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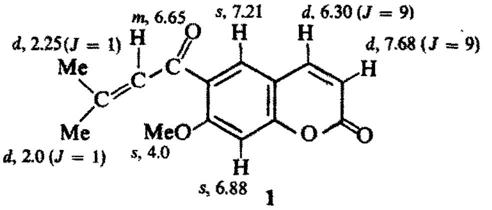
TWO COUMARINS FROM THE AEREAL PARTS OF *AMYRIS MADRENSIS*

X. A. Domínguez, G. Cano, Irene Luna and Antonieta Dieck
Departmento de Química, I.T.E.S.M. Monterrey, N.L., México

Key Word Index—*Amyris madrensis*; Rutaceae; coumarins; dehydrogeijerin; hopeyhopin; triterpene; lupenone; sitosterol.

As part of our research [1] on Mexican Rutaceae, we have studied *Amyris madrensis* Watt, a shrub common in northeastern Mexico. The aereal parts have been used occasionally as folk medicine, but there are no chemical reports on this plant. The petrol ether extract of dried stems and leaves of *A. madrensis* on chromatography yielded the triterpene lupenone, sitosterol, the rare coumarin dehydrogeijerin (1) and the new one, hopeyhopin (2). Lupenone was identified by its physical properties and conversion to lupeol.



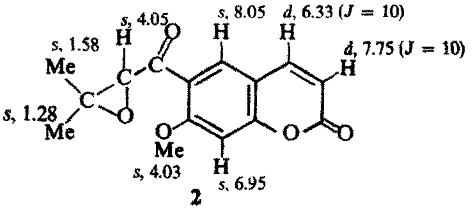
1

Dehydrogeijerin (1), mp 129° (M^+ 258), has been previously isolated only in *Geijera parviflora* [2]; this coumarin was identified by its mp and spectroscopic properties. The crystals of hopeyhopin 2 $C_{15}H_{14}O_5$, mp 200–201°, M^+ 274, are optical active and fluorescent. The NMR spectrum corresponding to a coumarin [3, 4]. It showed the presence of a methoxyl group, which on its UV and biogenetic grounds was positioned at C-7 and the five carbon epoxy ketone was positioned at C-6. Further, there are only two aromatic singlet protons (δ 8.05, 6.95) which could only be in the 5- and 8-positions. The MS was easily rationalized for the expected fragmentation pattern of such coumarins [5]. On *m*-chloroperbenzoic acid treatment of 1 a compound was obtained, which showed the same IR, NMR and TLC characteristics as 2 (hopeyhopin).

EXPERIMENTAL

Mp's are uncorr. The 60-MHz NMR spectra were recorded in a Varian A60-A in $CDCl_3$ with TMS (δ 0.00) as internal standard. IR in KBr, optical activity in $CHCl_3$.

Isolation of lupenone, sitosterol and the coumarins. Dried powdered stems and leaves (350 g) of *A. madrensis* (Voucher specimen 7420), were extracted in a Soxhlet with petrol (30–60°). The greenish brown residue (13 g) left after removal of petrol was refluxed 1 hr with 300 ml MeOH [6]. The MeOH soluble portion was evaporated to dryness, the 10 g brownish residue was chromatographed on Si gel. Elution with C_6H_6 with increasing proportions of MeOH afforded successively: lupenone $C_{30}H_{48}O$, M^+ 424 (23 mg, mp 160°), IR, NMR, [α], MS, on reduction of lupenone with $NaBH_4$ lupeol was identified; sitosterol (87 mg, mp 137°), IR, NMR, [α], coTLC and acetate; dehydrogeijerin (1) $C_{15}H_{14}O_4$, M^+ 258 (178 mg, mp 129°), *IR* ν_{max} KBr cm^{-1}, 3030, 2920. 1724, 1670, 1600, 1480, 1430, 1375, 1370, 1330, 1270, 1200, 1150, 1140, 990, 905, 805, 765, 745. *MS*: *m/e* 258 (100%), 257 (90), 243 (M-15) (23), 230 (1.8), 227 (49), 215 (3.6), 213 (9), 203 (40), 189 (7.2), 176 (15), 175 (21), 161 (9), 150 (5.4), 136 (5.4), 118 (7), 96 (6), 88 (9), 82 (24), 68 (13), 56 (16), 43 (13), 41 (15). Treatment of 1 with *m*-chloroperbenzoic acid in $CHCl_3$ gave crystals of a racemate with IR and NMR spectra identical with the corresponding spectra of hopeyhopine 2.



2

Hopeyhopin 2. $C_{15}H_{14}O_5$ (M^+ 274) (100 mg) mp 200–201°, in $CHCl_3$ $[\alpha]^{26}_{589}$ − 3.7°, $[\alpha]_{578}$ − 4.2°, $[\alpha]_{546}$ − 2.2°, $[\alpha]_{436}$ + 58°. UV λ^{MeOH}_{max} nm (ε), 202 (34837), 256 nm (4892), 308 (2266), 331 (2544). *IR*, ν_{max} KBr cm^{-1} 3033, 2925, 2875, 1780, 1725, 1650, 1500, 1475, 1450, 1420, 1400, 1360, 1280, 1200, 1160, 1140, 1110, 1010, 905, 895, 815, 805, 735. *MS*: *m/e* 274 (19), 259 (5), 245.5*, 216 (2.0), 203 (100), 186 (5), 175 (7), 160 (11), 144 (3), 131 (3), 119 (3), 115.5* (2), 104 (3), 89 (8), 76 (6), 71 (2), 69 (5).

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