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REVISED STRUCTURE OF BROUSSOFLAVONOL G AND THE 2D NMR SPECTRA OF SOME RELATED PRENYLFLAVONOIDS

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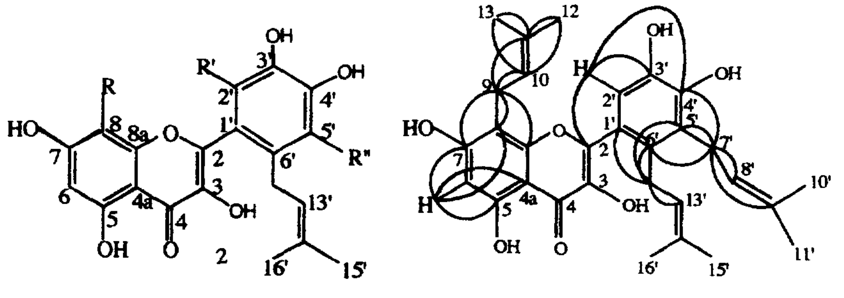
Key Word Index—*Broussonetia papyrifera*; Moraceae; broussoflavonol G; 2D NMR; prenylflavonoids.

Abstract—The structure of broussoflavonol E (8,2′, 6′-triprenyl-3,5,7,3′,4′-pentahydroxyflavone), renamed broussoflavonol G, from Formosan *Broussonetia papyrifera*, has been revised to be 8,5′,6′-triprenyl-3,5,7,3′,4′-pentahydroxyflavonol. The ^{13}C NMR spectra of the prenylflavonoids, cyclomorusin, cycloartomunin and dihydroisocycloartomunin, from Formosan *Artocarpus communis*, were reassigned using 2D techniques.

INTRODUCTION

In a previous paper [1], we reported the isolation of two new *iso*prenylated flavonols, broussoflavonols E (**1**) and F from Formosan *Broussonetia papyrifera*. The structure of **1** was determined by spectral methods and comparison of chemical shifts with those of corresponding data for broussoflavonol C (**2**) [2]. In the ^{13}C NMR spectrum of **1**, the chemical shift value of C-12′ was not in agreement with the value observed by Fukai and Nomura [3]. Therefore, the two prenyl groups of **1** were incorrectly assigned at C-2′ and C-6′, respectively. In the present paper, we rename **1** as broussoflavonol G (**3**) because of broussoflavone E, a prenylflavonol isolated from the root bark of *B. papyrifera* (L.) Vent. × *B. Kazinoki* Sieb [3], report the revised structure of **1** and reassign the ^{13}C NMR spectra of the prenylflavonoids, cyclomorusin



1: $R=R'=CH_2\text{-}CH=C(CH_3)_2$, $R''=H$

2: $R=CH_2\text{-}CH=C(CH_3)_2$, $R'=C(CH_3)_2\text{-}CH=CH_2$, $R''=H$

2′: $R=C(CH_3)_2\text{-}CH=CH_2$, $R'=H$, $R''=CH_2\text{-}CH=C(CH_3)_2$

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Fig. 1. Structure of compounds **1**, **2**, **2′**, **3** and HMBC of **3**.

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Table 1. ^{13}C NMR chemical shifts of compounds **2′** [2], **3**, **4** [4], **5** [4] and **6** [5]

C	2′*	3†	C	4‡	5‡	6†
C-2	148.7	151.1	C-2	159.6	151.2	153.1
C-3	136.2	137.9	C-3	110.3§	110.2§	111.1*
C-4	175.8	177.6	C-4	179.8	178.5	181.0
C-4a	105.2	105.2	C-4a	106.3§	105.6§	106.5
C-5	159.5	160.5	C-5	156.9	151.3	153.1
C-6	100.9	99.1	C-6	100.7	100.2	100.3
C-7	161.8	162.2	C-7	163.2	161.8	162.3§
C-8	110.1	107.5	C-8	102.6§	101.4§	108.5§
C-8a	155.7	156.2	C-8a	160.4	159.1	163.4§
C-9	40.5	22.4	C-9	70.5	69.6	70.6
C-10	27.5	123.5	C-10	122.4	120.8	123.2
C-11	28.1	131.8	C-11	139.3	139.2	139.7§
C-12	149.1	17.8	C-12	18.7	18.6	18.8
C-13	113.6	25.9	C-13	26.0	25.9	26.1
C-1′	122.7	122.9	C-14	115.7	114.8	22.5
C-2′	114.2	115.8	C-15	129.1	127.5	124.5
C-3′	142.0	143.3	C-16	79.1	78.0	133.2
C-4′	144.8	146.2	C-17	28.4	28.1	18.4
C-5′	127.1	128.7	C-18	28.4	28.2	26.1
C-6′	132.7	131.4	C-1′	108.6§	108.0	109.4§
C-7′	26.2	26.4	C-2′	152.4	140.5	143.9
C-8′	121.9	124.6	C-3′	105.2	100.8	102.9
C-9′	134.4	133.4	C-4′	164.8	155.1	157.8§
C-10′	18.0	18.1	C-5′	111.3	151.3§	155.1§
C-11′	25.8	25.9	C-6′	126.9§	108.0	110.3
C-12′	29.2	29.4	OMe	—	56.2	57.1
C-13′	123.5	125.4	—	—	—	—
C-14′	131.4	132.2	—	—	—	—
C-15′	17.8	17.8	—	—	—	—
C-16′	25.4	25.6	—	—	—	—

*Measured in $CDCl_3 + CD_3OD$.
†Measured in $(CD_3)_2CO$.
‡Measured in $CDCl_3$.
§Signals revised.

(**4**), cycloartomunin (**5**) and dihydroisocycloartomunin (**6**), from *Atrocarpus communis* by 2D spectra.

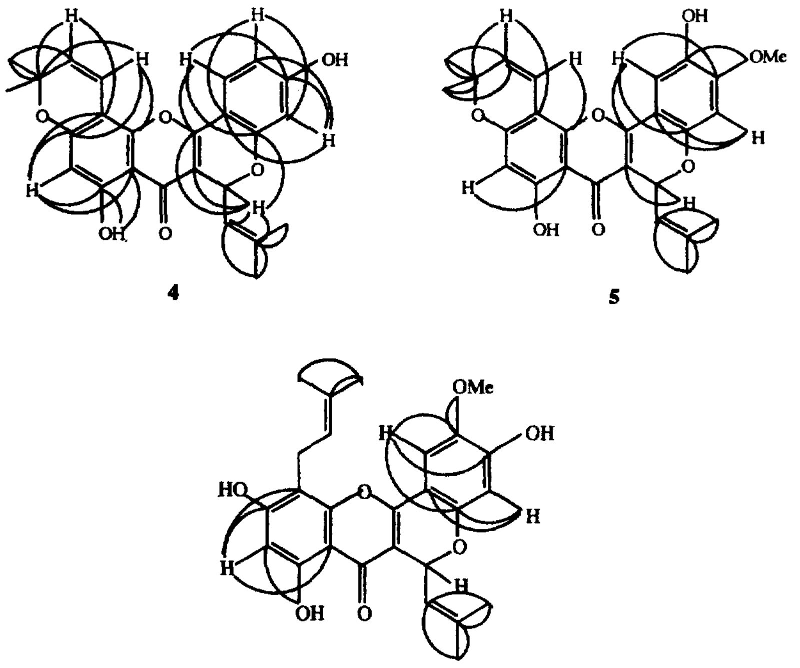
RESULTS AND DISCUSSION

The EI mass spectrum of **3** indicated the presence of a prenyl group in the A-ring and two prenyl groups in the B-ring [1]. The ^{1}H NMR spectrum and an $AlCl_3$-induced shift in the UV spectrum of **3** clearly indicated that the prenyl group in the A-ring of **3** was placed at C-8 [1]. The ^{13}C NMR spectrum of **3** (Table 1) was reassigned by ^{1}H-decoupled spectra, DEPT pulse sequence, HMQC and HMBC correlations (Fig. 1) and comparison of chemical shifts with those of corresponding data for revised broussoflavonol C (**2′**) [3]. In the ^{13}C NMR spectrum of **3**, the chemical shift values of the C-1 position of the prenyl groups were observed at δ22.4, 26.4 and 29.4, respectively. These chemical shifts clearly indicated that the prenyl groups were at C-8, C-5′ and C-6′, respectively [3]. The remeasured HMBC correlations (Fig. 1) also supported the revised structure as **3**. Thus, in the ^{1}H NMR spectrum of **3**, the signal at δ6.90 was revised and assigned to H-2′.

Assignment of the ^{13}C NMR spectra of cyclomorusin (**4**), cycloartomunin (**5**) and dihydroisocycloartomunin (**6**) have been reported [4, 5]. For further confirmation of these assignments, the ^{13}C NMR spectra of **4**–**6** were reassigned by ^{1}H-decoupled spectra, DEPT pulse sequence, ^{1}H–^{1}H and ^{1}H–^{13}C COSY spectra and ^{1}H–^{13}C long-range HETCOR, respectively (Table 1 and Fig. 2). These clearly indicated that the C-3 carbon signal of a flavone induced a downfield shift of *ca* 11–12 ppm due to its 2′-hydroxyl group being oxidatively cyclized with the doubly allylic methylene of a prenyl chain in the 3-position, as in cyclomorusin (**4**).

EXPERIMENTAL

^{1}H and ^{13}C NMR were measured using a Bruker AM-400 or Varian Gemini 200 MHz FT-NMR; spectral data are reported as ppm downfield from TMS ($\delta = 0$).



4 5 6

Fig. 2. ^1H–^{13}C long-range HETCOR of compounds 4–6.

For ^{13}C assignments, broad-band decoupled ^{13}C and DEPT expts were carried out. In order to make unambiguous characterization of compound or assignment of carbon signals, additional ^1H–^1H and ^1H–^{13}C shift-correlated 2D-NMR expts were also performed for the compounds.

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