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# STRUCTURAL ELUCIDATION IN ANTHRAQUINONES USING $^1$H NMR GLYCOSYLATION AND ALKYLATION SHIFTS

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**Key Word Index**—Emodin; citreoresin; questin; fallacinol; nalgiovensin; frangilin; islandicin; catenarin; glucoside; primveroside; $^1$H NMR; alkylation/glycosylation shifts; peracetates.

**Abstract**—The trend shown by the alkylation/glycosylation $^1$H NMR shifts in the A ring in anthraquinones is not affected by B ring substituents and this observation helps in structural elucidation.

## INTRODUCTION

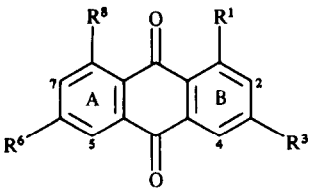
The position of *O*-glycosylation/alkylation in anthraquinones may be determined with the help of $^1$H NMR acylation shifts [1]. In an earlier report [2], an alternative procedure was proposed. It involves $^1$H NMR comparison of the peracetates of the aglycone and glycoside. The proton, *para* to the site of *O*-glycosylation, undergoes a larger shift. In the absence of a *para* proton, the *ortho* protons undergo larger shifts. The position of *O*-alkylation can be determined in a similar way. In the new method [2], the two anthraquinones being compared differ at one site only, and the shifts pinpoint the site of *O*-glycosylation/alkylation. In the former [1]*, the two anthraquinones (pertrimethylsilyl ether and peracetate) differ at many sites and the shifts cannot be attributed to *O*-glycosylation/alkylation alone. It is now shown that the trend of the shifts in the A ring is not affected by the B ring substitution pattern and this observations helps in structural elucidation in anthraquinones.

## DISCUSSION

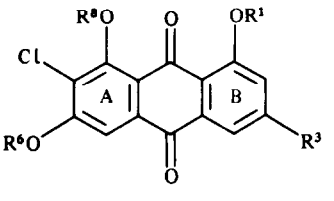
A comparison of **8** and **9**, having same A ring, shows $\Delta'$H-2 = +0.08 and $\Delta'$H-4 = +0.32 for 1-*O*-alkylation (Tables 1 and 2). Shifts from **2** and **7**, with different A rings are $\Delta'$H-2 = +0.17 and $\Delta'$H-4 = +0.31. A trend $\Delta'$H-4 > $\Delta'$H-2 is true in all of the 39 comparisons made (Table 2). A similar trend, $\Delta$H-4 > $\Delta$H-2, is observed for 1-*O*-glycosylation in 28 comparisons (Table 2). The shifts from **31** and **17** are $\Delta$H-2 = −0.18 and $\Delta$H-4 = −0.02 (Table 2) and considering the signs of the shifts, $\Delta$H-4 > $\Delta$H-2, in this extreme case with lowest $\Delta$H-4 (Table 2).

The 6-*O*-alkylation shifts from 30 comparisons are shown in Table 3. The shifts, $\Delta'$H-5 and $\Delta'$H-7, are > +0.20 in 29 comparisons. There is deviation in one case only, that is, comparison of **34** and **6** shows $\Delta'$H-5 = +0.18 ($\leqslant$ +0.2) and $\Delta'$H-7 = +0.25. Despite slight deviation ($\Delta'$H-5 $\leqslant$ +0.20) in this particular case, it cannot be confused with 8-*O*-alkylation (Table 4) which requires $\Delta'$H-5 > $\Delta'$H-7 (here $\Delta'$H-7 > $\Delta'$H-5). Of the four 6-*O*-glycosylation shifts shown in Table 3, three are as predic-

*This method [1] is less sensitive than the new one [25].




**1** $R^1,R^6,R^8$ = OH, $R^3$ = $CH_2OH$
**2** $R^1,R^6$ = OH, $R^3$ = Me, $R^8$ = OMe
**3** $R^1,R^6$ = OH, $R^3$ = $CH_2OH$, $R^8$ = OMe
**4** $R^1,R^8$ = OH, $R^3$ = $CH_2OH$, $R^6$ = OMe
**5** $R^1,R^6,R^8$ = OH, $R^3$ = Me
**6** $R^1,R^8$ = OH, $R^3$ = Me, $R^6$ = OMe
**7** $R^1,R^6$ = OMe, $R^3$ = Me, $R^8$ = OH
**8** $R^1$ = OH, $R^3$ = Me, $R^6,R^8$ = OMe
**9** $R^1,R^6,R^8$ = OMe, $R^3$ = Me
**10** $R^1$ = Me, $R^3,R^6,R^8$ = OMe
**11** $R^1,R^6,R^8$ = OMe, $R^3$ = $CH_2$·CH(OH)·Me
**12** $R^1,R^8$ = OH, $R^3$ = Me, $R^6$ = H
**13** $R^1,R^6$ = OH, $R^3$ = Me, $R^8$ = O-glc
**14** $R^1,R^6$ = OH, $R^3$ = Me, $R^8$ = -O-gent
**15** $R^1,R^6$ = OH, $R^3$ = Me, $R^8$ = O-prim
**16** $R^1,R^8$ = OH, $R^3$ = Me, $R^6$ = O-glc
**17** $R^1$ = -O-glc, $R^3$ = Me, $R^6,R^8$ = OH
**18** $R^1$ = OH, $R^3$ = Me, $R^6$ = OMe, $R^8$ = -O-glc
**19** $R^1$ = OH, $R^3$ = Me, $R^6$ = OMe, $R^8$ = O-gent
**20** $R^1$ = OH, $R^3$ = Me, $R^6$ = OMe, $R^8$ = -O-prim

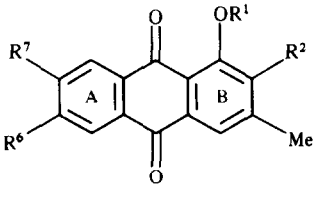



**21** $R^1,R^6,R^8$ = Me, $R^3$ = $CH_2$·CHOH·Me
**22** $R^1,R^6,R^8$ = H, $R^3$ = Me
**23** $R^1,R^3,R^6,R^8$ = Me
**24** $R^1,R^6,R^8$ = H, $R^3$ = $CH_2OH$

Table 1. Chemical shifts of aromatic protons in the $^1$H NMR of the peracetates of anthraquinones

| Peracetates of anthraquinones | Chemical shifts† ($\delta$, $CDCl_3$) H-2 | H-4 | H-5 | H-7 |
|---|---|---|---|---|
| Citreoresin (**1**) [3] | 7.42 | 8.19 | 7.99 | 7.29 |
| Questin (**2**) [3] | 7.22 | 8.01 | 7.65 | 7.11 |
| Questinol (**3**) [3] | 7.42 | 8.18 | 7.67 | 7.14 |
| Fallacinol (**4**) [4] | 7.35 | 8.15 | 7.65 | 6.88 |
| Emodin (**5**) [1] | 7.24 | 8.03 | 7.98 | 7.26 |
| Physcion (**6**) [1] | 7.24 | 8.03 | 7.69 | 6.92 |
| 1-*O*-Methylphyscion (**7**) [5] | 7.05 | 7.70 | 7.60 | 6.95 |
| 8-*O*-Methylphyscion (**8**) [1] | 7.18 | 7.96 | 7.36 | 6.77 |
| *1,8-Di-*O*-methylphyscion (**9**) [6] | 7.10 | 7.64 | 7.33 | 6.77 |
| *3,6,8-Tri-*O*-methyl-1-methylanthraquinone (**10**) | 6.92 | 7.53 | 7.32 | 6.74 |
| *Di-*O*-methylnalgiovensin (**11**) [8] | 7.17 | 7.68 | 7.28 | 6.75 |
| Chrysophanol (**12**) [9] | 7.21 | 8.01 | 8.21 | 7.38‡ |
| Emodin-8-*O*-glucoside (**13**) [1] | 7.23 | 7.97 | 7.76 | 7.31 |
| Emodin-8-*O*-gentiobioside (**14**) [10] | 7.19 | 7.97 | 7.78 | 7.29 |
| Emodin-8-*O*-primveroside (**15**) [11] | 7.17 | 7.96 | 7.78 | 7.21 |
| Emodin-6-*O*-glucoside (**16**) [1] | 7.19 | 7.91 | 7.54 | 6.98 |
| Emodin-1-*O*-glucoside (**17**) [1] | 7.35 | 7.88 | 7.97 | 7.29 |
| Physcion-8-*O*-glucoside (**18**) [1] | 7.15 | 7.90 | 7.42 | 6.94 |
| Physcion-8-*O*-gentiobioside (**19**) [12] | 7.18 | 7.92 | 7.50 | 6.88 |
| Physcion-8-*O*-primveroside (**20**) [13] | 7.13 | 7.88 | 7.45 | 6.97 |
| *Di-*O*-methylnalgiolaxin (**21**) [8] | 7.18 | 7.68 | 7.53 | — |
| Norfrangilin (**22**) [14] | 7.23 | 7.98 | 8.0 | — |
| *Di-*O*-methylfrangilin (**23**) [15] | 7.07 | 7.64 | 7.55 | — |
| 1,6,8-Trihydroxy-3-hydroxymethyl-7-chloroanthraquinone (**24**) [14] | 7.40 | 8.16 | 8.03 | — |
| 1,3,8-Trihydroxy-6-*O*-methyl-2-methylanthraquinone (**25**) [16] | — | 7.89 | 7.65 | 6.83 |
| *2-Carbomethoxy-3,6,8-tri-*O*-methyl-1-methylanthraquinone (**26**) [7] | — | 7.63 | 7.31 | 6.77 |
| Alaternin (**27**) [17] | — | 8.11 | 7.95 | 7.24 |
| 6-*O*-Methylalaternin (**28**) [18] | — | 7.95 | 7.50 | 6.80 |
| Xanthorin (**29**) [19] | 7.17 | 7.90 | — | 6.95 |
| *Tri-*O*-methylaxanthorin (**30**) [19] | 7.05 | 7.55 | — | 6.80 |
| Dermocybin (**31**) [1] | 7.17 | 7.86 | — | — |
| Dermocybin-1-*O*-glucoside (**32**) [1] | 7.24 | 7.70 | — | — |
| Islandicin (**33**) [20] | 7.24 | — | 8.05 | 7.32‡ |
| Catenarin (**34**) [21] | 7.23 | — | 7.87 | 7.17 |

*$^1$H NMR of the unacetylated compound.
†Multiplicities and $J$ values have been excluded in this Table.
‡H-6 = $\delta$7.74 and 7.68 for **12** and **33** respectively.




**35** $R^1,R^2,R^7$ = H, $R^6$ = OH
**36** $R^1,R^2,R^6$ = H, $R^7$ = OH
**37** $R^1$ = Me, $R^2$ = OH, $R^6$ = OMe, $R^7$ = H
**38** $R^1$ = Me, $R^2$ = OH, $R^6$ = H, $R^7$ = OMe

ted (> +0.20). The fourth has a slight deviation, i.e. shifts from **34** and **16** are ΔH-5 = +0.33 and ΔH-7 = +0.19 (≤ +0.2). Although ΔH-5 is larger than ΔH-7 it cannot be confused with 8-*O*-glycosylation which has ΔH-7 < +0.10 (Table 4) (here ΔH-7 > +0.10). When shifts for H-5 and H-7 are both > +0.20, there are indications for 6-*O*-alkylation/glycosylation and in such cases no attention is required whether ΔH-5 > ΔH-7 or ΔH-7 > ΔH-5 etc.

The 8-*O*-alkylation shifts from 28 comparisons are shown in Table 4. The trend Δ′H-5 > Δ′H-7 is always true. There is a similar trend for 8-*O*-glycosylation (ΔH-5 > ΔH-7) from a comparison of 24 pairs. The glycosylation shifts from **28** and **19** are ΔH-5 = 0.00 and ΔH-7 = −0.08 and ΔH-5 > ΔH-7 in this peculiar case with no shift for H-5. The 6,8-di-O-alkylation shifts from 24 comparisons are shown in Table 5. The trend is Δ′H-5 > +0.40 and Δ′H-7 > +0.40 and Δ′H-5 is always > Δ′H-7.

There are reports of partial structures 1,6-dihydroxy-3-methylanthraquinone **35**/1,7-dihydroxy-(**36**) [21] and 2-hydroxy-1,6-di-*O*-methyl-3-methylanthraquinone (**37**)/2-hydroxy-1,7-di-*O*-methyl-(**38**) [22]. Of these, those preferred on biogenetic considerations are **35** [21] and **37** [23].

Table 2. 1-*O*-Alkylation/glycosylation shifts

| 1-*O*-Alkylation (Δ′H*) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Anthra-quinones | Δ′H-2 | Δ′H-4 | Anthra-quinones | Δ′H-2 | Δ′H-4 | Anthra-quinones | Δ′H-2 | Δ′H-4 | Anthra-quinones | Δ′H-2 | Δ′H-4 |
| **2, 7** | +0.17 | +0.31 | **8, 9** | +0.08 | +0.32 | **15, 9** | +0.07 | +0.32 | **19, 30** | +0.13 | +0.37 |
| **2, 9** | +0.12 | +0.37 | **8, 30** | +0.13 | +0.41 | **15, 30** | +0.12 | +0.41 | **20, 7** | +0.08 | +0.18 |
| **2, 30** | +0.17 | +0.46 | **12, 30** | +0.16 | +0.46 | **16, 7** | +0.14 | +0.21 | **20, 9** | +0.03 | +0.24 |
| **5, 7** | +0.19 | +0.33 | **13, 7** | +0.16 | +0.27 | **16, 9** | +0.09 | +0.27 | **20, 30** | +0.08 | +0.33 |
| **5, 9** | +0.14 | +0.39 | **13, 9** | +0.13 | +0.33 | **16, 30** | +0.14 | +0.36 | **22, 30** | +0.18 | +0.43 |
| **5, 30** | +0.19 | +0.48 | **13, 30** | +0.18 | +0.42 | **18, 7** | +0.10 | +0.20 | **29, 30** | +0.12 | +0.35 |
| **6, 7** | +0.19 | +0.33 | **14, 7** | +0.14 | +0.27 | **18, 9** | +0.05 | +0.26 | **31, 7** | +0.12 | +0.16 |
| **6, 9** | +0.14 | +0.39 | **14, 9** | +0.09 | +0.33 | **18, 30** | +0.10 | +0.35 | **31, 9** | +0.07 | +0.22 |
| **6, 30** | +0.19 | +0.48 | **14, 30** | +0.14 | +0.42 | **19, 7** | +0.13 | +0.22 | **31, 30** | +0.12 | +0.31 |
| **8, 7** | +0.13 | +0.26 | **15, 7** | +0.12 | +0.26 | **19, 9** | +0.08 | +0.28 | | | |
| | 1-*O*-glycosylation (ΔH†) | | | | | | | | | | |
| | ΔH-2 | ΔH-4 | | ΔH-2 | ΔH-4 | | ΔH-2 | ΔH-4 | | ΔH-2 | ΔH-4 |
| **2, 17** | −0.13 | +0.13 | **12, 32** | −0.03 | +0.31 | **16, 17** | −0.16 | +0.03 | **20, 32** | −0.11 | +0.18 |
| **2, 32** | −0.02 | +0.31 | **13, 17** | −0.12 | +0.09 | **16, 32** | −0.05 | +0.21 | **22, 17** | −0.12 | +0.10 |
| **5, 17** | −0.11 | +0.15 | **13, 32** | −0.01 | +0.27 | **18, 17** | −0.20 | +0.02 | **22, 32** | −0.01 | +0.28 |
| **5, 32** | 0.0 | +0.33 | **14, 17** | −0.16 | +0.09 | **18, 32** | −0.09 | +0.20 | **29, 17** | −0.18 | +0.02 |
| **6, 17** | −0.11 | +0.15 | **14, 32** | −0.05 | +0.27 | **19, 17** | −0.17 | +0.04 | **29, 32** | −0.07 | +0.20 |
| **6, 32** | 0.0 | +0.33 | **15, 17** | −0.18 | +0.08 | **19, 32** | −0.06 | +0.22 | **31, 17** | −0.18 | −0.02 |
| **12, 17** | −0.14 | +0.13 | **15, 32** | −0.07 | +0.26 | **20, 17** | −0.22 | 0.0 | **31, 32** | −0.07 | +0.16 |

*Δ′H = δ value of the aromatic proton in anthraquinone peracetate minus that in *O*-alkyl peracetate.
†ΔH = δ value of the aromatic proton in aglycone peracetate minus that in *O*-glycosyl peracetate.

Table 3. 6-*O*-Alkylation/glycosylation shifts.

| 6-*O*-alkylation (Δ′H) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Anthra-quinones | Δ′H-5 | Δ′H-7 | Anthra-quinones | Δ′H-5 | Δ′H-7 | Anthra-quinones | Δ′H-5 | Δ′H-7 |
| **1, 4** | +0.34 | +0.41 | **3, 8** | +0.31 | +0.37 | **13, 18** | +0.32 | +0.37 |
| **1, 6** | +0.30 | +0.37 | **3, 9** | +0.34 | +0.37 | **14, 19** | +0.28 | +0.41 |
| **1, 7** | +0.39 | +0.34 | **3, 10** | +0.35 | +0.40 | **15, 20** | +0.33 | +0.24 |
| **1, 25** | +0.34 | +0.46 | **3, 11** | +0.39 | +0.39 | **27, 6** | +0.26 | +0.32 |
| **1, 28** | +0.49 | +0.49 | **3, 26** | +0.36 | +0.37 | **27, 7** | +0.35 | +0.29 |
| **2, 8** | +0.29 | +0.38 | **5, 4** | +0.33 | +0.38 | **34, 4** | +0.22 | +0.29 |
| **2, 9** | +0.32 | +0.34 | **5, 6** | +0.29 | +0.34 | **34, 6** | +0.18 | +0.25 |
| **2, 10** | +0.33 | +0.37 | **5, 7** | +0.38 | +0.31 | **34, 7** | +0.27 | +0.22 |
| **2, 11** | +0.37 | +0.36 | **5, 25** | +0.33 | +0.43 | **34, 25** | +0.22 | +0.34 |
| **2, 26** | +0.34 | +0.34 | **5, 28** | +0.48 | +0.46 | **34, 28** | +0.37 | +0.37 |
| | 6-*O*-glycosylation (ΔH) | | | | | | | |
| | ΔH-5 | ΔH-7 | | ΔH-5 | ΔH-7 | | ΔH-5 | ΔH-7 |
| **1, 16** | +0.45 | +0.31 | **5, 16** | +0.44 | +0.28 | **27, 16** | +0.41 | +0.26 |
| | | | | | | **34, 16** | +0.33 | +0.19 |

Table 4. 8-*O*-Alkylation/glycosylation shifts

| 8-*O*-alkylation (Δ'H) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Anthraquinones | Δ'H-5 | Δ'H-7 | Anthraquinones | Δ'H-5 | Δ'H-7 | Anthraquinones | Δ'H-5 | Δ'H-7 |
| **1, 2** | +0.34 | +0.18 | **6, 9** | +0.36 | +0.15 | **27, 3** | +0.28 | +0.10 |
| **1, 3** | +0.32 | +0.15 | **6, 10** | +0.37 | +0.18 | **28, 8** | +0.14 | +0.03 |
| **4, 8** | +0.29 | +0.11 | **6, 11** | +0.41 | +0.17 | **28, 9** | +0.17 | +0.03 |
| **4, 9** | +0.32 | +0.11 | **6, 26** | +0.38 | +0.15 | **28, 10** | +0.18 | +0.06 |
| **4, 10** | +0.33 | +0.14 | **25, 8** | +0.29 | +0.06 | **28, 11** | +0.22 | +0.05 |
| **4, 11** | +0.37 | +0.13 | **25, 9** | +0.32 | +0.06 | **28, 26** | +0.19 | +0.03 |
| **4, 26** | +0.34 | +0.11 | **25, 10** | +0.33 | +0.09 | | | |
| **5, 2** | +0.33 | +0.15 | **25, 11** | +0.37 | +0.08 | **34, 2** | +0.22 | +0.06 |
| **5, 3** | +0.31 | +0.12 | **25, 26** | +0.34 | +0.06 | **34, 3** | +0.20 | +0.03 |
| **6, 8** | +0.36 | +0.15 | **27, 2** | +0.30 | +0.13 | | | |
| 8-*O*-glycosylation (ΔH) | | | | | | | | |
| | ΔH-5 | ΔH-7 | | ΔH-5 | ΔH-7 | | ΔH-5 | ΔH-7 |
| **1, 13** | +0.23 | −0.02 | **5, 15** | +0.20 | +0.05 | **27, 14** | +0.17 | −0.05 |
| **1, 14** | +0.21 | 0.0 | **6, 18** | +0.27 | −0.02 | **27, 15** | +0.17 | +0.03 |
| **1, 15** | +0.21 | +0.08 | **6, 19** | +0.19 | +0.04 | **28, 18** | +0.08 | −0.14 |
| **4, 18** | +0.23 | +0.06 | **6, 20** | −0.24 | −0.05 | **28, 19** | 0.0 | −0.08 |
| **4, 19** | +0.15 | 0.0 | **25, 18** | +0.23 | −0.11 | **28, 20** | +0.05 | −0.17 |
| **4, 20** | +0.20 | +0.09 | **25, 19** | +0.15 | −0.05 | **34, 13** | +0.11 | −0.14 |
| **5, 13** | +0.22 | −0.05 | **25, 20** | +0.20 | −0.14 | **34, 14** | +0.09 | −0.12 |
| **5, 14** | +0.20 | −0.03 | **27, 13** | +0.19 | −0.07 | **34, 15** | +0.09 | −0.04 |

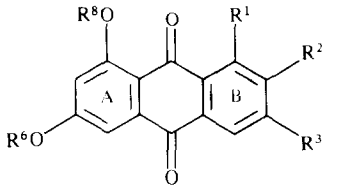
Table 5. 6,8-Di-*O*-alkylation shifts

| Anthraquinones | Δ'H-5 | Δ'H-7 | Anthraquinones | Δ'H-5 | Δ'H-7 | Anthraquinones | Δ'H-5 | Δ'H-7 |
|---|---|---|---|---|---|---|---|---|
| **1, 8** | +0.63 | +0.52 | **5, 11** | +0.70 | +0.51 | **27, 10** | +0.63 | +0.50 |
| **1, 9** | +0.66 | +0.52 | **5, 26** | +0.67 | +0.49 | **27, 11** | +0.67 | +0.49 |
| **1, 10** | +0.67 | +0.55 | **22, 21** | +0.47 | — | **27, 26** | +0.64 | +0.47 |
| **1, 11** | +0.71 | +0.54 | **22, 23** | +0.45 | — | **34, 8** | +0.51 | +0.40 |
| **1, 26** | +0.68 | +0.52 | **24, 23** | +0.48 | — | **34, 9** | +0.54 | +0.40 |
| **5, 8** | +0.62 | +0.49 | **24, 21** | +0.50 | — | **34, 10** | +0.55 | +0.43 |
| **5, 9** | +0.65 | +0.49 | **27, 8** | +0.59 | +0.47 | **34, 11** | +0.59 | +0.42 |
| **5, 10** | +0.66 | +0.52 | **27, 9** | +0.62 | +0.47 | **34, 26** | +0.56 | +0.40 |

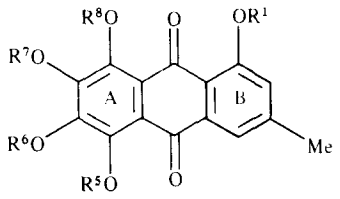
Table 6. Chemical shifts of A ring protons in the $^1$H NMR of anthraquinones and alkylation shifts

| | Chemical shifts (δ) | | | |
|---|---|---|---|---|
| Anthraquinones | H-5 | H-6 | H-7 | H-8 |
| †1,6-Dihydroxy-3-methylanthraquinone (**35**) [20] | 7.95 | — | 7.98 | 8.25 |
| ‡2-Hydroxy-1,6-*O*-methyl-3-methylanthraquinone (**37**) [21] | 7.68 | — | 7.22 | 8.19 |
| Alkylation shifts (Δ'H) | | | | |
| | Δ'H-5 | Δ'H-6 | Δ'H-7 | Δ'H-8 |
| **35, 37** | +0.27 | — | +0.26 | +0.06 |

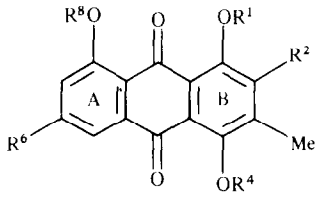
†As peracetate in $CDCl_3$.
‡Unacetylated in $CDCl_3$.



**25** $R^1,R^3$ = OH, $R^2,R^6$ = Me, $R^8$ = H
**26** $R^1,R^6$ = Me, $R^2$ = $CO_2Me$, $R^3$ = OMe, $R^8$ = Me
**27** $R^1,R^2$ = OH, $R^3$ = Me, $R^6,R^8$ = H
**28** $R^1,R^2$ = OH, $R^3,R^6$ = Me, $R^8$ = H



**29** $R^1,R^5,R^7,R^8$ = H, $R^6$ = Me
**30** $R^1,R^5,R^6,R^8$ = Me, $R^7$ = H
**31** $R^1,R^5,R^7,R^8$ = H, $R^6$ = Me
**32** $R^1,R^5,R^7$ = H, $R^6$ = Me, $R^8$ = glc



**33** $R^1,R^2,R^4,R^6,R^8$ = H
**34** $R^1,R^4,R^8$ = H, $R^2$ = H, $R^6$ = OH

The identity of **35** has been confirmed by comparison with a synthetic sample [24]. The $^1$H NMR data are shown in Table 6 and the 6-*O*-alkylation shifts $\Delta'$H-5 = +0.27, $\Delta'$H-7 = +0.26 are consistent with the preferred structure (**37**).

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