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THE TRITERPENOIDS—LVI

THE CHEMISTRY OF THE SOYASAPOGENOLS A, B AND C

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Abstract—Soyasapogenol A, B, and C are shown to be 3β:21:22:24-tetrahydroxyolean-12-ene, 3β:21α:24-trihydroxyolean-12-ene (XVIII) and 3β:24-dihydroxyoleana-12:21-diene (IX, R = H), respectively. Of the two possible configurations, α and β, for the *cis*-glycol group in soyasapogenol A the former is preferred, and soyasapogenol A tetra-acetate is represented by (X, R = Ac). The stereoisomeric soyasapogenol A tetra-acetate, which is obtained together with soyasapogenol A tetra-acetate by the oxidation of soyasapogenol C diacetate with osmium tetroxide, is consequently represented as 3β:21β:22β:24-tetra-acetoxyolean-12-ene (XI, R = Ac). Oxidation of soyasapogenol A tetra-acetate (X, R = Ac) and of the stereoisomeric soyasapogenol A tetra-acetate (XI, R = Ac) with selenium dioxide give the corresponding dioxodiene derivatives (XII) and (XVII), respectively. Treatment of each of the dioxodienes (XII) and (XVII) with alkali, and acetylation of the products, gives the same isomeric dioxodiene (XIII). These epimerisations include a reversed aldol-type condensation, followed by a direct intramolecular aldol-type condensation, and they prove that the *cis*-glycol group in soyasapogenol A is in ring E.

Soyasapogenol B (XVIII) forms a 3β:24-*iso*propylidene derivative (XIX), from which the 21-epimer of soyasapogenol B triacetate (XXII) is obtained by unambiguous procedures. Treatment of the dioxodiene derivative (XXIII) of the last compound with alkali, and subsequent acetylation, gives the dioxodiene derivative of soyasapogenol B triacetate (XXIV). This epimerisation again includes the opening and closing of ring E by a reversed aldol-type condensation and a direct intramolecular aldol-type condensation.

The identification of soyasapogenol B, which has been converted into soyasapogenol C, proves that the latter is 3β:24-dihydroxyoleana-12:21-diene (IX, R = H).

ACID hydrolysis of the saponin from soya bean gives a mixture from which four triterpenoid sapogenols, the soyasapogenols A, B, C and D, may be isolated.* Recently, soyasapogenols B and C, and possibly soyasapogenol A, have been obtained from a saponin mixture from ladino clover (*Trifolium repens*)[1] and soyasapogenol C has been isolated from whin (*Ulex europaeus*).[2] Preliminary studies by Japanese chemists* led to the views that the soyasapogenols are triterpenoids and contain a 1:3-glycol system similar to that in hederagenin; these views were confirmed and extended by Meyer *et al.*,[3] whose conclusions are summarised in the provisional formulae (I), (II), (III) and (IV) for soyasapogenols A, B, C and D, respectively. Meyer *et al.*, found that dihydrosoyasapogenol C, which is obtained by catalytic reduction of soyasapogenol C, is 3β:24-dihydroxyolean-12-ene, the reference specimen of which was prepared from α-boswellic acid. This incisive identification established the structure and stereochemistry of soyasapogenol C except for the position of the double bond susceptible to catalytic hydrogenation. The structure of soyasapogenol

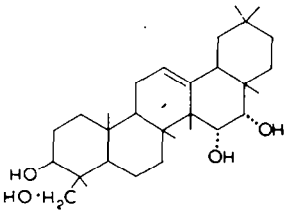
* References to early work on the soyasapogenols are listed in *Elsevier's Encyclopaedia of Organic Chemistry* (Ed. E. Josephy and F. Radt) Vol. 14, p. 592. Elsevier, New York and Amsterdam (1940). *Op. cit.* (Ed. F. Radt) Vol. 14–Supplement, p. 979 s. Elsevier, Amsterdam, Houston, London and New York (1952).

[1] E. D. Walter, E. M. Bichoff, C. R. Thompson, C. A. Robinson and C. Djerassi, *J. Amer. Chem. Soc.* **77**, 4936 (1955).

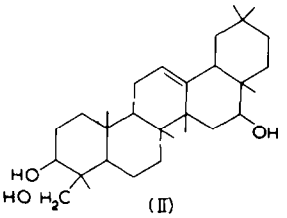
[2] J. McLean and J. B. Thomson, Unpublished work; we thank Dr J. McLean for this information.

[3] A. Meyer, O. Jeger and L. Ruzicka, *Helv. Chim. Acta* **33**, 672, 687, 1835 (1950).

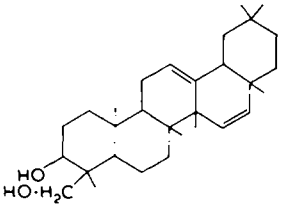
A follows from that of soyasapogenol C, since oxidation of the diacetate of the latter with osmium tetroxide, and acetylation of the product, gives soyasapogenol A tetra-acetate. The conversions, first, of soyasapogenol D and soyasapogenol C into a common derivative, and, secondly, of soyasapogenol B and soyasapogenol D into a common derivative, relate the position of the reactive double bond in soyasapogenol



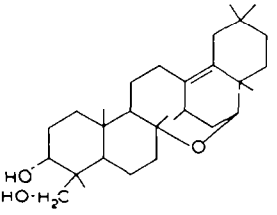
(I)



(II)



(III)



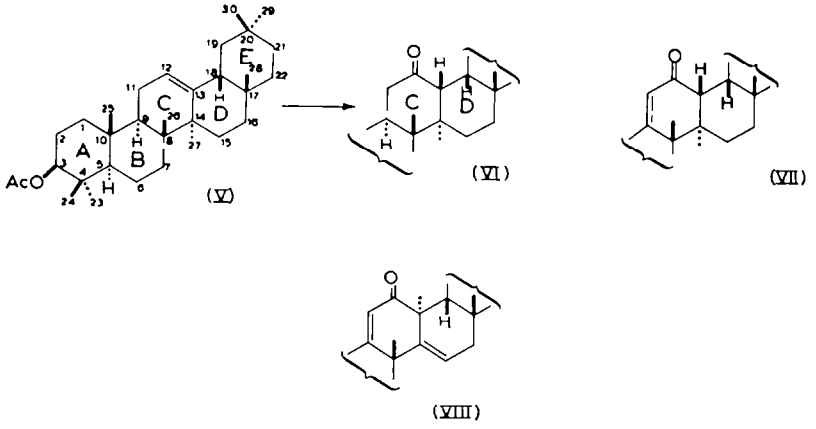
(IV)

C with the position of the isolated hydroxyl group in soyasapogenol B and with the position of one terminal of the oxide bridge in the tetracarbocyclic soyasapogenol D. In preliminary experiments, we converted soyasapogenol B into soyasapogenol C. Treatment of the former with acetone and sulphuric acid gives a 3β:24-*iso*propylidene derivative, which was dehydrated by reaction with phosphorus oxychloride and pyridine. Subsequent removal of the protecting *iso*propylidene group furnished soyasapogenol C, which was identified as its diacetate.

Meyer *et al.*[3] provided proof that the more reactive double bond in soyasapogenol C is of the type —CH=CH—, that this double bond is not located in ring A, and that the two double bonds in the sapogenol are not conjugated. Consequently, possible positions for the reactive double bond in soyasapogenol C are C_6–C_7, C_{15}–C_{16} and C_{21}–C_{22}, and the first of these was considered unlikely. In preliminary discussion, we designate the positions of the unlocated hydroxyl groups in soyasapogenol A as *x* and *y*.

Our interest in the soyasapogenols was aroused by the structure ascribed to soyasapogenol D by Meyer *et al.* and, as an essential prelude to a study of this compound, we undertook a further investigation of the soyasapogenols A, B and C. Our first objective was to test the structure (III) ascribed to soyasapogenol C. If this structure allocation is correct, soyasapogenol A must be 3β:15ξ:16ξ:24-tetrahydroxyolean-12-ene, e,g. (I), and to test this formula we applied to this sapogenol a series of reactions which involves ring D in an olean-12-ene derivative. Oxidation of β-amyrin acetate (V) with performic acid gives the saturated ketone, 12-oxo-oleanan-3β-yl acetate (VI), which reacts with bromine to furnish 12-oxo-olean-9(11)-en-3β-yl acetate (VII). Oxidation of this $\alpha\beta$-unsaturated ketone with selenium dioxide induces

rearrangement with the formation of 12-oxotaraxera-9(11):14-dien-3β-yl acetate (VIII).[4] Oxidation of soyasapogenol A tetra-acetate, $C_{38}H_{58}O_8$ [24:x:y-triacetoxy derivative of (V)] with performic acid gives a saturated ketone, $C_{38}H_{58}O_9$ [24:x:y-triacetoxy derivative of (VI)]. Bromine converts this saturated ketone into an $\alpha\beta$-unsaturated ketone, $C_{38}H_{56}O_9$ [24:x:y-triacetoxy derivative of (VII)], which shows



(V) (VI) (VII) (VIII)

an intense ultra-violet absorption maximum at 2470 Å. Oxidation of the latter compound with selenium dioxide yields a tetra-acetoxy-12-oxotaraxera-9(11):14-diene, $C_{38}H_{54}O_9$ [24:x:y-triacetoxy derivative of (VIII)], which gives a yellow colour with tetranitromethane and shows an intense absorption maximum at 2440 Å. Alkaline hydrolysis of the tetra-acetoxy-oxodiene, $C_{38}H_{54}O_9$, furnishes the corresponding tetrahydroxy-oxodiene, $C_{31}H_{46}O_5$. Normal acetylation of the tetrahydroxy-oxodiene regenerates the tetra-acetoxy-oxodiene. That these reactions of β-amyrin acetate and of soyasapogenol A tetra-acetate are structurally analogous is confirmed by the comparison of molecular rotation differences in Table 1.

TABLE 1

β-Amyrin series	M_D	Δ	Soyasapogenol A series	M_D	Δ
3β-Acetoxyolean-12-ene (V)	−374°	−447°	3β:24:x:y-Tetra-acetoxy-olean-12-ene	+546°	−417°
3β-Acetoxy-12-oxo-oleanane (VI)	− 73	+367	3β:24:x:y-Tetra-acetoxy-12-oxo-oleanane	+129	+347
3β-Acetoxy-12-oxo-olean-9(11)-ene (VII)	+294	−486	3β:24:x:y-Tetra-acetoxy-12-oxo-olean-9(11)-ene	+476	−487
3β-Acetoxy-12-oxo-taraxera-9(11):14-diene (VIII)	−192		3β:24:x:y-Tetra-acetoxy-12-oxo-taraxera-9(11):14-diene	−11	

[4] J. Green, N. Mower, C. W. Picard and F. S. Spring, *J. Chem. Soc.* 527 (1944); O. Jeger and L. Ruzicka, *Helv. Chim. Acta* **28**, 209 (1945); G. G. Allen, J. D. Johnston and F. S. Spring, *J. Chem. Soc.* 1546 (1954).

The formation of tetra-acetoxy-12-oxotaraxera-9(11):14-diene [24:x:y-triacetoxy derivative of (VIII)] from soyasapogenol A tetra-acetate, and its recovery after alkaline hydrolysis and reacetylation, proves that the α-glycol system in soyasapogenol A cannot include C_{15} and C_{16}. Consequently the formulae (I), (II), (III) and (IV) cannot represent the structures of the soyasapogenols.

The proof that ring D is not the seat of the α-glycol system in soyasapogenol A focussed attention on ring E as the most likely alternative site.[3] To test this possibility, we attempted to prepare the 18α-isomer of soyasapogenol B, since 21- or 22- substituents equatorially bonded in an oleanane derivative become axially bonded in the 18α-oleanane isomer, and similarly 21- or 22- substituents axially bonded in an oleanane derivative become equatorially bonded in the derived 18α-oleanane isomer. We attempted to apply to soyasapogenol B triacetate the method used for the conversion of β-amyrin acetate into 18α-olean-12-en-3β-ol.[5] Oxidation of soyasapogenol B triacetate with chromium trioxide gave a mixture, m.p. 242–248°, from which pure 3β:24-x-triacetoxy-11-oxo-olean-12-ene could not be separated. Its ultra-violet absorption spectrum (λ_{max} 2480 Å, ε 6000) showed that this mixture contains an appreciable amount of the required αβ-unsaturated ketone, but chromatography and fractional crystallisation failed to purify this component. The mixture was treated with strong alkali in the hope that the αβ-unsaturated ketone would be inverted at C_{18}. Surprisingly, the product did not show any appreciable absorption in the neighbourhood of 2480 Å, but it did show strong absorption in the ethylenic region of the spectrum, from which we conclude that the αβ-unsaturated ketone component had been converted into a non-conjugated unsaturated ketone [11-oxo-13(18)-ene]. Acetylation of this product and chromatography of the acetate mixture yielded a saturated ketone as the only crystalline fraction. This ketone is 3β:24:x-triacetoxy-12-oxo-oleanane, the reference specimen of which we prepared by oxidation of soyasapogenol B triacetate with performic acid; this saturated ketone has been obtained by Tsuda and Kitagawa[6] by oxidation of soyasapogenol B triacetate with either chromium trioxide or hydrogen peroxide in acetic acid. Finally, the mixture, m.p. 242–248°, was treated with hydrochloric and acetic acids. The product, m.p. 285–300°, showed an absorption maximum at 2420 Å. The shift in the position of the absorption maximum indicated that the αβ-unsaturated ketone component had been converted into its 18α-isomer. The latter compound, however, could not be separated from the mixture either by fractional crystallisation or by chromatography. Consequently this route was abandoned.

We next prepared the 11:13(18)-dienes from soyasapogenol A and soyasapogenol B to determine whether the consequential change in the conformation of ring E is reflected in a change in the ease of esterification of the x and y hydroxyl groups. Soyasapogenol B is converted into its triacetate by treatment with pyridine and acetic anhydride at 5°. Oxidation of soyasapogenol B triacetate with selenium dioxide in acetic acid gives 3β:24:x-triacetoxyoleana-11:13(18)-diene, which shows the characteristic ultra-violet absorption spectrum of oleana-11:13(18)-dienes with intense maxima at 2410, 2490 and 2590 Å. Acetylation of the corresponding triol, using acetic anhydride and pyridine at 5°, regenerates the parent triacetate. The trihydroxydiene was characterised as its *iso*propylidine derivative, and oxidation of this compound

[5] R. Budziarek, W. Manson and F. S. Spring, *J. Chem. Soc.* 3336 (1951).
[6] K. Tsuda and S. Kitagawa, *Ber. Dtsch. Chem. Ges.* 71, 790 (1938).

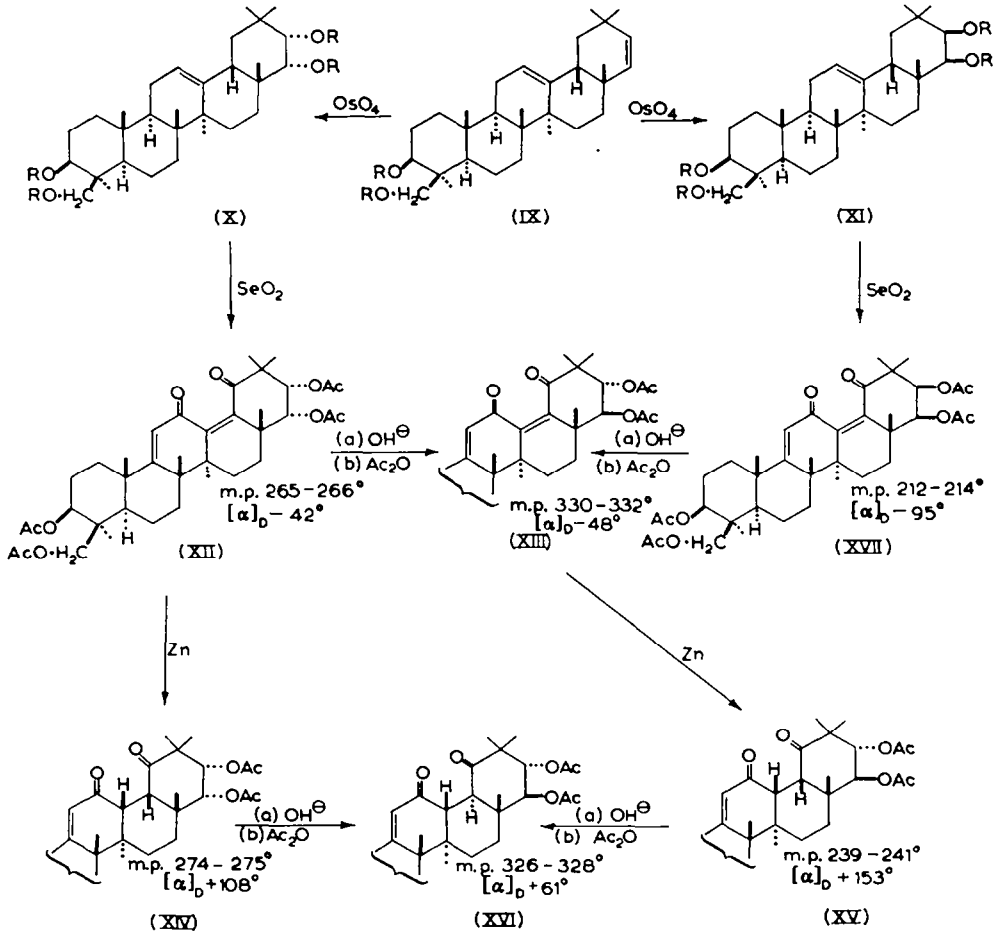
yielded *x*-oxo-3β:24-*iso*propylidenedioxyoleana-11:13(18)-diene. Acid hydrolysis of the protecting *iso*propylidene group and acetylation of the product furnished 3β:24-diacetoxy-*x*-oxo-oleana-11:13(18)-diene.

Oxidation of soyasapogenol A tetra-acetate with selenium dioxide in acetic acid yields 3β:24:*x*:*y*-tetra-acetoxyoleana-11:13(18)-diene. Acetylation of 3β:24:*x*:*y*-tetrahydroxyoleana-11:13(18)-diene, itself obtained by alkaline hydrolysis of the tetra-acetate, using acetic anhydride and pyridine at 5°, gave a mixture of a triacetate and the tetra-acetate. The triacetate is converted into the tetra-acetate by treatment with acetic anhydride and pyridine at 100°. Acetylation of soyasapogenol A, using acetic anhydride and pyridine at 5°, also gives a mixture of a triacetate and the tetra-acetate, and the former is converted into the tetra-acetate by hot acetylation. Oxidation of soyasapogenol A triacetate with selenium dioxide yields the triacetate of 3β:24:*x*:*y*-trihydroxyoleana-11:13(18)-diene, thus showing that the same hydroxyl group resists acetylation at 5° in both soyasapogenol A and in 3β:24:*x*:*y*-tetrahydroxyoleana-11:13(18)-diene. Although one interpretation of these reactions is that the α-glycol system in soyasapogenol A does not include C_{21} and C_{22}, an alternative explanation is that the method employed is not sufficiently delicate to detect the conformational change in ring E associated with the conversion of an olean-12-ene derivative into the related 11:13(18)-diene. That the latter is the correct explanation was shown by a study of the behaviour of 12:19-dioxo-9(11):13(18)-dienes derived from soyasapogenol A and soyasapogenol B.

Meyer *et al.* oxidised soyasapogenol A tetrabenzoate with selenium dioxide at 200° and obtained an amorphous oxidation product, which was not obtained crystalline after chromatography.[3] The amorphous product was hydrolysed by alkali, and the neutral product acetylated to give 3β:24:*x*:*y*-tetra-acetoxy-12:19-dioxo-oleana-9(11):13(18)-diene, m.p. 323–324°, $[\alpha]_D$ −48°, which shows the characteristic absorption spectrum of a 12:19-dioxo-oleana-9(11):13(18)-diene with a maximum at 2780 Å. We find that oxidation of soyasapogenol A tetra-acetate with selenium dioxide gives a different 3β:24:*x*:*y*-tetra-acetoxy-12:19-dioxo-oleana-9(11):13(18)-diene, m.p. 265–266°, $[\alpha]_D$ −42°, λ_{max} 2780 Å. When the tetra-acetoxy-dioxodiene, m.p. 265–266°, is hydrolysed with alkali and the product is acetylated, the higher melting isomer (m.p. 330–332°, $[\alpha]_D$ −48°, λ_{max} 2780 Å) is obtained. Since soyasapogenol A tetra-acetate is recovered unchanged after alkaline hydrolysis and acetylation of the product, the conversion of the tetra-acetoxy-dioxodiene, m.p. 265–266°, into the isomer, m.p. 330–332°, is supported by the 12:19-dioxo-9(11):13(18)-diene group or by part of this group, and this conversion is to be represented as a base-induced epimerisation of the groups attached to C_x and/or C_y. Now, 3β:24:*x*:*y*-tetra-acetoxy-12-oxo-olean-9(11)-ene [24:*x*:*y*-triacetoxy derivative of (VII)], prepared as described above, is recovered unchanged after hydrolysis with alkali and acetylation of the product, thus showing that the 12-oxo-9(11)-ene part of the dioxodiene chromophore is not in itself sufficient to support the base-induced epimerisation at C_x or C_y. That the 19- carbonyl is the activating group was shown as follows. Reduction of the tetra-acetoxy-dioxodiene, m.p. 265–266°, with zinc dust gives its 13β:18β-dihydro derivative, m.p. 274–275°, $[\alpha]_D$ +108°, λ_{max} 2440 Å. Similar reduction of the tetra-acetoxy-dioxodiene, m.p. 330–332°, gives its 13β:18β-dihydro derivative, m.p. 239–241°, $[\alpha]_D$ +153°, λ_{max} 2440 Å. Treatment of each of the isomeric dihydro derivatives with alkali and subsequent acetylation gives the same

(third) isomeric dihydro derivative, m.p. 326–328°, $[\alpha]_D$ +61°, λ_{max} 2430 Å. A rational interpretation of these isomerisations requires that the *cis*-1:2-glycol system in soyasapogenol A includes C_{21} and C_{22} (X, R = H, or XI, R = H), from which it follows that soyasapogenol C is 3β:24-dihydroxyoleana-12:21-diene (IX, R = H).

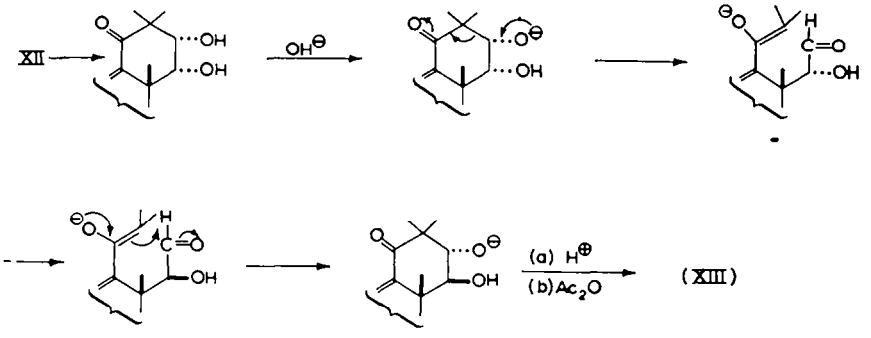
Meyer *et al.*[3] showed that oxidation of soyasapogenol C diacetate with osmium tetroxide, followed by decomposition of the reaction product with sodium sulphite, and subsequent acetylation, gave a mixture from which soyasapogenol A tetra-acetate, a stereoisomeric soyasapogenol A tetra-acetate and the 11-oxo derivative of the last compound were isolated. The stereoisomer of soyasapogenol A tetra-acetate and its 11-oxo derivative were obtained in approximately 25 per cent total yield, and soyasapogenol A tetra-acetate in approximately 6 per cent yield. We have repeated the oxidation of soyasapogenol C diacetate with osmium tetroxide; the reaction product was decomposed with lithium aluminium hydride and acetylated. We isolated the stereoisomeric soyasapogenol A tetra-acetate in 30 per cent yield and soyasapogenol A tetra-acetate in 8 per cent yield. The method used by us for isolating the reaction products would convert the 11-oxo derivative of the epimeric



(X) (IX) (XI) (XII) (XIII) (XVII) (XIV) (XVI) (XV)

soyasapogenol A tetra-acetate into the corresponding 9(11):12-diene, and, although this compound was not isolated in a pure state, the presence of a 9(11):12-diene was confirmed by the ultra-violet spectra of later fractions from the chromatograph used for the separation of the two stereoisomeric tetra-acetates. Since soyasapogenol A is formed as a minor oxidation product of soyasapogenol C, and the stereoisomeric tetrol is the major product, the latter is probably formed by attack at the less hindered β-face, and the former by attack at the more hindered α-face of ring E. Consequently, we provisionally represent soyasapogenol A as 3β:21α:22α-24-tetrahydroxyolean-12-ene (X, R = H). Soyasapogenol A tetra-acetate is (X, R = Ac) and the stereoisomeric soyasapogenol A tetra-acetate is 3β:21β:22β-24-tetra-acetoxyolean-12-ene (XI, R = Ac). These steric assignments at 21 and 22, in our view, require a more stringent proof; although it may transpire that they are to be reversed, the interpretations given below would still be valid in principle.

The dioxodiene, m.p. 265–266°, obtained by direct oxidation of soyasapogenol A tetra-acetate is (XII) and the isomeric dioxodiene, m.p. 330–332°, is (XIII). The conversion of (XII) into (XIII) is represented as a reversed aldol-type condensation, followed by an intramolecular direct aldol-type condensation whereby a *cis*-(equatorial: axial) glycol diacetate group is converted into a *trans*-(di-equatorial) glycol diacetate group:



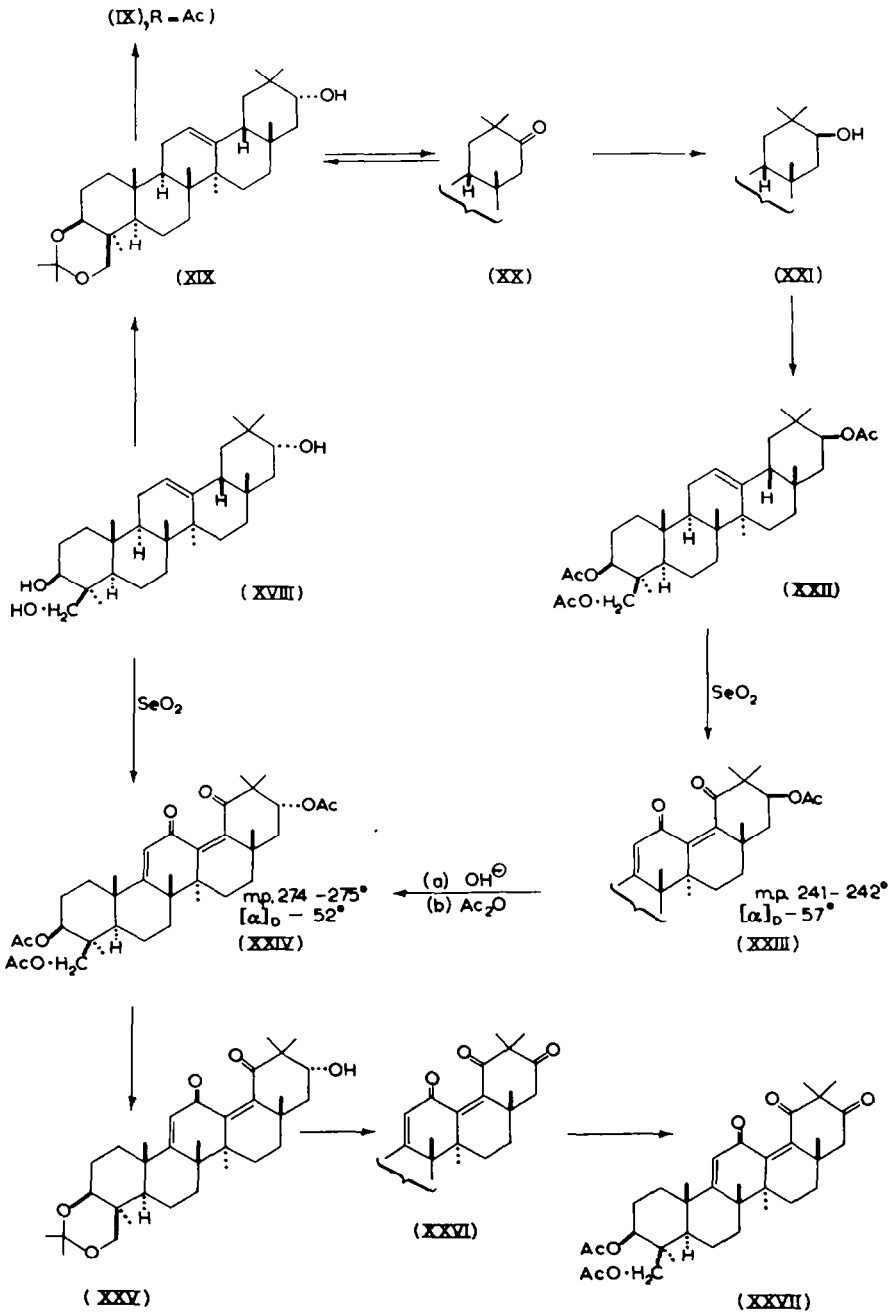
The dihydro derivative of the dioxodiene, m.p. 265–266°, is (XIV) and the dihydro derivative of the dioxodiene, m.p. 330–332°, is (XV). Treatment of (XV) with alkali inverts C_{18}, thereby giving, after acetylation, 3β:21α:22β:24-tetra-acetoxy-12:19-dioxo-18α-olean-9(11)-ene (XVI). In addition to inversion at C_{18}, treatment of (XIV) with alkali causes epimerisation at C_{22} by a reversed aldol: direct intramolecular aldol condensation sequence with the formation, after acetylation, of (XVI), the *cis*-(axial-equatorial) glycol diacetate group in (XIV) changing into a *trans*-(di-equatorial) glycol diacetate group.

Confirmation of the general validity of the mechanism suggested for the conversion of the dioxodiene, m.p. 265–266°, into the isomer, m.p. 330–332°, was obtained as follows. Vigorous oxidation of the stereoisomeric soyasapogenol A tetra-acetate (XI, R = Ac) with selenium dioxide gives its dioxodiene derivative (XVII), m.p. 212–214°, $[\alpha]_D$ −95°, λ_{max} 2780 Å, which, after treatment with alkali and subsequent acetylation, yields the tetra-acetoxy-dioxodiene, m.p. 330–332° (XIII). This isomerisation is represented again as a reversed aldol: direct aldol condensation sequence, which, in this case, effects epimerisation of a *cis*-(axial-equatorial) glycol diacetate group to a *trans*-(di-equatorial) glycol diacetate group.

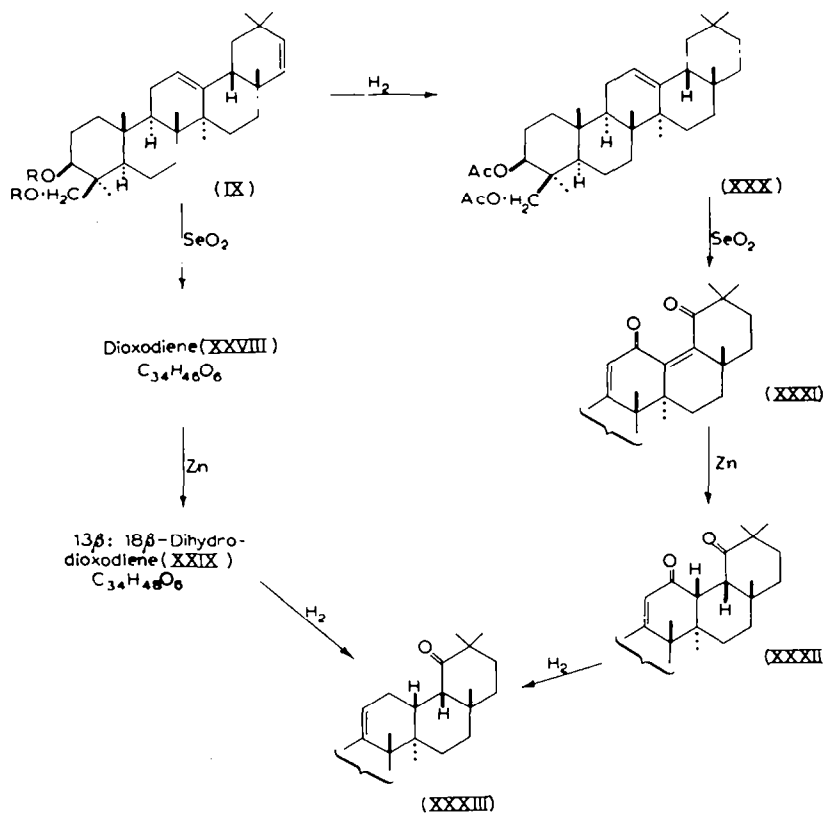
We next turn to a consideration of soyasapogenol B. Oxidation of soyasapogenol B triacetate with selenium dioxide gives 3β:24:*x*(or *y*)-triacetoxy-12:19-dioxo-oleana-9(11):13(18)-diene, m.p. 274–275°, $[\alpha]_D$ −52°, which is converted into the corresponding trihydroxy-dioxodiene by alkaline hydrolysis.[3] Acetylation of the last-named compound regenerates the parent triacetoxy-dioxodiene, m.p. 274–275°, $[\alpha]_D$ −52°. Considered together with the established relationship between soyasapogenol C (IX, R = H) and soyasapogenol B, this behaviour suggests that the latter compound is either a 3β:22:24-triol, in which case the related dioxodiene is not a β-hydroxyketone and therefore not suceptible to a reversed aldol-type condensation, or that it is 3β:21α:24-trihydroxyolean-12-ene (XVIII), in which case the 21-hydroxyl group in the related dioxodiene is an equatorial substituent and will not epimerise with alkali. A decision was made between these alternatives in favour of the latter by the following experiments. Treatment of soyasapogenol B (XVIII) with acetone and sulphuric acid furnished the *iso*propylidene derivative (XIX), which was oxidised by the chromium trioxide–pyridine complex to the 21-ketone (XX). Reduction of this ketone with lithium aluminium hydride gave a mixture of stereoisomers, which was separated by chromatography into the 21α-hydroxy compound (XIX) and its 21β-epimer (XXI). Hydrolysis of the *iso*propylidene derivative (XXI) with mineral acid and acetylation of the product produced 3β:21β:24-triacetoxyolean-12-ene (XXII). Vigorous oxidation of (XXII) with selenium dioxide furnished the corresponding dioxodiene (XXIII), m.p. 241–242°, $[\alpha]_D$ −56·8°, λ_{max} 2800 Å. Treatment of (XXIII) with alkali and subsequent acetylation gave 3β:21α:24-triacetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (XXIV), m.p. 274–275°, $[\alpha]_D$ −52°, identical with the product obtained by direct oxidation of soyasapogenol B triacetate with selenium dioxide. These experiments prove that the ring E hydroxyl group of soyasapogenol B is attached to C_{21} and that it is axially (α) bonded. In the derived dioxodiene triacetate (XXIV), the 21α-substituent is equatorially bonded and consequently alkali does not induce epimerisation. The 21-substituent in the epimer of soyasapogenol B triacetate (XXII) is equatorially bonded (β) and in the derived dioxodiene triacetate (XXIII) this substituent is axial. Consequently, when the dioxodiene triacetate (XXIII) is treated with alkali, a reversed aldol: direct aldol condensation sequence results in epimerisation to give, after acetylation, the 21α-(equatorial) acetate (XXIV).

As stated above, the oxidation of soyasapogenol B triacetate with selenium dioxide gives the dioxodiene derivative (XXIV), hydrolysis of which with alkali gives the related triol now identified as 3β:21α:24-trihydroxy-12:19-dioxo-oleana-9(11)-:13(18)-diene. With acetone and sulphuric acid this triol forms its 3β:24-*iso*propylidine derivative (XXV), which when oxidised with the chromium trioxide–pyridine complex gives the 3β:24-*iso*propylidene derivative of the 12:19:21-trioxo-9(11):13(18)-diene (XXVI). Hydrolysis of the last-named compound with mineral acid and acetylation of the product gave 3β:24-diacetoxy-12:19:21-trioxo-oleana-9(11):13(18)-diene (XXVII). Attempts were made to hydrolyse this α:γ-diketone with alkali and with alkaline hydrogen peroxide; the alkali-soluble reaction products were not, however, obtained crystalline.

We record some related experiments with soyasapogenol C diacetate (IX, R = Ac). Vigorous oxidation of the diacetate with selenium dioxide gives a dioxodiene derivative (XXVIII), which, surprisingly, does not give a colour with tetranitromethane. Reduction of the 13:18-double bond in this dioxodiene derivative with zinc gave the


(IX), R = Ac)
OH
(XIX)
(XX)
OH
(XXI)
OAc
AcO
AcO·H2C
(XXII)
OH
HO
HO·H2C
(XVIII)
SeO2
SeO2
OAc
mp. 274 -275°
[α]D − 52°
(XXIV)
(a) OH⊖
(b) Ac2O
OAc
mp. 241- 242°
[α]D − 57°
(XXIII)
OH
(XXV)
(XXVI)
AcO
AcO·H2C
(XXVII)

13β:18β-dihydro derivative (XXIX), which, again surprisingly, does not show isolated ethylenic absorption in the ultra-violet and does not give a colour with tetranitromethane. Vigorous oxidation of dihydrosoyasapogenol C diacetate (XXX) with selenium dioxide gives the dioxodiene derivative (XXXI), which is reduced by zinc to the 13β:18β-dihydro derivative (XXXII). Hydrogenolysis of 3β:24-diacetoxy-12:19-dioxo-olean-9(11)-ene (XXXII) gave 3β:24-diacetoxy-19-oxo-olean-9(11)-ene (XXXIII) and this ketone was also obtained by reduction of the dihydro-dioxodiene (XXIX) with hydrogen and platinum. In the latter case, hydrogenolysis of the 12-oxygen function is accompanied by reduction of the ring É double bond or its equivalent.



The identification of the soyasapogenols A, B, and C has a direct bearing upon the structure of soyasapogenol D. In particular, the identification of soyasapogenol B as 3β:21α:24-trihydroxyolean-12-ene (XVIII) shows that the oxide bridge in soyasapogenol D is attached to C_{21}. It is hoped to discuss the chemistry of this triterpenoid sapogenol in a later paper.

EXPERIMENTAL

M.p.'s are uncorrected. Rotations were measured in chloroform (unless otherwise stated) at 15–20°, and ultra-violet absorption spectra were measured in ethanol solutions. Grade II alumina and light petroleum, boiling range 60–80°, were used for chromatography.

Soya bean meal, which had been exhaustively extracted with light petroleum, was refluxed with boiling 80% alcohol and the extracted matter was hydrolysed successively with methanolic hydrochloric acid and with methanolic potassium hydroxide, essentially the method described by Meyer *et al.*[3] being used. A mixture of soyasapogenols and sterol was obtained from the alkaline liquor by extraction with benzene; approximately 10 g of this mixture was obtained from 3 kg of meal. The soyasapogenols were obtained from this mixture by using the preferred procedures described below; the physical constants of the sapogenols and their acetates observed by us are in good agreement with literature values. The sterol component of the mixture was identified as β-sitosterol.

Soyasapogenols A and B. The soyasapogenol-sterol mixture (65 g) was crystallised from benzene (650 ml) and the solid (25 g) was collected (mother liquor A) and acetylated with acetic anhydride and pyridine at 100°. A solution of the acetate mixture in light petroleum–benzene (5:1, 800 ml) was chromatographed on alumina (1 kg). Elution of the column with light petroleum–benzene mixtures (5:1, 5 l.; 4:1, 3 l.; 3:1, 4 l.) gave fractions which did not crystallise. Continued elution with light petroleum–benzene (1:1, 9·6 l.) gave crystalline fractions (total, 11 g), which were combined and crystallised from chloroform–methanol to yield soyasapogenol B triacetate as needles, m.p. 177–178°, $[\alpha]_D$ +79° (*c*, 1·2) (Found: C, 73·9; H, 9·8. Calc. for $C_{36}H_{56}O_6$: C, 73·9; H, 9·65 per cent). A solution of the triacetate in ether was refluxed with excess of lithium aluminium hydride for 1 hr and the product was crystallised from chloroform–methanol to give soyasapogenol B as needles, m.p. 260–261°, $[\alpha]_D$ +90° (*c*, 1·1).

A solution of soyasapogenol B (100 mg) in a cold mixture of acetic anhydride (5 ml) and pyridine (5 ml) was kept at 0–5° for 17 hr. Isolation of the product in the usual way gave soyasapogenol B triacetate (105 mg), as needles (from chloroform–methanol), m.p. and mixed m.p. 179–180°, $[\alpha]_D$ +77·5 (*c*, 1·0).

Continued elution of the alumina column with light petroleum–benzene (1:2, 16 l.), with benzene (12 l.) and with benzene–ether (20:1, 4 l.) gave fractions which crystallised with difficulty. Benzene–ether (10:1, 11 l.) then eluted crystalline fractions which were combined (total, 6·2 g) and recrystallised from chloroform–methanol to yield soyasapogenol A tetra-acetate as needles, m.p. 228–229°, $[\alpha]_D$ +85° (*c*, 1·0) (Found: C, 71·1; H, 9·1. Calc. for $C_{38}H_{58}O_8$: C, 71·0; H, 9·1 per cent). Hydrolysis of the tetra-acetate by boiling its solution in 3% methanolic potassium hydroxide for 3 hr gave soyasapogenol A as needles (from chloroform–methanol), m.p. 310–313°, $[\alpha]_D$ +103° (*c*, 0·5). Acetylation of soyasapogenol A by using acetic anhydride and pyridine at 100° regenerated the tetra-acetate as needles (from chloroform–methanol), m.p. and mixed m.p. 228–229°, $[\alpha]_D$ +85°.

Soyasapogenol D and β-sitosterol. The benzene mother liquor A (see above) was concentrated to half bulk. The amorphous solid (6·0 g) separating on standing was collected and acetylated by using pyridine and acetic anhydride at 100°, and a solution of the dry acetylated product in light petroleum–benzene (10:1, 1 l.) was chromatographed on alumina (180 g). Elution with light petroleum–benzene (10:1, 2 l.) gave amorphous fractions; continued washing with the same solvent mixture (9 l.) eluted crystalline fractions (total, 1·3 g), m.p.'s between 124° and 130°. These were combined and crystallised from chloroform–methanol to give β-sitosteryl acetate as plates, m.p. and mixed m.p. 128–129°, $[\alpha]_D$ −39·5° (*c*, 1·4). Alkaline hydrolysis of the acetate

and crystallisation of the product from chloroform–methanol gave β-sitosterol as needles, m.p. and mixed m.p. 135–136°, $[\alpha]_D$ −34° (*c*, 0·9).

Continued elution of the column with light petroleum–benzene (9:1, 2 l.; 4:1, 3·5 l.; 2:1, 2 l; 1:1, 4 l.) gave fractions (total 1·2 g) which after crystallisation from chloroform–methanol gave soyasapogenol D diacetate as plates, m.p. 191–192°, $[\alpha]_D$ −44° (*c*, 1·2) (Found: C, 75·3; H, 10·2. Calc. for $C_{34}H_{54}O_5$: C, 75·2; H, 10·0 per cent). Its infra-red spectrum (Nujol) includes a strong band at 1100 $cm.^{-1}$

A solution of the diacetate in ether was refluxed for 2 hr with an excess of lithium aluminium hydride and the product crystallised from chloroform–methanol to give soyasapogenol D as prisms, m.p. 297–299°, $[\alpha]_D$ −56·2° (*c*, 0·6).

Soyasapogenol C diacetate. The sapogenol-sterol mixture (60 g) was crystallised from methanol (200 ml). The separating solid (11 g) was recrystallised from benzene (150 ml). The solid was collected and the mother liquor was evaporated to dryness. The residue (6·5 g) was acetylated by using pyridine and acetic anhydride at 100°. A solution of the dry acetylated product in light petroleum–benzene (6:1, 500 ml) was chromatographed on alumina (250 g). After elution with light petroleum–benzene (6:1, 2 l.; 4:1, 1 l.), light petroleum–benzene (3:1, 4 l.) gave crystalline fractions (total, 1·4 g), which were combined and crystallised from chloroform–methanol to give soyasapogenol C diacetate as needles, m.p. 202–203°, $[\alpha]_D$ +59·5° (*c*, 1·3) (Found: C, 77·7; H, 10·2. Calc. for $C_{34}H_{52}O_4$: C, 77·8; H, 10·0 per cent).

Reactions of soyasapogenol A

3β:24-21α:22α-*Bis*-iso*propylidenedioxy-olean*-12-*ene.* A solution of soyasapogenol A (200 mg) in dry acetone (50 ml) and dry ether (200 ml) containing concentrated sulphuric acid (1 ml) was kept at 17° for 27 hr. The product was isolated in the usual way and purified by chromatography on alumina and crystallisation from chloroform–methanol to yield the *bis*-iso*propylidene derivative* as needles, m.p. 236–238°, $[\alpha]_D$ +93° (*c*, 1·5) (Found: C, 77·6; H, 10·6. $C_{36}H_{58}O_4$ requires C, 77·9; H, 10·5 per cent).

Soyasapogenol A triacetate. A solution of soyasapogenol A (130 mg) in a cold mixture of pyridine and acetic anhydride (1:1, 10 ml) was kept at 0–5° for 17 hr. The product was isolated in the usual way and its solution in light petroleum–benzene (2:1, 100 ml) was chromatographed on alumina (5 g). Elution with light petroleum–benzene (1:3, 7 × 150 ml) gave fractions (total, 85 mg) which crystallised from chloroform–methanol to yield soyasapogenol A tetra-acetate as needles, m.p. and mixed m.p. 228–230°, $[\alpha]_D$ +85° (*c*, 1·2). Further elution with benzene (500 ml), benzene–ether (20:1, 400 ml; 10:1, 500 ml; 4:1, 500 ml) gave fractions (total 45 mg) which crystallised from chloroform–methanol to yield *soyasapogenol A triacetate* as plates, m.p. 256–258°, $[\alpha]_D$ +71·7° (*c*, 0·8) (Found: C, 71·6; H, 9·3. $C_{36}H_{56}O_7$ requires C, 72·0; H, 9·4 per cent). Acetylation of the triacetate by using pyridine and acetic anhydride at 100° gave soyasapogenol A tetra-acetate as needles (from chloroform–methanol), m.p. and mixed m.p. 228–230°, $[\alpha]_D$ +83° (*c*, 0·6). Chromatography of soyasapogenol A tetra-acetate on the same preparation of alumina as that used for the separation of the triacetate gave an almost quantitative recovery of tetra-acetate.

Oxidation of soyasapogenol A tetra-acetate with performic acid. Soyasapogenol A tetra-acetate (1·0 g) in ethyl acetate (40 ml) was treated at 45° with a solution of

hydrogen peroxide (100 volume, 6·5 ml) in formic acid (99–100%, 34 ml) added dropwise over 3 hr. The solution was kept at 45° for 3 hr and then concentrated to one-third bulk. The crystals (750 mg) separating were recrystallised from chloroform–methanol, from which 3β:21α:22α:24-*tetra-acetoxy*-12-*oxo-oleanane* separated as needles, m.p. 308–310°, $[\alpha]_D$ +19·6° (*c*, 1·2) (Found: C, 69·1; H, 8·8. $C_{38}H_{58}O_9$ requires C, 69·3; H, 8·9 per cent). It does not give a colour with tetranitromethane in chloroform.

3β:21α:22α:24-*Tetra-acetoxy*-12-*oxo-olean*-9(11)-*ene*. A solution of bromine (0·38 g) in glacial acetic acid (25 ml) was added over 20 min to a solution of the saturated 12-ketone (1·4 g) in glacial acetic acid (100 ml) at 60–63°. The mixture was kept at 100° for 5 hr and at room temperature overnight. Water was added to the heated solution until crystals formed. After standing, the crystals (1·1 g) were collected and recrystallised from chloroform–methanol, from which 3β:21α:22α:24-*tetra-acetoxy*-12-*oxo-olean*-9(11)-*ene* separated as needles, m.p. 275–276°, $[\alpha]_D$ +72·6° (*c*, 1·0), λ_{max} 2470 Å (ε 11,000) (Found: C, 69·7; H, 8·4. $C_{38}H_{56}O_9$ requires C, 69·5; H, 8·6 per cent). It does not give a colour with tetranitromethane.

A solution of the tetra-acetoxy-αβ-unsaturated ketone (120 mg) in methanolic potassium hydroxide (3%, 30 ml) was refluxed for 2½ hr. The product was isolated by means of ether and acetylated by using pyridine and acetic anhydride at 100°. Crystallisation of the acetylated product from chloroform–methanol gave 3β:21α:22α-24-tetra-acetoxy-12-oxo olean-9(11)-ene as needles, m.p. and mixed m.p. 272–274°, $[\alpha]_D$ +72·9° (*c*, 1·1).

Oxidation of tetra-acetoxy-12-*oxo-olean*-9(11)-*ene with selenium dioxide*. Selenium dioxide (1·5 g) was added to a solution of the tetra-acetoxy-αβ-unsaturated ketone (900 mg) in glacial acetic acid (30 ml) and the mixture was heated under reflux for 24 hr. Water was added to the filtered solution, and the product was isolated by means of ether. It was purified by chromatography on alumina, and crystallisation from aqueous methanol gave 3β:21α:22α:24-*tetra-acetoxy*-12-*oxo-taraxera*-9(11):14-*diene* as plates, m.p. 240–241°, $[\alpha]_D$ −1·7° (*c*, 4·1). λ_{max} 2440 Å (ε 11,200 and $\varepsilon_{2\cdot80}$ 8000) (Found: C, 69·8; H, 8·4. $C_{38}H_{54}O_9$ requires C, 69·7; H, 8·3 per cent). It gives a pale yellow colour with tetranitromethane in chloroform.

3β:21α:22α:24-*Tetrahydroxy*-12-*oxo-taraxera*-9(11):14-*diene*. A solution of 3β:21α:22α:24-tetra-acetoxy-12-oxo-taraxera-9(11):14-diene (200 mg) in 3% methanolic potassium hydroxide was refluxed for 3 hr. The product was isolated by means of ether and crystallised from aqueous methanol to give the *tetrol* as prismatic needles, m.p. 296–298°, $[\alpha]_D$ −54·8° (*c*, 1·6 in methanol), λ_{max} 2440 Å (ε 11,000 and ε_{2080} 7500) (Found: C, 74·1; H, 9·6. $C_{30}H_{46}O_5$ requires C, 74·0; H, 9·5 per cent). Acetylation of the tetrol, using pyridine and acetic anhydride, gave the tetra-acetate as plates (from aqueous methanol), m.p. and mixed m.p. 240–241°, $[\alpha]_D$ −1·6° (*c*, 2·0).

Oxidation of soyasapogenol A tetra-acetate with selenium dioxide to 3β:21α:22α:24-*tetra-acetoxy-oleana*-11:13(18)-*diene*. Selenium dioxide (200 mg) was added to a solution of soyasapogenol A tetra-acetate (200 mg) in glacial acetic acid (30 ml) and the mixture was refluxed for 1 hr. The hot mixture was filtered and the product was isolated by means of ether and purified by chromatography on alumina and by crystallisation from chloroform–methanol to give 3β:21α:22α:24-*tetra-acetoxy-oleana*-11:13(18)-*diene* (150 mg) as needles, m.p. 242–243°, $[\alpha]_D$ +13·1° (*c*, 1·5), λ_{max} 2410, 2490 and 2590 Å (ε 30,000, 34,400 and 21,800) (Found: C, 71·2; H, 8·8.

$C_{38}H_{56}O_8$ requires C, 71·2; H, 8·8 per cent). Hydrolysis of the tetra-acetoxy-diene by refluxing its solution in 3% methanolic potassium hydroxide for 3 hr and crystallisation of the product from methanol gave 3β:21α:22α:24-*tetrahydroxyoleana*-11:13-(18)-*diene* as plates, m.p. 322–324°, $[\alpha]_D$ −42·6° (*c*, 1·3 in ethanol), λ_{max} 2410, 2490 and 2590 Å (ε 30,000, 34,200 and 21,800) (Found: C, 76·15; H, 10·4. $C_{30}H_{48}O_4$ requires C, 76·2; H, 10·2 per cent).

3β:21α:22α:24-*Tetrahydroxyoleana*-11:13(18)-*diene triacetate.* (a) A solution of the tetrahydroxy-diene in a mixture of pyridine and acetic anhydride (1:1, 10 ml) was kept overnight at 0–5°. The product, isolated in the usual way, was dissolved in light petroleum–benzene (2:1, 100 ml) and the solution was chromatographed on alumina (5 g). Elution with light petroleum–benzene (1:3, 5 × 130 ml) gave fractions (total 60 mg) which crystallised from chloroform–methanol to yield 3β:21α:22α:24-tetra-acetoxy-oleana-11:13(18)-diene as needles, m.p. and mixed m.p. 241–242°, $[\alpha]_D$ +13° (*c*, 1·0). Continued elution with ether and ether–methanol (20:1) gave fractions (total, 50 mg), which crystallised from chloroform–methanol to yield 3β:21α:22α:24-*tetrahydroxyoleana*-11:13(18)-*diene triacetate* as rods, m.p. 256–258°, $[\alpha]_D$ −10·5° (*c*, 1·1), λ_{max} 2420, 2500 and 2600 Å (ε 30,000, 34,200 and 21,900) (Found: C, 71·6; H, 9·3. $C_{36}H_{54}O_7$ requires C, 72·2; H, 9·1 per cent). Acetylation of the triacetate by using pyridine and acetic anhydride at 100° gave the tetra-acetate as needles (from chloroform–methanol), m.p. and mixed m.p. 241–242°, $[\alpha]_D$ +12° (*c*, 0·9). Chromatography of tetra-acetoxy-oleana-11:13(18)-diene on the same preparation of alumina as that employed for the separation of the triacetate gave a nearly quantitative recovery of the tetra-acetate.

(b) A solution of soyasapogenol A triacetate (70 mg) in glacial acetic acid (20 ml) was refluxed with selenium dioxide (70 mg) for 1 hr. The product was isolated by means of ether and its solution in light petroleum–benzene (1:1, 100 ml) was chromatographed on alumina (4 g). Elution with ether–methanol (20:1, 3 × 50 ml) gave fractions (total, 45 mg) which crystallised from chloroform–methanol to yield 3β:21α:22α:24-tetrahydroxyoleana-11:13(18)-diene triacetate as rods, m.p. and mixed m.p. 256–258°, $[\alpha]_D$ −9·0° (*c*, 0·5).

Oxidation of soyasapogenol A tetra-acetate (X, R = Ac) *with selenium dioxide to* 3β-21α:22α:24-*tetra-acetoxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene* (XII). A solution of soyasapogenol A tetra-acetate (2·1 g) in benzyl acetate (30 ml) was refluxed with powdered selenium dioxide (2·1 g) for 24 hr. The filtered solution was evaporated to dryness under reduced pressure and the product was purified by chromatography on alumina and by crystallisation from chloroform–methanol to yield 3β:21α:22α:24-*tetra-acetoxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene* (850 mg) as needles, m.p. 265–266° $[\alpha]_D$ −42·5° (*c*, 1·0), λ_{max} 2780 Å (ε 13,600) (Found: C, 68·4; H, 8·0. $C_{38}H_{52}O_{10}$ requires C, 68·2; H, 7·8 per cent). It does not give a colour with tetranitromethane in chloroform.

3β:21α:22β:24-*Tetra-acetoxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene* (XIII). A solution of 3β:21α:22α:24-tetra-acetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (100 mg) in methanolic potassium hydroxide (3%, 30 ml) was refluxed for 2½ hr. The product was isolated by means of ether and chloroform and acetylated by using acetic anhydride and pyridine. Crystallisation of the acetylated product from chloroform–methanol gave 3β:21α:22β:24-*tetra-acetoxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene* (75 mg) as prismatic needles, m.p. 330–332° (dec.), $[\alpha]_D$ −48·4° (*c*, 1·8), λ_{max}

2780 Å (ε 13,200) (Found: C, 68·0; H, 7·9. $C_{38}H_{52}O_{10}$ requires C, 68·2; H, 7·8 per cent). It does not give a colour with tetranitromethane in chloroform. A mixture with the isomeric 3β:21α:22α:24-tetra-acetate had m.p. 254°.

From the mother liquors of the dioxo-3β:21α:22β:24-tetra-acetate, unchanged 3β:21α:22α:24-tetra-acetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (10 mg), m.p. and mixed m.p. 263–267°, $[\alpha]_D$ −44° (*c*, 0·5), was isolated.

3β:21α:22α:24-*Tetra-acetoxy*-12:19-*dioxo-olean*-9(11)-*ene* (XIV). A solution of 3β:21α:22α:24-tetra-acetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (400 mg) in ethanol (50 ml) was refluxed with freshly activated zinc dust (4 g) for 5 hr. The product was isolated in the usual way and crystallised from chloroform–methanol to yield 3β:21α:22α:24-*tetra-acetoxy*-12:19-*dioxo-olean*-9(11)-*ene* (330 mg) as plates, m.p. 274–275°, $[\alpha]_D$ +108·4° (*c*, 1·5), λ_{max} 2440 Å (ε 12,100) (Found: C, 68·2; H, 8·3. $C_{38}H_{54}O_{10}$ requires C, 68·0; H, 8·1 per cent).

3β:21α:22β:24-*Tetra-acetoxy*-12:19-*dioxo-olean*-9(11)-*ene* (XV). 3β:21α:22β:24-Tetra-acetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (310 mg) was reduced in ethanol with zinc dust as described above. The product was crystallised from chloroform–methanol to give 3β:21α:22β:24-*tetra-acetoxy*-12:19-*dioxo-olean*-9(11)-*ene* (220 mg) as blades, m.p. 239–241°, $[\alpha]_D$ +153·5° (*c*, 1·0), λ_{max} 2440 Å (ε 12,000) (Found: C, 68·2; H, 8·3. $C_{38}H_{54}O_{10}$ requires C, 68·0; H, 8·1 per cent).

3β:21α:22β:24-*Tetra-acetoxy*-12:19-*dioxo*-18α-*olean*-9(11)-*ene* (XVI). (a) A solution of 3β:21α:22α:24-tetra-acetoxy-12:19-dioxo-olean-9(11)-ene (150 mg) in aqueous methanolic potassium hydroxide (10%, 100 ml) was refluxed for 6 hr in an atmosphere of nitrogen. The product was isolated by means of chloroform and re-acetylated by treatment with pyridine and acetic anhydride for 16 hr at 15°. Crystallisation of the acetylated product from chloroform–methanol gave 3β:21α:22β:24-*tetra-acetoxy*-12:19-*dioxo*-18α-*olean*-9(11)-*ene* (110 mg) as needles, m.p. 326–328°, $[\alpha]_D$ +60·2° (*c*, 0·85), λ_{max} 2430 Å (ε 11,400) (Found: C, 68·0; H, 8·2. $C_{38}H_{50}O_{10}$ requires C, 68·0; H, 8·1 per cent).

(b) 3β:21α:22β:24-Tetra-acetoxy-12:19-dioxo-olean-9(11)-ene (87 mg) was treated with alkali in an atmosphere of nitrogen and the product was re-acetylated as described under (a) above. Crystallisation from methanol–chloroform yielded 3β:21α:22β:24-tetra-acetoxy-12:19-dioxo-18α-olean-9(11)-ene (60 mg) as needles, m.p. and mixed m.p. 326–328°, $[\alpha]_D$ +61° (*c*, 0·8), λ_{max} 2430 Å (ε 11,200).

When the isomerisations described under (a) and (b) were effected in air, and not in an atmosphere of nitrogen, the product was in each case contaminated with 3β:21α:22β:24-tetra-acetoxy-12:19-dioxo-oleana-9(11):13(18)-diene. For example, repetition of experiment (b) in air gave a product, m.p. 326–328°, $[\alpha]_D$ +39° (*c*, 1·0), λ_{max} 2440 (ε 10,000) and 2780 Å (ε 2000), which could not be resolved into its components by crystallisation.

Reactions of soyasapogenol B

Oxidation of soyasapogenol B triacetate with performic acid. Soyasapogenol B triacetate (1·0 g) was oxidised with performic acid by the method described for the oxidation of soyasapogenol A tetra-acetate. The product was crystallised from chloroform–methanol to yield 3β:21α:24-triacetoxy-12-oxo-oleanane (700 mg) as plates, m.p. 264–265°, $[\alpha]_D$ −44° (*c*, 3·1) (Found: C, 72·1; H, 9·3. Calc. for $C_{36}H_{56}O_7$: C, 72·0; H, 9·4 per cent). Tsuda and Kitagawa[6] give m.p. 254–256° for this keto-acetate.

A solution of the keto-acetate in 3% methanolic potassium hydroxide was refluxed for 3 hr, and the product was crystallised from aqueous methanol to yield 3β:21α:24-trihydroxy-12-oxo-oleanane as needles, m.p. 258–260°, $[\alpha]_D$ −10·2° (*c*, 1·5) (Found; C, 75·6; H, 10·3. Calc. for $C_{30}H_{50}O_4$: C, 75·9; H, 10·6 per cent). Tsuda and Kitagawa[6] give m.p. 253–254° for this keto-triol.

Oxidation of soyasapogenol B triacetate with chromium trioxide. A solution of soyasapogenol B triacetate (1·0 g) in glacial acetic acid (50 ml) was treated at room temperature with a solution of chromium trioxide (0·75 g) in water (0·7 ml) and acetic acid (7·5 ml) was added with stirring over 20 min. After 17 hr, the neutral product was isolated in the usual way and crystallised from chloroform–methanol to give plates (540 mg), m.p. 242–248°, $[\alpha]_D$ +30° (*c*, 2·0), λ_{max} 2480 Å (ε 6000). Attempts to separate the $\alpha\beta$-unsaturated ketone component of this mixture by careful chromatography, by fractional crystallisation and by fractional solution all failed. Oxidation of soyasapogenol B triacetate with chromium trioxide at 60° gave a similar inseparable mixture of saturated ketone and $\alpha\beta$-unsaturated ketone.

A solution of the mixture [m.p. 242–248°, λ_{max} 2480 Å (ε 6000), 340 mg] in 3% methanolic potassium hydroxide was refluxed for 6 hr. The product, a gum, did not show selective absorption near 2500 Å, but did show strong end absorption (ε_{2340} = 5000). The gum (310 mg) was acetylated by using pyridine and acetic anhydride, and a solution of the dry acetylated product in light petroleum–benzene (3:1, 50 ml) was chromatographed on alumina (10 g). Elution with benzene (200 ml) gave fractions (150 mg) which crystallised from chloroform–methanol to give 3β:21α:24-triacetoxy-12-oxo-oleanane as plates, m.p. and mixed m.p. 264–265°, $[\alpha]_D$ −4·4°(*c*, 1·2) (Found: C, 72·3; H, 9·3. Calc. for $C_{36}H_{56}O_7$: C, 72·0; H, 9·4 per cent).

A solution of the mixture (200 mg), m p. 242–248°, in acetic acid (20 ml) containing concentrated hydrochloric acid (2 ml), was heated on a steam-bath for 3 hr. The product crystallised from chloroform–methanol as plates, m.p. 285–300°, λ_{max} 2420 Å (ε 6000). The mixture could not be separated by crystallisation or by chromatography.

Oxidation of soyasapogenol B triacetate with selenium dioxide to 3β:21α:24-*triacetoxyoleana*-11:13(18) *diene.* A solution of soyasapogenol B triacetate (1·0 g) in glacial acetic acid (150 ml) was refluxed with selenium dioxide (1·0 g) for 1 hr. The product was isolated in the usual way and purified by chromatography on alumina and crystallisation from chloroform–methanol to yield 3β:21α:24-*triacetoxyoleana*-11:13(18)-*diene* as needles, m.p. 250–251°, $[\alpha]_D$ −16·3° (*c*, 1·0), λ_{max} 2410, 2490 and 2590 Å (ε 30,000, 34 000 and 21,800) (Found: C, 74·0; H, 9·4. $C_{36}H_{54}O_6$ requires C, 74·2; H, 9·3 per cent). The triacetoxy-diene was hydrolysed by means of lithium aluminium hydride in ether. The trihydroxy-diene, which was not purified, was dissolved in a cold mixture of acetic anhydride and pyridine (1:1) and the solution was kept at 5° for 17 hr. The product was purified by chromatography on alumina and by crystallisation from chloroform–methanol to give the triacetoxy-diene as needles, m.p. and mixed m.p. 250–251°, $[\alpha]_D$ −16·1° (*c*, 1·0).

21α-*Hydroxy*-3β:24-iso*propylidenedioxyoleana*-11:13(18)-*diene.* A solution of 3β:21α:24-trihydroxyoleana-11:13(18)-diene (400 mg) in dry acetone (60 ml) and dry ether (300 ml) was treated with concentrated sulphuric acid (2 ml). After standing at 17° for 18 hr, the mixture was diluted with ether and washed with aqueous sodium hydrogen carbonate. The product was purified by chromatography on alumina and

crystallisation from chloroform–light petroleum to yield the *hydroxy-isopropylidene derivative* as plates, m.p. 235–236°, $[\alpha]_D$ −84° (*c*, 0·9) λ_{max} 2430, 2510 and 2600 Å (ε 29,000, 33,700 and 22,500) (Found: C, 79·8; H, 10·6; $C_{33}H_{52}O_3$ requires C, 79·8; H, 10·55 per cent).

21-*Oxo*-3β:24-iso*propylidenedioxyoleana*-11:13(18)-*diene*. The hydroxy-*iso*propylidene derivative (210 mg) was oxidised by treatment with the pyridine–chromium trioxide complex in the usual way. The product was purified by chromatography on alumina. Crystallisation from chloroform–light petroleum yielded 21-*oxo*-3β:24-iso*propylidenedioxyoleana*-11:13(18)-*diene* (170 mg) as rods, m.p. 243–245°, $[\alpha]_D$ −65° (*c*, 2·8), λ_{max} 2420, 2500 and 2590 Å (ε 25,800, 30,400 and 20,000). The infra-red spectrum includes bands at 1704 (carbonyl) and at 1155, 1105 and 1093 cm^{-1} (*iso*propylidenedioxy) (Found: C, 79·9; H, 10·2. $C_{33}H_{50}O_3$ requires C, 80·1; H, 10·2 per cent).

3β:24-*Diacetoxy*-21-*oxo-oleana*-11:13(18)-*diene*. A solution of the oxo-*iso*propylidene derivative (130 mg) in methanol (100 ml) containing concentrated hydrochloric acid (25 ml) was refluxed for 20 min. The product was isolated in the usual way and acetylated by treatment with acetic anhydride and pyridine at 100°. Crystallisation of the acetylated product from methanol gave 3β:24-*diacetoxy*-21-*oxo*-*oleana*-11:13(18)-*diene* (100 mg) as plates, m.p. 239–241°, $[\alpha]_D$ −33° (*c*, 0·8) λ_{max} 2420, 2520 (ε 30,000) and 2590 Å (Found: C, 75·6; H, 9·6. $C_{34}H_{50}O_6$ requires C, 75·8; H, 9·4 per cent). The infra-red spectrum (Nujol) includes bands at 1715 (carbonyl), 1736, 1266 and 1239 cm^{-1} (acetate).

Treatment of soyasapogenol B with acetone and sulphuric acid. A solution of soyasapogenol B (6·0 g) in dry ether (2 l.) and dry acetone (500 ml) containing sulphuric acid (20 ml) was kept at 17° for 60 hr. The mixture was diluted with ether and washed with aqueous sodium hydrogen carbonate. The product, isolated in the usual way, was purified by chromatography on alumina followed by crystallisation from aqueous methanol to give 21α-*hydroxy*-3β:24-iso*propylidenedioxyolean*-12-*ene* (XIX) as needles, m.p. 200–201°, $[\alpha]_D$ +73·6° (*c*, 2·2) (Found: C, 79·6; H, 10·9. $C_{33}H_{54}O_3$ requires C, 79·5; H, 10·9 per cent).

Conversion of soyasapogenol B (XVIII) *into soyasapogenol C* (IX, R = H). A solution of the *iso*propylidene derivative of soyasapogenol B (120 mg) in pyridine (20 ml) and phosphorus oxychloride (5 ml) was refluxed for 2 hr. The product was isolated by means of ether, and its solution in methanolic hydrochloric acid (2 N, 5 ml) was refluxed for 20 min. The crystalline product was isolated by using ether and acetylated by means of acetic anhydride and pyridine at 100°. The acetylated product was purified by chromatography on alumina and by crystallisation from chloroform–methanol to give soyasapogenol C diacetate (66 mg) as needles, m.p. and mixed m.p 200–201°, $[\alpha]_D$ +59° (*c*, 1·1). The infra-red spectrum of this specimen was identical with that of a specimen of soyasapogenol C diacetate isolated directly from soya bean.

Oxidation of 21α-*hydroxy*-3β:24-iso*propylidenedioxyolean*-12-*ene* (XIX). The complex prepared from chromium trioxide (3·0 g) and pyridine (30 ml) was added to a solution of the *iso*propylidene derivative of soyasapogenol B (3·0 g) in pyridine (30 ml) and the mixture was kept for 18 hr at 17° with occasional shaking. The product was isolated in the usual manner and its solution in light petroleum (300 ml) was chromatographed on alumina (100 g). Elution with the same solvent (2 l.) gave fractions which were combined and recrystallised from methanol to yield 21-*oxo*-3β:24-iso*propylidenedioxyolean*-12-*ene* (XX) (1·9 g) as prisms, m.p. 208–209°, $[\alpha]_D$

+14·3° (*c*, 0·9) (Found: C, 80·1; H, 10·7. $C_{33}H_{52}O_3$ requires C, 79·8; H, 10·55 per cent). The infra-red spectrum includes a strong band at 1703 cm^{-1}.

Reduction of 21-*oxo*-3β:24-iso*propylidenedioxyolean*-12-*ene* (XX) *with lithium aluminium hydride.* A solution of the ketone (1·8 g) in dry ether was refluxed with an excess of lithium aluminium hydride for 2½ hr. The product was isolated in the usual way and its solution in light petroleum (250 ml) was chromatographed on alumina (120 g). Elution with benzene (2·5 l.) gave fractions (total, 800 mg) which crystallised from methanol to yield 21α-hydroxy-3β:24-*iso*propylidenedioxyolean-12-ene as needles, m.p. and mixed m.p. 200–201°, $[\alpha]_D$ −73° (*c*, 1·1). Benzene (500 ml) and then benzene–ether (10:1, 2·5 l.) eluted fractions (800 mg) which crystallised from aqueous methanol as rosettes of needles, m.p. 127–140°. A solution of these fractions in light petroleum–benzene (1:1, 50 ml) was again chromatographed on alumina (70 g). Elution with light petroleum–benzene (1:9, 125 ml) gave a fraction (260 mg), m.p. 168–170°, $[\alpha]_D$ +70° (*c*, 0·6), which appeared to be a mixture. Continued elution with the same solvent mixture (1·8 l.) gave a fraction (500 mg), which after crystallisation from methanol yielded 21β-*hydroxy*-3β:24-iso*propylidenedioxyolean*-12-*ene* (XXI as needles, m.p. 128–130°, $[\alpha]_D$ +57·8° (*c*, 1·7) (Found: C, 79·3; H, 11·2 $C_{33}H_{54}O_3$ requires C, 79·5; H, 10·9 per cent). The infra-red spectrum includes a band at 3509 cm^{-1}.

3β:21β:24-*Triacetoxyolean*-12-*ene* (XXII). A solution of the 21β-hydroxy-*iso*propylidene derivative (500 mg) in methanol (150 ml) and concentrated hydrochloric acid (37·5 ml) was refluxed for 15 min. The mixture was diluted with water and the crystalline product was isolated by means of ether. The hydrolysis product was acetylated by treatment with acetic anhydride and pyridine for 48 hr at 17°. The acetylated product was isolated in the usual way and purified by chromatography on alumina and crystallisation from chloroform–methanol from which 3β:21β:24-*triacetoxy-olean*-12-*ene* separated as blades, m.p. 214–215°, $[\alpha]_D$ +64·5 °(*c*, 2·5) (Found: C, 74·0; H, 9·7. $C_{36}H_{56}O_6$ requires C, 73·9; H, 9·65 per cent).

Vigorous oxidation of soyasapogenol B triacetate with selenium dioxide to 3β:21α:24-*triacetoxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene* (XXIV). A solution of soyasapogenol B triacetate (1·8 g) in benzyl acetate (35 ml) was refluxed with powdered selenium dioxide (1·8 g) for 21 hr. The product was isolated in the usual way and purified by chromatography on alumina. Subsequent crystallisation of the product from chloroform–light petroleum and from chloroform–methanol gave 3β:21α:24-triacetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (800 mg) as rods, m.p. 274–275°, $[\alpha]_D$ −52° (*c*, 2·5), λ_{max} 2780 Å (ε 12,800) (Found: C, 70·6; H, 8·5; Calc. for $C_{36}H_{50}O_8$: C, 70·8; H, 8·25 per cent). Meyer *et al.*[3] give m.p. 267·5–268° and $[\alpha]_D$ −48° for this compound.

3β:21α:24-*Trihydroxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene*. A solution of the dioxodiene triacetate (500 mg) in 3% methanolic potassium hydroxide (100 ml) was refluxed for 2½ hr. The product was isolated by means of chloroform and crystallised from aqueous methanol to give 3β:21α:24-trihydroxy-12:19-dioxo-olcana-9(11):13(18)-diene (405 mg) as plates, m.p. 301–303°, $[\alpha]_D$ −145° (*c*, 0·4 in pyridine), λ_{max} 2800 Å (ε 11,900). Meyer *et al.*[3] give m.p. 300–301°, $[\alpha]_D$ −145° (pyridine) for this compound. The triol was acetylated by using acetic anhydride and pyridine at 100° and the product was crystallised from chloroform–methanol to give 3β:21α:24-triacetoxy-12:19-dioxo-oleana-9(11):13(18)-diene as rods, m.p. and mixed m.p. 273–274°, $[\alpha]_D$ −52° (*c*, 2·6), λ_{max} 2780 Å (ε 12,750.)

Vigorous oxidation of 3β:21β:24-*triacetoxyolean*-12-*ene* (XXII) *with selenium dioxide.* A solution of the triacetate (450 mg) in benzyl acetate (10 ml) was refluxed with selenium dioxide (400 mg) for 18 hr. The reaction product was isolated in the usual manner and purified by chromatography on alumina followed by crystallisation from chloroform–light petroleum to yield 3β:21β:24-*triacetoxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene* (XXIII) as needles, m.p. 241–242°, $[\alpha]_D$ −56·8° (*c*, 1·1), λ_{max} 2800 Å (ε 12,600) (Found: C, 70·6; H, 8·1. $C_{36}H_{50}O_8$ requires C, 70·8; H, 8·25 per cent). A mixture with 3β:21α:24-triacetoxy-12:19-dioxo-oleana-9(11):13(18)-diene had m.p. 230°.

Conversion of 3β:21β:24-*triacetoxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene* (XXIII) *into* 3β:21α:24-*triacetoxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene* (XXIV). A solution of the 3β:21β:24-triacetate (120 mg) in methanolic potassium hydroxide (3%, 100 ml) was refluxed for 2½ hr. Isolation by means of chloroform yielded a crystalline solid which was treated with pyridine and acetic anhydride at 100° for 1 hr. The acetylated product crystallised from chloroform–light petroleum to give 3β:21α:24-triacetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (90 mg) as rods, m.p. and mixed m.p. 274–275° $[\alpha]_D$ −52·1° (*c*, 1·4), λ_{max} 2780 Å (ε 12,700).

Treatment of the dioxodiene derivative of soyasapogenol B with acetone and sulphuric acid. A solution of 3β:21α:24-trihydroxy-12:19-dioxo-oleana-9(11):13(18)-diene (380 mg) in dry acetone (50 ml) and dry ether (200 ml) containing concentrated sulphuric acid (2 ml) was kept at 17° for 60 hr. The product was isolated in the usual way and purified by chromatography. Crystallisation from light petroleum–chloroform gave 21α-*hydroxy*-12:19-*dioxo*-3β:24-iso*propylidenedioxyoleana*-9(11):13(18)-*diene* (XXV) (250 mg), as needles, m.p. 288–290°, $[\alpha]_D$ −77·3° (*c*, 1·2), λ_{max} 2800 Å (ε 12,000) (Found: C, 75·6; H, 9·4. $C_{33}H_{48}O_5$ requires: C, 75·5; H, 9·2 per cent).

12:19:21-*Trioxo*-3β:24-iso*propylidenedioxyoleana*-9(11):13(18)-*diene* (XXVI). Oxidation of the 21α-hydroxy-*iso*propylidene derivative (800 mg) with the pyridine–chromium trioxide complex, in the usual way, gave 12:19:21-trioxo-3β:24-iso*propylidenedioxy-oleana*-9(11):13(18)-*diene* (750 mg) as needles (from chloroform–light petroleum), m.p. 282–284°, $[\alpha]_D$ −208° (*c*, 1·1), λ_{max} 2800 Å (ε 13,;000) (Found C, 75·8; H, 9·1. $C_{33}H_{46}O_5$ requires C, 75·8; H, 8·9 per cent).

3β:24-*Diacetoxy*-12:19:21-*trioxo-oleana*-9(11):13(18)-*diene* (XXVII). The *iso*propylidene derivative of the trioxodiene (750 mg) in methanol (100 ml) containing concentrated hydrochloric acid (25 ml) was refluxed for 15 min. The product was isolated by using ether and acetylated by treatment with acetic anhydride and pyridine at 100° for 3 hr. Crystallisation of the acetylated product from chloroform–light petroleum gave 3β:24-*diacetoxy*-12:19:21-*trioxo-oleana*-9(11):13(18)-diene (500 mg) as needles, m.p. 203–205°, $[\alpha]_D$ −131° (*c*, 2·3), λ_{max} 2800 Å (ε 12,000) (Found: C, 72·0; H, 8·4. $C_{34}H_{46}O_7$ requires C, 72·05; H, 8·2 per cent). Addition of methanolic potassium hydroxide (10%, 30 ml) to a methanol solution of the diacetoxy-trioxodiene (70 mg) gave a deep-orange solution. The solution was refluxed for 1 hr and then diluted with water. The product was not extracted from the alkaline solution by means of ether. Acidification of the aqueous solution with hydrochloric acid precipitated a solid, which was isolated by means of ether as an amorphous powder. Attempts to crystallise this acid and attempts to obtain a crystalline derivative by acetylation and by esterification with diazomethane all failed. Treatment of the amorphous acid with chloroform gives an intense blue solution.

Reactions of soyasapogenol C

Oxidation of soyasapogenol C diacetate (IX, R = Ac) *with osmium tetroxide.* Soyasapogenol C diacetate (850 mg) in pyridine (20 ml) was mixed with a solution of osmium tetroxide (0·6 g) in pyridine (6 ml) and the mixture was kept at 17° in the dark for 14 days. The mixture was diluted with ether (150 ml) and, after the addition of lithium aluminium hydride (2·0 g), refluxed for 1 hr. The product was isolated in the usual way and acetylated by means of acetic anhydride and pyridine. A solution of the acetylated product (900 mg) in light petroleum–benzene (10·1, 200 ml) was chromatographed on alumina (30 g). The column was washed successively with light petroleum–benzene mixtures (9:1, 320 ml; 6:1, 1120 ml; 7:3, 2720 ml; 3:2, 1280 ml; 2:3, 800 ml; 1:4, 320 ml) with benzene (800 ml) and finally with benzene–ether (3:1, 440 ml) to give fractions (50 × 160 ml). Evaporation of fractions 3–8 gave a solid (170 mg), which after crystallisation from chloroform–methanol furnished unchanged soyasapogenol C diacetate as needles, m.p. and mixed m.p. 203–204°, $[\alpha]_D$ +59°. Fractions 43–46 furnished soyasapogenol A tetra-acetate (70 mg) (X, R = Ac) as needles (from chloroform–methanol), m.p. and mixed m.p. 228–230°, $[\alpha]_D$ +89°. Fractions 9–42 were evaporated and the crystalline residues were combined (total, 600 mg) and rechromatographed on alumina (20 g). The column was washed successively with light petroleum–benzene mixtures (4:1, 800 ml; 3:7, 600 ml; 1:1, 1200 ml; 1:2, 1000 ml; 1:4, 2600 ml) with benzene (1 l.) and with benzene–ether (19:1, 2 l.) to give fractions (40 × 200 ml). Fractions 20–38 were evaporated and the combined solids (330 mg) were crystallised from chloroform–methanol to give 3β:21β:22β:24-tetra-acetoxyolean-12-ene (XI, R = Ac) as needles, m.p. 228–229°, $[\alpha]_D$ +41° (*c*, 1·1). Meyer *et al.*[3] give m.p. 226–227°, $[\alpha]_D$ +38°, for the stereoisomeric soyasapogenol A tetra-acetate. The crude solids obtained from fractions 16–33 showed selective absorption at 2800 Å (ε 1000). During recrystallisations, absorption at 2800 Å gradually diminished to $\varepsilon \simeq 50$.

Vigorous oxidation of the stereoisomeric soyasapogenol A tetra-acetate (XI, R = Ac) *with selenium dioxide.* A solution of 3β:21β:22β:24-tetra-acetoxyolean-12-ene (300 mg) in benzyl acetate (10 ml) was refluxed for 24 hr with selenium dioxide (250 mg). The product was isolated in the usual way and purified by chromatography on alumina and crystallisation from chloroform–methanol to give 3β:21β:22β:24-*tetra-acetoxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene* (XVII) (150 mg) as prisms, m.p. 212–214°, $[\alpha]_D$ −95° (*c*, 0·9), λ_{max} 2780 Å (ε 13,000) (Found: C, 68·4; H, 7·6. $C_{38}H_{52}O_{10}$ requires C, 68·2; H, 7·8 per cent).

3β:21α:22β:24-*Tetra-acetoxy*-12:19-*dioxo-oleana*-9(11):13(18)-*diene* (XIII). A solution of 3β:21β:22β:24-tetra-acetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (100 mg) in methanolic potassium hydroxide (3%, 30 ml) was refluxed for 2½ hr. The product was isolated in the usual way and acetylated by means of acetic anhydride and pyridine at 100°. The acetylated product was crystallised from chloroform–methanol to give 3β:21α:22β:24-tetra-acetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (40 mg) as prisms, m.p. and mixed m.p. 330–332° (dec.), $[\alpha]_D$ −48° (*c*, 0·6), λ_{max} 2780 Å (ε 13,200). From the chloroform–methanol mother liquor, unchanged 3β:21β:22β:24-tetra-acetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (40 mg) was isolated, m.p. and mixed m.p. 210–212°, $[\alpha]_D$ −95·4° (*c*, 0·95).

Vigorous oxidation of soyasapogenol C diacetate (IX, R = Ac) *with selenium dioxide.* A solution of soyasapogenol C diacetate (250 mg) in benzyl acetate was

refluxed with powdered selenium dioxide (300 mg) for 18 hr. The product was purified by chromatography, followed by crystallisation from light petroleum–chloroform, from which the *dioxodiene* derivative separated as needles, m.p. 217–218°, $[\alpha]_D$ −78·5° (*c*, 0·8), λ_{max} 2740 Å (ε 12,500) (Found: C, 74·2; H, 8·5. $C_{34}H_{46}O_6$ requires C, 74·15; H, 8·4 per cent). The dioxodiene derivative does not give a colour with tetranitromethane in chloroform.

Reduction of the dioxodiene derivative of soyasapogenol C diacetate. The dioxodiene derivative (70 mg) in ethanol (10 ml) was refluxed with freshly activated zinc dust (1 g) for 5 hr. The product was isolated in the usual way and crystallised from chloroform–methanol, from which the dihydro derivative (45 mg) separated as plates, m.p. 266–268°, $[\alpha]_D$ +106° (*c*, 0·8), λ_{max} 2450 Å (ε 12,600) (Found: C, 74·0; H, 8·9. $C_{34}H_{48}O_6$ requires C, 73·9; H, 8·75 per cent). The dihydro derivative does not give a colour with tetranitromethane in chloroform.

The dihydro derivative (30 mg) in acetic acid (50 ml) was shaken with hydrogen and platinum (from 250 mg of PtO_2) for 4 days. The crude product (ε_{2450} 2000) was purified by chromatography on alumina, followed by crystallisation from methanol to give 3β:24-*diacetoxy*-19-*oxo-olean*-9(11)-*ene*-(XXXIII) (12 mg) as plates, m.p. 237–239°, $[\alpha]_D$ +104° (*c*, 0·9), ε_{2480} 50 (Found: C, 75·8; H, 10·0. $C_{34}H_{52}O_5$ requires C, 75·5; H, 9·7 per cent). It gives a pale-yellow colour with the tetranitromethane reagent.

Vigorous oxidation of dihydrosoyasapogenol C diacetate (XXX) *with selenium dioxide.* Dihydrosoyasapogenol C diacetate (3β:24-diacetoxyolean-12-ene) was prepared as described by Meyer *et al.*[3] by catalytic reduction of soyasapogenol C diacetate; it had m.p. 188–189°, $[\alpha]_D$ +81·7° (*c*, 1·5). A solution of the dihydrodiacetate (200 mg) in benzyl acetate was oxidised with selenium dioxide as described above. The product was purified by chromatography on alumina and crystallisation from chloroform–methanol to give 3β:24-diacetoxy-12:19-dioxo-oleana-9(11):13(18)-diene (XXXI) (110 mg) as needles, m.p. 247–248°, $[\alpha]_D$ −76·7° (*c*, 1·8), λ_{max} 2760 Å (ε 13,000) (Found: C, 73·9; H, 9·0. $C_{34}H_{48}O_6$ requires C, 73·9; H, 8·75 per cent). It does not give a colour with tetranitromethane in chloroform.

3β:24-*Diacetoxy*-12:19-*dioxo-olean*-9(11)-*ene* (XXXII) A solution of the dioxodiene from dihydrosoyasapogenol C diacetate (70 mg) was reduced with zinc dust in ethanol in the usual way The product was purified by crystallisation from chloroform–methanol to give the 3β:24-*diacetoxy*-12:19-*dioxo-olean* 9(11)-*ene* as laminae, m.p. 249–251° (dec.), $[\alpha]_D$ +120° (*c*, 1·0), λ_{max} 2450 Å (ε 12,700) (Found: C, 73·7; H, 9·3. $C_{34}H_{50}O_6$ requires C, 73·6; H, 9·1 per cent). It does not give a colour with the tetranitromethane reagent. Hydrogenolysis of 3β:24-diacetoxy-12:19-dioxo-olean-9(11)-ene by shaking its solution in acetic acid with hydrogen and platinum for 4 days gave 3β:24-diacetoxy-19-oxo-olean-9(11)-ene as plates (from methanol), m.p. and mixed m.p. 238–239°, $[\alpha]_D$ +102° (*c*, 0·8).

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