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STRUCTURAL REVISION OF AJUGOL AND MYOPOROSIDE

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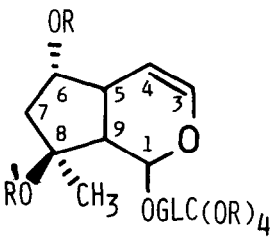
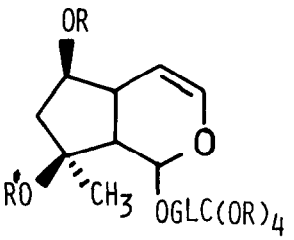
Abstract: An analysis of existing ^{13}C NMR data shows that the structures reported for the iridoid glucosides ajugol and myoporoside should be interchanged. Consequently, the structures of ajugoside and laterioside, both acyl-derivatives of ajugol, as well as that of 8-O-acetylmyoporoside need revision.

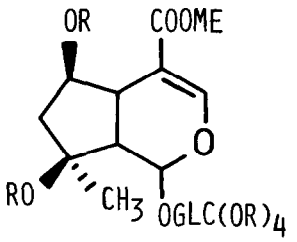
The iridoid glucosides ajugol and myoporoside have been assigned the structures 1 and 2, respectively.[1,2] In a recent paper[3] we compared the ^{13}C NMR data for ajugol[4,5] with those of shanzhiside[6] (3) and suggested that ajugol should be assigned the structure 2.[7] Its stereochemical relationship with myoporoside remained undecided, however, as no ^{13}C NMR data for this compound were available at that time. Recently, the ^{13}C NMR spectrum of 8-O-acetylmyoporoside was published,[9] and a comparison with the spectra of ajugoside (8-O-acetylajugol)[8] and laterioside (8-O-cinnamoylajugol)[4] is now possible. The spectra are compiled in Table 1.



1 R = R' = H
1a R = H; R' = Ac



2 R = R' = H
2a R = H; R' = Ac
2c R = H; R' = t-cinn.



3 R = H

Notable solvent effects are visible for certain signals; since these are larger than the differences caused by the change in acyl substituent, we prefer to compare only the two spectra recorded in CD_3OD. We have shown[3] that the C-9 shift is susceptible only to configurational changes at C-8. In the two spectra, the shifts for C-9 are identical; this fact, together with the expected[3,4] large shift differences for C-4, C-5 and C-6, confirm that the epimery resides at C-6.

Using a number of iridoid glucosides epimeric at C-6, we have demonstrated[3] that when

Table 1: ^{13}C NMR data for ajugol- and myoporoside-derivatives. The spectra have been aligned to C-6' = 61.5 ppm (cf. ref. 3).

Compound	Solvent	C-1	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
Ajugoside	D_2O	94.4	140.4	104.2	40.5	76.2	47.5	90.0	48.2	22.4
Laterioside	D_2O	93.9	140.3	104.0	40.5	75.9	47.8	89.8	48.2	22.4
	CD_3OD	93.1	140.0	102.6	40.2	75.3	47.4	88.6	48.0	21.5
8-O-acetyl-myoporoside	CD_3OD	92.7	140.6	99.9	35.7	70.5	46.0	86.6	47.9	21.0

considering ($\delta_{C-3} - \delta_{C-4}$) for each compound, the 6α-epimer gives always the largest value. In this case, 8-O-acetylmyoporoside gives 40.7 ppm while laterioside gives 37.4 ppm, demonstrating that the former belongs to the 6α-series, and the latter to the 6β-series.

Due to lack of appropriate model compounds (i.e. pairs of compounds lacking substitution both at C-4 and C-5) the other differences between the two spectra can only be analysed in a general way. Thus the shifts of C-5 and C-6 in laterioside (40.2 and 75.3 ppm) are ca. 5 ppm larger than the corresponding values for 8-O-acetylmyoporoside (35.7 and 70.5 ppm). This is consistent[3] with the trans-disposition of the substituents on C-5 and C-6 (i.e. C-4 and OH) relative to the five-membered ring in laterioside and a corresponding cis-disposition in 8-O-acetylmyoporoside. The conclusion is the same as that reached above.

Thus we find that the spectroscopic evidence satisfactorily demonstrates that ajugol and myoporoside are epimeric at C-6, and that the former is represented by 2, the latter by 1. Consequently, ajugoside and laterioside possess the structures 2b and 2c, respectively, and 8-O-acetylmyoporoside 1b. The previously reported configurations at C-6 were derived by using Horeau's method.[10]

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