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CRYSTAL STRUCTURE OF ARTEMETIN BROMIDE *

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Laggeria Alata is a major ingredient in an ointment for skin tumor in Chinese medicine. The dried powder of Laggeria Alata was extracted with n-hexane, and a yellow needle-shape crystalline was obtained with an empirical formula of $C_{20}H_{20}O_8$. The NMR ^1H spectra showed that it contains five methoxy groups. The compound was brominated with bromine in CCl_4. Crystal data of the brominated compound are: Space group $P2_1/c$; Cell dimensions: a=15.767, b=7.419, c=17.810 Å

TABLE 1 FRACTIONAL COORDINATES (X10^4) AND TEMPERATURE FACTORS FOR

The Crystal Structure of Artemetin in Laggeria Alata

T=EXP(-(B11*HH + B22*KK + B33*LL + B12*HK + B13*HL + B23*KL)) FOR ANISOTROPIC TEMPERATURE FACTORS (X10^4

ATOM	X/A	Y/B	Z/C	B11	B22	B33	B12	B13	B23
BR	2871(0)	1976(1)	-2298(0)	55(0)	238(2)	23(0)	-13(2)	32(0)	14(1)
O11	983(3)	978(7)	-2444(2)	43(3)	296(13)	27(2)	-18(11)	7(4)	20(8)
O12	394(3)	389(7)	-1168(3)	35(2)	223(13)	38(2)	5(9)	25(4)	8(8)
O13	1659(3)	306(7)	421(3)	51(3)	314(14)	31(2)	-38(11)	45(4)	1(8)
O21	4025(3)	1960(6)	-483(2)	33(2)	178(10)	21(2)	-8(9)	16(3)	-4(7)
O22	3349(3)	853(7)	1433(2)	54(3)	283(13)	21(2)	-12(10)	36(4)	13(8)
O23	5156(3)	1451(6)	174(2)	44(2)	202(12)	22(2)	-3(9)	14(3)	9(7)
O31	8014(3)	3689(7)	1743(3)	39(2)	280(13)	32(2)	-37(9)	15(4)	-7(8)
O32	8109(3)	4489(7)	364(3)	45(3)	257(13)	44(2)	-25(10)	43(4)	20(9)
C11	2492(4)	1426(8)	-1447(3)	40(4)	145(15)	22(2)	8(11)	26(5)	10(9)
C12	1573(4)	965(8)	-1636(3)	35(3)	162(14)	26(2)	11(12)	16(4)	18(10)
C13	1281(4)	601(9)	-1003(4)	35(4)	167(16)	32(3)	1(13)	18(5)	-9(11)
C14	1942(4)	658(8)	-189(3)	38(3)	170(15)	29(3)	2(12)	29(2)	-8(10)
C15	2869(4)	1085(9)	0(3)	41(4)	137(14)	24(3)	11(12)	22(5)	1(10)
C16	3134(4)	1510(8)	-637(3)	38(4)	127(16)	25(3)	4(11)	23(5)	1(9)
C17	248(5)	-363(10)	-2756(4)	51(4)	228(19)	36(3)	-25(16)	13(6)	-28(13)
C18	98(5)	-1340(11)	-949(5)	49(5)	273(22)	48(4)	-46(15)	41(7)	0(14)
C21	3559(5)	1170(9)	841(4)	43(4)	133(14)	28(3)	7(13)	23(5)	11(10)
C22	4481(4)	1651(8)	955(3)	41(4)	125(16)	25(3)	-7(12)	15(5)	-5(10)
C23	4701(4)	2055(9)	305(3)	39(3)	133(14)	25(2)	-3(13)	23(5)	-5(11)
C24	5122(6)	3235(11)	2225(4)	77(5)	282(21)	32(3)	-47(17)	49(7)	-69(14)
C31	5589(4)	2649(8)	312(4)	37(3)	145(14)	26(3)	1(12)	21(5)	-10(10)
C32	6386(4)	2847(9)	1046(4)	39(4)	167(15)	29(3)	-11(13)	24(5)	-12(11)
C33	7207(5)	3459(9)	1049(4)	40(4)	193(17)	34(3)	0(12)	21(6)	-20(11)
C34	7267(5)	3890(9)	296(4)	40(4)	147(16)	36(3)	3(13)	39(5)	10(10)
C35	6483(5)	3682(9)	-428(4)	48(4)	163(16)	32(3)	10(13)	36(6)	22(11)
C36	5652(4)	3091(10)	-433(4)	40(4)	195(15)	27(3)	-18(15)	27(5)	-8(12)
C37	7979(6)	3307(14)	2514(4)	54(5)	284(27)	33(3)	-10(19)	26(6)	-13(13)
C38	8221(5)	4806(12)	-387(5)	52(5)	336(24)	55(4)	-17(17)	62(7)	49(15)

ATOM	X/A	Y/B	Z/C	B	ATOM	X/A	Y/B	Z/C	B
H11	192(59)	-432(115)	-3312(52)	6.17(2.26)	H12	-413(60)	-73(115)	-2828(52)	4.36(2.28)
H13	474(56)	-1617(119)	-2431(50)	5.79(2.37)	H14	-930(60)	-1720(116)	-1315(50)	6.86(2.93)
H15	99(56)	-1002(118)	-351(51)	6.90(2.28)	H16	508(60)	-2407(114)	-1147(53)	6.57(2.36)
H17	2227(60)	282(117)	870(50)	2.95(2.35)	H21	4536(64)	3568(115)	2263(52)	6.59(2.36)
H22	5351(57)	4255(122)	2011(50)	3.50(2.32)	H23	5611(63)	3273(117)	2787(55)	6.13(2.32)
H31	6501(56)	3946(112)	-994(49)	2.01(2.34)	H32	5097(56)	3133(112)	-911(50)	3.39(2.33)
H33	6354(59)	2627(107)	1543(53)	5.46(2.36)	H34	7508(59)	3932(132)	2567(49)	2.97(2.32)
H35	8571(60)	3831(115)	2925(50)	2.19(2.34)	H36	8021(57)	1901(129)	2601(48)	6.89(2.40)
H37	8904(57)	5107(116)	-169(48)	3.58(2.36)	H38	8205(59)	3296(118)	-612(52)	6.95(2.30)
H39	7698(56)	5417(118)	-753(49)	4.14(2.35)					

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and β=114.32°, Z=4. A total of 1820 independent reflections($I > 3\sigma$) were collected on a Syntex P1 autodiffractometer using Ni-filtered CuK_α radiation, 2θ scan being used. After correction of Lp and absorption factors, the structure was solved by heavy-atom procedure, and refined by difference Fourier and full matrix least square. The final R factor is 0.043. The atomic form factors were corrected for dispersion effect. The relevant parameters are listed in Table 1 and in Fig. 1. There are no abnormal bonding and packing distances.

The structure was confirmed to be 8-bromo-5-hydroxy-3,3',4',6,7-pentamethoxy flavone which is also known as artemetin (1) with one H replaced by Br.

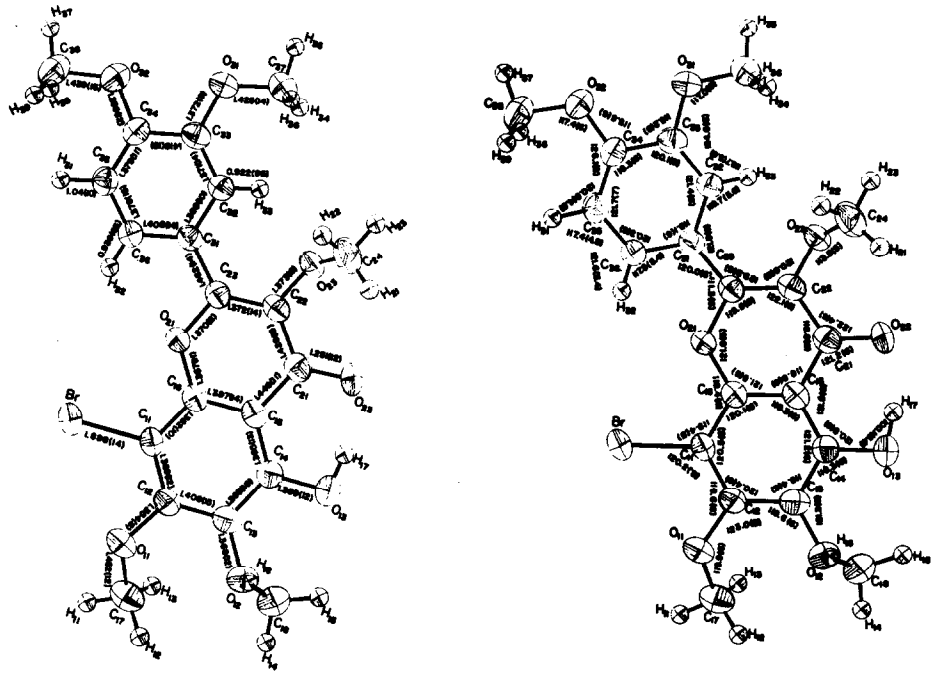

Fig.1. Bond lengths and angles (The isotropic temperature factors of hydrogen are assigned to be 1.5 in above plots)

References:

1. (a) L.S.Akhmedov, Sh.Z.Kasymov and G.P.Sidyakin, Khim. Prir. Soedin. 5(1), 57-8, (1969). (b) P.K.Bose, A.K.Barua and P.Chakrabarti, J. Indian Chem. Soc. 45(9) 851-2, (1968). (c) Z.Cekan and V.Herout, Chem.Listy 49, 1053-6 (1955) (d) W.Hertz, J. Org. Chem. 3014-5, (1961). (e) Y.Mazur and A.Meisels. Bull. Research Council Israel, 5A,67-9 (1955). (f) P.Tunmann and O.Issac, Arch. Pharm. 290, 37-43 (1957).