Sir:

Rotundifolone, the principal component of the oil of Japanese Mentha rotundifolia, was established to be 1-methyl-4-isopropylidene-1,2-epoxy-cyclohexanone-3 in our previous report. It has also been pointed out that "mintglyoxal" isolated from Indian Mentha viridis, was presumably identical with rotundifolone, but the glyoxal structure proposed by Chakravarti and Bhattacharyya \(^1\) cannot be accepted as that for rotundifolone\(^{**}\). Independently, Reitsema \(^2\) isolated the same substance as ours, and he has also indicated that rotundifolone was identical with "lippione", which had been isolated from the oil of Argentine Lippia turbinata by Fester et al.\(^3\).

We obtained dihydro-rotundifolone by the reduction of rotundifolone over palladium, while Reitsema did not succeed in hydrogenation of rotundifolone by the use of a platinum catalyst. Our dihydro-rotundifolone semi-carbazone showed no depression, upon admixture with l-piperitone oxide semi-carbazone which Reitsema and Varnis\(^4\), isolated from the American Mentha sylvestris.

As regards to the reduction product of rotundifolone by lithium aluminum hydride, Reitsema has assumed it to be 2,3-diol (II)\(^3\) on the basis of its positive periodic test. In our previous report,\(^*\) we gave 1,3-diol structure (II a, b) for two stereoisomers of the diol of m.p. 145° and of m.p. 85°. Neither of the dihydro-diols (III a and b), obtained by the catalytic hydrogenation of diols (II a, b) over palladium gave a positive periodic acid test. Dihydro-diol (III a) from diol of m.p. 145° (II a) is a levorotatory needle, m.p. 165°, \([\alpha]_D^{19} -33.0^\circ\), and the one (III b) from diol of m.p. 85° (II b) a dextrorotatory oil, \([\alpha]_D^{19} +20.35^\circ\), d\(_{10}^0\) 0.975, n\(_{10}^D\) 1.4712.

Macbeth and Robertson\(^5\), have determined the configuration of various stereoisomers of \(\beta\)-menthane-diol-2, 3, but neither of our dihydro-diols coincides with any stereo-isomer of their 2,3-diols.

Recently, Chatterjee and Majumder\(^6\) reported that periodic acid was a promising reagent for the detection of both terminal and exocyclic double bonds. Consequently, in such diols as (II a, b), which possess an exocyclic double bond, a positive periodic reaction does not necessarily indicate the presence of \(\alpha\)-glycol grouping.

---

\(^{*}\) Part II. This Bulletin, 21, 107 (1957).
\(^{**}\) This report was presented at the Annual Meeting of Agric. Chem. Soc. Japan, Univ. of Tokyo. April 11, (1957).

As the tertiary hydroxyl group resists to chromic acid, \( p \)-menthane-1, 3-diol (III) will yield 1-hydroxy-menthone (IV) by this oxidation, whereas, \( p \)-menthane-2, 3-diol should give diosphenol (VI), which is easily detectable by the ferric chloride reaction and the intense absorption maximum at 273\( \text{nm} \).

The chromic acid oxidation products of (III a, b) were the oil which were assumed to be the mixture of 1-hydroxy-menthone (IV) and a small amount of piperitone (V). When oil (IV), was refluxed with 10% sulfuric acid solution for 2 hrs., \( dl \)-piperitone (V) was obtained almost quantitatively. 2, 4-Dinitro-phenylhydrazone of (V) is a red crystal, melting at 118\( ^\circ \). Anal. Found: C, 57.70; H, 6.30. Calcd, for C\(_{16}\)H\(_{26}\)O\(_{\text{N1}}\): C, 57.82; H, 6.70%. It showed no depression of melting point when mixed with the corresponding derivative of an authentic \( dl \)-piperitone, isolated from the Japanese peppermint oil. Semi-carbazone of (V) was a crystal, hardly soluble in methanol, melting at 214\( ^\circ \). It also did not depress the melting point upon admixture with an authentic \( dl \)-piperitone semicarbazone.

By lithium aluminum hydride reduction, a secondary oxide linkage is attacked in preference to a tertiary, and tertiary alcohol is produced, although some exceptions have been reported. In the case of rotundifolone, the formation of \( p \)-menthane-1, 3-diol is dominant. The synthesis of piperitone from rotundifolone does not only support the presence of an epoxide linkage, but also establishes the relation between rotundifolone and menthol series.

Sumio Shimmizu

Laboratory of Agricultural Chemistry,
Faculty of Agriculture, Shinshu University
Received May 18, 1957