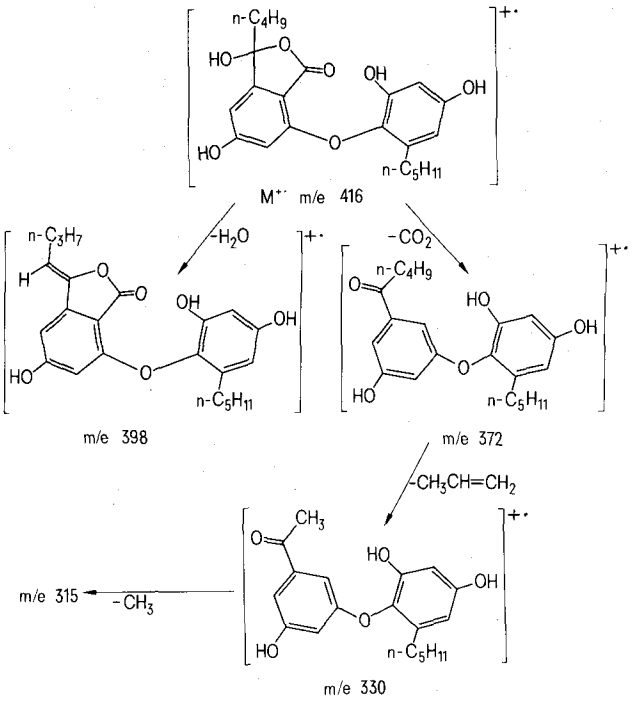
Mass spectral data (above m/e 398) of the principal products of acetylation of compound **I**

Product (R_f value in benzene/acetone 4:1)	m/e (% relative intensity)
III (0.80)	524 (2), 482 (65), 456 (5) 440 (100), 414 (35), 412 (55), 398 (80)
IV (0.60)	584 (5), 542 (3), 525 (5), 524 (3), 560 (3) 482 (100), 458 (5), 440 (100), 412 (30), 398 (30)
V (0.35)	482 (15), 440 (45), 398 (100)



Proposed fragmentation scheme for compound (**I**).

other major fragments at m/e 398, 330 and 315. The TLC and mass spectral data of the compound were identical to those of norlobariol which was obtained by treatment of norlobaridone with hot sodium hydroxide solution. Further, treatment of the compound with boiling formic acid yielded a product which was identical to isonorlobaridone[2]. The NMR (60 MHz) spectrum of the compound in deuterated acetone showed 4 sets of doublets attributable to aromatic protons at δ 6.60 (J, 1.8 Hz, 1 H), 6.42 (J, 2.6 Hz, 1 H), 6.32 (J, 2.6 Hz, 1 H), and 6.07 (J, 1.8 Hz, 1 H) and other signals at δ 2.10 (m, 4 H), 1.30 (m, 10 H), and 0.90 (m, 6 H) which are consistent with the structure of norlobariol. The identity of the lichen metabolite was further confirmed by its inertness to sodium bicarbonate solution and by its reaction with excess diazomethane which yielded a product with the highest mass at m/e 458 thus confirming the presence of 3 phenolic hydroxyls. In addition, acetylation of the metabolite yielded 3 principal products (**III, IV** and **V**) which could be logically explained from the structure of norlobariol. The mass spectral data of the acetylated products are shown in the table. Product (**III**) could arise by the loss of water from (**II**) under the dehydrating conditions of the reaction to yield a triacetylated product, while (**IV**) was the expected tetraacetylated product. Product (**V**) was identical to the product obtained by acetylating norlobaridone. This presumably could arise by the cleavage of the lactol ring followed by intramolecular cyclizatioo with the concomitant formation of the depsidone ring.

Thermally induced chemical artifacts in lichens have been known to occur[3]. As norlobaridone is also a major constituent of this lichen, the authenticity of norlobariol could be suspect. However, it is unlikely that norlobariol was produced from norlobaridone under the experimental conditions employed in this work. Cold extraction of the lichen with acetone over a short period yielded norlobariol. Norlobaridone under these conditions remained unchanged. It is therefore concluded that norlobariol is a natural metabolite of this lichen.

1 Acknowledgment. The authors wish to acknowledge the assistance of Dr D. Galloway in identifying the lichen sample and Dr A.W. Campbell for the microanalytical data.

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New bibenzyls of the liverwort, *Radula variabilis*

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Summary. 3 new bibenzyls having a 7-membered heterocyclic ring have been isolated from the liverwort, *Radula variabilis* and their structures have been established to be **1, 3** and **5.**

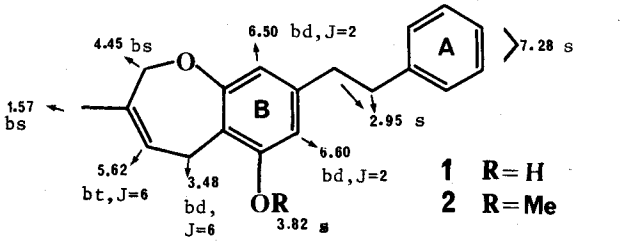
In the course of the investigation of the aromatic components of the liverwort, we have recently reported the isolation and the structures of 4 new aromatic esters containing the isoprene units, from *Trichocolea tomentella*[1]. The liverworts, *Radula* species, also contain various aromatic compounds. We now wish to describe the isolation and the structures of 3 new bibenzyls (**1**), (**3**) and (**5**) with 7-membered heterocycle from *Radula variabilis*[2].

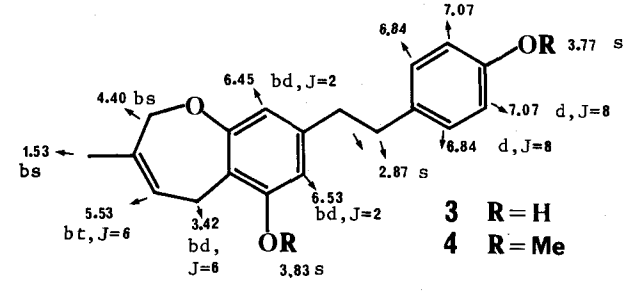
R. variabilis, growing on rock, was collected in June 1977. Column and preparative TLC on silica gel of the methanol extract (9 g) of air-dried and ground material resulted in the isolation of 3 new bibenzyls, **1** (9.4%, total weight of the extract), **3** (1.1%) and **5** (8.8%), respectively.

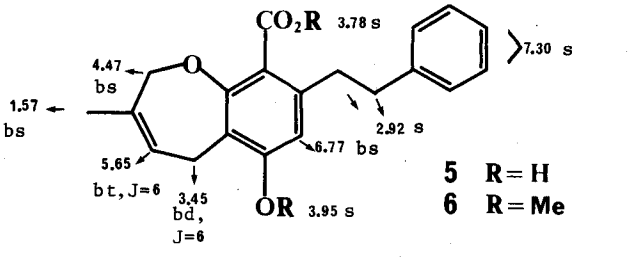
Bibenzyl (**1**), $C_{19}H_{20}O_2$ (M^+280), showed the presence of the hydroxyl group (3370 cm^{-1}) and a benzene ring (1625, 1590 and 700 cm^{-1}; λ_{max} 221 and 279 nm). The presence of a phenolic hydroxyl group was confirmed by methylation to give a monomethyl ether (**2**), $C_{20}H_{22}O_2$ (M^+ 294), NMR (figure) 3.82 ppm (s, 3H).

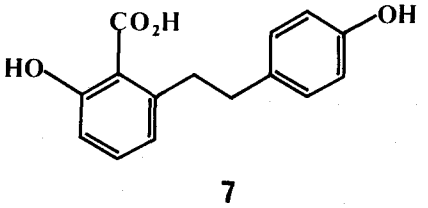
Hydrogenation of **2** afforded a dihydroderivative, $C_{20}H_{24}O_2$ (M^+ 296), indicating the presence of a double bond. The presence of a non-substituted benzyl group was confirmed

by the intense peak at m/e 91 (70%) and 189 (M^+-91, 99%) in the mass spectrum and by the singlet signal at 7.25 ppm (5H). The NMR-spectrum of **1** contained the signals for 2 equivalent methylene groups (2.90, s), assignable to ph-CH_2-CH_2-ph, 2 non-equivalent aromatic protons (6.42, bs and 6.55, bs), indicating the substituents being asymmetrical and 2 protons placing at meta position. The NMR- and NMDR-spectra further showed the presence of a cyclized isoprene unit: a vinyl methyl (1.57, bs), a vinyl proton (5.62, bt, J=6 Hz), 1 methylene (4.43, bs) located between an aromatic ether oxygen, and a double bond and an additional methylene group (3.40, bd, J=6) located between an aromatic ring and a double bond. The above chemical and spectral evidence, coupled with the molecular formula, indicates that **1** is the bibenzyl derivative and 1 of the methyl group of γ, γ-dimethyl allyl group attached on 1 of the benzene rings is connected with a phenolic ether oxygen. The relative positions of the substituents at the benzene ring B was proved by an NOE experiment with **2.** Irradiation of the singlet signal of 2.95 ppm (ph-CH_2-CH_2-ph) indicated the increase of the intensity of the signal at 6.50 and 6.60 ppm, assignable to 2 aromatic protons. Consequently, the structure of the new bibenzyl has been established to be **1**.









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The new bibenzyls (**1**, **3** and **5**) and the NMR spectral data of their permethylated compounds (**2**, **4** and **6**).

Bibenzyl (**3**). The compound **3** which possessed no methoxyl group, contained a very small amount of a non-identified dihydrochalcone derivative. The bibenzyl **3** was purified by methylation. The NMR-spectrum (figure) of the methylated bibenzyl (**4**), $C_{21}H_{24}O_3$ (M^+324), strikingly resembled that of **2**, except for the presence of AB doublet signals of 4 protons on benzene ring instead of the singlet signal (5H) of the non-substituted benzyl group of **2**, and the presence of the signal of the additional methoxyl group. This observation suggested that the methyl ether possessed the same skeleton as the compound **2**, and the para position of A-ring was substituted by a methoxyl group. This assignment was further confirmed by the base peak at m/e 121 (MeO-C_6H_5-CH_2^+) and the intense peak at m/e 203 (M^+-121, 53%) in the mass spectrum. Thus, the structure of the methyl ether was shown by **4**, hence the original bibenzyl was represented by **3.**

Bibenzyl (**5**), $C_{20}H_{20}O_4$ (M^+324), displayed the presence of a carboxylic group (3500-2600 cm^{-1} and 1710 cm^{-1}). The NMR-spectrum showed the signals at 8.22 (bs, 1H) and 5.38 ppm (bs, 1H), which disappeared upon the addition of D_2O, assignable to a COOH and a phenolic OH proton, respectively. This assignment was confirmed by the methylation of **5.** Treatment of **5** with diazomethane gave a methyl ester (**6**), $C_{22}H_{24}O_4$ (M^+352); 1735 cm^{-1}, whose NMR-spectrum (figure) was quite similar to that of **2,** except the presence of the signal of the methyl ester and the absence of 1 aromatic proton. This evidence, together with the molecular formula, indicated that **6** possessed the same skeleton as the compound **2** and 1 proton on the aromatic B-ring was substituted by a carbomethoxyl group. The NMR-and IR-spectra of the original acid exhibited no hydrogen-bonded hydroxyl group, suggesting that the carboxylic and the phenolic hydroxyl groups were in the para position. On the basis of the above results and coexistence of the compounds **1** and **3,** coupled with the biogenetic basis[3], the structure of the acidic bibenzyl was determined to be **5.**

The number of bibenzyl derivatives found in the liverworts is steadily increasing and lunularic acid (**7**) is particularly significant as the plant growth inhibitor[4]. The compounds containing the nucleus of 2,2-dimethyl chromene and 2,2-dimethyl chromane are largely distributed in the higher plants. The present new bibenzyls have a 7-membered chromene skeleton. As far as we are aware, this heterocycle is the 1st member of a new group of the natural products, and it is very interesting from the biogenetic view-point.

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2 The authors are indebted to Dr S. Hattori of the Hattori Botanical Laboratory for his identification of the species and helpful suggestion.
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