104. *Sapogenins. Part XV. Siaresinolic Acid.*

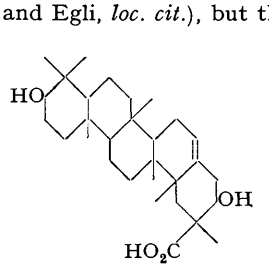
By Philip Bilham, George A. R. Kon, and Walter C. J. Ross.

Siaresinolic acid is shown to belong to the β-amyrin group of triterpene acids by its conversion into oleanene III, a hydrocarbon obtained from oleanolic acid by Winterstein and Stein (*Annalen*, 1933, **502**, 223). One hydroxyl group of siaresinolic acid occupies a position at C_2 in ring A; the second hydroxyl is attached to C_{21} in the other terminal ring, E, as shown by measurements of unimolecular films of *dihydronorsiaresinol*. The double bond of siaresinolic acid is situated in the βγ-position with respect to the carbon atom carrying this group; it is also shown to occupy the same position as the double bond of oleanolic acid by the dehydration of *methyl 2-acetylsiaresinolate* to methyl acetyldehydro-oleanolate. This also shows that, apart from the additional hydroxyl at C_{21}, siaresinolic acid is identical with oleanolic acid.

The reactions of siaresinolic acid cannot be satisfactorily interpreted on the basis of the older formulæ for the compounds of the β-amyrin group, but support the new structure put forward in Part XIII (this vol., p. 533).

Siaresinolic acid, which occurs in Siamese gum benzoin, has the formula $C_{30}H_{48}O_4$ (Zinke and Lieb, *Monatsh.*, 1918, **39**, 95, 627). On dehydrogenation with selenium it gives most of the products obtainable from triterpenes, notably 1 : 8-dimethylpicene, sapotalene, and hydroxyagathalene (2-hydroxy-1 : 5 : 6-trimethylnaphthalene) (Ruzicka, Brüngger, Egli, Ehmann, Furter, and Hösli, *Helv. Chim. Acta*, 1932, **15**, 431; Ruzicka, Brüngger, Egli, Ehmann, and Goldberg, *ibid.*, p. 1496), from which it follows that the acid must have a skeleton based on 1 : 8-dimethylpicene, and that, like oleanolic acid, it has a hydroxyl group at C_2 in ring A. Moreover, the formation of a bromo-lactone on treatment of the acid with bromine (Winterstein and Egli, *Z. physiol. Chem.*, 1931, **202**, 207) shows that it is a βγ-, γδ- or δε-unsaturated acid and suggests a similarity in structure with the acids of the β-amyrin group. The experiments described below lead to the conclusion that siaresinolic acid is 21-hydroxyoleanolic acid and is represented by the formula (I).

Siaresinolic acid has two hydroxyl groups, as shown by determinations of active hydrogen (Winterstein and Egli, *loc. cit.*), but these are of unequal reactivity, like those of echinocystic acid (compare Bergsteinsson and Noller, *J. Amer. Chem. Soc.*, 1934, **56**, 1403). The acid forms a monobenzoate (Zinke and Lieb, *loc. cit.*) and a monoacetate (Winterstein and Egli, *loc. cit.*); the methyl ester similarly gives a *monoacetyl* derivative, whereas the second hydroxyl group does not react. The more reactive hydroxyl group, which may be designated as $OH^{(1)}$, is doubtless that attached to C_2, since a hydroxyl group in that position is known to be reactive; separate proof of this is given on p. 541. The less reactive hydroxyl group, $OH^{(2)}$, is secondary and can be oxidised; *e.g.*, the monoacetyl ester mentioned above gives the *acetate* of a *ketohydroxy-ester* (methyl 21-keto-oleanolate), $C_{33}H_{50}O_5$, on treatment with chromic acid.



(I.)

The position of the hydroxyl $OH^{(2)}$ in proximity to the carboxyl group follows from the observation that, although methyl siaresinolate resists hydrolysis even under very vigorous conditions, and the carbomethoxyl group therefore occupies a sterically protected position, hydrolysis becomes easy once $OH^{(2)}$ has been oxidised. The above acetylketo-hydroxy-ester at once develops a strong yellow colour with alkali and undergoes rapid hydrolysis. Similarly, *methyl siaresinonate*, the diketo-ester obtained by the oxidation of methyl siaresinolate with chromic acid, is also easily hydrolysed. In this respect these esters resemble the diketo-esters derived from echinocystic acid (Noller and White, *J. Amer. Chem. Soc.*, 1939, **61**, 983) and from quillaic acid (Elliott, Kon, and Soper, J., 1940, 612). The diketo-ester is evidently capable of enolisation, because, apart from the yellow colour which it develops with alkali, it liberates one molecule of methane under the conditions of the Zerevitinov test. The diketo-ester derived from echinocystic acid also has been found to behave in this way by Noller and White (*loc. cit.*; confirmed by Carson and Noller, *ibid.*, 1941, **63**, 621), although under the conditions used in our Microanalytical Department (*iso*-amyl ether as solvent, room temperature) this was not observed (Elliott, Kon, and Soper, *loc. cit.*); it may be safely inferred that methyl siaresinonate is appreciably more acidic than the isomeric compound.

An important difference lies in the fact that the ketonic acids formed by the hydrolysis of siaresinonic ester and of the acetoxy-keto-ester do not lose carbon dioxide with the production of ketones, but are isolated as such, although they are readily decarboxylated. In spite of their apparent stability they are formulated as β-ketonic esters (see p. 542).

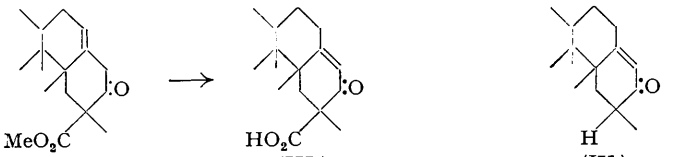
When methyl siaresinonate is reduced by the Clemmensen method, only one carbonyl group, namely that at C_2, is attacked, and the ester undergoes hydrogenation at the same time; the product, *methyl-2-deoxo-dihydrosiaresinonate*, no longer gives a colour with tetranitromethane. The formation of hydrogenation products in the course of the Clemmensen reaction has been noted in certain alkaloid derivatives (Awe and Unger, *Ber.*, 1937, **70**, 472) and another case is reported in Part XVI (this vol., p. 546). The carbonyl group which escapes reduction must be that derived from $OH^{(2)}$, because the new ester also is readily hydrolysed.

The same carbonyl group resists reduction when methyl siaresinonate is heated with hydrazine hydrate and sodium ethoxide. The product is β-*2-deoxosiaresinonic acid*. The apparent resistance to reduction of the carbonyl group in this and other similar cases is probably due to a tendency to enolisation rather than the effect of steric hindrance, and has also been encountered in derivatives of glycyrrhetic acid.

β-Deoxosiaresinonic acid is converted on melting into *norsiaresinone*, a ketone $C_{29}H_{46}O$ (IV). This com-

pound also resists reduction by the hydrazine method; the carbonyl group is, however, easily reduced by the Clemmensen method with the formation of a hydrocarbon, which has been identified as oleanene III by its m. p., mixed m. p., and rotation. Oleanene III has previously been obtained from oleanolic acid (Winterstein and Stein, *Annalen*, 1933, **502**, 222) and from echinocystic acid (Todd, Harris, and Noller; *J. Amer. Chem. Soc.*, 1940, **62**, 1624) and its formation shows that siaresinolic acid must have the carbon skeleton common to these triterpenes. In particular, it may be inferred that the carboxyl group is similarly situated in ring E (compare Bilham and Kon, J., 1941, 552); the position of the double bond cannot be inferred from this, because oleanene III is probably a secondary product formed by the movement of the double bond from its original position.

It can, however, be shown that the double bond of siaresinolic acid is situated in a $\beta\gamma$-position with respect to the carbon atom carrying $OH^{(2)}$. Methyl siaresinonate (II), which is optically transparent, is hydrolysed to β-*siaresinonic acid* (III) and this is re-esterified with diazomethane to a β-ester isomeric with the starting material; the latter is therefore designated as the α-ester. The β-ester shows selective absorption of light with a maximum at 2510 A., having an intensity log $\varepsilon_{max.} = 3{\cdot}95$.



The isomerisation of the α- to the β-compound is evidently due to the wandering of the double bond in the course of alkaline hydrolysis, with the formation of a conjugated system. A similar change is observed when the acetoxy-keto-ester previously mentioned is hydrolysed; the product is the β-*hydroxyketo-acid*, which is re-esterified to a strongly lævorotatory β-*ester* (light absorption: maximum at 2520 A., log $\varepsilon_{max.} = 3{\cdot}99$) and this is oxidised by chromic acid to methyl β-siaresinonate. The hydroxy-keto-ester is isomeric with methyl 22-keto-oleanolate and methyl glycyrrhetate (compare preceding paper), but differs from them in rotation.

β-Deoxosiaresinonic acid, which has already been described, gives a *methyl* ester having a spectrum with a maximum at 2510 A., log $\varepsilon_{max.} = 4{\cdot}02$; on the other hand, the saturated deoxo-dihydro-ester formed by the Clemmensen reduction of methyl α-siaresinonate is hydrolysed without isomerisation, as would be expected. The acid so formed is re-esterified to a dextro-rotatory ester identical with the starting material.

The movement of the double bond in derivatives of siaresinonic acid is accompanied by remarkably large changes of optical rotation; the compounds of the α-series, with the double bond in the original position, have positive rotations of the order of + 130°. The compounds of the β-series, with the double bond in the αβ-position with respect to the carbonyl group, are strongly lævorotatory, with $[\alpha]_D$ of the order of — 200° or more. It seems hardly possible that such large changes would have been observed if the isomerisation from the α- to the β-series had been incomplete, as might be inferred from the somewhat low intensities of the absorption spectra; these appear to be due to some constitutive influence, such as is observed, for example, in 3-hydroxy-6-keto-Δ^4-cholestene (Heilbron, Jones, and Spring, J., 1937, 801), Δ^4-androstene-6 : 7-dione (Ruzicka, Grob, and Raschka, *Helv. Chim. Acta*, 1940, **23**, 1518), and Δ^1-steroids (Butenandt, Mamoli, Dannenberg, Masch, and Paland, *Ber.*, 1939, **72**, 1617; see also Inhoffen and Huang-Minlon, *ibid.*, 1938, **71**, 1720; Barnett and Reichstein, *Helv. Chim. Acta*, 1938, **21**, 926).

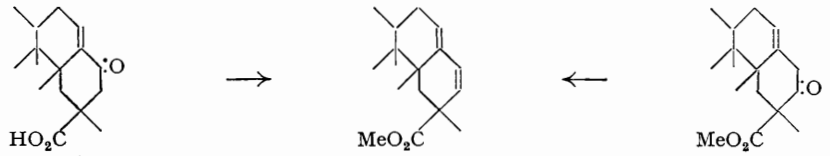
It might have been expected that methyl siaresinolate would undergo oxidation by the Oppenauer reagent, which is generally regarded as specific for $\beta\gamma$-unsaturated alcohols. The ester does indeed undergo oxidation when treated with aluminium *tert.*-butoxide and *cyclo*hexanone, but the *ester*, $C_{31}H_{48}O_4$, which is produced shows no selective absorption of light in the expected region of the spectrum. The oxidation thus either involves the hydroxyl group at C_2, or $OH^{(2)}$ is oxidised without movement of the double bond.

Methyl monoacetylsiaresinolate is dehydrated on boiling with phosphoric oxide in benzene solution, yielding methyl acetyldehydro-oleanolate, identical with the product obtained by the action of selenium dioxide on methyl acetyloleanolate (Ruzicka, Grob, and Sluys-Veer, *Helv. Chim. Acta*, 1939, **22**, 788), as shown by its m. p., mixed m. p., rotation and absorption spectrum. This shows that the skeleton of siaresinolic acid must be identical with that of oleanolic acid, except for the additional hydroxyl group $OH^{(2)}$ in the former acid, and in particular, that the position of the double bond must be the same. Since this is situated in a $\beta\gamma$-position with respect to the carbon atom carrying $OH^{(2)}$, the latter would be placed at C_{21} on the basis of the new formula for oleanolic acid (Part XIII; this vol., p. 533).

Decisive evidence as to the position of $OH^{(2)}$ in the molecule is also afforded by surface-film measurements. Norsiaresinone forms a very weak, unstable film, which appears to have a small limiting area of the order of 47 sq. A. On reduction with sodium and alcohol the ketone is converted into the saturated alcohol, *dihydronorsiaresinol*; this is to be expected since norsiaresinone is an αβ-unsaturated ketone as shown by its absorption spectrum (maximum at 2490 A., log ε_{max} 3·97). The new alcohol forms films of good stability, which do not exhibit spontaneous contraction and have a limiting area of 43·5 sq. A., with $\mu = 171$ e.s.u. $\times 10^{-21}$. Such a limiting area is only compatible with a position of the polar group in a terminal ring, and since the alternative

positions in ring A are excluded, it can only be attached to C_{21} or C_{23}. In agreement with this, methyl 2-deoxodihydrosiaresinonate has a limiting area of 65 sq. A. and $\mu = 872$ e.s.u. $\times 10^{-21}$. These results are in complete accord with the formulation deduced from purely chemical considerations.

Now the dehydro-ester (VI) mentioned above has also been obtained from keto-oleanolic acid (V), the acetyl ester of which is isomeric, and not identical, with the acetyl-keto-ester (VII) described on p. 540; the former is an αβ- and the latter a βγ-unsaturated ketone. The double bond must occupy the same position in both compounds and they differ by the position of the carbonyl group, which must, however, be placed in a terminal ring in both compounds :



(V.) (VI.) (VII.)

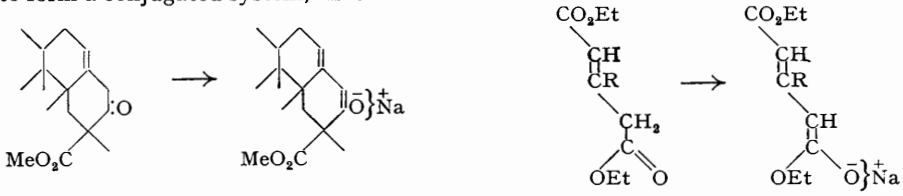
It follows from this that the two carbonyl groups of (V) and (VII) severally represent two methylene groups of oleanolic acid, which are situated in proximity to the carboxyl group and in a different ring from that which houses the double bond.

Certain by-products isolated in the reduction of norsiaresinone are of interest. One of these is a *diene* with a system of conjugated double bonds, as shown by the absorption spectrum. The position of the maximum (2400 A., log $\varepsilon_{max.}$ 4·31) suggests that the double bonds are situated in different rings; it is impossible to say why the position of the maximum is about 100 A. further from the visible region of the spectrum than in the dehydro-ester (VI). In addition to this diene, another compound is found in such small amount that it has not been isolated in the pure state, but from the fact that it gives an intense colour with antimony trichloride, whereas the above diene does not, it may be assumed that it is the diene (VIII) with two double bonds in one ring, analogous to amyradienol I (Picard and Spring, J., 1941, 35). This compound could be formed from norsiaresinone by reduction and loss of water :

(VIII.) (IX.)

The diene previously described (IX) is doubtless formed by a similar mechanism either from the βγ-isomeride of norsiaresinone, which might be expected to be produced to some extent by the action of alkali on norsiaresinone, or by the isomerisation of (VIII).

The stability of the ketonic acids derived from siaresinolic acid is in marked contrast to the instability of the otherwise similarly constituted acids derived from quillaic and echinocystic acids, and appears at first sight to constitute a serious objection to formula (I). Stable β-ketonic acids have, nevertheless, been observed (compare, *e.g.*, Bredt, *J. pr. Chem.*, 1937, **148**, 221; Böttger, *Ber.*, 1937, **70**, 316); Bredt suggests that the loss of the carboxyl group is due to a tendency on the part of the keto-group to enolise towards the carbon atom carrying the carboxyl group, and this does not take place when this carbon atom occupies a bridge head, since the structure formed would be contrary to Bredt's rule. In the case under consideration, however, it is possible for this keto-group to enolise in the opposite direction, the process being facilitated by the βγ-double bond, which tends to form a conjugated system, thus :



The system of double bonds is similar to that found in the glutaconic esters, which are also shown above. Once the enolate has been formed in the manner shown, the mechanism which normally provides the driving force for the elimination of the carboxyl group no longer operates and hydrolysis of the ester can proceed normally.

This and other reactions of siaresinolic acid cannot be satisfactorily interpreted on the basis of Haworth's original triterpene formula or the variant of it put forward by Bilham and Kon (*Nature*, 1941, **147**, 745) (these formulæ will be found on p. 533), in which the double bond is placed in ring C, because this double bond cannot migrate to an adjacent position to become conjugated with the carbonyl group produced by the oxidation of OH[2].

Added in proof: The authors have recently obtained access to a Thesis by R. Egli (Zürich, 1933), in which some of the compounds now described are mentioned, notably methyl siaresinonate and (β) siaresinonic acid. It is remarkable that this lævorotatory acid is described as giving a dextrorotatory ester identical with methyl siaresinonate.

Experimental.

M. p.'s were determined in sealed capillaries and are uncorrected; analysis specimens were dried for 2 hours at 100°/1—2 mm.; rotations were determined in chloroform solution.

Siaresinolic Acid.—Crude sodium siaresinolate, prepared as described by Winterstein and Egli (*loc. cit.*), after being extracted with aqueous acetone (20% of water) to remove most of the colour, was suspended in water, and the acid liberated with hydrochloric acid and taken up in ether. The extract was shaken with 10% sodium hydroxide solution and the aqueous suspension of the re-formed sodium salt was separated from the ethereal layer and warmed on the steam-bath until all adhering ether had been driven off. The amorphous salt, thus rendered crystalline, was collected and washed with a little sodium hydroxide solution. The colourless salt obtained was dissolved in hot acetic acid; on cooling, the solution deposited the complex of siaresinolic acid and acetic acid, m. p. 268—270°. The yields of this product varied considerably with different samples of gum benzoin: samples A, B, and C, supplied by Messrs. Brome and Schimmer, of 6 Leather Market, S.E. 1, of moderate quality gum gave, respectively, 0·5, 0 and 0·05% of the complex; sample B contained a small amount of another triterpene (?) acid giving an ester of m. p. 244°. Specimen D, supplied by the British Drug Houses Ltd., gave a yield of 3·3% of the complex, but a specimen of equally high quality material and of exactly similar appearance, purchased from Messrs. Wright, Layman, and Umney, again contained no siaresinolic acid.

Methyl siaresinolate was prepared from the complex by treatment with diazomethane in ether and was recrystallised from methyl alcohol, forming large plates, m. p. 176°, $[\alpha]_D$ + 45° (c = 0·75). The ester (100 mg.) was recovered unchanged after boiling for 4 hours with 10 c.c. of 4% potassium hydroxide in 95% alcohol; the solution remained colourless throughout.

Methyl Acetylsiaresinolate.—500 Mg. of methyl siaresinolate were warmed with 10 c.c. of pyridine–acetic anhydride (1 : 1) until dissolved. The solution, after being left at room temperature overnight, was diluted with water, and the acetylated *ester* recrystallised from methyl alcohol, forming needles (400 mg.), m. p. 110—120°, not altered by further crystallisation (Found: C, 74·6, 74·5; H, 9·8, 9·9. $C_{33}H_{52}O_5$ requires C, 75·0; H, 9·9%).

Oxidation. The above monoacetyl ester (300 mg.) was dissolved in acetic acid (20 c.c.) and treated with a solution of 150 mg. of chromic acid in 1 c.c. of water and 5 c.c. of acetic acid. After ½ hour the solution was warmed to 60° and kept at that temperature for ½ hour; it was then cautiously diluted with hot water until crystals formed. *Methyl acetyl-21-keto-oleanolate* was then recrystallised from methyl alcohol; m. p. 232—234°; yield, 200 mg. (Found: C, 75·2; H, 9·7. $C_{33}H_{50}O_5$ requires C, 75·3; H, 9·5%).

Hydrolysis of the Acetoxy-keto-ester.—200 Mg. of the above ester were treated with 20 c.c. of 4% alcoholic potassium hydroxide, a bright yellow colour being developed at once. After 4 hours' boiling, the mixture was diluted, acidified, and extracted with ether. The acid obtained could be crystallised with some difficulty from alcohol; m. p. *ca.* 280°. It was esterified with diazomethane to the *β-hydroxy-keto-ester*, which crystallised from dilute acetone in needles, m. p. 189—190°, $[\alpha]_D$ − 195° (c = 0·935) (Found: C, 76·6, 76·6; H, 10·3, 10·3. $C_{31}H_{48}O_4$ requires C, 76·8; H, 10·0%).

Methyl α-Siaresinonate.—5 G. of methyl siaresinolate were dissolved in 200 c.c. of "AnalaR" acetic acid, and 1·5 g. of chromic acid in 50 c.c. of 90% acetic acid gradually added at room temperature. After ½ hour the mixture was kept at 60° for a further ½ hour and diluted with its own volume of hot water. Crystals gradually separated from the warm solution and were collected (3 g.); they had m. p. 207—208° and this rose to 210° on crystallisation from methyl alcohol; $[\alpha]_D$ + 135° (Found: C, 77·4; H, 9·5. $C_{31}H_{46}O_4$ requires C, 77·1; H, 9·6%). The *ester* was recovered unchanged after being kept for some time with sodium *iso*propoxide (warm) or sodium ethoxide (cold).

Methyl β-Siaresinonate.—500 Mg. of the above ester were boiled for 4 hours with 2 g. of potassium hydroxide in 50 c.c. of 95% alcohol. The solution at once developed a bright yellow colour. The acid, obtained by acidification and extraction with ether, crystallised from methyl alcohol in needles or prisms, m. p. 295° (decomp.), $[\alpha]_D$ − 187° (c = 0·37). On treatment with diazomethane it gave the *β-methyl* ester, which formed plates from methyl alcohol, m. p. 190° (mixed m. p. with α-ester *ca.* 165°), $[\alpha]_D$ − 192° (c = 0·79) (Found: C, 77·4; H, 9·7. $C_{31}H_{46}O_4$ requires C, 77·1; H, 9·6%). This ester was also prepared by the oxidation of the β-form of the hydroxy-keto-ester, obtained from the acetoxy-keto-ester, and identified by its m. p. and mixed m. p.

Reduction of α-Siaresinonic Ester.—250 Mg. of the α-ester were boiled for ½ hour with 4 g. of amalgamated zinc, 12 c.c. of acetic acid, and 2·6 c.c. of hydrochloric acid. *Methyl 21-ketodihydro-oleananate*, obtained in 40% yield by dilution and extraction with ether, crystallised from methyl alcohol in needles, m. p. 200—201°, $[\alpha]_D$ + 25·3° (c = 1·145) (Found: C 78·8, 78·6, 78·9; H, 10·5, 10·5, 10·4. $C_{31}H_{50}O_3$ requires C, 79·1; H, 10·6%). The ester showed no selective absorption of light and gave no colour with tetranitromethane. It was hydrolysed as described above; no yellow colour developed in the course of hydrolysis. The product was separated into a neutral and an acidic portion, the former of which proved to be the potassium salt of the acid. Both portions gave the same ester on warming with ethereal diazomethane, m. p. and mixed m. p. 200°, $[\alpha]_D$ + 26·7° (c = 2·285).

β-Deoxosiaresinonic Acid.—1·5 G. of methyl α-siaresinonate, 3·4 c.c. of 90% hydrazine hydrate, and 1·25 g. of sodium in 25 c.c. of alcohol were heated in a sealed tube for 12 hours at 200°. The acid obtained by acidification and extraction with ether did not crystallise. It was dissolved in ether and shaken with 10% sodium hydroxide solution, but no precipitate formed at the interface. The aqueous layer gave no precipitate on acidification, showing that the sodium salt of the acid had remained in the ethereal layer. This was therefore dried and concentrated, then diluted with light petroleum. The sodium salt separated in fine needles and could be further purified by extraction with dry ether, in which it was now sparingly soluble. The solid was dissolved in alcohol–acetic acid, giving needles of the acid, m. p. *ca.* 297° (decomp.), which were collected, washed with petroleum, and dried in a high vacuum. An attempt to reduce this acid by Clemmensen's method gave a product, m. p. 275—280° after three crystallisations from methyl alcohol, which was unaffected by diazomethane and was probably a lactone. The *methyl* ester prepared from the crude acid formed plates from methyl alcohol, m. p. 214°, $[\alpha]_D$ − 225° (c = 1·18) (Found: C, 79·2, 79·0; H, 10·2, 10·2. $C_{31}H_{48}O_3$ requires C, 79·4; H, 10·3%).

Norsiaresinone.—The above acid was heated until no more gas was evolved, care being taken to avoid charring; the product was dissolved in light petroleum (b. p. 60—80°) and percolated through a column of activated alumina, the *ketone* being adsorbed. It was eluted with benzene (yield, nearly 40%) and crystallised from acetone, giving needles, m. p. 237—238°, $[\alpha]_D$ + 152° (c = 0·80); it could also be crystallised from alcohol or light petroleum (Found: C, 84·5; H, 11·2. $C_{29}H_{46}O$ requires C, 84·8; H, 11·3%). On one occasion a crude specimen of the acid, evidently containing some diketo-acid, was pyrolysed; after repeated crystallisation of the product from light petroleum a less soluble fraction, forming tufts of needles, m. p. 290°, was isolated; this consisted of *norsiaresinodione* (Found: C, 82·4, 82·0; H, 10·4, 10·4. $C_{29}H_{44}O_2$ requires C, 82·0; H, 10·4%).

Reduction of Norsiaresinone.—(1) The ketone was treated with hydrazine and sodium ethoxide as described on p. 543, and the product extracted with ether without previous acidification. The extract gave on evaporation a jelly, insoluble in all the solvents tried, which crystallised on digestion with methyl alcohol and acetic acid and could then be recrystallised from the latter solvent and finally from light petroleum, forming needles, m. p. 294—295°; it gave a yellow colour with tetranitromethane. The amount obtained was insufficient for analysis.

(2) 200 Mg. of norsiaresinone were reduced with zinc and acid as described on p. 543, and the product purified by percolation of its solution in light petroleum through a column of activated alumina. The solid recovered, after crystallisation from acetone and then from ethyl acetate, had m. p. and mixed m. p. with oleanene III, 218—219°, $[\alpha]_D$ + 32·1° (c = 1·93 in toluene); slow cooling of an acetone solution gave the characteristic hexagonal plates of the hydrocarbon (Found: C, 88·0; H, 11·9. Calc.: C, 87·8; H, 12·2%).

(3) 200 Mg. of the ketone in 40 c.c. of boiling absolute alcohol were gradually treated with sodium until no more would dissolve. The solution was diluted and extracted with ether, and the extract washed, dried, and evaporated. In a preliminary run it had been found that crystallisation did not give a good separation of the products formed; the residue was therefore dissolved in light petroleum (b. p. 60—80°) and percolated through a column of alumina. The first 100 c.c. of percolate contained a very small amount of solid, which could not be purified; it gave an intense colour with tetranitromethane and a deep port-wine colour with antimony trichloride in chloroform solution. The column was then eluted with benzene; the first 100 c.c. of eluate contained a solid which crystallised from methyl alcohol in flattened needles, m. p. 166—167°, consisting of *dihydronorsiaresinol*, which gave no colour with tetranitromethane (Found: C, 83·8; H, 12·1. $C_{29}H_{48}O$ requires C, 84·1; H, 12·1%).

Further elution of the column gave a solid which was unsaturated to tetranitromethane and apparently constituted a major product of the reaction. Crystallisation from methyl alcohol at first gave a product, m. p. *ca.* 180°; after crystallisation from acetic acid a product of lower m. p. was obtained, consisting of the *diene hydrocarbon*, which crystallised from methyl alcohol in plates, m. p. 126—127°, $[\alpha]_D$ − 33° (c = 0·385) (Found: C, 88·4; H, 11·8. $C_{29}H_{44}$ requires C, 88·3; H, 11·7%).

Dehydration of Methyl 2-Acetylsiaresinolate.—500 Mg. of the ester in 50 c.c. of benzene were boiled for 3 hours with 3 g. of phosphoric oxide, which assumed a deep purple colour. The colourless benzene solution was percolated through a column of activated alumina and evaporated, and the residue crystallised from methyl alcohol, giving the characteristic flattened needles of methyl acetyldehydro-oleanolate, m. p. and mixed m. p. 223—224°, $[\alpha]_D$ − 130° (c = 0·93); its absorption spectrum showed the expected maxima at 2510 A. and 2600 A. (log $\varepsilon_{max.}$ 4·45 and 4·33 respectively) (Found: C, 77·2; H, 10·0. Calc.: C, 77·5; H, 9·9%).

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