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PERACID OXIDATION PRODUCTS OF SWERTANONE, THE NOVEL TRITERPENE OF SWERTIA CHIRATA

AJIT KUMAR CHAKRAVARTY*, BINAYAK DAS AND SIBABRATA MUKHOPADHYAY

Indian Institute of Chemical Biology
Calcutta 700032, India

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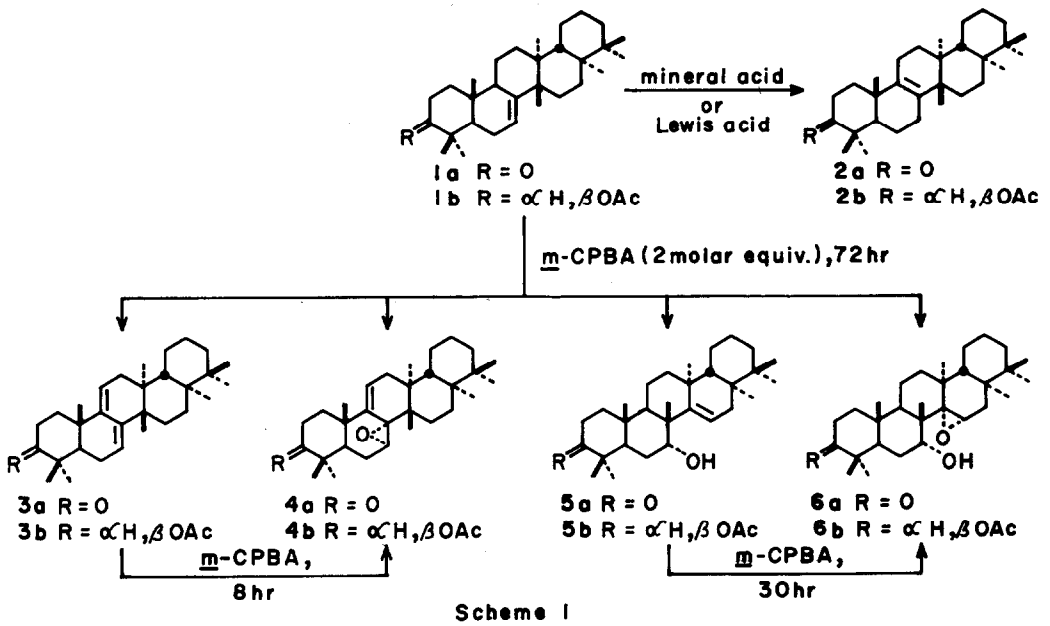
Abstract : While treatment of swertanone (**1a**) with mineral acids and Lewis acids yielded isoswertanone (**2a**) as the only isolable product, its reaction with m-chloroperbenzoic acid afforded 7α,8α -epoxyswertanone (**7**), 7α -hydroxy-swert-8-en-3-one (**8**), swerta-7,9(11)-dien-3-one (**3a**), its 7α,8α -epoxide (**4a**), 7α -hydroxy-friedogammacer-14-en-3-one (**5a**) and its 14α,15α -epoxide (**6a**). The structures of the products have been elucidated mainly on the basis of ^{1}H and ^{13}C NMR spectroscopy and, in some cases, by chemical correlation.

Assignments of ^{13}C NMR signals of the products have been done and those of some of the signals of **1a**, swertenyl acetate (**1b**) and swertenol (**16**) have been revised. In this connection, spectra of bauerenyl acetate (**18**), isobauerenyl acetate (**19**) and multiflorenyl acetate (**20**) have been recorded.

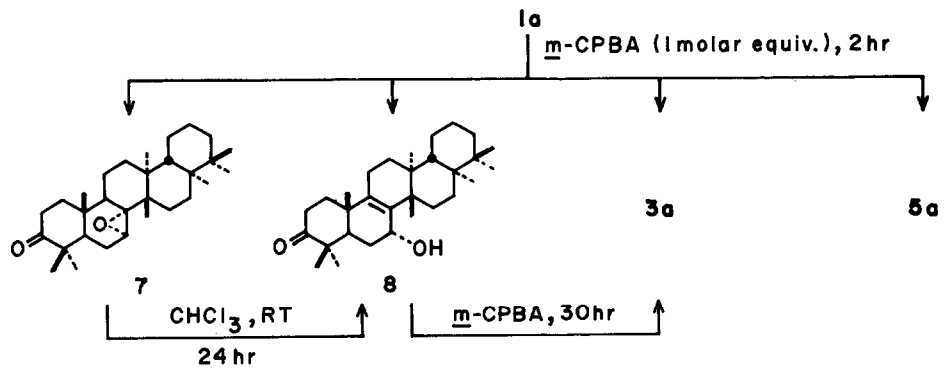
Recently we reported[1] the isolation and structure elucidation of swertanone (**1a**), a triterpene with a new skeletal type named swertane. Because of the novelty in structure, it was of interest to investigate the possible rearrangement of **1a** with mineral acid or Lewis acid, and its reaction with m-chloroperbenzoic acid. Interesting products could thereby be isolated and their structures established through spectral studies. The large number of ^{13}C NMR spectral data thus available showed that the original spectral assignment[1] of **1a**, **1b** and **16** needed some revision. For comparison, we also recorded the spectra of related triterpenoids *viz.* bauerenyl acetate (**18**), isobauerenyl acetate (**19**) and multiflorenyl acetate (**20**) whose ^{13}C NMR data are not available in the literature. The results are discussed herein.

Swertanone (**1a**) on heating for a short period with AcOH-HCl or AcOH-H_2SO_4, or refluxing with AcOH-$ZnCl_2$, or stirring with CH_2Cl_2-BBr_3 yielded isoswertanone (**2a**) as the only isolable product. When **1a** was treated with two molar equivalents of m-chloroperbenzoic acid at 4°C for 72 hr, four distinct products (**3a-6a**) could be isolated (Scheme 1). When, however, **1a** was treated with one molar equivalent of m-chloroperbenzoic acid for short periods (2 hr or 24 hr), two more new products (**7** and **8**) were obtained besides **3a** and **5a** (Scheme 2).

Swertenyl acetate (**1b**)[1] was also subjected separately to AcOH-HCl and m-chloroperbenzoic acid (2 molar equivalent, 72 hr) treatment leading to the formation of analogous products. Thus, the former reagent yielded isoswertenyl acetate (**2b**) while the later afforded **3b-6b** (Scheme 1).



Scheme 1



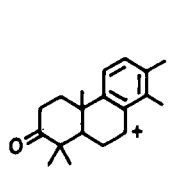
Scheme 2

Characterisation of products :

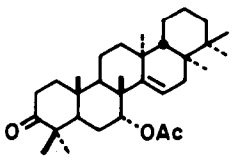
Isoswertanone (2a). Its EIMS showed intense peaks at m/z 245, 257 and 271, and thus indicated that the double bond of **2a** could have isomerised only to 8,9 or 9,11 position[2]. The absence of any vinylic proton signal in its ^{1}H NMR spectrum and the appearance of two quaternary carbon signals at δ 132.8 and 135.4 ppm in the ^{13}C NMR spectrum suggested that the double bond must be located between C-8 and C-9.

Swerta-7,9(11)-dien-3-one (3a). The EIMS of the compound showed M^+ at m/z 422 which is 2 mass units less than that of **1a** indicating the presence of one more double bond in the molecule supported by its ^{1}H and ^{13}C NMR spectra. While the former displayed two one-proton multiplets at δ 5.20 and 5.44 ppm for two vinylic protons, the latter exhibited two

doublets at δ 115.1 and 117.3 ppm and two singlets at δ 141.4 and 143.9 ppm for two sets of trisubstituted olefinic carbons. That the two double bonds are conjugated and heteroannular in nature was demonstrated by the UV absorption maximum at 238 nm (log ε 4.03). Finally, the location of the diene system at $\Delta^{7,9(11)}$ was evident[3] from the mass spectral fragment ion at m/z 269 (species a).



a, m/z 269



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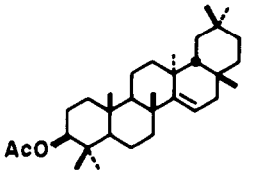

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7α,8α-Epoxy-swert-9(11)-en-3-one (4a). The M^+ in the EIMS of the compound was found to be at m/z 438 which is 14 mass units higher than that of **1a**. The presence of a trisubstituted double bond and a trisubstituted epoxide in the molecule was evident from ^1H NMR signals at δ 5.74 ppm as double doublet (J=5,3 Hz) and δ 3.33 ppm as broad singlet as well as ^{13}C NMR signals at δ 142.1(s), 126.0(d), 62.0(s) and 51.2(d) ppm.

The compound **4a** can be obtained from the diene (**3a**) on treatment with m-chloroperbenzoic acid (Scheme 1) indicating that one of the double bonds of **3a** must have undergone epoxidation in **4a**. That the epoxide is located between C-7 and C-8 rather than C-9 and C-11 and that the epoxide oxygen is α oriented was clearly demonstrated by the up-field shift of ^{13}C NMR signals for C-5, C-6 and C-15 by 8.6, 3.3 and 5.0 ppm when compared with those of the diene (**3a**) (Table 1). Its structure was finally confirmed by its correlation with 7α,8α-epoxy-swertan-3-one (**7**) (vide infra).

7α-Hydroxy-friedogammacer-14-en-3-one (5a). The EIMS of the compound showed M^+ at m/z 440 which is 16 mass units higher than that of **1a**. Its ^1H NMR spectrum displayed, besides the signal for a vinylic proton of a trisubstituted double bond at δ 5.51 ppm, a one proton triplet-like signal at δ 3.92 ppm (J=3 Hz) indicating the presence of an axial OH group located at a carbon flanked by a methylene group and a quaternary carbon. The up-field shift of C-5 signals in the ^{13}C NMR spectra of **5a** and its acetate (**9**) by 5.4 and 4.1 ppm respectively as against that of **1a** (Table 1) established the location of the axial OH group at C-7. Though mechanistically, several structures are possible through back-bone rearrangement, careful examination of ^{13}C NMR spectrum of the compound pointed to structure **5a** for it. Thus, the down-field shift of C-16 methylene and, C-27 and C-28 methyl carbons by 6, 4.5 and 2.4 ppm respectively compared to those of **1a** (Table 1) indicated the location of the trisubstituted double bond between C-14 and C-15. The assigned structure also received support from ^{13}C chemical shifts of other B, C and D ring carbons when compared with those of taraxeryl acetate (**10**)[4] (Table 1) which lacks the axial OH group at C-7. Thus, as expected, deshielding of C-6, C-7, C-8 and C-15, and shielding of C-9, C-26 and C-14 induced by the axial OH group were observed.

7α-Hydroxy-14α,15α-epoxy-friedogammaceran-3-one (6a). The EIMS of the compound showed M^+ at m/z 456 which is 16 mass units higher than that of **5a**. The ^{13}C NMR spectrum displayed two signals at δ 71.4(s) and 59.8(d) ppm commensurate with the presence of a trisubstituted epoxide ring. Moreover, it exhibited a doublet at δ 71.0 ppm indicating the presence of a secondary OH group in the molecule which was also supported by the appearance of a D_2O exchangeable broad singlet at δ 5.17 ppm. Selective decoupling experiment showed that the two protons associated with the quartet-like signal at δ 3.47 ppm in its ^1H NMR spectrum are attached to two different carbons having chemical shifts of δ 71.0 and 59.8 ppm. That the compound is 14,15-epoxide of **5a** was confirmed by the conversion of **5a** to **6a** on treatment with m-chloroperbenzoic acid. The orientation of the epoxide oxygen could be concluded to be α from the fact that the 7α-OH proton signal appears at a down-field position (δ 5.17 ppm) ascribed to intramolecular hydrogen bonding with the α oriented oxygen of the epoxide ring.

7α-8α-Epoxy-swertan-3-one (7). Its EIMS showed M^+ at m/z 440 which is 16 mass units higher than that of **1a**. A one proton triplet-like signal at δ 3.18 ppm (J=2 Hz) in its ^1H NMR spectrum and the signals at δ 63.8 ppm (s) and 53.1 ppm (d) in its ^{13}C NMR spectrum suggested that the compound must be the 7,8-epoxide of **1a**. Moreover, the up-field shift of C-5 and C-15 carbon signals by 4.2 and 5.5 ppm respectively in the spectrum of **7** when compared with those of **1a** (Table 1) indicated that the oxygen of the 7,8-epoxide must be α oriented.

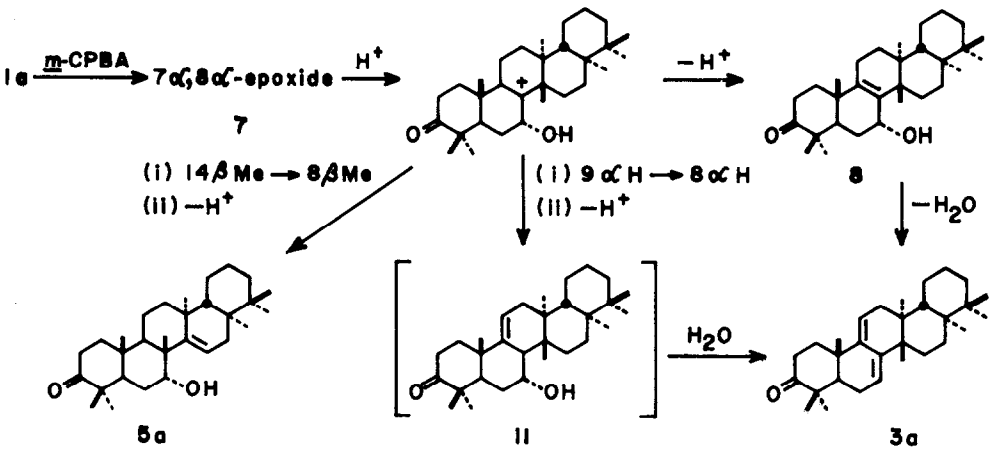
7α-Hydroxy-swert-8-en-3-one (8). The EIMS showed the M^+ of the compound at m/z 440. Its ^1H NMR spectrum displayed a one-proton multiplet at δ 4.25 ppm with $W_{\frac{1}{2}}$=8 Hz indicating the presence of an axial OH function in the molecule. The ^{13}C NMR spectrum showed the presence of two low-field singlets at δ 137.1 and 138.8 ppm suggesting the presence of one tetrasubstituted double bond in it. The structure of the compound could finally be confirmed by its formation from **7** on standing in $CHCl_3$ solution at room temperature for 24 hr.

The structures of the products **2b-6b** obtained from swertenyl acetate (**1b**) could similarly be deduced from their spectral data.

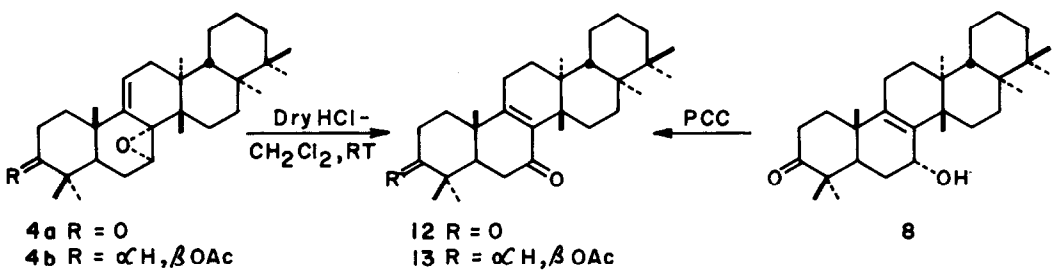
Mechanism of formation :

A plausible mechanism for the formation of the products has been suggested as shown in Scheme 3. It may be mentioned here that the formation of the diene (**3a**) was found to be very facile even on treatment of **1a** with the reagent for short period (2 hr). It was also observed the compound **8** can be converted to the diene (**3a**) with the same reagent though the reaction is extremely slow. We, therefore, believe that the diene (**3a**) must have formed mainly *via* some other labile intermediate **e.g. 11.**

Interestingly enough, 7α,8α-epoxy-swert-9(11)-enes (**4a** and **4b**) on treatment with dry HCl in CH_2Cl_2 for a short period yielded the α,β-unsaturated ketones (**12** and **13**). Their structures were elucidated from spectral data and finally confirmed by direct comparison (^1H NMR, IR) of **12** with a sample prepared from **8** on PCC oxidation[5] (Scheme 4).

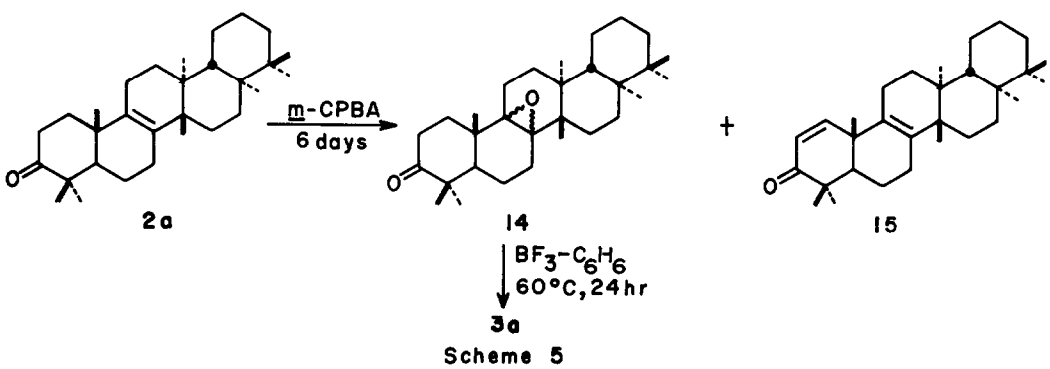


Scheme 3



Scheme 4

Isoswertanone (**2a**) on treatment with m-chloroperbenzoic acid yielded a mixture of 8α,9α and 8β,9β -epoxides (**14**) as the major product besides swerta-1,8-dien-3-one (**15**) as a minor compound. Attempted opening of the epoxide ring of **14** with BF_3 led to the formation of the diene (**3a**) as the only isolable produce (Scheme 5).



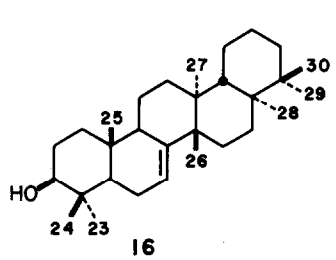
Scheme 5

On the basis of the above observations, it can be reasonably concluded that the swertane skeleton is quite stable to rearrangement. This appears to be due to the increased

steric interactions in the products arising from migration of the double bond to Δ^{12} or $\Delta^{13(18)}$ with shift of C(13)-Me to C-14 as is evident from Dreiding model studies.

^{13}C NMR signal assignment

In our earlier paper[1], we reported the assignment of ^{13}C chemical shifts to specific carbon centres of **1a**, **1b** and **16** on the basis of reported data of gammaceran-3β-ol (tetrahymanol, 17)[6] as well as amyrins[7,8] and Δ^7-steroids[9]. Therein the most up-field methyl and methylene signals at $\sim\delta$ 13.0 and $\sim\delta$ 17.0 ppm were assigned respectively to C-28 and C-19 based on the number of γ_g interactions experienced. However, during the present investigation, it was found that the same methyl and methylene signals in that case must have shifted down-field by $\sim$7.0 ppm and 3-4 ppm respectively in the spectra of Δ^8-isomers (viz. **2a** and **2b**). Examination of Dreiding models revealed that isomerisation of the double bond from 7,8 to 8,9 position is not expected to affect significantly either C-28 or C-19 carbon signal. A revision of ^{13}C signal assignments of **1a**, **1b** and **16** was, therefore, taken up. This was facilitated by the fact that the present rearrangement studies resulted in the isolation of a large number of analogs. Moreover, some other Δ^7 and Δ^8 triterpenoids (**18-20**) having identical A, B and C ring substitutions also became available to us. It was, therefore, possible to do a detailed comparative study of their ^{13}C chemical shifts leading to reasonable assignments to specific carbons in most of the compounds as discussed below.



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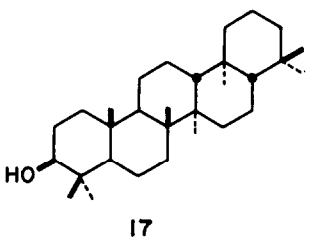

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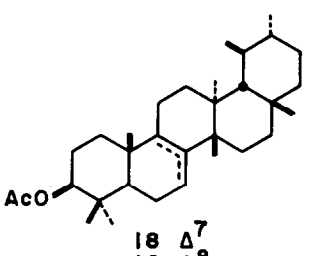
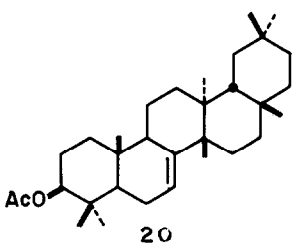


18 Δ^7
19 Δ^8



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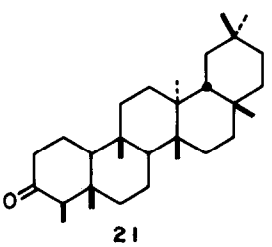

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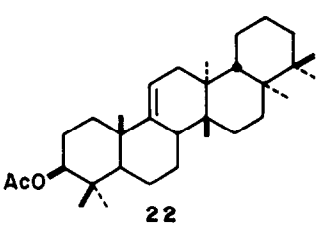

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The ^{13}C NMR spectra of bauerenyl acetate (**18**) and multiflorenyl acetate (**20**) (Table 1) showed that like **1a**, **1b** and **16**, they contained one methyl carbon signal at $\sim\delta$ 13.0 ppm and one methylene carbon signal at $\sim\delta$ 17.0 ppm in spite of different substitution pattern in the E ring and cis D:E ring fusion. It was, therefore, presumed that these two signals must be due to two carbons associated with the A, B or C ring rather than the E ring. Since both these signals were shifted down-field in the spectra of isobauerenyl acetate (**19**) and isoswertane derivatives (**2a** and **2b**), these may be reasonably assigned to C-25 and C-11 respectively.

Among the other methyl signals, those for the two (C-23 and C-24) attached to C-4 could easily be assigned on the basis of reported[7-9] data of similar systems. For the three methyl carbons attached to ring E, viz. C-28, C-29 and C-30 in swertane series, it is expected that the derivatives differing only with respect to functionalities in A, B and/or C rings (viz. **1a-4a, 1b-4b, 7, 8, 13, 15** and **16**) should show close chemical shifts. Table 1 indeed shows that three signals exist at δ 16.0-16.7, 22.8-23.0 and 25.2-25.3 ppm in the spectra of these compounds and were accordingly assigned respectively to C-28, C-30 and C-29 taking into account their involvement in γ_g interactions. The two remaining methyl signals for C-26 and C-27 in Δ^7 compounds (**1a, 1b** and **16**) were assigned by comparison of their chemical shifts with those of 7α,8α-epoxide (**7**) with the reasonable assumption that introduction of the 7α,8α-epoxide is not expected to affect C-27 carbon signal significantly. In case of Δ^8 isomers (**2a, 2b, 8** and **19**), however, one of those methyl carbons invariably experienced significant up-field shift (δ 16.0-17.0 ppm) compared to Δ^7 derivatives (δ 22.0-23.0 ppm in **1a, 1b, 16** and **18**). Examination of Dreiding model showed that the severe steric interaction (flagpole-flagpole) experienced by C-27 with C(9)-H in the Δ^7 compounds is absent in Δ^8 isomers and a distinct difference in resonance frequency is, therefore, expected. The up-field signal of the latter was, therefore, assigned to C-27.

Though an adequate number of data sets were not available for bauerene and multiflorene series, ^{13}C chemical shifts of the four methyl carbons, viz. C-26, C-28, C-29 and C-30 of multiflorenyl acetate (**20**) could be assigned satisfactorily on the basis of reported data[10] (Table 1) for friedelin (**21**). The assignments for bauerenyl acetate (**18**) and isobauerenyl acetate (**19**) remain, however, tentative.

In case of friedogammacer-14-enes (**5a, 5b** and **9**), four methyl carbons (C-23 to C-26) attached to A and B rings were assigned on the basis of reported data[4] (Table 1) of taraxeryl acetate (**10**), the up-field shift of C-26 signal being ascribed to γ_t effect of the 7α-OH group, while the assignment of three methyl carbons (C-28 to C-30) attached to E ring could be done by comparison of their chemical shifts with those of swertane derivatives already discussed. A slight deshielding of C-28 signal must be due to removal of one of its γ_g interactions with C-15 consequent upon the introduction of 14,15-double bond.

Now, A, B and C ring carbons of swertenyl acetate (**1b**) are expected to show chemical shifts close to those of bauerenyl acetate (**18**) and multiflorenyl acetate (**20**). The assignment of C-1 to C-10 carbons could be satisfactorily done on the basis of reported[7-9,11] data for similar systems. Besides, the most up-field methylene signal has already been assigned to C-11 (vide supra). Of the remaining signals, the close lying methylene carbon signal in the spectra of **1b, 18** and **20** at δ 32.5-34.6 ppm was assigned to C-12 while the two non-protonated carbon signals at δ 36.5-37.8 and 41.0-41.6 ppm were assigned respectively to C-13 and C-14 considering the degree of substitution at the β-carbons.

Table 1. Carbon-13 NMR data[a] (δ ppm, $CDCl_3$)

Comp.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1a	38.3	34.8	216.5	47.8	52.3	24.5	116.1	145.1	47.4	35.3	16.8	33.9	36.5	41.0	29.1	27.9
2a	35.7	34.4	218.0	47.0	51.0	19.5	25.7	132.8	135.4	37.4	20.5	30.4	37.2	40.7	26.9	27.9
3a	36.7	34.9	216.2	47.7	49.9	24.4	115.1	141.4	143.9	36.2	117.3	38.2	37.4	39.7	27.4	27.8
4a	36.7	34.6	215.8	46.6	41.3	21.1	51.2	62.0	142.1	36.3	126.0	39.0	37.7	38.6	22.4	27.3
5a	38.5	34.7	217.4	46.9	46.9	25.0	72.5	45.4	46.5	37.2	15.9	33.9	36.6	151.2	119.4	32.8
6a	37.7	33.8	217.2	46.5	46.1	26.0	71.0	42.4	45.2	37.5	16.4	32.8	36.6	71.4	59.8	30.3
1b	36.5	24.2	81.1	37.8	50.8	24.0	115.9	145.1	47.7	35.1	16.7	33.9	36.5	41.0	29.1	27.9
2b	35.1	24.3	81.0	37.8	50.6	19.0	25.8	134.0[b]	134.4[b]	37.4	19.6	30.3	37.2	40.6	27.0	28.0
3b	35.2	23.7	81.0	37.9	48.2	24.3	114.5	141.3	144.8	36.2	117.4	38.4	37.4	39.7	27.5	27.9
4b	35.8	24.1	80.5	36.9	39.9	22.4	51.2	62.0	143.1	36.5	125.1	39.1	37.9	38.5	22.4	27.4
5b	37.6	23.9	80.9	37.7	46.9	23.6	72.9	45.6	46.6	37.3	16.0	34.8	36.3	151.6	119.4	32.9
6b	37.1	23.4	80.9	37.6	46.0	24.9	71.6	42.5	45.4	37.0	16.6	32.9	36.7	71.6	59.8	30.3
7	37.9	34.5	215.9	46.8	48.1	23.5[b]	53.1	63.8	46.5	34.9	16.4	33.3	37.7	39.5	23.6[b]	26.9
8	35.1	34.2	217.6	46.5	44.2	26.3	63.3	138.8	137.1	37.2	19.7	30.4[b]	36.8	41.0	30.3[b]	27.9
9	38.8	34.3	216.6	46.8	48.2	24.5	75.8	43.2	46.8	37.1	15.9	33.4	36.9	148.7	117.8	33.9
10	37.8	23.4	81.1	37.9	55.7	18.8	33.2	39.1	49.3	37.6	17.6	36.7	37.8	158.0	116.9	33.7
13	34.4	23.9	79.8	37.7	47.5	36.5	197.9	139.9	164.3	39.0	21.6	29.5	37.4	40.2	24.2	28.0
15	156.2	126.1	205.1	44.3	47.5	19.3	25.8[b]	130.6	136.7	41.0	21.0	30.3	37.1	40.6	25.9[b]	27.9
16	36.9	27.8	79.3	39.0	50.7	24.2	116.2	145.0	47.9	35.3	16.7	34.1	36.5	41.0	29.1	27.9
18	36.5	24.2	81.1	37.8	50.0	24.0	116.2	145.4	48.2	35.1	16.9	32.5	37.8	41.3	28.9	31.5
19	34.8	24.2	80.9	37.8	50.6	19.0	25.3	134.0[b]	134.5[b]	37.4	20.5	33.1	38.2	41.1	27.3	29.6
20	36.6	24.2	81.1	37.7	50.2	24.0	117.5	147.6	48.7	35.1	17.1	34.6	37.0	41.6	31.7	36.1
21[10]	22.4	41.5	213.0	57.9	42.1	41.3	18.2	53.1	37.4	59.6	35.4	30.5	38.4	39.7	32.5	36.0
22[d]	37.2 (39.1)	24.7	81.1	37.6	44.6	17.4	19.0	40.3	150.2	37.3	116.7	39.1 (37.2)	37.2	38.2	28.1[b]	27.9[b] (37.6)

Comp.	17	18	19	20	21	22	23	24	25	26	27	28	29	30	$\underline{C}OCH_3$	$CO\underline{C}H_3$
1a	**38.1**	43.4	23.2	21.5	37.0	39.0	24.5	21.4	12.5	23.8	22.2	16.0	25.3	22.9	-	-
2a	38.3	41.4	23.1	21.8	36.9	39.1	26.7	21.0	19.7	21.8	16.9	16.5	25.2	22.8	-	-
3a	38.1	41.1	23.1	21.4	37.0	39.1	24.4	22.0	19.7	20.6	17.4	16.2	25.2	22.9	-	-
4a	38.1	41.6	23.4	21.1	36.9	39.0	25.2	22.7	22.9	18.5	18.3	16.2	25.2	22.8	-	-
5a	37.2	41.1	22.7	22.1	37.2	37.2	26.3	21.1	15.0	20.5	27.4	18.4	25.7	23.7	-	-
6a	37.7	40.6	23.1	22.5	36.5	37.9	26.9	21.3	15.2	17.9	23.1	16.8	25.4	23.6	-	-
1b	38.1	43.4	23.2	21.5	37.1	39.0	27.5	15.7	12.9	23.7	22.1	16.0	25.3	23.0	170.9	21.2
2b	38.4	41.4	23.2	21.7	36.9	39.2	28.0	16.3	20.1	22.2	17.0	16.6	25.3	22.8	170.9	21.3
3b	38.2	41.3	23.2	21.5	37.1	39.2	27.5	16.4	20.6[b]	20.7[b]	17.4	16.4	25.3	23.0	170.9	21.3
4b	38.1	41.7	23.0	21.2	37.0	39.1	27.7	17.2	23.6	18.7	18.3	16.3	25.2	22.9	170.6	21.2
5b	37.3	42.0	22.7	22.2	37.3	37.3	27.9	16.5	15.6	20.4	27.6	18.5	25.8	23.8	170.9	21.3
6b	38.0	41.5	23.1	22.5	36.5	38.2	27.7	16.9	15.5	18.0	23.6	16.8	25.4	23.6	170.7	21.2
7	38.0	43.7	23.2	21.3	37.0	39.1	24.8	21.3	14.2	19.3	22.8	16.0	25.2	22.8	-	-
8	38.2	41.6	23.1	21.8	36.8	39.2	27.1	21.0	18.6	23.4	16.9[c]	16.7[c]	25.2	22.8	-	-
9	36.3	42.7	22.8	22.1	37.3	37.1	25.9	21.0	15.2	19.9	27.2	17.9	25.7	23.9	169.9	21.1
10	35.8	48.9	41.3	28.8	35.2	37.5	28.0	16.5	15.5	26.0	29.9	29.9	33.4	21.3	171.1	21.3
13	38.4	40.6	23.1	21.6	36.8	39.2	27.1	16.0[b]	18.8	21.8	17.0	16.2[b]	25.3	22.8	170.8	21.2
15	38.4	41.3	23.1	21.7	36.9	39.2	26.5	21.4	24.1	22.4	17.0	16.3	25.3	22.8	-	-
16	38.2	43.4	23.3	21.3	27.2	39.0	27.6	14.6	12.9	23.8	22.2	16.1	25.3	23.0	-	-
18	32.1	55.0	35.4	38.0	29.2	37.8	27.5	15.8	13.0	23.6	22.7	32.1	25.6	22.5	170.9	21.2
19	31.8	52.4	35.9	38.2	29.1	37.8	27.9	15.6	19.9	22.1	16.2	32.0	25.2	22.4	170.8	21.2
20	30.9	46.9	36.1	28.2	33.9	36.8	27.6	16.0	13.2	27.1	26.1	31.7	34.1	33.7	170.8	21.2
21[10]	30.0	42.9	35.7	28.2	32.8	39.2	6.7	14.6	17.9	20.2	18.6	31.8	35.0	32.1	-	-
22[d]	38.2	41.2	23.3	21.8	37.6 (27.9)	39.3	27.4	16.2	25.3	15.2	16.5	16.4 (23.0)	25.3 (16.4)	23.0 (25.3)	171.0	21.3

[a]The multiplicity of each signal was ascertained by INEPT experiment. [b,c]Assignments may be reversed in case of a particular compound. [d]The values in parentheses are the original assignments[13].

The chemical shift assignments for C-15 to C-22 carbons in swertenyl acetate (**1b**) and other derivatives of the series, having chair conformations[1] of both D and E rings with their trans ring juncture, were found to be straight forward. Thus, of the remaining five methylene carbon signals, the most down-field one at ~δ 37.0 ppm was assigned to C-21 with two β-substitutions and one γ_g interaction. C-20 was assigned the chemical shift of ~δ 21.5 ppm in analogy with the chemical shift of C-2 of triterpene hydrocarbons[12]. C-15 and C-16 having almost identical β-substitutions and steric interactions were assigned two close signals at δ 29.1 and 27.9 ppm, the up-field one being due to C-16 with one more γ_g interaction. The changes in chemical shifts (Table 1) observed on introduction of functional groups in A, B, C and/or D ring of swertenyl acetate (**1b**) or swertanone (**1a**) fully supported the above assignment of ^{13}C NMR signals to specific carbons.

^{13}C chemical shifts of D and E ring carbons of **20** could be assigned on the basis of reported[10] data (Table 1) of friedelin (**21**). In case of **18** and **19**, however, only tentative assignments have been done for the same carbons.

With all these data and their assignments in hand, some of the recently reported[13] ^{13}C chemical shift assignments for pichierenyl acetate (**22**) could also be revised (Table 1).

Experimental

Melting points are uncorrected. IR spectra were recorded on a Perkin Elmer Model 177 spectrophotometer. UV spectra were registered on Hitachi U-3200 spectrophotometer. Optical rotations were measured in $CHCl_3$ solution on a Jasco DIP 360 polarimeter. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as internal standard on a JEOL FX-100 FT NMR instrument and mass spectra on a Hitachi RMU-6L instrument. Unless mentioned otherwise, all chromatography were done over neutral alumina.

Reaction of swertanone (1a) with mineral acids

(i) With conc. H_2SO_4 : To a solution of **1a** (0.09 g, 0.212 mmol) in glacial AcOH (25 ml) was added dropwise conc. H_2SO_4 (1 ml) with stirring and the reaction mixture was heated at 100°C for 15 min. Usual work-up followed by chromatography over Si-gel gave isoswertanone (**2a**, 0.081 g, 90%) crystallising out of EtOAc as shining flakes; m.p. 226-227°C, $[\alpha]_D$+31° (c 0.4); IR (KBr): ν_{max} 1700 cm^{-1}; ^1H NMR :δ 0.75, 0.78, 0.98(x2), 1.05(x3) and 1.09 (Me) ppm; m/z (%) : 424 (M^+, 26), 409(35), 271(16), 257(100) and 245(79). Anal. Found : C, 84.60; H, 11.13. $C_{30}H_{48}O$ requires : C, 84.84; H, 11.39.

(ii) With conc. HCl : A solution of **1a** (0.08 g, 0.189 mmol) in glacial AcOH (15 ml) on treatment with conc. HCl (0.6 ml) under above conditions gave **2a** (0.07 g, 88%).

Reaction of swertanone (1a) with Lewis acids

(i) With BBr_3 : To a solution of **1a** (0.06 g, 0.142 mmol) in dry CH_2Cl_2 (5 ml) was added BBr_3-SMe_2 (0.053 g, 0.168 mmol) and the mixture was stirred at 0°C for 2 h. Usual work-up followed by chromatographic purification and crystallisation afforded **2a** (0.05 g, 84%).

(ii) With $ZnCl_2$: To a solution of **1a** (0.1 g, 0.236 mmol) in glacial AcOH (20 ml) was added anh. $ZnCl_2$ (1 g, 7.34 mmol) and the mixture was heated at 100°C for 4 h. Usual work-up followed by chromatography of the product yielded **2a** (0.08 g) in 80% yield.

Reaction with swertenyl acetate (1b) with conc. HCl

Treatment of **1b** (0.06 g, 0.128 mmol) with conc. HCl (0.8 ml) in glacial AcOH (10 ml) yielded isoswertenyl acetate (**2b**) crystallising out of $CHCl_3$-CH_3OH in shining flakes (0.05 g, 84%); m.p. 264-265°C; $[\alpha]_D$-3.35° (c 0.477); IR(KBr) : ν_{max} 1725 and 1245 cm^{-1}; ^1H NMR : δ 0.75, 0.77, 0.88(x2), 0.96, 0.98(x2) and 1.04(Me), 2.04(OAc) and 4.49 (dd, J=10,6 Hz, 3-H) ppm; m/z (%) : 468 (M^+, 33), 453(37), 408(8), 393(34), 301(100), 289(76), 257(12), 255(20), 241(90) and 229(76). Anal. Found : C, 82.18; H, 11.02. $C_{32}H_{52}O_2$ requires : C, 81.99, H, 11.18.

Reaction of swertanone (1a) with m-chloroperbenzoic acid

(a) With two molar equiv. of reagent : To a solution of **1a** (0.25 g, 0.589 mmol) in dry CH_2Cl_2 (20 ml) was added m-CPBA (0.25 g, 1.45 mmol) and the reaction mixture was kept at 4°C for 72 h. Removal of the solvent at room temp. under reduced pressure gave a residue which on chromatography furnished four products as follows.

(i) Swerta-7,9(11)-dien-3-one (3a) : Elution with light petrol-$CHCl_3$ (7:3) afforded **3a** crystallising out of $CHCl_3$-CH_3OH as fine needles (0.095 g, 38%); m.p. 262-263°C; $[\alpha]_D$-244.22° (c 0.345); IR(KBr) : ν_{max} 1700 cm^{-1}; UV (MeOH) : λ_{max} (log ε) 238 (4.03); ^1H NMR : δ 0.66, 0.79, 0.92, 0.96, 1.05(x2), 1.13 and 1.15(Me), 2.83 (ddd, J=15,15,6 Hz, 2-H_{ax}), 5.20 (m, 7-H) and 5.44 (m, 11-H) ppm; m/z (%) : 422 (M^+, 81), 407(18), 269(37), 255(17), 243(15), 221(13), 190(34) and 179(100). Anal. Found : C, 85.01; H, 10.80. $C_{30}H_{46}O$ requires : C, 85.24; H, 10.97.

(ii) 7α,8α-Epoxy-swert-9(11)-en-3-one (4a) : Continued elution with the same solvent yielded **4a.** It was crystallised from $CHCl_3$-CH_3OH as colourless flakes (0.038 g, 15%); m.p. 244-245°C; $[\alpha]_D$-102.54° (c 0.256); IR(KBr) : ν_{max} 1705, 1460 and 1380 cm^{-1}; ^1H NMR : δ 0.79, 0.99(x2), 1.00, 1.05, 1.08(x2) and 1.16(Me), 3.33 (br s, 7-H) and 5.74 (dd, J=5,3 Hz, 11-H) ppm; m/z (%) : 438 (M^+, 15), 423(4), 233(22) and 109(100). Anal. Found : C, 82.30; H, 10.50. $C_{30}H_{46}O_2$ requires : C, 82.13; H, 10.57.

(iii) 7α-Hydroxy-friedogammacer-14-en-3-one (5a) : Further elution with the above solvent gave **5a** as colourless prisms ($CHCl_3$-CH_3OH) (0.085 g, 33%); m.p. 235-236°C; $[\alpha]_D$-38.88° (c 0.252); IR(KBr) : ν_{max} 3400 (br) and 1700 cm^{-1}; ^1H NMR : δ 0.81, 0.93, 1.00(x2), 1.05 and 1.10(x3) (Me), 3.92 (t-like J=3 Hz, 7-H) and 5.51 (t, J=4 Hz, 15-H) ppm; m/z (%) : 440 (M^+, 12), 422(12), 407(14), 337(17), 271(34), 255(82), 204(63) and 185(100). Anal. Found : C, 81.60; H, 11.06. $C_{30}H_{48}O_2$ requires : C, 81.76; H, 10.98.

(iv) 7α-Hydroxy-14α,15α-epoxy-friedogammaceran-3-one (6a) : Elution with light petrol-$CHCl_3$ (1:1) yielded **6a**, crystallised in fine needles from $CHCl_3$-CH_3OH (0.02 g, 8%); m.p. 166-168°C; $[\alpha]_D$+5.77° (c 0.347); IR(KBr) : ν_{max} 3600-3400 (br), 1700 cm^{-1}; ^1H NMR : δ 0.79, 0.92, 0.98, 1.02, 1.05, 1.07, 1.08 and 1.10 (Me), 3.47 (q-like J=2 Hz, 7-H and 15-H) and

5.17 (br s, OH) ppm, m/z(%) : 456 (M^+, 3), 441(2), 438(5), 423(3), 407(3), 275(73), 257(32), 207(13), 182(97) and 137(100). Anal. Found : C, 79.15; H, 10.70. $C_{30}H_{48}O_3$ requires : C, 78.89; H, 10.59.

(b) With one molar equiv. of reagent : Compound **1a** (0.11 g, 0.259 mmol) was treated with m-CPBA (0.048 g, 0.278 mmol) in dry CH_2Cl_2 (15 ml) at 4°C for 24 h. Usual work-up and chromatography of the product gave in addition to **3a** (0.055 g, 50%) and **5a** (0.025 g, 22%), two other products, **viz. 7** and **8** as detailed below.

(i) 7α,8α-Epoxy-swertan-3-one (7) : M.p. 234-235°C (yield 9%), $[\alpha]_D$-99.03° (c 0.208); IR(KBr) : ν_{max} 1700 cm^{-1}; ^1H NMR : δ 0.77, 0.95, 1.04(x4), 1.07 and 1.10 (Me) and 3.18 (t-like, J=2 Hz, 7β-H) ppm; m/z(%) : 440 (M^+, 10), 422(100), 407(40), 337(6), 269(30), 255(24), 243(18) and 179(48). Anal. Found : C, 81.60; H, 10.74. $C_{30}H_{48}O_2$ requires : C, 81.76; H, 10.98.

(ii) 7α-Hydroxy-swert-8-en-3-one (8) : M.p. 239-240°C (yield 9%); $[\alpha]_D$+40° (c 0.1); IR(KBr) : ν_{max} 3550-3400 (br) and 1700 cm^{-1}; ^1H NMR : δ 0.79(x2), 0.97, 0.99, 1.01, 1.06(x2) and 1.13 (Me), 4.25 (m, $W_{\frac{1}{2}}$=8 Hz, 7-H$_{eq}$); m/z(%) : 440 (M^+, 17), 422(100), 407(80), 337(15), 269(10), 255(8), 243(9) and 179(16). Anal. Found : C, 81.92; H, 10.80. $C_{30}H_{48}O_2$ requires : C, 81.76; H, 10.98.

Reaction of swertenyl acetate (1b) with m-chloroperbenzoic acid

(a) With two molar equiv. of reagent : Treatment of **1b** (0.2 g, 0.427 mmol) with m-CPBA (0.19 g, 1.03 mmol) in dry CH_2Cl_2 (8 ml) under conditions mentioned above yielded four products on chromatographic resolution.

(i) 3β-Acetoxy-swerta-7,9(11)-diene (3b) : Elution with light petrol-$CHCl_3$ (4:1) afforded **3b** crystallising out of $CHCl_3$-CH_3OH as fine needles (0.016 g, 8%); m.p. 228-230°C; $[\alpha]_D$-151.66° (c 0.345); IR(KBr) : ν_{max} 1730 and 1240 cm^{-1}; UV (MeOH) : λ_{max} (log ε) 238 (4.0); ^1H NMR : δ 0.66, 0.79, 0.86, 0.88, 0.93, 0.96(x2) and 1.06(Me), 2.05(OAc), 4.50 (m, $W_{\frac{1}{2}}$=13 Hz, 3-H), 5.17 (m, 7-H) and 5.38 (m, 11-H) ppm; m/z(%) : 466 (M^+, 40), 451(32), 407(12), 406(10), 313(24), 253(45), 190(44) and 179(100). Anal. Found : C, 82.62; H, 10.66. $C_{32}H_{50}O_2$ requires : C, 82.34; H, 10.80.

(ii) 3β-Acetoxy-7α,8α-epoxy-swert-9(11)-ene (4b) : Continued elution with light petrol-$CHCl_3$ (7:3) yielded **4b** (0.085 g, 42%); m.p. 260-262°C ($CHCl_3$-light petrol); $[\alpha]_D$-32.48° (c 0.314); IR(KBr) : ν_{max} 1725 and 1240 cm^{-1}; ^1H NMR : δ 0.78, 0.87, 0.91, 0.98(x2), 1.01 and 1.04(Me), 2.04(OAc), 3.27 (d, J=2 Hz, 7-H), 4.66 (dd, J=10,5 Hz, 3-H) and 5.66 (dd, J=5,3 Hz, 11-H) ppm; m/z(%) : 482(M^+, 41), 467(19), 422(47), 407(27), 278(26), 272(21), 271(18), 255 (16), 243(13) and 135(100). Anal. Found : C, 79.88; H, 10.39. $C_{32}H_{50}O_3$ requires : C, 79.62; H, 10.44.

(iii) 3β-Acetoxy-7α-hydroxy-friedogammacer-14-ene (5b) : Continued elution with the above solvent gave **5b** as needles (0.035 g, 17%), m.p. 318-319°C ($CHCl_3$-MeOH); $[\alpha]_D$-47.56° (c 0.185); IR(KBr) : ν_{max} 3560 (br), 1725 and 1250 cm^{-1}; ^1H NMR : δ 0.81, 0.87(x2), 0.90, 0.93, 1.00, 1.06 and 1.10(Me), 2.04(OAc), 3.88 (m, $W_{\frac{1}{2}}$=6 Hz, 7-H), 4.55 (dd, J=10,6 Hz, 3-H)

and 5.48 (t, J=4 Hz, 15-H) ppm; m/z(%) : 484 (M^+, 100), 469(30), 466(74), 445(49), 424(4), 406(21), 391(49), 381(29), 321(35), 271(56), 255(59), 204(40) and 185(100). Anal. Found : C, 79.36; H, 10.75. $C_{32}H_{52}O_3$ requires : C, 79.28; H, 10.81.

(iv) 3β-Acetoxy-7α-hydroxy-14α,15α-epoxy-friedogammacerane (6b) : Further elution with the same solvent afforded **6b** crystallising out of $CHCl_3$-CH_3OH as colourless needles (0.035 g, 16%); m.p. 228-229°C; $[\alpha]_D$-13.55° (c 0.413); IR(KBr) : ν_{max} 3460 (br), 1725 and 1250 cm^{-1}; ^1H NMR : δ 0.78, 0.84, 0.86, 0.92(x2), 1.01, 1.05 and 1.08(Me), 2.03(OAc), 3.45 (q-like, J=2 Hz, 7-H and 15-H), 4.53 (dd, J=10,6 Hz, 3-H) and 5.28 (br s, OH) ppm; m/z(%) : 500 (M^+, 12), 485(26), 440(10), 313(10), 275(97), 257(74), 179(70) and 137(100). Anal. Found : C, 76.53; H, 10.59. $C_{32}H_{52}O_4$ requires : C, 76.75; H, 10.47.

7α-Acetoxy-friedogammacer-14-en-3-one (9)

Compound **5a** (0.06 g, 0.136 mmol) on acetylation gave **9** crystallising out of $CHCl_3$-CH_3OH in fine needles (0.05 g, 76%); m.p. 236°C; $[\alpha]_D$-50° (c 0.352); IR(KBr) : ν_{max} 1725, 1700 and 1250 cm^{-1}; ^1H NMR : δ 0.78, 0.91, 0.93, 1.01, 1.03(x2), 1.11 and 1.14(Me), 1.98(OAc), 5.19 (m, $W_{\frac{1}{2}}$=6 Hz, 7-H) and 5.29 (t, J=4 Hz, 15-H) ppm; m/z(%) : 482 (M^+, 56), 467(39), 422(35), 283(27), 271(54), 270(43), 255(100), 229(20), 215(15), 204(20) and 185(94). Anal. Found : C, 79.81; H, 10.59. $C_{32}H_{50}O_3$ requires : C, 79.62; H, 10.44.

Swert-8-en-3,7-dione (12) from 4a

Dry HCl gas was passed slowly for 25 min with constant stirring through a solution of **4a** (0.02 g, 0.045 mmol) in anhydrous CH_2Cl_2 (20 ml). Usual work-up and crystallisation of the product from $CHCl_3$-CH_3OH afforded fine needles of **12** (0.015 g, 75%); m.p. 252°C; $[\alpha]_D$-14.89° (c 0.284); IR(KBr) : ν_{max} 1700 and 1640 cm^{-1}; UV (MeOH) : λ_{max} (log ε) 255 (3.95); ^1H NMR : δ 0.77, 0.79, 0.98, 1.06(x2), 1.13, 1.19 and 1.23(Me) ppm; m/z(%) : 438 (M^+, 100), 423(95), 298(20), 285(30), 284(25), 271(23) and 259(92). Anal. Found : C, 82.40; H, 10.73. $C_{30}H_{46}O_2$ requires : C, 82.13; H, 10.57.

3β-Acetoxy-swert-8-en-7-one (13) from 4b

Compound **4b** (0.015 g, 0.031 mmol) on treatment with HCl gas under identical condition as mentioned above yielded **13** (0.009 g, 60%) in fine needles ($CHCl_3$-CH_3OH); m.p. 306°C; $[\alpha]_D$-12.65° (c 0.395); UV (MeOH) : λ_{max} (log ε) : 255 (3.95); ^1H NMR : δ 0.78(x2), 0.87, 0.96, 0.99, 1.01, 1.05 and 1.16(Me), 2.06(OAc) and 4.52 (m, $W_{\frac{1}{2}}$=16 Hz, 3-H) ppm; m/z(%): 482 (M^+, 100), 467(76), 422(22), 407(22), 320(16), 315(12), 303(29), 272(8), 271(7), 270(8), 255(10) and 243(40). Anal. Found : C, 79.93; H, 10.62. $C_{32}H_{50}O_3$ requires : C, 79.62; H, 10.44.

Oxidation of 7α-hydroxy-swert-8-en-3-one (8) with PCC

Compound **8** (0.01 g, 0.22 mmol) dissolved in dry CH_2Cl_2 (10 ml) on oxidation with PCC[5] gave **12** (0.008 g, 80%).

Reaction with isoswertanone (2a) with m-chloroperbenzoic acid

A solution of **2a** (0.37 g, 0.87 mmol) in dry CH_2Cl_2 (30 ml) was treated with m-chloroperbenzoic acid (0.40 g, 2.5 mmol) for 6 days at 4°C. Usual work-up and chromato-

graphic purification of the product yielded, besides the starting material **2a** (79%), the following compounds.

(i) 8,9-Epoxy-swertan-3-one (14) : M.p. 208-211°C (yield 8%); IR(KBr) : ν_{max} 1710 cm^{-1}; m/z(%) : 440 (M^+, 55), 425(29), 422(10), 289(60), 205(26), 193(45), 191(63), 189(63) and 105(100); ^1H and ^{13}C NMR showed it to be a mixture of α and β epoxides.

(ii) Swerta-1,8-dien-3-one (15) : M.p. 250-252°C (yield 4.5%); IR(KBr) : ν_{max} 1680 cm^{-1}; ^1H NMR : δ 0.75, 0.78, 0.99, 1.01, 1.05, 1.07, 1.15 and 1.17(Me), 5.89 (d, J=10 Hz, 2-H), 7.30 (d, J=10 Hz, 1-H); m/z(%) : 422 (M^+, 50), 407(70), 269(17), 255(100), 243(70) and 229(20). Anal. Found : C, 85.50; H, 11.22. $C_{30}H_{46}O$ requires : C, 85.24; H, 10.97.

Reaction of 8,9-epoxy-swertan-3-one (14) with BF_3

A solution of **14** (0.025 g, 0.057 mmol) in dry C_6H_6 (10 ml) was treated with BF_3-etherate (1 ml) and the mixture was heated with stirring at 60°C for 4 hr. The product on chromatographic purification and crystallisation afforded **3a** (0.010 g, 39%).

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