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TRITERPENE COMPOUNDS—VIII[1]

THE CONSTITUTION OF PHILLYRIGENIN

C. S. CHOPRA, (the late) D. E. WHITE and (in part) G. J. H. MELROSE
Department of Organic Chemistry, University of Western Australia, Nedlands, Western Australia

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Abstract—Phillyrigenin, the dihydroxy lactone isolated from *Pittosporum phillyraeoides* D.C., has been degraded to ψ-taraxastene (VIe), and a tentative structure (Ia) has been suggested.

IN AN earlier paper[2] we described the isolation of phillyrigenin from the sapogenins derived from *Pittosporum phillyraeoides* D.C. Phillyrigenin, $C_{30}H_{48}O_4$, was characterized as a saturated δ-lactone containing a primary and a secondary hydroxyl group and evidence is now presented limiting the configuration of the sapogenin to Ia or Ib. For convenience, the argument is presented in terms of Ia.

Oxidation of phillyrigenin with chromic acid and acetic acid gave a keto-acid[2] and in an attempt to prepare the keto-aldehyde oxidation with chromium trioxide in pyridine[3] was used. The product (IIa) retained the primary hydroxyl group and the keto-aldehyde (IIb) was obtained ultimately by oxidation in chromic and acetic acids and chloroform solution.[4] Huang-Minlon[5] reduction of IIb gave the lactone III. However, because of the poor yield in the oxidation step, an alternative method of deoxygenation of phillyrigenin was examined. The dimesylate[2] was treated with sodium benzylmercaptide in dimethylformamide[6] to give the benzylthioether (IVa), whose NMR spectrum showed a multiplet centred at 5·37[7] (2H) attributed to the vinylic protons on a *cis*-disubstituted double bond. Elimination at C_3 under these conditions has been found in analogous cases.[8,9] The thioether (IVa) was desulphurized with Raney nickel[10] to give the lactone (IVb) which, on hydrogenation over platinum, gave the saturated lactone (III) identical to that obtained *via* the keto-aldehyde (IIb).

The lactone (III) was reduced to the diol (Va) by heating with LAH for 20 hr in refluxing dioxan. This diol (Va) afforded the monoacetate (Vb) whose IR absorption (in CS_2) at 3615 cm^{-1} indicated the presence of a tertiary hydroxyl group[11] which was supported by the NMR spectrum which showed a 3H singlet (1·32) expected for a

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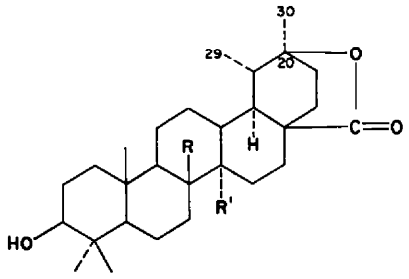
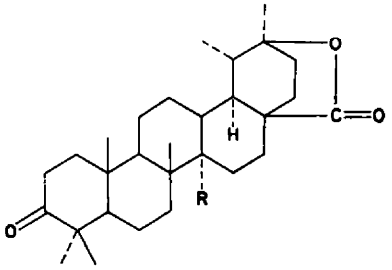
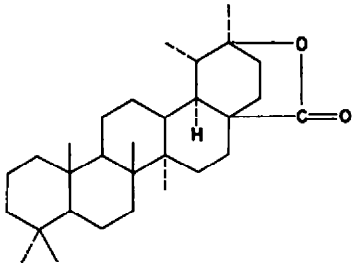


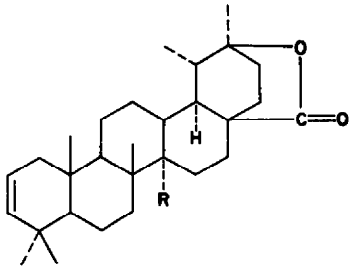
Ia ; R = CH_3, R' = CH_2OH
Ib ; R = CH_2OH, R' = CH_3



IIa ; R = CH_2OH
IIb ; R = CHO
IIc ; R = CO_2H
IId ; R = CO_2CH_3



III

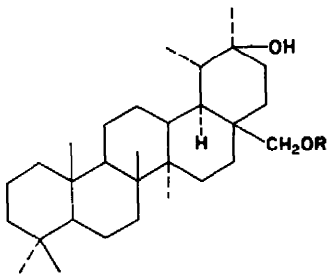


IVa ; R = $CH_2SCH_2C_6H_5$
IVb ; R = CH_3

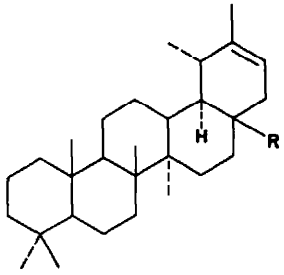
methyl group adjacent to a tertiary hydroxyl group. The acetate (Vb) was dehydrated by phosphoryl chloride in pyridine[12] to give the acetoxy-olefin (VIa), the NMR spectrum of which showed absorption due to one vinylic proton (5·33) and one vinylic methyl group (1·66). The physical constants of the acetate (VIa; m.p. 185–186°, $[a]_D$ +20°) and of the derived alcohol (VIb; m.p. 200–201°, $[a]_D$ +50°) closely resembled those reported for 3-desoxyheterobetulin acetate (m.p. 186–186·5°, $[a]_D$ +19°)[13] and 3-desoxyheterobetulin (m.p. 201–202°, $[a]_D$ +47°).[13] To establish these identities, the alcohol (VIb) was converted to ψ-taraxastene in the following manner.

Mesylation of VIb afforded the methane sulphonate (VIc) which reacted with sodium benzylmercaptide in dimethyl formamide[6] to give the benzylthioether (VId) which was desulphurized by Raney nickel.[10] The hydrocarbon obtained was identified as ψ-taraxastene (heterolupene; VIe)[14] by comparison with an authentic sample.

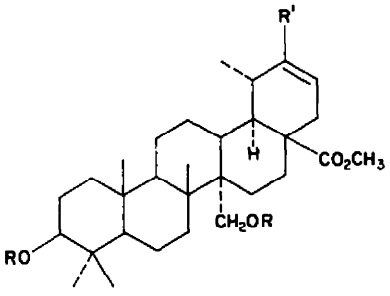
Saponification of phillyrigenin had been shown to give an unsaturated dihydroxyl acid.[2] The derived diacetoxy methyl ester (VIIa) was oxidized with selenium dioxide to give the conjugated aldehyde (VIIb), λ_{max} 234 mμ (ε = 12,200), whose structure was supported by the NMR spectrum which showed a signal at 9·37 (1H) corresponding to an aldehyde proton. Similar oxidation of VIa gave the corresponding



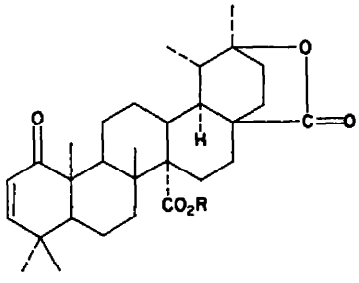
Va ; R = H
Vb ; R = $COCH_3$



VIa ; R = CH_2OCOCH_3
VIb ; R = CH_2OH
VIc ; R = $CH_2OSO_2CH_3$
VId ; R = $CH_2SCH_2C_6H_5$
VIe ; R = CH_3



VIIa ; R = $COCH_3$, R' = CH_3
VIIb ; R = $COCH_3$, R' = CHO



VIIIa ; R = CH_3
VIIIb ; R = H

aldehyde. The unhindered nature of the olefinic group in VIIa follows from its ready hydrogenation. These results are expected for the ψ-taraxastene system,[13,15–17]

The conditions used in the conversion of phillyrigenin to ψ-taraxasene suggest that skeletal rearrangement in this process was most unlikely and that phillyrigenin is based on this skeleton. In addition, evidence for a δ-lactone and the correspondence of the physical constants of the degradation products (VIb and VIa) with those reported for 3-desoxyheterobetulin and its acetate are strong evidence for the location of the lactone ring in phillyrigenin bridging C_{28}–C_{20}.

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The location of the hydroxyl groups in phillyrigenin are based on the following evidence. The secondary hydroxyl was placed tentatively at C_3 in view of the positive Zimmermann test[18] given by the keto-acid (IIc)[2] and the derived ester (IId).[2] The conjugated ketone (VIIIa) was prepared from IIa by LAH reduction, dehydration and chromic acid oxidation. Its UV spectrum was found to have λ_{max} 222 mμ (ε = 8,000) as expected for a 1-oxo-2-ene.[19] Reduction of the ester (IId) by LAH did not affect the ester or lactone groups but converted the ketone to an equatorial (absorption at 3629 cm^{-1}).[20] this being the expected product from an unhindered C_3 ketone.[21] The 3β hydroxyl configuration was supported by the differences in molecular rotations detween phillyrigenin diacetate ($[M]_D$ +117°)[2] and phillyrigenin monoacetate A ($[M]_D$ +82°)[2], and between phillyrigenin monoacetate B ($[M]_D$ +160°)[2] and phillyrigenin ($[M]_D$ +109°)[2] which are expected for 3β-hydroxylated triterpenoids.[22] Thus, in all probability, phillyrigenin contains the normal structure (Ia) of a $C_{3\beta}$-hydroxylated triterpenoid.

Phillyrigenin failed to give an isopropylidene, a benzylidene or an ethylidene derivative, restricting the relationship of the two hydroxyl groups. The absence of a 1:3 glycol was established by the facile isolation and the stability of the keto-acid (IIc), eliminating C_{23} and C_{24} as the location of the carboxyl group. The derived methyl ester (IId) was not hydrolysed by 10% methanolic potassium hydroxide under reflux during 8 hr. This evidence excluded, C_{23} C_{29} and C_{30},[23] for the position of the methoxycarbonyl group and, therefore, of the primary hydroxyl group in phillyrigenin.

Of the three remaining possibilities (C_{25}, C_{26}, C_{27}) for the primary hydroxyl group, C_{27} was favoured, [24–26] since only one triterpene is recorded with oxygenation at C_{25},[27] and none is known with oxygenation at C_{26}.[28]

The keto-ester (VIIIa) was hydrolysed to the acid (VIIIb), and the acid was recovered unchanged after heating at 200–205°. This result excluded the presence of a C_{10} methoxycarbonyl group in the ester (VIIIa).

At this stage it is not possible to distinguish between C_8 and C_{14} for the location of the primary hydroxyl group, leaving the alternative formulations (Ia and Ib) for phillyrigenin.

EXPERIMENTAL

M.ps. were recorded on a Kofler block. Optical rotations, UV and IR spectra were recorded for $CHCl_3$, EtOH and CS_2 solutions respectively. NMR spectra were recorded, on a Varian A60 high-resolution spectrometer, for $CDCl_3$ solutions with tetramethylsilane as internal reference. All peak positions are recorded on δ-scale. Alumina for chromatography was Peter Spence grade H standardized[29] at activity II. Light petroleum refers to the fraction b.p. 56–60°. Microanalyses were carried out by the C.S.I.R.O. Microanalytical Service, University of Melbourne.

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Attempted oxidation of phillyrigenin (Ia) *with chromium trioxide in pyridine*

A solution of Ia (100 mg) and CrO_3 (150 mg) in pyridine (15 ml) was allowed to stand at room temp for 12 hr. The reaction mixture was poured into water and extracted with $CHCl_3$ to give 3-*oxo*-27-*hydroxytaraxastan*-28,20*β*-*olide* (IIa; 25 mg) as prisms from $CHCl_3$–MeOH, m.p. 278–279°, $[\alpha]_D$ +60° (*c*, 0·62), ν_{max} (in $CHCl_3$) 3620, 1740, 1700 cm^{-1}. A Zimmermann test[18] gave a violet colour changing to pink on dilution, identical with lupenone and α-amyrenone. (Found: C, 76·4; H, 10·0. $C_{30}H_{46}O_4$ requires: C, 76·6; C, 9·9%.)

3-*Oxotaraxastan*-27-*al*-28,20*β*-*olide* (IIb)

To an ice-cooled solution of phillyrigenin (160 mg) in $CHCl_3$ (8 ml) and acetic acid (80 ml) was added during 10 min a solution of CrO_3 (450 mg) in water (4 ml) and acetic acid (12 ml). After 75 min at room temp MeOH was added, the mixture diluted with water and extracted with $CHCl_3$. The organic layer was washed with 3% KOH aq and evaporated to give the *keto-aldehyde* (IIb; 40 mg) as needles from $CHCl_3$–MeOH, m.p. 260–262°, $[\alpha]_D$ + 52° (*c*, 0·68). (Found: C, 76·9; H, 9·4. $C_{30}H_{44}O_4$ requires: C, 76·9; H, 9·5%.)

Huang-Minlon reduction of 3-*oxotaraxastan*-27-*al*-28,20*β*-*olide* (IIb)

A solution of IIb (50 mg), 80% hydrazine hydrate (2 ml) and EtOH (6 ml) were heated under reflux for 1 hr. Potassium hydroxide (1 g) and diethylene glycol (25 ml) were added and the mixture distilled until the internal temp reached 195°. The solution was then heated under reflux for 4 hr, diluted with water, acidified and extracted with $CHCl_3$. The organic layer was washed with 3% KOH aq and evaporated to give the crude product (25 mg) which was dissolved in $CHCl_3$ and filtered through alumina (1 g) to give *taraxastan*-28,20*β*-*olide* (III) as needles from MeOH–CH_2Cl_2, m.p. 280–281°, $[\alpha]_D$ + 21° (*c*, 0·70), ν_{max} 1755. (Found: C, 81·7; H, 11·1. $C_{30}H_{46}O_2$ requires: C, 81·8; H, 11·0%.)

Taraxast-2-*en*-28,20*β*-*olide*-27-*benzylthioether* (IVa)

Sodium benzylmercaptide prepared from benzyl mercaptan (1 g) and Na (250 mg) was taken up in dimethylformamide (10 ml) and a solution 3*β*,27-dimethanesulphonyloxytaraxastan-28,20*β*-olide (1 g)[3] in dimethylformamide (40 ml) added and the mixture heated at 100° for 7 hr under dry N_2. The cold solution was added to 3% KOH aq (200 ml) and extracted with ether, and the extract washed successively with 3% KOH aq and water, then dried and evaporated. The residue (1 g) was dissolved in light petroleum (100 ml) and chromatographed on alumina (20 g). Elution with light petroleum–benzene (1:2) gave the *benzylthioether* (IVa; 700 mg) as needles from MeOH–CH_2Cl_2, m.p. 203–204°, $[\alpha]_D$ + 50° (*c*, 0·80). (Found: C, 79·2; H, 9·4; S, 5·9. $C_{37}H_{52}O_2S$ requires: C, 79·2; H, 9·4; S, 5·7%.)

Taraxast-2-*en*-28,20*β*-*olide* (IVb)

Taraxast-2-en-28,20*β*-olide-27-benzylthioether (500 mg) in EtOH (150 ml) was heated under reflux with Raney Ni (10 g) for 10 hr. The catalyst was filtered off and washed with ether, at the pump, and the filtrates evaporated. The residue was dissolved in light petroleum–$CHCl_3$ (4:1) and chromatographed on alumina (10 g). Elution with light petroleum–$CHCl_3$ (1:1) gave the *lactone* (IVb; 350 mg) as needles from MeOH–CH_2Cl_2, m.p. 260–261°, $[\alpha]_D$ + 26° (*c*, 0·64). (Found: C, 82·1; H, 10·5. $C_{30}H_{46}O_2$ requires: C, 82·1; H, 10·6%.)

Taraxstan-28,20*β*-*olide* (III)

Taraxast-2-en-28,20*β*-olide (300 mg) in acetic acid (60 ml) absorbed H_2 (1 mole) in the presence of Pt catalyst (50 mg). The catalyst was filtered off and washed with ether and the filtrate evaporated to give III (280 mg) as needles from MeOH–CH_2Cl_2, m.p. and mixed m.p. 280–281°, $[\alpha]_D$ + 20° (*c*, 0·62).

Taraxastan-20*β*,28-*diol* (Va)

Taraxastan-28,20*β*-olide (200 mg) was heated in refluxing dioxan (100 ml) with LAH (500 mg) for 20 hr. After the cautious addition of water (200 ml), the mixture was worked up with ether to give the *diol* (Va; 100 mg) as plates from MeOH, m.p. 216–218°, $[\alpha]_D$ + 29° (*c*, 0·75). (Found: C, 81·3; H, 11·7. $C_{30}H_{52}O_2$ requires: C, 81·0; H, 11·8%.)

28-Acetoxytaraxastan-20β-ol (Vb)

Taraxastan-20β,28-diol (100 mg) was treated with acetic anhydride (10 ml) in pyridine (10 ml) at room temp for 12 hr, and the mixture poured into water (100 ml) and extracted with ether to give the *monoacetate* (Vb; 70 mg) as prisms from MeOH–ether, m.p. 118–120°, $[\alpha]_D$ + 65° (*c*, 0·92). (Found: C, 79·3; H, 11·1%. $C_{31}H_{54}O_3$ requires: C, 79·0; H, 11·2%.)

Taraxast-20-en-28-yl acetate (VIa)

28-Acetoxytaraxastan-20β-ol (500 mg) in pyridine (20 ml) was heated at 100° with $POCl_3$ (5 ml) for 6 hr. The solution was cooled and poured into ice and extracted with ether to give a crude product (425 mg) which was dissolved in light petroleum (100 ml) and chromatographed on neutral alumina (10 g). Elution with light petroleum–benzene (4:1) gave the *acetoxy-olefin* (VIa; 300 mg) as needles from MeOH, m.p. 185–186°, $[\alpha]_D$ + 20° (*c*, 0·83). The acetoxy-olefin gave a yellow coloration with tetranitromethane. (Found: C, 81·9; H, 11·3. $C_{32}H_{52}O_2$ requires: C, 82·0; H, 11·2%.)

Taraxast-20-en-28-ol (VIb)

Taraxast-20-en-28-yl acetate (200 mg) was heated under reflux with EtOH (20 ml) containing KOH (700 mg) for 2 hr. The reaction mixture was then cooled, poured into water, and extracted with ether to give the *alcohol* (VIb; 170 mg) as needles from MeOH, m.p. 200–201°, $[\alpha]_D$ + 50° (*c*, 0·64). ν_{max} 3625 cm^{-1}. (Found: C, 84·6; H, 11·7. $C_{30}H_{50}O$ requires: C, 84·4; H, 11·8%.)

28-Methanesulphonyloxytaraxast-20-ene (VIc)

Methanesulphonyl chloride (0·5 ml) was added to the taraxast-20-en-28-ol (150 mg) in pyridine (3 ml) at 0°. The mixture was allowed to stand at 20° for 12 hr, when the excess of reagent was destroyed by the careful addition of water and the mixture worked up with $CHCl_3$ to give a crude product (170 mg). This was dissolved in $CHCl_3$–benzene (1:10) and filtered on neutral alumina (5 g) to give the *methanesulphonate* (VIc; 110 mg) as needles from $CHCl_3$–MeOH, m.p. 164–165°, $[\alpha]_D$ + 10° (*c*, 0·70). The NMR spectrum showed a singlet at 2·8 (3H) attributed to the protons of methanesulphonyl group and a multiplet 5·33 (H) (vinylic proton of trisubstituted double bond). (Found: C, 73·7; H, 10·4; S, 6·5. $C_{31}H_{52}O_3S$ requires: C, 73·8; H, 10·4; S, 6·3%.)

Taraxast-20-en-28-benzylthioether (VId)

28-Methanesulphonyloxytaraxast-20-ene (100 mg) was treated with sodium benzylmercaptide, from benzylmercaptan (0·5 ml) and Na (25 mg) in dimethylformamide (10 ml) at 100° for 8 hr under an atm. of dry N_2. The deep red solution was poured into 2 N NaOH (50 ml) and worked up as described before to give the *benzylthioether* (VId; 70 mg) as prisms from MeOH, m.p. 172–173°, $[\alpha]_D$ + 25° (*c*, 0·56). (Found: C, 83·6; H, 10·6; S, 5·8. $C_{37}H_{56}S$ requires: C, 83·4; H, 10·6; S, 6·0%.)

Taraxast-20-ene (VIe)

Taraxast-20-en-28-benzylthioether (50 mg) in EtOH (25 ml) was heated under reflux with Raney Ni (2 g) for 12 hr and the mixture then allowed to stand at room temp for 16 hr. The solution was decanted and the residual Ni washed with light petroleum. The combined liquor and washings were concentrated to 5 ml, poured into water (50 ml) and worked up with ether to give the hydrocarbon as needles from $CHCl_3$–MeOH, m.p. and mixed m.p. 180–181·5°, $[\alpha]_D$ + 48° (*c*, 0·68). (cf. lit.[14] m.p. 181–182°, $[\alpha]_D$ + 48°.)

The NMR spectrum showed a multiplet at 5·33 (H) attributed to the vinylic proton of a trisubstituted double bond, and a singlet at 1·66 (3H) (protons of one vinylic methyl group). The hydrocarbon (VIe) gave a yellow coloration with tetranitromethane.

Methyl 3β,27-diacetoxytaraxast-20-en-28-oate (VIIa)

3β,27-Dihydroxytaraxastan-28,20β-olide (3 g) was dissolved in diethylene glycol (75 ml) KOH (30 g) added and the solution heated in an oil bath at ca. 210° for 7 hr. A potassium salt (2·8 g), m.p. >350°, which separated on the addition of water, was filtered. The salt was dissolved in a solution of KOH (6 g) in MeOH (25 ml), EtOH (25 ml) and water (50 ml). Dimethyl sulphate (10 ml) was added in portions and when the vigour of the reaction had ceased, the solution was heated over a steam bath for 1·5 hr. On cooling, it was retreated with KOH (6 g), dimethyl sulphate (10 ml) and

MeOH (15 ml) and refluxed a further hr. The reactants were stood for 2 days and the crude mixture of esters (2·5 g) filtered off.

The product (2·5 g) was dissolved in pyridine (50 ml) and treated with acetic anhydride (50 ml) for 24 hr. After pouring into water, a colourless glass (2·5 g) was obtained by working up with ether. The glass (2·5 g) in pyridine (80 ml) was heated at 100° with $POCl_3$ (14 ml) for 5 hr. The solution was cooled, poured into water, and worked up with ether to give a crude product (2·3 g) which was dissolved in benzene–$CHCl_3$ (1:1) and chromatographed on alumina (50 g). Elution with $CHCl_3$ gave the *unsaturated diacetoxy ester* (VIIa; 1·3 g) as plates from $CHCl_3$–MeOH, m.p. 195–196°, $[\alpha]_D$ + 32°, (*c*, 0·92). (Found: C, 73·4; H, 9·4. $C_{35}H_{54}O_6$ requires: C, 73·6; H, 9·5%.)

Oxidation of methyl 3*β*,27-*diacetoxytaraxast*-20-*en*-28-*oate* (VIIa)

The diacetoxy-ester (VIIa; 1 g) in acetic acid (70 ml) was heated under reflux with SeO_2 (1 g) for 2 hr. The solution was decanted and the residual Se washed with ether. The combined liquor and washings were poured into water and worked up with ether to give a crude product (800 mg) which was dissolved in benzene and filtered through alumina (20 g) to give *methyl* 3*β*,27-*diacetoxy*-30-*oxotaraxast*-20-*en*-28-*oate* (VIIb; 600 mg) as plates from MeOH–water, m.p. 194–195°, $[\alpha]_D$ + 55° (*c*, 0·98). (Found: C, 71·8; H, 8·9. $C_{35}H_{52}O_7$ requires: C, 71·9; H, 9·0%.)

30-*Oxotaraxast*-20-*en*-28-*yl* acetate

Taraxast-20-en-28-yl acetate (40 mg) in acetic acid (5 ml) was heated under reflux with SeO_2 (50 mg) for 2 hr. The reaction mixture was worked up as described in the previous experiment to give a crude product (45 mg) which was dissolved in benzene and filtered through alumina (2 g) to give the *acetoxy-aldehyde* (35 mg) as needles from MeOH, m.p. 197–198°, $[\alpha]_D$ + 22° (*c*, 1·8). (Found: C, 79·8; H, 10·3. $C_{32}H_{50}O_3$ requires: C, 79·6; H, 10·4%.)

Methyl 3*β*,27-*diacetoxytaraxastan*-28-*oate*

Methyl 3*β*,27-diacetoxytaraxastan-20-en-28-oate (100 mg) in acetic acid (30 ml) was catalytically reduced over Pt catalyst (30 mg) to give the *dihydro ester* (80 mg) as prisms from MeOH, m.p. 145–146°, $[\alpha]_D$ −65° (*c*, 1·1). (Found: C, 73·3; H, 9·8. $C_{35}H_{56}O_6$ requires: C, 73·4; H, 9·9%.)

Zimmermann tests

The compound (1 mg) was dissolved in 5% ethanolic KOH (1 ml) and a 1% solution of *m*-dinitrobenzene in EtOH (1 ml) added. The colour was observed 3 times; namely, on the addition, after standing for 45 min, and finally after dilution with EtOH (8 ml).

Compound	Colour		
	Initially	After 45 mins	After dilution
Blank	brown	brown	brown
11-Oxo-urs-12-ene	brown	brown	brown
3-Oxo-lup-20(29)-ene	purple	purple	cyclamen
3-Oxo-lanostane	purple	purple	purple
3-Oxotaraxastan-28,20*β*-olide-27-oic acid (IIc)[a]	purple	cyclamen	cyclamen
Methyl-3-oxotaraxastan-28,20*β*-olide-27-oate (IId)[a]	purple	cyclamen	cyclamen

Oxime formation of methyl-3-*oxotaraxastan*-28,20*β*-*olide*-27-*oate* (IId)[a]

The keto-ester (IId; 170 mg), hydroxylamine hydrochloride (300 mg) and pyridine (1 ml) were heated at 100° for 6 hr to give the *oxime* as needles from MeOH, m.p. 240–241°, $[\alpha]_D$ −32° (*c*, 0·98). (Found: C, 72·1; H, 9·1. $C_{31}H_{47}O_5N$ requires: C, 72·5; H, 9·2%.)

Methyl 3β-hydroxytaraxastan-28,20β-olide-27-oate

The keto-ester (IId; 560 mg) was refluxed in ether (500 ml) with excess of LAH for 1·5 hr. The unreacted reagent was decomposed with water and the mixture worked up with ether to give the *hydroxy-ester* as prisms from MeOH–water, m.p. 264–265°, $[\alpha]_D^{20}$ + 52° (c, 0·90). ν_{max} 3629, 1748, 1717 cm^{-1}. (Found: C, 74·5; H, 9·6; O, 15·6. $C_{31}H_{48}O_5$ requires: C, 74·4; H, 9·7; O, 16·0%.)

Methyl taraxast-2-en-28,20β-olide-27-oate

Methyl 3β-hydroxytaraxastan-28,20β-olide-27-oate (300 mg) in pyridine (20 ml) was heated at 100° with $POCl_3$ (5 ml) for 12 hr. The solution was poured into ice and worked up with ether to give the *ester* (170 mg) as needles from MeOH, m.p. 205–206°, $[\alpha]_D$ + 130° (*c*, 0·92). (Found: C, 76·9; H, 9·6. $C_{31}H_{46}O_4$ requires: C, 77·1; H, 9·6%.)

Methyl 1-oxotaraxast-2-en-28,20β-olide-27-oate (VIIIa)

Sodium dichromate (150 mg) was added to methyl-taraxast-2-en-28,20β-olide-27-oate (150 mg) in acetic acid (5 ml) and the solution refluxed for 1 hr, after which time it had turned completely green. Sodium dichromate (140 mg) was added and refluxing continued for 5 hr, when the excess reagent was removed with EtOH. The solution was poured into water and extracted with ether to give the *conjugated ketone* (VIIIa; 50 mg) as needles from MeOH–water, m.p. 304–305°, $[\alpha]_D$ +80° (*c*, 0·98). (Found: C, 74·7; H, 9·1. $C_{31}H_{44}O_5$ requires: C, 75·0; H, 8·9%.)

Attempted preparation of (a) *an isopropylidene*, (b) *a benzylidene, and* (c) *an ethylidene derivative of phillyrigenin* (Ia)

(a) Phillyrigenin (150 mg) was shaken with a mixture of ether (50 ml), acetone (25 ml), and H_2SO_4 (1 ml) until dissolution occurred. The solution was stood at room temp for 20 hr, poured into water (25 ml) and extracted with $CHCl_3$ to give phillyrigenin m.p. and mixed m.p. 339–341°.

(b) Phillyrigenin (150 mg) was treated with benzaldehyde (20 ml) and conc. H_2SO_4 (0·5 ml) at room temp overnight. The reaction mixture was worked up as described above to give phillyrigenin m.p. and mixed m.p. 339–341°.

(c) Phillyrigenin (150 mg) was shaken in ether (50 ml) with paraldehyde (3 ml) and conc. HCl (0·3 ml) until dissolution occurred. The solution was stood at room temp. for 20 hr. The reaction mixture was worked up as described above to give phillyrigenin m.p. and mixed m.p. 339–341°.

Saponification of methyl 3-oxotaraxastan-28,20β-olide-27-oate (IId)

The keto-ester (IId; 100 mg) was refluxed with 10% methanolic KOH (30 ml) for 8 hr. The reaction mixture was then cooled, poured into water, and extracted with ether to give IId (95 mg) as needles from MeOH–CH_2Cl_2, m.p. 251–252°, with no depression in m.p. on admixture of starting material.

The aqueous solution was acidified and extracted with ether, but gave no acidic product.

Saponification of methyl 1-oxotaraxast-2-en-28,20β-olide-27-oate (VIIIa)

The keto-ester (VIIIa; 60 mg) and KOH (500 mg) in diethylene glycol (8 ml) were brought to reflux temp during 1 hr and then maintained at the temp for another hr. The mixture was acidified, diluted with water, and extracted with $CHCl_3$. The organic layer was washed several times with 5% NaOH aq and evaporated to give VIIIa (10 mg) as needles from MeOH, m.p. and mixed m.p. 304–305°.

The NaOH washings were re-acidified and extracted with $CHCl_3$ to give *1-oxotaraxast-2-en-28,20β-olide-27-oic acid* (VIIIb; 30 mg) as needles from MeOH–water, m.p. 328–330°, $[\alpha]_D$ + 62° (*c*, 0·68). (Found: C, 74·6; H, 8·7. $C_{30}H_{48}O_5$ requires: C, 74·7; H, 8·8%.)

Attempted decarboxylation of 1-oxotaraxast-2-en-28,20β-olide-27-oic acid (VIIIb)

The keto-acid (VIIIb; ·25 mg) was heated during 15 min at 200–205° under an atm. of N_2. The product in $CHCl_3$, was washed with 5% NaOH aq leaving no residue. The NaOH washings were acidified and extracted with $CHCl_3$ to give a crude acid (20 mg) which was methylated to give VIIIa, m.p. and mixed m.p. 304–305°.

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