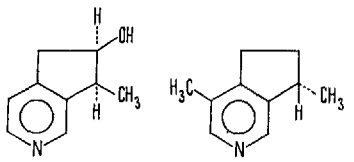
The curves (all measurements in methanol) are in fact identical within experimental limits. The very minor differences in properties are most likely due to the presence of slight impurities, poor stability of the alkaloid, and the different histories of the 2 samples. Unfortunately, the 2 materials are rare and sufficient quantities are not available for a more detailed comparison.

Comparison of the ORD-CD spectra with that of L-(−)-actinidine (II), whose absolute configuration is unambiguously known[6], demonstrated an enantiomeric relationship at the benzylic position. The stereochemistry of the benzylic position in diastereoisomeric aryl compounds is known to determine the sign of the derived Cotton effects, and asymmetry at more distant centers affect the intensity of the peaks[7]. Since detailed NMR studies on RW-47 clearly demonstrate a *cis* relationship between the methyl and hydroxyl groups, the ORD-CD findings require expression I for the absolute configuration of RW-47-venoterpine[2]. The poor asymmetry of II relative to its extinction coefficients prevent obtention of accurate CD values. The signs of the peaks are qualitatively consistent with the assignment.



I II

I. $[\Phi]_{300}$ +300, $[\Phi]_{265}$ −860, $[\Phi]_{260}$ −360, $[\Phi]_{258}$ −710, $[\Phi]_{235}$ +2060. $[\theta]_{264}$ +900, $[\theta]_{253}$ −4840.

II. $[\Phi]_{300}$ −2, $[\Phi]_{270}$ +4.5, $[\Phi]_{265}$ −5, $[\Phi]_{255}$ −12.5, $[\Phi]_{235}$ −6.5, $[\Phi]_{225}$ −12. $[\theta]_{268}$ neg., $[\theta]_{260}$ pos., $[\theta]_{240}$ neg.

It is interesting to note that the actinidine alkaloids occasionally have the opposite absolute configuration to the glycosides implicated in indole biosynthesis and, presumably, present in these same plants. The potential significance of this finding is not clear, especially as current thinking about the detailed pathways between the glycosides and the complex indole alkaloids involves destruction of the stereochemistry at both centers corresponding to those in RW-47-venoterpine during the course of their further biological elaboration[1].

Further details of these experiments and stereochemical relationships of the complex indole bases of *Alstonia venenata* will be reported in a full paper in preparation[8].

Zusammenfassung. RW-47 und Venoterpin sind identisch. Die absolute Konfiguration ist durch ORD-CD-Vergleiche mit L-(−)-Actinidin ableitbar.

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Acidolytic Cleavage of Peptide Bonds During Acetylation

Gas-chromatographic determination of amino acids was performed by JOHNSON et al.[1] using N-acetyl amino acid *n*-butyl esters. The derivatization was carried out by esterification followed by acetylation. In the present experiments acetylation was carried out first in order to allow quantitative methyl ester formation by diazomethane. Derivatization of some simple dipeptides led to formation of considerable quantities of the N-acetyl methyl esters of the constituent amino acids (Figure), presumably through oxazolone formation. A similar observation recently published[2] has made us communicate the results presented below.

For calibration purposes a number of N-acetyl amino acids described in the literature[3] were synthesized and characterized by CHN-analysis. The flame-ionization detector response to each derivative was determined by dissolving a weighed quantity of N-acetyl amino acid in a measured volume of methanol containing an internal standard. Methylation was carried out quantitatively[4] by adding an excess of ethereal diazomethane. 1–5 µl of the resulting solution was injected into the gas-chromatograph (Panchromatograph, Pye Scientific Instruments Ltd., Cambridge, England).

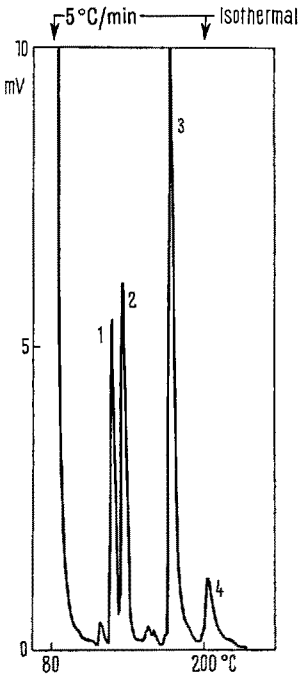
Values within ± 5–10% were found for the derivatives of Gly, Ala, Val, Ile, Leu, Pro, Lys, Glu, Met, Phe, Tyr and Trp. Acetylation of the individual free amino acids was effected by boiling for 1 h in acetic acid containing by volume 10% acetic anhydride and 10% pyridine. After evaporation of the solvents and several evaporations with water to decompose residual anhydride, the

Yields of N-acetyl amino acids from peptides

Peptide	Derivative of	Yield (%)[a]	Peptide	Derivative of	Yield (%)[a]
Val-Leu	Val	37	Gly-Phe	Gly	78
	Leu	36		Phe	85
Glu-Val-Phe	Glu	ca. 50	Gly-Lys-HCl	Gly	105
	Val	68		Lys	88
	Phe	100	Gly-Trp	Gly	105
				Trp	88
Cys-Gly / Glu	Glu	ca. 80	Leu-Tyr	Leu	66
	Cys	–		Tyr	80
	Gly	69			

Reaction time: 1 h. For Glu-Val-Phe the reaction time was 4 h.
[a] Average of 2 determinations.

residue was methylated with diazomethane as above. Reproducible yields of 70–100% of the above-mentioned derivatives (except for Glu), identified by their retention times, were obtained. Formation of by-products e.g. acetylamino acetone derivatives[5], was not observed. Glu, however, was transformed into N-acetyl pyroglutamic acid in agreement with the finding of DAKIN and WEST[5]. By brief heating with N HCl prior to the methylation, the normal derivative of Glu appeared in the chromatogram. This treatment was necessary in the presence of Pro, as the retention times of the 2 cyclic derivatives were identical on all the columns studied.



1, valine; 2, leucine; 3, internal standard; 4, valyl-leucine. Column: 1 ft. 3% carbowax 20M.

During an attempt to derivatize the dipeptide Val-Leu for gas-chromatography by the above-mentioned procedure, additional peaks corresponding to the derivatives of Val and Leu were observed. The same result was obtained for other dipeptides and two tripeptides. As the described acetylation procedure is similar to that employed for the racemization of optically active amino acids[3], it is reasonable to assume that the breakdown takes place via oxazolone formation. However, an acetylation of the peptide bond[6], making it labile to water, could also account for the results obtained. With the aid of the calibration values obtained above, the yields of N-acetyl amino acids on treatment of the peptides mentioned with the acetylation mixture could be calculated (Table)[7].

Zusammenfassung. Eine Spaltung von Peptiden tritt auf, wenn versucht wird, gewisse Derivate in an sich üblicher Weise herzustellen. Damit wird auf die Möglichkeit einer Fehlinterpretation hingewiesen.

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Synthesis and Photolysis of 2-Formyl-4,4-Dimethyl-2,5-Cyclohexadienone

It is known that certain substituents influence the pathways of photochemical rearrangements of bicyclic cross-conjugated cyclohexadienones[1,2]. In pursuing our interest in photolytic reactions, we now wish to report the synthesis and photolysis of a monocyclic compound of this type with an electron withdrawing formyl substituent.

Synthesis of 2-formyl-4,4-dimethyl-2,5-cyclohexadienone (III) was carried out by a procedure similar to that employed by EDWARDS et al.[3]. Condensation of I[4] with ethyl formate in the presence of sodium methoxide and reaction of the hydroxymethylene derivative II [b.p. 43–45° (0.1 mm); 69% yield; $\lambda_{max}^{95\%\,EtOH}$ 235 (ε 13,400) and 307 nm (ε 5400); Anal.[5]] with 2,3-dichloro-5,6-dicyanobenzoquinone[6] in dioxane gave III [mp 66.5 to 67°; 61% yield; $\lambda_{max}^{95\%\,EtOH}$ 237 nm (ε 14,350); $\lambda_{max}^{95\%\,EtOH+NaOH}$ 350 nm (ε 13,560); λ_{max}^{KBr} 5.90, 5.98, 6.03, 6.15, and 6.25 μ; $\delta_{TMS}^{CDCl_3}$ 1.40 (s, 6H); H_1:6.3 (doublet, $J_{1-2} = 10$ Hz); H_2:6.9 (2 doublets, $J_{2-3} = 2.5$ Hz); H_3:7.6 (doublet); H_4:10.2 ppm[5]].

A 0.5% solution of III was irradiated in 45% acetic acid using a 450 watt Hanovia high pressure mercury lamp in an all Pyrex cell. UV-absorption after 45 min indicated a 90–95% conversion. Solvent removal in vacuo afforded the crude photoproduct. Efforts to unequivocally characterize the nature of the photoproduct without further chemical transformations were without success. Interpretation of the NMR data indicated an

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