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NEW TRITERPENES AND FLAVONOIDS FROM  
THE LEAVES OF *BOSISTOA BRASSII*

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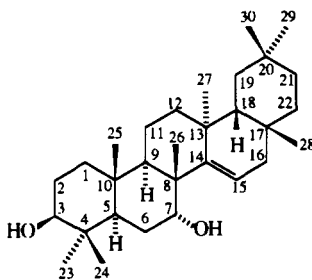
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**ABSTRACT.**—Four triterpenes and five flavonoids were isolated from the leaves of *Bosistoa brassii* (Rutaceae) and identified using spectroscopic methods. The triterpenes were characterized as baurenol and multiflorenol (isolated as a mixture), friedelan-3 $\beta$ -ol, and D-friedoolean-14-ene-3 $\beta$ ,7 $\alpha$ -diol [1]. Four of the flavonoids were identified as kumatakenin (5,4'-dihydroxy-3,7-dimethoxyflavone) [2], 5,7-dihydroxy-3-methoxy-4'-(3-methylbut-2-enyloxy)flavone [3], 5,7-dihydroxy-4'-methoxy-8-(3-methylbut-2-enyl)flavanone [4], and 5,7-dihydroxy-4'-methoxy-8-(2-hydroxy-3-methylbut-3-enyl)flavanone [5]. The fifth flavonoid is a dimer [5,7-dihydroxy-4'-methoxy-8-(3-methylbut-2-enyl)flavanon-6-yl]-[5,7-dihydroxy-4'-methoxyflavanon-8-yl]methane [6], to which we have assigned the trivial name bosistoabiflavanone dimer.

The genus *Bosistoa* F. Muell. ex Benth. (Rutaceae) is confined to the rain forests of eastern Australia, and *Bosistoa brassii* T. Hartley is a small tree found in the coastal strip of northeastern Queensland (1). No previous chemical work has been carried out on this species, and all that is known about the chemistry of the genus is the occurrence of the triterpenes taraxerol and taraxerol methyl ether in *Bosistoa pentacocca* (F. Muell.) Baill. (2). Another taxon, *Bosistoa euodiiformis* F. Muell., was reported to contain acetophenones, furoquinoline alkaloids, limonoids, and the tetracyclic triterpene bosistoin, but this has now been moved from *Bosistoa* and placed in *Acradenia*, as *Acradenia euodiiformis* (F. Muell.) T. Hartley (3). In this paper we report the results of an examination of the leaf of *B. brassii* with the isolation and identification of novel triterpenes and flavonoids.

The leaves of *B. brassii* were extracted sequentially with petroleum ether (bp 60–80°), CH<sub>2</sub>Cl<sub>2</sub>, and MeOH. Each extract was separately concentrated, and preliminary separation was achieved by use of vlc over Si gel, eluting with solvents of increasing polarity. Compounds were isolated from the crude fractions obtained by means of further vlc, preparative tlc, or centrifugal preparative tlc. These procedures yielded two pure triterpenes and a mixture of two further triterpenes from the petroleum ether extract, while five flavonoids were obtained from the CH<sub>2</sub>Cl<sub>2</sub> extract.

Of the triterpenes, one was identified as friedelan-3 $\beta$ -ol by direct comparison with literature data (4) and an authentic sample, and the mixture was characterized as being



made up of equal amounts of baurenol (urs-7-en-3 $\beta$ -ol) and multiflorenol (olean-7-en-3 $\beta$ -ol). The remaining triterpene, which appears to be novel, was identified as D-friedoolean-14-ene-3 $\beta$ ,7 $\alpha$ -diol (7-hydroxytaraxerol) [1] on the basis of the following evidence.

The hreims of 1 indicated the molecular formula C<sub>30</sub>H<sub>50</sub>O<sub>2</sub>, and inspection of the <sup>1</sup>H-nmr spectrum (Table 1) revealed eight Me singlets, carbinolic protons at  $\delta$  3.28 and  $\delta$  4.03 (both showing two couplings only), and an olefinic proton at  $\delta$  5.71. Coupling constants indicated that the  $\delta$  3.28 carbinol was axial while the  $\delta$  4.03 carbinol was equatorial. The presence of a 14,15-olefin was suggested by the occurrence, in the eims, of a major fragment at  $m/z$  318 [C<sub>21</sub>H<sub>34</sub>O<sub>2</sub>]<sup>+</sup> which could derive from rDA fragmentation in ring D. If such a skeleton were present and C-3 were assumed to be oxygenated, then suitable sites for the second OH would be C-1, C-7, and C-12, as in these positions the carbinol would exhibit only two couplings. A further fragment at  $m/z$  236 [C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>]<sup>+</sup>, attributable to rings A and B, eliminated C-12 as a possible hydroxylation site. A COSY-45 study revealed no common couplings for the two carbinols, rul-

TABLE 1. <sup>1</sup>H- and <sup>13</sup>C-nmr Chemical Shift Data and Selected <sup>2</sup>J and <sup>3</sup>J <sup>1</sup>H-<sup>13</sup>C Coupling for Compound 1.\*

Carbon	$\delta_H$	<i>J</i>	$\delta_C$	<sup>2</sup> <i>J</i>	<sup>3</sup> <i>J</i>
C-1 . . . . .	1.0–1.1 m 1.55–1.6 m		37.7 (38.8)		
C-2 . . . . .	1.57–1.67 m		27.4 (28.7)		
C-3 . . . . .	3.28 dd	11.2, 5.1 Hz	79.1 (78.9)		
C-4 . . . . .			38.5 <sup>b</sup> (39.4 <sup>b</sup> )		
C-5 . . . . .	1.50–1.60 m		46.5 (47.3)		
C-6 . . . . .	1.79 td 1.88 dt	13.0, 3.0 Hz 13.0, 4.0 Hz	23.9 (25.5)	46.5 d	38.5/6s
C-7 . . . . .	4.03 dd	4.0, 3.0 Hz	71.6 (72.2)		
C-8 . . . . .			45.7 (46.3)		
C-9 . . . . .	1.95 m		42.1 (43.0)	38.5/6s, 45.7 s	15.6 q, 17.1 t, 26.7 q
C-10 . . . . .			38.6 <sup>b</sup> (39.5 <sup>b</sup> )		
C-11 . . . . .	1.45–1.60 m		17.1 (17.8)		
C-12 . . . . .	1.47–1.55 m 1.60–1.65 m		34.1 (35.3)		
C-13 . . . . .			37.5 (38.0)		
C-14 . . . . .			155.2 (155.1)		
C-15 . . . . .	5.71 dd	8.2, 3.3 Hz	118.7 (119.1)		
C-16 . . . . .	1.71 m 2.00 dd	15.0, 3.0 Hz	36.9 (37.5 <sup>c</sup> )	36.0s, 118.7 d	29.6 q, 49.0 d, 155.2s
C-17 . . . . .			36.0 (36.3)		
C-18 . . . . .	1.00 m		49.0 (49.8)		
C-19 . . . . .	0.9–1.1 m 1.3 m		37.2 (37.8 <sup>c</sup> )		
C-20 . . . . .			29.3 (29.8)		
C-21 . . . . .	1.25 m 1.35 m		33.2 (34.0)		
C-22 . . . . .	1.10 m 1.40 m		35.2 (35.9)		
C-23 . . . . .	1.01 s		27.9 (29.0)	38.5/6s	15.8 q, 46.5 d, 79.1 d
C-24 . . . . .	0.81 s		15.8 (17.0)	38.5/6s	27.9 q, 46.5 d, 79.1 d
C-25 . . . . .	0.93 s		15.6 (16.3)	38.5/6s	42.1 d, 46.5 d, 35.2/34.1 t
C-26 . . . . .	1.17 s		26.7 (27.6)	45.7 s	42.1 d, 71.6 d, 155.2s
C-27 . . . . .	0.93 s		21.1 (21.5)	37.5 s	35.2/34.1 t, 49.0 d, 155.2s
C-28 . . . . .	0.83 s		29.6 (30.2)	36.0s	35.2 t, 36.9 t, 49.0 d
C-29 . . . . .	0.96 s		33.1 (33.5)	29.3 s	29.8 q, 33.2 t, 37.2 t
C-30 . . . . .	0.91 s		29.8 (30.1)	29.3 s	33.1 q, 33.2 t, 37.2 t

\* $\delta_C$  values in parentheses are from C<sub>5</sub>D<sub>5</sub>N solvent; all other data obtained in CDCl<sub>3</sub>. Under <sup>2</sup>*J* and <sup>3</sup>*J* couplings the use of s, d, t, q refers to whether the carbon is quaternary (s), methine (d), methylene (t) or methyl (q).

<sup>b,c</sup>Values may be interchanged.

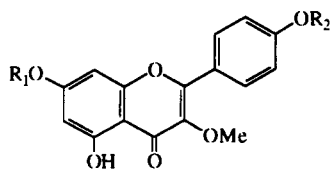
ing out the possibility of C-1 oxygenation, while a NOESY spectrum revealed a strong interaction between the olefinic proton and the carbinol at  $\delta$  4.03, which strongly suggested hydroxylation at C-7.

As all eight methyls occurred as singlets, it seemed probable that this triterpene possessed a taraxerane skeleton. This was confirmed by an exhaustive analysis of long-range C-H coupling obtained using the HMBC technique (5). This revealed two instances of  $^3J$  coupling between the protons of one Me and the carbon of a second Me, a situation that requires the two methyls to be geminal (Table 1). Assuming placement of the geminal methyls at C-4 and C-20 then by identifying long range interactions with the Me protons, C-3, -5, -7, -8, -9, -13, -14, -17, -18, and -20 of the carbon skeleton could be unambiguously assigned while the pairs of carbon resonances for C-1/C-12, C-4/C-10, C-19/C-21, and C-16/C-22 could be identified but not separated. Of these pairs, C-16 and C-22 were separated by reference to the NOESY spectrum (H-15/H-16 interaction), and the COSY-45 revealed the H-18/H-19 interaction and, thus, separated C-19 and C-21. Of the remaining carbons, C-6 was located through direct correlation with the clearly visible H-6, C-15 was confirmed by  $^2J$  correlation to H-16, and C-11 was confirmed by  $^2J$  coupling with H-9 (Table 1). C-2 was assigned by default, and C-1 and C-12 were tentatively separated by comparison of data with that published for taraxerol (6). Differentiation between C-4 and C-10 was not achieved.

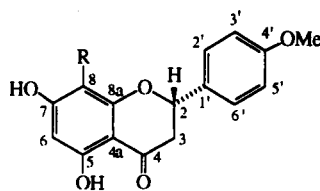
The  $\text{CH}_2\text{Cl}_2$  extract, on vlc, gave three fluorescent fractions (assigned A-C on basis of increasing polarity). Further vlc of bands A and C yielded one pure compound in each case. Circular preparative tlc of B gave three pure compounds (B1-B3 in increasing polarity). The compound from band C was identified as the known flavone kumatakenin (5,4'-dihydroxy-3,7-dimethoxyflavone [2]) (7,8).

Compound B1 analyzed by hreims for  $\text{C}_{21}\text{H}_{20}\text{O}_6$  and gave uv and nmr spectral data similar to those of 2, indicating a kaempferol skeleton. In this case the nmr data (Table 2) indicated a single MeO, two OH (one hydrogen bonded), and 3-methylbut-2-enyloxy substituents. Placement of the MeO at C-3 followed from the chemical shift for the MeO carbon (60.2 ppm). The relatively deshielded resonance for this carbon requires that both positions ortho to it are substituted (9). This was confirmed by a NOESY experiment which revealed interaction of the MeO with H-2'/H-6' of the B ring. The NOESY also showed an interaction between the methyleneoxy protons of the prenyloxy side chain and H-3'/H-5'. This defined the positions of both substituents unambiguously, identifying this flavonoid as 5,7-dihydroxy-3-methoxy-4'-(3-methylbut-2-enyloxy)flavone [3], which appears to be a new natural product.

The compound from band A and that from B2 analyzed (hreims) for  $\text{C}_{21}\text{H}_{22}\text{O}_5$  and  $\text{C}_{21}\text{H}_{22}\text{O}_6$ , respectively. The simple uv spectra and ABX system for H-3/H-2 protons in the  $^1\text{H}$ -nmr spectra suggested that both were flavanones. Other features in the nmr spectra were an AA'BB' system for a para disubstituted aromatic ring, a single MeO, a hydrogen-bonded 5-OH proton, and a single aromatic proton which must be placed in the A ring (Table 2). Further resonances in A could be attributed to a 3-methylbut-3-



- 2  $\text{R}_1 = \text{Me}, \text{R}_2 = \text{H}$   
 3  $\text{R}_1 = \text{H}, \text{R}_2 = \text{CH}_2\text{CH}=\text{C}(\text{Me})_2$



- 4  $\text{R} = \text{CH}_2\text{CH}=\text{C}(\text{Me})_2$   
 5  $\text{R} = \text{CH}_2\text{CH}(\text{OH})\text{C}(\text{=CH}_2)\text{Me}$

TABLE 2.  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr Chemical Shift Data for Flavonoids **3**, **4**, and **5**.<sup>a</sup>

Position	Compound					
	$^1\text{H}$			$^{13}\text{C}$		
	3	4	5	3	4	5
2 . . . . .	—	5.36 dd 12.9, 3.0 Hz	5.48 dd 12.8, 3.0 Hz	155.9	78.7	79.1
3 . . . . .	—	3.06 dd 17.1, 12.9 Hz 2.80 dd 17.1, 3.0 Hz	3.16 dd 17.0, 12.8 Hz 2.91 dd 17.0, 3.0 Hz	139.0	43.0	43.3
4 . . . . .	—	—	—	179.1	196.5	196.8
4a . . . . .	—	—	—	105.6	103.1	103.1
5 (OH) . . .	13.40 s	12.01 s	12.78 s	157.6	162.1	163.3
6 . . . . .	6.74 d 2.1 Hz	6.02 s	6.50 s	99.9	96.7	97.2
7 (OH) . . .	—	6.55 s	—	166.0	163.7	167.2
8 . . . . .	6.79 d 2.1 Hz	—	—	94.7	106.4	106.6
8a . . . . .	—	—	—	163.0	159.8	161.3
1' . . . . .	—	—	—	123.2	130.7	131.8
2'/6' . . . .	8.18 d 9.0 Hz	7.37 d 8.7 Hz	7.57 d 8.7 Hz	130.6	127.5	128.2
3'/5' . . . .	7.17 d 9.0 Hz	6.95 d 8.7 Hz	7.04 d 8.7 Hz	115.2	114.1	114.5
4' . . . . .	—	—	—	161.5	159.8	160.3
3-OMe . . . .	3.95 s	—	—	60.1	—	—
4'-OMe . . .	—	3.84 s	3.69 s	—	55.3	55.3
1'' . . . . .	4.64 d 6.4 Hz	3.30 d 7.0 Hz	3.32 d 6.4 Hz	65.3	21.7	30.5
2'' . . . . .	5.54 t 6.4 Hz	5.20 t 7.0 Hz	4.89 t 6.4 Hz	120.1	121.6	75.6
3'' . . . . .	—	—	—	138.2	134.6	149.2
3''-Me . . . .	1.65	1.70 s	1.97 s	18.1	25.6	18.4
3''-Me . . . .	1.67 s	1.71 s	—	25.6	17.8	—
3''=CH <sub>2</sub> . . .	—	—	5.23 br s 4.92 br s	—	—	110.2

<sup>a</sup>Compounds **3** and **5** run in C<sub>5</sub>D<sub>3</sub>N, **4** in CDCl<sub>3</sub>.

enyl substituent. In the other flavanone these were replaced by signals which could be assigned to a 2-hydroxy-3-methylbut-3-enyl group.

NOESY experiments revealed that in both compounds the MeO was placed at C-4'. Resonance patterns in the  $^{13}\text{C}$ -nmr spectra confirmed oxygenation at C-5 and C-7 in ring A, which meant that the 3-methylbutyl substituents must be placed at C-6 or C-8 with the single aromatic proton occupying the other position. Placement of the prenyl substituent, in both cases, at C-8 followed from HMBC studies that showed a  $^3J$  interaction between the 5-OH proton and the methine carbon for the single unsubstituted position on the A ring. On this basis the two compounds can be identified as 5,7-dihydroxy-4'-methoxy-8-(3-methylbut-2-enyl)flavanone [**4**] and 5,7-dihydroxy-4'-methoxy-8-(2-hydroxy-3-methylbut-3-enyl)flavanone [**5**]. Flavanone **5** appears to be novel. Compound **4** has previously been reported from *Wyethia mollis* (Compositae) although no data was recorded (10).

The  $^1\text{H}$ -nmr spectrum of the final compound (from band B3) showed signals suggesting a 1:1 mixture of two flavanones. However, fabms indicated a molecular formula C<sub>38</sub>H<sub>36</sub>O<sub>10</sub>, establishing that this was a flavanone dimer. Analysis of the  $^1\text{H}$ -nmr spectrum (Table 3) revealed two ABX and two AA'BB' systems, two methoxyls, two hydrogen bonded 5-hydroxyls, and two other acidic hydroxyls (typical of 7-OH). Other signals, not duplicated, could be assigned to a single A-ring aromatic proton, a 3-methylbut-3-enyl system, and an isolated methylene in which the protons were non-equivalent. As with **4** and **5**, an HMBC experiment revealed  $^3J$  coupling linking a 5-OH proton to a C-6 methine carbon. From these data, the dimer must be linked through C-8 of one monomer to either C-6 or C-8 of the second monomer with the other position on the second monomer being occupied by the prenyl substituent. Returning

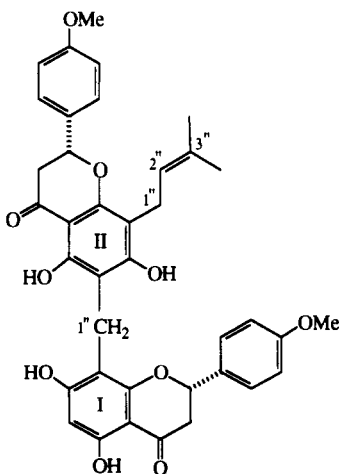
TABLE 3.  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr Chemical Shift Data for Flavanone Dimer **6**.<sup>a</sup>

Position	$^1\text{H}$		$^{13}\text{C}$	
	monomer I	monomer II	monomer I	monomer II
2 . . . . .	5.50 dd 13.3, 2.6 Hz	5.35 dd 12.7, 3.0 Hz	81.4	78.9
3 . . . . .	3.29 dd 17.3, 13.3 Hz 2.81 dd 17.3, 2.6 Hz	3.06 dd 17.3, 12.7 Hz 2.84 dd 17.3, 3.0 Hz	43.0	43.0
4 . . . . .	—	—	195.6	197.1
4a . . . . .	—	—	102.7	102.5
5 (OH) . . . . .	11.96 s	13.64 s	163.3	157.0
6 . . . . .	6.18 s	—	99.1	105.6
7 (OH) . . . . .	9.04 s	7.95 s	165.0	162.2
8 . . . . .	—	—	105.1	109.6
8a . . . . .	—	—	158.3	159.0
1' . . . . .	—	—	128.9	130.9
2'/6' . . . . .	7.49 d 8.7 Hz	7.36 d 8.6 Hz	128.8	127.7
3'/5' . . . . .	7.02 d 8.7 Hz	6.94 d 8.6 Hz	114.7	114.3
4' . . . . .	—	—	161.0	160.1
4'-OMe . . . . .	3.87 s	3.84 s	55.6	55.6
1'' . . . . .	3.66/3.72 ABq 16.0 Hz	3.21 dd 12.0, 7.4 Hz 3.18 dd 12.0, 7.4 Hz	15.6	22.2
2'' . . . . .	—	5.12 t 7.4 Hz	—	122.3
3'' . . . . .	—	—	—	131.7
3''-Me . . . . .	—	1.62 s	—	18.0
3''-Me . . . . .	—	1.65 s	—	26.0

<sup>a</sup>Data obtained in  $\text{CDCl}_3$ .

to the HMBC study, the protons of the isolated methylene showed the six anticipated  $^2J$  and  $^3J$  couplings. Three of these could be attributed to C-7, C-8, and C-8a of the monomer to which it was bonded at C-8. The other couplings were found to involve C-5, C-6, and C-7 of the second monomer, so requiring attachment to be at C-6. On this basis the dimer must be assigned structure **6** which is, once again, novel, and has been assigned the trivial name bosistoabiflavanone dimer.

Complete, unambiguous assignments of all carbon resonances were obtained



through HMBC and HMQC experiments. However, while these allowed assignments to be made for the two cinnamic-acid-derived units (C-2 to C-4 plus C-1' to C-6'), it did not differentiate which unit was part of monomer I and which was part of monomer II. This distinction was achieved by means of a NOESY experiment which revealed interactions between the 7-OH proton of monomer II and H-2 and H-2' of monomer I (Figure 1).

Bosistoabiflavanone probably arises through loss of an isobutyl moiety from a biflavanone linked through C-1 of a prenyl substituent attached to C-8 of monomer I to C-6 of monomer II. A plausible biosynthetic route is shown in Scheme 1. Two similar compounds found in the Rutaceae, but in which the prenyl linking group remains intact, are the acetophenone, acrovstone (11), and the mixed acridone/coumarin dimer, acrimarin A (12). The coumarin dimer gerberinol (13) from *Gerbera lanuginosa* (Compositae) has two 4-methylcoumarins linked by a methyl bridge which may arise in the same way.

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv, Perkin-Elmer 552 in MeOH; ir, Perkin-Elmer 781, KBr disks; specific rotations  $[\alpha]_D$ , Perkin-Elmer 241; nmr, Bruker AMX-400 ( $^1\text{H}$  400 MHz,  $^{13}\text{C}$  100.6 MHz); eims AEI-MS902 double-focussing at 70 eV; fabms, VG ZAB-E with nitrobenzyl alcohol matrix; mp's (uncorrected), Reichert Hot Stage. Petroleum ether refers to the bp 60–80° fraction.

PLANT MATERIAL.—Plant material was collected from coastal forests north of Cairns, Queensland, in 1989 and was oven dried. A voucher (T.G. Hartley 15145) has been deposited at the Australian National Herbarium, Canberra.

EXTRACTION AND ISOLATION.—The ground leaves (650 g) were extracted sequentially in a Soxhlet with petroleum ether,  $\text{CH}_2\text{Cl}_2$ , and MeOH. The concentrated petroleum ether extract was fractionated by vlc over Si gel eluting with petroleum ether containing increasing amounts of EtOAc. Elution with 12% EtOAc yielded a mixture of baurenol and multiflorenol (520 mg, identified by direct comparison with authentic samples of both components); 15% EtOAc followed by preparative tlc [Si gel, solvent  $\text{CHCl}_3$ -hexane (2:1)] gave friedelan-3 $\beta$ -ol (10 mg); 45% EtOAc and subsequent vlc with  $\text{CHCl}_3$ -MeOH (3:2) yielded **1** (11 mg).

Identical treatment of the concentrated  $\text{CH}_2\text{Cl}_2$  extract gave three bands from vlc: A, eluted with 35% EtOAc, B, eluted with 35–45% EtOAc, and C, eluted with 55–70% EtOAc. Further vlc of band A gave **4** (80 mg) on elution with 30–40%  $\text{CHCl}_3$  in MeOH. Band B was further fractionated by circular preparative tlc using 20% EtOAc in petroleum ether which gave, in order of elution, **3** (11 mg), **5** (18 mg), and **6** (10 mg). Finally, further vlc of band C, eluting with  $\text{CHCl}_3$ , gave **2** (8 mg).

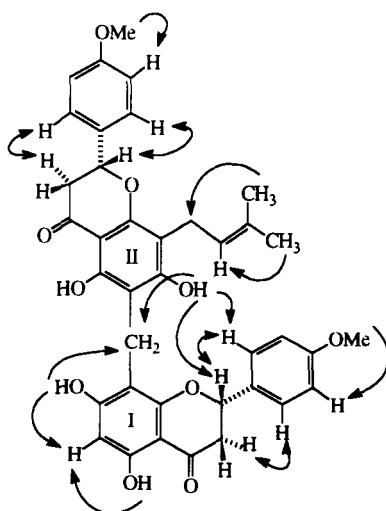
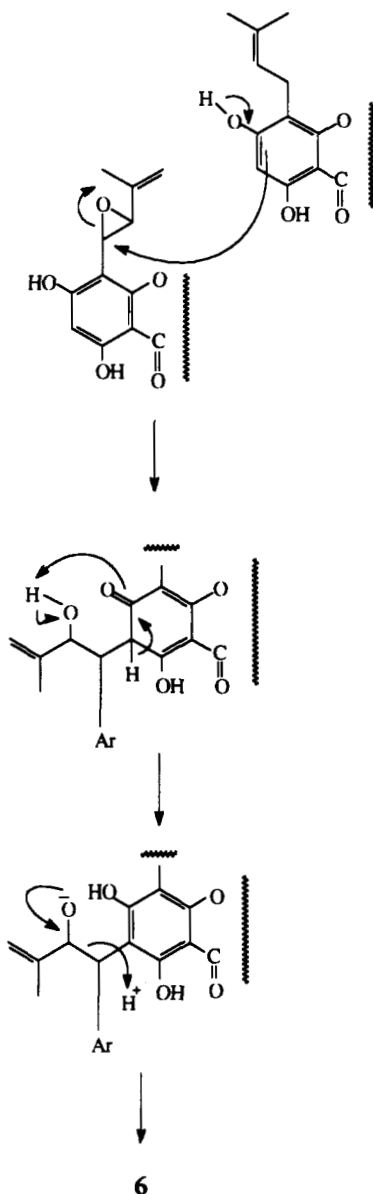


FIGURE 1. The nOe of bosistoabiflavanone [6].



SCHEME 1. Putative route for the formation of bosistoabiflavanone [6].

*Friedelan-3 $\beta$ -ol.*—Needles from EtOAc: mp 294–295° [lit. (4) 290°];  $^1\text{H}$  nmr ( $\text{CDCl}_3/\text{CD}_3\text{OD}$ )  $\delta$  0.68 (3H, d), 0.63, 0.70, 0.72, 0.75, 0.76, 0.78, 0.93 ( $7 \times 3\text{H}$ ,  $7 \times \text{s}$ ), 3.46 (1H, m, H-3); eims  $m/z$  (%)  $[\text{M}]^+$  428.4007 (calcd for  $\text{C}_{30}\text{H}_{52}\text{O}$ , 428.4018) (100), fragmentation in agreement with published data (14).

*D-Friedoolan-14-ene-3 $\beta$ ,7 $\alpha$ -diol* [1].—Needles from EtOAc/MeOH: mp 275–279°;  $[\alpha]_{\text{D}} -14$  ( $c = 0.14$ ,  $\text{CHCl}_3$ ); ir  $\nu$  max 3565, 3470, 1470, 1380, 1360, 1255, 1070, 1045, 1025  $\text{cm}^{-1}$ ;  $^1\text{H}$  and  $^{13}\text{C}$  nmr see Table 1; eims  $m/z$  (%)  $[\text{M}]^+$  442.3798 (calcd for  $\text{C}_{30}\text{H}_{50}\text{O}_2$  442.3811) (74), 427 (20), 409 (25), 318 (100), 285 (15), 272 (75), 236 (44), 204 (31), 147 (20), 145 (23), 135 (26), 134 (20), 133 (20), 123 (18), 121 (34), 119 (29), 109 (26), 107 (27), 105 (24), 95 (35), 93 (23), 91 (20), 81 (31).

*Kumatakenin* [2].—Yellow needles from EtOAc/petroleum ether: mp 254–256° [lit. (7) 252–254°]; uv  $\lambda$  max 265, 292, 350 nm;  $^1\text{H}$  nmr ( $\text{C}_5\text{D}_5\text{N}$ )  $\delta$  3.59 (3H, s), 3.77 (3H, s), 6.39 (1H, d,  $J = 2$  Hz), 6.47



(1H, d,  $J = 2$  Hz), 7.07 (2H, d,  $J = 8.5$  Hz), 7.96 (2H, d,  $J = 8.5$  Hz), 13.36 (1H, s); eims  $m/z$  (%)  $[M]^+$  314.0795 (calcd for  $C_{17}H_{14}O_6$ , 314.0791) (100), 313 (99), 296 (30), 295 (28), 285 (33), 271 (62), 167 (18), 143 (21), 131 (11), 121 (30).

**5,7-Dihydroxy-3-methoxy-4'-(3-methylbut-2-enyloxy)flavone [3].**—Yellow needles from EtOAc/petroleum ether: mp 202–203°; uv  $\lambda$  max (log  $\epsilon$ ) 268 (3.84), 300 (3.63), 352 (3.61) nm; ir  $\nu$  max 3140, 1645, 1610, 1570, 1495, 1360, 1295, 1245, 1220, 1180, 1160, 985, 805  $cm^{-1}$ ;  $^1H$  and  $^{13}C$  nmr see Table 2; eims  $m/z$  (%)  $[M]^+$  368.1262 (calcd for  $C_{21}H_{20}O_6$ , 368.1260) (43), 300 (90), 299 (100), 282 (37), 271 (37), 257 (34), 153 (20), 121 (19), 69 (77).

**5,7-Dihydroxy-4'-methoxy-8-(3-methylbut-2-enyl)flavanone [4].**—Yellow clusters from MeOH: mp 165–167°;  $[\alpha]_D -30$  ( $c = 1.05$ ,  $CHCl_3$ ); uv  $\lambda$  max (log  $\epsilon$ ) 290 (3.76), 333 (2.96) nm; ir  $\nu$  max 3160, 1630, 1605, 1585, 1515, 1435, 1355, 1295, 1255, 1250, 1230, 1170, 1085, 1075, 830, 820  $cm^{-1}$ ;  $^1H$  and  $^{13}C$  nmr see Table 2; eims  $m/z$  (%)  $[M]^+$  354 ( $C_{21}H_{22}O_5$ ) (100), 311 (22), 299 (27), 220 (34), 205 (47), 192 (40), 177 (36), 165 (56), 134 (48), 121 (42), 119 (19), 91 (21), 77 (16), 65 (18).

**5,7-Dihydroxy-4'-methoxy-8-(2-hydroxy-3-methylbut-3-enyl)flavanone [5].**—Cream needles from EtOAc/petroleum ether: mp 215–218°;  $[\alpha]_D -53$  ( $c = 1.36$ ,  $CHCl_3$ ); uv  $\lambda$  max (log  $\epsilon$ ) 289 (4.05), 328 (3.45) nm; ir  $\nu$  max 3260, 1640, 1610, 1510, 1360, 1345, 1305, 1260, 1195, 1170, 1095, 835  $cm^{-1}$ ;  $^1H$  and  $^{13}C$  nmr see Table 2; eims  $m/z$  (%)  $[M]^+$  370.1409 (calcd for  $C_{21}H_{22}O_6$ , 370.1416) (43), 300 (61), 299 (100), 166 (44), 165 (95), 135 (26), 134 (40), 121 (15).

**Bosistoabiflavanone dimer [5,7-Dihydroxy-4'-methoxy-8-(3-methylbut-2-enyl)flavanon-6-yl]-[5,7-dihydroxy-4'-methoxyflavanon-8-yl]methane [6].**—Yellow needles from EtOAc/petroleum ether: mp 188–191°;  $[\alpha]_D -20$  ( $c = 0.65$ ,  $CHCl_3$ ); uv  $\lambda$  max (log  $\epsilon$ ) 301 (4.00), 326 sh nm; ir  $\nu$  max 3380, 1635, 1610, 1515, 1445, 1250, 1170, 1110, 830  $cm^{-1}$ ;  $^1H$  and  $^{13}C$  nmr see Table 3; fabms  $m/z$  (%)  $[M + H]^+$  653, 367 (100), 311 (39), 299 (57), 233 (25).

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