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SAPOGENINS OF *ACACIA CONCINNA* DC—IV

WAGNER–MEERWEIN REARRANGEMENTS IN ACACIC ACID LACTONE AND SOME SELECTED TRITERPENES†

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Abstract—Dehydration reactions involving the 3-OH of ring-A in acacic acid lactone (**1**), sapogenin-B (**2**), methyl exhinocystate (**3**) and methyl oleanolate (**4**) have been carried out with different reagents: $POCl_3$/pyridine, PCl_5/hexane and solvolysis of their 3-tosylates. Structures of the different products obtained have been assigned based on the study of their PMR and mass spectra. Dependence of the conformational strain of the rest of the molecule other than ring-A is felt considerably on the course of dehydration with milder reagents, e.g. $POCl_3$/pyridine and solvolysis but not with PCl_5.

The dehydration reactions of the 3-OH in triterpenes[1] and steroids[2] are often followed by molecular rearrangements. These rearrangements could be effected by a variety of reactions: (a) treatment of the free alcohols with common dehydrating reagents like PCl_5/hexane,[3] $POCl_3$/pyridine[4] or P_2O_5/hexane,[5] (b) solvolysis of the corresponding tosyl or mesyl derivatives[6] and (c) by passing of the tosyl or mesyl derivatives over a column of alumina.[7] A large number of triterpenes recently studied have given an insight into varying conformational features of the molecules.[8]

It was ealier reported[9] that acacic acid lactone (**1**) with $POCl_3$/pyridine underwent dehydration giving A-nor product, anhydroacacic acid lactone-I (**5**) with a 5–6 double bond. Formation of this unusual product with preferential elimination of 6 –H was attributed to the strained conformations of ring-D (twist boat) and ring-E (boat).

The above observation led us to investigate the dehydration reactions in detail with a view to ascertain whether this behaviour is solely dependant on the structural features of the molecule or the reagent has any role to play. This present study reports the dehydration reactions of acacic acid lactone (**1**) with PCl_5/hexane and solvolysis of its tosylate. Effect of these reagents on some related triterpenes, e.g. sapogenin-B (**2**) which bears similar strained conformation in rings D/E as in acacic acid lactone, methyl echinocystate and methyl oleanolate has also been studied.

Rearrangements of acacic acid lactone (**1**)

Dehydration of acacic acid lactone (**1**) with PCl_5/hexane gave anhydroacacic acid lactone-II m.p. 218°, $(\alpha)_D$ + 87°. This anhydro-compound-II differed very much from the anhydro-compound-I (m.p. 294–96°) earlier obtained with $POCl_3$/pyridine.[9] Its IR spectrum showed the absence of any OH function indicating that both the 3 and 16 OH's were dehydrated and its UV showed no conjugation. In its PMR spectrum (Table 1) the 21-hydrogen (α = to the lactone) appeared as a doublet at δ 4.15, 4.20, J = 5 Hz as in the parent compound and also as in the anhydroacacic acid lactone-I (**5**). A significant difference between these two anhydro-compounds-I and II could be noticed in the olefinic region, the latter contained three protons while the former had four.

Of the three olefinic protons of anhydro-compound-II the AB quartet at δ 5.60, 5.70, 6.04, 6.14; J = 10 Hz is clearly assignable to the 15, 16 Hs and the remaining multiplet at δ 5.45 represents the 12-H. This obviously shows that the third double bond formed during the dehydration of 3-OH must be tetra substituted. No Me on a double bond was noticed, ruling out the structures **6**, **7** and **8** for the new anhydrolactone-II. It can, therefore, be concluded that ring-A contraction occurred with the formation of a 3–5 double bond suggesting structure **9**. This structure was further supported by its mass spectrum which showed the complete absence of M-43 (due to loss of the isopropyl group) peak unlike anhydrolactone-I (**5**)[9] and the usual RDA fragments at *m/e* 244 (15%) and 189 (100%) are quite in agreement with the structure proposed.

Solvolysis of acacic acid lactone 3, 16-ditosylate was next studied. Acacic acid lactone when treated with *p*-toluenesulphonyl chloride in pyridine formed readily the ditosylate (**1a**) m.p. 134–38°. The ditosylate was then solvolysed. The anhydro-product crystallised from chloroform-methanol as colourless needles m.p. 293–95°, $(\alpha)_D$ + 32° was found to be identical with the anhydrolactone-I (**5**) (m.p., IR and PMR, Table 1).

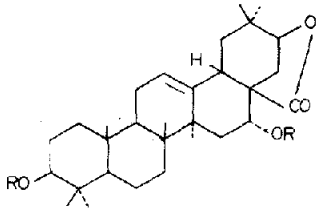
Action of $POCl_3$*/pyridine on sapogenin-B.* Acacic acid lactone (**1**) can be considered as 16-hydroxy sapogenin-B (**2**) and sapogenin-B might, therefore, be expected to exhibit similar behaviour towards dehydration as the former. The dehydration reaction on the latter was earlier performed by Djerassi *et al.*[10] who gave the structure **10** for the anhydro-compound formed with $POCl_3$/pyridine. The structure **10** was not supported by spectroscopic evidence. The reaction has now been reported to establish the structure of the anhydro-compound beyond doubt.

Sapogenin-B when dehydrated with $POCl_3$/pyridine gave the anhydro-compound which crystallised from methanol as colourless crystals m.p. 295–96°. It analysed for $C_{30}H_{44}O_2$, M^+ 436 and was transparent in UV beyond 220 nm and showed the presence of a γ-lactone at 1772 cm^{-1} in its IR spectrum.

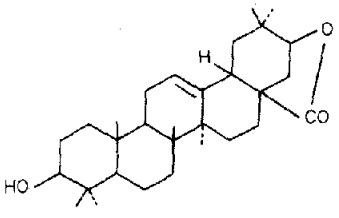
†In part from the Ph.D. thesis of A. Sree submitted to the Andhra University, Waltair (1977). Part III *Phytochemistry* (in press).

Table 1. PMR spectra, chemical shift in δ, in $CDCl_3$ with TMS

Anhydroacacic acid lactone-I (5) 100 MHz	Anhydroacacic acid lactone-II (9) XL-100	Solvolysis product of tosylate (5) XL-100	Anhydrosapogenin-B (11), 60 MHz	Assignment
0.81, 0.91, 0.93, 0.98 1.07 and 1.11 all s	0.98, 1.00, 1.05, 1.10 all s	0.80, 0.90, 0.91, 0.98, 1.06, 1.12 all s	0.88, 0.98, 1.00, 1.05, 1.10, 1.18, all s	7-CH_3 (21 H)
4.15, 4.20 d J=5Hz	4.15, 4.20 d J=5Hz	4.15, 4.20 d J=5Hz	4.20, 4.25 d J=5Hz	21α-H
5.40 br s	----	5.40 br s	5.50 br s	6-H
5.45 m	5.45 m	5.45 m	5.66 m	12-H
5.61, 5.71, 6.05, 6.15 AB q J=10, 10 Hz	5.60, 5.70, 6.04, 6.14 AB q J=10, 10 Hz	5.60, 5.70, 6.04, 6.14 AB q J=10, 10 Hz	-------	15-H 16-H



1 R=H
1a R=Tosyl



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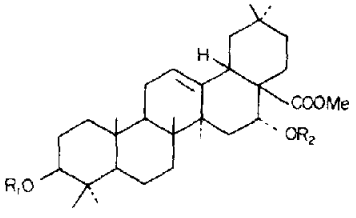
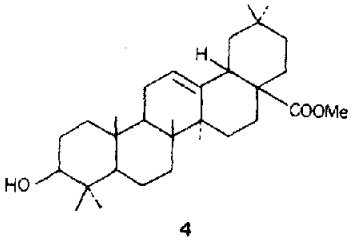


3 $R_1=R_2=H$
3a R_1=Ac $R_2=H$
3b R_1=Tosyl $R_2=H$



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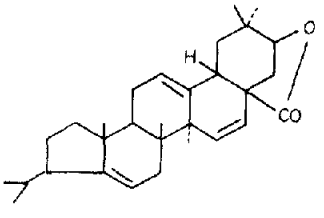

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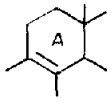

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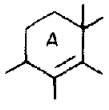

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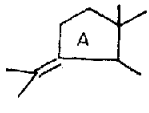

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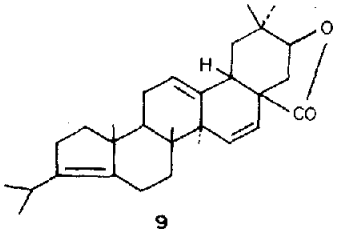

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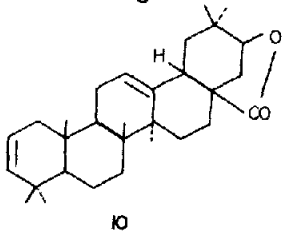


10

Its PMR spectrum (Table 1) showed the usual doublet at δ 4.20, 4.25 J = 5 Hz assignable to the lactone proton at C-21 and two olefinic protons, one at δ 5.66 m assignable to 12-H and the other at 5.50 to another proton on a trisubstituted double bond, thus ruling out the structure **10** proposed by Djerassi *et al.*[10] Its PMR spectrum is quite similar to that of anhydroacacic acid lactone-I (**5**) and the signal of the second olefinic proton is quite remniscent of the 6-H as observed in **5**. The presence of M-43 peak (7%) in the mass spectrum of anhydrosapogenin-B as in anhydroacacic acid lactone-I (**5**), confirms its structure as **11** ruling out the other alternative structure **11a**. The RDA fragments at *m/e* 246 (100%) and 189 (100%) also support the structure **11** proposed. The behaviour of sapogenin-B in $POCl_3$ dehydration is similar to that of acacic acid lactone thus confirming the effect of steric compression of rings D/E carried on and felt on the 6-β hydrogen. The reaction of PCl_5 or the solvolysis of sapogenin-B 3-tosylate could not be studied for want of sufficient quantity of the compound.

Rearrangements of methyl echinocystate. The dehydration reactions of echinocystic acid isolated for this purpose from the seeds of *Albizzia lebbeck*,[11] were followed stepwise eliminating first the 16-OH and then the 3-OH.

Methyl echinocystate (**3**) was partially acetylated to give the 3-monoacetate (**3a**) which on treatment with $POCl_3$/pyridine yielded 16-anhydro methyl echinocystate 3-acetate (**12a**). It was hydrolysed with alkali to give 3-hydroxy 16-anhydro methyl echinocystate (**12b**), m.p. 191–93°, $(\alpha)_D$ + 18°, $C_{31}H_{48}O_3$, M^+ 468 (17%). Its PMR spectrum (Table 2) contained three olefinic protons appearing one at δ 5.50 m assigned to 12-H and a singlet at δ 5.60 for two protons assigned to 15-H and 16-H. The appearance of 15, 16 protons as a singlet in it is noteworthy in contrast to the quartet (Table 1) observed for these protons in the anhydroacacic acid lactone-I (**5**).[9] The mass spectrum of the 16-anhydro methyl echinocystate (**12b**) showed the usual RDA fragments at *m/e* 260 (100%) and 189 (36%).

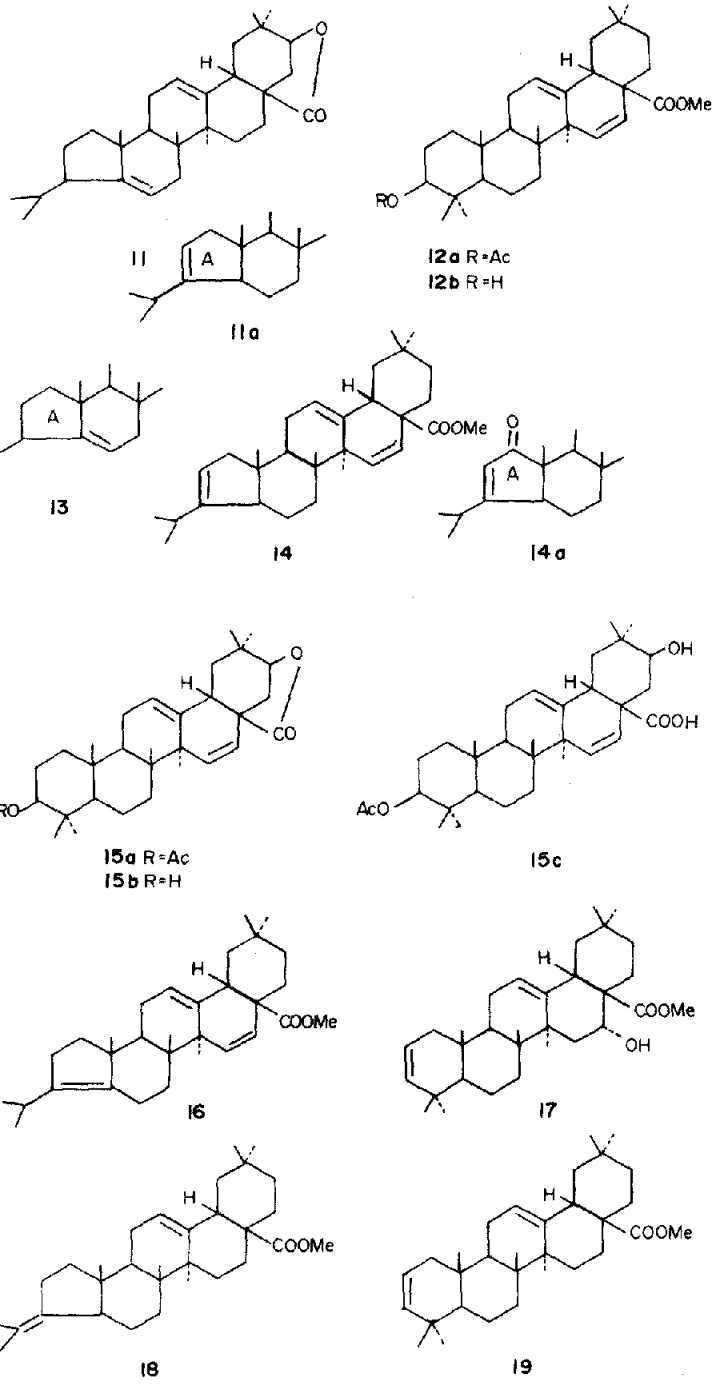
3-β hydroxy 16-anhydro methyl echinocystate (**12b**) was subsequently treated with $POCl_3$/pyridine as usual to give the anhydro methyl echinocystate-I. It crystallised from methanol, m.p. 137–39°, $(\alpha)_D$ + 48.7° and analysed for $C_{31}H_{48}O_2$, M^+ 450 (9%). No conjugation was observed in its UV. Four olefinic protons were noticed in its PMR spectrum (Table 2). The signal at δ 5.66 represents the 15, 16-protons as in the parent 16-anhydro compound (**12b**). The presence of the extra fourth olefinic proton at δ 5.48 br s shows the formation of a new trisubstituted double bond during dehydration of 3-OH. The newly formed double bond can be accommodated in the two alternative structures (**13** and **14**). The former corresponds to the structure of anhydroacacic acid lactone-I (**5**) and anhydrosaogenin-B (**11**). The absence of M-43 peak in its mass spectrum favours structure **14**. The usual RDA fragments appeared at *m/e* 201 (100%) and 189 (37%).

Further proof for the structure **14** was provided when it was oxidised with CrO_3/AcOH to give a mixture of three compounds. The major compound separated by chromatography did not crystallise but showed an UV absorption at 228 nm (log ϵ 3.85) suggesting the presence of an α,β-unsaturated CO in a 5-membered ring (**14a**). Its IR spectrum also showed a broad absorption from 1700 to 1735 cm^{-1} (α,β-unsaturated 5-membered ketone and $-COOCH_3$). Based on these facts anhydro methyl echinocystate-I was assigned the structure **14**.

Methyl echinocystate (**3**) underwent simultaneous dehydration of 16-OH (with $POCl_3$/pyridine) to yield the same anhydro methyl echinocystate-I (**14**) as obtained in the stepwise dehydration. From this it can be infered that the prior formation of 15–16 double bond has little effect on the course of dehydration of the 3-OH. Similar observation was in fact noticed with acacic acid lactone also during stepwise dehydration. 16-Anhydro acacic acid lactone 3-acetate[9] (**15a**) obtained was hydrolysed with mild alkali to give a mixture of two compounds: one, 3-hydroxy 16-anhydroacacic acid lactone (**15b**) and two, 3-acetoxy 16-anhydro acacic acid (**15c**) obtained by partial hydrolysis of the 3-OAc and the lactone respec-

Table 2. PMR spectra, chemical shift in δ, in $CDCl_3$ with TMS

16-Anhydro methyl echinocystate (12b), 60 MHz	Anhydro methyl echinocystate-I (14) 60 MHz	Anhydro methyl echinocystate-II (16) XL-100	Anhydro methyl echinocystate-III (17) XL-100	Assignment
0.62, 0.88, 0.95, 1.02, 1.17 all s	0.66, 0.95, 1.02, 1.22, 1.32 all s	0.88, 0.94, 1.24 all s	0.78, 0.90, 0.96, 1.24, 1.34 all s	7-C$\underline{H}_3$ (21 H)
2.80 m, 3.20 m	----	------	-------	3-O$\underline{H}$, 3-$\underline{H}$
-----	-------	------	3.10	16-O$\underline{H}$
3.58 s	3.63 s	3.56 s	3.60 s	17-COOC$\underline{H}_3$
-----	------	--------	4.50 m	16-$\underline{H}$
------	5.48 br s	------	-------	2-$\underline{H}$
-----	-------	-------	5.40 br s	2-$\underline{H}$, 3-$\underline{H}$
5.50 m	5.45 m	5.52 m	5.63m	12-$\underline{H}$
5.60 br s	5.66 s	5.66 s	-----	15-$\underline{H}$, 16-$\underline{H}$



tively. The former (**15b**) on dehydration with $POCl_3$/Py gave the same anhydroacacic acid lactone-I (**5**) as obtained in the simultaneous dehydration.

With PCl_5/hexane methyl echinocystate (**3**) gave the anhydro-compound-II, m.p. 156–58°, $(\alpha)_D + 32°$ which differed from the anhydro methyl echinocystate-I (**14**). Its IR spectrum showed the absence of an OH function and presence of a $-COOCH_3$ at 1735 cm^{-1}. It was transparent to UV. Its PMR spectrum (Table 2) exhibited three olefinic protons; one at δ 5.52 for the usual 12-H and the singlet at δ 5.66 integrated for two protons at 15 and 16-positions suggesting a tetrasubstituted double bond to have formed from the dehydration of the 3-OH. No Me on a double bond could be noticed and all the 7-Me's were at the usual positions as in the parent compound (**3**). From this the anhydromethyl echinocystate-II was assigned the structure **16** as in anhydro acacic acid lactone-II (**9**). The structure was further supported by its mass spectrum by the absence of M-43 peak and with the usual RDA fragments at *m/e* 260 (50%), 201 (80%) and 189 (100%).

Echinocystic acid methyl ester (**3**) was tosylated with PTS and pyridine to give the 3-monotosylate as major product (**3b**). The tosylate (**3b**) crystallised from methanol, m.p. 141–44° and showed in IR a peak at 3610 cm^{-1} for the OH. On solvolysis, it gave an an-

hydro-compound-III. m.p. 174–76°, $(\alpha)_D + 39°$ which showed the presence of an OH at 3615 cm^{-1} and a methyl ester at 1736 cm^{-1} in IR. Its PMR spectrum (Table 2) contained the 16-βH at δ 4.5 m showing that the compound is 3-anhydro methyl echynocystate. Of the three olefinic protons observed, the one at δ 5.63 m is assigned to 12-H and the other two at δ 5.40 br s integrated for the two protons of the newly formed disubstituted double bond. These data fit in very well with the structure 17 for the anhydro methyl echinocystate-III.

Rearrangements of methyl oleanolate. The reaction of PCl_5/hexane on methyl oleanolate (4) gave the A-nor isopropylidene product (18) m.p. 176–78°, $(\alpha)_D + 24°$ as noticed in oleanolic acid lactone.[12] With $POCl_3$/pyridine it yielded Δ^2-methyl oleanolate (19), m.p. 182–84°, $(\alpha)_D + 105°$ as was earlier reported.[13] Its PMR and mass spectra clearly conform to the structure.

RESULTS AND CONCLUSIONS

Acacic acid lactone (1) was found to give the same Wagner-Meerwein product (5) with 5–6 double bond in the tosylate solvolysis as well as with $POCl_3$/pyridine. This suggests similar course of ring contraction in both the processes. Formation of similar unusual 5–6 double bond was also noticed in sapogenin-B thus confirming the influence of the peculiar twist boat and boat conformations of rings D and E respectively, present in these molecules on the course of dehydration of 3-OH and consequent formation of double bond with ring contraction. The steric compressional effect in rings D and E is transmitted to rings A and B increasing 1,3-diaxial interactions on 6-βH. It was also observed that the prior formation of 15–16 double bond has little effect on the course of this reaction.

These features can be well conceived by looking at the Dreiding model of acacic acid lactone (1). The distance between 6β-H and the 1,3-diaxial Me groups at C-8, C-4 and C-10, particularly the former two has considerably reduced as compared with the normal oleanene skeleton thus making the 6β-H (axial) more sterically hindered and labile to escape. The course of this reaction might presumably be going through the mechanism suggested in Chart A.

In methyl echinocystate (3), where the special conformational effects of rings D and E as found in the above lactones are absent, the loss of 6β-H was not found with any of the reagents used. $POCl_3$/pyridine gave A-nor product with less common 2–3 double bond. Presumably through the mechanism (Chart B), PCl_5 gave A-nor product with 3–5 double bond and solvolysis of the tosylate gave the product with 2–3 double bond. The formation of different products with different reagents in such reactions has been already reported in literature, where PCl_5 is noted to invariably cause ring contraction while the reaction with milder reagents such as $POCl_3$/pyridine or solvolysis could yield different products giving way to the conformational features of the molecule as a whole. Thus acacic acid lactone, with PCl_5, gave the normal product 9 with 3–5 double bond and ring contraction unlike with other reagents, supporting the above observations. Similarly methyl oleanolate gave with PCl_5A-nor isopropylidene derivative and with $POCl_3$ 3-anhydro compound.

EXPERIMENTAL

Action of PCl_5 on acacic acid lactone (1). Acacic acid lactone (250 mg) in hexane (100 ml) was refluxed with PCl_5 (300 mg) for 4 hr on a water bath. The soln was then washed with water and dried over K_2CO_3. The residue after removal of the solvent crystallised from MeOH–$CHCl_3$ to give colourless crystals of 9 m.p. 218°, $(\alpha)_D + 87°$(*c*, 0.8 in $CHCl_3$). (Found: C, 82.78; H, 9.56. $C_{30}H_{42}O_2$ requires: C, 82.90; H, 9.74%). ν_{max}^{Nujol} 1770 (γ-lactone), 1660, 1460, 1380, 1185, 1150, 1100, 1040, 970, 780 and 730 cm^{-1}.

Solvolysis of acacic acid lactone ditosylate (1a). Acacic lactone ditosylate prepared from acacic acid lactone (py + PTS at 50° for 5 hr) 150 mg in dry AcOH (20 ml) containing fused NaOAc (250 mg) was refluxed for 3 hr on an oil-both. Most of the solvent was removed under vacuum, ice-water was added and

Chart A

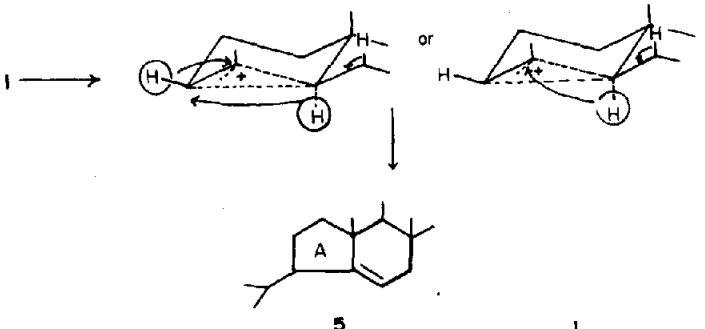
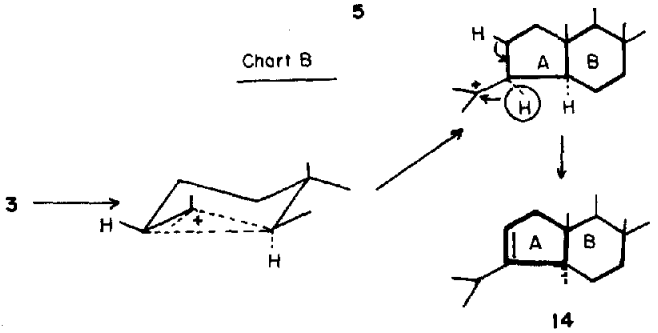


Chart B



the product was extracted with ether. The ether extract was washed with 2N $NaHCO_3$, water and dried over $MgSO_4$. The residue after removal of ether crystallised from $CHCl_3$–MeOH to give colourless needles of **5**, 90 mg, m.p. and m.m.p. with the product obtained from $POCl_3$/pyridine dehydration 293–95°. $(\alpha)_D + 32°$ (*c*, 0.9 in $CHCl_3$). Found: C, 82.72; H, 9.83 $C_{30}H_{42}O_2$ requires: C, 82.90; H, 9.74%. ν_{max}^{Nujol} 1770 (γ-lactone), 1660, 1460, 1380, 1190, 1155, 1110, 1075, 1045, 995, 975, 950, 935, 815, 740 and 720 cm^{-1}.

Action of $POCl_3$ *on sapogenin-B* (**2**). Sapogenin-B (**2**, 70 mg) in dry pyridine (6 ml) was heated on a water-bath for 2 hr with $POCl_3$ (0.5 ml) and then refluxed for 2 hr on an oil-bath. The mixture was worked up in the usual way and the product crystallised from $CHCl_3$–MeOH to afford colourless needles of **11** (45 mg), m.p. 295–96°, $(\alpha)_D + 26°$ (*c*, 1.0 in $CHCl_3$). Dehydro compound of sapogenin-B prepared by Djerassi[10] has m.p. 300.5–301°). (Found: C, 82.31; H, 10.05. $C_{30}H_{44}O_2$ requires: C, 82.52; H, 10.16%). ν_{max}^{Nujol} 1770 (γ-lactone), 1470, 1380, 1300, 1280, 1220, 1180, 1150, 1110, 1070, 1020, 970, 880, 820 and 730 cm^{-1}.

Action of $POCl_3$ *on methyl echinocystate* (**3**). Compound **3a** was obtained by acetylation of **3** (with Py/Ac_2O, room temp. overnight) m.p. 206–8° $(\alpha)_D + 28°$ (*c*, 1.0 in EtOH). ν_{max}^{Nujol} 3520 (16-OH), 1735 br (OAc and $COOCH_3$), 1370, 1240, 1150, 1100, 1030, 940 cm^{-1}.

Compound **3** | (500 mg) when dehydrated with $POCl_3$/pyridine gave **12a** (400 mg) which crystallised from alcohol as colourless needles m.p. 192–94°. $(\alpha)_D + 20.4°$ (*c*, 1.0 EtOH). ν_{max}^{Nujol} 1730–35 br (OAc and $COOCH_3$) 1375, 1250, 1130, 1095, 1040 and 930 cm^{-1}.

Alkaline hydrolysis of the above compound (4% KOH–EtOH, 3 hr on steam-bath) gave **12b** which crystallised from alcohol as colourless heavy needles. m.p. 191–93°, $(\alpha)_D + 18°$ (*c*, 1.1 EtOH). (Found: C, 79.21; H, 10.04. $C_{31}H_{48}O_3$ requires: C, 79.44; H, 10.32%). ν_{max}^{Nujol} 3380 br (3-OH), 1735 ($COOCH_3$), 1380 1245, 1160, 1110, 1050, 1020 and 970 cm^{-1}.

Compound **12b** (250 mg) was dissolved in dry pyridine (15 ml) and $POCl_3$ (3 ml) was added slowly in cold. The mixture was heated on a steam-bath for 2 hr and then refluxed on an oil-bath for 2 hr. The product after usual work up was crystallised from $CHCl_3$–MeOH to give **14** (180 mg) as colourless needles, m.p. 137–39°, $(\alpha)_D + 48.7°$ (*c*, 0.85 in $CHCl_3$). (Found: C, 82.43; H, 10.42, $C_{31}H_{46}O_2$ requires: C, 82.61; H, 10.29%) ν_{max}^{Nujol} 1738 br ($COOCH_3$), 1450, 1380, 1230, 1170, 1100, 1070, 980, 920, 790 and 730 cm^{-1}.

CrO_3–AcOH *oxidation of anhydro methyl echinocystate-I* (**14**). Compound **14** (100 mg) in dry glacial AcOH (15 ml) containing CrO_3 (75 mg) was refluxed for 3 hr on an oil-bath. The mixture was cooled, poured in ice-water and extracted with ether. The ether extract was washed with $NaHCO_3$aq, water and dried over $MgSO_4$. The gummy residue after complete removal of ether was chromatographed over a small column of neutral alumina by eluting with hexane and benzene. The benzene eluent gave a keto compound as a low melting solid which did not crystallise, but showed a single spot on tlc ν_{max}^{Nujol} 1700–1735 br (α,β-unsaturated 5 membered ketone and –$COOCH_3$), 1375, 1270, 1070, 880 cm^{-1}. λ_{max}^{EtOH} 228 nm (log 3.85).

Stepwise dehydration of acacic acid lactone (**1**). Mild hydrolysis of **15a** with 0.5 N KOH in EtOH gave a mixture of two compounds which were separated by column chromatography: Compound-I crystallised from alcohol as light needles, m.p. 263–65°, $(\alpha)_D + 52°$. Its IR showed peaks for OH (3400 br) and acetoxyl (1730) suggesting it to be **15c**. Compound-II identified as **15b** ν_{max}^{Nujol} 3450 (OH) and 1770 cm^{-1} (γ-lactone).

Compound **15b** (100 mg) in dry pyridine (10 ml) and $POCl_3$ (1.5 ml) was heated on a steam-bath for 2 hr and then refluxed on an oil-bath for 2 hr. The product after usual work up gave colourless needles from $CHCl_3$–MeOH m.p. and m.m.p. with an authentic sample obtained from the dehydration of acacic acid lactone directly with $POCl_3$, 295–97°, $(\alpha)_D + 36°$ (*c*, 1.0 in $CHCl_3$). ν_{max}^{Nujol} 1770, 1660, 1330, 1190, 1155, 1110, 1075, 995, 975, 950, 935, 815, 740 and 720 cm^{-1}.

Action of PCl_5 *on methyl echinocystate* (**3**). Compound **3** (250 mg) in dry hexane (35 ml) was treated with PCl_5 (300 mg) in cold and then refluxed on a water-bath for 4 hr. The mixture was then cooled thoroughly washed with water and dried over K_2CO_3. Complete removal of the solvent afforded a semisolid mass which was passed over a column of neutral alumina and then crystallised from MeOH to afford colourless crystals of **16** (180 mg) m.p. 156–58°, $(\alpha)_D + 32°$ (*c*, 1.0 in $CHCl_3$). (Found: C, 82.42; H, 10.35, $C_{31}H_{46}O_2$ requires: C, 82.61, H, 10.29%). $\nu_{max}^{CHCl_3}$ 1735 (–$COOCH_3$), 1380, 1330, 1270, 1100, 980, 970 cm^{-1}.

Solvolysis of methyl echinocystate 3-tosylate (**3b**). Compound **3b** was prepared from **3** in pyridine with PTS at 50° for 4 hr. m.p. 141–44°. Its IR showed the peak at 3610 cm^{-1} (–OH).

3b (160 mg) in dry AcOH (20 ml) containing fused NaOAc (200 mg) was gently refluxed on an oil-bath for 2.5 hr. The mixture was cooled, poured in ice-water and extracted with ether. The product after usual working up was crystallised from alcohol as colourless small needles of **17** (100 mg), m.p. 174–76°, $(\alpha)_D + 39°$ (*c*, 0.8 EtOH). (Found: C, 79.31, H, 10.19, $C_{31}H_{48}O_3$ requires: C, 79.31, H, 10.32%). ν_{max}^{Nujol} 3615 (16-OH9, 1736 (–$COOCH_3$), 1450, 1370, 1280, 1130, 1070, 980 and 880 cm^{-1}.

Action of PCl_5 *on methyl oleanolate* (**4**). Compound **4** (300 mg) in petroleum ether (75 ml) was refluxed with PCl_5 (250 mg) on a water-bath for 2.5 hr. The mixture was cooled, thoroughly washed with water, dried over $MgSO_4$, filtered and evaporated. Crystallisation from MeOH yielded **18** as colourless needles, m.p. 176–78°, $(\alpha)_D + 24°$ (*c*, 1.0 in $CHCl_3$). PMR in δ 0.67, 0.75, 0.80 (all s, 5 CH_3), 1.60 and 1.62 (s, 2=C–CH_3), 3.54 (s, –$COOCH_3$), 5.25 (m, 12-H). (Found: C, 82.75; H, 10.74. $C_{31}H_{48}O_2$ requires: C, 82.75, H, 10.69%). ν_{max}^{Nujol} 1730 ($COOCH_3$), 1450, 1360, 1300, 1280, 1120, 980 and 950 cm^{-1}.

Action of $POCl_3$ *on methyl oleanolate* (**4**). Compound **4** (250 mg) in dry pyridine (10 ml) was treated with freshly distilled $POCl_3$ (1.5 ml) and heated on a stream-bath for 2 hr and then refluxed on an oil-bath for 2 hr. The product was worked up in the usual way to give **19** as colourless needles from alcohol m.p. 182–83°, $(\alpha)_D + 106$ (*c*, 1.0 in $CHCl_3$). PMR in δ 0.77, 0.92, 0.88, 1.15 (all s, 7 CH_3), 3.68 (s, $COCH_3$), 5.40 (m, 12-H), 5.45 (br s, 2-H, 3-H). ν_{max}^{Nujol} 1730 ($COOCH_3$), 1460, 1380, 1320, 1270, 1240, 1200, 1170, 1130, 1080, 1050, 1000, 820 and 735 cm^{-1}. (Found: C, 82.02; H, 10.76, $C_{31}H_{48}O_2$ requires: C, 82.25; H, 10.69%). Mass: M^+ 452 (20%), *m/e* 392 (10%), 262 (85%), 202 (100%), 189 (72%).

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