# 7β,8β-Epoxycardenolide Glycosides of *Asclepias eriocarpa*

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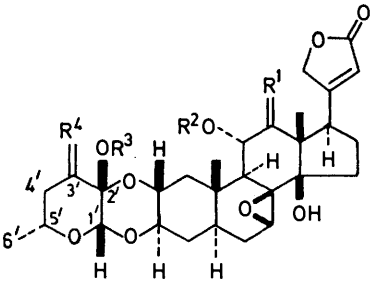
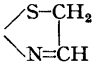
The identity of eriocarpin with desglucosyrioside (1) has been established by comparison of their triacetates. $^{13}C$ and $^{1}H$ N.m.r. spectra show that the conversion of labriformidin into desglucosyrioside involves solely the reduction of a 3-keto-function in the carbohydrate portion (*B*) which is identical (in structure and stereochemistry) with that in uscharidin (7). Structures are proposed for labriformidin and labriformin. $^{13}C$ N.m.r. data establish the β-configuration of the 7,8-epoxide in labriformidin, desglucosyrioside, and in the 5β-cardenolide sarverogenin (11).

RECENTLY the toxic cardenolide glycosides, labriformidin, labriformin, and eriocarpin were isolated from *Asclepias eriocarpa* of the milkweed family (Asclepiadaceae), and shown to be present also in *A. labriformis* and *A. erosa*.[1] In this paper we propose structures (2)

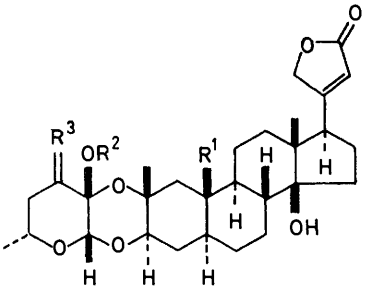


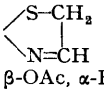
| | | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|---|
| Desglucosyrioside | (1) | O | H | H | β-OH, α-H |
| | (1a) | O | Ac | Ac | β-OAc, α-H |
| Labriformidin | (2) | O | H | H | O |
| | (2a) | O | Ac | H | O |
| Labriformin | (3) | O | H | H |  |
| | (4) | O | H | H | β-O-glu, α-H |
| | (5) | α-OH, β-H | H | H | β-OH, α-H |

and (3) respectively for the former two glycosides, and show that eriocarpin is identical with the known desglucosyrioside (1).

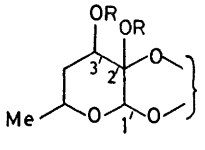
The three cardiac glycosides are closely related. Thus labriformin was hydrolysed by acid to labriformidin which in turn could be reduced to eriocarpin.[1] The high degree of oxygenation (labriformidin for example has a molecular formula $C_{29}H_{36}O_{11}$) suggests a close relationship to the cardenolides of *Asclepias syrica*. The glycosides syrioside and syriobioside from *A. syrica* were recently re-examined by Reichstein and his collaborators [2] and were given structures (4) and (5) which incorporate an epoxide group at positions 7β,8β of the cardenolide skeleton, and oxygen functions at positions 11α and 12. The carbohydrate portion (*A*) of syrioside and syriobioside is, as was first put forward for gomphoside (6) [3] from *A. fruticosa*, based on a 4,6-dideoxyhexosulose group which is attached to positions 2α and 3β of the steroid aglycone. The complete stereochemistry of the carbohydrate in these and several other cardenolides of the Asclepiadaceae has been described in the preceding paper.[4]

A feature of the 4,6-dideoxyhexosulose moiety (*A*) of the Asclepiadaceae cardenolides is that the tertiary 2'-hydroxy-group may be acetylated.[2-4] While eriocarpin formed a diacetate under mild conditions,[1] with increase of temperature a triacetate is obtained. The $^{1}H$ and $^{13}C$ n.m.r. spectra of the triacetate are identical with those of 2',3',11-triacetyldesglucosyrioside (1a) [2] (Tables 1 and 2). This establishes the identity of eriocarpin with desglucosyrioside (1) † which was the product of enzymic cleavage of glucose from the cardenolide

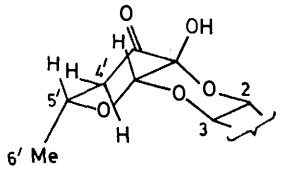


| | | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|---|
| | (6) | Me | H | β-OH, α-H |
| | (6a) | Me | Ac | β-OAc, α-H |
| Uscharidin | (7) | CHO | H | O |
| | (8) | CHO | H |  |
| | (9) | CHO | Ac | β-OAc, α-H |

syrioside (4).[2] As desglucosyrioside itself occurs naturally (albeit in low yield) in *A. syrica* [2], the name 'eriocarpin' should now be discarded.



(A)



(B)

Labriformidin on sodium borohydride reduction gave desglucosyrioside (1) as one of the products.[1] Comparison of the $^{13}C$ n.m.r. spectra shows that the process involves reduction of *one* ketone function to a

† Also shown by t.l.c. (see Experimental Section).

TABLE 1

$^1$H Chemical shifts in δ (*J*/Hz values in parentheses)

| | Uscharidin (7) [a] | Labriformidin (2) [b] | 11-Acetyl-labriformidin (2a) [b] | Triacetyldesglucosyrioside (1a) [c] |
|---|---|---|---|---|
| H-1′ | 4.54 | 4.63 | 4.64 | 4.83 |
| H-3′ | | | | 5.74 |
| H-4′ | | 2.76 (*J* 14, 12) | 2.77 (*J* 14, 12) | |
| | | 2.43 (*J* 14, 2) | 2.43 (*J* 14, 2) | |
| H-6′ | 1.29 (*J* 6) | 1.39 (*J* 6) | 1.39 (*J* 6) | 1.21 (*J* 6) |
| H-5′ | ↑ | *ca.* 3.7 (m) | *ca.* 3.7 (m) | ↑ |
| H-2β | 3.5—4.1 (m) | 3.6—4.1 (m) | 3.8—4.1 (m) | 3.7—4.1 (m) |
| H-3α | ↓ | 3.6—4.1 (m) | 3.8—4.1 (m) | ↓ |
| H-7α | | 3.46 (br d) (*J* 5) | 3.52 (br d) (*J* 5) | 3.50 (br d) (*J* 5) |
| H-9α | | 1.69 (*J* 13) | 2.06 (*J* 13) | |
| H-11β | | 4.76 (*J* 12) | 5.69 (*J* 13) | 5.67 (*J* 13) |
| H-17α | | 3.93 (t) ($J_{AX}$ + $J_{BX}$ 16) | *ca.* 3.95 | 3.93 (t) ($J_{AX}$ + $J_{BX}$ 16) |
| H-18 | 0.79 | 1.21 | 1.12 | 1.12 |
| H-19 | 9.96 | 1.07 | 1.02 | 1.01 |
| H-21 | *ca.* 4.8 | 4.83, 4.83 | 4.80, 4.80 | 4.80, 4.80 |
| H-22 | 5.82 | 6.00 | 5.97 | 5.96 |
| Ac | | | 2.21 | 2.06, 2.06, 2.23 |

[a] In octadeuteriodioxan. [b] In $CDCl_3$; $D_2O$-exchanged for (2). Chemical shifts as given here for a sample from *A. eriocarpa* in $CDCl_3$ are within 0.01 p.p.m. of those recorded in ref. 2.

secondary hydroxy-group. Of the two secondary hydroxy-groups in desglucosyrioside (1), one is attached to C-3′ on the carbohydrate, and the other is part of an α-ketol function at ring C. The decoupling experiments described below show that the 11α-hydroxy-12-ketone function in desglucosyrioside (1) occurs also in labriformidin, and establishes the position of the reducible ketone group in labriformidin to be at C-3′. The structure of labriformidin (2) follows then from that given to syrioside (4) by Reichstein and his collaborators.[2]

In deuteriochloroform, H-11β of labriformidin (2) gives rise to a doublet of doublets (*J* 13 and 4.5 Hz) at δ 4.76 which becomes a doublet (*J* 13 Hz) upon deuterium exchange (with removal of coupling with the

TABLE 2

$^{13}$C Chemical shifts (p.p.m. downfield from $SiMe_4$) [a]

| Carbon | Diacetylcalactin (6a) [b] | Uscharidin (7) [a] | Triacetyldesglucosyrioside (1a) [c] | 11-Acetyl-labriformidin (2a) | Labriformidin (2) |
|---|---|---|---|---|---|
| C-1′ | 93.2 | 97.2 | 93.1 | 97.3 | 97.2 [d] |
| C-2′ | 95.6 | | 95.5 | 91.2 | 91.1 |
| C-3′ | 70.5 | 207.5 * | 70.2 | 201.7 | 201.7 |
| C-4′ | 35.0 | 45.1 | 34.8 | 44.7 | 44.7 [d] |
| C-5′ | 66.6 | 68.0 | 66.6 | 67.9 | 67.8 |
| C-6′ | 20.8 | 21.5 | 20.8 | 21.5 | 21.4 |
| C-1 | 35.7 | 36.0 | 43.8 | 44.1 | 43.9 |
| C-2 | 70.8 | 69.5 | 69.7 | 68.6 | 68.7 |
| C-3 | 71.2 | 72.1 | 70.8 | 71.8 | 71.9 |
| C-4 | 32.4 | 32.0 | 31.4 | 31.7 | 31.6 |
| C-5 | 43.6 | 43.5 | 40.4 | 40.5 | 40.6 |
| C-6 | 27.7 | 27.7 | 35.6 | 35.6 | 35.9 |
| C-7 | 27.4 | 27.5 | 54.2 | 54.3 | 53.9 |
| C-8 | 42.6 | 42.3 | 62.5 | 62.6 | 62.1 * |
| C-9 | 48.6 | 48.7 | 45.1 | 45.2 | 48.2 [d] |
| C-10 | 52.8 | 53.1 | 37.6 | 37.8 | 37.8 |
| C-11 | 22.0 | 22.0 | 75.3 | 75.5 | 73.5 [d] |
| C-12 | 39.5 | 39.4 | 204.5 | 204.8 | 212.5 |
| C-13 | 49.4 | 49.6 | 64.0 | 64.1 | 63.1 * |
| C-14 | 85.0 | 84.5 | 80.8 | 80.9 | 81.1 |
| C-15 | 33.1 | 33.3 | 28.3 | 28.5 | 28.4 |
| C-16 | 26.9 | 26.9 | 26.6 | 26.7 | 26.7 |
| C-17 | 50.7 | 50.8 | 41.7 | 41.8 | 42.4 [d] |
| C-18 | 15.6 | 15.6 | 17.2 | 17.4 | 18.3 |
| C-19 | 206.4 | 208.1 * | 13.6 | 13.6 | 13.5 |
| C-20 | 174.2 | 175.5 | 170.9 | 170.9 | 170.6 |
| C-21 | 73.4 | 73.9 | 73.6 | 73.7 | 73.7 |
| C-22 | 118.0 | 117.7 | 118.8 | 118.9 | 118.8 [d] |
| C-23 | 173.9 | 175.5 | 173.8 | 173.8 | 173.8 |
| $CH_3CO$ | 20.8, 21.6 | | 20.7, 21.7, 21.1 | 21.1 | |
| $CH_3CO$ | 168.5, 168.8 | | 168.3, 168.8, 169.8 | 160.6 | |
| $CDCl_3$ (as reference) | 77.05 | 77.3 | 77.0 | 77.1 | 77.05 |

[a] In $CDCl_3$ [except for compound (7) in $CDCl_3$–$CD_3OD$ (3 : 1 v/v)]. [b] Ref. 2. [c] Chemical shifts as given here for a sample from *A eriocarpa* are within 0.1 p.p.m. of those recorded in ref. 2. [d] Assignment confirmed by ' Birdsall plots.' [13]

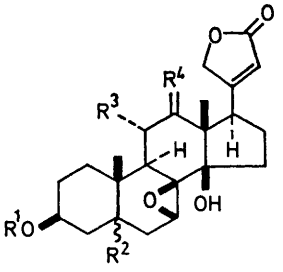
* Signals within a vertical column may be reversed.

hydroxy-proton). Mutual decoupling confirms that the 13 Hz coupling is due to vicinal (axial–axial) coupling to H-9α resonating at δ 1.69 (doublet with $J$ 13 Hz). The two protons α to the 3′-keto-group in labriformidin (H-4′) give rise to a signal consisting of an AB quartet at δ 2.43 and 2.76 ($J$ 14 Hz), the upfield and downfield halves of which are further split (by H-5′) by 2 Hz ($J_{ax\text{-}eq}$) and 12 Hz ($J_{ax\text{-}ax}$) respectively. Irradiation of a multiplet at δ 3.72 (H-5′) causes the removal of the latter couplings, as well as the collapse of a methyl doublet (H-6′) at δ 1.39.

The structure of labriformin (3), $C_{31}H_{39}O_{10}NS$, may be deduced from that of labriformidin (2). The transformation of labriformin to labriformidin in acid consists of the generation of the 3′-ketone in labriformidin by hydrolysis of a thiazoline system (δ 7.65, –CH=N–; δ 3.91, $-SCH_2-$) in labriformin.[1] The analogous conversion among the *Calotropis* cardenolides, *viz.* uscharin (8) into uscharidin (7), is well documented.[5]

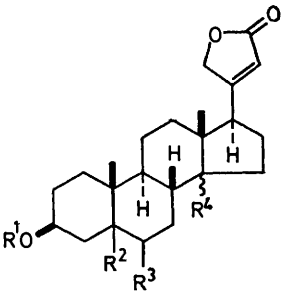
From the $^{13}C$ n.m.r. data, deduction may be made on the stereochemistry of labriformidin and some other cardenolides. First, it is observed that the shieldings of the six carbohydrate carbons of labriformidin or its 11-acetate are nearly identical to those of uscharidin (7) (see Table 2) which has the same carbohydrate structure. Labriformidin must have the same *cis* fusion of pyranose and 1,4-dioxan rings [see (*B*)] as was shown [4] for uscharidin.

It was pointed out by Tori, Lukacs, and their co-workers [6] that the configuration of the epoxide group in an epoxy-steroid may be determined by comparison of the $^{13}C$ chemical shifts with those of the corresponding unsaturated steroid which is conformationally similar. Instead of referring to 2,3- and 3,4-epoxides examined by these workers, we illustrate below their approach using the published data [7] on the cardenolides (15) and (16). Replacement of a $\Delta^5$ double-bond by a 5α,6α-



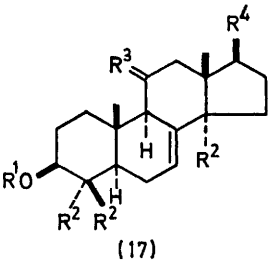
| | | R¹ | R² | R³ | R⁴ |
|---|---|---|---|---|---|
| Tanghinigenin | (10) | H | β-H | H | $H_2$ |
| Sarverogenin | (11) | H | β-H | OH | O |
| | (11a) | Ac | β-H | OAc | O |
| | (12a) | Ac | α-H | OAc | O |

epoxide ring results in increased shielding of those carbon atoms which are γ to the epoxide oxygen *and* which bear an axial hydrogen *cis* to the oxygen, *viz.* 4.7 p.p.m. at C-1, and 7.7 p.p.m. at C-9. In contrast there is only slight shielding (2.1 p.p.m.) of C-8 which has an axial hydrogen *trans* to the oxygen.

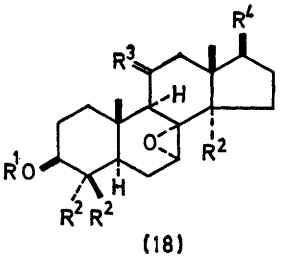


| | R¹ | R²/R³ | R⁴ |
|---|---|---|---|
| (13) | Ac | H/H (5β) | β-OH |
| (14) | Ac | H/H (5α) | β-OH |
| (15) | H | $\Delta^{5,6}$ | α-H |
| (16) | H | α-epoxy | α-H |

On the basis of the steric γ-*gauche* effect of an epoxide referred to above, the α-configuration of the 7,8-epoxide (18a) obtained from 3β-acetoxy-7-lanosten-11-one (17a)[8]

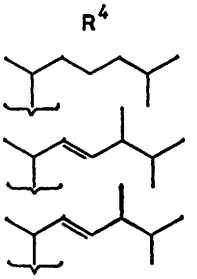


(17)



(18)

| | R¹ | R² | R³ |
|---|---|---|---|
| a; | Ac | Me | O |
| b; | H | H | $H_2$ |
| c; | Ac | H | $H_2$ |



is strikingly shown by $^{13}C$ n.m.r. Thus compared with the $\Delta^7$-compound, the 7,8-epoxy-triterpene shows increased shielding of 5 to 7.5 p.p.m. for three carbon atoms γ to the oxygen, *viz.* C-5 (42.3 *vs.* 49.7/49.9 p.p.m.), C-15 (26.3 *vs.* 31.4 p.p.m.), and C-28 (14α-Me) (18.0/18.8 *vs.* 23.7 p.p.m.).[8]

For configurational assignment of the 7,8-epoxide in the *Asclepias* glycosides, we compare the shielding data of labriformidin (2), its 11-acetate (2a), and 2′,3′,11-triacetyldesglucosyrioside (1a) (Table 2) with those reported for the $\Delta^7$-5α-ergostanes (17b) and (17c).[9] Substantial chemical-shift changes at C-5 are not expected to be caused by the structural differences between the two series at carbons 2 and 3,* nor at the remote C-14, nor by the introduction of an equatorial

* For example the shielding of C-5 is 44.2 p.p.m. in 3-acetyluzarigenin (14) (with a 3β-acetate) and is 44.8 p.p.m. in 2′,3′-diacetylgomphoside (6a) [4] [with the same diacetylated sugar moiety (A) as in 2′,3′,11-triacetyldesglucosyrioside].

11α-hydroxy- or -acetoxy-group.* The chemical shifts of C-5 in the five compounds (all in $CDCl_3$) agree to within 0.4 p.p.m. showing that the 7,8-epoxide in labriformidin and 2′,3′,11-triacetyldesglucosyrioside does *not* cause shielding of C-5, and therefore has the β-configuration.

*Configuration of the 7,8-Epoxide in Sarverogenin.*—A number of cardenolide glycosides are known which also possess a 7,8-epoxide ring, but with a 5β-skeleton. Of the three genins related to such glycosides, tanghinigenin (10) and 17βH-tanghinigenin have been well characterised structurally by degradation and interconversions.[11] The following analysis supports the postulated β-configuration of the epoxide in the remaining genin, sarverogenin (11).[12] The first three columns of Table 3 give the $^{13}C$ shifts of 3,11-diacetylsarverogenin (11a),[2] its 5α-epimer (12a), and the difference between the chemical shifts of these two compounds. The shielding data of the hypothetical 5α-epimer of 3,11-diacetylsarverogenin was estimated from those of 2′,3′,11-triacetyldesglucosyrioside (1a) as described in footnote *d* of Table 3. These shift-difference data (column 3) were then compared with a similar set of data (column 6) obtained from the chemical shifts of 3-acetyldigitoxigenin (13) with 5β-H (column 4), and 3-acetyluzarigenin (14) with 5α-H (column 5). The two sets of shift differences, between 5α- and 5β-epimers (columns 3 and 6), agree to within 2 p.p.m. for all carbons except C-4 and C-7. Each of these two carbons has an axial hydrogen and is more shielded in 3-acetyldigitoxigenin (13) than 3-acetyluzarigenin (14) (by 3 and 5 p.p.m. respectively) because of the mutual *γ-gauche* ' interaction ' across the folded A/B-*cis* system in the former. However, in the 7,8-epoxycardenolides, H-7 becomes approximately coplanar with carbons 6, 7, 8, and 9, irrespective of the configuration of the epoxide, and does not ' interact ' with C-4; carbons 4 and 7 in the A/B-*cis* compound are not expected to be significantly more shielded. Indeed, C-4 in 3,11-diacetylsarverogenin (11a) is about 3 p.p.m. *less* shielded, while C-7 is only 1.5 p.p.m. more shielded when compared to its 5α-epimer (12a). The above analysis of the shieldings of C-4 and C-7 demonstrates

TABLE 3

$^{13}C$ Chemical shifts (p.p.m.), and shift differences between 5α- and 5β-epimers

| Carbon | Diacetylsarverogenin (11a) [a,c] | Estimated for 5α-epimer of diacetylsarverogenin (12a) [a,d] | Shift differences δ(11a) − δ(12a) | Acetyldigitoxygenin (13) [a,b] | Acetyluzarigenin (14) [a] | Shift differences [e] δ(13) − δ(14) |
|---|---|---|---|---|---|---|
| C-1 | 32.0 | 39 | −7 | 30.3 | 36.8 | −6.5 |
| C-2 | 25.5 | 26 | −1 | 24.8 | 27.3 | −2.5 |
| C-3 | 69.0 | 72 | −3 | 70.3 | 73.5 | −3 |
| C-4 | 36.2 * | 33 | +3 | 30.3 | 33.8 | −3.5 |
| C-5 | 32.9 | 40 | −7 | 36.6 | 44.2 | −7.5 |
| C-6 | 35.5 * | *h* | 0 | 26.2 | 28.4 | −2 |
| C-7 | 52.7 | *h* | −2 | 21.0 | 27.3 | −6 |
| C-8 | 63.0 | *h* | 0 | 41.5 | 41.5 | 0 |
| C-9 | 32.9 | *h* | −12 | 35.4 | 49.6 | −14 |
| C-10 | 34.4 | 35 | −1 | 35.0 | 35.7 | −1 |
| C-11 | 75.5 | *h* | 0 | 21.0 | 21.1 | 0 |
| C-12 | 204.6 | *h* | 0 | 39.7 | 39.7 | 0 |
| C-13 | 64.3 | *h* | 0 | 49.5 | 49.6 | 0 |
| C-14 | 81.1 | *h* | 0 | 85.1 | 85.1 | 0 |
| C-15 | 28.5 | *h* | 0 | 32.9 | 33.0 | 0 |
| C-16 | 26.6 | *h* | 0 | 26.7 | 26.9 | 0 |
| C-17 | 41.8 | *h* | 0 | 50.8 | 50.9 | 0 |
| C-18 | 17.5 | *h* | 0 | 15.6 | 15.8 | 0 |
| C-19 | 23.0 | 12 | +11 | 23.5 | 12.1 | +11.5 |
| C-20 | 171.1 | | | 174.9 * | 175.1 | |
| C-21 | 73.7 | | | 73.4 | 73.5 | |
| C-22 | 118.7 | | | 117.3 | 117.4 | |
| C-23 | 173.9 | | | 174.5 * | 174.7 | |
| $CH_3CO$ | 20.8 ,21.4 | | | 21.0 | 21.4 | |
| $CH_3CO$ | 169.5, 170.4 | | | 170.6 | 170.6 [g] | |

[a] In $CDCl_3$. [b] Data shown here as obtained on a $CDCl_3$ solution are within 1.5 p.p.m. of those recorded on a $CDCl_3$–$CD_3OD$ (3 : 2 v/v) solution (K. Tori, H. Ishii, Z. W. Wolkowski, C. Chachaty, M. Sangaré, F. Piriou, and G. Lukacs, *Tetrahedron Letters*, 1973, 1077). [c] Data from ref. 2 with assignments of C-1/C-4 and C-20/C-23 reversed. [d] The carbon shifts of 2′,3′,11-triacetyldesglucosyrioside (1a) [2] (Table 2) are modified by the following shift changes expected upon replacement of a diacetylated sugar moiety (*A*) by a 3β-acetate [estimated from the shieldings of 2′,3′-diacetylgomphoside (6a) [4] and of 3-acetyluzarigenin (14)]: C-1, −4.9; C-2, −43.8; C-3, +1.7; C-4, +1.8; C-5, −0.6; C-10, −2.3; C-19, −1.6 p.p.m.; other carbons, less than ±1 p.p.m. [e] Shift differences as shown on this column are within 1.5 p.p.m. of those calculated from data measured in [$^2H_5$]pyridine (T. Yamauchi, F. Abe, and M. Nishi, *Chem. Pharm. Bull.*, 1978, **26**, 2894). [f] Doublet in single-frequency off-resonance (s.f.o.r.d.) spectrum due to $J_{CCH}$. [g] Quartet in s.f.o.r.d. spectrum due to $J_{CCH}$. [h] This chemical shift is estimated to be within 1 p.p.m. of that for 2′,3′,11-triacetyldesglucosyrioside (1a) (Table 2).

* Signals within a vertical column may be reversed.

* An 11α-hydroxy- or 11α-acetoxy-substituent on 5α-androstane causes, respectively, 0.1 and 0.4 p.p.m. shielding on C-5.[10] This substituent effect is not expected to change substantially if structural changes in ring B do not cause severe distortion of ring C.[7]

that sarverogenin (11) and the *Asclepias* epoxycardenolides such as desglucosyrioside have structurally and configurationally the same epoxide system.

With respect to C-5, the shift differences between the 5α- and 5β-series provide specific information on the configuration of the epoxide. A 7,8-epoxide with the α-configuration would exert a *γ-gauche* shielding effect on C-5 in a 5α-H, but not in a 5β-H steroid (see discussion above). Absence of such extra shielding in the 5α-epimer (12a) (see columns 3 and 6) confirms the β-configuration of the epoxide.

$^{13}$C N.m.r. assignments for labriformidin, its 11-acetate, and uscharidin (7) are based on multiplicities, chemical-shift theory, and comparison with those of 2′,3′-diacetylcalactin (9) [2] and 2′,3′,11-triacetyldesglucosyrioside (1a).[2] In the case of labriformidin, confirmation of assignments comes from 'Birdsall plots' [13] which provide distinction between signals of like carbons having attached protons of dissimilar $^{1}$H chemical shifts. Methine signals at 48.2 and 45.2 p.p.m. in the spectra of labriformidin (with 11α-hydroxy) and 11-acetyl-labriformidin (2a), respectively, are assigned to C-9 since in the latter compound C-9 is expected to be shielded by the 11-acetoxy-carbonyl carbon. Another methine signal appearing at about 42 p.p.m. in both compounds is assigned on the basis of Birdsall plots to C-17 which has a low-field attached proton (compared to C-5 and C-9) and which is not affected by acetylation at position 11. However, C-17 is strongly shielded by the oxygen atom of the 12-carbonyl group, and in uscharidin (7) and 2′,3′-diacetylcalactin (9) (each of which lacks the 12-ketone) this carbon resonates near 51 p.p.m. Methylene signals of C-4′ [44.7 p.p.m. in labriformidin and its 11-acetate, 34.8 p.p.m. in 2′,3′,11-triacetyldesglucosyioside (1a)] are distinguished from those of C-1 (near 44 p.p.m. for each compound) in view of the expected effect of structural changes at position 3′. The full assignment for uscharidin (*e.g.* the distinction between C-2 and C-3 and between the three methylene signals near 27 p.p.m. due to carbons 6, 7, and 16) is consistent with the extensive data we have collated for the derivatives of the Asclepiadaceae cardenolides gomphoside (6) and afroside (15β-hydroxygomphoside).[4] Finally, noting the structural relationship between the glycosides listed in Table 2, the internal consistency of the assignments is confirmed by the following equalities (to ±1.5 p.p.m.) * of shift differences: δ (6a) − δ (7) = δ (1a) − δ (2a), and δ (6a) − δ (1a) = δ (7) − δ (2a).

* Except for the carbonyl carbons which are deshielded by hydrogen-bonding with $CD_3OD$ added to increase the solubility of uscharidin (7) in $CDCl_3$.

## EXPERIMENTAL

N.m.r. spectra were determined on Varian HA-100 (100 MHz, $^{1}$H) or CFT-20 (20 MHz, $^{13}$C) spectrometers. N.O.e measurements in uscharidin (from *Asclepias curassavica* latex [14]) were made in the continuous-wave mode using a 0.05M-solution in octadeuteriodioxan which had been degassed.

*Conversion of Eriocarpin into 2′,3′,11-Triactyldesglucosyrioside* (1a).—A mixture of eriocarpin (8 mg), acetic anhydride (0.02 ml), and dry pyridine (1.0 ml) was sealed under vacuum and kept for 8 days at 35 °C. The residue obtained on evaporation of the reaction mixture under vacuum was dissolved in chloroform, washed with dilute hydrochloric acid and sodium hydrogencarbonate, and worked-up to give 2′,3′,11-triacetyldesglucosyrioside (1a), identical [$^{13}$C and $^{1}$H n.m.r. spectra (Tables 1 and 2)] with an authentic sample.[2]

*Chromatographic Comparison of Eriocarpin and Desglucosyrioside.*—Under thin-layer chromatographic conditions, as recorded in ref. 14, eriocarpin and desglucosyrioside (*A. syrica*) [2] had identical $R_F$ values with respect to digitoxin: *viz.* 1.17 in chloroform–methanol–formamide (90 : 6 : 1 v/v/v), and 1.63 in ethyl acetate–methanol (97 : 3 v/v).

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