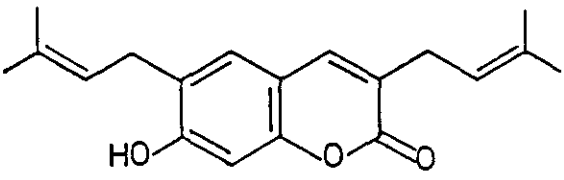
AMYRIS OF JAMAICA. NEW COUMARINS FROM AMYRIS ELEMIFERA L. (RUTACEAE)

Saleela Philip[1] and Basil A. Burke[2]

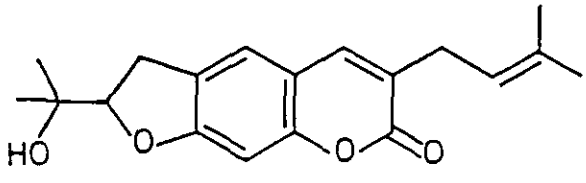
Department of Chemistry, University of West Indies, Mona, Kingston 7, Jamaica

Abstract - The isolation of elemiferone, elemiferone monoacetate and elemiferone diacetate constitutes further evidence for the use of 3-(3',3'-dimethylallyl)-coumarins as taxonomic markers for the genus Amyris.

In our previous reports[3,4] on the chemical investigations of the Amyris genus of Jamaica, we presented the coumarins (1) and (2) as metabolites of Amyris balsamifera and Amyris elemifera and suggested that 3-(3',3'-dimethylallyl)-coumarins could be used as chemotaxonomic markers of the genus Amyris. The further isolation of the three new coumarins, elemiferone (3), elemiferone monoacetate (4) and elemiferone diacetate (5) from Amyris elemifera - the subject of this report - gives support to our earlier suggestion.



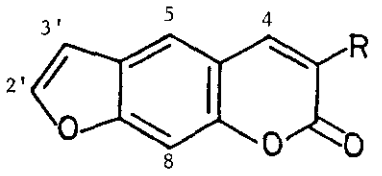
1



2

Purification by column and preparative layer chromatography of the toluene extract of dried, milled leaves and twigs of Amyris elemifera furnished the coumarins (3), (4) and (5).

The coumarin (3), elemiferone, mp 184-185°C, $[\alpha]_D^{25}$ + 39.0° (c, 0.88; EtOH), analysed for $C_{16}H_{16}O_5$. The ultraviolet absorptions at 240, 245, 262, 292 and 325 nm (log ε 4.38, 4.40, 3.79, 4.11 and 3.95 respectively, no base shift) were analogous to that of psoralen (6)[5], thus signalling the presence of a linear furanocoumarin moiety. The infrared spectrum exhibited bands at 3400 and 1708 cm^{-1} for the hydroxy and coumarin carbonyl functionalities.



R

3. $-CH_2-CH(OH)-C(OH)(CH_3)_2$

4. $-CH_2-CH(OAc)-C(OH)(CH_3)_2$

5. $-CH_2-CH(OAc)-C(OAc)(CH_3)_2$

6. H

7. $-CH_2COOH$

8. $-CH_2COOCH_3$

The ^1H NMR spectrum (100 MHz) in $CDCl_3$ was consistent with the structure (3). The linear furanocoumarin moiety was represented by signals at δ 6.83 (1H, dd, J = 1 Hz, 2.5 Hz, H-3'), 7.72 (1H, d, J = 2.5 Hz, H-2'), 7.37 (1H, d, J = 1 Hz, H-8), 7.68 (1H, s, H-5) and 7.78 (1H, s, H-4). The prenyl side chain was recognized from an ABX system, the methylene group constituting the AB protons [δ 2.40 (1H, dd, J = 10, 14 Hz); 2.92 (1H, dd, J = 3, 14 Hz)] while the methine hydrogen at the base of the hydroxyl portion formed the X portion [δ 3.65 (1H, dd, J = 3, 10 Hz)]. A six-proton singlet at δ 1.24 together with an exchangeable (with D_2O) signal at δ 3.57 (2H) completed the signals for this linear five-carbon C-3 substituent.

Jones oxidation of elemiferone (3) provided the acid (7), sublimes at 198-202°C. The infrared spectrum showed an absorption at 1692 cm^{-1}, due to the acid carbonyl while the ^1H NMR spectrum indicated the loss of the prenyl diol side chain but showed a two-proton singlet at δ 3.53 which was assigned to the methylene group adjacent to the carboxylic acid functionality. Methylation of (7) employing ethereal diazomethane furnished (8), mp 143-145°C, which analysed for $C_{14}H_{10}O_5$. The product (7) obtained by Jones oxidation also proved that the hydroxyl groups were attached to adjacent carbons as in the structure (3).

The coumarin (4), mp 178.5-179.5°C, $[\alpha]_D^{25}$ + 13.2° (c, 1.83; $CHCl_3$), $C_{18}H_{18}O_6$, had ultraviolet absorptions [238 (shoulder), 242, 260 (shoulder), 289 and 323 nm (log ε 4.41, 4.43, 3.80, 4.12 and 3.96 respectively)] similar to those of (3). The infrared spectrum indicated a hydroxy function (3456 cm^{-1}), an ester carbonyl (1743 cm^{-1}) and coumarin lactone (1720 cm^{-1}) moiety. The ^1H NMR spectrum agreed well with the structure (4). A three-proton singlet at δ 1.93 for the

acetoxy group and a downfield shift of the methine proton to δ 5.12 - the remaining signals being virtually superimposable with those of elemiferone (3) - confirmed that this natural product was the monoacetate derivative of (3). Mild hydrolysis of (4) yielded (3), identical by direct comparison to the natural product.

Elemiferone diacetate (5), mp 156-157°C, $[\alpha]_D^{25}$ - 6.5° (c, 1.80; $CHCl_3$), $C_{20}H_{20}O_7$, exhibited bands in the infrared spectrum at 1748 (ester carbonyl) and 1718 (coumarin carbonyl) cm^{-1}. The ^1H NMR spectrum contained no exchangeable signals but instead showed two three-proton singlets at δ 1.98 and δ 2.01 (2X-O-$\overset{O}{\overset{\|}{C}}$-$CH_3$). The rest of the resonances were similar to those of (4). Hydrolysis of this natural product, once again, furnished (3), identical in every respect to the natural product, and confirming its structure as the diacetate derivative (5).

Elemiferone, elemiferone monoacetate and elemiferone diacetate were present in the crude extract, obtained on percolation of the plant material with toluene at room temperature and before subjection of it to purification by chromatographic methods.

REFERENCES

1. Present address: Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6.

2. Present address: ARCO Plant Cell Research Institute, 6560 Trinity Court, Dublin, California, U.S.A.

3. B. A. Burke and H. Parkins, Phytochemistry, 1979, 18, 1073.

4. B. A. Burke and S. Philip, Heterocycles, 1981, 16, 897.

5. E. C. Horning and D. B. Reisner, J. Am. Chem. Soc., 1950, 72, 1514.

Received, 19th April, 1985