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CORIALSTONINE, A NOVEL QUINOLINE ALKALOID FROM *ALSTONIA CORIACEA*

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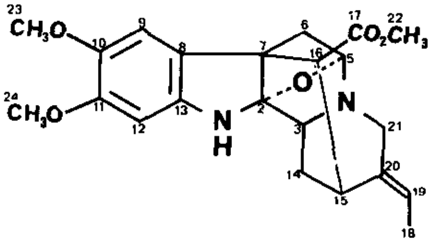
Abstract — *Corialstonine is a novel quinoline alkaloid isolated from Alstonia coriacea*. Its structure illustrates a possible new transformation of indoles into quinolines.

The propensity of some indoles to transform themselves into quinolines is exemplified by the *Cinchona*[1] or *Camptotheca*[2] alkaloids and to a lesser extend by lanceomigine from *Alstonia* and *Hunteria* species[3]. We wish to describe a novel quinoline alkaloid, corialstonine 1, which also illustrates an alternative means of transposition of indoles into quinolines.



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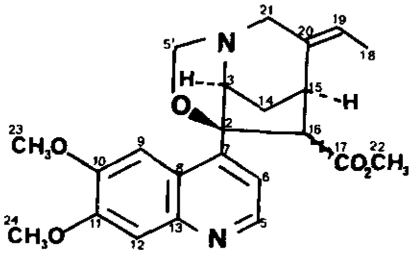
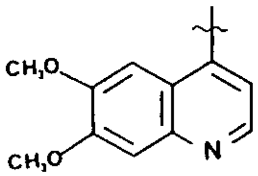


1

Alstonia coriacea is a shrub from New-Caledonia[4] whose stem bark main alkaloid is nor-quaternine 2 [5]. It is accompanied by corialstonine[6], an amorphous base which is slightly fluorescent on TLC ($(\alpha)_D$ +102°, $CHCl_3$, C=1). Corialstonine does not react with the Ce-IV spray but stains orange after Dragendorff pulverization. Its uv spectrum does not resemble those of the usual indole alkaloids ; two maximum appear at 317 and 330 nm, which are shifted at 354 nm upon acidification : the ms of 1 displays molecular ion at m/z 410, analyzed for $C_{23}H_{26}N_2O_5$ (410.176 ; calc:410.184) ; it is accompanied by an m/z 424 probably due to transmethylation.

^{1}H nmr and ^{13}C nmr spectra for 1 were obtained at 300 and 75MHz respectively. They were uneventfully interpreted by means of homonuclear (^{1}H-^{1}H) and heteronuclear (^{1}H-^{13}C) correlated spectroscopy[7]. It is thus found an isolated eight-carbon system 3 corresponding to the core of all type -I indole alkaloids[8] and a quinoline 4. Other systems are a methoxycarbonyl unit, a quaternary carbon and an isolated methylene with an unusually low geminal coupling constant (J=6.7Hz) ; worthy of note is the absence of "tryptamine-like" CH_2-CH_2 protons.



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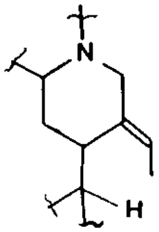
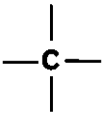
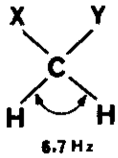


3

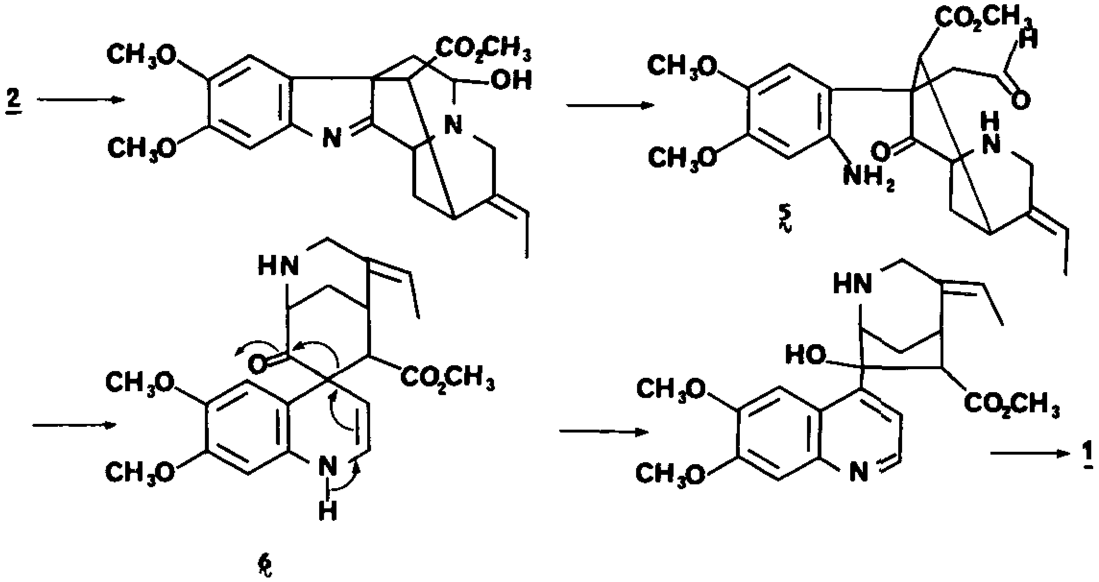
—CO_2CH_3





Structure 1 was finally deduced from biogenetic considerations and from observation of long range ^{1}H-^{1}H and ^{1}H-^{13}C couplings. Of particular value are the correlations of and across quaternary carbons such as : C-2→H-6 (3_J) ; H-6→H-3 (5_J) ; C-3→H-5' ; C-2→H-14. These experiments have also allowed complete assignment of both proton and carbon spectra including methoxyls and quaternary carbons. Configurations of C-15 and of the 19→20 double bond are assumed to be the "biogenetic" configurations ; stereochemistry of the methoxylcarbonyl group has not been determined.

From biosynthetic standpoint, 1 may arise from 2 via keto-aldehyde 5 resulting from opening of the carbinolamine ether, ring closure of a six-membered ring 6 and 1,2 carbon shift whose driving force would be aromatization of the quinoline system. Natural or artificial origin of C-5' is still questionable . Other pathways originating form an earlier biosynthetic intermediate such as geissoschizine may also be envisionned ; in this latter case, it is possible to propose mechanisms in which C-5' would be C-17 of the precursors.



	1	2		1	2
C-2	89.7	109.7	C-14	31.4	21.6
C-3	73.4	49.4	C-15	40.2	33.2
C-5	146.9	86.9	C-16	59.4	57.9
C-6	115.2	44.7	C-18	12.9	13.1
C-7	146.5	52.5	C-19	119.5	120.0
C-8	122.2	123.4	C-20	135.8	137.8
C-9	107.9	111.2	C-21	53.1	46.6
C-10	152.0	143.5	C-5'	89.2	-
C-11	148.9	145.6	Ar-OCH_3-23	55.9	57.0
C-12	105.8	95.2	Ar-OCH_3-24	55.7	57.7
C-13	148.0	150.0	$CO_2\underline{C}H_3$	50.8	51.6
			$\underline{C}O_2CH_3$	169.2	174.5

^{13}C nmr data for 1 and 2 ($CDCl_3$, 75 MHz)

REFERENCES

1. M.R.Uskokovic and G.Grethe, in "The Alkaloids", Vol.XIV, R.H.F.Manske Ed., Academic Press, New-York, 1973, p.181.
2. J.C.Cai and C.R.Hutchinson, in "The Alkaloids", Vol.XXI, A.Brossi Ed., Academic Press, New-York, 1983, p.101.
3. J.Vercauteren, G.Massiot, L.Le Men-Olivier, J.Lévy, T.Prange, and C.Pascard, *Tetrahedron Letters*, 1981, **22**, 2871.
4. Plant material was collected by Dr.Sevenet, J.Pusset, and S.Labarre, whom we thank ; this article is n°117 in the series "Plants from New Caledonia". For part 116 see H.E.Saad, R.Anton, J.C.Quirion, G.Chauvière and J.Pusset, submitted to Tetrahedron Letters.
5. G.Lewin, O.Tamini, P.Cabalion, and J.Poisson, *Ann.Pharm.Fr.*, 1981, **39**, 273.
6. Corialstonine (complementary data) : uv : λmax (MeOH) : 218, 238, 317, 330 nm ; (MeOH + HCl) : 220, 246, 354 nm ; ir ($CHCl_3$) : 1745, 1620, 1580, 1500, 1480, 1430, 1345, 1250, 1160 cm^{-1} ; ms (electron impact) : m/z (rel.int.) : 424(5), 410(30), 258(10), 188(12), 135(25), 122(40), 121(100) ; ms (NH_3 chemical ionization) : 425(30), 411(100) ; ^1H nmr ($CDCl_3$, 300MHz) : 8.65(d,J=4.8Hz,H-5), 8.32(s,H-12), 7.4(s,H-9), 7.08(d,J=4.8Hz,H-6), 5.4(br q,J=7Hz,H-19), 4.7(d,J=6.7Hz,H-5'), 4.35 (d,J=6.7Hz,H-5'), 4.3(d,J=4.1Hz,H-3), 4.02(s,3H,OCH_3-24), 4.00(s,3H,OCH_3-23), 3.95(dq,J=16.5,2.4Hz,H-21), 3.65(br s,H-15), 3.45(s,3H,CO_2CH_3), 3.2(br d,J=16.5Hz, H-21), 2.85(d,J=5.1Hz,H-16), 2.5(d,J=13.2Hz,H-14), 2.1(dt,J=13.2,4.1Hz,H-14), 1.5 (dd,3H,J=7,2.4Hz,CH_3-18).
7. A.Bax, Two-Dimensional Nuclear Magnetic Resonance in Liquids, Delft University Press, Dordrecht, 1984.
8. W.I.Taylor and J.Le Men, *Experientia*, 1965, **21**, 508.

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