AMYRIS OF JAMAICA. COUMARINS OF AMYRIS ELEMIFERA D.C., (RUTACEAE)

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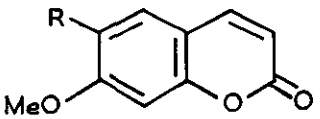
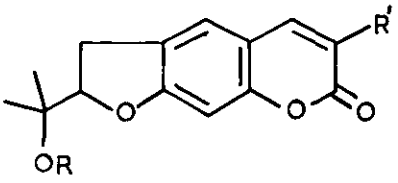
Abstract - Two new coumarins, marmesin acetate and 3-(3',3'-dimethylallyl)-marmesin, are reported from A.elemifera.

Amyris elemifera is one of only three Jamaican species of the genus Amyris[1]. Though typically rutaceous in other locations the Jamaican genus has been the subject of dichotomous classification[1,2]. Our previous reports[3,4] on the two other species, A. balsamifera and A. plumieri,have provided substantial chemical evidence for placing the genus in Rutaceae. Oxazoles, β-phenylethylamides and coumarins - typical constituents of the family Rutaceae - are present in these species. On the contrary, ligans[5] which are widely distributed in the family Burseraceae are significantly absent among the secondary metabolites found to date in the species of Amyris investigated. The constituents of the title plant[6] - the subject of our present report - fully concur with our earlier findings. In addition, a possible generic marker for use in chemotaxanomy has emerged from this study.

The toluene extract of the dried, milled leaves and twigs of A. elemifera gave products from which several coumarins have been identified.





1. R = CH=CHCOHMe$_2$
2. R = COCH=CMe$_2$
3. R = COCHCMe$_2$ (O)
4. R = H; R^1 = H
5. R = Ac; R^1 = H
6. R = H; R^1 = $CH_2CH=CMe_2$

Compound (1), $C_{15}H_{16}O_4$, m.p. 174-175°, showed maxima at λ_{max} 224, 255, 294, 304 and 343 (log ε 4.29, 4.59, 3.59, 3.94 and 4.15 respectively) nm but did not give a base shift[7]. The IR spectrum contains bands at 3425 and 1720 cm^{-1} for the hydroxy and α-pyrone carbonyl functionalities. The presence of two doublets (J = 9 Hz) at δ 6.17 and 7.72 and two singlets at 6.77 and 7.52 (each 1H) signalled the presence of a 6-alkyl-7-oxycoumarin[8]. The remaining PMR signals at 1.35 (6H, s), 3.88 (3H, s), 4.30 (1H, s, exchangeable with D_2O) and 6.30 and 6.80 (each 1H, d, J = 16 Hz) supported the structure (1) with the E - geometry of the side chain. This compound is suberenol previously isolated from Zanthoxylum suberosum[9].

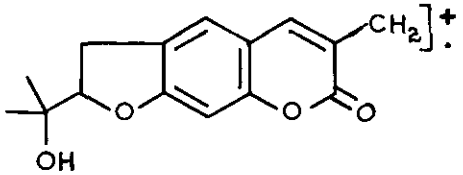
Compound (2), m.p. 129-130°, analysed for $C_{15}H_{14}O_4$. The UV [λ_{max} 232, 267, 307 and 328 (log ε 3.92, 4.21, 3.91, 4.01) nm]and IR (ν_{max} 1663, 1723 cm^{-1}) spectra were in agreement with the α, β-unsaturated arylketone and the 7-methoxycoumarin moieties. The dimethylacryloyl side chain was fully identified by singlets (3H each) at δ 1.98 and 2.22 and by a broad singlet (1H) at 6.57. The influence of the acyl substituent on the C-5 proton (δ 7.65, 1H, s) confirmed its position at C-6. Other signals, at 6.22 and 7.62 (each, 1H, d, J = 9 Hz) and 6.78 (1H, s) were assigned to H-3, H-4, and H-8 respectively. These features identified this compound as dehydrogejerin, a metabolite of Geijera parviflora[10]. Epoxidation of (2) with m-chloroperbenzoic acid gave hopeyhopin (3) which was isolated from A. madrensis[11].

Compound (4), $C_{14}H_{14}O_4$, m.p. 188-190° $[\alpha]_D^{25}$ + 26.0 (c 1.54 $CHCl_3$) had characteristic UV absorptions of a 6-alkyl-7-oxycoumarin at λ_{max} 224, 248, 258, 285, 297 sh and 335 (log ε 4.12, 3.78, 3.75, 3.67, 3.86 and 4.30) nm, and IR bands at 3450 and 1720 cm^{-1}. The compound was not phenolic. The PMR spectrum (60 MHz) of (4) displayed a triplet at δ 4.70 (1H, J = 8 Hz), a doublet at δ 3.20 (2H, J = 8 Hz), and two singlets at δ 1.23 and 1.37 (each 3H), in addition to the usual signals for a 6-alkyl-7-oxycoumarin. These features pointed to the presence of a linear dihydrofuranocoumarin[8] rather than the isomeric chromanocoumarins. Compound (4), was resistant to oxidation by Jones' reagent. Together with the molecular rotation this evidence confirmed that (4) is marmesin, already found in Aegle marmelos[12] which also belongs to the family Rutaceae.

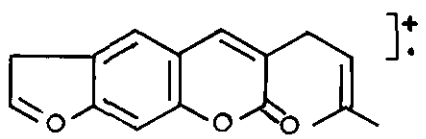
Compound (5), $C_{16}H_{16}O_5$, m.p. 135-136°, $[\alpha]_D^{25}$ + 13.5 (c 1.97, $CHCl_3$) showed spectral features similar to (4) the accompanying difference being associated with the replacement of the hydroxy group by an acetoxy group. Significantly the IR spectrum had no hydroxy bands, while the PMR spectrum showed a three proton singlet at δ 1.93 for the acetate and deshielded methyl signals at δ 1.50 and 1.53 (each 3H, s). Compound (5), is therefore marmesin acetate which has not previously been isolated as a natural product, although its enantiomer nodakentin acetate has been[13]. This assignment was confirmed by mild hydrolysis of (5) to marmesin (4).

Compound (6), m.p. 199-200°, $[\alpha]_D^{25}$ + 23.1 (c 0.85, $CHCl_3$) analysed for $C_{19}H_{22}O_4$. Its UV [λ_{max} 219,

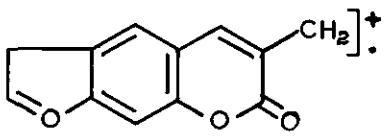
245 (sh), 255 (sh), 282 (sh), 295 (sh) and 329 (log ε 4.15, 3.80, 3.69, 3.80, 3.99 and 4.42 respectively)] and IR (3450 and 1710 cm^{-1}) spectra were consistent with this structure. The PMR spectrum showed all the features of the dihydrofuran moiety of marmesin. On the other hand the usual two doublets for the protons at C-3 and C-4 in marmesin were replaced by a one-proton singlet at δ 7.34 for the proton at C-4 and other signals [δ 5.30 (1H, bt, J = 8 Hz), 3.20 (2H, d, J = 8 Hz) and 1.68 and 1.80 (each 3H, bs)] diagnostic of the 3',3'-dimethylallyl group. The mass spectrum of (6) supported this structural assignment[14,15]. Especially informative were the major fragments a-d shown in Figure I. The molecular ion was also the base peak.



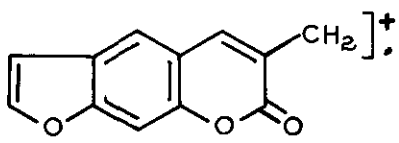
a. m/e 259 (99%)



b. m/e 255 (26%)



c. m/e 200 (51%)



d. m/e 199 (34%)

Figure I

A comparison of the rotation of (6) with that of marmesin, nodakenetin and their derivatives reveals that a remote (e.g. C-3) achiral functionality does not affect the direction of molecular rotation. The similarity in rotation between compound (6) and marmesin therefore indicates that compound (6) is 3-(3',3'-dimethylallyl)-marmesin, a new natural product. Together with balsamiferone of A. balsamifera[3] and 3-(3',3'-dimethylallyl)-xanthyletin of A. simplicifolia[16] this compound forms a series of 3-(3',3'-dimethylallyl)-coumarins which are emerging as potential taxanomic markers of the genus Amyris. The corresponding 3-(1', 1'-dimethylallyl)-coumarins appear commonly in the genus Ruta[17], also belonging to Rutaceae.

References and Notes

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