

Desacetoxy VLB hydrazide (V) was prepared in boiling absolute ethanol and hydrazine, analogously to that of VLB³, and crystallized from CH₂Cl₂-MeOH, m.p. 202–207° (d). High resolution mass spectrum, C₄₁H₅₄N₆O₄ Calcd. 694.4206; Found: 694.4209. Anal. Calcd for:

C₄₁H₅₄N₆O₄·CH₃OH. C, 69.39; H, 8.04; N, 11.56. Found: C, 69.73; H, 7.80; N, 11.51.

Zusammenfassung. Auf Grund spektroskopischer Untersuchungen konnte die Struktur eines neuen Alkaloids aus *Vinca rosea* L. als Desacetoxy-VLB aufgeklärt werden.

⁶ Acknowledgments. We wish to thank Mr. J. L. OCCOLOWITZ for the high resolution mass spectral data, Mr. T. K. ELZEY for the ¹H-NMR spectra, Mr. G. M. MACIAK for microanalyses and Mr. R. J. ARMSTRONG for the isolation of the partially purified alkaloid.

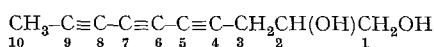
N. NEUSS, A. J. BARNES and L. L. HUCKSTEP

Lilly Research Laboratories, Eli Lilly and Company, Indianapolis (Indiana 46206, USA), 26 August 1974.

The Structure of a Polyacetylenic Diol Isolated from *Vernonia appendiculata* Less. (Compositae)

In continuation of our studies on the sesquiterpene lactones of the genus *Vernonia* (Compositae)¹, we were interested in the investigation of the species *Vernonia appendiculata* Less. originating from Madagascar.

Working up of the chloroform extract of the leaves in the usual manner² did not yield any sesquiterpene, but led to the isolation of a crystalline substance which is unstable on exposure to light. This new compound, deca-4,6,8-triyn-1,2-diol, C₁₀H₁₀O₂, M⁺·162, m.p. 113–116°, [α]_D²⁰ -13° (c = 1, MeOH:CHCl₃ 2:8) has been assigned the structure **1** on the basis of the following evidence: I.R.



1

(Nujol): 3300 cm⁻¹ (OH) and 2240 cm⁻¹ (C≡C)³. U.V. (EtOH): λ_{max} 214 (ε 16,000), 238 (ε 980), 252 (ε 630), 268 (ε 570), 285 (ε 570) and 305 nm (ε 630), characteristic for -(C≡C)₃-system⁴. M.S.: m/e 162 (M⁺·), and 144 (M⁺·-H₂O). ¹H N.M.R. (CDCl₃-Pyr., D₂O): 1.92 (3H, s.); -CH₂-CH(OH)- 2.56 (2H, d., 6). The chemical shifts due to the vicinal glycol system -CH-CH₂-OH are observed

OH

as two complex signals centered at 3.65 (2H) and 3.95 (1H) which are displaced in the spectrum of the amorphous diacetate, C₁₄H₁₄O₄, [α]_D²⁰ -67° (c = 1, CHCl₃) to 4.18 (1H, d.d., 12 and 6.0), 4.37 (1H, d.d., 12 and 4) and 5.14 (1H, q.d., 6.0 and 4) (ABX system)⁵.

The formation of the diacetate was confirmed by the examination of the mass spectrum: m/e 246 (M⁺·), 204 (M⁺·-42), 186 (M⁺·-60) and 126 (M⁺·-60×2).

¹³C N.M.R. (Pyridine-d₅): 10 carbons from pulsed⁶ and off-resonance⁷ decoupling measurements, ppm from TMS reference: 3.9 (q), 25.4 (t), 60.7 (s)⁸, 61.2 (s)⁸, 65.4 (s), 66.0 (t), 67.1 (s), 71.2 (d), 76.3 (s) 78.7 (s); assignments based on alcohol substituent effects⁹ and alkyne data^{9,10}: C₁₀, C₃, C₇, C₆, C₅, C₁, C₈, C₂, C₉, C₄, respectively.

Résumé. La structure d'un diol polyacétylénique isolé de *Vernonia appendiculata* Less. a été déterminée essentiellement par son étude en résonance magnétique nucléaire (H et ¹³C).

R. TOUBIANA, C. M. HO, B. MOMPON, M. J. TOUBIANA¹¹, A. L. BURLINGAME and D. M. WILSON

Institut de Chimie des Substances Naturelles, C.N.R.S., F-91190 Gif sur Yvette (France); and Space Sciences Laboratory, University of California, Berkeley (California 94720, USA), 4 July 1974.

¹ R. TOUBIANA and A. GAUDEMER, *Tetrahedron Lett.* 1967, 1333. – R. TOUBIANA, C. r. Acad. Sci., Paris, 268(c), 82 (1969). – C. M. HO and R. TOUBIANA, *Tetrahedron*, 26, 941 (1970). – R. TOUBIANA, M. J. TOUBIANA and B. C. DAS, C. r. Acad. Sci., Paris, 270(c), 1033 (1970). – B. MOMPON, C. M. HO and R. TOUBIANA, C. r. Acad. Sci., Paris, série A, 276, 1799 (1973).

² W. HERZ, P. S. SUBRAMANIAM, P. S. SANTHANAM, K. AOTA and A. L. HALL, *J. org. Chem.* 35, 1453 (1970).

³ R. K. BENTLEY, Sir EWART R. H. JONES, R. A. M. ROSS and V. THALLER, *J. chem. Soc. Perkin 1*, 1973, 140.

⁴ R. K. BENTLEY, Sir EWART R. H. JONES and V. THALLER, *J. chem. Soc. (C)*, 1969, 1096.

⁵ R. H. BIBLE JR., *Guide to the NMR Empirical Method* (Plenum Press, New York 1967), p. 104.

⁶ R. FREEMAN, H. D. W. HILL and R. KAPTEIN, *J. magn. Resonance* 7, 327 (1972).

⁷ K. G. R. PACHLER, *J. magn. Resonance* 7, 442 (1972).

⁸ Very slow relaxation.

⁹ J. B. STOTHERS, ¹³C NMR Spectroscopy (Academic Press, New York 1972).

¹⁰ D. E. DORMAN, M. JAUTELAT and J. D. ROBERTS, *J. org. Chem.* 38, 1026 (1973).

¹¹ Acknowledgments: We are indebted to Professor E. LEDERER for his general interest in this work and to Doctor B. C. DAS for valuable suggestions.

A Single-Chain Triple Helical Structure in Synthetic Polypeptides

The existence of a single-chain triple helical structure, in which a single polypeptide chain folds back on itself to form a stable collagen-like triple helix, was first suggested for the subunit of *Ascaris* collagen by McBRIDE and HARRINGTON¹, and for the synthetic polypeptide (Pro-Pro-Gly)_n by ENGEL². On the basis of model building studies, RAMACHANDRAN, DOYLE and BLOUT³ were able to give the details of such a structure for (Pro-Pro-Gly)_n. They suggested that the single-chain triple helix is a

possible conformation for polypeptides of the type (X-Y-Gly)_n, where X and Y are any amino or imino acids.

¹ O. W. McBRIDE and W. F. HARRINGTON, *Biochemistry* 6, 1499 (1967).

² J. ENGEL, in *Conformation of Biopolymers* (Ed. G. N. RAMACHANDRAN; Academic Press, London 1967), vol. 2, p. 483.

³ G. N. RAMACHANDRAN, B. B. DOYLE and E. R. BLOUT, *Biopolymers* 6, 1771 (1968).