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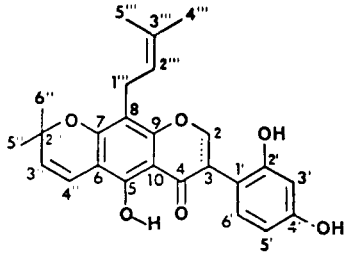
2,3-DIHYDROAURICULATIN, A NEW PRENYLATED ISOFLAVANONE FROM *ERYTHRINA SENEGALENSIS*.[1] APPLICATION OF THE SELECTIVE INEPT TECHNIQUE

RICHARD B. TAYLOR, DAVID G. CORLEY, MICHAEL S. TEMPESTA,*
Department of Chemistry, University of Missouri, Columbia, Missouri 65211
Z. TANEE FOMUM,* J. FOYERE AYAFOR, JEAN WANDJI,
Department of Chemistry, University of Yaounde, B.P. 812, Yaounde, Cameroon
and P. NGOZI IFEADIKE
Department of Chemistry, University of Port Harcourt, Nigeria

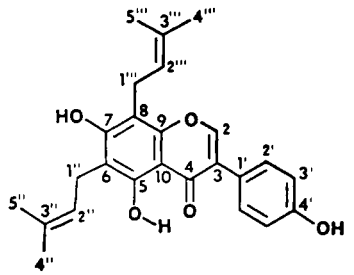
Our studies of Cameroonian medicinal plants in the genus *Erythrina* have yielded a number of new flavanones (1-2). In this paper, we report the structure of a new isoflavanone, 2,3-dihydroauriculatin (**1**), isolated from *Eythrina senegalensis* DC., as well as the ^{13}C-nmr spectral data on the co-occurring auriculatin (**2**) and 6,8-diprenylgenistein (**3**) (2-5).

The air-dried, ground stem bark of *E. senegalensis* was defatted with hexane and then extracted with $CHCl_3$. The hexane extract was concentrated and chromatographed over SiO_2 using hexane/Et_2O to give **3** as a powder whose spectral properties matched those published (4,5). After concentration, the $CHCl_3$ extract was chromatographed over SiO_2 using hexane-EtOAc (17:3) to give a mixture. The mixture was chromatographed further to yield **2**, which was identified by comparison of its spectral features with published data (3). Hexane-EtOAc (4:1) gave a mixture, which was chromatographed further to yield **1**.

Pure **1** was analyzed for $C_{25}H_{26}O_6$ through exact mass measurement. The ir spectrum exhibited bands at νmax (film) 3161 (free OH) and 1643 cm^{-1} (chelated C=O); the uv spectrum λmax 275 (log ϵ 4.72) indicated that **1** was related to **2** (3). The ^{1}H nmr in DMSO-d_6 indicated the presence of a chelated hydroxyl (δ 12.63) as well as two free phenolic groups (δ 9.35, 9.50). Comparison with the ^{1}H-nmr spectrum of **2** (3) indicated that the singlet assigned to H-2 (δ 7.95) in **2** was absent in **1** and that three additional signals were present in **1**, assigned to H-2 (δ 4.48, dd, J=7.7, 14.4 Hz; δ 4.56, t, J=14.4 Hz) and H-3 (δ 4.25, dd, J=7.7, 14.4 Hz).



1 2,3-dihydro
2 2-ene



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Comparison of the ^{13}C-nmr spectra of **1** and **2** (Table 1) indicated that the two compounds were very similar. The major differences were found in the

[1]Part 7 in the series "*Erythrina* Studies."

TABLE 1. ^{1}H-nmr Assignments for 2,3-Dihydroauriculatin (**1**) and ^{13}C-nmr Assignments for **1**, Auriculatin (**2**), and 6,8-Diprenylgenistein (**3**)

Atom	Compound			
	1		**2**	**3**
	^{1}H	^{13}C	^{13}C	^{13}C
2	4.48 dd(7.7,14.4) 4.56 t(14.4)	69.6 t	155.6 d	153.8 d
3	4.25 dd(7.7,14.4)	46.3 d	120.4 s	1231.9 s
4	—	198.6 s	181.0 s	180.6 s
5	—	156.0 s	153.9 s	156.7 s
6	—	101.9 s	104.6 s	111.5 s
7	—	158.3 s	155.8 s	158.9 s
8	—	107.5 s	106.8 s	106.2 s
9	—	159.4 s	154.0 s	152.8 s
10	—	102.5 s	105.2 s	104.6 s
1′	—	111.8 s	108.4 s	121.4 s
2′	—	156.1 s	156.4 s	130.1 d
3′	6.30 d(2.3)	102.6 d	102.6 d	115.0 d
4′	—	157.8 s	158.6 s	157.3 s
5′	6.17 dd(2.3,4.6)	106.3 d	106.2 d	115.0 d
6′	6.83 d(4.6)	131.2 d	132.1 d	130.1 d
1″	—	—	—	21.4 t
2″	—	77.9 s	77.7 s	122.3 d
3″	5.64 d(10)	126.6 d	128.8 d	130.7 s
4″	6.53 d(10)	115.0 d	115.0 d	25.5 q
5″	1.39 s	27.8 q	27.6 q	17.8 q
6″	1.39 s	27.9 q	27.6 q	—
1‴	3.11 bs	20.8 t	20.8 t	21.4 t
2‴	5.09 bs	122.3 d	121.7 d	122.3 d
3‴	—	130.4 s	130.4 s	131.1 s
4‴	1.70 bs	25.5 q	25.5 q	25.5 q
5‴	1.62 bs	17.8 q	17.8 q	17.8 q
5-OH	12.63			
2′-OH	9.50[a]			
4′-OH	9.35[a]			

[a]Assignments may be reversed.

chemical shifts of carbons 2-4, consistent with **1** being an isoflavanone and **2** an isoflavone. It remained for us, to establish unambiguously the position of the free prenyl and cyclized prenyl groups. A new nmr technique based on ^{13}C-^{1}H long-range couplings, Selective INEPT (6), was used to verify the prenyl attachments in **1**, **2**, and **3**. When H-2 is irradiated, we observed polarization transfer to the C-4 carbonyl and C-9. When H-1‴ was irradiated, polarization transfer was seen to C-3″, C-7, and C-9. This showed clearly that the free prenyl group was attached at C-8, as shown in Figure 1. This technique is also useful in making ^{13}C assignments (7) and, since it is sensitive, should find wide use in the structure elucidation of natural products.

EXPERIMENTAL

GENERAL.—All mp's were determined on a Kofler hot-stage apparatus and are uncorrected. Mass spectra were obtained with a Kratos MS-25 with a DS-55 Data System. Ir spectra were run on a Nicolet 20 DXB, and uv spectra on a Beckman 25 spectrophotometer. Silica gel GF_{254} (Merck) and silica gel 60 (70-230 mesh ASTM) (Merck) were used for tlc and column chromatography, respectively. All nmr experiments were performed

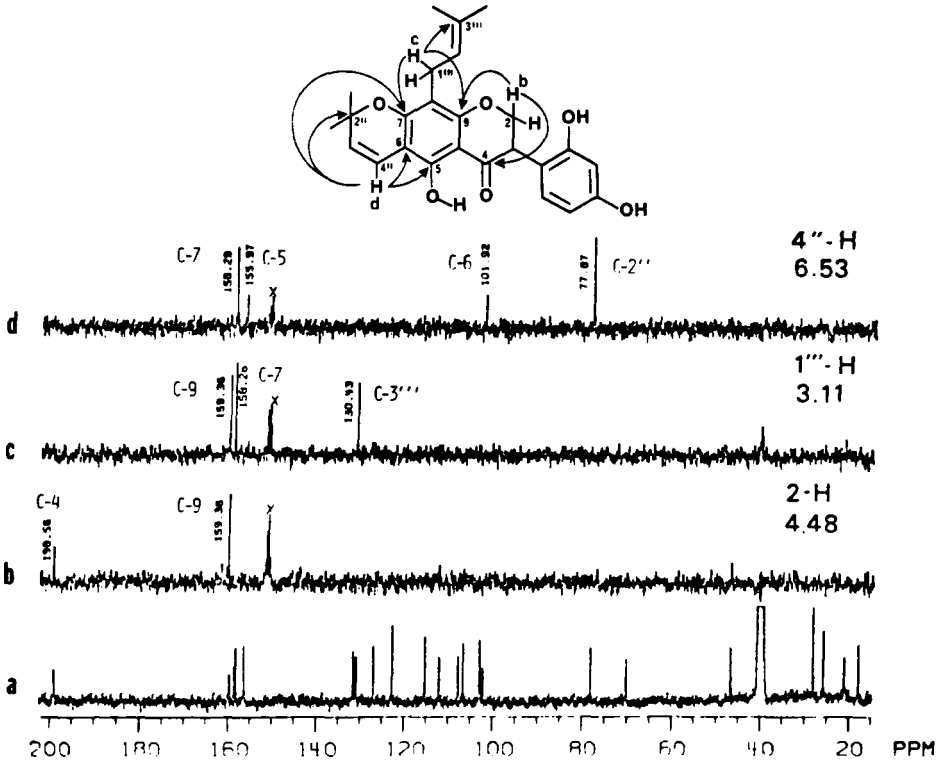

FIGURE 1. Summary of selective INEPT data obtained on 2,3-dihydroauriculatin (**1**), showing long-range heteronuclear couplings. (a) The ^{13}C-nmr broad band decoupled spectrum on 2,3-dihydroauriculatin (**1**) at 75.45 MHz in DMSO-d_6; (b) irradiation of H-2 (δ 4.48), observing polarization transfer to C-4 and C-9; (c) irradiation of H-1''' (δ 3.11), observing polarization transfer to C-3''', C-7, and C-9; (d) irradiation of H-4'' (δ 6.53), observing polarization transfer to C-2'', C-5, C-6, and C-7. X peaks are quadrature images of the solvent peak due to pulse imperfections.

on a Nicolet NT-300 WB spectrometer equipped with 5mm ^{1}H and ^{13}C probes operating at 300.06 and 75.45 MHz, respectively. Each sample was run in DMSO-d_6 at 22°, and all chemical shifts were referenced to internal TMS (0.0 ppm) for ^{1}H-nmr spectra and to DMSO-d_6 (39.5 ppm) for ^{13}C-nmr spectra. Selective INEPT experiments used the pulse sequence by Bax (6). A decoupler field strength $\gamma H_2 = 25$ Hz was used to generate a selective 90° proton pulse = 10 ms. The polarization transfer delays Δ_1 and Δ_2 were optimized for $J_{CH} = 6$ Hz. Between 600 and 2000 16K acquisitions were signal averaged in double precision acquisition mode and processed in floating point mode with standard Nicolet software.

PLANT MATERIAL.—*E. senegalensis* stem bark was collected at Abagana, eastern Nigeria, in March 1983. Voucher material documenting the collection was identified by the Director of the National Herbarium, Yaounde, Cameroon, and is on deposit there.

EXTRACTION AND ISOLATION.—Dried ground stem bark (3 kg) was successively extracted with hexane and $CHCl_3$. The $CHCl_3$ extract (90 g) was chromatographed using cc on SiO_2 (silica gel 60, 900 g), and elution with hexane-EtOAc (17:3) gave a mixture (10 g). Further cc on SiO_2 (300 g) using hexane-EtOAc (7:3) gave **2** (600 mg), mp 135-136°. Further cc on the main column with hexane-EtOAc (4:1) gave a mixture (12 g). The mixture was chromatographed using cc on SiO_2 (300 g) with hexane-EtOAc (4:1), and gave **1** (200 mg).

2,3-DIHYDROAURICULATIN (**1**).—Pale yellow powder, mp 100° (Me_2CO); $[\alpha]^{22}D = 0.0°$ (c = 0.017, MeOH); no cd; uv λmax (MeOH) 275 nm (log ε 4.72); ir νmax (film) 3161, 1643, 1622 cm^{-1}; ms obs. M^+ *m/z* 422.1715, calc. for $C_{25}H_{26}O_6$ 422.1729, *m/z* (rel. int.) 422(M^+, 60), 407(100), 285(25), 123(28) and 43(28)); ^{1}H nmr (300.06 MHz, DMSO-d_6) see Table 1; ^{13}C nmr (75.45 MHz, DMSO-d_6) see Table 1.

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