Tetrahedron Letters No. 5, pp 405 - 406.
©Pergamon Press Ltd. 1979. Printed in Great Britain.

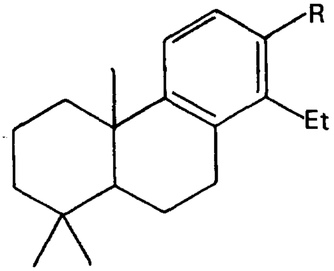
0040-4039/79/0129-0405$02.00/0

TWO NAPHTHALENIC NOR-DITERPENES FROM VELLOZIACEAE[1]

A. da C. Pinto, R. Pinchin, D.H.T. Zocher, and C.C. Lopes,
Núcleo de Pesquisas de Produtos Naturais,
Centro de Ciências da Saúde, Bloco H,
Universidade Federal do Rio de Janeiro,
Rio de Janeiro, Brazil.

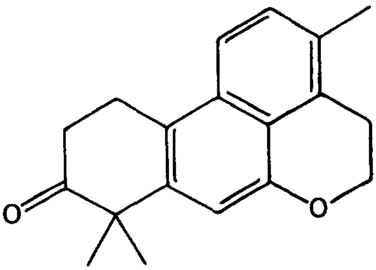
Recently two diterpenes (1, 2), with the cleistanthane skeleton, were isolated from the South American plant *Vellozia flavicans*.[2] Now, a related nor-diterpene (3), with the unusual feature of a naphthalenic nucleus in rings B and C, has been isolated from *V. stipitata* and *V. declinans* in 0.021 and 0.012% of dry plant weight, respectively.

Compound 3, m.p. $147-8^{\circ}$, $C_{19}H_{20}O_2$, was isolated from the hexane extract of the stem, roots, and leaf-sheaths of the plants by chromatography and subsequent recrystallization from hexane. The UV spectrum, λ_{max}^{EtOH} 224 nm (log ε 4.703), 242 (4.697), 307 (3.907), 322 (3.782), and 338 (3.715), was similar to the spectra of some substituted naphthalenes.[3] Examination of the ^1H and ^{13}C NMR spectra (δ in $CDCl_3$, TMS=0, 107.9 d, 121.1 d, 121.8 s, 127.7 s, 129.3 d, 129.6 s, 130.4 s, 140.8 s, and 151.8 s) confirmed the presence of a pentasubstituted naphthalene nucleus, with two of the aromatic protons *ortho* with respect to each other, δ ($CDCl_3$, TMS=0) 7.34 (1H, d, *J*=9Hz) and 7.76 (1H, d, *J*=9Hz), and indicated that the third, a singlet at δ 6.90, was located on the other ring *ortho* to an alkoxy substituent. The three methyl groups were also readily identified; a geminal dimethyl function, δ 1.50 (6H, s), and an aromatic methyl substituent, δ 2.40 (3H, s). The nature of the other aromatic substituents, comprising of two ring systems, was deduced from the NMR spectra. Two triplets, δ 2.84 and 3.42 (*J*=5Hz), were assigned to an $ArCH_2CH_2CO-$ grouping. As the carbonyl group was not conjugated with the aromatic nucleus, UV, IR (1712 cm^{-1}), and ^{13}C NMR (δ 214.5) spectrum, then this ring must be completed by the geminal dimethyl group. The other ring was shown to be a dihydropyran fused to the aromatic nucleus, δ 3.16 (2H, d, *J*=5Hz) and 4.42 (2H, d, *J*=5 Hz).

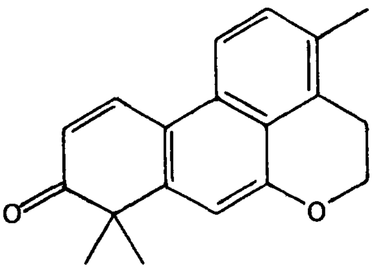


1 R=CH_2OH

2 R=CO_2H



3



4

Of the several structures compatible with the above evidence, that depicted by formula 3, 4,5,10,11-tetrahydro-3,8,8-trimethylphenanthro[10,1-bc]pyran-9(8H)-one, was proved to be correct. Reduction with sodium borohydride gave the corresponding alcohol. Comparison of the relative downfield shifts observed for the signals in the ^{1}H NMR spectrum of the alcohol upon addition of the shift reagent Eu(fod)$_3$ with the calculated relative shift values comfirmed structure 3.

The $\Delta^{10,11}$ dehydro derivative of 3 was also obtained from the hexane extract of *V. declinans* (0.0009% of dry plant weight). This compound (4), m.p. 122-3°, had an intense yellow colour, λ_{max}^{EtOH} 215 nm (log ε 4.850), 250 (4.676), 272 (4.456), and 397 (4.155). It was observed that samples of 3, upon prolonged exposure to air, became yellowed due to the formation of 4. The ^{1}H NMR spectrum of 4 was consistent with the structure proposed, containing, *inter alia*, two doublets at δ 6.22 and 8.24 (J=10Hz) and only one pair of triplets, at δ 3.18 and 4.46 (J=5Hz), assigned to the $\Delta^{10,11}$ double bond and the dihydropyran methylenes, respectively.

It seems evident that these novel nor-diterpenes are derived biogenetically from the cleistanthane group. Already several such diterpenes have been identified in Velloziaceae.[1,2] One, bearing a carboxaldehyde function at C-10,[4] could well be an intermediate in the biosynthesis of 3, in which oxidative decarboxylation gives rise to aromaticity in ring B.

Acknowledgements. The authors are indebted to Dra. Nanuza L. de Menezes for identification of the plants and to the Ministry of Planning (FINEP), the National Research Council (CNPq), and to the Research Council of this University (CEPG) for financial assistance.

References and Footnotes.

1. Part V of "The Chemistry of S. American Velloziaceae"; for part IV see, E.M. Peixoto, R.Pinchin and A. da C. Pinto, Ciência e Cultura, in press.
2. R. Pinchin, L.M.U. Mayer, and A. da C. Pinto, Phytochem., 17, 1671 (1978).
3. A.I. Scott, Interpretation of the Ultraviolet Spectra of Natural Products, Pergamon Press, Oxford, 1964, p.128-9.
4. R. Pinchin and A. da C. Pinto, unpublished results.

(Received in USA 7 November 1978)