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COMMENTS ON THE STRUCTURE AND SYNTHESIS OF JASMINOL, A TRITERPENE REPORTED FROM *JASMINUM AURICULATUM*

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Abstract—The assignment of the lup-20(29)en-28-ol structure for jasminol, and subsequent synthetic proof, are shown to be insecure.

In 1970, a report [1] appeared describing the structure of jasminol, a new triterpene from *Jasminum auriculatum* (Vahl), as lup-20(29)en-28-ol (**1**). The structural assignment was based on spectral data; subsequently, synthetic lup-20(29)en-28-ol was stated [2] to be identical with jasminol.

As regards the spectral data [1, 3] of the natural product, there are a number of features incompatible with the structure **1**. Among the major discrepancies, a ^{1}H NMR signal at *ca* δ 3.15 was assigned to the C-28 C$\underline{H}_2$OH protons, but these normally appear [4] in betulin (**2**) and related compounds as an AB quartet at *ca* δ 3.5 (ΔAB 14 Hz, J_{AB} = 11 Hz). Further, in the mass spectrum of jasminol, peaks at *m/z* 220 and 249 were ascribed to the well-known ring C cleavage modes of triterpenes. These peaks cannot, however, be readily reconciled with structure **1** since the ring C fragmentation peaks would be expected to appear at *m/z* 191, 204, 205 and 234 [5]. Finally, in 1970, two unambiguous syntheses of **1** were already on record [6, 7]. While no spectral data were given for the synthetic lup-20(29)en-28-ols, the reported mps and $[\alpha]_D$s deviate to a large degree from those given for jasminol (Table 1). Also, we have recently [8] developed a very short synthesis of **1**. The mp and $[\alpha]_D$ of our product are in accord with those given earlier [6, 7] for **1**; the ^{13}C NMR spectrum was identical to that published [9]; and the mass spectrum indeed showed peaks at *m/z* 191, 204, 205 and 234, while peaks at *m/z* 220 and 249 were absent. Finally, lup-20(29)en-28-ol has a much larger R_f (0.39) in TLC than that reported [10] for jasminol (0.22), whereas in our extract (see below) of *J. auriculatum* leaves, no component appeared on TLC within R_f 0.39 ± 20%. We thus conclude that the identity of jasminol with lup-20(29)en-28-ol is doubtful.

Table 1. Reported values of mp and $[\alpha]_D$ for various specimens of lup-20(29)en-28-ol (**1**)

Source	mp	$[\alpha]_D$	Ref.
Jasminol (natural product)	208–210°	+41.50	1
Ruzicka	140–141°	+16° ± 2°	6
Djerassi	140–142°	not given	7
Hase	144°	+16.8°	8
'Synthetic jasminol'	209°	+40°	2

Regarding the reported [2] synthesis of jasminol, it turns out that this synthesis is the same as had previously been reported by Djerassi [7] for the preparation of **1**, involving successive Huang-Minlon and $LiAlH_4$ reductions of methyl 3-oxobetulate. However, it is remarkable that while the spectra of the newly synthesized material clearly show that the product is indeed **1**, it was claimed to have a mp and $[\alpha]_D$ closely similar to those reported for jasminol, and unlike those given for **1** by Ruzicka [6] and Djerassi [7] and us [8] (Table 1). Finally, it should be mentioned that the synthetic paper [2] also contains the statement, "the identity was later confirmed by the usual procedure", without any supporting experimental details whatever. We conclude that lup-20(29)-28-ol (**1**) was certainly being synthesized

and therefore the product's identity with natural jasminol is in doubt.

In trying to establish the true identity of jasminol, we have repeated the extraction and purification procedure [10] for this compound from *Jasminum auriculatum* leaves. We confirm that another triterpene, lup-20(29)en-3β-ol (lupeol) is present as reported, and also isolated a second major component, having a practically identical R_f on TLC with that of lupeol, again as originally indicated (R_f 0.214 for lupeol, 0.22 for jasminol). However, our material bears little resemblance to jasminol in terms of mp, $[\alpha]_D$ and spectral characteristics, and is in fact identical with β-amyrin (olean-12-en-3β-ol), another pentacyclic triterpene monoalcohol, isomeric with lupeol and jasminol. Our material, as the free alcohol and as the derived acetate, had mp [11], $[\alpha]_D$ [11], ^{1}H NMR [12, 13], ^{13}C NMR (peak deviation max. 0.1 ppm) [14] and MS [13] in agreement with the β-amyrin structure and with literature data for this substance and its acetate.

As a precaution against having overlooked the presence of yet another isomeric triterpene, i.e. jasminol, we have examined the mass spectrum (at various temperatures and eV values) of our crude extract for the presence of a peak at m/z 249, the single significant MS peak originally reported [1] for jasminol (other peaks given were $M^{+\cdot}$ and $M^{+\cdot}-18$ which obviously lack diagnostic value, and m/z 220 which also occurs in the MS of lupeol [15] with 9.5% relative intensity). No m/z 249, however, could be discerned, for example in a spectrum where m/z 191, 204, 205 and 234 (see above) are 20.2, 62.6, 34.1 and 3.9%, respectively, of the base peak, and where m/z 189 of lupeol is 48.3% (reported for lupeol, 43.1% [15]).

The true identity of jasminol thus remains obscure. We are unable to account for our failure to obtain jasminol from *J. auriculatum* leaves, unless this is due to seasonal or some other variation in the triterpene contents of the plant.

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