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SESQUITERPENE LACTONES OF THE UMBELLIFERAE*

MIROSLAV HOLUB and MILOŠ BUDĚŠÍNSKÝ

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6, Czechoslovakia

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Key Word Index—Umbelliferae; sesquiterpene lactones; new stereostructural types; biogenesis; chemotaxonomy.

Abstract—A survey of sesquiterpene lactones from the species of Umbelliferae is presented. The structures based on predominantly undescribed stereostructural types were derived for the majority of these lactones.

INTRODUCTION

At present the number of described sesquiterpene lactones† isolated from members of the Umbelliferae amounts to about 100. While studying them systematically, we have found recently that practically all the sesquiterpene lactones of this family so far described are based on new stereostructural types.

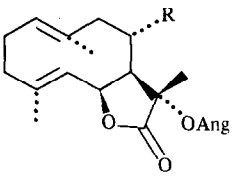
* Part 292 in the series "On Terpenes". For Part 291 see *Collect. Czech. Chem. Commun.* (1986) **51**, 1323.

† 'Sesquiterpene lactones' here means those substances only the lactone carbonyl of which can be derived by oxidation of the methyl of the isopropyl group of the basic sesquiterpene carbon skeleton.

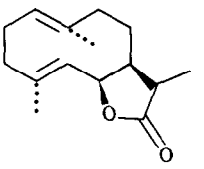
RESULTS

Germacranolides

So far in the species of Umbelliferae five germacranolides have been identified, among which laserolide (**1**) [1, 2], 8-deacetoxylaserolide (**2**) [3] and gallicolide (**3**) [4], isolated from the tribe Laserpitieae, belong according to their structure to the new stereostructural type of germacranolide which we described recently. It is based on the fundamental skeleton 6*R*,7*S*-germacra-*E*1(10),*E*(4)-dien-6,12-olide (**4**) [5, 6]. We confirmed the structure of this new stereostructural type by X-ray analysis of ursiniolide A (**5**) [7] and laserolide (**1**) [8]. The further two germacranolides described, isolated from *Smyrnium rotundifolium* Mill. (tribe Smyrnieae), i.e. 1β,10α-epoxy-4-methoxy-8-hydroxyglechomanolide (**6**) and 1β,10α-epoxy-4-methoxyglechomanolide (**7**), still do not have their complete relative and absolute configurations de-



1 R = OAc
2 R = H
3 R = OMebu



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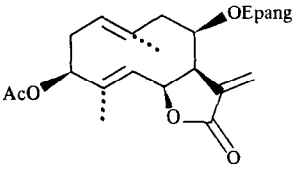

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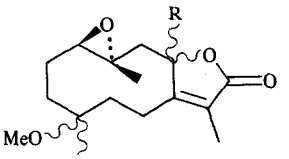
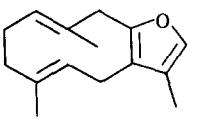


6 R = OH
7 R = H



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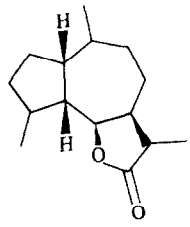
termined. It is possible that they are artifacts formed from the furodiene **8**, which was also detected in the same plant material [9].

Guaianolides

As regards guaianolides, we have demonstrated that the predominant lactones of this type, isolated from the species of Umbelliferae—especially from the tribes Laserpitieae and Peucedaneae—belong to the new stereostructural type which we have also described [10] and the fundamental skeleton is 1*S*,5*R*,6*R*,7*S*-guaian-6,12-olide (**9**) or slovanolide [11]. We confirmed the structure of this new type of guaianolide by X-ray analysis of the ketolactone **10** [12] which we prepared from 8α-angeloyloxy-10β,11α-diacetoxyslov-3-enolide (**11**) [10], and by the correct interpretation [12] of the X-ray data of the lactone from *Laserpitium marginatum* [13] leading to the correct structure **12** for this compound [12]. About 20 natural sesquiterpene lactones can be classed as slovanolides, which we isolated from *Laserpitium siler* [10,11,14], *L. archangelica* [15] and *Laser trilobum* [3], all being derived from 8α,10β,11α-trihydroxyslov-3-enolide (**13**), 2β,8α,10β,11α-tetrahydroxyslov-3-enolide (**14**) or 4α,8α,10β,11α-tetrahydroxyslov-2-enolide (**15**). Grilactone (**16**) also belongs in this group. Its structure was proved by X-ray structural analysis [16] several years ago and completed by us by its absolute configuration [17]. The guaianolides such as 8-deangeloylshairidin (**17**) [18], guillonein (**18**) [19] and others are structurally closely related to the slovanolides. The structure for the natural lactones **17** and **18** (including absolute configur-



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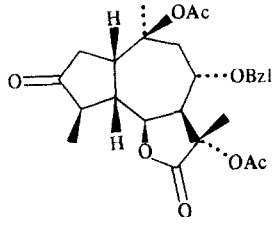

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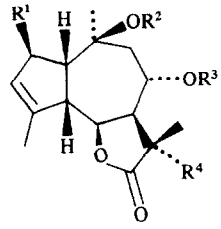
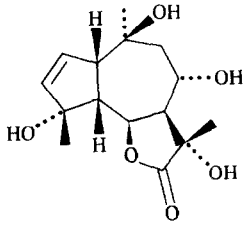


11 R^1 = H, R^2 = Ac; R^3 = Ang; R^4 = OAc
12 R^1, R^4 = H; R^2 = Ac; R^3 = Ang
13 R^1, R^2, R^3 = H; R^4 = OH
14 R^1, R^4 = OH; R^2, R^3 = H



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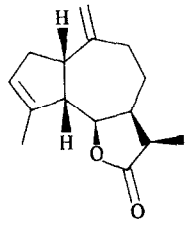

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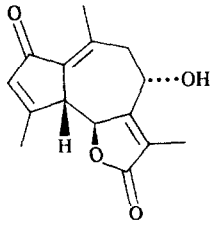

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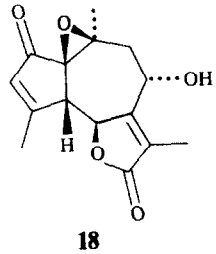

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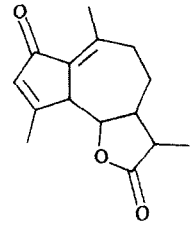

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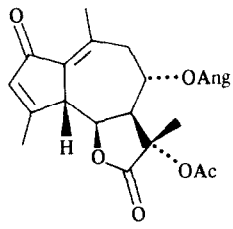

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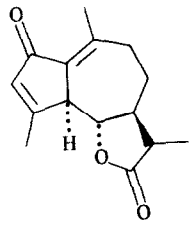

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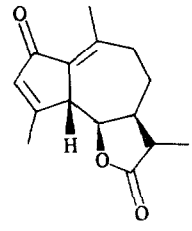

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