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STRUCTURES OF THREE NEW *ENT*-LONGIPINANE TYPE SESQUITERPENOIDS FROM THE LIVERWORT *MARSUPELLA EMARGINATA* SUBSP. *TUBULOSA*

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Three new sesquiterpenoids were isolated from the liverwort *Marsupella emarginata* subsp. *tubulosa*. The structures and absolute configurations of the compounds have been shown to be (-)-marsupellone(1), (+)-marsupellol(2) and (+)-acetoxymarsupellone(3), containing an *ent*-longipinane skeleton, on the basis of chemical and spectral evidence.

In our course of the investigation on terpene constituents of liverworts, several enantiomeric sesquiterpenoids, which are antipodes of those from higher plants, have been isolated.[1-4] From a methanol extract of *Marsupella emarginata* (Ehrh.) subsp. *tubulosa* (Steph.) N. Kitag., now three new *ent*-longipinane type sesquiterpenoids, named (-)-marsupellone(1), (+)-marsupellol(2) and (+)-acetoxymarsupellone(3), were isolated by means of combination of column and preparative thin layer chromatographies on silica gel. The structures and absolute configurations of these compounds were determined, and we now report the chemical and spectral evidence for the proposed enantiomeric structures.

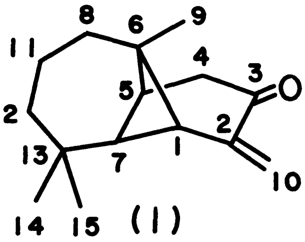
(-)-Marsupellone(1), $C_{15}H_{22}O(M^+ 218)$; oil; $[\alpha]_D$ -1.94°(c 3.50, $CHCl_3$); Rf 0.76(hexane-EtOAc, 4 : 1), was isolated as a major constituent of the extract. The spectroscopic evidence showed that the compound was a tricyclic α,β-unsaturated sesquiterpene ketone having a ketone group conjugated with an exocyclic methylene[λ_{max}^{EtOH} 241 nm(ε 4470); ν_{CCl_4} 3015, 1710, 1630 and 935 cm^{-1}; δ_{CCl_4} 4.81 and 5.77(each 1H, d, J=1.5 Hz)], an active methylene[ν 1415 cm^{-1}; δ 2.48(2H, complex)] adjacent to the carbonyl group, three characteristic methines[δ 1.34

(1H, s), 2.24(1H, d.t, J=6.5 and 3.0 Hz) and 2.77(1H, d, J=6.5 Hz)] and three tertiary methyls[δ 0.76(3H, s) and 0.92(6H, s)].

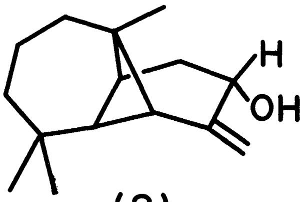
The ^{1}H-NMR spectrum of this ketone had a close resemblance to that of pinocarvone,5) a bicyclic α,β-unsaturated monoterpene ketone, along with the UV and IR spectra, except an additional tertiary methyl and three normal methylenes. On addition of Eu(fod)$_3$ (15 mg to 27 mg of sample), the signals of the active methylene were clearly observed at δ 4.03 and 4.29(each 1H, d.d, J=18.5 and 3.0 Hz; H-4) and the three methines were shifted to δ 2.12(1H, s; H-7), 2.69(1H, d.t, J=6.5 and 3.0 Hz; H-5) and 3.22(1H, d, J=6.5 Hz; H-1), respectively. The value of coupling(J_{1-5}=6.5 Hz) was interpreted by a long range coupling due to W letter configuration as observed in pinocarvone,5) verbenone6) and vulgarones7,8) containing a bicyclo[3.1.1]heptane system. Besides, irradiation of one methine(δ 2.69) deformed another methine(δ 3.22) to a broad singlet and simplified the two double doublets of the active methylene to two doublets of AB-type(each 1H, J=18.5 Hz), and reversely irradiation at δ 3.22 transformed the methine at δ 2.69 to a triplet(J=3.0 Hz). These spectral behaviors are reasonably explained in terms of the longipinane type structure(1), which has an additional isoprene unit between C-7 and C-8 in the structure of pinocarvone.

The ketone was subjected to hydrogenation over 5% Pd-C in ethanol followed by LiAlH$_4$ reduction to furnish a saturated secondary alcohol(4), $C_{15}H_{26}O$(M^+ 222); mp 113.5-114.5 °C; $[\alpha]_D$ -46.9°(c 0.64, CHCl$_3$); ν_{CCl_4} 3630 and 3450 cm^{-1}; δ_{CCl_4} 4.32 (1H, t.d, J=10.0 and 5.0 Hz), containing one secondary methyl[δ 1.05(3H, d, J=7.0 Hz)] and three tertiary methyls[ν 0.87(6H, s) and 1.03(3H, s)]. The alcohol was then treated with POCl$_3$ to give an unsaturated hydrocarbon(5), $C_{15}H_{24}$(M^+ 204); oil; $[\alpha]_D$ -31.5°(c 0.89, CHCl$_3$), in 10% yield. The hydrocarbon was identified as (-)-α-longipinene(5)1), the enantiomer of (+)-α-longipinene,9) based on coincidence of the spectral data and specific rotation. Thus, the structure and absolute configuration of (-)-marsupellone(1) was determined.

(+)-Marsupellol(2), $C_{15}H_{24}O$(M^+ 220); oil; $[\alpha]_D$ +13.4°(c 1.34, CHCl$_3$); Rf 0.53 (hexane-EtOAc, 4 : 1), was isolated as a minor constituent. It contained a secondary hydroxyl group[ν_{CCl_4} 3590 and 3435 cm^{-1}; δ_{CDCl_3} 4.47(1H, d, J=7.0 Hz)], an exocyclic methylene[ν 3050, 1642 and 893 cm^{-1}; δ 4.78 and 4.95(each 1H, br.s)] and three tertiary methyls[δ 0.62(3H, s) and 0.92(6H, s)]. The IR, ^{1}H-NMR and mass spectra closely resembled those of (-)-marsupellone(1) and its reduced alcohol(4),



(1)



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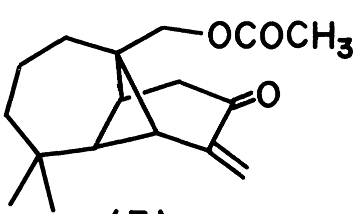

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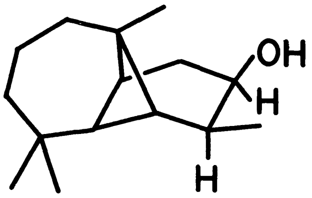

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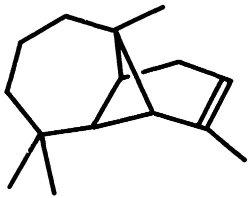

(5)

and suggested that marsupellol would be a reduction product(2) of marsupellone(1).

The Sarett oxidation(CrO_3/pyridine) of the alcohol provided an α,β-unsaturated ketone, $C_{15}H_{22}O$(M^+ 218); $[\alpha]_D$ -3.05°(c 1.31, $CHCl_3$), which was identified with (-)-marsupellone(1) in the spectral data and optical rotation. On the other hand, reduction of marsupellone with $LiAlH_4$ gave, in a ratio of 1 : 4, (+)-marsupellol and its diastereoisomer[ν_{CCl_4} 3610, 3440, 3080, 1652 and 867 cm^{-1}; δ_{CCl_4} 0.72(3H, s), 0.89(6H, s), 4.59(1H, m), 4.73(1H, br.s) and 4.99(1H, br.s)]. The configuration of the hydroxyl group in (+)-marsupellol(2) was recognized to be *trans* on similarity of both ^1H-NMR spectra of the compound and *trans*-pinocarveol prepared from β-pinene.[10] Alternatively, according to the Brewster's benzoate rule[11] ($[M]_D^{benzoate} - [M]_D^{alcohol} = +12.3°$), the absolute configuration of the secondary carbinyl carbon was defined to have *S* chirality. Consequently, the absolute structure of (+)-marsupellol should be represented by the formula(2).

(+)-Acetoxymarsupellone(3), $C_{17}H_{24}O_3$(M^+ 276); oil; $[\alpha]_D$ +6.9°(c 1.02, $CHCl_3$); Rf 0.48(hexane-EtOAc, 4 : 1), contained a primary acetoxyl group[ν_{CCl_4} 1735 and 1230 cm^{-1}; δ_{CDCl_3} 2.00(3H, s) and 3.77(2H, s)], a ketone group conjugated with an exomethylene[λ_{max}^{EtOH} 239 nm(ε 4070); ν 3010, 1705, 1625 and 935 cm^{-1}; δ 5.00 and 5.89(each 1H, d, J=1.5 Hz)] and two tertiary methyls[δ 0.95(6H, s)]; the UV, IR and ^1H-NMR spectra were also extremely similar to those of marsupellone. However, this compound lacked the most shielded tertiary methyl which was present in marsupellone and contained the acetoxyl group instead. (+)-Acetoxymarsupellone was thus thought to have the structure(3). This deduction was supported by the ^{13}C-NMR spectrum: the spectrum of acetoxymarsupellone was quite similar to that of marsupellone in the chemical shift and peak multiplicity, except that a quartet

^{13}C-NMR Chemical shifts of (-)-marsupellone(1), (+)-marsupellol(2) and (+)-acetoxymarsupellone(3) (δ from TMS, in $CDCl_3$)

Carbon No.	(1)	(2)	(3)
1	47.8 (d)	50.1 (d)	45.4 (d)
2	150.5 (s)	158.5 (s)	149.3 (s)
3	200.6 (s)	67.5 (d)	199.4 (s)
4	44.7 (t)	37.6 (t)	44.2 (t)
5	37.3 (d)	39.0 (d)	35.8 (d)
6	42.5 (s)	41.9 (s)	44.0 (s)
7	59.3 (d)	53.5 (d)	59.3 (d)
8	39.4 (t)	39.5 (t)	35.8 (t)
9	23.1 (q)	24.0 (q)	67.8 (t)
10	115.4 (t)	109.7 (t)	116.6 (t)
11	21.4 (t)	21.7 (t)	20.9 (t)
12	41.1 (t)	41.3 (t)	39.4 (t)
13	33.1 (s)	32.7 (s)	33.1 (s)
14	27.5 (q)	27.7 (q)	27.4 (q)
15	27.8 (q)	28.2 (q)	27.8 (q)
$-OCOCH_3$			171.0 (s) 20.7 (q)

(δ 23.1) in marsupellone was replaced by a triplet(δ 67.8) and two signals of a singlet(δ 171.0) and a quartet(δ 20.7) were present as additional carbon atoms. (+)-Acetoxymarsupellone was, therefore, depicted as the structure(3).

We have already isolated (-)-α-longipinene(5), which has been defined to be an enantiomer of that isolated from higher plants, from the liverwort *Scapania undulata*.1) Now (-)-marsupellone(1), (+)-marsupellol(2) and (+)-acetoxymarsupellone(3) can be added to new members of the naturally occurring *ent*-longipinane type sesquiterpenoids. This is very interesting in the viewpoints of terpenoid biogenesis and chemosystematics.

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References

1) A. Matsuo, M. Nakayama and S. Hayashi, Chem. Lett., 1973, 769.
2) A. Matsuo, M. Nakayama, S. Sato, T. Nakamoto, S. Uto and S. Hayashi, Experientia, 30, 321 (1974).
3) A. Matsuo, M. Nakayama, T. Maeda, Y. Noda and S. Hayashi, Phytocnemistry, 14, 1037 (1975).
4) A. Matsuo, H. Nozaki, M. Nakayama, Y. Kushi, S. Hayashi, N. Kamijo, V. Benešová and V. Herout, J. Chem. Soc., Chem. Commun., 1976, 1006.
5) Y. Bessière-Chrétien and C. Grison, Bull. Soc. Chim. Fr., 1970, 3103.
6) M. A. Cooper, J. R. Salmon and D. Whittaker, J. Chem. Soc. (B), 1967, 1259.
7) Y. Uchio, A. Matsuo, M. Nakayama and S. Hayashi, Tetrahedron Lett., 1976, 2963.
8) Y. Uchio, A. Matsuo, S. Eguchi, M. Nakayama and S. Hayashi, ibid., 1977, 1191.
9) H. Erdtman and L. Westfelt, Acta Chem. Scand., 17, 2351 (1963).
10) L. E. Gruenewald and D. C. Johnson, J. Org. Chem., 30, 1673 (1965).
11) J. H. Brewster, Tetrahedron, 13, 106 (1961).

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