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SEVEN NEW BIBENZYLS AND A DIHYDROCHALCONE FROM *RADULA VARIABILIS*

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Key Word Index—*Radula variabilis*; Hepaticae; liverwort; bibenzyls; seven-membered heterocyclic skeleton; isoprene unit; structure elucidation.

Abstract—Six new bibenzyls have been isolated from the liverwort, *Radula variabilis* and their structures have been established by chemical and spectral evidence. In addition, a new dihydrochalcone and a new bibenzyl have been isolated as their methyl ethers. Except for two of the bibenzyls, the present compounds have a unique seven-membered heterocyclic ring and they are the first members of a new group of natural product.

INTRODUCTION

In the course of the systematic investigation of the biologically active substances in the Bryophyta, we have reported the isolation, structures and allergenic properties of the sesquiterpene lactones of *Frullania* species [1, 2]. The liverworts, *Radula* species (Radulaceae) also contain allergenic agents [3]; however, the hapten of allergenic contact dermatitis has not been proved. We have now investigated the chemical constituents of *Radula variabilis* and found it to lack sesquiterpene lactones; instead, it elaborates new bibenzyls and a dihydrochalcone which possess a unique seven-membered heterocyclic ring.

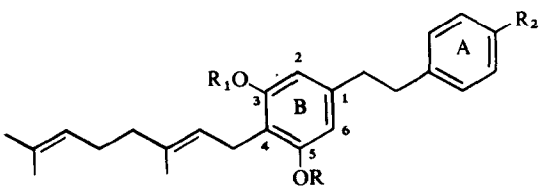
RESULTS AND DISCUSSION

Column and PLC on Si gel of the methanol extract of the air-dried material resulted in the isolation of the bibenzyls, **1**, **4**, **8**, **10**, **17** and **24**, respectively. In addition to the above bibenzyls, a dihydrochalcone (**15**) and an acidic bibenzyl (**20**), after methylation with excess diazomethane, were isolated by the combination of column and PLC on Si gel.

Bibenzyls (**1**) *and* (**4**)

The major component, $C_{24}H_{30}O_2$ (M^+ 350) exhibited the presence of hydroxyl group (3450 cm^{-1}) and aromatic groups (1610, 1595, 703 cm^{-1}; λ_{max} 225, 280 nm) in IR and UV spectra. Methylation of **1** gave a dimethyl ether (**2**), $C_{26}H_{34}O_2$ (M^+ 378) and acetylation of **1** afforded diacetate (**3**) (δ, 2.28 (*s*, 6H), 1767 cm^{-1}), indicating the presence of two hydroxyl groups in **1**. Hydrogenation of **1** and its dimethyl ether (**2**) gave the corresponding tetrahydroderivatives (**5**), $C_{24}H_{34}O_2$ (M^+ 354) and (**6**), $C_{26}H_{38}O_2$ (M^+ 382), respectively. The presence of an unsubstituted benzyl group was confirmed by the base peak at *m/e* 91 in the mass spectrum and by the singlet signal at 7.27 ppm (5H) in the NMR spectrum. The NMR (Table 1) and NMDR spectra of **1** also contained the signals of two equivalent aromatic protons and two equivalent methylene groups, characteristic of the bibenzyl. The presence of a geranyl group attached on an aromatic ring was proved by the signals due to three vinylic methyls, two vinylic protons appearing as broad triplet, two methylenes located between double bonds and a methylene group located between an aromatic ring and a double bond. The signal pattern of the former three groups were identical to those of geraniol. The presence of an allylic benzyl group was confirmed by the intense fragment ion at *m/e* 227 (M^+-C_9H_{15}). Treatment of **1** with conc HCl in HOAc gave a chromane derivative (**7**), $C_{24}H_{31}O_2Cl$ (M^+ 386) with a chlorine atom in the side chain, indicating the *ortho* position between the geranyl group and a hydroxyl group. The equivalent chemical shift of two protons on a benzene ring showed the symmetrical substitution of the benzene ring, and a geranyl group and a phenethyl group being in *para* position and two hydroxyl groups being in *ortho* position with respect to isoprene chain. Nuclear Overhauser effect experiments on the dimethyl ether (**2**) indicated 11% increase of the intensity of the signal of the atomatic protons, after irradiation of the singlet signal at 2.80 ppm (4H), attributable to two methylene groups of the bibenzyl. On the basis of the above chemical and spectral evidence, coupled with the biogenetic consideration, the structure of the new bibenzyl was thus established as 3,5-dihydroxy-4-(3,7-dimethyl-2,6-octadienyl)-bibenzyl (**1**).

The mass spectrum of **4** showed the molecular ion at *m/e* 366 and its fragmentation pattern was strikingly similar to that of the bibenzyl (**1**). The base peak at *m/e*

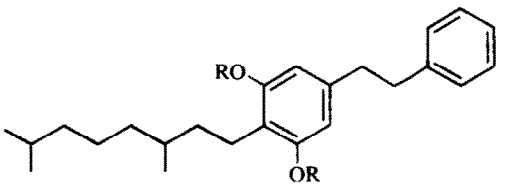


1 R_1 = H R_2 = H
2 R_1 = Me R_2 = H
3 R_1 = Ac R_2 = H
4 R_1 = H R_2 = OH

Table 1. NMR data* of the new

Compounds	1	2	3	5	6	8	9
Ar (A-ring)	7.27 (*s*)	7 37 (*s*)	7.32 (*s*)	7 28 (*s*)	7 30 (*s*)	7.25 (*s*)	7 28 (*s*)
Ar (B-ring)	6.28 (*bs*)	6.47 (*bs*)	6.80 (*d*, *J* = 2) 6.93 (*d*, *J* = 2)	6.21 (*d*, *J* = 2) 6.34 (*d*, *J* = 2)	6 35 (*bs*)	6.42 (*d*, *J* = 2) 6 55 (*d*, *J* = 2)	6 50 (*bs*) 6 60 (*bs*)
Ar—$(CH_2)_2$—Ar	2.80 (*s*)	2 93 (*s*)	2.92 (*s*)	2.83 (*s*)	2 88 (*s*)	2 90 (*s*)	2 87 (*s*)
Ar—CH_2—C=	3.27 (*d*, *J* = 7)	3.41 (*d*, *J* = 7)	3.26 (*d*, *J* = 7)			3 40 (*bd*, *J* = 7)	3 48 (*bd*, *J* = 7)
=CH—	5.10 (*bt*, *J* = 7)	5.20 (*bt*, *J* = 7)	5.03 (*m*)			5.62 (*bt*, *J* = 7)	5.62 (*m*)
	1.57 (*bs*)	1.60 (*bs*)	1.65 (*bs*)			1 57 (*bs*)	1.58 (*bs*)
=C—Me	1.65 (*bs*)	1 67 (*bs*)	1.75 (*bs*)				
	1 77 (*bs*)	1 80 (*bs*)	1.85 (*bs*)				
—CH_2—CH_2—	2 00 (*bs*)	2 03 (*bs*)	2 20 (*bs*)				
—C—Me				0.88 (*d*, *J* = 6)	0.87 (*d*, *J* = 7)		
Ar—OMe		3.80 (*s*)					
Ar—OAc			2 28 (*s*)				
OH	5.50 (*bs*)					6.23 (*bs*)	
Ar—CH_2—CH_2—				2.55 (*t*, *J* = 7)	2 57 (*t*, *J* = 7)		
—O—CH_2—						4 43 (*bs*)	4 45 (*bs*)
COOMe							
Ar—CH=CH—							
Ar—$(CH_2)_2$—CO							

* Chemical shifts in ppm. Signal multiplicity *s* = singlet, *d* = doublet, *t* = triplet, *bs* = broad singlet, *bd* = broad doublet, *bt* = broad triplet, *m* = multiplet. †The signals of COOMe and one proton of —OCH_2 were overlapped.



5 R = H
6 R = Me

107 was assigned to be HO–$C_7H_6^+$ and the intense peak at *m/e* 243 was confirmed to be the fragment, M^+-C_9H_{15} (isoprene side chain). The presence of dimethylallyl group was suggested by the peak at *m/e* 69. The above mass spectral evidence, together with the co-occurrence with **1**, led us to the structure (**4**) for the minor bibenzyl.

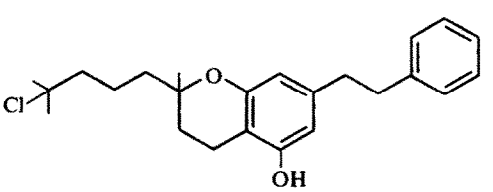
Bibenzyls (**8**) *and* (**10**)

The less polar component, $C_{19}H_{20}O_2$ (M^+ 280), showed the presence of hydroxyl (3370 cm^{-1}) and aromatic groups (1625, 1590, 700 cm^{-1}; 221, 279 nm). The presence of one hydroxyl group was confirmed by methylation to give monomethyl ether (**9**), $C_{20}H_{22}O_2$ (M^+ 294). Hydrogenation of **9** gave a dihydro derivative (**13**), $C_{20}H_{24}O_2$ (M^+ 296), indicating the presence of a double bond. The presence of an unsubstituted benzene ring was established by the intense peak at *m/e* 91 and by the singlet signal at 7.25 ppm (5H). The NMR and NMDR spectra showed the presence of two equivalent methylene groups (4H), assignable to benzylic methylenes and two non equivalent aromatic protons (*J* = 2), indicating the substituents being asymmetrical and two protons placing in *meta* position. The NMR spectrum of **8** further contained the signals of one isoprene unit; a vinylic methyl, a vinylic proton, one methylene located between a double bond and an aromatic ether oxygen, an additional methylene group placed between a double bond and an aromatic ring. This assignment was confirmed by the double resonance experiment. The above chemical and spectral evidence, coupled with the molecular formula showed that **8** was the bibenzyl derivative having an unsubstituted benzene ring (A) and one methyl group of γ,γ-dimethylallyl group attached on another benzene ring (B), condensed with a phenolic hydroxyl group at the *ortho* position in the same ring. The arrangement of the substituents of B-ring was proved by the NOE experiment of **9**. Irradiation of the singlet signal at 2.87 ppm, due to two benzylic methylenes, caused the increase of the intensity of the signals of 6.50 and 6.60 ppm, assignable to two protons on the benzene ring (**B**). From the above results, together with biogenetic consideration, the third bibenzyl is represented by structure **8** [4].

Treatment of the bibenzyl (**10**), $C_{19}H_{20}O_3$ (M^+ 296) with $(Me)_2SO_4$ gave a dimethyl ether (**11**) [4], $C_{21}H_{24}O_3$ (M^+ 324). Acetylation of **10** afforded a diacetate (**12**) (δ, 2.30 ppm, *s*; 1760 cm^{-1}), indicating **10** to have two hydroxyl groups. The signal pattern of NMR spectrum of **10** and its dimethyl ether (**11**) were almost identical to **8** and **9**, respectively, except for the presence of AB doublet signals of four protons on the benzene ring instead of the singlet signal (5H) of the unsubstituted benzene ring. The mass spectrum of **10** showed the base peak at *m/e* 189 (M^+-107) and the intense peak at *m/e* 107 (HO-$C_7H_6^+$). On the basis of these results, the structure of the fourth bibenzyl was established as **10**.

Dihydrochalcone (**15**)

The compound (**15**) could not be isolated as the original state, because of the presence of a small amount of an unknown bibenzyl. The mixture including **15** was directly methylated with diazomethane to afford the methyl ether (**16**), after purification by PLC. The methyl ether (**16**), $C_{21}H_{22}O_4$ (M^+ 338), displayed the presence of a con-



7

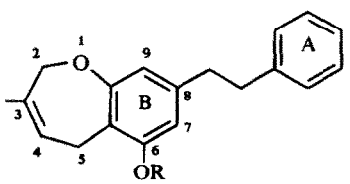
bibenzyls and their derivatives

10	11	12	16	18	21	22
6.80 (*d*, *J* = 8)	6.84 (*d*, *J* = 8)	7.1–7.28 (*m*)	7.30 (*s*)	7.30 (*s*)	7.27 (*s*)	7.26 (*s*)
7.02 (*d*, *J* = 8)	7.07 (*d*, *J* = 8)					
6.38 (*d*, *J* = 2)	6.43 (*d*, *J* = 2)	6.64 (*d*, *J* = 2)	6.50 (*s*)	6.77 (*s*)	6.73 (*s*)	6.60 (*bs*)
6.53 (*d*, *J* = 2)	6.53 (*d*, *J* = 2)	6.80 (*d*, *J* = 2)				
2.85 (*s*)	2.87 (*s*)	2.83 (*s*)		2.92 (*s*)	2.90 (*s*)	2.86 (*s*)
3.40 (*bd*, *J* = 7)	3.42 (*m*)	3.23 (*bd*, *J* = 6)	3.51 (*d*, *J* = 6)	3.45 (*m*)		
5.57 (*m*)	5.53 (*m*)	5.53 (*bt*, *J* = 6)	5.75 (*m*)	5.65 (*m*)		
1.55 (*bs*)	1.53 (*bs*)	1.53 (*bs*)	1.65 (*bs*)	1.57 (*bs*)		
					1.42 (*s*)	1.33 (*s*)
	3.77 (*s*)		4.05 (*s*)	3.95 (*s*)	3.95 (*s*)	3.93 (*s*)
	3.83 (*s*)					
		2.30 (*s*)				
			12.00 (*s*)			
4.42 (*bs*)	4.40 (*bs*)	4.42 (*bs*)	4.53 (*bs*)	4.47 (*bs*)	3.93 (*d*, *J* = 11)	3.8+ (*d*, *J* = 12)
					4.50 (*d*, *J* = 11)	4.20 (*d*, *J* = 12)
				3.78 (*s*)	3.85 (*s*)	3.83 (*s*)
					5.96 (*d*, *J* = 12)	6.01 (*bd*, *J* = 12)
					6.83 (*d*, *J* = 12)	6.63 (*d*, *J* = 12)
			2.7–3.2 (*m*)			

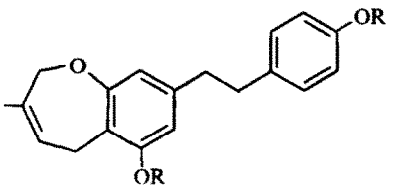
jugated carbonyl group (1660 cm^{-1}) and aromatic group (1620, 1580, 700 cm^{-1}). The NMR and NMDR spectra of **16** contained the signals of one methoxyl group, one proton on aromatic ring, unsubstituted benzene ring (*m/e* 91, 56%, 7.30 ppm, *s*, 5H), two methylene groups located between benzene ring and carbonyl group, and a chelated hydroxyl group (12 ppm, *s*), indicating the characteristic of a 6′-hydroxydihydrochalcone in which the A-ring was unsubstituted. The UV spectrum of 16 showed the absorption bands at 260 and 312 nm, and the bands shifting to 273 and 355 nm, upon addition of $AlCl_3$. These bathochromic shifts supported **16** to be 6′-hydroxydihydrochalcone derivative. The NMR and NMDR spectra further indicated the presence of a vinylic methyl, a vinylic proton, a methylene located between the benzene ring and a double bond and an additional methylene group bearing an ether oxygen, whose chemical shifts and signal pattern were strikingly similar to those of the methyl ethers (**9**) and (**11**). The spectral evidence, along with the biogenetic consideration led us the structure **16** for the methylated dihydrochalcone; hence, the original compound is **15**.

Bibenzyl (**17**)

The most polar fraction was composed of aromatic acid mixture and one acidic bibenzyl (**17**) isolated as a viscous liquid. The compound (**17**) possessed a carboxylic (3500–2600, 1715 cm^{-1}) and an aromatic group (1605, 1582 cm^{-1}). The NMR signal pattern was very similar to that of the bibenzyl **8**, except the presence of the complex signal at 2.7–3.3 ppm (4H) and the broad singlets at 8.22 and 5.38 ppm, which disappeared upon addition



8 R = H
9 R = Me



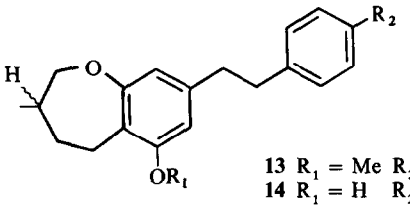
10 R = H
11 R = Me
12 R = Ac

of D_2O. Methylation of **17** gave a methyl ester (**18**), $C_{22}H_{24}O_4$ (M^+ 352) (δ, 3.78 ppm, *s*; 1735 cm^{-1}), followed by oxidation with *m*-chloroperbenzoic acid to afford the stereoisomeric monoepoxides (**19**), $C_{22}H_{24}O_5$ (M^+ 368), indicating the presence of one double bond. The NMR spectrum of **18** was closely similar to that of the methyl ether (**9**), except the presence of the signals of the methyl ester and the absence of one singlet signal of the aromatic proton. These results, coupled with the molecular formula, showed that the methyl ester (**18**) possessed the same skeleton as the bibenzyl (**9**), in which one aromatic proton of **8** was replaced by a carbomethoxyl group. The NMR spectrum of **17** exhibited no hydrogen bonded hydroxyl group, indicating that the carboxylic and the phenolic hydroxyl groups are *para* to each other and one methyl group of γ,γ-dimethyl-allyl group being linked to phenolic ether oxygen in the *ortho* position. Irradiation of the signal at 2.92 ppm due to benzylic methylene groups caused the increase of the intensity of the signal of one aromatic proton. The above results lead to structure **17** [4].

Bibenzyl (**20**)

The most polar acidic bibenzyl (**20**) was isolated as the methylated form, after methylation with large excess diazomethane, followed by purification on PLC. The methylated compound (**21**), $C_{22}H_{24}O_5$ (M^+ 368) showed the presence of carbomethoxyl group (1730 cm^{-1}; δ 3.85 ppm, *s*), hydroxyl group (3350 cm^{-1}), conjugated double bond (265 nm) and an unsubstituted benzyl

group (δ 7.27, *s*, 5H). The NMR spectrum also contained the signals of one methoxyl group, a tertiary methyl group on carbon bearing an hydroxyl group, non equivalent protons of methylene (3.93, $J = 11$; 4.50 ppm, $J =$

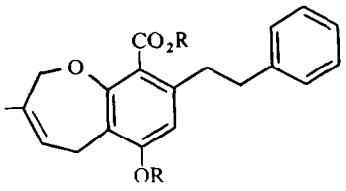


13 R_1 = Me R_2 = H
14 R_1 = H R_2 = OH

11, each, 1H) bearing an ether oxygen and *cis*-ethylenic protons (5.96, $J = 12$; 6.83, $J = 12$). This spectral evidence, along with the similar cracking pattern to that of **18** in the MS showed that **21** possessed the same skeleton as that of **18** or its rearranged skeleton in which a hydroxyl group was placed at C-3 position and a double bond at C-4/C-5 position. Treatment of **21** in the presence of PtO_2 in EtOAc resulted in the formation of a rearranged isomer, $C_{22}H_{24}O_5$ (M^+ 368), whose IR, UV and mass spectra were similar to those of the methyl ester (**21**). Hydrogenation of the rearranged isomer in the presence of pre-reduced PtO_2 in EtOH gave a dihydro derivative (**26**), $C_{22}H_{26}O_5$ (M^+ 370). The NMR signal pattern of the rearranged isomer also closely resembled that of **21**, except the signal pattern of *cis* ethylenic protons. In the rearranged isomer, one olefinic proton at 6.01 ppm showed the broad doublet and it was coupled by the aromatic proton (6.60 ppm, $J = 0.5$) and the another olefinic proton at 6.63 ppm appeared as sharp doublet. On the other hand, in the methyl ester (**21**), both *cis* ethylenic protons showed as a sharp doublet. This fact and the facile rearrangement of **21** supported structure **22** for the rearranged product. Consequently, the structure of the methyl ester of the natural acidic bibenzyl was established to be **21**; hence, the acidic bibenzyl was deduced to be **20**. The absolute configuration at C-2 remains to be established.

Bibenzyl (**24**)

The minor bibenzyl (**24**), $C_{19}H_{20}O_4$ (M^+ 312), was directly methylated with diazomethane to give a dimethyl ether (**25**), $C_{21}H_{24}O_4$ (M^+ 340), followed by hydrogenation to afford a dihydro derivative (**26**), $C_{21}H_{26}O_4$ (M^+ 342), which showed the presence of hydroxyl group (3500 cm^{-1}) and a tertiary methyl group (1.22 ppm). The mass spectrum of **26** indicated the presence of the fragment ion at *m/e* 121 (base) assignable to MeO-$C_7H_6^+$, and *m/e* 221 (M^+-121) and their fragmentation pattern was closely related to that of the bibenzyl **23**. Dehydration of **26** with $SOCl_2$ afforded the less



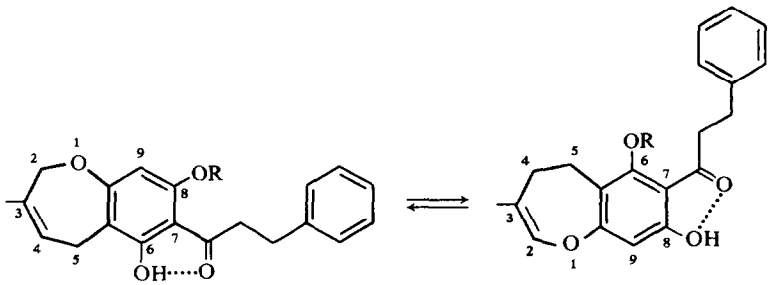
17 R = H
18 R = Me

polar bibenzyl whose chromatographic behaviour and the mass spectrum were completely identical to those of the bibenzyl (**11**). Thus, the structure (**24**) of the original bibenzyl was deduced from the above chemical and spectral evidence.

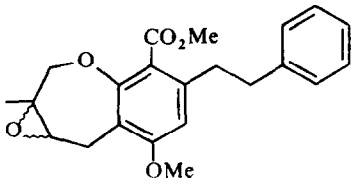
Bibenzyls occur naturally in a few families of higher plants, notably the Combretaceae [5, 6], Dioscoreaceae [7] and Pinaceae [8]. On the other hand, the number of these compounds is steadily increasing in liverworts [9–12] and lunularic acid is particularly significant as the endogenous growth regulator in the liverworts [13, 14]. Compounds containing the nuclear of 2,2-dimethylchromene and 2,2-dimethylchromane are widely distributed in the higher plants. The present new compounds, except for the bibenzyl (**1**) and (**4**), contain the seven-membered heterocyclic ring. As far as we are aware, the present compounds with this heterocyclic ring are the first members of a new group of natural product. Flavonoids and stilbenes have often been found together in the higher plants [8, 15, 16] and the chalcone is an important intermediate to flavonoid. It is known that lunularic acid is synthesized by the shikimate–malonate pathway [14]. The coexistence of the bibenzyls and a dihydrochalcone with one or two isoprene units in *Radula variabilis* suggests that the present compounds might be synthesized by the same route as lunularic acid and that the isoprene chain is introduced into benzene ring (B) and cyclized before or after decarboxylation.

EXPERIMENTAL

UV spectra were in 95% EtOH; NMR spectra were run in $CDCl_3$ at 90 or 60 MHz. IR spectra were in liquid film unless otherwise stated. MS were recorded using a direct inlet system or GC-Mass at 70 eV. GLC for the GC–MS were recorded using glass column, OV-1 5%. ORD curves and optical rotation were



15 R = H
16 R = Me



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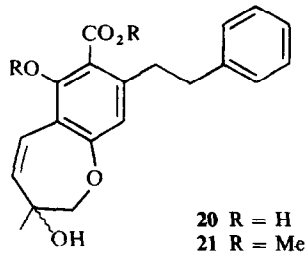
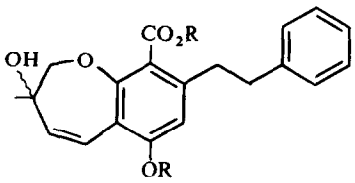
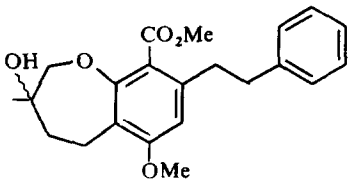


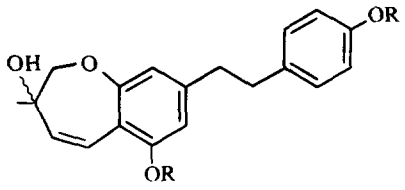
20 R = H
21 R = Me



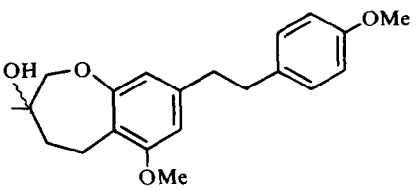
22 R = Me



23



24 R = H
25 R = Me



26

measured in MeOH. TLC spots were detected with UV light and 50% H_2SO_4 spraying, then heating at 120°. TLC and PLC solvent system: C_6H_6–EtOAc (4:1) and C_6H_6–EtOAc–MeOH (10:5:1).

Extraction and isolation. Radula variabilis collected in Tokushima Prefecture, Ananshi, Kamodani (150 m) in June 1977, was washed with H_2O. After being air-dried for 1 week, the ground material (120 g) was extracted with MeOH for 2 weeks and the crude extract (6.06 g) was directly chromatographed on Si gel using *n*-hexane–EtOAc gradient. The first fraction eluted by *n*-hexane contained *n*-paraffin mixtures (12 mg). The next fraction (*n*-hexane-EtOAc 19:1) gave a mixture of sesquiterpene hydrocarbons (292 mg), not identified. The third fraction (4:1) contained a blue fluorescent compound and yielded the bibenzyl (**8**) (72 mg), $C_{19}H_{20}O_2$, λ_{max} 221 nm (ε, 6584), 279 (1573); ν_{max} 3370, 1625, 1590, 1500 and 700 cm^{-1}; *m/e* (%) 280 (M^+, 88), 265 (M^+-15, 100), 189 (M^+-91, 99), 174 (M^+-15-91, 41), 105 ($C_6H_5CH_2$-CH_2^+, 29), 91 ($C_7H_7^+$, 70). Monomethyl ether (**9**), $C_{20}H_{22}O_2$, λ_{max} 206 nm (ε, 4018), 216sh (2744); ν_{max} 1615, 1585, 1495, 1208, 1110, 700 cm^{-1}; *m/e* (%) 294 (M^+, 73), 279 (M^+-15, 100), 203 (M^+-91, 66), 105 (29), 91 (65), 41 (38). Dihydro derivative (**13**) $C_{20}H_{26}O_2$, $[\alpha]_D$ ±0°, ν_{max} 1625, 1585, 1010, 700 cm^{-1}; δ 7.28 ppm (*s*, 5H), 6.36 (*bs*, 1H), 6.30 (*bs*, 1H), 3.86 (OMe), 3.80 (*m*, 2H), 2.90 (*s*, 4H), 2.8 (overlapped, 2H), 1.20 (*d*, *J* = 6, 3H); *m/e* (%) 296 (M^+, 40), 205 (M^+-91, 70), 105 (27), 91 (100).

From the fraction (20:7), the bibenzyl (**10**) (105 mg) and the dihydrochalcone (30 mg) including a small amount of unknown bibenzyl were obtained. Bibenzyl (**10**), $C_{19}H_{20}O_3$, λ_{max} 206 nm (ε, 10360), 227sh (3848), 275 (1322); ν_{max} 3350 (OH), 1610, 1580, 1495, 1060, 745 (*p*-substituted benzene ring); *m/e* (%) 296 (M^+, 90), 281 (M^+-15, 74), 189 (M^+-107, 100), 174 (M^+-15-107, 38), 107 (HO-$C_7H_6^+$, 92). The dimethyl ether (**11**), $C_{21}H_{24}O_3$, λ_{max} 206 nm (ε, 8208), 217sh (6855), 272 (3078), 277sh (2865); ν_{max} 1612, 1582, 1494, 1240, 1100, 750 cm^{-1}; *m/e* (%), 324 (M^+, 47), 309 (M^+-15, 37), 203 (M^+-121, 53), 121 (MeO-$C_7H_6^+$, 100). The diacetate (**13**), $C_{23}H_{24}O_5$, λ_{max} 204 nm (ε, 2150), 206 (2032), 260 (344); ν_{max} 1760, 1220 (OAc), 1620, 1577, 1488, 755 cm^{-1}; *m/e* (%) no molecular peak, 91 (77), 43 ($MeCO^+$, 100), 69 (33). The dihydro derivative (**14**), $C_{19}H_{22}O_3$, λ_{max} 207 nm (ε, 3378), 277 (353); $\nu_{max}^{CHCl_3}$ 3440 (OH), 1620, 1585, 1115 cm^{-1}; *m/e* (%) 298 (M^+, 82), 191 (M^+-107, 100), 107 (30). The dihydrochalcone mixture was methylated with CH_2N_2, followed by PLC to give pure methyl ether (**16**) (25 mg), $C_{21}H_{22}O_4$, λ_{max} 205 nm (ε, 2894), 217 (3143), 260 (823), 312 (462); $\lambda_{max}^{EtOH+AlCl_3}$ 206 nm (ε, 3232), 218 (3189), 273 (820), 292sh (570), 355 (464); ν_{max} 1660 (C=C—CO), 1620, 1580, 1500, 1295, 1160, 810, 750, 700 cm^{-1}; *m/e* (%) 338 (M^+ 72), 306 (M^+-32, 100), 291 (M^+-32-15, 75), 263 (31), 215 (56), 91 (56).

The yellow viscous oil eluted with *n*-hexane–EtOAc (1:1) was rechromatographed on Si gel using C_6H_6–EtOAc gradient to give pure bibenzyls (**1**) (2.30 g), $C_{24}H_{30}O_2$ and (**4**) (4 mg), $C_{24}H_{30}O_3$. The bibenzyl (**1**): λ_{max} 225 nm (ε, 9648), 280 (3831); ν_{max} 3450, 1610, 1595, 1495, 1135, 840, 750, 703 cm^{-1}; *m/e* (%) 350 (M^+, 13), 227 (M^+-C_9H_{15}, 98), 105 (40), 91 (100), 69 (51), 41 (50). The bibenzyl (**4**): *m/e* (%) 366 (M^+, 10), 243 (M^+-C_9H_{15}, 94), 107 (100), 69 (39), 41 (26).

From the fraction eluted with *n*-hexane–EtOAc (7:20), the acidic bibenzyl (**17**) (120 mg) and the bibenzyl (**24**) (17 mg) were obtained. The bibenzyl (**17**): $\nu_{max}^{CHCl_3}$ 3500–2600, 1715 (COOH), 1605, 1582, 1498, 850, 750 cm^{-1}. The methyl ester (**18**), C_{22}-$H_{24}O_4$, λ_{max} 215 nm (ε, 4452); ν_{max} 1735, 1272, 1158 (COOMe), 1610, 1579, 1077, 755, 702 cm^{-1}; *m/e* (%) 353 (M^++1, 63), 352 (M^+, 100), 337 (M^+-15, 43), 321 (M^+-31, 77), 261 (M^+-91, 50), 262 (50), 231 (29), 105 (20), 91 (50), 43 (32), 41 (21). The bibenzyl (**24**), $C_{19}H_{20}O_4$, *m/e* (%) 312 (M^+ 12), 299 (M^+-15, 15), 297 (M^+-17, 26), 207 (M^+-HO-C_7H_6, 77), 107 (100). The methyl ether (**25**), $C_{21}H_{24}O_4$, *m/e* (%) 340 (M^+, 20), 325 (M^+-15, 10), 323 (M^+-17, 19), 219 (M^+- 121, 68), 121 (100). The dihydro derivative (**26**), $C_{21}H_{26}O_4$, ν_{max} 3500 (OH), 1615, 1580, 1498, 1245, 1100, 755 cm^{-1}; 7.06 (*d*, *J* = 8, 2H), 6.80 (*d*, *J* = 8, 2H), 6.58 (*bs*, 1H), 6.50 (*bs*, 1H), 3.88 (*s*, 3H), 3.32 (*s*, 3H), 2.90 (*s*, 4H), 4.1–3.5 (2H, overlapped), 2.66 (*t*, *J* = 6, 2H), 1.78 (*t*, *J* = 6, 2H), 1.22 (*s*, 3H); *m/e* (%) 342 (M^+, 57), 327 (M^+-15,

5), 325 (M^+-17, 5), 309 (M^+-15-18, 14), 221 (M^+-121, 11), 203 (M^+-121-18, 33), 121 (100).

From the fraction (EtOAc 100%), a more polar acidic bibenzyl mixture (105 mg) was obtained. The mixture in MeOH was treated with a large excess of CH_2N_2 and the product purified by PLC to afford pure methyl ester (**21**), (75 mg), $C_{22}H_{24}O_5$, $[\alpha]_D$ ±0°; $[\phi]_{300-600\,nm}$ no absorption; λ_{max} 203 nm (ε, 8025), 206sh (6790), 220 (4345), 265 (2440); $\nu_{max}^{CHCl_3}$ 3400 (OH), 1730, 1265, 1145 (COOMe), 1605, 1560, 1060, 750, 700 cm^{-1}; *m/e* (%) 368 (M^+, 30), 353 (M^+-15, 16), 351 (M^+-17, 25), 350 (M^+-18, 7), 337 (M^+-31, 37), 293 (34), 277 (M^+-91, 68), 105 (17), 91 (100).

Methylation of **1** with $Me_2SO_4/K_2CO_3/Me_2CO$ gave dimethyl ether (**2**), $C_{26}H_{34}O_2$, λ_{max} 207 nm (ε, 2035); ν_{max} 1610, 1590, 1495, 1205, 1120, 910, 830, 740, 700 cm^{-1}; *m/e* (%) 378 (M^+, 50), 309 (M^+-69, 32), 255 (M^+-C_9H_{15}, 100), 105 (68), 91 (77), 69 (36), 41 (50).

Acetylation of **1** overnight with Ac_2O–Py gave the diacetate (**3**), $C_{28}H_{34}O_4$, λ_{max} 206 nm (2411), 217sh (1672); ν_{max} 1767, 1200 (OAc), 1613, 1595, 1495, 1118, 904, 757, 703 cm^{-1}; *m/e* (%) no molecular peak, 91 (77), 69 (33), 43 (100).

Hydrogenation of **1**. EtOAc soln of 1 (113 mg) was hydrogenated in the presence of pre-reduced PtO_2 (50 mg). After absorption of 2 mol of H_2, the catalyst was filtered. Treatment in the usual manner afforded a viscous tetrahydro derivative (**5**), $C_{24}H_{34}O_2$, λ_{max} 207 (ε, 1889); ν_{max} 3238 (OH), 1620, 1600, 1499, 1140, 840, 760, 700 cm^{-1}; *m/e* (%) 354 (M^+, 34), 227 (M^+-C_9H_{19}, 100), 137 (15), 127 ($C_9H_{19}^+$, 10), 91 (18), 43 (10). The methyl ether (**6**), $C_{26}H_{38}O_2$, λ_{max} 227 (8420), 273 (3595); ν_{max} 1610, 1590, 1495, 1202, 1150, 910, 830, 740, 700 cm^{-1}; *m/e* (%) 382 (M^+, 25), 255 (M^+-C_9H_{19}, 100), 151 (11), 91 (10).

Cyclization of **1**. The bibenzyl **1** (250 mg) in HOAc (5 ml) and conc HCl (1 ml) was heated at 115° for 2 hr. The product, a pale brown oil, was purified by PLC to afford the chromane derivative (**7**) (120 mg), $C_{24}H_{31}O_2Cl$, λ_{max} 211 nm (ε, 19275), 233sh (5979), 285 (1739); ν_{max} 3400 (OH), 1620, 1600, 1500, 1145, 845, 750, 700 cm^{-1}; δ 7.35 (*s*, 5H), 6.37 (*bs*, 1H), 6.28 (*bs*, 1H), 4.83 (*bs*, 1H, OH), 2.87 (*s*, 4H), 2.55 (*t*, *J* = 6, 2H), 1.80 (*t*, *J* = 6, 2H, overlapped), 1.60 (*s*, 6H, $(Me)_2CCl$); *m/e* (%) 388 (M^+, $C_{24}H_{31}O_2Cl^{37}$, 2), 386 (M^+, $C_{24}H_{31}O_2Cl^{35}$, 6), 352 (M^+-HCl^{37}, 12), 350 (M^+-HCl^{35}, 46), 265 (36), 259 (M^+-91, 7), 227 (100, $C_{15}H_{15}O_2^+$), 91 (39).

Oxidation of **18**. The bibenzyl (**18**) (55 mg) in $CHCl_3$ (3 ml) was treated with *m*-chloroperbenzoic acid (80 mg) for 12 hr. Work up as usual afforded stereoisomeric monoepoxides (**19**) (52 mg). $C_{22}H_{24}O_5$, λ_{max} 205 nm (ε, 2229), 215sh (1385); ν_{max} 1735, 1274 (COOMe), 1602, 1570, 1150, 1060, 694 cm^{-1}; δ 7.33, (*s*), 7.40 (*s*), 6.73 (*bs*), 4.50 (*d*, *J* = 12), 4.03 (*d*, *J* = 12), 4.00 (*s*, OMe), 3.83 (*s*, COOMe), 3.36 (*m*, 2H), 2.90 (*s*), 1.90 (*m*), 1.56 (*s*, Me—C—O), 1.26 (*s*, Me—C—O); *m/e* (%) 368 (M^+, 70), 337 (M^+-31, 37), 279 (52), 277 (M^+-91, 57), 219 (37), 105 (31), 91 (100).

Rearrangement of **21**. **21** (50 mg) in EtOAc (2 ml) was added to PtO_2 (10 mg) in EtOAc (0.5 ml) and stirred for 30 min at room temp. Filtration of catalyst and then evapn of solvent gave a more polar methyl ether (**22**) (42 mg), $C_{22}H_{24}O_5$, $[\alpha]_D$ ±0° $[\phi]_{300-600\,nm}$ no absorption; λ_{max} 207 nm (ε, 6567), 215 (6284), 263 (2660), 275 sh (1811), ν_{max} 3450 (OH), 1730, 1270, 1140 (COOMe), 1065, 750, 700 cm^{-1}; *m/e* (%) 368 (M^+, 34), 337 (M^+-31, 35), 293 (32), 279 (43), 278 (51), 277 (M^+-91, 100), 91 (85).

Hydrogenation of **22**. The rearranged product (**22**) (25 mg) in EtOH (2 ml) was hydrogenated in the presence of pre-reduced PtO_2 for 3 hr. Work up as usual gave a dihydro derivative (**23**) (18 mg), $C_{22}H_{26}O_5$, λ_{max} 213 nm (ε, 8695); ν_{max} 3450, 1728 (COOMe), 1605, 1565, 1300, 1270, 1150, 1060, 700 cm^{-1}; δ 7.28 (*s*, 5H), 6.73 (*s*, 1H), 4.01 (*d*, *J* = 10, 1H), 3.96 (*s*, OMe), 3.80 (*s*, COOMe), 3.61 (*d*, *J* = 10, 1H), 2.86 (*s*, 4H), 2.85 (*t*, *J* = 6, 2H), 1.73 (*t*, *J* = 6, 2H), 1.25 (*s*, 3H); *m/e* (%) 370 (M^+, 24), 339 (M^+-31), 281 (55), 280 (M^+-31-59, 100), 279 (M^+-91, 36), 261 (M^+-91-18, 20), 91 (80).

Dehydration of **26**. The bibenzyl (14 mg) was treated with redistilled $SOCl_2$ (0.5 ml) and Py (0.8 ml). After passing through a short Si gel column, the product was obtained as a mixture; the GC–MS and R_f of the main peak was completely identical to that of bibenzyl (**11**).

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