CHAPTER IX

Synthesis of DL-Ar-Turmerone

The essential oil from the rhizomes of Curcuma Longa Linn contains a high percentage of two closely related sesquiterpene ketones, turmerone (XLVIIIa) and ar-Turmerone (124,125). Rupe and coworkers (126,127) have proposed the structure (XLVIII) for ar-turmerone on the basis of extensive degradation experiments, most important being treatment of (XLVIII) with aqueous methanolic potassium hydroxide (126) which gave acetone and curcumone (XLIX) and thus established the conjugation character of the side chain triply substituted double bond with that of ketone, in ar-turmerone.

Later on curcumone (XLIX) was synthesised by Rupe and Wiederkehr (127) by treatment of the acid chloride of \( \beta \)-(p-tolyl)-butyric acid with zinc methyl as depicted below and thus the structure (XLVIII) for ar-turmerone further confirmed.
Constitution of ar-turmerone having been established its absolute configuration was not determined till recently. In 1965 Rao (128) determined the absolute configuration of this compound on the basis of comparison of the molecular rotations of (-)-3-phenyl butanoic acid of known absolute configuration and (+)-3-(p-tolyl)-butanoic acid, a degradation product of ar-turmerone, and represented it by the structure (XLVIIIa).

The structure (XLVIII) for ar-turmerone was confirmed by a number of syntheses (126, 127, 129). In 1959, Mukherji et al (130) achieved another synthesis of ar-turmerone as depicted below:

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\text{\begin{align*}
\text{CH}_3 & \quad \text{H}_3\text{C} \\
\text{CO} & \quad \text{H}_3\text{C} \\
\text{\text{XLVIII}} & \quad \text{\text{a}}
\end{align*}}
\]
The present dissertation, however, describes a new synthesis of ar-turmerone using isobutylene magnesium bromide and subsequent oxidation of the alcohol with Jones reagent to provide the title compound (XLVIII). Its structure was confirmed on the basis of its I.R. spectral data. The following scheme depicts the sequence of reactions.

The carbinol (L) obtained according to the method reported by Vig et al (132) was submitted to oxidation with Collin's reagent (86) when it furnished the aldehyde (LI)
in 69 per cent yield. The aldehyde showed characteristic bands at 1710, 2720 (-CHO) and 1610, 1500, 810 (1,4-disubstituted benzene nucleus) cm\(^{-1}\).

The aldehyde (LI) was subjected to Grignard reaction with isobutylene magnesium bromide in THF to provide the secondary carbinol (LII) in 60 per cent yield after distillation. The carbinol (LII) gave characteristic I.R. absorption bands at 3400 (-OH), 1600, 1500 and 810 (1,4-disubstituted benzene nucleus) cm\(^{-1}\). The 810 cm\(^{-1}\) peak (triply substituted double bond) was overlapped by the 810 cm\(^{-1}\) peak (1,4-disubstituted benzene nucleus). The above carbinol (LII) was oxidised with Jones's reagent (131) to give the ketone (XLVIII) in 50 per cent yield after distillation under vacuum. The ketone was characterised through its semicarbazone derivative m.p. 104-106\(^\circ\). Lit. (130) reports m.p. 105-106\(^\circ\).

I.R. absorption spectra of the ketone (XLVIII) showed characteristic bands at 1705 (\(\text{C} = \text{O}\)), 1670, 810 (triply-substituted double bond), 1610, 1500 and 810 (1,4-disubstituted benzene nucleus) cm\(^{-1}\), and other prominent bands at 3020, 2910, 1890, 1450, 1360, 1260, 1160, 1010, 960, 880, 720 and 700 cm\(^{-1}\).