Isolation of Enantiomeric Type Sesquiterpenoids from the Liverwort Riccardia jackii

Akihiko Matsuo, Osamu Ishii, Michihiko Suzuki, and Mitsuru Nakayama
Department of Chemistry, Faculty of Science, Hiroshima University, Naka-ku, Hiroshima 730

Shūichi Hayashi
Department of Chemistry, Faculty of Science, Okayama University of Science, Okayama 700, Japan

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A series of the enantiomeric sesquiterpenoids corresponding to the antipodes of those obtained from higher plants were isolated from the liverwort Riccardia jackii. This result is an additional example suggesting the special position taxonomical of the liverworts in plant kingdom.

Introduction

In the course of our study on sesquiterpenoids of the liverworts which are placed in a special group considered an early stage of the evolution of the terrestrial plants, we found that almost all of the liverworts metabolite the enantiomeric (abbr. ent) sesquiterpenoids corresponding to the antipodal form of those in higher plants [1-5]. In general, the sesquiterpenoids special to plants are produced from cis-farnesyl pyrophosphate and trans-isomer through appropriate stereospecific cyclizations and rearrangements on enzyme surface. We have, therefore, recognized the phenomena, that is, the biogenesis of liverwort sesquiterpenoids, as one of the most important biochemical characteristics of the liverworts.

In this paper, as an additional result supporting the significant feature, we describe the isolation of a series of enantiomeric sesquiterpenoids from a thalloid liverwort, Riccardia jackii Schiffn. belonging to the Aneuraceae [6, 7].

Results and Discussion

The liverwort, R. jackii, was digested with methanol to afford a brownish oily substance. A neutral fraction was separated by usual manner from the methanol extract in a yield of 1.1% to the dried material. The neutral part was subjected to column chromatography using silica gel to separate the hydrocarbon and alcohol fractions. From the hydrocarbon part ent-(-)-a-ompene (1) (syn. ent-(-)-isogymnomitrene), ent-(-)-ß-pompe (2) (syn. ent-(-)-gymnomitrene), ent-(-)-cuparene (3), ent-(-)-bicyclogermacrene (4), and ent-(-)-ledrene (7) were isolated by a combination of column chromatography and preparative TLC in pure state, respectively. The two selinene isomers, ent-(-)-a-selinene (5) and ent-(-)-ß-selinene (6), were obtained only by a preparative TLC using silica gel impregnated silver nitrate. From the polar fraction three sesquiterpene alcohols, ent-(-)-selin-11-en-4a-ol (8), ent-(-)-spathulenol (9), and ent-(-)-aristol-10β-ol (10), were isolated by rechromatography through a silica gel column together with a diterpene alcohol phytol [8] and a new 9,10-dihydrophenanthrene derivative. The structure of the last compound was elucidated by X-ray analysis to be 3,4-dimethoxy-5-hydroxy-9,10-dihydrophenanthrene and the result will be reported elsewhere.

ent-(-)-a-Pompe (1) and ent-(-)-ß-pompe (2) were identified to be the enantiomeric forms by coincidence of both the spectral data and the optical rotations (see Experimental Section) with those of the specimens obtained from other liverworts [9-12]. They are widely distributed in many liverworts, but are never isolated from other kinds of plants. These sesquiterpenoids are, therefore, one of the diagnostic components for showing chemotaxonomical position of the liverworts in plant kingdom. The structures including the absolute configurations of ent-(-)-cuparene (3) [13, 14] and ent-(--)-bicyclogermacrene (4) [4, 15] were presented...
as the enantiomeric forms by determination of
$^1$H NMR, IR, and mass spectra as well as the optical
rotations. The two bicyclic carbon skeletons are
important precursors for converting into the tri-
cyclic carbon skeletons such as gymnomitrane,
aromadendrane, alloaromadendrane, and maaliane
groups being common in the liverworts [5]. The
identification of three selinane sesquiterpenoids,
$\text{ent-} (+)-a$-selinene (5), $\text{ent-} (-)-\beta$-selinene (6) [16–18],
and $\text{ent-} (-)$-selin-11-en-4-$\alpha$-ol (8) [19], was per-
formed by coincidence of the spectral data with
those of the authentic compounds. The structures
were also certified by determination of $^1$C-NMR
spectra [20] (see Experimental Section). The optical
rotations of these selinene compounds, furthermore,
indicated the stereostructures as the enantiomeric
forms being the antipodes of those isolated from
higher plants. The spectral data of the seventh
hydrocarbon (7) exhibited the same properties as
those of ledrene derived from bicyclogermacrene
and ledrol [14]. The absolute configuration is not
certain because of no report of the rotation value of
the synthetic ledrene, but it is deduced to be the
enantiomeric type (7) in relationship with the ab-
olute configuration of $\text{ent-} (-)$-bicyclogermacrene
(4) which is a possible precursor of the sesquiterpene
ledrene. $\text{ent-} (-)$-Spathulenol (9) [21] was identified
by superimposition of $^1$H NMR and IR spectra to the
reported ones, and the optical rotation showing an
opposite sign to the value of normal stereostructure
suggested the enantiomeric structure. The spectra
of the last sesquiterpenoid were similar to those of
$\text{ent-} (+)$-maalian-10$\beta$-ol isolated from another liver-
wort Plagiochila ovalifolia [22], and the structure
was tentatively proposed as $\text{ent-} (+)$-aristlan-10$\beta$-ol
(10) by analysis of the spectra features and by con-
sideration of the biosynthetic sequence of all of
these sesquiterpenoids in this liverwort. However,
the structure and absolute configuration of both
compounds (7 and 10) should be certified in a future.

As described above, we isolated ten kinds of the
enantiomeric sesquiterpenoids corresponding to the
optical antipodes of those of higher plants from the
thalloid liverwort, $R$. jackii. This result suggests the
special position of the liverworts in plant kingdom,
and furthermore supported that the enantiomeric
sesquiterpenoids in the liverworts may be cyclized
by action of the liverwort enzymes having some
active sites in a contrary to the position of normal
enzymes, i.e. the sesquiterpenoid synthetases of
liverworts hold a reverse conformation to the
sesquiterpenoid synthetic enzymes of higher plants.

Experimental

IR Spectra were recorded on a grating spectrom-
eter for CCl$_4$ solutions and optical rotations were
taken on an automatic polarimeter for CHCl$_3$
solutions. $^1$H NMR Spectra were measured at 60 MHz
and $^1$C-NMR at 22.63 MHz for CCl$_4$ solutions with
TMS as the internal standard. Mass spectra were
determined at 70 eV. For column chromatography
Merk Kieselgel 60 was used and Merk Kieselgel PF$_254$
was used for TLC and preparative TLC. Analytical
plates were visualized under UV light or were
sprayed with 10% H$_2$SO$_4$ in EtOH and then heated
at 100 °C for 10 min.

Material and its extraction

The liverwort, $R$. jackii, was collected on
granite rocks in a valley at the suburbs of Hiroshima
city. The whole plant (1.7 kg), after washing with
water and drying in the shade for several days, was
digested with MeOH for a week at room tempera-
ture. The solvent was distilled off under reduced
pressure to give a viscous brownish oil. A neutral
part (18.2 g) was obtained by washing the extract
with 5% NaOH solution for removing an acid
part.

Isolation and identification of the constituents

The neutral part thus obtained was chromato-
graphed through a silica gel-column to divide some
fractions. The following compounds were isolated
from the fractions by a further combination of
column chromatography and preparative TLC using
silica gel. For the selinene mixture the TLC plates
impregnated with silver nitrate (10%) were used:
$\text{ent-} (+)$-$\alpha$-pompene (1) (15 mg), $\text{ent-} (-)$-$\beta$-pompene
(2) (80 mg), $\text{ent-} (-)$-cuparene (3) (7 mg), $\text{ent-} (-)$-
marianol (4) (35 mg), $\text{ent-} (+)$-$\alpha$-selinene (5)
50 (mg), $\text{ent-} (-)$-$\beta$-selinene (6) (160 mg), $\text{ent-} (-)$-

ledrene (7) (25 mg), ent-(—)-selin-11-en-4-α-ol (8) (20 mg), ent-(-)-spathulenol (9) (30 mg), ent-(+)-aristol-10-β-ol (10) (60 mg), phytol (130 mg), and 3,4-dimethoxy-5-hydroxy-9,10-dihydrophenanthrene (150 mg). The physical and spectral properties of these compounds are as follows: ent-(—)-ledrene (7): C_{15}H_{18}O (M^+ m/z 204, base peak m/z 204); [α]_D^20 +45°; IR 3515, 3460, 1635, 890 cm^{-1}; 1H NMR 0.57, 1.08, 1.25, 2.29 (each 3H, s), 6.95, 7.12 (each 2H, d, J = 8.0). ent-(—)-Bicyclogermacrene (4): C_{15}H_{18}O (M^+ m/z 204, base peak m/z 204). [α]_D^20 -28°; IR 1520, 1385, 1375, 1365, 812 cm^{-1}; 1H NMR 0.57, 1.08, 1.25, 2.29 (each 3H, s), 6.95, 7.12 (each 2H, d, J = 8.0). ent-(—)-Aristol-10-β-ol (10): C_{15}H_{18}O (M^+ m/z 222, base peak m/z 222); [α]_D^20 +6°; m.p. 87-88 °C; IR 3605, 3420, 1108, 978, 940, 893 cm^{-1}; 1H NMR 0.53-0.7 (2H, complex). 0.92 (3H, s, 1.30 (3H, s), 1.23 (3H, s); 1H, mm). 4.70 (2H, br. s),). ent-(—)-Aristol-10-β-ol (10): C_{15}H_{18}O (M^+ m/z 222, base peak m/z 222); [α]_D^20 +6°; m.p. 87-88 °C; IR 3605, 3420, 1108, 978, 940, 893 cm^{-1}; 1H NMR 0.53-0.7 (2H, complex). 0.92 (3H, s, 1.30 (3H, s), 1.23 (3H, s), 1H, mm). Phytol: C_{30}H_{40}O (M^+ m/z 296); IR 3640, 3450, 1650, 1380, 1370 cm^{-1}; 1H NMR 0.86 (12H, d, J = 7.0). 1.65 (3H, s), 1.40 (2H, d, J = 7.0). 1.93 (1H, t, J = 7.0). 3.4-Dimethoxy-5-hydroxy-9,10-dihydrophenanthrene: C_{15}H_{18}O (M^+ m/z 256); m.p. 125.5-126.5 °C; UV 218, 260, 267, 300 nm (e 4.3 × 10^4, 1.3 × 10^5, 1.3 × 10^4, 6.6 × 10^5); IR 3430, 1605, 1581, 1485, 1263, 1128 cm^{-1}; 1H NMR 2.65 (4H, s), 3.70, 3.85 (each 3H, s), 6.6-7.2 (5H, complex). 8.28 (1H, s).

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[6] Part of this work has been reported at the 24th Symposium of Chemistry of Terpenes, Essential Oils and Aromatics, Koriyama, 1989, Symposium Papers, p. 224.