

STEREOCHEMISTRY OF NATURAL COUMARINS CONTAINING

THE 3-HYDROXY-2,2-DIMETHYLCHROMAN SYSTEM (1)

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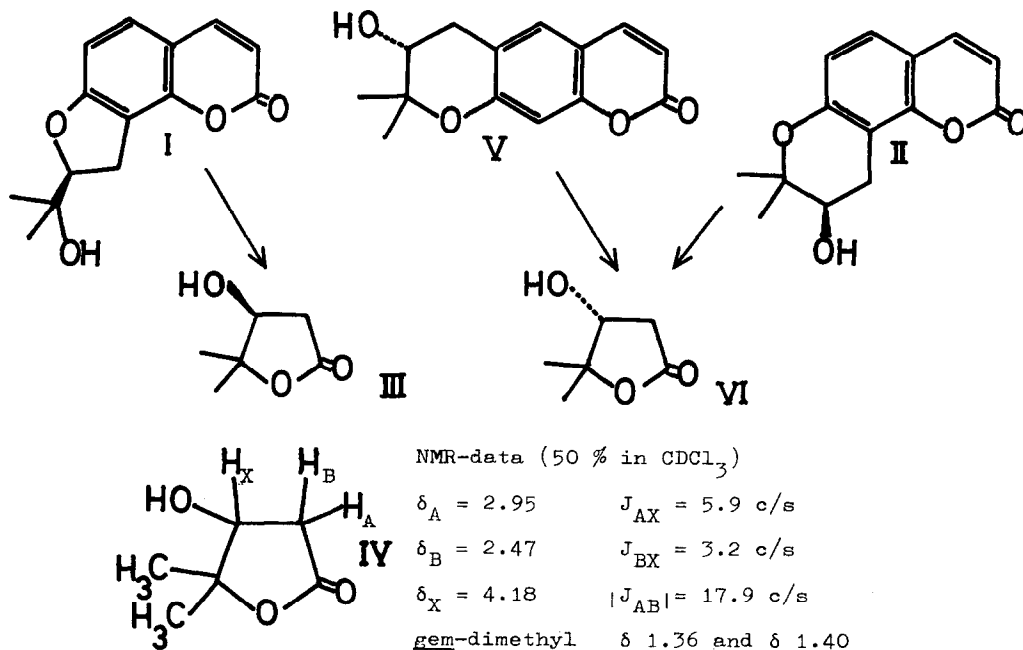
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Many natural products, especially within the fields of coumarins, chromones, isoflavones, and quinolines possess a 2,3-dioxygenated isopentanyl group attached to an aromatic or heteroaromatic ring. A number of variations of this structural feature is known. The oxygen functions frequently occur as a 2,3-epoxy group, possibly arising by biological oxidation of a 3,3-dimethylallyl group. The epoxides may in turn be hydrolyzed to the corresponding glycols or may, by biologically induced cyclizations, give structural types exemplified by (I) and (II).

Recently (+)-8,9-dihydrooroselol (I) was shown (2) to possess the configuration 8(S). Now, degradation of (I), m.p.163.5-164.0°,  $[\alpha]_D^{20} +273$  (c 0.3 MeOH) by exhaustive ozonolysis (3) has afforded 3(S)-3,4-dihydroxy-4-methylpentanoic acid  $\gamma$ -lactone (III) in moderate yield. The lactone (III) is a viscous liquid,  $[\alpha]_D^{23} -11$ ,  $[\alpha]_{365}^{23} -50$  (c 1.5 CHCl<sub>3</sub>), 3,5-dinitrobenzoate m.p.151.0-151.5°,  $[\alpha]_D^{23} -5.4$ ,  $[\alpha]_{436}^{23} -15.4$  (c 1.7 CHCl<sub>3</sub>). The IR-spectrum of (III) was identical with that of synthetic (R,S)-3,4-dihydroxy-4-methylpentanoic acid  $\gamma$ -lactone (IV). The racemic lactone (IV), b.p.118-120°, 1 mm Hg, was prepared from 2,3-dihydroxy-isopentanyl bromide using procedures very similar to those described (4) for the preparation of 3,4-dihydroxybutyric acid  $\gamma$ -lactone. (IV) gave a satisfactory NMR-spectrum and a 3,5-dinitrobenzoate m.p.134.0-134.5°. The natural coumarins, lomatin (II)\*), m.p.182.5-183.5,  $[\alpha]_D^{23} +52$  (c 0.4 EtOH) and (-)-3'-hydroxy-3',4'-dihydroxanthyletin (V) (5), m.p.180.5-181.5,  $[\alpha]_D^{23} -11$  (c 0.7 CHCl<sub>3</sub>),  $[\alpha]_D^{23} -102$  (c 0.5 pyridine), both on exhaustive ozonolysis afforded 3(R)-3,4-dihydroxy-4-methylpentanoic acid  $\gamma$ -lactone (VI). The 3,5-dinitrobenzoates, m.p.150.0-151.0°,  $[\alpha]_D^{23} +5$ ,  $[\alpha]_{436}^{23} +16$  (CHCl<sub>3</sub>), gave IR-spectra identical with that of the 3,5-di-

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nitrobenzoate of (III). These results prove the configurations of lomatin (II) and (-)-3'-hydroxy-3',4'-dihydroxyethyl (V) to be 3'(R). The natural coumarin decursinol (6),  $[\alpha]_D^{17} +103.8^\circ$  (pyridine) (7), which is the antipode of (V), accordingly possesses the configuration 3'(S).

The optically active lactone (III) will be useful as a key compound in our studies establishing the stereochemistry of compounds possessing the structural features discussed above.

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