SYNTHESIS OF 7-(2,3-EPOXY-3-METHYLBUTYLLOXY)-5,6-METHYLENEDIOXYCOUMARIN AND DERIVATIVES

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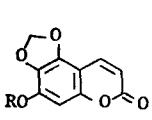
Abstract. The synthesis of 7-(3-methylbutenyl-loxy)-6,7-methylenedioxycoumarin as well as its correspondents epoxy- and diol- side chain derivatives, suggests a structural revision for natural products.

In a previous communication[1] we mentioned the isolation of 8 coumarins from aereal parts of Pterocaulon balansae and P. lanatum. One of them (1) had been previously isolated from Pteronia glabrata by Bohlmann et al[2].

Based on spectral data, including the use of solvent-induced chemical shift technique in PMR and chemical interchanges starting from 1, we proposed[1] structures of two (2 and 3) of the four new coumarins which were isolated.

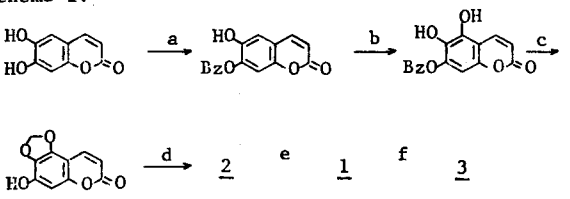


1. R = $-CH_2-CH\overset{O}{\frown}C(CH_3)_2$
2. R = $-CH_2-CH=C(CH_3)_2$
3. R = $-CH_2-CH(OH)-C(OH)(CH_3)_2$

In this communication we report the unambiguous synthesis of substances 1 - 3 (scheme I), starting from aesculetin (4), which was prepared according to the literature[3], and compared directly with an authentic sample. All the final compounds, as well as intermediates, presented spectral data (UV, IR, MS and NMR) compatible with their molecular structures. During our studies, however, we found that the solvent-induced chemical shift technique, so largely used in PMR for structural elucidation[4], failed several times with these our compounds.

To our surprise, none of the final synthetic products (1, 2 and 3) presented physical constants in agreement with those reported for the natural products which were isolated by Bohlmann[2] and by ourselves[1]. Thus, the natural coumarins probable have alternative structures whose synthesis we are now developing. Nevertheless, we emphasize that the coumarins represented by 1, 2 and 3 are new synthetic compounds.

Scheme I:



legend: Bz = $-CH_2-C_6H_5$; a) Ac_2O/Py than BzCl/KI/K_2CO_3[5]; b) AcOH/HMT than H_2O_2/NaOH[6]; c) CH_2I_2/CuO/DMF[7]; d) C_5H_9Br/K_2CO_3[8]; e) mCPBA/$CHCl_3$[9]; f) H_3O^+.

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Título em Português:

Sínteses da 7-(2,3-epoxido-3-metilbutiloxido)-5,6-metileno dióxido-cumarina e derivados.