Acetone extract. This was evaporated to dryness *in vacuo*; 20 g of reddish syrup was chromatographed over Si gel affording besides grevillol, three more compounds.

Mono-norstriatol (**1a**). From C_6H_6–EtOAc (9:1) fractions, brownish syrupy liquid (2.2 g). (Found: C, 75.9; H, 9.6. $C_{27}H_{40}O_4$ requires C, 75.7; H, 9.3%.) λ_{max}^{MeOH} 273, 276 nm; +KOH 281, 283 nm. ν_{max}^{KBr} 3500 br (OH), 2976, 1621, 1595, 1440, 1144, 1068, 830, 719 and 693 cm^{-1}; MS: *m/e* 428 (M^+) *tetraacetate* (**1d**) with Py–Ac_2O at room temp., colourless syrup, PMR δ 6.80 (*br*, 5 H, Ar-H), 2.58 (*t*, 4 H, Ar-CH_2), 2.24 (*s*, 6 H, phenolic O*Ac*), 2.19 (*s*, 6 H, phenolic O*Ac*), 1.92 (*s*, 3 H, Ar-Me), 1.25 (*br s*, 24 H, $-(CH_2)_{12}-$); *tetramethyl ether* (**1e**) with K_2CO_3–$(Me)_2CO$–$(Me)_2SO_4$, brown syrup. PMR: δ 6.53 (*br*, 5 H, Ar-H), 4.06 (*s*, 6 H, –OMe), 4.01 (*s*, 6 H, –OMe), 2.80 (*t*, 4 H, Ar-CH_2), 2.28 (*s*, 3 H, Ar-Me), 1.47 (*br s*, 24 H, $-(CH_2)_{12}-$).

Bis-norstriatol (**1b**). From C_6H_6–EtOAc (17:3) eluates, brownish syrup, crystallized as colourless needles (C_6H_6) (5.3 g) mp 97–99°. (Found: C, 75.1; H, 8.9. $C_{26}H_{38}O_4$ requires C, 75.3; H, 9.1%.) λ_{max}^{MeOH} 276 nm; +KOH 282 nm. ν_{max}^{KBr} 3390 (OH), 2950, 1623, 1595, 1480, 1156, 998, 831, 727 and 676 cm^{-1}. PMR(DMSO-D_6, δ) 9.8 (*s*, 4 H, Ar-OH), 6.18 (*br*, 6 H, Ar-H), 2.4 (*t*, 4 H, Ar-CH_2), 1.23 (*br. s*, 24 H $(CH_2)_{12}$–). MS: *m/e* 414 (M^+) 167, 163, 149, 137, 124 (base), 123, 71, 57 and 43. *Tetraacetate* (**1f**) by Py–Ac_2O method in cold, colourless syrup, PMR 6.75 (*br*, 6 H, Ar-H), 2.52 (*t*, 4 H, Ar-CH_2), 2.1 (*s*, 12 H, phenolic O*Ac*), 1.18 (*br s*, 24 H, $-(CH_2)_{12}-$), *tetramethyl ether* (**1g**) by K_2CO_3–$(Me)_2CO$–$(Me)_2SO_4$ method. Colourless rods (EtOAc), mp 63–64°, PMR: δ 6.39 (*br*, 6 H, Ar-H), 3.75 (*s*, 12 H, –OMe), 2.55 (*t*, 4 H, Ar-CH_2), 1.28 (*br*, 24 H, $-CH_2)_{12}-$). MS: *m/e* 470 (M^+) 165, 152, 151, confirmed by direct comparison with synthetic sample [3] (co-TLC, mmp, co-IR).

Acknowledgements—The authors are grateful to Prof. E. Ritchie, University of Sydney, Australia for a sample of bis-norstriatol tetramethyl ether. One of the authors (RSV) thanks the University of Delhi for a Senior Research Fellowship.

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TWO NEW COUMARINS FROM *TODDALIA ACULEATA**

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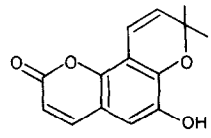
(*Received* 10 *February* 1976)

Key Word Index—*Toddalia aculeata*; Rutaceae; alkaloids; coumarins; norbraylin; 5,7,8-trimethoxycoumarin.

Toddalia aculeata was collected and supplied by Mukerjee & Co., Algarah, Darjeeling, India and is widely distributed in subtropical Himalayas, Southern India and Ceylon. The plant is used in medicine as a tonic, stimulant, and antipyretic.

The plant has been extensively investigated and a number of coumarins and alkaloids have been reported [1,2]. From the chloroform extract of the stem two new coumarins, norbraylin (**1**) and 5,7,8-trimethoxycoumarin have been isolated. In addition 3 alkaloids, robustine, dictamnine and γ-fagarine, and 2 coumarins, bergapten and luvangetin, have been isolated for the first time from this plant.



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The total chloroform extract of the stem was chromatographed over silica gel column and eluted successively with C_6H_6, C_6H_6–$CHCl_3$, $CHCl_3$ and finally $CHCl_3$–MeOH. Some of the fractions were rechromatographed for further purification. From the first few fractions toddalinine, robustine, skimmianine, dictamnine, bergapten, luvangetin and isopimpinellin have been isolated. The final fractions were further separated into phenolic and neutral compounds. The phenolic portion was purified by passing through a short column of Si gel using hexane–Me_2CO (4:1). One compound crystallized as needles, mp 132–34°, M^+ 244 (Found: C, 69.0; H, 5.0. $C_{14}H_{12}O_4$ requires C, 68.9; H, 4.9%). IR, ν_{max} (cm^{-1}) 1720 (C=O of α-pyrone) and 3535 (phenolic OH). NMR ($CDCl_3$, τ60 MHz,) 3.13 and 4.3 (two, *d*, J = 10 Hz) vinylic H, 8.5 (s, *C*–Me_2) presence of 2,2-dimethylchromene ring; 3.7 and 2.5 (two *d* J = 10 Hz) 3- and 4-H of coumarin ring and 3.14 (*s*, 5-H). Hence the compound should have structure (**1**). The linear structure was ruled out as its TLC and mmp was not identical with norluvangetin, MS (*m/e*): 244 (28%), 229 (100) M-15; 243 (2) M-1; 201 (9) (M-43). The coumarin was methylated with diazomethane which gave a crystalline monomethyl ether, mp 150° (lit. [3] mp 150°). The MS fragmentation was consistent with braylin. Thus this phenolic compound is norbraylin, not reported previously. The neutral fraction was purified by passing through a short column of alumina

* NCL communication No. 1969.

using hexane–Me_2CO (4:1). One crystalline compound was isolated mp 165°, M^+ 236 (Found: C, 61.5; H, 5.3. $C_{12}H_{12}O_5$ requires C, 61.0; H, 5.1). IR ν_{max} (cm^{-1}) 1715 (C=O). NMR ($CDCl_3$) 3.81 and 2.03 (two *d*; J = 10 Hz) 3- and 4-H of coumarin, 3.62 (*s*, 6-H); 6 and 6.1 (*s*; 3 OMe). The C_6H_6-induced solvent shifts of OMe groups are seen at 6.2, 6.5 and 6.6, indicating that two OMe groups have suffered a significant upfield shift, suggesting that at least one adjacent position to the two OMe groups is unsubstituted. MS (*m/e*) 236 (100%); 221 (80), M-15; 195 (11), M-41; 194 (93) M-42; 178 (2), M-58; 165 (5) M-71; 150 (11), M-86; 135 (4) M-101; 107 (3) M-129. The compound is therefore 5,7,8-trimethoxycoumarin.

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CHRYSOERIOL 7-*O*-RHAMNOSIDE FROM *SEDUM FORMOSANUM*

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(*Received* 18 *March* 1976)

Key Word Index—*Sedum formosanum*; Crassulaceae; sterols; flavonoid; chrysoeriol 7-*o*-rhamnoside.

Sedum formosanum Hay. has been used in folk-medicine for the treatment of diabetes [1]. We have isolated from it campesterol, stigmasterol and sitosterol and a new flavone glycoside, identified as chrysoeriol 7-*o*-rhamnoside. The sugar was identified as rhamnose by co-chromatography with an authentic sample and confirmed by oxidation of the glycoside with periodate [2]. The NMR spectrum of the glycoside showed the characteristic rhamnoside H-1″ proton and rhamnosyl C-Me group [3]. The aglycone was identified as chrysoeriol from UV, NMR [3] and MS data [4] and this was confirmed by its demethylation to give luteolin. The glycoside lost its sugar on acid hydrolysis, indicating that it was an *o*-glycoside. Comparing the NMR spectrum of glycoside and aglycone showed a downfield shift for H-8 and H-6 indicating that the sugar unit was attracted to oxygen at C-7, a fact confirmed by the absence of a UV shift with NaOAc. Thus the compound is chrysoeriol 7-*o*-rhamnoside. Although a number of chrysoeriol glycoside are known, this is the first report of the 7-rhamnoside.

EXPERIMENTAL

Air-dried whole plants of *Sedum formosanum* were obtained from the beach of Yee-Leou (Taiwan) in May, 1973. NMR spectra were recorded in DMSO-d6. GLC was used with 3% SE-30 column. Mp's are uncorrected.

Extraction and isolation. Plants (5.3 kg) were extracted with *n*-hexane and EtOH successively. Evaporation of the *n*-hexane extract left 1 l. of viscous residue, which was then deposited a precipitate at 4°. The supernatant was further concentrated and then subjected to column chromatography on Si gel and eluted with *n*-hexane–Me_2CO (4:1 l.) giving 1.6 g of the sterol mixture. The EtOH extract was concentrated and the syrupy mass was dissolved in 3% HOAc. The filtered acidic soln was extracted with Et_2O, and a brown ppt. formed. This was dissolved in EtOH, filtered, and the filtrate was conc. and dried. The yellow mass was subjected to column chromatography over Si gel and eluted with 25% MeOH in $CHCl_3$, and MeOH, giving the flavone glycoside, eventually as fine yellow needles from MeOH (15 mg). The sterol mixture crystallized from *n*-hexane as needles, mp 139–40°, which gave a positive Liebermann–Burchard test. It was identified as a mixture of campesterol, stigmasterol and sitosterol by GLC comparison with soybean sterols [5]. Chrysoeriol 7-rhamnoside had mp 287–9° (Found: C, 54.82; H, 5.13. $C_{22}H_{22}O_{10}.2H_2O$ requires: C, 54.77; H, 5.43%). It showed a single spot of polyamide plate (EtOH, FeCl, brown–gray), and gave a violet colour with Mg–HCl, UV maxima 350, 268 *sh*, 253; $AlCl_3$ 388, 355, 296 *sh* 276, 261; NaOAc 418, 356, 268 *sh*, 254; NaOAc + H_3BO_3 351, 268 *sh*, 254, EtONa 418, 261. NMR δ:7.5 (2H, *m*,) 6.93 (1H, *d*, *J*, 9 Hz,) 6.75 (1H, *d*, *J* 2 Hz,) 6.38 (1H, *d*, *J* 2 Hz,) 5.18 (1H, *br*,) 1.25 (3H, *m*,). Its identification was carried out by standard procedures [3].

Acknowledgements—This work was partially supported by the National Council of Science, Republic of China. The authors thank Dr. H. H. Li, Director, National Research Institute of Chinese Medicine, for his encouragement. Thanks are also due to Dr. Y. M. Lin, National Taiwan University, for advice and to Mr. J. H. Lin, for his gift of luteolin.

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