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COUMARINS AND OTHER CONSTITUENTS OF *HESPERETHUSA CRENULATA*

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Key Word Index—*Hesperethusa crenulata*; Rutaceae; coumarins; suberosin epoxide; 4-methoxy-1-methy-2-quinolone.

Abstract—Sitosterol, 4-methoxy-1-methy-2-quinolone and four coumarins, one of which is a 1,2-epoxide, were isolated from the petrol. extract of the root bark of *Hesperethusa crenulata*.

A PREVIOUS communication[1] from this laboratory reported the isolation and characterization of 4-methoxy-1-methyl-2-quinolone from the stem bark of *Hesperethusa crenulata*.

We now report on the chemical constituents in the petrol. extract of the root bark of the same plant. The concentrated petrol. extract was chromatographed on neutral alumina and the column was eluted successively with petrol., petrol.–benzene (19:1, 9:1, 1:3) and benzene–$CHCl_3$ mixtures and finally with $CHCl_3$.

The early fraction eluted with petrol. gave mainly a waxy material and was not examined in detail; the later fractions gave a crystalline substance which on rechromatography and recrystallization from acetone–petrol. gave a TLC pure substance m.p. 139–140°. It gave an acetyl derivative m.p. 126–127°. The compound was identified as sitosterol by comparison of its m.p., m.m.p. with authentic sample and also by m.p. and m.m.p. of the acetates.

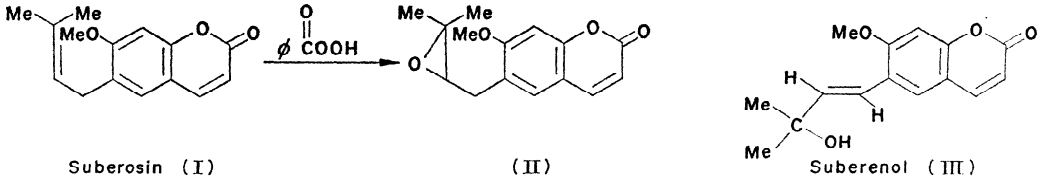
The fraction eluted with petrol.–benzene (19:1) gave two crystalline compounds, as revealed by TLC (silica gel G). The mixture was separated by rechromatography and purified by crystallization from acetone–petrol.; one of these melted at 88–89° and the other 121–121·5°.

The compound m.p. 88–89° analysed for $C_{15}H_{16}O_3$ (M^+ *m/e* 244); showed λ_{max}^{EtOH} at 224 (log ϵ 4·31) 256 (log ϵ 3·68) 297 (log ϵ 3·86) and 332 nm (log ϵ 4·15) suggestive of a 7-allyloxycoumarin.[2] The IR spectrum in Nujol showed peaks at 1725 (C=0), 1615 (C=C), 1575 and 1508 cm^{-1} (aromatic). The MS in addition to its molecular ion peak *m/e* 244, showed peaks at *m/e* 229 (M^+ –Me) and also at *m/e* 189, 159 and 131 which are expected in the case of prenylated 7-methoxycoumarins.[3] All these data coupled with the NMR spectrum (see Table 1) confirmed the identity of the compound as suberosin (I).

The compound m.p. 121–121·5°, molecular formula $C_{15}H_{16}O_4$ (M^+ *m/e* 260) had λ_{max}^{EtOH} at 223 (log ϵ 4·12) 258 (log ϵ 3·58) 297 (log ϵ 3·75) and 328 nm (log ϵ 3·98). The IR spectrum in KBr showed peaks at 1725 (C=O), 1638 (C=C stretching), 1575, 1508 (aromatic), 1385, 1365 (Me bending), 1260 (C=C–O–C symmetric stretching), 1030 (C–O–C symmetric stretching) 950 (asymmetric stretching of the ring, the so-called 11 μ band of epoxides) and

[1] M. N. S. NAYAR, C. V. SUTAR and M. K. BHAN, *Phytochem.* **10**, 2843 (1971).
[2] J. P. KUTNEY, R. N. YOUNG and A. K. VARMA, *Tetrahedron Letters* 1845 (1969).
[3] G. B. GUISE, E. RITCHIC, R. G. SENIOR and W. C. TAYLOR, *Austral. J. Chem.* **20**, 2429 (1967).

840 cm^{-1} (expoide, the so-called 12 μ band).[4] The MS showed a molecular ion peak at *m/e* 260 and peaks at *m/e* 245 (M^+–Me), 189, 159 and 131. There was also another peak at *m/e* 231, probably representing the loss of CHO which can be expected in the case of epoxides.[5] These data together with the NMR spectrum (see Table 1) indicated that the compound is 7-methoxy-6-(2,3-epoxy-6-methylbutyl)coumarin* (II), previously synthesized by King *et al.*[6] (reported m.p. 1114–114·5°) and to the best of our knowledge isolated for the first time from a natural source. The previous report does not give any spectral details.



Suberosin (I) (II) Suberenol (III)

The final conformation of the structure was established by the epoxidation of suberosin (I) with perbenzoic acid in $CHCl_3$ at 0°. The reaction mixture was purified by column chromatography on alumina and recrystallization from petrol.–acetone. The synthetic product was identical (IR, UV, NMR, MS and m.p.) with the natural product.

TABLE 1. 60 MHz—NMR SPECTRA OF COUMARINS IN $CDCl_3$ WITH TMS AS INTERNAL REFERENCE CHEMICAL SHIFT IN δ AND J IN Hz

Compound	H_3	H_4	H_5	7-*o*-Me	H_8	H'$_1$	H'$_2$	Me_2 C–C	3'OH
Suberosin	6·24 *d* (1H) $J = 9·5$	7·62 *d* (1H) $J = 9·5$	7·19 *s* (1H)	4·0 *s* (3H)	6·8 *s* (1H)	3·3 *d* (2H) $J = 8·0$	5·3 *t* (1H) $J = 8·0$	1·7, 1·8 } 6H	—
Epoxysuberosin	6·25 *d* (1H) $J = 9·5$	7·67 *d* (1H) $J = 9·5$	7·35 *s* (1H)	3·92 *s* (3H)	6·85 *s* (1H)	2·9 (3H) unresolved multiplet		1·30, 1·39 } 6H	
Suberenol	6·33 *d* (1H) $J = 9·5$	7·58 *d* (1H) $J = 9·5$	7·55 *s* (1H)	4·0 *s* (3H)	6·85 *s* (1H)	6·99 *d* (1H) $J = 16$	6·40 *d* (1H) $J = 16$	1·46 *s* (6H)	1·73 *s* (1H) disappeared on D_2O exchange

The fraction eluted with petrol.–benzene (9:1) on rechromatography separated into its two components which on further crystallization gave 4-methoxy-1-methyl-2-quinolone and marmesin. These compounds were identified by comparison of their m.p., m.m.p., IR, UV and NMR spectra with those of authentic samples.

Eluates from the column with petrol.–benzene (1:3) gave a single substance which after one rechromatography and recrystallization gave a TLC pure substance m.p. 172–173°. It analysed for $C_{15}H_{16}O_4$ (M^+ 260). The UV absorption showed λ_{max}^{EtOH} at 255 (log ϵ 4·33) 295 (log ϵ 3·8) 306 (log ϵ 3·81) and was very similar to suberosin; and showed IR absorption peaks at 3460 (OH), 1735 (C=O), 1615 (C=C), 1565 and 1505 cm^{-1} (aromatic). The MS, in addition to the molecular ion peak at *m/e* 260, showed peaks at *m/e* 245 (M^+ –Me) and also

* The sample isolated was in very small quantity and hence the optical rotation could not be determined.

[4] K. NAKASHI, *IR and Absorption Spectroscopy*, p. 36, Holden Day, San Francisco (1964).
[5] F. BROWN, J. KOSSANYI and C. DJERANSI, *Tetrahedron* **22**, Suppl. 8, 241 (1966).
[6] F. E. KING, J. R. HONSKY and T. J. KING, *J. Chem. Soc.* 1392 (1954).

at *m/e* 189, 159 and 131. The final confirmation of the identity of the compound as suberenol (III) previously isolated from *Xanthoxylum* species[3] was possible from the NMR spectrum (see Table 1).

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