The correctness of the structure (IV) was further verified by the following experiments. Tetrahydro-α-dicarvelone (V) on reduction with LAH as well as with $NaBH_4$ furnished the diol (VIII), m.p. 215–216 °C; ν_{max} 3330 and 1024 cm^{-1} (hydroxyl), no carbonyl band; NMR ($CDCl_3$) τ: 9.04, 9.11 (doublet, partly overlapped, two CH_3–CH– and two CH_3–CH–CH_3), 8.48 (sharp singlet, >CHO*H*, disappeared after exchange with D_2O). Benzoylation of the diol (VIII) in pyridine at room temperature afforded dibenzoate (IX), m.p. 199 °C; IR-spectrum: 1714, 1276 and 1110 cm^{-1} (aromatic ester); NMR ($CDCl_3$) τ: 1.91, 2.46 (10H, multiplet, two C_6H_5–C(=O)–), 4.62 (2H, broadened singlet, two –C*H*–O–), 9.03 and 9.12 (18H, doublet, partly overlapped, two CH_3–CH– and two CH_3–CH–CH_3). Pyrolysis of dibenzoate (IX) at 280 ± 10 °C in atmosphere of nitrogen yielded an olefin (X), b.p. 150–160 °C (bath)/2 mm; single spot on TLC plate; IR-spectrum (liquid film): 816 and 1649 cm^{-1} (trisubstituted double bond); NMR (CCl_4) τ: 4.50 (2H, sharp singlet, two *H*C=C–), 8.36 (6H, singlet, two CH_3–C=CH)[11], 9.09 (12H, doublet, J = 5.5 c/s, two –CH(CH_3)$_2$); M.S.: m/e 274 (3.23% Σ_{41}, M^+), m/e 164 (9.24% Σ_{41}, base peak), m/e 55 (2.51% Σ_{41}). High resolution measurements with (X) demonstrate that the ion of mass 55 is almost due to $C_4H_7^+$ and its formation can be rationalized by invoking a reverse DIELS-ALDER fragmentation of (X) followed by elimination of a methyl radical[12]. Thus, the formation of a trisubstituted olefin (X) coupled with earlier results clearly rule out the structure (III) and establish unequivocally the structure (IV) for α-dicarvelone whose formation can be satisfactorily explained by the pathway[13] depicted in Chart I (Scheme II).

We are currently investigating the structure of β- and γ-isomer reported by WALLACH. This work along with their stereochemistry will be reported in our next communication[14].

Zusammenfassung. Die Struktur des Terpens α-Dicarvelon wird endgültig aufgeklärt.

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Department of Chemistry, University of Victoria, Victoria (B.C., Canada), 6 September 1967.

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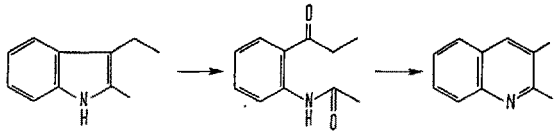
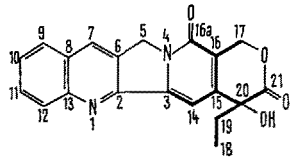
A Numbering System for Camptothecin Based on Its Biogenesis

The unusual pentacyclic alkaloid camptothecin (I), isolated by WALL and co-workers from *Camptotheca acuminata* (Nyssaceae)[1], is most probably of tryptophane-terpene origin.

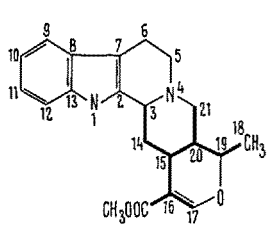
The quinoline system must be formed by oxidation of an indole double bond, followed by recyclization and aromatization:



The remainder of the camptothecin (I) molecule incorporates the well recognized 10 carbon moiety (here represented by thick lines) which is also present in ajmalicine (II). In the case of the indole alkaloids, this 10 carbon fragment has been clearly shown to be of terpenoidal origin[2–6].



I



II

Following the LE MEN-TAYLOR system[7], the numbering system below is therefore suggested for camptothecin (I), in analogy with ajmalicine (II).

The pyridone carbonyl carbon in camptothecin has been designated 16a for convenience, although this atom is not assigned a number in the LE MEN-TAYLOR scheme.

Résumé. Un mode de numérotation pour la camptothecin est proposé, basé sur la biogenèse de cet alcaloïde.

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