Chemical Constituents of *Corchorus capsularis* and *C. olitorius* (Jute Plant), III * Structure of Corosin

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Corosin, Triterpenoids, *Corchoros capsularis*

Corosin (**8**; R=R¹=H) has been reisolated through a modified procedure, as its *acetate* (**8**; R=H, R¹=Ac), in an overall yield of 0.2% from jute roots.

On pyrolysis *in vacuo*, corosin gave *pyro corosin* (**1a**; R¹=OH, R²=COOH, R³=R⁵=H, R⁴=R⁶=Me), shown to have a 12:18 (17) di-ene formed by elimination of the 19-OH and the angular C-28 carboxyl in the molecule. On rearrangement with concentrated sulphuric acid in acetic acid, corosin acetate gave *corosin anhydro lactone acetate* (**7**; R¹=Ac, R=H), having a 13(18) double bond and a lactone bridge between the 28-carboxyl and the 20-carbon atom. *Corosin acetate ester* (**8**; R=Me, R¹=Ac), on treatment with sulphuric-acetic acid reagent, gave as the main product *anhydro corosin acetate ester* (**7**; R=Me, R¹=Ac), with a 12:18(19)-diene. The structure of corosin is proposed to be *urs*-12-*ene*-2α, 3β, 19α-*trihydroxy*-24, 28-*dioic acid* (**8**; R=R¹=H).

During earlier investigations a convenient proceedure had been developed for isolation of sterols, triterpenoids, acids, bases etc.[1–14]. The fresh undried jute roots were extracted at room temperature with ethanol and the isolation carried out as indicated in the experimental part. The mild technique avoiding use of strong chemicals minimises possible changes in labile molecules. The extraction depends on the process of dialysis through the plant membranes and consequently the extract contains little polymeric products, which otherwise complicate the isolation proceedure. Isolation of corosin by direct fractional crystallisation of the triterpenoid fraction, has previously been described[1] and is a laborious process. This has now been modified, by first acetylating the crude triterpenoid fraction and then isolating the *acetate* (**8**; R¹=Ac, R=H), m.p. 267–268 °C decomp. The acetate could be easily hydrolysed to give hexagonal plates of *corosin* (**8**; R=R¹=H), m.p. 284–286 °C decomp (gas bubbling).

The molecular formula of corosin had been established as $C_{30}H_{46}O_7$ and shown to contain two carboxyl groups and three hydroxyl groups, two of which were readily acetylated to give corosin acetate. Corosin or its acetate was not hydrogenated over platinum catalyst in ethyl acetate, but gave a pale yellow colour with tetranitromethane, indicating the presence of a non-reducible double bond. It was not vinylic as seen from the infra-red and NMR spectra and also expected from its resistance to hydrogenation. All corosin derivatives showed a triplet near 4.68 τ in the NMR spectra, which is characteristic of a C-12 proton in the Δ^{12}-triterpenes[15]. Corosin and its acetate exhibited peaks at M-H_2O, M-HCOOH and M-(H_2O + HCOOH) in their mass spectra and their esters gave a strong M-60 peak obviously due to elimination of H-COOMe from the molecules. The decomposition of corosin at its melting point with gas evolution, also suggested an elimination of a carboxyl group by carbon dioxide evolution. When corosin was heated *in vacuo*, it readily sublimed with decomposition near its m.p., to give after purifications a product now designated as *pyro corosin* (**1a**; R¹=OH, R²=COOH, R³=R⁵=H, R⁴=R⁶=Me) m.p. 255–256 °C, $[\alpha]_{578}^{22}$ + 99°, λ_{max} 238, 245, 252 nm (ε: 15,500; 16,900; 12,800). It gave a molecular ion peak at 456 in its mass spectrum and analysed for $C_{29}H_{44}O_4$ establishing that pyro corosin is formed by elimination of one mole of water and one carboxyl group from the corosin molecule. Indeed, the ready de-

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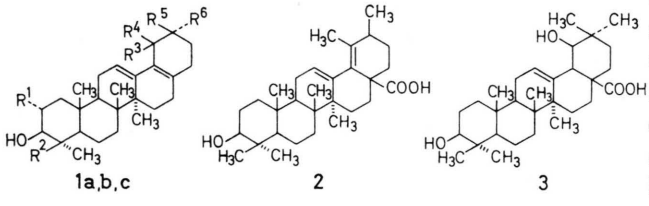
carboxylation of β,γ-unsaturated C-28 carboxyl is well known as in morolic [16] and vanguerolic acids [17]. *Corosin acetate dimethyl ester* (**8**; R = Me, R^1 = Ac) on refluxing with 10% methanolic caustic potash gave *corosin dimethyl ester* (**8**; R = Me, R^1 = H). This resistance of the two ester groups to hydrolysis will be in conformity with assigning C-28 and C-24 positions for the two carboxyl groups [18] in the corosin molecule. The NMR bands of the C-28 and C-24 methyl esters of triterpenoids have been assigned positions greater than 146.2 c.p.s. (6.35 τ) and between 144 – 146.2 c.p.s. (6.4 to 6.35 τ) [19] respectively. The ester methyls in corosin derivatives were in agreement with the above assignments (Table IV). The pyrolysis of corosin is thus explained by a simultaneous elimination of water and carbon dioxide to give a 12:18(17)-diene as in pyrolysed vanguerolic acid (**1b**; $R^1 = R^4 = R^6$ = H, $R^2 = R^3 = R^5$ = Me), λ_{max} 237, 245, 253 nm (ε: 17,000; 18,300; 11,600) [17]. It seems reasonable to assume that such an elimination of water is most likely due to the presence of a 19-OH in the corosin molecule, resulting in the formation of a 18,19-double *cf.* vanguerolic acid (**2**) which then readily decarboxylates to give pyro corosin. The M_D* of *nor*-olean 12:18(17)-dienol (**1c**; $R^1 = R^3 = R^4$ = H, $R^2 = R^5 = R^6$ = Me) and siaresinolic acid (**3**) [20] is 14,000° and is of a comparable order to that of pyro corosin and corosin, +17,500°.



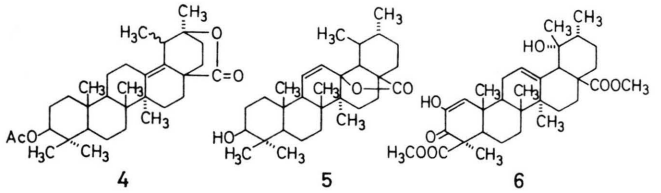
19α and β-OH in the β-amyrin compounds are known not to form acetates [20, 21] and the tertiary 19-OH cannot form an acetate in the α-amyrin series under normal conditions. If corosin has a β-amyrin skeleton, it should give a 19-keto compound on chromic acid oxidation of the acetate. Corosin acetate or the acetate ester did not form an olean 19-keto compound, under mild conditions it was recovered in fair yield. An dilute acetic soluble product formed under more forcing conditions, has been isolated in impure form and clearly shows the presence of two keto methyls in addition to the acetate methyls and can be formulated as a 19,20-seco-19,20-diketo-13(18)-en triterpenoid (λ_{max} 250 nm). This suggested an α-amyrin skeleton for the corosin molecule. Snatzke [22] observed a characteristic difference in the infra-red absorption patterns between β- and α-amyrin skeletons in pyridine solution. The former showed two bands in the first region (A) and three bands in the second region (B). The latter (α-amyrin) series possesses in both the regions three bands, at 1392 – 1386, 1383 – 1370 and 1364 – 1359 cm^{-1} and with increasing intensities at 1312 – 1308, 1276 – 1270 and 1250 – 1245 cm^{-1}. Corosin and its derivatives exhibited three weak bands in both the regions (Table I) in their KBr pellet infra-red spectra thus supporting an α-amyrin skeleton in the molecule.

Table I.

	Region A [cm^{-1}]			Region B [cm^{-1}]		
Corosin	1390	1375	1363	1310	1268	1235
Corosin acetate	1385i	1380	1367	1322	1270	1252
Corosin methyl ester	1385	1375	1365	1309	1270	1260
Corosin acetate ester	1390i	1380	1370	1320	1245	1230

An acid isolated from *Barringtonia acutangula* [23], as its diester, formulated as $C_{32}H_{50}O_7$ has been assigned the structure of olean-12-ene-2,3,19-trihydroxy-24,28-dioic-acid. The diacetate diester has been indicated to melt at 196 °C as compared to m.p. 187 – 188 °C for corosin diacetate dimethyl ester. The free hydroxyl at C-19 absorbed at 3560 cm^{-1} in the infra-red spectrum. In the corosin molecule such a sharp band at 3550 cm^{-1} can be assigned also to a 19-OH. The olean ester acetate has been reported to dehydrate with $POCl_3$-pyridine reagent to give a 11:13-diene, λ_{max} 243, 251, 260 nm. Corosin ester acetate was very resistant to such a dehydration and was recovered in high yield. Under more forcing conditions, a small yield of a low melting solid was obtained which showed strong ultra-violet absorption at 242, 251 and 261 nm. Corosin acetate on treatment with acetic acid-sulphuric acid reagent [24] gave a product, m.p. 300 – 305 °C decom., $[\alpha]_{578}^{19}$ – 89°. The product sublimed unchanged near its m.p. in vacuo. In the infra-red it showed bands at 1740 s (shoulders at 1735 s and 1745 s), 1715 ms, 1700 mi, 1685 mi cm^{-1} and gave ultra-violet absorption maxima at

210 and 227 nm (ε: 7,900 and 6,500). The unusual ultra-violet absorption had a striking resemblance with the lactone (**4** or alternatively with a C-19 lactone bridge) described by Barton [17], obtained by heating vanguerolic acid (**2**) with hydrochloric acid in acetic acid solution, λ_{max} 209, 228 nm (ε: 9,100 and 5,500). The lactone (**5**) [25] on the other hand has a normal ultra-violet absorption, showing only a strong end absorption.



4 **5** **6**

The strong negative optical rotation was clearly indicative of a 13(18)-double bond and the mass spectral molecular ion and analysis were also in agreement with formulation of the product as *corosin anhydro lactone acetate* (**7**; R = H, R^1 = Ac). The lactone on treatment with 8% methanolic caustic potash gave *corosin anhydro lactone* (**7**; R = R^1 = H), $[\alpha]_{578}^{22}$ −80°, ν_{max} 1735 s (shoulder at 1740 s), 1720 msi, 1690 m, 1670 mwi cm^{-1}. The strong C − O bands at 1285 and 1240 cm^{-1} of the acetate were replaced by a weak band at 1240 cm^{-1} in the infra-red spectrum, and no acetate methyls were visible in the NMR spectrum. On the basis of the lactone peak position in the infra-red spectrum a normal δ-lactone structure with the C-20 carbon atom is clearly favoured, which is formed by a rearrangement under the influence of the sulphuric acid reagent. The *anhydro lactone ester* (**7**; R = Me, R^1 = H) is obtained by heating corosin acetate ester with aqueous hydrochloric acid in acetic acid, and its *diacetate* (**7**; R = Me, R^1 = Ac) is identical with the *methyl ester* (**7**; R = Me, R^1 = Ac) of corosin anhydro lactone acetate described above.

The ease of hydrolysis with which corosin acetate gave corosin (10% methanolic caustic potash at room temperature), has been observed in medicagenic acid diacetate [18] which gave the 2α,3β-diol under similar conditions. Corosin or its ester did not form an acetonide [18] thus eliminating the possibility of a *cis*-diol, namely 2β,3β- or 2α,3α-diols in corosin. On copper pyrolysis [26] no formaldehyde was detected from corosin ester, thus also excluding the possibility of a 3,23-diol. The presence of a *vicinal* diol was confirmed by chromic acid oxidation of the ester, when in addition to various other products, formed due to the presence of reactive centres at 2, 3, 12 and 19 carbon atoms, a small yield of a *diosphenol* (**6**) [27], λ_{max} 212, 274 nm shifting to 217, 317 nm with caustic soda, was obtained on separation on preparative TLC plates (silica-gel). On lead tetra-acetate oxidation corosin ester oxidised slowly [28] favouring a *trans*-diol [29]. The positive Liebermann-Buchard reaction of corosin derivatives is expected of a 3-hydroxy triterpene [30]. Corosin derivatives, however give a yellow colour (changing very slowly to red) with conc. sulphuric acid [31]. The molecular rotation difference between the diols and the diacetates of corosin and corosin ester have been measured as 24,500. The only triterpene with a 2β,3α-diol, bredemolic acid is olean-12-ene-2β,3α-diol-28-oic acid [32] and the ΔM_D of the diol and the diacetate is 600 (in pyridine). The ΔM_D values for the 5α-steroid diols and diacetates calculated from tables [33] are observed to be high for a 2α,3β-diol, and in the oleanane series maslinic acid [34], barringtogenic acid [35] and stryphnodendron sapogenin F [36] have high ΔM_D values between the acid-alcohol and the acid-acetates *viz.* 11,000; 9,700 and 27,900 respectively. These observations strongly suggest the presence of a 2α,3β-diol in the corosin molecule, which is accordingly formulated as, *urs*-12-*ene*-2α,3β, 19-*trihydroxy* 24,28-*dioic acid* (**8**; R = R^1 = H). The assignment of a C-24 carboxyl is also in agreement with the observations of Barton [37] of a comparatively large ΔM_D value between the acid and their esters when present within a molecule containing a 3β-OH. Some values are given in Table II for comparison.

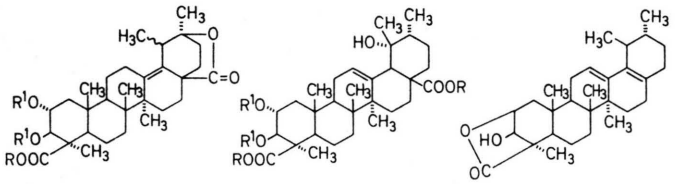
Table II.

	ΔM_D (Acid minus ester)
Barringtogenic acid	2,700
β-Boswellic acid	3,700
Medicagenic acid acetate	1,700
Corosin	3,150
Corosin acetate	1,800

An inversion at the carbon atom C-2 will explain the formation of *pyro anhydro corosin* (**9**), $C_{29}H_{42}O_3$, $[\alpha]_{578}^{22}$ +46°, λ_{max} 239, 246 and 254 nm (ε: 18,400; 19,300 and 16,250), isolated in small yield, from a mainly polymeric product, when corosin is pyrolysed at atmospheric pressure. It gave a strong infra-red band at 1776 cm^{-1} (shoul-

der at 1770 cm^{-1}), explained by the formation of a γ-lactone with C-2 carbon atom. A medium weak inflexion at 1756 cm^{-1} also detected, appears to be due to Fermi resonance observed earlier on in some γ- and δ-lactones [39]. This lactone was also isolated in a small amount from the combined mother liquors of the pyrolysed corosin carried out *in vacuo*.

The lactone formation is also confirmed by the NMR spectra in which the 2α-H appears as a doublet at 5.36 and 5.41 τ as compared to the 2β-H attached to the free 2α-OH of pyro corosin appearing at 6.97 and 7.06 τ. The 3α-H of both the products appeared at 6.2 τ.



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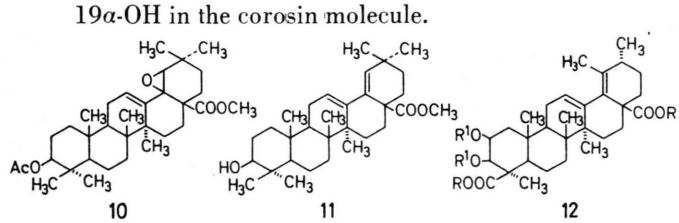
When corosin acetate dimethyl ester (**8**; R = Me, R^1 = Ac) in acetic acid solution is treated with concentrated sulphuric acid at room temperature, a complex reaction mixture is obtained, which does not separate on TLC on silica gel plates, showing only one spot ($CHCl_3$: EtOAc = 3 : 2 elution). On careful crystallisations from methanol-water, of the first crop obtained from petroleum ether, shiny flakes of a product now designated as *anhydro corosin acetate ester* (12; R = Me, R^1 = Ac), m.p. 232 – 234 °C, $[\alpha]_{578}^{22}$ +203.5°. λ_{max} 212.5 i, 228, 235 i, 239 i nm (ε: 7,200; 8,800; 8,300 and 7,600) were obtained. Methyl morolate acetate oxide (**10**) in presence of sulphuric acid in refluxing methanol has been shown to form *iso*-dehydro oleanolate (**11**) by Barton [16]. This had a λ_{max} 237 nm (ε: 10,200) and showed a strong positive rotation $[\alpha]_D$ +214°. 18-Dehydro-2-*epi*ursolic acid (**2**) in the ursane series has been recorded to give λ_{max} 228 nm (ε: 7,200). From the above comparison it becomes obvious that the anhydro acetate ester should be formulated as a 12:18(19)-diene (**12**) and is formed by elimination of water after protonation of the 19α-OH in the corosin molecule.

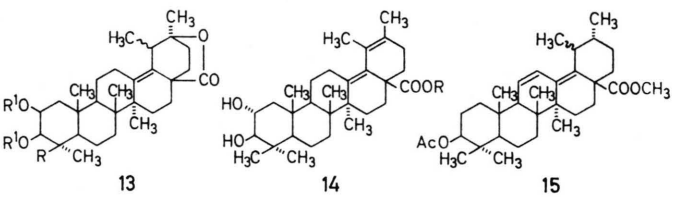


10 11 12

The mother liquors from the 12:18-anhydro acetate ester also gave additional anhydro products, which could not be purified satisfactorily, but from their spectral and optical rotations are indicated to be 13:19(20) and 12:19(20)-dienes.

The two 19α-hydroxy compounds described by Brieskorn *et al.* have been assigned a normal ursane skeleton [40, 41] and the 19α-hydroxy-28-carboxy-pomolic acid [41] has also been observed to yield the C-20,28-anhydro lactone as formed in the corosin molecule. Corosin acetate in acetic acid solution also when treated with bromine at room temperature resulted in the lactone formation (**7**) as reported for pomolic acid.

Corosic acid described previously, has now been established to be a mixture of anhydro corosin (**12**; R = R^1 = H) and corosin anhydro lactone (**7**; R = R^1 = H) by separation of its acetate ester. It cristallised as rhombs and cannot be resolved. Corosic acid acetate gives corosin anhydro lactone acetate in nearly quantitive yield on sulphuricacetic acid treatment. No transformation takes place on passage of gaseous HCl through the acetate solution in chloroform at room temperature.



13 14 15

The C-24 carboxyl in corosin could be reduced to the aldehyde by Rosenmund reduction and *corosin anhydro lactone acetate C-24 aldehyde*, m.p. 260 – 265 °C (changing to needles) and 300 – 305 °C decomp., $[\alpha]_{578}^{22}$ – 90° (**13**; R = CHO, R^1 = Ac) was obtained from the lactone acetate. The aldehyde under Huang Minlon reduction gave a *diene diol-28-carboxylic acid* (**14**; R = H), m.p. 284 – 286 °C decomp. (gas bubbling), $[\alpha]_{578}^{22}$ – 240°, λ_{max} 245 251.5 nm (ε: 18,100; 17,100). The acid gave *methyl ester* (**14**; R = Me), $[\alpha]_{578}^{24}$ – 248°, λ_{max} 245, 251.5 nm (ε: 21,370; 20,300) which in its NMR spectrum clearly showed the C-28 ester methyl at 6.41 τ, together with the two methyls on the double bond at 19,20 (conjugated) at 8.12 and 8.37 τ thus establishing the formation of a 13:19(20)-diene. The 11:13(18)-dienoic ester (**15**) described from pomolic acid clearly differed from the above dienoic acid in its ultra-violet absorption spectrum and had

λ_{max} 250, 256, 265 nm (ε: 20,500; 22,500; 14,600). The acid as expected gave a *lactone* (**13**; R = Me, R^1 = H) on sulphuric acid rearrangement.

The data published so far for the NMR spectra of various triterpenoids [15, 42, 43] are inadequate for the assignment of NMR bands to particular C-methyls of the triterpenoid molecules, and the correlations presented in the Table IV for the C-methyls should be clearly understood to be tentative, particularly because of the complex patterns obtained in this region of the spectra.

The optical rotations presented in Table III were determined in methanol solution at the wavelengths mentioned and extrapolated to 589 nm for the α_D values, except for the compounds indicated to have been measured directly.

Experimental

Unless otherwise stated, all infra-red spectra were determined in KBr, ultra-violet spectra were determined in methanol solution, optical rotations were determined in methanol solution and melting points were determined on electric blocks and are uncorrected. In the text the symbols s, m, v, w and i denote strong, medium, very, weak and inflexion respectively. Analytical samples were dried at 90 °C (unless otherwise stated), in evacuated drying pistols over P_2O_5 (24 hours).

1. Extraction of Corchorous capsularis roots

Fresh undried roots were chopped into small pieces (101 kg, dry wt. 25.4 kg), soaked in ethanol (142 l) for about a month, the extractive (110 l) concentrated under reduced pressure in a cyclone evaporator to a smaller volume (9 l) and cooled in a refrigerator to give after filtration, a blackish crude solid (dried, 332 g). This was leached with benzene and the benzene soluble fraction (42 g) was separated. The insoluble residue was dissolved in hot methanol and charcoaled hot through a bed of filter aid (kieselgur) and allowed to crystallise after concentration to a smaller volume. After Collection of three crops the supernatant liquid was mixed with subsequent crystallisation of the second extract solids. The second extraction was carried out with ethanol (126 l) for 20 days and the roots washed with a further 5 l of ethanol and drained (over 4

Table III. Optical Rotations.

	α_{364}	α_{405}	α_{436}	α_{546}	α_{578}	α_D	Conc. *	t[°C]
Corosin (**8**; R=R^1=H)	+169	+123	+102	+65	+56	+53	0.715	22
Corosin acetate (**8**; R=H, R^1=Ac)	+18	+12	+10	+4	+3	+3	0.975	22
Corosin ester (**8**; R=Me, R^1=H)	+161	+121	+100	+57	+48	+45	0.845	22
Corosin ester acetate (**8**; R=Me, R^1=Ac)	+7	+4	±0	±0	±0	±0	0.953	22
Pyro corosin (**1a**; R^1=OH, R^2=COOH, R^3=R^5=H, R^4=R^6=Me)	+357	+255	+206	+115	+99	+94	0.648	22
Pyro anhydro corosin (**9**)	+112	+96	+80	+48	+46	+45	0.125	22
Corosin ester diosphenol (**6**)	+117	+117	+94	+54	+49	+49	0.35	22
Corosin anhydro lactone acetate (**7**; R=H, R^1=Ac) *1	−345	—	−192	−104	−89	−84	0.222	19
Corosin anhydro lactone (**7**; R=R^1=H)	−274	−195	−160	−92	−80	−78	0.088	23
Corosin anhydro lactone ester (**7**; R=Me, R^1=H) *1	−325	—	−170	−86	−75	−75	0.1	22
Corosin anhydro lactone acetate ester (**7**; R=Me, R^1=Ac) *1	−337	—	−180	−100	−87	−83	0.164	22
Anhydro corosin acetate ester (**12**; R=Me, R^1=Ac) *1	+855	—	+456	+236	+204	+192	0.197	22
Anhydro corosin ester diol (**12**; R=Me, R^1=H)	+1100	+769	+600	+313	+263	+248	0.16	23
Corosin anhydro lactone acetate C-24 aldehyde (**8**; R=CHO, R^1=Ac) *1	−363	—	−199	−105	−90	−82	0.107	22
Urs 13:19(20)-dien 28-oic 2α,3β-diol (**14**; R=H) *1	−1088	—	−558	−283	−240	−226	0.077	22
Urs 13:19(20)-dien 28-carbomethoxy 2α,3β-diol (**14**; R=Me) *1	−1118	—	−574	−290	−248	−229	0.077	24

* In g/100 ml. *1 Determined on Perkin Elmer 141 Polarimeter.

Table IV. NMR spectra * of corosin derivatives.

Substance	H-3			H-2		H-3 [a]	C-23 Me	C-25 Me	C-26 Me	C-27 Me	C-29 Me	C-30 Me	C-24 -OMe	C-28 -OMe	C-2 -OAc	C-3 -OAc
a. Free Alcohols																
Corosin * (**8**; R=R[1]=H)	4.65	4.71	4.75	7.14	7.25	5.89—6.14	9.12	8.83	9.18	8.73	8.67	9.03	—	—	—	—
Corosin ester (**8**; R=Me, R[1]=H)	4.62	4.66	4.71	7.06	7.16	5.84—6.14	9.20	9.04	9.30	8.80	8.75	9.10	6.34	6.42	—	—
Corosin ester diosphenol (**6**) [b]	4.63	4.67	4.71	Nil	Nil	Nil	9.10	8.92	9.24	8.80	8.74	9.04	6.38	6.41	—	—
Pyro corosin (**1a**; R[1]=OH, R[2]=COOH, R[3]=R[5]=H, R[4]=R[6]=Me)	4.50	4.52	4.57	6.97	7.06	6.20	9.01	8.79	9.13	8.74	8.79	8.82	—	—	—	—
Pyro anhydro corosin (**9**)	4.38	4.45	4.48	5.36	5.41	6.20	9.02	8.81	9.11	8.75	8.78	8.81	—	—	—	—
Corosin anhydro lactone (**7**; R=R[1]=H)		Nil		7.07	7.17	5.79—6.01	9.08	8.95	9.14	8.82	8.88	8.63	—	—	—	—
Urs 13:19(20)-dien 28-carbomethoxy 2α:3β-diol (**14**; R=Me) **		Nil		6.94	7.03	5.73—6.34	8.97 [d]	8.95	9.13	8.80	8.12	8.37	Nil	6.41	—	—
b. Acetates																
Corosin acetate (**8**; R=H, R[1]=Ac)	4.64	4.68	4.72	5.14	5.24	4.16—4.31	9.07	8.82	9.31	8.75	8.73	9.07	—	—	7.94	8.05
Corosin acetate ester (**8**; R=Me, R[1]=Ac)	4.63	4.66	4.70	5.12	5.22	4.15—4.42	9.09	8.80	9.32	8.74	8.74	9.04	6.32	6.42	7.94	8.04
Corosin anhydro lactone acetate (**7**; R=H, R[1]=Ac)		Nil		5.14	5.24	4.16—4.44	9.06	8.88	9.22	8.74	8.88	8.62	—	—	7.93	8.03
Corosin anhydro lactone acetate ester (**7**; R[1]=Ac, R=Me)		Nil		5.13	5.27	4.24—4.45	9.13	8.85	9.18	8.73	8.85	8.61	6.34	Nil	7.93	8.01
Anhydro corosin acetate ester (**7**; R=Me, R[1]=Ac) ***	4.63	4.66	4.70	5.12	5.22	4.21—4.46	9.05	8.74	9.17	8.74	8.31	9.03	6.31	6.40	7.93	8.02
c. Olean 12(13)-enes [42, 43, c]	4.50	to	5.07	Acetates		5.3 to 4.82	9.13	9.03	9.17	8.87	9.13	9.13	6.36 to 6.40	6.40 to 6.46		

* Spectra were taken in 100 Mcs Varian XL-100 instrument in $CDCl_3$ solution. The peak positions were read from the chart and are expressed in τ.
** The spectra were taken in CD_3OD.
*** The spectra were taken on Varian HA-100 instrument.
[a] A sextet obtained when clearly resolved.
[b] A multiplet obtained for the 1-en proton between 5.80 to 6.04 τ
[c] C-28 methyl at 9.17 τ. The 2,3 protons based on only two compounds. C-24 methyl at 9.07 τ.
[d] C-24 methyl appeared at 8.97 τ.

days). The total extractive was concentrated as above to give some further crops of solids from methanol solution (two crops collected). The total solid was 129 g (greyish white powder).

*2. Isolation of corosin acetate (**8**; R = H, R^1 = Ac)*

The crude powder obtained above (29.3 g) was dissolved in dry pyridine (40 ml) and acetic anhydride (20 ml) mixture, by warming (80 °C) and left at room temperature over two days. The solvents were removed under reduced pressure over water bath and traces removed by evaporation with methanol and benzene. The residue was immediately taken up in benzene and left at room temperature, when a crystalline mass was precipitated after cooling. The crystalline fraction was collected and washed with benzene and crystallised from ethanol. The first four crops collected were *corosin acetate* (9.5 g), (**8**; R = H, R^1 = Ac), m.p. 267 – 268 °C decomp., $[\alpha]_{578}^{22}$ +3°.

$C_{34}H_{50}O_9$ (602.7)

Calcd.: C 67.75 H 8.36;
Found: C 67.96 H 8.32.

The yield based on dry weight of roots was 0.167%. The acetate gave pale yellow coloration with tetranitromethane in chloroform solution.

3. Isolation of β-sitosteryl acetate

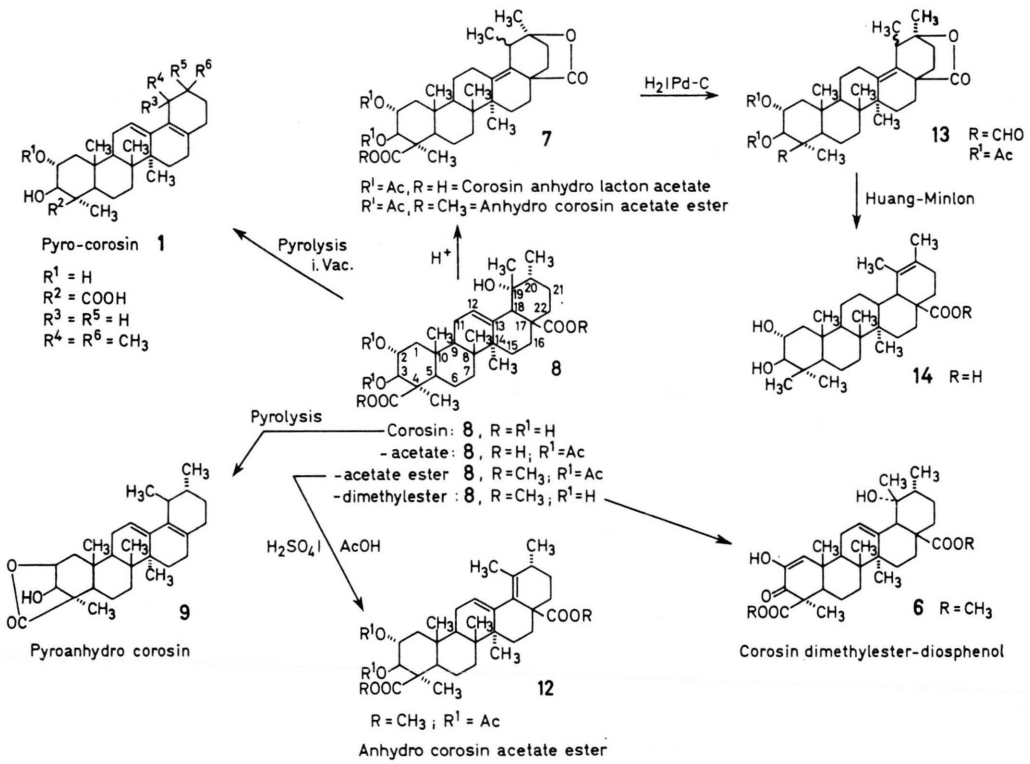
The benzene mother liquor obtained above was evaporated under reduced pressure to give a viscous oil. The oil was leached out with petroleum ether (9.65 g residue) followed by benzene, finally leaving behind a dark insoluble residue (1.5 g). The benzene soluble fraction was evaporated and once again leached out with petroleum ether (40 – 60 °C). The combined petroleum ether soluble oil (10.8 g) was allowed to crystallise from methanol (liquor M). The crystallised mass purified by several crystallisations from the same solvent gave shiny flakes of *β-sitosteryl acetate*, m.p. 134 °C, $[\alpha]_D^{22}$ −48° (*c*, 0.82% Chloroform). Melting point of an authentic specimen on mixed m.p. determination was not depressed.

$C_{31}H_{52}O_2$ (454.7)

Calcd.: C 81.52 H 11.48;
Found: C 81.58 H 11.63.

4. Isolation of hexadecanoic acid

The methanol mother liquor (M above) on evaporation gave an oil (9.8 g), which was distilled in vacuo and the distillate was refractionated under reduced pressure into four fractions, i. b.p. 108 – 138 °C/0.3 mm, ii. b.p. 138 – 150 °C/0.3 mm, iii.



b.p. 150 °C/0.3 mm and iv. b.p. 152 – 158 °C/0.3 mm. The fraction iii. has been established as *ethyl hexadecanoate.* n_D^{22} 1.4495.

$C_{18}H_{36}O_2$ (284.5)

Calcd.: C 76.00 H 12.75;
Found: C 75.75 H 12.05.

The ester oil prepared from another batch was hydrolysed by dissolving in methanolic (5 ml) caustic potash (0.38 g) solution by refluxing over 45 min. The acidified (HCl) mass was diluted with water and extracted with chloroform. The dried (Na_2SO_4) extract was evaporated to give a waxy solid which after three crystallisations from methanol-water gave waxy flakes of *hexadecanoic acid* (palmitic acid, m.p. 62 – 64 °C, $[\alpha]_{578}^{22}$ ±0° (*c*, 0.66% chloroform). The infra-red spectrum was superimposable on that of authentic palmitic acid and they did not depress each others melting point.

$C_{16}H_{32}O_2$ (256.2402)

Calcd.: C 74.94 H 12.57;
Found: C 75.37 H 12.41.

Mass m.wt. found: 256.2386.

*5. Isolation of corosin (***8***; R = R¹ = H)*

a. Corosin acetate (1.11 g) was dissolved in methanol (50 ml) and refluxed with caustic potash (5.0 g) for 1½ hours, the solvent removed under reduced pressure, the residue taken up in water and acidified with HCl and filtered. The filtered precipitate was washed with water, and crystallised from methanol to give hexagonal plates of *corosin*, m.p. 284 – 286 °C decomp., $[\alpha]_{578}^{22}$ + 56°. The first two crops were pure (0.74 g) and a third crop collected (0.12 g) had m.p. 280 – 285 °C (decomp.). This was found to be identical in all respect with the corosin described previously and gave a pale yellow colour with tetranitromethane. When left in concentrated sulphuric acid it dissolved slowly to give initially a yellow changing after a few hours to orange-red.

b. Corosin acetate (61 mg) was dissolved in 10% methanolic caustic potash solution (5 ml) and left at room temperature overnight. The clear solution was diluted with water and acidified with hydrochloric acid. The gelatinuous precipitate was filtered, washed with water and crystallised from methanol to give conglomerates of hexagonal plates of corosin, m.p. 275 – 283 °C (decomp.).

*6. Corosin methyl ester (***8***; R = Me, R¹ = H)*

a. Corosin (82 mg) was dissolved in pure methanol (approx. 7 ml), an excess of etherial diazomethane solution added and left at room temperature for a few minutes. After removing the solvent under reduced pressure, the residue was dissolved in petroleum ether (60 – 70 °C) and allowed to crystallise. The first crop was *corosin methyl ester* (70 mg), m.p. 152 – 153 °C (foams up above 100 °C and subsides to a glass, no sharp melting point), $[\alpha]_{578}^{22}$ + 45°.

$C_{32}H_{50}O_7$ (629.1).

Calcd.: C 70.33 H 9.15 O-Me (for two) 11.4%;
Found: C 70.47 H 9.50 O-Me 9.00%.

b. Corosin acetate methyl ester (125 mg) in methanol (5 ml) and potassium hydroxide (0.6 mg) was refluxed for 2 hours, cooled and then diluted with water and extracted with ether (3×). The etherial extract was dried (Na_2SO_4) and evaporated to dryness (0.12 g). The alkaline aqueous layer did not show any turbidity on acidification with HCl. The solid obtained above was crystallised from petroleum ether to give *corosin methyl ester*, m.p. and mixed m.p. with the above sample was undepressed.

c. Corosin methyl ester (0.12 g) was mixed with electrolytic copper powder (0.3 g) and heated slowly to 260 °C and then slowly to 350 °C over 15 min, under a stream of nitrogen. The effluent gas did not show any traces of formaldehyde when passed through a solution of dimedone in water.

7. Attempted acetonide formation

a. Corosin (59 mg) was stirred in pure acetone (20 ml) with anhydrous copper sulphate powder (100 mg) for 3½ days. The filtered mass gave unchanged corosin.

b. Corosin methyl ester (53 mg) was left at room temperature for three days in acetone (5 ml) containing two drops of conc. sulphuric acid. After neutralisation with solid $NaHCO_3$ and water the filtered solution was evaporated to dryness and chromatographed on a column of alumina. The chloroform elute gave unchanged corosin methyl ester on crystallisation from methanol-water, which did not depress m.p. of authentic sample of the ester.

*8. Corosin acetate methyl ester (***8***; R = Me, R¹ = Ac)*

a. Corosin acetate (1 gm) was dissolved in methanol (50 ml), etherial solution of diazomethane added in excess (until yellow) and left for 15 min at room temperature. The solvents were removed and the residue crystallised from hot petroleum ether (60 – 70 °C) – a slight coloured principitate appearing on initial cooling was rejected. The first crop was collected as well formed crystals of *corosin acetate methyl ester*, m.p. 187 – 188 °C, $[\alpha]_{578}^{22}$ ±0° (0.72 g). A second crop (0.15 g) was also

collected as micro-crystalline solid, m.p. 162 – 163 °C (puffing up above 100 °C to a foam, subsiding to a glass later giving ill defined m.p.). The anhydrous form of the acetate ester is obtained only when the petroleum ether solution is allowed to concentrate by boiling from a larger volume. It gave a pale yellow colour with tetranitromethane in chloroform solution. The well formed crystals had ν_{max} 3550 ms, 2995 mi, 2980 ms, 2963 mi, 2935 m, 2920 m, 2876 mi, 2860 m, 2840 wi, 1742 si, 1735 s, 1717 s, 1683 w, 1475 wi, 1465 wi, 1458 wi, 1448 m, 1428 m, 1385 wi, 1365 ms, 1245 s, 1230 s, 1200 mi, 1145 ms, 1128 mi, 1090 w, 1055 mw, 1038 m, 1022 m, 995 mw, 965 m, 948 mw, 910 w, 860 w, 845 w, 820 vw, 772 wi, 764 mw, 755 wi, 695 vw, 645 w, 608 wi, 600 w cm^{-1}.

$C_{36}H_{54}O_9$ (630.8)
Calcd.: C 68.56 H 8.56 O-Me, 9.80%;
Found: C 68.75 H 8.94 O-Me, 8.08%.

b. Corosin methyl ester (0.11 g) was dissolved in dry pyridine (2.5 ml) and acetic anhydride (3 ml) by slight warming and left at room temperature overnight. The excess solvents were removed, and the residue crystallised from hot petroleum ether twice to give micro-crystalline corosin methyl ester acetate, identical with similar crystals obtained above; no depression of each others melting point.

c. Corosin acetate (0.125 g) was dissolved in hot (approx. 90 °C ½ hour) acetic acid (9.0 ml) and chromic acid (35 mg) were added. After separation of an initial crop of impure corosin acetate, the diluted aqueous filtrate was extracted with ethyl acetate. The ethyl acetate extractive was a complex mixture and on TLC separation, a fraction could be collected which showed strong ultra-violet absorption at 250 nm. It could not be crystallised satisfactorily, but showed infra-red bands at 1730 s (broad), 1720 msi, 1700 msi, 1690 mi and unsaturation at 1660 ms cm^{-1}. α-Amyrin compounds normally give an 11-keto compound on chromic acid oxidation [43], but the oxidised product clearly showed two keto methyls (7.94 and 8.05 τ) in addition to the two acetate methyls (7.93 and 8.02 τ in the NMR spectrum. The H-2 and H-3 protons appeared at the expected positions. A ring cleavage at the 19.20 carbon atoms together with a 13(18)-en modification of the molecule will clearly explain the above observations and will further confirm the α-amyrin skeleton for corosin (C-29 and C-30 keto methyls).

d. Corosin acetate methyl ester (53 mg) was taken up in pure acetone (5.0 ml) and chromic acid (6.5 mg) in water (0.5 ml) and conc. H_2SO_4 (0.1 ml) was added at room temperature. After one and a half hour, methanol (0.5 ml) was added and diluted with water, the precipitate was filtered, washed with water and crystallised from petroleum ether (60 – 70 °C), to give unchanged corosin acetate methyl ester (30 mg), mixed m.p. with authentic sample was undepressed.

*10. Pyro corosin (***1a***; $R^1 = OH$, $R^2 = COOH$, $R^3 = R^5 = H$, $R^4 = R^6 = Me$)*

Corosin (210 mg) was taken in a cold finger apparatus and heated *in vacuo* to 290 °C (bath temperature) and during 15 min allowed to sublime between 290 – 300 °C. The sublimate (150 mg; m.p. 191 – 206 °C) was charcoaled in methanol and allowed to crystallise after a little dilution with water. The first crop obtained (m.p. 241 – 245 °C) was recrystallised from the same solvent after evaporation of some added chloroform, to give conglomerates of flat needles. Another crystallisation from the same solvent gave flat bars of *pyro corosin* (33 mg), m.p. 255 – 257 °C decomp (earlier softening), $[\alpha]_{578}^{22}$ +99°, λ_{max} 252 i, 245.5, 238 nm (ε: 12,800; 16,900; 15,500).

$C_{29}H_{44}O_4$ (456.6)
Calcd.: C 76.27 H 9.71;
Found: C 75.92 H 9.40.

On thin layer chromatography of the mother liquor on silica-gel G with chloroform/ethyl acetate/formic acid (55/40/5), a total of five spots were detected having R_F values 0.2, 0.23, 0.27, 0.34, 0.44. Of these pyro corosin had the value 0.23.

Corosin ester diosphenol (**6**)

Corosin ester (0.2 g) was taken in pure acetone (10 ml) and a solution of chromic acid (50 mg) in water 0.75 ml) and conc. H_2SO_4 (0.25 ml) was added dropwise during 15 min, stirring at room temperature. The reacted mixture was diluted with water and extracted with ether (3 ×). The etherial layer was washed with water and dried (Na_2SO_4). After removal of the solvent a faint yellow foam (0.2 g) was obtained, which showed five spots on TLC separation. It was transferred on to a preparative large silica-gel G plate and eluted twice with chloroform/ethyl acetate (100/30) mixture (the plate was dried after first elution). The plate was cut into eight zones under ultra-violet light. The sixth band from the starting line was visible as a brilliant pink band and on extraction with methanol-chloroform gave a powdery foam (25 mg), which on crystallisation from methanol-water gave *corosin dimethyl ester diosphenol, (*foams up above 100 °C, no sharp melting point), $[\alpha]_{578}^{22}$ +49°, λ_{max} 212,

274 nm (ε: 5,100; 6,500), which shifted to λ_{max}^{NaOH} 217, 317 nm (ε: 5,100; 3,500). It gave a mass molecular ion peak at 512 ($C_{32}H_{46}O_7$) and in the infra-red spectrum gave bands at 1738 s, 1730 s, 1680 ms, 1670 msi, 1660 mw, 1650 mw cm^{-1}.

$C_{32}H_{46}O_7 \cdot 0.5\,H_2O$ (551.7)
Calcd.: C 69.66 H 8.59;
Found: C 69.31 H 8.50.

Lead tetra-acetate oxidation

Corosin methyl ester (21 mg) was treated with excess of lead tetra-acetate solution in acetic acid (35 ml). Aliquot portions (5 ml) were titrated with sodium thiosulphate (0.02 N) after addition of sodium iodide. A blank was also similarly titrated. It was found that about one mole equivalent of lead tetra acetate was taken up by the ester during 40 hours.

Corosin anhydro lactone acetate (**7**; R = H, R^1 = Ac)

a. Corosin acetate (0.228 g) was dissolved in acetic acid (12.0 ml), and to the solution at room temperature concentrated sulphuric acid (4.0 ml) was added slowly. The viscous solution was left at room temperature over a 60 min period (turned green), it was then diluted with water and filtered. On crystallisation from ethanol large prismatic rods of *corosin anhydro lactone acetate*, m.p. 305 – 310 °C decomp. (0.139 g) were obtained, on recrystallisation from methanol; flat needles, m.p. 300 – 310 °C decomp., $[\alpha]_{578}^{19}$ −89°, λ_{max} 210, 227 nm (ε: 7,900; 6,500), ν_{max} 3510 m, 3020 mi, 2990 m, 2960 ms, 2880 m, 1755 si, 1740 s, 1715 s, 1685 mi, 1285 m, 1114 m, 1108 m, 1000 mw, 975 mw, 930 m, 890 w, 870 mw, 790 mw cm^{-1}. In chloroform solution the lactone and the acetate band appeared as one band at 1740 – 1745 cm^{-1}.

$C_{34}H_{48}O_8 \cdot C_2H_5OH$ (630.8)
Calcd.: C 68.54 H 8.63;
Found: C 68.51 H 8.89.

b. Corosic acid (30 mg) was acetylated with acetic anhydride – pyridine mixture at room temperature and the crude acetate obtained was dissolved in acetic acid (3 ml) and concentrated sulphuric acid (1 ml). The solution was left at room temperature for 60 min. It was worked up as above to give *corosin anhydro lactone acetate* (21 mg), m.p. 295 – 300 °C.

$C_{34}H_{48}O_8$ (584.7); dried at 160 °C
Calcd.: C 69.83 H 8.27;
Found: C 69.34 H 8.25.

c. Corosin acetate (90 mg) was dissolved in acetic acid (7.0 ml) and to the solution at room temperature bromine in acetic acid (5% wt./vol.) was added dropwise (0.25 ml, and then after 30 min 0.25 ml). It was left in dark for 3 days and worked up to give corosin anhydro lactone acetate on recrystallisation from methanol – water; needles of m.p. 285 – 302 °C decomp., identical with the acetate described above.

*11. Corosin anhydro lactone (**7**; R = R^1 = H)*

Corosin acetate anhydro lactone (42 mg) was dissolved in methanolic (7.5 ml) caustic potash (0.6 g) solution by slight warming and left at room temperature overnight. It was diluted with water, acidified with HCl and the solid obtained on filtration, was washed with water and crystallised from methanol-water to give rectangular plates of *corosin anhydro lactone*, m.p. 300 – 305 °C decomp., $[\alpha]_{578}^{22}$ −80°. It had ν_{max} 1750 mi, 1740 si, 1735 s, 1720 si, 1690 ms, 1670 msi, 1625 w, 1120 m, 940 m cm^{-1} and λ_{max} 212.5, 230 nm (ε: 9,500; 7,000).

$C_{30}H_{44}O_6$ (502.6); dried at 150 °C
Calcd.: C 71.97 H 8.86;
Found: C 71.70 H 8.95.

*12. Pyro anhydro corosin (**9**)*

a. Corosin (160 mg) was taken in a cold finger apparatus and heated on a metal bath to 280 °C briskly, the volatile condensate was removed and the melt heated between 300 – 320 °C for 5 min, cooled and the total product chromatographed on a silica gel column (6 g) with benzene. The benzene, 25 and 50% chloroform benzene elutes were small and the 75% chloroform benzene gave about 30 mg substance which was crystallised from methanol-chloroform-water to give silky needles after two crystallisations from the same solvent, of *pyro anhydro corosin*, m.p. 251 – 253 °C (starts subliming over 210 °C), $[\alpha]_{578}^{22}$ +46°, λ_{max} 239, 246, 254 nm (ε: 18,400; 19,300; 16,250). The molecular ion peak appeared at 438 in the mass spectrum confirming $C_{29}H_{42}O_3$ formulation.

b. Corosin acetate ester (158 mg) was dissolved in dry pyridine (5 ml) and refluxed with pure phosphorous oxychloride (2.5 ml) under dry conditions for 4 hours. The cooled reaction mixture was poured slowly in ice-water and extracted with ether (3 ×). The etherial extract was washed with water, dried (Na_2SO_4) and solvent removed. The residue was chromatographed on a column of neutral alumina (10 g). The main fraction was eluted with 25% and 50% chloroform in benzene mixture. The substance eluted was crystallised from petroleum ether (60 – 70 °C: well formed crystals of unreacted corosin acetate ester (123 mg), m.p. 188 – 189 °C, undepressed on admixture with authentic sample.

*14. Corosin anhydro lactone ester (**7**; R = Me, R^1 = H)*

Corosin acetate methyl ester (178 mg) was dissolved in acetic acid (8 ml) and heated on steam bath for 15 min together with conc. hydrochloric acid (2 ml). It was diluted with water and extracted with ether. The etherial extract was washed with sodium carbonate solution, dried (Na_2SO_4) and evaporated. The first crop collected from petroleum ether (60 – 80 °C), on recrystallisation from methanol gave colourless rods (73 mg) of *corosin anhydro lactone ester*, which after several recrystallisations gave crystals, m.p. 293 – 295 °C, λ_{max} 210, 228 nm (ε: 10,500; 7,000), ν_{max} 1735 s, 1705 ms, 1695 msi cm^{-1}.

$C_{31}H_{46}O_6$ (514.7)

Calcd.:	C 72.34	H 9.01;
Found:	C 72.00	H 8.69.

*15. Corosin anhydro lactone acetate ester (**7**; R = Me, R^1 = Ac)*

Corosin anhydro lactone acetate (27 mg) taken in methanol, was treated with excess of etherial diazomethane. After removal of solvents, it crystallised from methanol to give *corosin anhydro lactone acetate ester* (24 mg), m.p. 255 – 257 °C $[\alpha]_{578}^{22}$ – 86.5°, λ_{max} 212.5, 228 nm (ε: 8,300; 6,200), ν_{max} 1735 s, 1715 ms, 1700 m cm^{-1}.

$C_{35}H_{50}O_8 \cdot H_2O$ (616.7)

Calcd.:	C 68.15	H 8.50;
Found:	C 68.21	H 8.35.

The corosin anhydro lactone ester described above (43 mg) on acetylation with acetic anhydride (2.5 ml) and dry pyridine (1.5 ml) at room temperature overnight on working up and crystallisation from methanol, gave corosin anhydro lactone acetate ester, m.p. 249 – 251 °C, identical in all respects with the acetate ester described above.

16. Corosic acid ester acetate

Corosic acid (17 mg) was dissolved in methanol (4 ml) and treated with excess of etherial diazomethane. After removal of the solvents, the residue was dissolved in acetic anhydride (1 ml) and dry pyridine (0.5 ml) and left at room temperature overnight. The solvents were removed, and the residue after several crystallisations from methanol-water gave flat bars of *corosic acid acetate ester*, m.p. 232 – 234 °C, $[\alpha]_{578}^{22}$ + 192°, λ_{max} 212.5 i, 227, 235 i nm (ε: 6,600; 8,700; 8,300). The infra-red spectrum was superimposable with that of anhydro corosin acetate ester described below.

$C_{36}H_{52}O_8 \cdot 0.5\,H_2O$ (621.7)

Calcd.:	C 69.53	H 8.59;
Found:	C 69.33	H 8.25.

17. HCL-Treatment of corosic acid

Corosic acid (35 mg) was dissolved in acetic acid (1.0 ml) and hydrochloric acid gas was passed through it for 65 min at room temperature. After removal of solvent and drying over caustic potash *in vacuo*, the residue gave back corosic acid.

*18. Anhydro corosin acetate ester (**12**; R = Me, R^1 = Ac)*

Corosin acetate ester (209 mg) was dissolved in acetic acid (4 ml) and concentrated sulphuric acid (0.5 ml) at room temperature and left standing for 75 min. After an initial warming up the colour darkened slowly to a bottle green shede. It was diluted with water and extracted with ether. The etherial extracts were washed with water, sodium bicarbonate solution and dried (Na_2SO_4). After removal of solvent the residue was crystallised from petroleum ether (60 – 70 °C). The first crop was crystallised thrice from methanol-water to give shiny flakes of *anhydro corosin acetate ester* (45 mg), m.p. 232 – 234 °C, $[\alpha]_{578}^{22}$ + 203.5°, λ_{max} 212.5 i, 228, 235 i, 239 i nm (ε: 7,200; 8,800; 8,300; 7,600).

$C_{36}H_{52}O_8$ (612.7)

Calcd.:	C 70.56	H 8.52;
Found:	C 70.27	H 8.59.

*19. Anhydro corosin ester diol (**12**; R = Me, R^1 = H)*

Anhydro corosin ester acetate (flakes, 27 mg) was taken in 11% methanolic caustic potash (5 ml) and refluxed for 45 min. The solution was evaporated at the filter pump, diluted with water and extracted with ether. The etherial extract on evaporation and crystallisation from methanol-water, gave flat bars of *anhydro corosin ester*, m.p. 126 – 130 °C, $[\alpha]_{578}^{23}$ + 262°, λ_{max} 216 i, 228, 238 i nm (ε: 8,500; 9,000; 8,600).

$C_{32}H_{48}O_6$ (528.7)

Calcd.:	C 71.48	H 9.18;
Found:	C 71.11	H 8.78.

*20. Corosin anhydro lactone acetate C-24 aldehyde (**13**; R = CHO, R^1 = Ac)*

Corosin anhydro lactone acetate (0.87 g) was dissolved in thionyl chloride (7.0 ml), when an immediate reaction started. It was refluxed under low heat for 15 min, excess thionyl chloride was removed at the pump and traces over KOH *in vacuo*. The powdery foam (0.98 g) was taken in dry toluene (35.0 ml) and Pd./charcoal (10%; 0.52 g) added. A stream of hydrogen gas was bubbled through the solution, which was slowly raised to

reflux. The effluent gas was passed through water and titrated with 0.1 N caustic soda to determine the progress of reaction. After an initial rapid reaction it slowed down and after 22 hours, the catalyst was filtered off and fresh quantity (0.42 g) was added to the solution in dry toluene (25 ml). After a further six hours reduction under reflux, the absorption again became imperciptible, and the catalyst was filtered off (celite). The solution was evaporated *in vacuo* and the residue crystallised from chloroform-methanol, to give *corosin anhydro lactone acetate C-24 aldehyde* (0.52 g), which after recrystallisation from the same solvent gave m.p. 260 – 265 °C (transforms to needles) and 300 – 305 °C decomp., $[\alpha]_{578}^{22}$ −90°, λ_{max} 213.5, 227, 260, 271 nm (ε: 7,200; 5,500; 600 and 400), ν_{max} 2750 w, 1738 s, 1718 ms, 1700 mi, 1682 w cm^{-1}. In the NMR it gave bands at ($CDCl_3$ solution in T-60 Varian Spectrophotometer) 9.20, 9.10, 8.87, 8.77, 8.66 (C-Me), 7.99 and 7.94 (acetate Me), 5.11, 4.99, (H-2), multiplet 4.71 – 4.22 (H-3), and 0.01 τ (CHO).

$C_{34}H_{48}O_7$ (568.7)

Calcd.:	C 71.80	H 8.51;
Found:	C 71.52	H 8.53.

*21. Urs-13:19(20)-dien-28-oic-2α,3β-diol (**14**; R = H)*

Corosin-anhydro-lactone-acetate-C-24-aldehyde (80 mg) was taken in diethylene glycol (7 ml) with hydrazine hydrate (99 – 100%, 0.7 ml) and refluxed under nitrogen for 15 min. It was transferred to a two necked flask and under dry nitrogen bubbling heated for 90 min during which ca. 3 ml digol was allowed to distill over (up to 180 °C). After slight cooling pellets of caustic potash (0.4 g) were added and the mixture refluxed for a further 90 min. It was cooled and poured into dilute HCl and extracted with ether, dried (Na_2SO_4) and evaporated. The chloroform insoluble portion was crystallised from a large volume methanol to give plates of *urs-13:19 (20)-dien-28-oic-2α,3β-diol* (23 mg in two crops), m.p. 284 – 286 °C decomp. (gas bubbling), $[\alpha]_{578}^{22}$ −240°, λ_{max} 209 i, 245, 251.5 nm (ε: 2,900; 18,100; 17,200). It gave mass molecular ion at 470 in the mass spectra and a strong peak at 426 indicated decarboxylation expected of the β,γ-unsaturated C-28 acid.

$C_{30}H_{46}O_4$ (470.6)

Calcd.:	C 76.55	H 9.85;
Found:	C 76.33	H 9.81.

*22. Methyl-urs-13:19(20)-dien-2α,3β-diol-28-oate (**14**; R = Me)*

Urs-13:19(20)-dien-2α,3β-diol-28-oic acid (14 mg) was taken in excess etherial diazomethane and methanol (2 ml). The solvents were removed and the residue crystallised from methanol-water to give waxy plates of methyl-*urs-13:19(20)-dien,2α,3β-diol-28-oate*, m.p. 162 – 165 °C, $[\alpha]_{578}^{24}$ −248°, λ_{max} 207, 245, 251.5 nm (ε: 7,070; 21,400; 20,300).

$C_{31}H_{48}O_4$ (484.7)

Calcd.:	C 76.81	H 9.98;
Found:	C 76.69	H 9.81.

*23. Urs-13:19(20)-dien-2α,3β-diol-20,28-lactone (**13**; R = Me, R^1 = H)*

Urs-13:19(20)-dien-28-oic2α,3β-diol (35 mg) without purification was taken in acetic acid (1.5 ml) and concentrated sulphuric acid (0.5 ml) added at room temperature; after 15 min, the solution was poured in water, extracted with ether containing ethyl acetate, and washed with bicarbonate solution. The dried (Na_2SO_4) organic layer was evaporated and the total extract chromatographed on a column of silica gel G (1.5 g). The chloroform elutes were greasy solid and were not investigated, the 20% methanol in chloroform elute gave a crystalline white solid identified as a 20,28 lactone from its infra-red (1730 cm^{-1}), UV (λ_{max} 209, 227 nm) and NMR spectrum. Once crystallised from methanol-water it gave the *lactone* (**13**; R = Me, R^1 = H) as a microcrystalline solid, m.p. 220 – 225 °C (earlier softening).

$C_{30}H_{46}O_4$ (470.6)

Calcd.:	C 76.55	H 9.85;
Found:	C 76.53	H 9.77.

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