THE MINOR ALKALOIDS OF *Monnieria trifolia* L.

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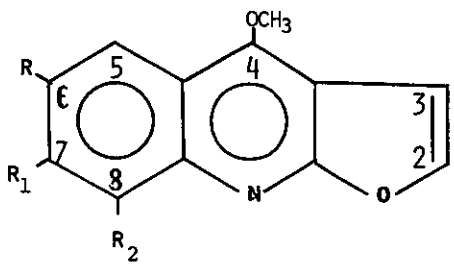
Abstract: Evolatine and 6-methoxy-7-hydroxydictamnine, alleged to have been isolated from the leaves of ***Monnieria trifolia*** L., appear to be identical to montrifoline and delbine respectively, the new alkaloids reported from the same source.

Recently, we reported[2] the structures of two new furoquinoline alkaloids, montrifoline(1) and delbine(2), isolated from the leaves of ***Monnieria trifolia*** L., a Rutaceous herb growing throughout the northeastern region of Brazil. About the same time, the isolation of the alkaloids alleged to be evolatine(3) and 6-methoxy-7-hydroxydictamnine(4) along with evoxine(5) and haplopine(6) were reported[3] from the same source. In this communication, we wish to report that based on all the published data, the alkaloids claimed[3] to be evolatine and 6-methoxy-7-hydroxydictamnine isolated from ***M. trifolia*** are actually montrifoline and delbine, respectively.



1, R = $-OCH_2CH(OH)C(OH)(CH_3)_2$; R_1= OCH_3; R_2= H

2, R = OH; R_1= OCH_3; R_2= H

3, R = OCH_3; R_1= $-OCH_2CH(OH)C(OH)(CH_3)_2$; R_2= H

4, R = OCH_3; R_1= OH; R_2= H

5, R = H; R_1= $-OCH_2CH(OH)C(OH)(CH_3)_2$; R_2= OCH_3

6, R = H; R_1= OH; R_2= OCH_3

7, R = R_1= R_2= H

8, R = R_1= OCH_3; R_2= H

9, RR_1 = $-OCH_2O-$; R_2 = H

For the convenience of discussion, the alkaloids isolated from the leaves of *M. trifolia* and alleged[3] to be evolatine and 6-methoxy-7-hydroxydictamnine will be referred to as Alkaloids A and B, respectively.

Alkaloid A has a reported[3] mp 188-190°C which is very close to that of montrifoline (1), mp 191-193°C, and much lower than that of evolatine(3), mp 201-202°C, isolated, so far, from *Evodia alata*[4] only. Alkaloid A, upon KOH fusion, furnished Alkaloid B. The latter was also isolated[3] from the leaves of *M. trifolia* as a new natural product. However, the reported mp 229°C of Alkaloid B is very close to that of delbine(7-methoxy-6-hydroxydictamnine; 2), mp 229-231°C, and much lower than that of 6-methoxy-7-hydroxydictamnine(4), mp 239-240°C, the KOH fusion product of evolatine(3) from *E. alata*[4]. Subsequently, heliparvifoline, isolated[5] from *Helietta parvifolia*, was unambiguously assigned the structure 6-methoxy-7-hydroxydictamnine (4), and was shown to have a mp 245-247°C, which is also considerately higher than 229°C, reported for the Alkaloid B isolated from *M. trifolia* and assigned[3] the same structure.

The spectral properties of montrifoline(1) and delbine(2) are expectedly very similar to those of evolatine(3) and 6-methoxy-7-hydroxydictamnine(4), respectively. However, the ^{1}H NMR spectrum of Alkaloid B from *M. trifolia* showed <u>para</u> aromatic proton signals at 7.24 and 7.54 ppm, assigned[3] to the C-5 and C-8 protons, respectively. When the OCH_3 signal at 3.99 ppm was irradiated, it resulted in the increased intensity of the aromatic proton signal at 7.24 ppm which was already assigned to C-5 proton. Therefore, the OCH_3 group was assigned to C-6. Also, the acetylation of the phenolic OH group resulted in a greater deshielding of the proton at 7.24 ppm than the proton at 7.54 ppm in the ^{1}H NMR spectrum of the acetate. Therefore, the OH group was assigned to C-7, <u>ortho</u> to the C-8 proton. However, a review of the ^{1}H NMR spectra of several naturally occurring furoquinoline alkaloids unsubstituted at C-5 and C-8 shows(Table 1) that irrespective of the nature of the substituents at C-6 and C-7 and the solvents used, the C-5 proton appears at a relatively lower field than the C-8 proton, without exception. Therefore, it appears that the aromatic protons at 7.24 and 7.54 ppm in the ^{1}H NMR spectrum of Alkaloid B, mp 229°C, assigned[3] erroneously to C-5 and C-8 protons, respectively, should be assigned in a reverse order to C-8 and C-5 protons, respectively. This would require the assignments of the OCH_3 group at 3.99 ppm and the phenolic OH group to C-7 and C-6, respectively, as in delbine(2), and not in a reverse order originally assigned[3]. Consequently, as Alkaloid B (mp 229°C) was also obtained by the KOH fusion of

TABLE 1

Chemical Shifts[a] of the C-5 and C-8 protons of some Naturally Occurring Furoquinoline Alkaloids

NAME OF THE ALKALOID	STRUCTURE	CHEMICAL SHIFTS (ppm) OF THE PROTON AT		REFERENCE
		C-5	C-8	
Heliparvifoline[b] (6-methoxy-7-hydroxydictamnine)	4	7.43	7.20	5
Dictamnine	1	8.11	7.88	5
Kokusaginine (6,7-dimethoxydictamnine)	8	7.44	7.30	5
Maculine (6,7-methylenedioxydictamnine)	9	7.50	7.33	6
Montrifoline[b]	1	7.53	7.28	2
Montrifoline	1	7.54	7.24	7
Delbine[b]	2	7.48	7.29	2
Delbine	2	7.53	7.25	7

a, in $CDCl_3$

b, in DMSO-d_6

Alkaloid A, mp 188-190°C, it appears that the latter compound is actually montrifoline(1) which yields delbine(2) by similar KOH fusion. This would also be consistant with the chemical shift assignments of the aromatic protons of Alkaloid A at 7.24 and 7.54 ppm to C-8 and C-5, respectively, as in montrifoline(1) and not in the reverse order to C-5 and C-8 protons, respectively, as in evolatine.

The slight difference in the chemical shift data between montrifoline and Alkaloid A and between delbine and Alkaloid B is due to the difference in the solvents used. To verify this, the ^1H NMR spectra of montrifoline and delbine which were previously run[2] in DMSO-d_6 were repeated in $CDCl_3$. It was observed that the chemical shift data were practically identical to those published[3] for the alleged evolatine (Alkaloid A) and 6-methoxy-7-hydroxydictamnine (Alkaloid B). Therefore, it appears on the basis of all the above evidence that the alkaloids reported[3] as evolatine and 6-methoxy-7-hydroxydictamnine, from the leaves of *M. trifolia* are actually,

montrifoline(1) and delbine(2), respectively, although the possibility of the presence of the former two alkaloids in this plant in trace amounts cannot be ruled out.

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