

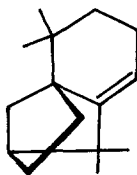
SYNTHESIS OF (+)-ISOLONGIFOLENE

R.R. Sobti and Sukh Dev

National Chemical Laboratory, Poona, India

(Received 5 May 1967)

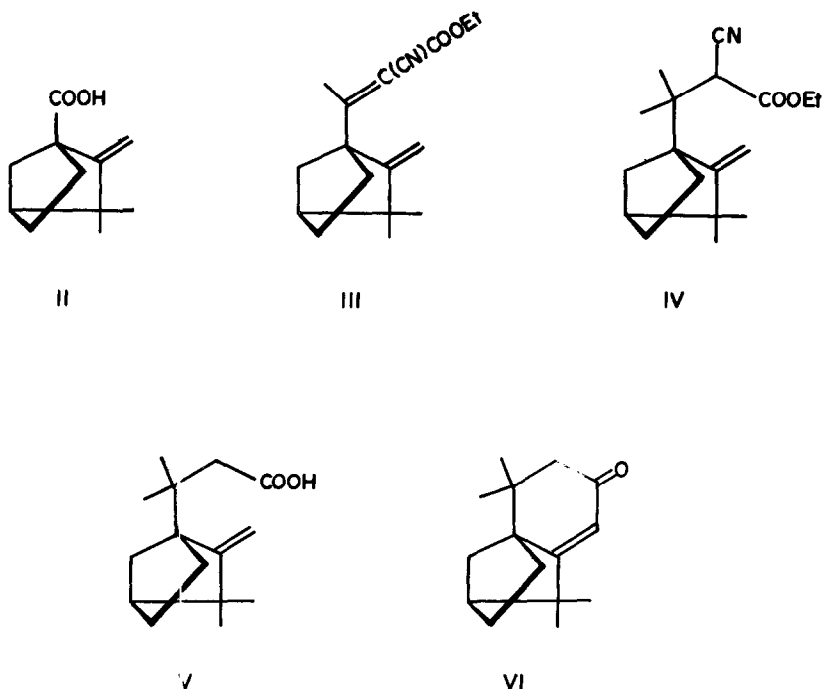
ISOLONGIFOLENE¹, the acid-catalysed rearranged product of longifolene, has been formulated as I, on the basis of spectral and degradation studies^{2,3,4}. We now report on its total synthesis by an unambiguous route.



I

(+)-Camphene-1-carboxylic acid⁵ (II, m.p. 109-110°. PMR spectrum⁶ : two quaternary methyls, 6H singlet at 67.5 c/s; C=CH₂, two 1H singlets at 281 and 300 c/s) was converted to the corresponding methyl ketone (PMR spectrum: CH₃CO, 3H singlet at 126 c/s; C=CH₂, two 1H singlets at 277 and 281 c/s) in 83% yield by its interaction with excess MeLi. This ketone smoothly condensed with ethyl cyanoacetate in the presence of NH₄OAc⁷ to furnish III ($\lambda_{\max}^{\text{EtOH}}$ 236 m μ , ϵ 13,970. PMR spectrum: vinylic Me, 3H singlet at 136 c/s; C=CH₂, two 1H singlets at 274.5 and 282 c/s) in 60% yield. Conjugate addition of lithium dimethylcopper⁸ to III gave, in 80% yield, a diastereoisomeric mixture of IV, which without separation was hydrolysed by KOH in ethylene glycol to give, in 90% yield, a single product, V (m.p. 87-88°. PMR spectrum: four quaternary methyls, 3H singlets at 60, 65, 71 and 75 c/s; -C¹-CH₂COOH, 2H singlet at 150 c/s; C=CH₂, two 1H singlets at 285 and 297 c/s). This acid was converted to its acid chloride (oxalyl

chloride), the intramolecular acylation of which proceeded smoothly at -15° , in CS_2 in the presence of SnCl_4 , to give in 84% yield the unsaturated ketone (VI), m.p. $54-55.5^{\circ}$, identical (mixed m.p., IR) with the (+)-ketone of structure VI, obtained earlier² as a $\text{Na}_2\text{Cr}_2\text{O}_7$ -AcOH oxidation product of



partially racemised isolongifolene. This unsaturated ketone was thio-ketalised (BF_3 - Et_2O) to give a product (PMR spectrum: four quaternary methyls, 3H singlets at 57, 60, 60 and 65 c/s; $\text{C}=\underline{\text{C}}\text{H}$ -, 1H singlet at 316.5 c/s) which on refluxing (16 hr) with Raney nickel in EtOH yielded a hydrocarbon (62%), which after separation of a trace impurity by chromatography over AgNO_3 - SiO_2 gel, was identified (GLC, TLC⁹, IR, PMR) as (+)-isolongifolene.

REFERENCES

- 1 U.R. Nayak and Sukh Dev, Tetrahedron **8**, 42 (1960).
- 2 J.R. Prahlad, R. Ranganathan, U.R. Nayak, T.S. Santhanakrishnan and Sukh Dev, Tetrahedron Letters 417 (1964).
- 3 T.S. Santhanakrishnan, Ph.D Thesis, Madras University (1965).
- 4 R.R. Sobti, Ph.D Thesis, Bombay University (1967).
- 5 J. Houben and E. Pfankuch, Liebig's Ann **483**, 271 (1930).
- 6 All PMR spectra were measured in 10-20% solutions in CCl_4 on a Varian A-60 spectrometer; the signals are recorded in c/s from tetramethylsilane as internal standard.
- 7 E.J. Cragoe, C.M. Robb and J.M. Sprague, J. Org. Chem. **15**, 381 (1950).
- 8 H.O. House, W.L. Respess and G.M. Whitesides, J. Org. Chem. **31**, 3128 (1966).
- 9 A.S. Gupta and Sukh Dev, J. Chromatog. **12**, 189 (1963).