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## FURANOCOUMARINS FROM THE ROOT OF HERACLEUM MANTEGAZZIANUM

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Key Word Index—Heracleum manteaazzianum. Umbelliferae furanocoumarins

Plant Heracleum mantegazzianum Somm & Lev Source Plants were collected at the Quartier-Léopold, Brussels Material was identified in the herbarium of the Jardin Botanique National de Belgique Previous work Roots<sup>1</sup>, fruit<sup>2</sup>

Roots Dry roots (135 g) were extracted with light petrol (25–50°)–Et<sub>2</sub>O (1 1), compounds were isolated by silica gel column chromatography, eluted with light petrol (25–50°) with increasing amounts of Et<sub>2</sub>O and by silica gel preparative TLC with CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> in various proportions Pimpinellin, angelicin, isobergapten, bergapten, xanthotoxin, isopimpinellin and sphondin were identified by UV, NMR and MS and m m p and by direct comparison with authentic samples by TLC<sup>3</sup> and GLC <sup>4</sup>

Acknowledgement - We thank Dr Th Beyrich for specimens of authentic samples

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## TERPENOIDS AND FLAVONES OF CALLICARPA MACROPHYLLA AND C LONGIFOLIA

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**Key Word Index**—Callicarpa macrophylla, C longifolia, Verbenaceae, calliterpenone and its monoacetate, sitosterol ursolic acid, 7-O-glucuronides of luteolin and apigenin

LEE, E. C., CATALFOMO, PH. and SCIUCHETTI A. (1966) J. Pharm. Sci. 55, 521

<sup>&</sup>lt;sup>2</sup> BEYRICH, TH (1968) Die Pharm 23, 336

<sup>&</sup>lt;sup>3</sup> Beyrich, Th (1965) Planta Med 13, 439

<sup>&</sup>lt;sup>4</sup> HAFSFN J P SZUM VORDFSIEVE VORDING J G M and KHO K F F (1971) Planta Med 19, 285

Plant Callicarpa macrophylla Vahl (voucher specimen No 1/73, deposited at JIPMER) Uses Medicinal 1,2 Previous work Calliterpenone and its monoacetate, 3 on sister species 4-6

Present work Dry leaves of C macrophylla were extracted with CHCl<sub>3</sub>, followed by 80% EtOH CHCl<sub>3</sub> conc after purification by adsorption chromatography over alumina yielded (a) sitosterol (petrol– $C_6H_6$ , 3 1 fraction), mp and mmp, acetyl, co-TLC (AgNO<sub>3</sub> impregnated silica gel), (b) calliterpenone ( $C_6H_6$ –CHCl<sub>3</sub>, 9 1 fraction), mp and mmp 156–158°,  $[\alpha]_5^{29}$  +308° (CHCl<sub>3</sub>) IR  $v_{max}^{KBr}$  3320 (br, OH) and 1708 (cyclohexanone) NMR ( $\delta$  values) 098, 101 and 106 (3H, s, each,  $C_{18}$ ,  $C_{19}$  and  $C_{20}$   $\rightarrow$  Me) and 371 (m, 2H,  $C_{17}$ –CH<sub>2</sub>OH), acetyl mp 121–123°, and co-TLC with authentic sample and (c) calliterpenone monoacetate (petrol– $C_6H_6$ , 3 2 fraction), mp and mmp 121–123°, co-TLC with synthetic and authentic calliterpenone monoacetate

EtOH extract gave luteolin and apigenin (ether fraction),  $R_f$ , mp,  $\lambda_{\rm max}$ , and co- $R_f$ , apigenin-7-O-glucuronide (EtOAc fraction),  $R_f$ , mp, products of hydrolysis and co- $R_f$  and luteolin-7-O-glucuronide (EtOAc fraction, less soluble in aq MeOH), mp 180–182° UV  $\lambda_{\rm max}$  (nm) 254, 268 sh, 345 (MeOH), 255, 268 sh, 360, 400 (NaOAc), 272, 298 sh, 425 (AlCl<sub>3</sub>) and 259, 368 (NaOAc + H<sub>3</sub>BO<sub>3</sub>)  $R_f$  048 (H<sub>2</sub>O), 023 (15% HOAc), 040 (BAW), 045 (phenol), 070 (Forestal) and 054 (t-BAW) and products of acid and glucuronidase hydrolysis

Plant Callicarpa longifolia Lam (voucher specimen No 2/73 deposited at JIPMER) Uses Medicinal 1,2 Previous work Nil

Present work Examination of the leaves  $CHCl_3$  extract contained calliterpenone and calliterpenone monoacetate (identified as above) and ursolic acid (mp, mmp and TLC of acetyl and methyl ester of acetyl derivative and co-TLC) and the alcohol extract, the same flavonoids as C macrophylla in minute quantities

Comment This appears to be the first record of isolation of luteolin-7-O-glucuronide though it has been identified earlier in Digitalis purpurea, Anisochilus carnosus and Trifolium pannonicum The isolation of calliterpenone and its monoacetate (11-oxo kaurane derivatives) from these 2 species of Callicarpa, together with the occurrence of callicarpone (tricyclic diketo diterpene) in C candicans and maingayic acid (furan diterpene acid) in C maingayi suggests that the occurrence of diterpenes in Callicarpa is common

Acknowledgements—We thank Professor A Chatterjee, Calcutta University for the authentic samples of calliterpenone and its monoacetate, Professor T R Govindachari for the spectral data, the Officer-in-charge, Systematic Botany Branch, Forest Research Institute, Dehra Dun for the supply of authentic leaves and the Principal, JIPMER, for encouragement

<sup>&</sup>lt;sup>1</sup> Anon (1950) Wealth of India, Raw Materials, Vol II, p 14, CSIR, New Delhi

<sup>&</sup>lt;sup>2</sup> CHOPRA, R N, NAYAR, S L and CHOPRA, I C (1956) Glossary of Indian Medicinal Plants, p 45, CSIR, New Delhi

<sup>&</sup>lt;sup>3</sup> Chatterjee, A, Desmukh, S K and Chandrasekharan, S (1972) Tetrahedron 28, 4319

<sup>&</sup>lt;sup>4</sup> Hosozawa, S., Natsuki, K. and Katsura, M. (1972) Phytochemistry 11, 2362

<sup>&</sup>lt;sup>5</sup> KAWAZU, K and MITSUI, T (1966) Tetrahedron Letters 3519

<sup>&</sup>lt;sup>6</sup> Nishino, C, Kawazu, K and Mitsui, T (1971) Tetrahedron Letters 1541

<sup>&</sup>lt;sup>7</sup> HARBORNE, J B (1967) Comparative Biochemistry of Flavonoids, p 48, Academic Press, London

<sup>&</sup>lt;sup>8</sup> Subramanian, S S and Nair, A G R (1972) Phytochemistry 11, 453

<sup>&</sup>lt;sup>9</sup> SCHULTZ, G and BOHRER, I (1971) Phytochemistry 10, 3315