Tetrahedron Letters No. 51, pp 4547 - 4548, 1977. Pergamon Press. Printed in Great Britain.

# THE STRUCTURE OF SILYCHRISTIN

A. Pelter*

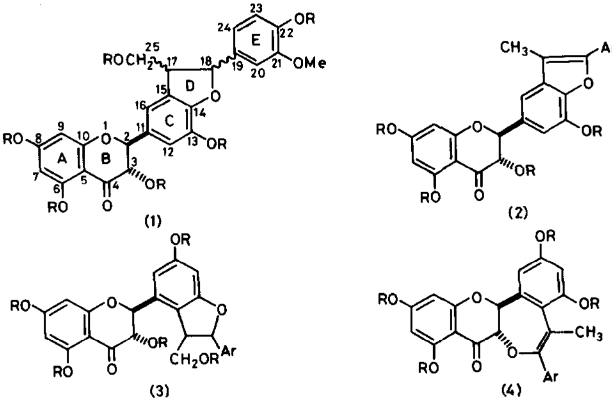
Department of Chemistry, University College of Swansea, Singleton Park, Swansea, U.K.

R. Hänsel and M. Kaloga

Institut für Pharmakognosie und Phytochemie der Freie Universität, Berlin

(Received in UK 7 October 1977; accepted for publication 27 October 1977)

Two structures (1a) and (3a) have been proposed[1,2] for silychristin, a flavonolignan isolated from <u>Silybum marianum</u>. Structure (1a) was put forward on the basis of the $^1H$ n.m.r. spectra of the parent compound and its acetate whilst (2a) was designed to reconcile the $^1H$ n.m.r. with the results of colour tests on the acid dehydration products of silychristin and dehydrosilychristin.[2] These tests reproducibly indicated that the anhydro-products did not contain a free 3-hydroxy group. Structure (4a) was proposed for anhydrosilychristin. The corresponding structure based on (1a) for silychristin would be (2a).



(a) R=H, (b) R=Ac. Ar is ring E of (1).

An examination (Table) of the $^{13}C$ n.m.r. spectra of silychristin and anhydrosilychristin and their acetates unequivocally support structures (1) and (2). Ring A and B corresponding to taxifolin are present in all four compounds. However C-14 in structure (3) would be expected to appear at the low value of <u>ca.</u> 100 p.p.m. due to the two adjacent oxygen atoms, and no such signal is evidenced. Furthermore the shifts of the C-3 signal on acetylation of silychristin (1a) and anhydrosilychristin (2a) are parallel showing that a free 3-hydroxy group remains in anhydrosilychristin. All other signals are compatible with structures (1a), (1b), (2a), and (2b). Evidently the colour tests that are reliable for simple dihydroflavonols and even for silybin and dehydrosilybin[3] must be treated with caution for other flavonolignans.

### TABLE

### $^{13}$C N.M.R. of Silychristin and Related Compounds$^{a}$

| Carbon atom | Taxifolin$^{b}$ | (1a) | (1b) | (2a) | (2b) |
|---|---|---|---|---|---|
| 2 | 83.1 | 83.5 | 80.9 | 83.5 | 81.4 |
| 3 | 71.7 | 72.1 | 73.2 | 71.9 | 73.6 |
| 4 | 197.1 | 197.3 | 185.1 | 197.6 | 185.9 |
| 5 | 163.3 | 163.6 | 151.8 | 163.3 | 151.4 |
| 6 | 96.1 | 96.6 | 111.4 | 96.1 | 111.3 |
| 7 | 166.8 | 167.0 | 156.4 | 166.8 | 156.4 |
| 8 | 95.1 | 95.2 | 109.0 | 95.0 | $109.1^{*}$ |
| 9 | 162.5 | 162.6 | 166.4 | 162.5 | 162.5 |
| 10 | 100.6 | 100.5 | 110.7 | 100.5 | 110.7 |
| 11 | 128.1 | 129.0 | 128.6 | 122.0 | 129.4 |
| 12 | 115.3 | $115.3^{*}$ | $122.7^{*}$ | $109.8^{\dagger}$ | 116.1 |
| 13 | $144.9^{*c}$ | 147.4 | 139.7 | 150.9 | 140.1 |
| 14 | $145.7^{*}$ | 140.9 | $151.9^{\ddagger}$ | $141.6^{*}$ | $152.1^{\ddagger}$ |
| 15 | 115.3 | 129.9 | 139.9 | 122.0 | 130.3 |
| 16 | 119.2 | $115.8^{*}$ | $123.0^{*}$ | $110.0^{\dagger}$ | 119.9 |
| 17 | | 53.7 | 51.0 | 109.5 | 112.0 |
| 18 | | 87.3 | 88.3 | $141.7^{*}$ | 145.2 |
| 19 | | 132.6 | $139.4^{\dagger}$ | 132.5 | 134.9 |
| 20 | | 110.2 | 109.6 | $110.4^{\dagger}$ | $109.3^{*}$ |
| 21 | | $147.6^{\dagger}$ | $151.5^{\ddagger}$ | $147.8^{\ddagger}$ | $151.3^{\ddagger}$ |
| 22 | | $147.4^{\dagger}$ | $139.7^{\dagger}$ | $147.1^{\ddagger}$ | 140.1 |
| 23 | | $115.1^{*}$ | 121.3 | 115.9 | 123.1 |
| 24 | | 118.7 | 117.6 | 119.7 | 117.2 |
| 25 | | 63.2 | 65.2 | 9.3 | 9.4 |

(a) Chemical shifts in p.p.m. downfield from T.M.S. All assignments supported by off resonance spectra. Signals due to acetate and methoxy carbon atoms are omitted. (b) B. Ternai and K. R. Markham, *Tetrahedron*, 1976, **32**, 565. (For convenience the same numbering used for taxifolin as for (1a) - (2b)). (c) Signals marked with the same superscript denote interchangeable assignments for any one compound.

## References

1. H. Wagner, O. Seligmann, L. Hörhammer, M. Seitz, and J. Sonnenbichler, *Tetrahedron Letters*, 1971, 1895.
2. R. Hänsel, M. Kaloga, and A. Pelter, *Tetrahedron Letters*, 1976, 2241.
3. A. Pelter and R. Hänsel, *Chem.Ber.*, 1976, **108**, 790.