CHEMISTRY LETTERS, pp. 1253-1256, 1983. © The Chemical Society of Japan 1983

ISOLATION OF OPPOSITANE- AND CYCLOEUDESMANE-TYPE SESQUITERPENOIDS FROM TORILIS JAPONICA D.C.

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Oppositane-, eudesmane-, and new cycloeudesmane-type sesquiterpenes were isolated from Torilis japonica D.C. All the compounds can be biogenetically correlated to epoxygermacrene-D.

In the previous paper, we reported the isolation of humulene, germacrene-D, and germacra-4(14),5(E),10(15)-trien-1β-ol(1) from the fruits of Torilis japonica D.C.(Umberiferae).[1)] The latter two sesquiterpenes were found to occur as enantiomeric mixtures. This paper is concerned with the isolation of oppositanes(4,5,6,10) from T. japonica. Oppositol(14), isolated from a red algae Laurencia subopposita, was made up of trans octahydro-1H-indene skeleton, and this type sesquiterpenes(14,15,16) are distributed in marine algae, Laurencia sp.[2)] Recently, Niwa et al. have reported biomimetic reaction of epoxygermacrene-D(8) with 80% acetic acid and with aluminum chloride leading to the formation of six oppositane derivatives(4,5,6,12, and others). This is the first case of the isolation of oppositanes from higher plant.

The fresh fruits of T. japonica were extracted in the same manner.[1)] The hexane-soluble fraction was further separated by silica gel column chromatography, and the eluates were finally purified by HPLC using a silica gel and a silver nitrate-coated silica gel columns[4)] to give five compounds(A-E). In order to eliminate a small amount of impurities, compound F was acetylated and the product was submitted to silica gel HPLC to afford a pure sample of the acetate Fa. Compounds D and E were also obtainable from the ethyl acetate-soluble fraction.

The IR and ^{1}H-NMR spectra of these compounds obviously indicate that each of them possesses a quaternary methyl(δ 0.6-0.8), an equatorial secondary hydroxyl(3640 cm^{-1}, δ 3.4-3.6, dd, J=11,5 Hz), and an exocyclic methylene groups (3090 and 890 cm^{-1}, δ 4.5-4.9, a pair of br s). By comparison of these data to those of 1α- and 1β-hydroxyeudesmane derivatives previously reported,[5)] it is strongly suggested that all of them have a partial structure 2 in the molecules.

The presence of another partial structure 3 in compound A ($[\alpha]_D$ +29.3^o) was revealed by the ^{1}H-NMR decoupling experiment. The coexistence of 2 and 3 led to the conclusion that compound A should be an oppositane-type sesquiterpene illustrated by the formula 4.

In the ^{1}H-NMR spectrum of compound B ($[\alpha]_D$ +40.3°), the signals of only one olefinic methyl group(δ 1.73,3H,s) and another exocyclic methylene group (δ 4.69,2H,br s) were observed together with those corresponding to 2. Therefore, compound B must be a double bond isomer of A, and can be represented by the formula 5.

The IR and ^{1}H-NMR spectra of compounds F and Fa(7) ($[\alpha]_D$ +40.7°) indicated the presence of a dimethylalkyl carbinol group (7: 3620 cm^{-1}; both F and 7: δ 1.23,6H,s). Although the ^{1}H-NMR spectrum of Fa is almost superimposable on that of 1β-hydroxy-β-eudesmol acetate,$^{6)}$ they are not identical. Thus, compound F must also possess the same carbon skeleton as those of A and B, and can be represented by the formula 6.

Compounds A, B, and F were identical with 4, 5, and 6 on comparison of the IR and ^{1}H-NMR spectra with authentic data from Niwa.$^{3)}$ Accordingly, this is the first example of occurrence of oppositane type sesquiterpenes in higher plants. The ^{1}H-NMR spectrum of compound C ($[\alpha]_D$ +12.4°) exhibited slightly resolved two methyl signals around δ 0.91 together with the proton signals corresponding to the partial structure 2. The ^{13}C-NMR spectrum showed that this compound must be a tricyclic sesquiterpene, because only a pair of sp^{2} carbon signals(δ 105.6 and 145.9) due to 4(15) double bond was observed. In addition, three methine carbon signals(δ 24.4, 24.6, and 32.4) which appeared in the significantly high field region indicated the presence of a 1,2,3-trisubstituted cyclopropane ring. These facts suggest that C may be the same compound as a tricyclic sesquiterpene(9), which has very recently been obtained by the biomimetic reaction of epoxygermacrene-D(8) with basic alumina,

Table 1. ^{13}C chemical shifts of compounds A(4), B(5), Fa(7), D(10), and E(11)

	4	5	7	10	11
1	79.2(d)	79.2(d)	80.5(d)	79.2(d)	79.3(d)
2	34.2(t)	34.7(t)	34.3(t)	34.9(t)	35.2(t)
3	31.5(t)	31.8(t)	30.4(t)	31.9(t)	32.1(t)
4	145.9(s)	145.9(s)	145.2(s)	146.0(s)	144.6(s)
5	58.0(d)	57.5(d)	57.9(d)	55.4(d)	51.2(d)
6	36.3(d)	34.5(d)	32.5(d)	39.0(d)	78.9(d)
7	129.8(d)	47.9(t)	49.5(t)	91.4(d)	45.4(d)
8	29.2(t)	28.0(t)	28.4(t)	26.1(t)	18.5(t)
9	36.8(t)	36.8(t)	37.2(t)	37.1(t)	36.4(t)
10	48.3(s)	48.5(s)	46.3(s)	49.3(s)	42.1(s)
11	130.2(s)	110.4(s)	71.3(s)	31.3(d)	25.8(d)
12	18.2(q)	145.3(t)	21.0(q)	16.3(q)	16.1(q)
13	25.7(q)	22.7(q)	21.2(q)	21.0(q)	21.2(q)
14	107.0(t)	106.1(t)	107.0(t)	107.2(t)	108.9(t)
15	12.4(q)	12.1(q)	13.0(q)	12.3(q)	11.8(q)
OCH_3	-	-	-	60.7(q)	52.5(q)

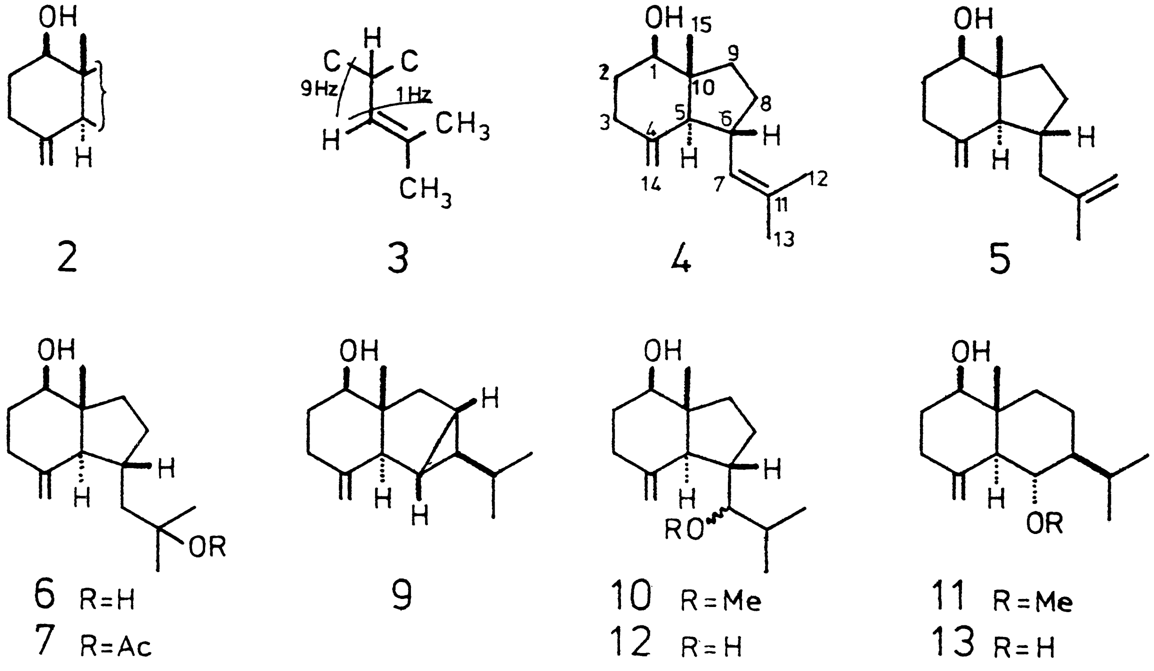
and whose structure has been determined by Yamamura et al.7) The identity was established by direct comparison of their IR, ^{1}H-NMR,and ^{13}C-NMR spectra. In order to determine the absolute configuration, epoxide of (-)-germacrene-D (optical purity: 35%) was treated with basic alumina according to the literature to give a dextro rotatory product. Therefore, the structure of natural sesquiterpene can be drawn as the formula 9.

Physical properties of two novel compounds are listed below.8)

Compound D: amorphous, $[\alpha]_D$ $+29.8^{\circ}$. IR 3640, 3080, 2950, 2885, 1650, 890 cm^{-1}. ^{1}H-NMR δ 0.63(3H,s), 0.88, 0.94(3H each, both d, J=6 Hz), 2.78(1H,dd,J=7,4 Hz), 3.30(3H,s), 3.53(1H,dd,J=11,5 Hz), 4.78, 4.84(1H each, both br s).

Compound E: amorphous, $[\alpha]_D$ $+7.8^{\circ}$. IR 3635, 3090, 2940, 2880, 1650, 890 cm^{-1}. ^{1}H-NMR δ 0.68(3H,s), 0.84, 0.93(3H each, both d,J=7 Hz), 3.16(3H,s), 3.37(1H, dd,J=11,5 Hz), 3.53(1H,t,J=10 Hz), 4.83, 4.93(1H each,br s). ^{13}C-NMR δ 11.8(q), 16.1(q), 18.5(t), 21.2(q), 25.8(d), 32.1(t), 35.2(t), 36.4(q), 42.1(s), 45.4 (d),51.2(d), 52.5(t), 78.9(d), 79.3(d), 108.9(t), 144.1(s).

^{1}H-NMR spectra of compounds D and E obviously exhibited that each possessed a methoxyl group. It was proved by comparison of the ^{13}C-NMR spectra that compound D had all the singnals corresponding to those of the carbons on the oppositane ring of compounds A and B, and Fa (Table 1), suggesting that this might also be the same type of compound. Niwa et al. have already obtained two hydroxyl compounds 12 and 13,3) whose chemical shifts and, in particular, coupling constants of the carbinyl protons in the ^{1}H-NMR spectra are quite similar to those of compounds D and E, respectively. Thus, these can be illustrated by the formulae 10 and 11, respectively.



2 3 4 5

6 R=H
7 R=Ac

9

10 R=Me
12 R=H

11 R=Me
13 R=H

Chart I.

All the compounds isolated from T. japonica could be biosynthesized from epoxygermacene-D by the same pathway described for the in vitro formation processes[3,7] as shown in chart II. The absolute configulations of all compounds except 9 have not been determined, however we assume that they have the same one as that of 9 because of the correlation to (-)-epoxygermacrene-D.

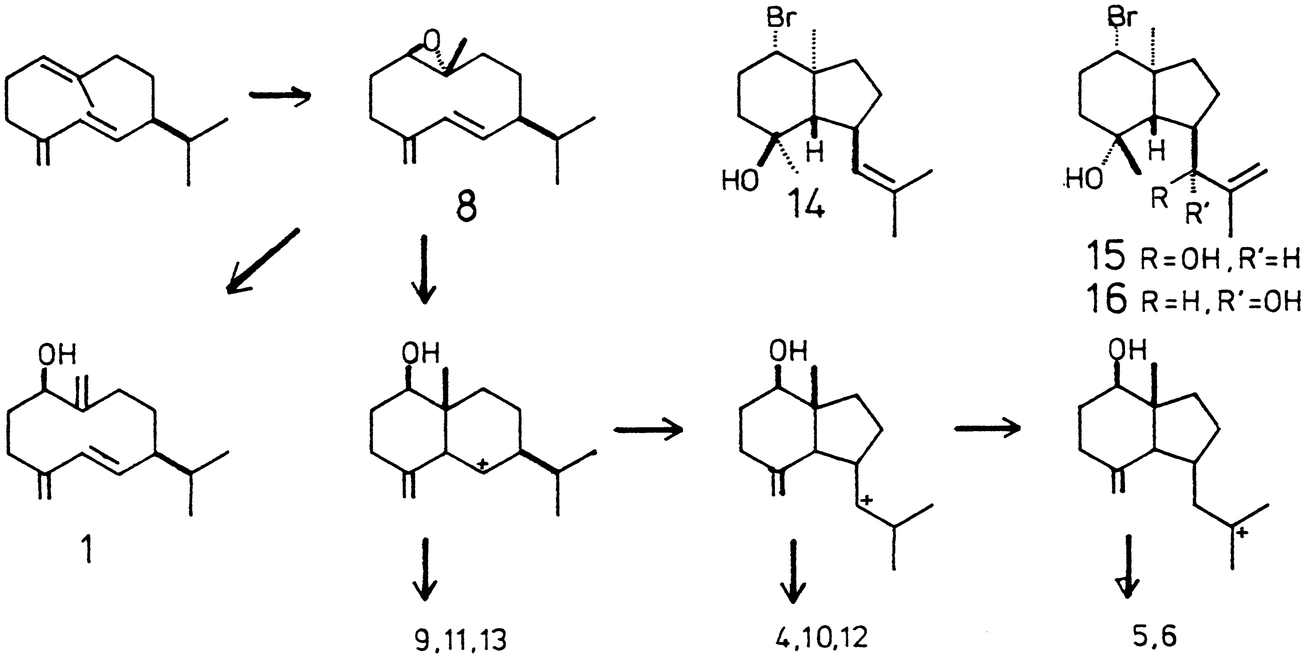


Chart II.

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8) All the spectral data were obtained under the following conditions; Optical rotation: JASCO DIP-4 in $CHCl_3$, IR: JASCO A-302 in CCl_4, ^1H-NMR: VARIAN EM-390 in $CDCl_3$, ^{13}C-NMR: JEOL FX-100 in $CDCl_3$.

(Received May 6, 1983)