supplementary material : Other X-ray data [e.g. structure factor amplitudes] are available upon request.

บทคัดย่อ

บทความนี้กล่าวถึงรายละเอียดการหาสูตรโครงสร้างของสาร Boesenbergin B โดยใช้เทคนิค Single-crystal low temperature X-ray diffraction analysis ข้อมูลที่ได้สนับสนุนสูตรโครงสร้างของสาร Boesenbergin B ที่หาได้จากการใช้เทคนิคทาง spectroscopy