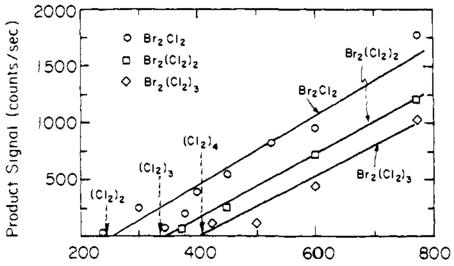

Figure 3. Variation with chlorine source pressure of scattered $Br_2(Cl_2)_m$ product molecules with m = 1-3 from reaction of Br_2 with chlorine polymers. Data pertain to a laboratory scattering angle of 70° (cf. Figure 2) and collision energy of 3.4 kcal/mol. Arrows indicate nominal "pressure thresholds" below which $(Cl_2)_n$ signals become very small.

below certain source pressures and the $(Cl_2)_n$ signals for n = 4-2, respectively, disappear below these same "pressure thresholds". This indicates that at least the regions between successive thresholds are governed by van der Waals exchange reactions of the form

$$Br_2 + (Cl_2)_n \rightarrow Br_2(Cl_2)_{n-1} + Cl_2 \qquad (R5)$$

As in the (R3) case, where n = 2, these reactions with n = 3 or 4 appear to be rebound processes. Results corresponding to (R4) and (R5) were also found for reactions of HI and CH_3Br with chlorine polymers.[9]

Recently, $Br_2 + (Cl_2)_n$ reactions in the high polymer regime have been studied in crossed-beams by Behrens et al.[10] Comparable aspects agree with our results. However, most of their work is complementary; it deals with larger polymers and scattering within 10° of the chlorine beam, which we did not study for high polymers. Behrens et al. find evidence for "condensation" to form $Br_2(Cl_2)_n$ adducts which for $n \gtrsim 10$ persist long enough ($\gtrsim 10^{-5}$ sec) to travel to the detector. Other polymer systems with large n also appear to form such adducts under single-collision conditions.[10-12] More complex polymer reactions, including proton transfer and solvation processes, have also been observed in beam experiments.[13] There is now much scope for reactive scattering studies of the weak but ubiquitous van der Waals bonding.

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(5) Since the work of ref 2, the electron bombardment ionizer and parts of the ion counting system have been rebuilt, with considerable improvement in detection sensitivity. This allowed use of a smaller chlorine nozzle and lower source pressure as well as higher mass resolution (~1%). Fragmentation in the electron bombardment region appears not to introduce significant ambiguity when higher chlorine polymers are absent. Some of the $BrCl^+$ signal could come from fragmentation of $BrCl_3^+$, since (R1) and (R2) are parallel paths with somewhat similar properties, but very little of the $BrCl^+$ can be attributed to fragmentation of $Br_2Cl_2^+$, in view of the drastic difference in the energy dependence and angular distribution for (R1) and (R3).

(6) Only a rough estimate can be obtained for the difference ΔE_T between the product and reactant relative translational energy because it is smaller than the spread in collision energy. Also, momentum conservation imposes constraints because the detected product Br_2Cl_2 is much heavier than its partner Cl_2. The difference ΔD_0 in the $Br_2 \cdots Cl_2$ and $Cl_2 \cdots Cl_2$ van der Waals bond strengths is related to the energy disposal in translation, vibration, and rotation by $\Delta D_0 = \Delta E_T + \Delta E_{V+R}$. The use of supersonic beams makes $E_{V+R} \sim 0$ for the reactants, so $\Delta E_{V+R} \gtrsim 0$ and $\Delta D_0 \gtrsim \Delta E_T$. The lower bounds probably apply in view of the weak bonds involved. Analysis of the data gives nominal most probable values of ΔE_T = 0.4 and 0.5 kcal/mol for the Br_2 and HI versions of (R3), respectively.

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(8) Molecules of the form $BrCl(Cl_2)_m$ with m = 2 or 3 were not observed.

(9) The (R5) reaction to form $Br_2(Cl_2)_2$ or $HI(Cl_2)_2$ is of particular interest. (R1) allows cyclic configurations of these n = 3 species to undergo facile six-center reaction (exoergic by 20 kcal/mol for the HI case). The cyclic configurations might be stable if formed in a "van der Waals well", but excitation of only a few kilocalories per mole would permit the six-center reaction. Stereochemical arguments as well as the observed resemblance of the Br_2, HI, and CH_3Br reactions suggest (R5) probably forms noncyclic polymers.

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(13) For example, ref 4 and 12 report HI + $(NH_3)_n$ in crossed-beams yields $NH_4^+I^-(NH_3)_m$; molecules with n up to 21 and m = 2-13 were observed.

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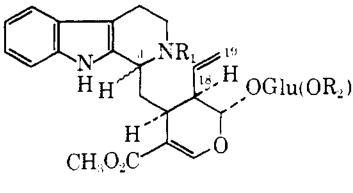
The Absolute Configuration of Vincoside

Sir:

The intricate pathway by which the structurally diverse indole and dihydroindole alkaloids are biosynthesized in several Apocynaceous plants has been elucidated by decisive research in several laboratories.[1] The keystone of this pathway is vincoside (**1a**), which results in vivo and in vitro along with isovincoside (strictosidine), **1b**, from the condensation of tryptamine with secologanin.[2] Originally,[2] **1a** was depicted with a C-3 (S) α-hydrogen, which was cis to the C-15 and C-20 hydrogens whose absolute configurations were known by correlation with loganin.[3] Such an assignment also seemed sensible since the Corynanthé alkaloids into which **1a** was shown to be efficiently incorporated[2] are S at C-3.[4] Smith[5] and Brown[6] and coworkers subsequently reported chemically and spectroscopically derived results that were discordant with Battersby's assignment, favoring instead a C-3 (R) β hydrogen for **1a**. Simultaneously, Battersby et al. revised the absolute C-3 stereochemistry of **1a** to R by implication from its comparison to *O,O*-dimethylipecoside, its tetrahydroisoquinoline analog, using X-ray analysis.[7] In view of the special significance of **1a** and **1b**[8] in the developing picture of indole alkaloid biosynthesis, we felt that an X-ray analysis of **1a** was necessary to absolutely secure its stereochemistry. Additionally, we have correlated **1c** to its lactam[2] (**2a**),[10] to its pentaacetyl 7-oxo-pyrrolo[3,4-*b*]quinoline derivative[9] (**3a**)[10] to provide readily accessible, crystalline standards of C-3 stereochemistry, and to the now



1a, C-3 R (βH), $R_1 = R_2 = H$
1b, C-3 S (αH), $R_1 = R_2 = H$
1c, C-3 R (βH), $R_1 = CH_2C_6H_4Br$; $R_2 = COCH_3$
1d, C-3 R (βH), $R_1 = R_2 = CO_2CH_2CCl_3$
1e, C-3 S (αH), $R_1 = R_2 = CO_2CH_2CCl_3$

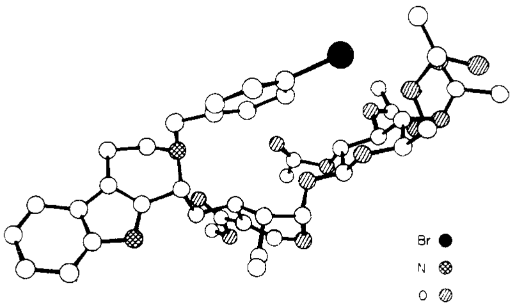


Figure 1. A computer generated perspective drawing of the N_b-*p*-bromobenzyltetraacetylvincoside derivative. Hydrogens are omitted for clarity.

readily obtainable **1a** (hydrochloride) via its 2,2,2-trichloroethoxycarbonyl derivative, **1d**, as well as **1b** via **1e.**

Small acircular crystals of N_b-*p*-bromobenzyltetraacetylvincoside[11] (**1c**) were used for an X-ray diffraction experiment. This derivative crystallizes in the common, chiral space group $P2_1$ with $a = 8.447(1)$ Å, $b = 18.515(3)$ Å, $c = 14.188\ (2)$ Å, and $\beta = 104.26\ (1)°$. A calculated ($Z = 2$) and approximately measured density of 1.34 g cm^{-3} indicated that one molecule of composition $C_{42}H_{47}N_2O_{13}Br$ formed the asymmetric unit.

All unique reflections with $2\theta \leq 114°$ were measured using graphite monochromated Cu K_α (1.5418 Å) X-rays and an ω-scan technique on an automated four-circle diffractometer. After corrections for Lorentz, polarization, and background effects 2050 (68%) of the measured intensities were judged observed ($F_o^2 > 3\sigma(F_o^2)$).

The bromine atom was easily located by standard Patterson techniques. Further elaboration of the structure from the bromine-phased electron density maps was frustrated by a pseudo-mirror plane generated by having only one atom in the asymmetric unit. The tangent formula recycling procedure[12] resolved this dilemma and after several cycles all nonhydrogen atoms had been located. Full-matrix, least-squares refinements with anisotropic temperature factors for the nonhydrogen atoms and no hydrogen atoms have reduced the standard crystallographic discrepancy index to its current minimum of 0.068 for the observed reflections.[13]

Figure 1 is a computer generated drawing of the current X-ray model. As can be seen, the configuration of the hydrogen at C-3 of **1c** is clearly β. Full crystallographic details will be published in a subsequent paper.

Hydrogenolysis (5% Pd/C, 3 atm, MeOH-AcOH) of **1c,** treatment with aqueous Na_2CO_3, and Zemplen deacetylation[2] gave 18,19-dihydro-**2a,** whose melting point (189.5-190.5°), mixture melting point, and TLC behavior were identical with a reference sample of 18,19-dihydrovincoside lactam prepared according to Battersby et al.[2] The 18,19-dihydro-**2a** can be shown also to be identical with **3a** by the reported chemical conversions.[9]

Treatment at 0° of a chloroform (4 ml) suspension of the freeze-dried reaction mixture (120 mg) obtained from the synthesis of **1a** and **1b**[2] with dry pyridine (1 ml) followed immediately with 2,2,2-trichloroethylchloroformate[14] (0.36 ml, twofold excess) gave a homogeneous red solution, which was allowed to stir for 12-18 hr (25°). The work-up described[15a] readily gave **1d**[15b] and **1e**[15c] as chromatographically pure compounds. Upon deblocking of **1d** (or **1e**) (Zn dust, glacial AcOH, 25°, 4 hr) **1a** (or **1b**) could be obtained (70%) as its hydrochloride,[16] which was shown to be uncontaminated with **1b** (or **1a**) by its conversion to **2a** (or **2b**). Thereby, the structure and stereochemistry of the actual biochemical intermediates are confirmed by correlation to **1c.** These results are being confirmed biologically in *Camptotheca acuminata*[8] and *Catharanthus roseus*.[2,17]

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(15) (a) The solvent and excess reagents were removed in vacuo at 40°. The resulting residue was partitioned between Et_2O and ice cold H_2O; the Et_2O layer was dried ($MgSO_4$) and evaporated. The resulting crude solid residue was PLC'd on silica gel PF_{254} (E-Merck & Co.) in hexane–ethyl acetate (3:1) to obtain **1d** and **1e** as colorless solids. (b) $R_f = 0.26$; NMR ($CDCl_3$) δ 3.68 (s, 3 H), 4.74 (s, 2 H), 4.78 (s, 8 H); ir (KBr) cm^{-1} 1780 (br s), 1710 (br s), 1635 (w); $[\alpha]^{25}{}_D = -90°$ (*c* 0.10; $CHCl_3$), $[M]_D$ −1266°. (c) $R_f = 0.37$; NMR ($CDCl_3$), δ 3.73 (s, 3 H), 4.74 (s, 2 H), 4.78 (s, 8 H); ir (KBr) cm^{-1} 1780 (br s), 1710 (br s), 1635 (w); $[\alpha]^{25}{}_D$ −44° (*c* 0.094; $CHCl_3$), $[M]_D$ −623°.

(16) The calculated amount of hydrochloric acid must be added to the filtered acetic acid solution before solvent evaporation to avoid formation of **2a** (or **2b**).

(17) This research was supported in part by a grant from the National Institutes of Health (CA 17127) to C.R.H.

(18) Camille and Henry Dreyfus Teacher–Scholar Grant Awardee 1972–1977 and Fellow of the Alfred P. Sloan Foundation 1973–1975.

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Structure of Crystalline (Hexatriene dianion)dilithium, an Ion-Paired *Z,Z*-Dianion

Sir:

Hoffmann and Olofson predicted on the basis of extended Hückel calculations that the most stable shape of hexa-