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24(*R*)-ETHYLLOPHENOL FROM *SOLANUM MELONGENA* SEEDS

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Key Word Index—*Solanum melongena*; Solanaceae; seeds; 4α-methylsterol; 24(*R*)-ethyllophenol; ^{13}C NMR spectroscopy.

During the course of our studies on the sterol and triterpene alcohol constituents of Solanaceae, 24-ethyllophenol (4α-methyl-24ξ-ethyl-5α-cholest-7-en-3β-ol) has been isolated from the 4α-methylsterol fraction of *Solanum melongena* seed oil, but the configuration at C-24 of the sterol remained to be determined [1]. Because 24-ethyllophenol was the major component (65%) in the 4α-methylsterol fraction of the oil [1], and is considered to be an important intermediate in the biogenesis of steroids in the plant, the configuration at C-24 of this sterol appears to be significant. Recently ^{13}C NMR spectroscopy has proved useful in determining the configuration at C-24 of alkyl sterols [2–4]. In this study, the technique has been applied to determine the C-24 configuration of the 24-ethyllophenol isolated from *S. melongena*. Off-resonance decoupling, acetylation and ketonization shifts, and lanthanide-induced shifts (LIS) were all used to aid assignment.

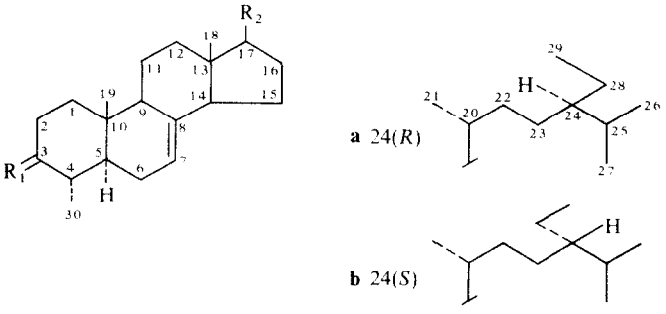
Most of the side chain carbons of the epimeric mixture of 24(*R*)- and 24(*S*)-ethyllophenols (**1** and **2**), prepared from citrostadienol (4α-methyl-5α-stigmasta-7,*Z*-24[28]-dien-3β-ol) by hydrogenation, showed split signals in the ^{13}C NMR spectrum, which enabled differentiation between the epimeric pair. The side chain signals of **1** and **2** were assigned as shown in Table 1 by direct comparison with those of the published spectral data [3] of sitosterol (24[*R*]-24-ethylcholest-5-en-3β-ol or stigmast-5-en-3β-ol) and its 24(*S*)-epimer, clionasterol, respectively. When the ^{13}C NMR spectrum of 24-ethyllophenol isolated from *S. melongena* was recorded, only the signals due to the 24(*R*)-epimer were observed as the side chain carbon signals, and the sterol therefore was identified as 24(*R*)-ethyllophenol (**1**). The signals arising from C-7, C-10 and rings-C and -D carbons (C-8, C-9 and C-11 through C-18) of 24(*R*)-ethyllophenol (**1**) were assigned by the comparison with those reported for 5α-cholest-7-en-3β-ol [5] and 24(*R*)-methyl-5α-cholesta-7,*E*-22-dien-3β-ol [6]. Furthermore, the characteristic changes that occur either on acetylation [5–8] or ketonization [7, 8] of the 3β-hydroxyl group enabled the signals for C-1 through C-6 and C-19 to be assigned. Assignment of a remaining C-30 (4α-methyl group) carbon signal was facilitated by the ketonization shift value ($\Delta\delta$ [**4**–**1**] = −3.7) which was identical with that reported for cycloeucalenol (4α,14α,24-trimethyl-9β,19-cyclo-5α-cholest-24[28]-en-3β-ol), a 4α-methylsterol [8]. The foregoing assignment (Table 1) was well supported by the LIS experiment in which the spectra were measured with various amounts of $Eu(fod)_3$, and then by the estimation of the approximate spacial distance between the expected co-ordinating site (hydroxyl function) of a lanthanide ion and the carbons under consideration.

The 24-ethyl group of 24-ethyllophenol isolated from *S. melongena* seed oil was thus unequivocally determined to have a 24(*R*)-configuration by ^{13}C NMR spectroscopy,

Table 1. ^{13}C NMR chemical shifts (δ) of 24-ethyllophenol and its derivatives

Carbon	**1**	**2**	**3**	**4**	**1** LIS*
C-1	37.0		36.6	39.4	3.6
C-2	31.0		27.1	38.0	10.9
C-3	76.2		78.4	213.3	24.3
C-4	40.2		37.0	45.6	5.4
C-5	46.7		46.7	50.2	2.9
C-6	26.7		26.6	28.0	1.9
C-7	117.4		117.2	117.1	1.1
C-8	139.1		139.1	139.2	1.4
C-9	49.7		49.4	49.2	1.4
C-10	34.8		34.7	35.1	3.4
C-11	21.4		21.3	21.5	1.2
C-12	39.6		39.5	39.6	0.8
C-13	43.4		43.3	43.3	0.6
C-14	55.0		54.9	54.9	0.7
C-15	23.0		22.9	23.0	0.3
C-16	28.0		28.0	28.0	0.5
C-17	56.0		56.0	56.0	0.6
C-18	11.8		11.8	12.0	0.4
C-19	14.2		14.0	13.7	2.7
C-30	15.2		15.2	11.5	7.0
$\underline{C}OMe$	—		170.8	—	—
$CO\underline{C}H_3$	—		21.3	—	—
C-20	36.6	36.7	36.6		0.4
C-21	18.9		18.9		0.3
C-22	33.9		33.9		0.3
C-23	26.2	26.5	26.2		0.2
C-24	45.9	46.1	45.9		0.2
C-25	29.1	29.0	29.1		0.3
C-26	19.8	19.0	19.8		0.2
C-27	19.0	19.6	19.0		0.2
C-28	23.1		23.1		0.5
C-29	12.0	12.3	12.0		0.5

* Lanthanide-induced shift ($\Delta\delta$): Extra shift produced by the addition of 100 mg of $Eu(fod)_3$ to the solution of 100 mg of substrate/0.9 ml of $CDCl_3$.



a 24(*R*)

b 24(*S*)

1 $R_1 = \alpha - H, \beta - OH, R_2 = \mathbf{a}$
2 $R_1 = \alpha - H, \beta - OH, R_2 = \mathbf{b}$
3 $R_1 = \alpha - H, \beta - OCOMe, R_2 = \mathbf{a}$
4 $R_1 = O, R_2 = \mathbf{a}$

and the carbon signals of the sterol were fully assigned. 24-Ethyllophenol has also previously been isolated from the same genus, *S. xanthocarpum*, and demonstrated to have a 24(*R*)-ethyl group by the chemical correlation with carpesterol (22[*R*]-hydroxy-6-oxo-4α-methyl-24[*R*]-ethyl-5α-cholest-7-en-3β-yl benzoate) [9].

EXPERIMENTAL

Recrystallizations were performed in Me_2CO–MeOH. Mps taken on a heated block were uncorr. The steryl acetate (**3**, mp 153–155°) was isolated from the acetylated 4α-methylsterol fraction separated from the unsaponifiable lipid of *Solanum melongena* seed oil [1]. Hydrolysis of the acetate (**3**) by refluxing for 1 hr with KOH in MeOH afforded free sterol (**1**, mp 175.5–176.5°). Oxidation of the free sterol (**1**) with CrO_3 in pyridine as described previously [10] gave ketone (**4**, mp 154.5–155.5°). A C-24 epimeric mixture of 24-ethyllophenol (**1** and **2**) was prepared from citrostadienol by partial hydrogenation (PtO_2 catalyst, Et_2O soln). ^{13}C FT NMR spectra were recorded on a JNM FX-100 spectrometer operating at 25.05 MHz using 0.1–0.26 M solns in $CDCl_3$. The chemical shifts (δ) are expressed in ppm relative to TMS and are estimated to be accurate to ±0.05 ppm. The probe temp. was *ca* 30°. FT NMR measurement conditions were as follows: spectral width: 5 or 6 KHz, pulse width: 6 μsec, acquisition time: 2 or 2.5 sec, and number of data points: 8192. The LIS experiment was performed using commercially available $Eu(fod)_3$ (tris[heptafluorobutanolypivaloylmethanato]europium).

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