

(R)-(-)- α -CUPARENONE FROM *Mannia fragrans* (BALBIS) FRYE et CLARK*

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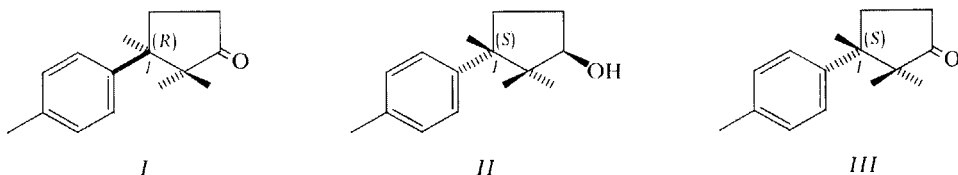
In addition to other components the sesquiterpenic ketone (R)-(-)- α -cuparenone was isolated from the liverwort *Mannia fragrans* (BALBIS) FRYE et CLARK. Its structure and absolute configuration have been determined; it is enantiomeric with the substances isolated from higher plants.

Approximately ten years ago we started an intensive study of liverworts (*Hepaticae*). Up till today about two percent of these sporangial green plants have been investigated chemically rather thoroughly, and there is a tendency to classify the obtained results in various ways. In view of the small number of plants investigated so far, this tendency may appear premature. Nevertheless, some properties of the substances isolated from liverworts so far are remarkable. One such feature is the optical activity of the typical components of liverworts — terpenic substances. These substances isolated both from the extracts and from the essential oils, prepared either from the extracts or by direct distillation from the plant material, are enantiomers of substances¹⁻¹¹ isolated earlier from higher plants. Ninety percent of chemically investigated liverworts in which enantiomeric components have been found belong to the *Jungermanniales* order. Among the liverworts belonging to the *Marchantiales* order δ -cadinene¹² has been isolated from the liverwort *Conocephalum conicum* (L.) LINDB. as the major sesquiterpenic component, for which it was proved¹³ that it is the enantiomer of (+)- δ -cadinene. This communication discusses another enantiomeric substance isolated from the intensively scented miniature liverwort *Mannia fragrans* (BALBIS) FRYE et CLARK (syn. *Grimaldia fragrans* (BALBIS) CORDA).

From the essential oil of the liverwort *M. fragrans* sesquiterpenic ketone I, C₁₅H₂₀O, was isolated by repeated chromatography. The infrared spectrum contained in addition to the carbonyl band (1745 cm⁻¹) a strong band (1520 cm⁻¹) characteristic of aromatic nucleus and also other bands (1378, 1387 cm⁻¹) corresponding to a geminal dimethyl arrangement. It also contained a band of a methylene group (1412 cm⁻¹) in α -position to a carbonyl group. The ¹H-NMR spectrum indicated the presence of a *para*-disubstituted benzene ring (aromatic H: 7.19; 4 H, AA', BB'), four tertiary methyls (0.61; 1.17; 1.25; 2.32) of which one (2.32) corresponded to

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a methyl on the benzene ring. The infrared spectrum of ketone *I* was identical with that of (+)- α -cuparenone *III*, isolated from the wood of "mayur pankhi" (probably *Thuja orientalis* L.)¹⁴ and also with the infrared spectrum of the same derivative prepared from α -cuparenone *II*, isolated from *Biota orientalis*¹⁵. The values of the



¹H-NMR spectra of both cuparenes were also in complete agreement. In the high resolution mass spectrum the molecular peak of mass 216·1512 (for C₁₅H₂₀O calculated 216·1514) was evident in addition to the characteristic ions C₁₁H₁₃ (*m/e* 145) and C₁₀H₁₂ (*m/e* 132), which are also present in the spectrum of (R)-(-)- α -cuparene¹⁶. Ketone *I* had a specific rotation $[\alpha]_D^{20} -169.9^\circ$ which corresponds, with the exception of its sign, to that of (+)- α -cuparenone¹⁴ *III*, $[\alpha]_D^{30} +177^\circ$. In view of these characteristic features ketone *I* isolated from the liverwort *M. fragrans* must be the optical antipode of (+)- α -cuparenone^{14,15}. Japanese authors¹⁶ have demonstrated that while the cuparene derivatives found in higher plants have an *S* configuration on the C₍₁₎ atom, the sesquiterpenes of the same type isolated from liverwort *Bazzania pompeana* are their optical antipodes. Therefore, the newly isolated (-)- α -cuparenone from the liverwort *M. fragrans* may be classified as another member among the *R*-chiral sesquiterpenes of cuparene type and hence as another member of enantiomeric terpenes isolated from liverworts.

EXPERIMENTAL

The melting points were determined on a Kofler block. The IR spectra were measured in tetrachloromethane with a Zeiss UR 20 spectrophotometer. The mass spectra were measured on a MS 902 spectrometer. The ¹H-NMR spectra were recorded with a Varian HA-100 instrument. Silica gel for column chromatography was prepared according to Pitra and Štěrba¹⁷.

Isolation of (R)-(-)- α -Cuparenone

M. fragrans was collected in October near Biskoupky in South Moravia. The vegetal material freed from impurities from the soil, which in fresh state had a volume of 400 ml, was steam distilled. The essential oil was collected in *n*-pentane. The *n*-pentane solution was dried over sodium sulfate and the solvent was evaporated to give a fragrant liquid residue (160 mg). This was chromatographed on silica gel deactivated with 10% of water. The fractions eluted with benzene gave a liquid product (35 mg) giving a single spot on TLC (*R_F* 0·36; benzene). An intensive band was present in the IR spectrum of this substance corresponding to a carbonyl group. According to

gas chromatography the distilled sample contained two components in a 91 : 9 ratio. By repeated chromatography on deactivated silica gel the major component was isolated in pure state, which had m.p. 52–55.5°C, $[\alpha]_D^{20} -169.9^\circ$. $C_{15}H_{20}O$ (216.1512), calculated 216.1514; m/e 145 ($M - C_4H_7O$; m/e 132 ($M - C_5H_8O$). IR spectrum: 822, 1378, 1387, 1520, 1745, 3035, 3070, 3105 cm^{-1} .

In addition to (–)- α -cuparenone five additional, as yet unknown isomeric hydrocarbons ($M^+ 204$) and three other oxygen-containing substances ($M^+ 218$) were isolated by gas chromatography from the essential oil, and identified by a combination of gas chromatography and mass spectrometry and subsequent measurement of the IR spectra.

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