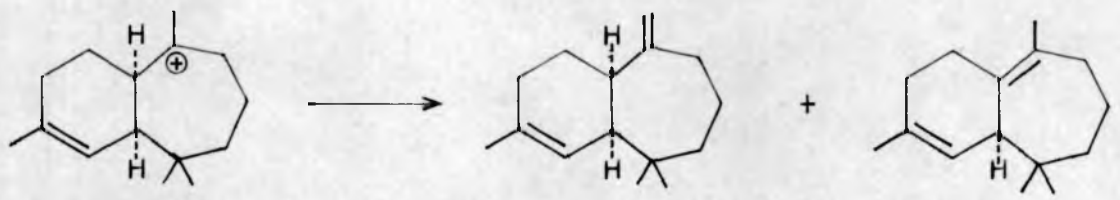
CHAPTER VI

BIOGENETIC CONSIDERATIONS

The biogenesis of sesquiterpenes has been very briefly dealt with in Chapter I wherein it has been indicated that ion (3) which has been considered by Hendrickson[1] as the precursor for longibornyl cation, can stabilize itself to yield himachalenes (Fig.I). The species (3) should give



(3) (4) (5)

rise to α-himachalene (4) with cis- junction and this has actually been shown to be the case as discussed in Chapter IV. Thus the biogenesis of himachalenes and related compounds and that of longifolene and its congeners(longipinene and longicyclene) is intimately linked (Fig.I). The botanical relationship between Pinus longifolia and Cedrus deodara is indicated in Fig.II and it is gratifying to note that the major sesquiterpene components of the two plants arise from a common species (3). The fact that in Cedrus deodara

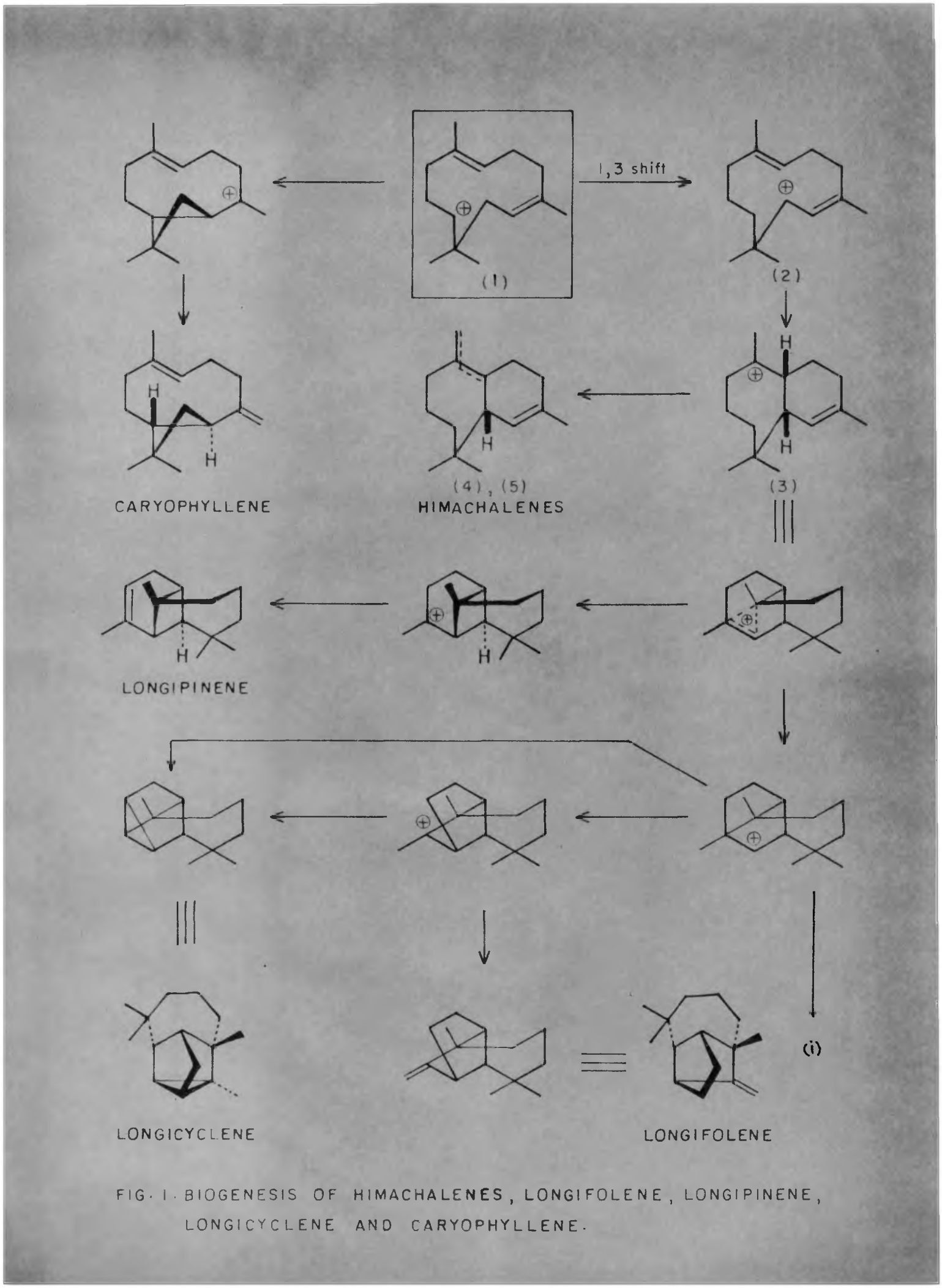


FIG. 1. BIOGENESIS OF HIMACHALENES, LONGIFOLENE, LONGIPINENE, LONGICYCLENE AND CARYOPHYLLENE.

DIVISION: GYMNOSPERMAE[2,3]
CLASS: CONIFERAE (~640 SPECIES)
ORDER: PINALES (~210 SPECIES)
FAMILY: PINACEAE

GENUS: ABIES | KETELEERIA | PSEUDOTSUGA | TSUGA | PICEA | PSEUDOLARIX | LARIX | CEDRUS (4 species) | PINUS (90 spec

SUBGENUS: HAPLOXYLON | DIPLOXYLON

SPECIES: C. DEODARA ROXB (LOUD)
LOCATION: WESTERN HIMALAYAS & MEDITERRANEAN

CONSTITUENTS OF THE ESSENTIAL OIL[4]:

- p-METHYL ACETOPHENONE + p-METHYL Δ^3-TETRAHYDROACETOPHENONE ---~5.0 %
- α-HIMACHALENE ---------- 9.6 %
- β-HIMACHALENE ---------- 38.0 %
- ALLOHIMACHALONE + ar-DIHYDROTURMERONE ---------- 1.4 %
- LONGIBORNEOL ---------- 3.4 %
- HIMACHALOL ---------- 13.0 %
- ALLOHIMACHALOL ---------- 7.5 %
- α- & β-ATLANTONE ---------- 14.6 %
- (UNIDENTIFIED FRACTION) ---------- 6.5 %

P. LONGIFOLIA
HIMALAYAN REGION

CONSTITUENTS OF THE ESSENTIAL OIL[4]:

- α-PINENE ---------- 7 %
- β-PINENE ---------- 18 %
- Δ^3-CARENE ---------- 52 %
- CARENE (other isomers) ---- 8 %
- LONGIFOLENE ---------- 10 %
- LONGIPINENE, LONGICYCLENE, LONGIBORNYL ACETATE, LONGIBORNEOL, CARYOPHYLLENE OXIDE, HUMULENE OXIDE, CARYOPHYLLENE, HUMULENE, BISABOLENE ---- ~1 %
- UNIDENTIFIED FRACTION ---~4 % (~14 COMPOUNDS)

FIG. II. BOTANICAL RELATIONSHIP BETWEEN PINUS LONGIFOLIA AND CEDRUS DEODARA

the biogenetic sequence essentially* terminates at the ion (3) would mean that the enzymatic facility for the folding over of the cation (3) to a conformation suitable for transformation to longibornyl cation, is not available in Cedrus deodara and the products arise from the stabilization of the species (3). It is worth noting that some of the usual pathways open for the stabilization of carbonium ion have indeed been followed in Cedrus deodara. Thus recent work[4] in this Laboratory has shown the presence of himachalol (6), a product of stabilization by anion collapse and allohimachalol (7), a product of rearrangement -

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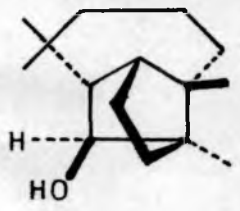
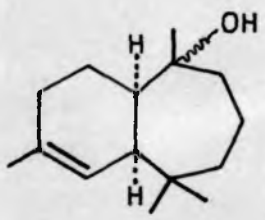
*In order to see if minor amounts of longifolene or longiborneol occur in Cedrus deodara and similarly if minor amounts of himachalenes could be detected in Pinus longifolia, work in this direction has been carried out in this Laboratory by S.C.Bisarya. These investigations reveal that the essential oil of Cedrus deodara contains small amount (~ 5%) of longiborneol (i), but himachalenes are absent in Pinus longifolia.

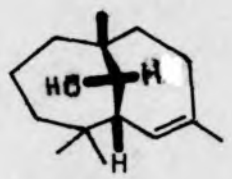


(i)

substitution, in the essential oil of Cedrus deodara besides himachalenes.



(6)



(7)

REFERENCES

1 J.B. Hendrickson, Tetrahedron 7, 83 (1959).

2 H. Erdtman in "Progress in Organic Chemistry" J.W.Cook ed., Vol.I, Butterworths, London (1952), p.22.

3 H. Erdtman, Pure and Appl. Chem., 6, 679 (1963).

4 S.C.Bisarya and Sukh Dev, Private communication.