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A REVISED STRUCTURE FOR THE TRITERPENE RIGIDENOL

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Abstract—The structure of the triterpene rigidenol has been revised to 11α-hydroxy-lup-20(30)-en-3-one.

Rigidenol was isolated from *Maytenus rigida* (Celastraceae) and the structure of 6α-hydroxy-lup-20(30)-en-3-one (**1**) was assigned [1]. The lup-20-ene skeleton was deduced from the NMR spectrum and the presence of a ketone at C-3 was given on the basis of the reduction product of rigidenol, by comparison of the ORD spectrum of one of the ridideno1 derivatives with the lup-20(30)-en-3-one and by biogenetic consideration. The hydroxyl group was assigned to C-6, C-11 or C-12 because an olefin with only one vinylic proton was obtained by dehydration. Of these three positions C-6 was chosen because the oxidation product of rigidenol was different from the 3,11- and 3,12-lupendione [2, 3]. The fact that the structure of thurberindione (calenduladione) was changed from 3,12-lupendione to 3,16-lupendione [4, 5] compelled us to carry out a reinvestigation of the structure of rigidenol.

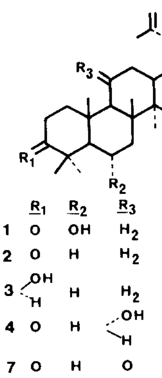
Considering that the chemical shifts of the methyl groups at C-4 in the ^{1}H NMR spectra of rigidenol and its reduction product are similar to those of the lupenone and lupeol respectively [6], it would seem that the presence of a hydroxyl group at C-6 must be excluded. On the other hand, given the displacement to downfield of the methyl group at C-10 in rigidenol in comparison with that of the lupenone it seems that the alcohol group is at C-11 [7]. Furthermore, the geminal proton to the hydroxyl presents the same chemical shift and coupling as in the 11α-hydroxygermanicol spectrum [13]. Moreover, in the rigidenol spectrum three protons appear between δ 2.30 and 2.80, assignable to two hydrogens at C-2 and one equatorial at C-1.

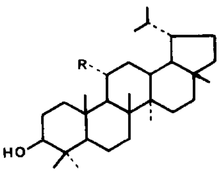
Rigidenol is an ideal substance for ^{13}C NMR analysis because the full assignment of carbon resonance in the lupeol series has been made [8]. In Table 1 we give the carbon chemical shifts of rigidenol, one of its derivatives (**5**), lupanol (**6**) and lupenone (**2**). The values of **6** and **2** are those published by Wenkert *et al.* [8]. Study of the table reveals that the structure of rigidenol is 11α-hydroxy-lup-20(30)-en-3-one (**4**). Thus, by comparison of rigidenol (**4**) with lupenone (**2**) it is seen that in the first the signal corresponding to C-11 has disappeared and that those of C-9 and C-12 were displaced downfield. It is characteristic that the signals due to C-1 of compounds **4** and **5** appear at a lower field (2.9) than in the lupenone (**2**) or lupeol (**3**) spectra respectively.

Table 1. ^{13}C NMR spectrum data of rigidenol and related triterpenes

	6	**2**	**5**	**4**	*
C-1	38.7	39.5	42.3	41.6	41.4
C-2	27.4	34.0	34.2	27.8	27.7
C-3	78.8	217.9	218.3	78.8	78.5
C-4	38.8	47.2	47.7	39.4	39.1
C-5	55.2	54.8	55.1	56.1	55.9
C-6	18.3	19.6	19.8	18.4	18.0
C-7	34.4	33.5	34.4	35.8	35.6
C-8	40.8	40.7	43.2	43.0	42.9
C-9	50.1	49.7	55.3	56.1	56.5
C-10	37.1	36.8	38.5	39.7	39.5
C-11	20.9	21.4	70.8	70.8	71.1
C-12	26.8	25.1	37.8	39.8	38.6
C-13	37.8	38.1	37.5	37.4	37.3
C-14	43.0	42.8	42.7	43.2	43.0
C-15	27.4	27.4	27.7	28.1	27.5
C-16	35.5	35.4	35.6	35.8	
C-17	43.1	42.9	42.9	43.5	
C-18	47.5	48.2	47.9	47.7	
C-19	43.8	47.8	48.0	45.0	
C-20	29.6	150.5	150.4	29.6	
C-21	21.9	29.8	29.8	22.2	
C-22	40.4	39.9	40.0	40.5	
C-23	28.0	26.6	27.6	28.6	
C-24	15.4	21.0	20.9	15.7	
C-25	16.0	15.8	17.0	17.5	
C-26	16.0	15.9	16.7	16.5	
C-27	14.4	14.4	14.6	14.8	
C-28	18.0	18.0	18.2	18.5	
C-29	15.1	109.2	110.0	15.3	
C-30	23.0	19.3	19.5	23.1	

*3β,11α-dihydroxy-olean-18-ene [9].





5 R = OH
6 R = H

This shift may be attributed to the presence of an equatorial OH group at C-11. In the germanicol series [9] it is also 2.9 and in the steroid derivatives [10] this shift is around 1.4. In comparison with the 11α-hydroxy-lup-20(30)-en-3-one (**4**) spectrum, in the 3β,11α-dihydroxy-lupane (**5**) spectrum the C-12 signal has undergone a downfield shift. This is attributable to the isopropyl configuration in **5** as compared with that which has the isopropylene group in **4** [8].

Finally, we verified by direct comparison that the NMR and IR spectra of the oxidation product of rigidenol and those of 3,11-lupendione (**7**) [2] were identical. Hence, the structure of rigidenol is 11α-hydroxy-lup-20(30)-en-3-one (**4**). Other lupane triterpenes with an OH group at C-11 have been isolated from *Salvia phlomoides* [11] and *Nepeta hindostana* [12].

EXPERIMENTAL

The ^{13}C NMR spectra were determined on a Brucker WM250 at 62.9 MHz and run with the solvent $CDCl_3$ providing an internal deuterium lock.

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