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# CHROMONES AND COUMARINS FROM *SKIMMIA LAUREOLA*

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**Key Word Index**—*Skimmia laureola*; Rutaceae; chromones; skimminin; coumarins; linear furanocoumarins.

**Abstract**—The isolation and characterisation of chromones and coumarins, including the new chromone, skimminin, from *S. laureola* is reported.

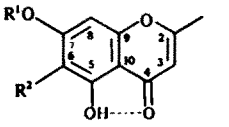
## INTRODUCTION

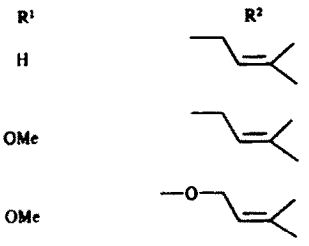
*Skimmia laureola* Seib et Zucc ex Walp. is the only temperate sub-alpine species of the genus endemic to forest shades of Kashmir [1]. Following our studies [2–4] on the chemistry of its essential oil, a detailed investigation on its crystalline constituents was undertaken to supplement the previous work [5–8] indicating the presence of coumarins, lupeol, lupenone and the lone alkaloid, skimmianine, in the plant. During the present investigation a new chromone, designated as skimminin has been isolated and characterised along with other compounds.

## RESULTS AND DISCUSSION

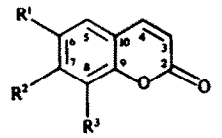
From the hot ethanolic extract of the aerial parts of *Skimmia laureola*, 24 compounds and sitosterol were isolated and characterized mainly by spectroscopic methods, including $^{13}$C NMR, some chemical transformations and comparison of mp with authentic sample or those reported in the literature [9–12].

Compounds **1**, **2** and **3** responded positively to the alcoholic ferric chloride test. Their UV absorptions were characteristic of 5,7-dioxygenated-2-methyl chromones [13, 14]. The IR spectra of the compounds, besides favouring the chromone structure [15], indicated the presence of a chelated hydroxyl. This was proved further by their $^1$H NMR signals at $\delta$12.73, 12.75 and 12.90 (1H, *br s*, exch. $D_2O$), respectively. While compound **1** was found to bear another hydroxyl, $\delta$6.1 (1H, *br s*, exch. $D_2O$), compounds **2** and **3** were found to carry a methoxyl, $\delta$3.85 and 3.92 (each 3H, *s*), respectively. The presence of a 2-methyl chromone nucleus in the compounds was proved by the resonance signals at $\delta$2.32–2.34 (3H, *s*), $\delta_c$21.30–21.40, due to vinylic methyl, and 6.20–6.34 (1H, *s*), due to H-3. The $^1$H NMR and $^{13}$C NMR spectra (Table 1) of the compounds revealed the presence of a 3,3-dimethylallyl side chain. However, the presence of extra oxygen in compound **3**, coupled with the downfield chemical shift and multiplicity [$\delta$4.41 (2H, *d*, $J$ = 7 Hz)] of the methylene protons, and also substantiated by the





| | $R^1$ | $R^2$ |
|---|---|---|
| **1** | H | |
| **2** | OMe | |
| **3** | OMe | |



| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **4** | H | OH | H |
| **5** | OH | OH | H |
| **6** | OH | OMe | H |
| **7** | OMe | OMe | H |
| **8** | OMe | OH | H |
| **9** | H | OMe | |
| **10** | H | OMe | |
| **11** | H | OMe | OMe |

$^{13}$C NMR chemical shift ($\delta_c$69.3), corroborated the presence of a 3,3-dimethylallyloxy chain attached to a benzene ring[16]. This is an unusual feature with the naturally occurring chromones. The position of the methoxyl in this compound was finally settled on the basis

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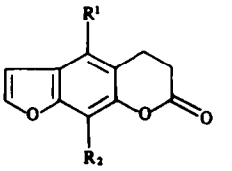
Table 1. $^{13}C$ NMR chemical shifts of chromones in $CDCl_3$ ($\delta_C$) ppm

| Carbon | 1 | 2 | 3 |
|---|---|---|---|
| C-2 | 105.20 | 105.34 | 105.08 |
| C-3 | 112.52 | 112.69 | 112.47 |
| C-4 | 182.40 | 182.33 | 183.70 |
| C-5 | 165.91 | 166.18 | 167.30 |
| C-6 | 108.52 | 108.70 | 150.04 |
| C-7 | 164.25 | 162.69 | 163.50 |
| C-8 | 89.00 | 89.30 | 89.50 |
| C-10 | 155.50 | 156.4 | 156.42 |
| C-9 | 157.30 | 158.3 | 158.21 |
| 2-Me | 21.32 | 21.40 | 21.30 |
| C-1′ | 25.65 | 25.65 | 69.73 |
| C-2′ | 122.72 | 122.02 | 119.0 |
| C-3′ | 132.03 | 131.63 | 138.6 |
| C-4′ | 20.23 | 20.20 | 25.4 |
| C-5′ | 17.65 | 17.60 | 18.3 |
| OMe | — | 55.7 | 56.7 |

of the large deuterobenzene induced diamagnetic shift, $\Delta\delta$0.65 ppm, resulting from a methoxyl having at least one *ortho*-position unsubstituted [17, 18]. The mass spectra of the compounds **1–3** exhibited features of 2-methyl chromones and indicated that they followed pathway I and II similar to those of flavones [19]. The loss of 68 amu, $C_5H_8$, from the molecular ion of compound **3** was in agreement with the presence of a dimethylallyloxy side chain. The base peak represented the hydroxy derivative of the original ether. The compounds **1** and **2** were thus identified as peucenin [20, 21] and peucenin-7-methyl ether [15]. The compound **3** is a new chromone and is designated as skimminin.

The compounds **4–24** were found to be coumarins by their colour reaction with alkaline hydroxylamine followed by ferric chloride [22], UV and IR absorptions. The UV absorptions [23] (Table 2), the mss spectral fragmentation [24] and the downfield $^1H$ NMR spectral patterns of the compounds **12–24** (Table 3) were typical of linear furanocoumarins [25].

The downfield $^1H$ NMR spectral patterns of the compounds **4–11** (Table 4) were identical and suggested that they were 7-substituted coumarin derivatives. The spectra contained two doublets, $J$ = 9–9.6 Hz, at $\delta$6.11–6.29 and



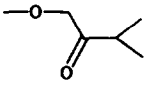
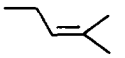
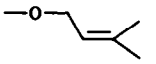
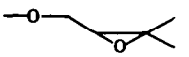
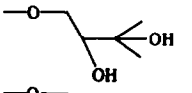
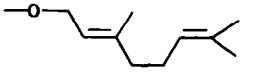
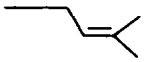
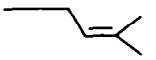
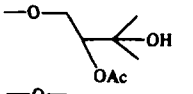
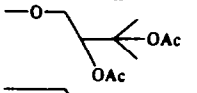
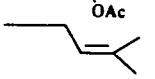
| | $R^1$ | $R^2$ |
|---|---|---|
| **12** | H | H |
| **13** | OH | H |
| **14** | OMe | H |
| **15** |  | H |
| **16** |  | OH |
| **17** | H | OH |
| **18** | H | OMe |
| **19** | H |  |
| **20** | H |  |
| **21** | H |  |
| **22** | H |  |
| **23** | OH |  |
| **24** | OMe | OMe |
| **25** | OAc | H |
| **26** |  | OAc |
| **27** | H | OAc |
| **28** | H |  |
| **29** | H |  |
| **30** | OAc |  |

Table 2. UV spectra of coumarins from *S. laureola*

| Compound | $\lambda_{max}$ nm | Compound | $\lambda_{max}$ nm |
|---|---|---|---|
| **4** | 222, 240, 245, 265, 308 | **15** | 252, 261, 268 |
| **5** | 230, 250, 260, 344 | **16** | 216, 249, 263, 299 |
| **6** | 230, 254, 260, 298, 346 | **17** | 243, 249, 262, 306 |
| **7** | 228, 245, 298, 308 | **18** | 208, 247, 293, 262 |
| **8** | 225, 240, 245, 346 | **19** | 243, 249, 263, 299 |
| **9** | 240, 245, 265, 315 | **20** | 225, 248, 265, 307 |
| **10** | 222, 245, 270, 310 | **21** | 218, 248, 263, 300 |
| **11** | 220, 243, 270, 312 | **22** | 244, 249, 264 |
| **12** | 240, 245, 289, 327 | **23** | 224, 244, 267, 274, 317 |
| **13** | 209, 248, 259, 296 | **24** | 209, 247, 262, 296 |
| **14** | 217, 247, 261, 308 | | |

Table 3. $^1$H NMR chemical shifts of the furobenzopyrone nucleus ($\delta$ values $CDCl_3$)

| Compound | H-3 (1H, *d*); *J* (Hz) | H-4 (1H, *d*); *J* (Hz) | H-5 (1H, *s*) | H-8 (1H, *s*) | H-2′ (1H, *d*, *J* = 2.2 Hz) | H-3′ (1H, *d*, *J* = 2.2 Hz) |
|---|---|---|---|---|---|---|
| **12** | 6.33; 9.0 | 7.76; 9.0 | 7.46 | 7.29 | 7.60 | 6.80 |
| **13** | 6.23; 9.0 | 8.04; 9.0 | — | 7.13 | 7.87 | 7.21 |
| **14** | 6.23; 9.0 | 8.04; 9.0 | — | 7.03 | 7.57 | 6.96 |
| **15** | 6.32; 9.5 | 8.32; 9.5 | — | 7.17 | 7.59 | 6.83 |
| **16** | 6.20; 9.3 | 7.96; 9.3 | — | — | 7.69 | 6.80 |
| **17*** | 6.28; 9.5 | 7.82; 9.5 | 7.23 | — | 7.63 | 6.73 |
| **18** | 6.30; 9.0 | 7.76; 9.0 | 7.30 | — | 7.70 | 6.80 |
| **19** | 6.30; 9.5 | 7.79; 9.5 | 7.56 | — | 7.86 | 6.80 |
| **20** | 6.31; 9.3 | 7.78; 9.3 | 7.40 | — | 7.76 | 6.86 |
| **21** | 6.36; 9.1 | 7.76; 9.1 | 7.36 | — | 7.72 | 6.85 |
| **22** | 6.13; 9.0 | 7.60; 9.0 | 7.16 | — | 7.49 | 6.66 |
| **23*** | 6.32; 9.0 | 8.03; 9.0 | — | — | 7.72 | 6.86 |
| **24** | 6.25; 9.5 | 8.08; 9.5 | — | — | 7.59 | 6.96 |
| **26** | 6.30; 9.5 | 7.85; 9.5 | — | — | 7.70 | 6.80 |
| **27** | 6.28; 9.5 | 7.72; 9.5 | — | 7.73 | 7.63 | 6.73 |
| **28** | 6.33; 9.0 | 7.78; 9.0 | 7.36 | — | 7.70 | 6.80 |
| **29** | 6.26; 9.5 | 7.70; 9.0 | 7.30 | — | 7.60 | 6.80 |
| **30** | 6.26; 9.5 | 7.90; 9.5 | 7.28 | — | 7.60 | 6.79 |

*Solvent DMSO-$d_6$.

Table 4. $^1$H NMR Chemical shifts of coumarins from *S. laureola* ($\delta$ values)

| Compound | H-3 (1H, *d*) | H-4 (1H, *d*) | H-5 | H-6 | H-8 | OH (1H, *s*, $D_2O$) *br*, exch. | OMe |
|---|---|---|---|---|---|---|---|
| **4** | 6.11 (*J* = 9.5 Hz) | 7.83 (*J* = 9.5 Hz) | 7.43 (*J* = 8.5 Hz) | 6.68 (1H, *dd*, *J* = 8.5, 2.5 Hz) | 6.62 (1H, *d*, *J* = 2.5 Hz) | 10.2 | — |
| **5*** | 6.14 (*J* = 9.6 Hz) | 7.84 (*J* = 9.6 Hz) | 6.96(*s*) | — | 6.73(*s*) | 8.9 (OH-6) 10.8 (OH-7) | |
| **6** | 6.12 (*J* = 9.3 Hz) | 7.82 (*J* = 9.3 Hz) | 7.12(*s*) | — | 6.72(*s*) | 10.9 (OH-7) | 3.80 |
| **7** | 6.25 (*J* = 9.5 Hz) | 7.58 (*J* = 9.5 Hz) | 7.20(*s*) | — | 6.82(*s*) | — | 3.89 3.92 |
| **8** | 6.18 (*J* = 9.6 Hz) | 7.87 (*J* = 9.6 Hz) | 7.18(s) | — | 6.73(s) | 10.2 (OH-7) | 3.80 |
| **10** | 6.29 (*J* = 9.3 Hz) | 7.63 (*J* = 9.3 Hz) | 7.20(*d*, *J* = 9.0 Hz) | 6.90 (1H, *d*,*J* = 9.0 Hz) | — | 8.20 | 3.95 |
| **11** | 6.20 (*J* = 9 Hz) | 7.88 (*J* = 9 Hz) | 7.33 (*d*, *J* = 9.5 Hz) | 6.70 (*d*, *J* = 9.5 Hz) | — | — | 3.70 3.95 |

*Solvent DMSO-$d_6$.

7.63–7.88, due to H-3 and H-4, respectively. The resonance signals at $\delta$6.96–7.18 (1H, *s*, H-5) in the spectra of the compounds **5–8** indicated that the compounds were substituted at C-6. Other compounds were found to be 7,8-disubstituted coumarins by the resonance signals at $\delta$7.20–7.46 (1H, *d*, *J* = 9–9.3 Hz, H-5) and 6.68–6.90 (1H, *d*, *J* = 9–9.3 Hz, H-6). A two proton triplet at $\delta$4.20, $\delta_C$ 72.6, and a two proton AB quartet at $\delta$ 3.62 and 3.50, $\delta_C$67.8, in the spectra of compound **10**, indicated the presence of two oxymethylenes. The NMR spectral data accounted for the 4-hydroxy-3-methyl butoxy chain which was placed at C-8 on the basis of the deuterobenzene induced shift, $\Delta\delta$0.70, for the methoxyl [17, 18]. The base peak in the mass spectrum of this compound originated from the loss of a $C_5H_8$ unit and represented the hydroxyl derivative of the original ether. The spectral

data, including $^{13}$C NMR (Table 5) was consistent with the structure of desoxylacarol [16].

The compounds **6** and **8** showed two aromatic singlets at $\delta$7.12 and 7.18, due to H-5, and 6.72 and 6.73, due to H-8 in their $^1$H NMR spectra [26]. The distinction between the compounds was made on the basis of the diamagnetic shift of their methoxyls. The low diamagnetic shift, $\Delta\delta$ 0.3 ppm, in the methoxyl of compound **8** excluded its presence at C-5 or C-7 [27] which was also supported by the presence of an $[M-15]^+$ peak in its mass spectrum [28]. Compound **6** showed a high diamagnetic shift, $\Delta\delta$0.65 placing the methoxyl at C-7. Likewise, the chemical shift and multiplicity of the aromatic protons distinguished between compounds **7** and **11**. The former exhibited two singlets, while the later showed two doublets with aromatic *ortho*-coupling, $J$ = 9.5 Hz, in their $^1$H NMR spectra.

Compound **11** underwent diamagnetic shift, $\Delta\delta$0.65 and 0.3 ppm, in its methoxyl signals indicating the presence of one of the methoxyls at C-5 or C-7. In view of the chemical shift and multiplicity of the H-5 and H-6 signals, one of the methoxyls was placed at C-7. The bathochromic shift of 20 nm with respect to the parent compound confirmed that the other methoxyl was at C-8.

On the basis of the detailed spectral analysis the simple coumarins were characterised as umbelliferone (**4**), esculetin (**5**), isoscopoletin (**6**), scoparone (**7**), scopoletin (**8**), osthol (**9**) and 7,8-dimethoxycoumarin (**11**).

The distinction between C-5 and C-8 substituted linear furanocoumarins **13–24** was made on the basis of the chemical shift of H-4 which appeared downfield at $\delta$7.96–8.32 in the compounds **13–16**, indicating that they were substituted at C-5 [29]. The aromatic proton in the compounds **17–22** resonated at $\delta$7.60–7.96 confirming that they were substituted at C-8 [30]. The compounds **23** and **24** exhibited no signal for an aromatic proton in their $^1$H NMR spectra. The $^1$H NMR and $^{13}$C NMR chemical shifts [31–33] of these compounds are presented in Tables 3, 6, 7 and 8. The compounds have been characterised as psoralen (**12**), bergaptol (**13**), bergapten (**14**), iso-

Table 5. $^{13}$C NMR chemical shifts of simple furanocoumarins ($\delta_C$) ppm ($CDCl_3$)

| Carbon | 4 | 5 | 6 | 7 | 8 | 9* | 10† | 11 |
|---|---|---|---|---|---|---|---|---|
| C-2 | 160.3 | 160.4 | 160.3 | 160.2 | 160.3 | 160.4 | 160.4 | 160.3 |
| C-3 | 111.4 | 112.4 | 113.2 | 114.9 | 114.4 | 111.5 | 114.9 | 115.2 |
| C-4 | 144.2 | 143.5 | 143.3 | 143.5 | 143.4 | 143.5 | 143.3 | 143.3 |
| C-5 | 129.5 | 114.2 | 114.1 | 113.6 | 113.9 | 125.3 | 120.5 | 120.7 |
| C-6 | 113.3 | 142.7 | 144.5 | 148.8 | 143.4 | 112.6 | 114.5 | 114.3 |
| C-7 | 161.6 | 150.2 | 150.3 | 149.4 | 149.8 | 148.4 | 148.4 | 147.3 |
| C-8 | 102.5 | 104.4 | 104.2 | 104.5 | 104.2 | 125.9 | 132.3 | 131.5 |
| C-9 | 155.7 | 148.1 | 149.4 | 147.5 | 147.2 | 148.3 | 146.1 | 146.3 |
| C-10† | 110.4 | 112.4 | 113.2 | 114.9 | 114.4 | 111.5 | 114.9 | 115.2 |
| OMe-6 | — | — | — | 56.3 | 56.3 | — | — | — |
| OMe-7 | — | — | 55.4 | 55.2 | — | 55.5 | 55.4 | 55.4 |
| OMe-8 | — | — | — | — | — | — | — | 61.7 |

*Side chain carbons ppm: **9**, 22.9 (C-1'), 120.7 (C-2'), 138.4 (C-3'), 18.0 (C-4'), 24.7 (C-5'). **10**, 72.6 (C-1'), 34.0 (C-2'), 33.5 (C-3'), 17.1 (C-4'), 67.8 (C-5').
†$CD_3OD/CDCl_3$.

Table 6. $^1$H NMR chemical shifts of the side chain protons of furanocoumarins

| Compound | H-1″ | H-2″ | H-3″ | H-4″ (3H, *s*) | H-5″ (3H, *s*) | OAc |
|---|---|---|---|---|---|---|
| **15** | 5.10 (2H, *s*) | — | 2.81 (1H, *m*) | 1.17 | 1.20 | — |
| **16** | 3.76 (2H, *d*, $J$ = 7Hz) | 5.20 (1H, *t*, $J$ = 8.5, 6Hz) | — | 1.76 | 1.90 | — |
| **19** | 4.96 (2H, *d*, $J$ = 7Hz) | 5.60 (1H, *t*, $J$ = 8.5, 6Hz) | — | 1.73 | 1.75 | — |
| **20** | 4.56 (2H, *m*) | 3.20 (1H, *m*) | — | 1.30 | 1.36 | — |
| **21** | 4.56 (2H, *m*) | 3.90 (1H, *m*) | — | 1.36 | 1.45 | — |
| **23** | 3.73 (2H, *d*, $J$ = 8Hz) | 3.20 (1H, *t*, $J$ = 9, 6Hz) | — | 1.76 | 1.89 | — |
| **26** | 3.76 (2H, *d*, $J$ = 7Hz) | 3.62 (1H, *t*, $J$ = 8, 6Hz) | — | 1.76 | 1.90 | 2.34 |
| **28** | 4.63 (2H, *m*) | 3.20 (1H, *m*) | — | 1.36 | 1.41 | 2.30 |
| **29** | 4.63 (2H, *m*) | 5.35 (1H, *m*) | — | 1.50 | 1.42 | 2.30<br>2.36 |
| **30** | 3.60 (2H, *d*, $J$ = 7Hz) | 5.12 (1H, *t*, $J$ = 9, 6Hz) | — | 1.63 | 1.79 | 2.43 |

Table 7. $^{13}$C NMR chemical shifts of the furobenzopyrone nucleus ($\delta_C$ ppm, $CDCl_3$)

| Compound | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 | C-10 | C-2′ | C-3′ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **12** | 161.1 | 114.7 | 144.2 | 120.0 | 125.0 | 156.2 | 99.5 | 152.2 | 115.6 | 147.0 | 106.6 |
| **13** | 161.1 | 112.6 | 139.3 | 149.6 | 114.3 | 158.2 | 94.2 | 152.8 | 107.5 | 144.8 | 105.1 |
| **14** | 160.3 | 112.7 | 139.4 | 149.6 | 113.0 | 158.2 | 94.4 | 152.7 | 106.7 | 145.0 | 105.2 |
| **15** | 160.8 | 113.3 | 139.1 | 128.7 | 113.6 | 158.1 | 95.1 | 152.7 | 107.5 | 145.5 | 104.1 |
| **16** | 161.1 | 113.9 | 144.6 | 128.2 | 124.6 | 147.7 | 93.8 | 139.5 | 107.3 | 144.8 | 105.3 |
| **17** | 160.0 | 113.7 | 145.3 | 110.0 | 125.2 | 145.3 | 130.1 | 139.8 | 116.2 | 147.2 | 106.9 |
| **18** | 160.1 | 114.3 | 144.1 | 112.8 | 125.9 | 147.3 | 132.4 | 142.7 | 116.2 | 146.4 | 106.4 |
| **19** | 160.2 | 114.2 | 143.3 | 113.2 | 125.7 | 148.3 | 131.3 | 143.5 | 116.2 | 146.4 | 106.3 |
| **20** | 160.1 | 114.3 | 144.2 | 113.3 | 126.2 | 147.9 | 131.2 | 143.0 | 116.2 | 146.7 | 106.3 |
| **21** | 160.3 | 114.5 | 144.3 | 113.5 | 126.0 | 147.7 | 131.5 | 143.0 | 116.3 | 146.7 | 106.3 |
| **22** | 160.2 | 114.4 | 144.1 | 113.3 | 126.1 | 147.5 | 130.4 | 143.1 | 116.7 | 146.8 | 105.2 |
| **23** | 161.1 | 112.4 | 138.8 | 149.5 | 114.7 | 152.5 | 111.7 | 148.2 | 107.3 | 145.4 | 105.2 |
| **24** | 160.7 | 112.9 | 139.3 | 144.4 | 114.9 | 149.9 | 128.3 | 143.7 | 107.1 | 146.0 | 105.1 |

Table 8. $^{13}$C NMR chemical shifts of the side chain carbons of linear furanocoumarins $\delta_C$ ppm

| Compound | C-1″ | C-2″ | C-3″ | C-4″ | C-5″ | OMe |
|---|---|---|---|---|---|---|
| **14** | — | — | — | — | — | 60.3 |
| **15** | 75.0 | 208.5 | 37.4 | 17.9 | 17.9 | — |
| **16** | 22.4 | 120.7 | 138.1 | 24.4 | 18.0 | — |
| **18** | — | — | — | — | — | 61.1 |
| **19** | 69.91 | 119.75 | 139.2 | 25.7 | 18.0 | — |
| **20** | 73.5 | 61.0 | 58.1 | 24.5 | 19.1 | — |
| **21** | 75.6 | 76.2 | 71.5 | 25.1 | 26.5 | — |
| **22*** | 69.91 | 117.8 | 141.5 | 38.5 | 25.5 | — |
| **23** | 25.3 | 121.7 | 137.2 | 24.2 | 18.1 | — |
| **24** | — | — | — | — | — | 61.5, 59.3 |

*122.6 (C-6″), 134.7 (C-7″), 24.8 (C-8″), 17.2 (C-9″), 15.7 (C-10″).

oxypeucedanin (**15**), alloimperatorin (**16**), xanthotoxol (**17**), xanthotoxin (**18**), imperatorin (**19**), heraclenin (**20**), heraclenol (**21**), 8-geranyloxypsoralen (**22**), alloisoimperatorin (**23**) and isopimpinellin (**24**).

This is the first report on the presence of chromones in the genus *Skimmia*. To our knowledge the natural existence of skimminin has not been documented so far. Lacarols are unusual natural coumarins being rarely distributed in nature [34]. They are mostly confined to the genus *Artemisia*. Desoxylacarol is reported for the second time from nature. Isoscopoletin and 7,8-dimethoxycoumarin is new to the genus *Skimmia*; the latter was previously reported from *Artemisia apiaceae* [35]. Among the linear furanocoumarins bergapten, iso-imperatorin, xanthotoxin and isopimpinellim alone have been reported from *S. laureola*. We have failed to isolate isoimperatorin from the plant.

## EXPERIMENTAL

Mps are uncorr. IR was recorded in KBr discs. $^1$H NMR spectra were run at 60, 90 and 250 MHz, $^{13}$C NMR at 62.89 MHz. MS were done at 70 eV.

*Extraction and isolation.* The plant material was obtained from Gulmarg (Kashmir Valley), ground and extracted with hot EtOH. After removing the solvent *in vacuo* the residue (650 g) was triturated successively with petrol (40–60°), $C_6H_6$ and EtOAc. Each of these fractions was worked up independently. The solvent was removed and the residues chromatographed over silica gel using gradient solvent systems. The mixtures obtained were separated by repeated CC, prep. TLC and argentation TLC, on silica gel.

*Characterisation of compounds.* Sitosterol, mp 135°, gave a positive LB test. Its identity was confirmed by co-TLC and determination of mmp with authentic sample.

*Peucenin* (**1**). $[M]^+$ *m/z* 260.1140 (calc. for $C_{15}H_{16}O_4$, 260.1048), mp 209° (lit. 210–212°) gave violet colour with alc. $FeCl_3$. UV $\lambda_{max}^{EtOH}$ nm: 265, 245, 238, 210. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3450 (OH), 3380 (OH), 1665, 1660, 1580, 1500, 1460 (aromatic), 1380, 1360 (*gem* dimethyl), 1230, 1200, 1105, 970, 840, 820. $^1$H NMR (90 MHz), $CDCl_3$: $\delta$ 1.65 (3H, *s*, H-4′), 1.72 (3H, *s*, H-5′), 2.32 (3H, *s*, Me-2), 2.32 (3H, *s*, Me-2), 6.20 (1H, *s*, H-3), 3.32 (2H, *d*, $J$ = 8.7 Hz, H-1′), 5.20 (1H, *m*, H-2′), 6.1 (1H, *br s*, exch. $D_2O$, OH-7), 6.40 (1H, *s*, H-8), 12.73 (1H, *br s*, exch. $D_2O$, OH-5). MS *m/z*: 260 $[M]^+$, 245, 217, 205 (100%), 192, 115.

*Peucenin-7-methyl ether* (**2**). $[M]^+$ *m/z* 274.1203 (calc. for $C_{16}H_{18}O_4$, 274.1205), mp 101° (lit. 102°), UV $\lambda_{max}^{EtOH}$ nm: 258, 240, IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3450 (OH), 1660, 1580, 1460 (aromatic), 1380, 1360 (*gem* dimethyl), 1220, 1200, 1650, 1110, 960, 840, 820, $^1$H NMR (250 MHz), $CDCl_3$: $\delta$ 1.65 (3H, *s*, H-4′), 1.75 (3H, *s*, H-5′), 2.32 (3H, *s*, Me-2) 3.30 (2H, *d*, $J$ = 8.7 Hz, H-1′), 3.85 (3H, *s*, OMe), 5.20 (1H, *m*, H-2′), 6.32 (1H, *s*, H-8), 12.75 (1H, *br s*, exch. $D_2O$,

OH-5). MS *m/z*: 274 $[M]^+$ 259, 231, 219, 206, 205 (100%) 189, 177.

*Skimminin* (**3**). $[M]^+$ *m/z* 290.1104 (calc. for $C_{16}H_{18}O_5$, 290.1154), mp 150–152°, UV $\lambda_{max}^{EtOH}$ nm: 268, 245, 235, 215. IR $\nu_{max}^{KBr}$ $cm^{-1}$ 3455 (OH) 1665, 1580, 1500, 1460 (aromatic), 1380, 1360 (*gem* dimethyl), 1220, 1195, 1650, 1110, 960, 820. $^1H$ NMR (90 MHz), $CDCl_3$: $\delta$ 1.54 (3H, *s*, H-4'), 1.65 (3H, *s*, H-5'), 2.34 (3H, *s*, Me-2), 3.92 (3H, *s*, OMe), 4.93 (2H, *d*, J = 9 Hz, H-1'), 5.43 (1H, *t*, *J* = 6, 9 Hz, H-2'), 6.34 (1H, *s*, H-8), 12.90 (1H, *br s*, exch. $D_2O$, OH-5); $C_6H_6$: $\delta$ 1.46 (3H, *s*, H-4'), 1.52 (3H, *s*, H-5'), 2.17 (3H, *s*, Me-2), 3.17 (3H, *s*, OMe), [$\Delta\delta$0.65 ppm], 4.62 (2H, *d*, *J* = 9 Hz, H-1'), 5.21 (1H, *br d*, $W_{0.5}$ 8.0 Hz, H-2'), 6.30 (1H, *s*, H-8), 12.52 (1H, *br s*, exch. $D_2O$, OH). MS *m/z*: 290 $[M]^+$, 275 $[M-Me]^+$, 260 $[M-2\times Me]^+$, 247, 222 (100%), 205, 192, 115.

*Umbelliferone* (**4**). $[M]^+$ *m/z* 162.0573 (calc. for $C_9H_6O_3$, 162.0316), mp 220° (lit. 223–224°). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3430 (OH), 1715 ($\alpha$, $\beta$-unsaturated-$\delta$-lactone), 1660, 1600, 1500, 1460, 1195, 960, 820, MS *m/z* 162 $[M]^+$, 144, 134, 106.

*Esculetin* (**5**). $[M]^+$ *m/z* 178.1402 (calc. for $C_9H_6O_4$ 178.0265), mp 267°(lit. 268–270°). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3450, 3435 (OH), 1710, 1660, 1610, 1530, 1450, 1190, 825. MS *m/z*: 178 $[M]^+$, 176, 160, 133, 132, 104.

*Isoscopoletin* (**6**). $[M]^+$ *m/z* 192.1342 (calc. for $C_{10}H_8O_4$, 192.0422) mp 207.5–209°. IR $\nu_{max}^{KBr}$ $cm^{-1}$ 3450 (OH), 1725, 1630, 1590, 1450, 1180, 940, 820. MS *m/z*: 192 $[M]^+$, 177 $[M-Me]^+$, 164, 149, 148, 133, 104 (100%). $^1H$ NMR (60 MHz) $C_6D_6$: $\delta$3.18 (3H, *s*, OMe), [$\Delta\delta$0.62], 6.11 (1H, *d*, *J* = 9.3 Hz, H-3), 6.72 (1H, *s*, H-8), 7.12 (1H, *s*, H-5), 7.82 (1H, *d*, *J* = 9.3 Hz, H-5), 10.7 (1H, *br s*, exch. $D_2O$, OH). On methylation with $Me_2SO_4$ gave **7**, mp 146, whose spectra were similar to scoporone.

*Scoporone* (**7**). $[M]^+$ *m/z* 206.1150 (calc. for $C_{11}H_{10}O_4$, 206.0579), mp 147°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1715, 1710, 1645, 1570, 1460, 1410, 1280, 825, $^1H$ NMR (60 MHz) $C_6D_6$: 3.22 (3H, *s*, OMe), [$\Delta\delta$0.70], 3.24 (3H, *s*, OMe), [$\Delta\delta$0.65], 6.20 (1H, *d*, *J* = 9.5 Hz, H-3), 6.70 (1H, *d*, *J* = 9.5 Hz, H-4), 7.32 (1H, *s*, H-5), 6.84 (1H, *s*, H-8). MS *m/z* 206 $[M^+]$, 181, 179, 178, 166, 164, 153.

*Scopoletin* (**8**). $[M]^+$ *m/z* 192.1240 (calc. for $C_{10}H_8O_4$, 192.0422), mp 205° (lit. 204°). IR and MS similar to **6**. $^1H$ NMR (90 MHz) $C_6D_6$: $\delta$ 3.10 (3H, *s*, OMe), [$\Delta\delta$0.70], 6.10 (1H, *d*, *J* = 9.6 Hz, H-3) 6.22 (1H, *s*, H-8) 7.16 (1H, *s*, H-5), 7.48 (1H, *d*, *J* = 9.6 Hz, H-4), 10.0 (1H, *br s*, exch. $D_2O$, OH).

*Osthol* (**9**). $[M]^+$ *m/z* 244.1123 (calc. for $C_{15}H_{16}O_3$ 244.1099), mp 83° (lit. 83°). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1715, 1600, 1495, 1385, 1365, $^1H$ NMR (90 MHz) DMSO-$d_6$: $\delta$ 1.86 (3H, *s*, H-4'), 1.83 (3H, *s*, H-5') 3.50 (2H, *d*, *J* = 7 Hz, H-1'), 5.23 (1H, *m*, H-2'), 6.20 (1H, *d*, *J* = 9 Hz, H-3), 6.96 (1H, *d*, *J* = 8.5 Hz, H-6), 7.46 (1H, *d*, *J* = 8.5 Hz, H-5), 7.80 (1H, *d*, J = 9 Hz, H-4). MS *m/z*: 244, 229, 214, 213, 175. Confirmed by co-TLC with authentic sample.

*Desoxylacarol* (**10**). $[M]^+$ 278.0149 (calc. for $C_{15}H_{18}O_5$, 278.1154), mp 102° (lit. 103°). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3530, 2850, 1740, 1600, 1375, 1340, 1260, 1070. $^1H$ NMR (90 MHz) $C_6D_6$: $\delta$6.25 (1H, *d*, *J* = 9.2 Hz, H-3), 6.54 (1H, *d*, *J* = 9.2 Hz, H-4), 6.45 (1H, *d*, *J* = 9.5 Hz, H-5), 6.22 (1H, *d*, *J* = 9.5 Hz, H-6), 3.23 (3H, *s*, OMe), 4.11 (2H, *t*, J = 6, 6Hz, H-1'), 1.82 (1H, *m*, H-2'), 1.61 (1H, *m*, H-2'), 2.14 (1H, *m*, H-3'), 3.50 (2H, ABq, *J* = 11 Hz, H-4), 0.97 (3H, *s*, H-5'), 4.35 (1H, *br s*, exch. $D_2O$, OH). MS *m/z*: 278 $[M]^+$, 264, 260, 250, 247, 232, 219, 208, 192 (100%), 180.

*7,8-Dimethoxycoumarin* (**11**). $[M]^+$ *m/z* 206.1032 (calc. for $C_{11}H_{10}O_4$, 206.0579). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1640, 1600, 1570, 1460, 1360, 1280, 940, 820. $^1H$ NMR (90 MHz) $C_6D_6$: $\delta$3.65 (3H, *s*, OMe), [$\Delta\delta$0.30]; 3.05 (3H, *s*, OMe), [$\Delta\delta$0.65], 6.12 (1H, *d*, *J* = 9 Hz, H-3), 6.72 (1H, *d*, *J* = 9.5 Hz, H-6), 7.36 (1H, *d*, J = 9.5 Hz, H-5), 7.76 (1H, *d*, *J* = 9 Hz, H-4). MS *m/z*: 206, 181, 153, 138, 120.

*Psoralen* (**12**). $[M]^+$ *m/z* 186.0310 (calc. for $C_{11}H_6O_3$, 186.0316) mp 156°, IR: $\nu_{max}^{KBr}$ $cm^{-1}$: 1710, 1600, 1560, 870. MS *m/z*: 186, 158, 129. Confirmed by co-TLC with authentic sample.

*Bergaptol* (**13**). $[M]^+$ *m/z* 202.0202 (calc. for $C_{11}H_6O_4$, 202.0249). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3310, 1710, 1598, 1492, MS *m/z*: 202 $[M]^+$ 185, 145, $^1H$ NMR (60 MHz) $CDCl_3$: $\delta$ 2.6 (1H, *s*, exch. $D_2O$, OH). On acetylation with $AC_2O$-pyridine gave the acetate **25**, mp 151–153°, $[M]^+$ *m/z* 244.6034 (calc. for $C_{13}H_8O_5$, 244.6354). IR: $\nu_{max}^{KBr}$ $cm^{-1}$ 1745, 1246, 1714, 1590, 1490. $^1H$ NMR (60 MHz) $CDCl_3$: $\delta$ 2.13 (3H, *s*, OCOMe), 6.26 (1H, *d*, *J* = 9 Hz, H-3), 7.13 (1H, *s*, H-8), 7.21 (1H, *d*, *J* = 2.2 Hz, H-3'), 7.87 (1H, *d*, *J* = 2.2 Hz, H-2'), 8.20 (1H, *d*, *J* = 9 Hz, H-4). MS *m/z*: 244, 202 $[M-COCH_2]^+$ (100%), 185, 145.

*Bergapten* (**14**). $[M]^+$ *m/z* 216.0416 (calc. for $C_{12}H_8O_4$ 216.0406), mp. mmp 180° (lit. 188°). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1725, 1607, 1500, 880. MS *m/z*: 216, 201 (100%), 185, 173, 145, 132, 76. $^1H$ NMR (60 MHz) $CDCl_3$: $\delta$ 3.93 (3H, *s*, OMe).

*Isooxypeucedanin* (**15**). $[M]^+$ *m/z* 286.0837 (calc. for $C_{16}H_{14}O_5$, 286.0841); mp. mmp 146°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1720, 1620, 1590, 1490, 1385, 1361. MS *m/z*: 286 $[M]^+$, 215, 202, 201 (100%), 189, 173, 145, 132, 71, 69.

*Alloimperatorin* (**16**). $[M]^+$ *m/z* 270.1054 (calc. for $C_{16}H_{14}O_4$, 270.0054); mp, mmp 232° (lit. 226–227). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3410, 1718, 1595, 1495, 1385, 1365. MS *m/z*: 270, 255, 202 (100%), 185. $^1H$ NMR (90 MHz) $CDCl_3$: 4.30 (1H, *s*, exch. $D_2O$, OH) on acetylation with $AC_2O$-pyridine **16** gave the acetate **26**, $[M]^+$ *m/z* 312.1021 (calc. for $C_{18}H_{16}O_5$, 312.1222), mp 120°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1746, 1248 (OCOMe). MS *m/z*: 312, 270, 255, 242, 202 (100%), 185.

*Xanthotoxol* (**17**). $[M]^+$ *m/z* 202.0240 (calc. for $C_{11}H_6O_4$, 202.0249) mmp mp 248° (lit. 251–252). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3280, 1710, 1600, 1495. MS *m/z*: 202, 201 (100%), 173, 145, $^1H$ NMR, (DMSO-$d_6$): $\delta$3.50 (1H, *s*, exch. $D_2O$, OH). On acetylation with $AC_2O$–pyridine at room temp. gave **27**, $[M]^+$ *m/z* 232.0518 (calc. for $C_{12}H_8O_5$, 232.0608), mp 186° IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1740, 1245 (OCOMe). $^1H$ NMR (60 MHz), $CDCl_3$: $\delta$2.35 (3H, *s*, $OCOCH_3$). MS *m/z*: 232 $[M]^+$ 202, 210 (100%), 173, 145. Methylation with $Me_2SO_4$ gave **18** which was identified by mmp (147°) and co-TLC with authentic sample.

*Xanthotoxin* (**18**). $[M]^+$ *m/z* 216.0332 (calc. for $C_{12}H_8O_4$, 216.0432), mp 147° (lit. 147°). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1710, 1610, 1585, 1400, 1290, 1090, 750. MS *m/z*: 216 $[M]^+$, 201 (100%), 185, 173. $^1H$ NMR (90 MHz), $CDCl_3$: $\delta$4.23 (3H, *s*, OMe).

*Imperatorin* (**19**). $[M]^+$ *m/z* 270.0882 (calc. for $C_{16}H_{14}O_4$ 270.1092), mp 102° (lit. 102°). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1710, 1595, 1497, 1383, 1360. MS *m/z*: 270, 255, 202, 201 (100%), 173, 145.

*Heraclenin* (**20**). $[M]^+$ *m/z* 286.0847 (calc. for $C_{16}H_{14}O_5$, 286.1086) mp 111° (lit. 111°). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1720, 1598, 1491, 1380, 1366. MS *m/z*: 286, 271, 270, 256, 202, 201 (100%), 173, 145. On hydrolysis with oxalic acid **18** gave **21**.

*Heraclenol* (**21**). $[M]^+$ *m/z* 304.1015 (calc. for $C_{16}H_{16}O_6$ 304.0946), mp 117° (lit. 117–118°). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3540, 3430, 1720, 1610, 1590, 1490, 1385, 1370, 850. MS *m/z*: 304 $[M]^+$, 289, 245, 202, 201 (100%), 173, 145. $^1H$ NMR (90 MHz), $CDCl_3$: $\delta$2.73 and 3.53 (1H, exch. or *s*, exch. $D_2O$, OH). On acetylation with $Ac_2O$–pyridine, at room temperature **21** afforded **28**, $[M]^+$ at *m/z* 346.1054 (calc. for $C_{18}H_{18}O_7$, 346.1393), mp 102°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3430, 1735, 1720, 1603, 1495, 1380, 1360, 1240, 850. MS *m/z*: 346 $[M]^+$, 331, 328, 287, 286, 279, 272, 202, 201 (100%), 173, 145. On heating with $Ac_2O$–pyridine for 6 hr **21** formed **29**, $[M]^+$ at *m/z* 388.1158 (calc. for $C_{20}H_{20}O_8$, 388.1546), mp 65°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1742, 1718, 1605, 1490, 1245, 1380, 1360. MS *m/z*: 388 $[M]^+$, 363, 328, 304, 303, 268, 244, 243, 202, 201 (100%), 173, 145.

*8-Geranyloxypsoralen* (**22**). $[M]^+$ 338.1510 (calc. for $C_{21}H_{22}O_4$, 338.1502), mp 53°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1710, 1600, 1560, 1490, 1380, 1360, 820. $^1H$ NMR (90 MHz) $CDCl_3$ (Side chain): $\delta$ 1.53, 1.63, 1.69 (3H each *s*, side chain Me's), 4.69 (2H, *d*, *J* + 9 Hz Ar–$OC\underline{H}_2$), 5.43 (2H, *t*, methine), 2.01 (4H, *d*, *J* = 11.5 Hz, –$C\underline{H}_2$–$C\underline{H}_2$–CH). Confirmed by $^{13}C$ NMR, co-TLC and mmp with authentic sample.

*Alloisoimperatorin* (**23**). $[M]^+$ *m/z* 270.0872 (calc. for $C_{16}H_{14}O_4$, 270.0875), mp 220°. IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3315, 1730, 1600, 1470, 1430, 1380, 1365, 1120, 660. MS *m/z*: 270, 255, 202, 201 (100%), 145. On acetylation with $Ac_2O$–pyridine **23** gave **30**, $[M]^+$ at *m/z* 312.1210 (calc. for $C_{18}H_{16}O_5$, 312.1245). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1750, 1600, 1590, 1380, 1360, 1245, 820.

*Isopimpinellin* (**24**). $[M]^+$ *m/z* 240.1256 (calc. for $C_{13}H_{20}O_4$, 240.1362). mp 152° (lit. 150–151°), IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3315, 1720, 1600, 1450, 1370, 1080, 820. MS *m/z*: 240 $[M]^+$, 225, 210, 202, 201 (100%), 173, 145. $^1H$ NMR (90 MHz) $CDCl_3$: $\delta$ 4.10, 4.14 (3H each *s*, OMe).

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