47), 244 (12), 235 (13), 232 (17), 230 (100), 207 (17), 203 (26), 193 (47), 181 (17), 175 (13), 167 (17), 161 (21), 153 (73), 148 (15), 140 (11), 139 (73), 123 (35), 115 (29).

Hydrogenation of **2**.—Hydrogenation of 5 mg of **2** in MeOH in the presence of 1 mg of 5% palladium-on-carbon for 12 h (1 atom H_2) followed by filtration, and evaporation of the solvent yielded 4.5 mg of a sticky white solid (**5**); ir 3600-2500 (br), 1710 cm^{-1}; ^1H nmr ($CDCl_3$) 0.86 (3 H, br t, J=6 Hz), 0.92 (6 H, br d, J=7 Hz, 2 sec. Me), 1.21 (10 H, br m), 2.49 (2H, m), 6.31 (1 H, s, H-3), 7.97 (1 H, s, H-1), 10.2 (1 H, br s, $-CO_2H$); ms (70 ev) *m/z* (rel. int.) 252 (M+, 7.1), 207 (4.8), 195 (8), 181 (22), 164 (9), 157 (26), 153 (71), 139 (56), 130 (72), 126 (56), 125 (50), 113 (40), 112 (100), 109 (16), 108 (11), 107 (26), 95 (24), 87 (28), 85 (45), 84 (29), 83 (16), 81 (25), 71 (44), 69 (46), 57 (53).

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MAJOR CONSTITUENTS OF THE ESSENTIAL OILS OF THE FIJIAN DACRYDIUMS

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The leaf oils of some *Dacrydium* species, particularly *Dacrydium cupressinum* Sol. ex. Lamb. have been extensively studied, and the diterpene hydrocarbon rimuene has been the subject of a number of structural investigations (1-3).

The essential oils of the Fijian species *Dacrydium nausoriense* de Laub., whose growth is confined to restricted highland areas, and *Dacrydium nidulum* de Laub. var. *nidulum* have not, to our knowledge, been examined. However, phenolic diterpenoids were extracted from the wood of Fijian *D. nidulum* (4).

Analysis of the freshly extracted, steam-volatile oils was achieved in this study by means of capillary glc and ms. The essential oil content of six trees of *D. nidulum* var. *nidulum* and five of *D. nausoriense* was determined. The results are summarized in Table 1.

Some of the major components of the volatile oils that were identified from the Dacrydiums include α-pinene (up to 58%), caryophyllene, aromadendrene, viridiflorene, camphene, bicyclogermacrene, β-farnesene, and rimuene (up to 58%). The α-pinene content was significantly higher for trees obtained from the Nausori Highlands area. Twenty-one compounds were detected in *D. nidulum* var. *nidulum*, of which 19 have been identified; 32 compounds were detected in *D. nausoriense*, of which 26 have been identified. Of the compounds detected, 19 were common to both *Dacrydium* species (Table 1).

TABLE 1. Percent Composition of Essential Oils of Fijian Dacrydiums

Oils	*D. nidulum* var. *nidulum*	*D. nausoriense*
α-Pinene	7.6-44.9	3.1-58.4
Camphene	ND[a]	9.4-22.4
β-Pinene	0.4-21.2	2.0- 4.8
Sabinene	ND	1.6- 4.5
Myrcene	1.0- 3.9	
α-Terpinene	0.2- 0.9	0.3- 0.8
Limonene	0.2- 2.4	0.6- 1.8
β-Phellandrene	0.2- 1.3	0.8- 1.2
γ-Terpinene	tr- 1.5	0.5- 1.4
Terpinolene	0.3- 1.5	0.7- 1.3
γ-Elemene	0.7- 0.9	ND
Undecan-3-one	ND	0.1- 1.0
α-Cubebene+$C_{15}H_{24}$	0.7- 3.4	0.1- 0.8
β-Ylangene (tent)	0.1- 3.2	0.2- 1.7
α-Copaene	ND	tr
Terpinen-4-ol	ND	- 0.6
Caryophyllene	0.7-10.4	0.4- 1.2
Aromadendrene	0.3- 1.2	0.2- 0.9
Alloaromadendrene	ND	tr- 0.2
α-Humulene	tr[b]	tr
β-Farnesene	2.2- 7.8	0.5- 7.9
α-Terpineol	ND	tr- 2.2
Viridiflorene	0.4- 1.8	tr- 2.5
Bicyclogermacrene	0.6- 1.5	1.5- 2.4
$C_{15}H_{24}$	0.6- 1.3	tr
Caryophyllene oxide	ND	tr
$C_{15}H_{26}O$	ND	tr
$C_{15}H_{26}O$	ND	tr
$C_{20}H_{32}$	ND	0.1- 0.6
$C_{20}H_{32}$	ND	0.2- 9.0
Viridiflorol	tr	tr- 4.0
$C_{20}H_{32}$, Rimuene	15.3-58.5	3.5-39.7

[a]ND=compound not detected.
[b]tr=<0.1%.

Rimuene, $C_{20}H_{32}$, was the major diterpene constituent of the leaf oils of the Dacrydiums. Its composition varied from about 15%-59% in *D. nidulum* var. *nidulum* to from 4%-40% in *D. nausoriense*. The sample of *D. nidulum* var. *nidulum* with the lowest rimuene content (15%) was obtained from the Nausori Highlands, Nadi. *D. nidulum* var. *nidulum* grown at Tamavua, Suva, contained higher amounts of rimuene than *D. nausoriense*.

Some of the trees, particularly those from the Nausori Highlands, contain some diterpenes (up to 9%), which are yet to be identified and are now being studied.

EXPERIMENTAL

COLLECTION OF PLANT MATERIAL AND ISOLATION OF VOLATILE OILS.—Fresh foliage of *D. nidulum* var. *nidulum* was collected mainly from Tamavua, Suva, and foliage of *D. nausoriense* from the Nausori Highlands. Voucher specimens are kept at the Herbarium, Institute of Natural Resources, USP, Suva. Terminal twigs and leaves (300 g) were steam distilled for 8 h, with a yield of the colorless oil of between 0.1-0.5% of the weight of the fresh plant.

IDENTIFICATION OF OIL COMPONENTS.—Analytical glc was conducted on a Perkin-Elmer Sigma 3B chromatograph using a 3 m×2 mm i.d. glass column containing 15% Carbowax 20 M on Chromosorb W with N_2 as carrier gas at 30 ml/min. The injector port was set at 250° and the FID temperature at 260°. Individual runs were linear-temperature-programmed from 120° to 180° at 5°/min following an initial holding period of 5 min at 120°. The major individual components were tentatively identified by their re-

tention times and by co-injection with authentic compounds. A Perkin-Elmer LCI-100 Computing Integrator was used to determine peak areas and retention times.

The glc-ms determinations were carried out with a Shimadzu GC6-AMP gas chromatograph equipped with a FFAP coated SCOT column (85 m×0.5 mm i.d.) using He as carrier gas. The gas chromatograph was programmed from 70 to 230° at 3°/min; and the mass spectrometer, AE1 MS12, was operated at 70 eV with the ion source at 200°. Spectra were aquired and processed by a VG Digispec Display data system.

FRACTIONATION OF VOLATILE OILS.—Micro-distillation of a sample of volatile oils (0.73 g) obtained from *D. nidulum* var. *nidulum* gave fraction 1, bp 160°-220° (0.53 g) and a 'still-pot' residue, fraction 2 (0.20 g). Plc (hexane) of fraction 2 (80 mg) gave rimuene (50 mg), mp 45°-50° (identical ir, ^{1}H nmr, ^{13}C nmr, ms to rimuene) (2,5).

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FLAVONOIDS FROM *BRICKELLIA SCOPARIA*

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In a continuation of our chemotaxonomic studies of the genus *Brickella* (Compositae, tribe Eupatorieae, subtribe Alomiinae) (1-10), eight 6-methoxyflavonoids were isolated from *Brickella scoparia* (DC) Gray, a member of the previously uninvestigated Section Bulbostylis subsection Clavigera. These compounds, previously reported from our other studies, are characteristic of the main evolutionary line in *Brickellia*, and include 3-*O*-glucosides of kaempferol 6-methyl ether, quercetin 6-methyl ether, and kaempferol 6,7-dimethyl ether as well as five aglycones: 5-hydroxy-3,4′,6,7-tetramethoxyflavone, 5,7-dihydroxy-3,6,4′-trimethoxyflavone, 5,7,3′-trihydroxy-3,6,4′-trimethoxyflavone, 5,7,4′-trihydroxy-3,6-dimethoxyflavone, and 5,7,3′,4′-tetrahydroxy-3,6-dimethoxyflavone.

EXPERIMENTAL

PLANT MATERIAL.—Several populations of *B. scoparia* were collected in the state of Oaxaca on the road between Oaxaca City and Huajuapan de Leon, Mexico, on January 10, 1984. Voucher material (Gage and Norris #1222) is deposited in the Plant Resources Center at The University of Texas at Austin, Austin, Texas.

EXTRACTION AND ISOLATION OF FLAVONOIDS.—Dried leaf material (600 g) was extracted three times with 85% and 50% aqueous MeOH, respectively. The combined extracts were concentrated to an aqueous layer under reduced pressure and the concentrate was partitioned against CH_2Cl_2 and EtOAc. The concentrate from the CH_2Cl_2 extract (16 g) yielded the five aglycones when chromatographed over a Polyclar AT(GAF Corp.) column initially packed in toluene-EtOAc (9:1) and then eluted with this solvent system which was then gradually altered during the chromatographic run in 10% increments to 100% MeOH; the column finally was washed with Me_2CO-H_2O (1:1). The concentrate of the EtOAc extract (8

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