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ISOLATION AND STRUCTURE OF NITENIN AND DIHYDRONITENIN, NEW FURANOTERPENES FROM *SPONGIA NITENS*

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Abstract—Two novel C-21 furanoterpenes, nitenin and dihydronitenin, have been isolated from *Spongia nitens* and shown to have structures I and XI, respectively.

IN PURSUING our chemical investigation on the metabolites of Porifera,[1] *Spongia nitens*, a common sponge in the Mediterranean Sea, has been examined. The ether soluble fraction of the methanolic extracts was chromatographed on silica gel to give two new furanoterpenes, designated as nitenin (I) and dihydronitenin (XI).

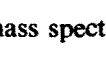
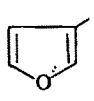
The present paper deals with the isolation and structure elucidation of these compounds.

Structure of nitenin I

The major compound, $C_{21}H_{24}O_4$ (elemental analyses and high resolution mass spectrum, M^+ 340·1638; $C_{21}H_{24}O_4$ requires 340·1674), is a colourless oil, $[\alpha]_D$ −45·4°, λ_{max} 221 (ε 14,000) nm.

The presence of two β-substituted furan rings is deduced from 100 MHz NMR spectrum (Fig 1a): signals at δ 7·26 (2H, t, J = 2 Hz), 7·16 (1H) and 7·12 (1H) are due to four α-furanohydrogens, while signals at δ 6·23 (1H) and 6·17 (1H) arise from two β-furanoprotons. These assignments are confirmed by double irradiation experiments: irradiation at δ 6·20, the centre of the two β-proton signals, collapses the δ 7·26 triplet to a broad singlet; the same experiment shows a sharpening of the two signals at δ 7·16 and 7·12; irradiation at δ 7·26 collapses the signals at δ 6·23 and 6·17 to two broad singlets. These data enable us to assign the δ 7·26 triplet to H in C-1 and in C-21, and the signals at δ 7·16 to H in C-4 and at δ 7·12 to H in C-19 or *vice versa*.

It is worth pointing out that the protons of the two furan rings are not chemically equivalent, in contrast with the behaviour of the protons of the furan rings in III (Fig 1b).

The presence of furan rings is confirmed by the positive Ehrlich test, IR (3140, 1570, 1500, 875 and 780 cm^{-1})[2] and mass spectra [ions at *m/e* 67  and 81 (base peak, )].

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Nitenin possesses an α,β-unsaturated γ-lactone ring since it exhibits strong bands at 1745 (>C=O) and 1670 (>C=C<) cm^{-1}; furthermore, by treatment with alkali, it gave a hydroxy α,β-unsaturated carboxylic acid (II, niteninic acid), $C_{21}H_{26}O_5$ (elemental analyses and mass spectrum), m.p. 89–95°, ν_{max} 3390, 1690 and 1645 cm^{-1}, from which nitenin is slowly regenerated upon acidification of the alkaline solution.

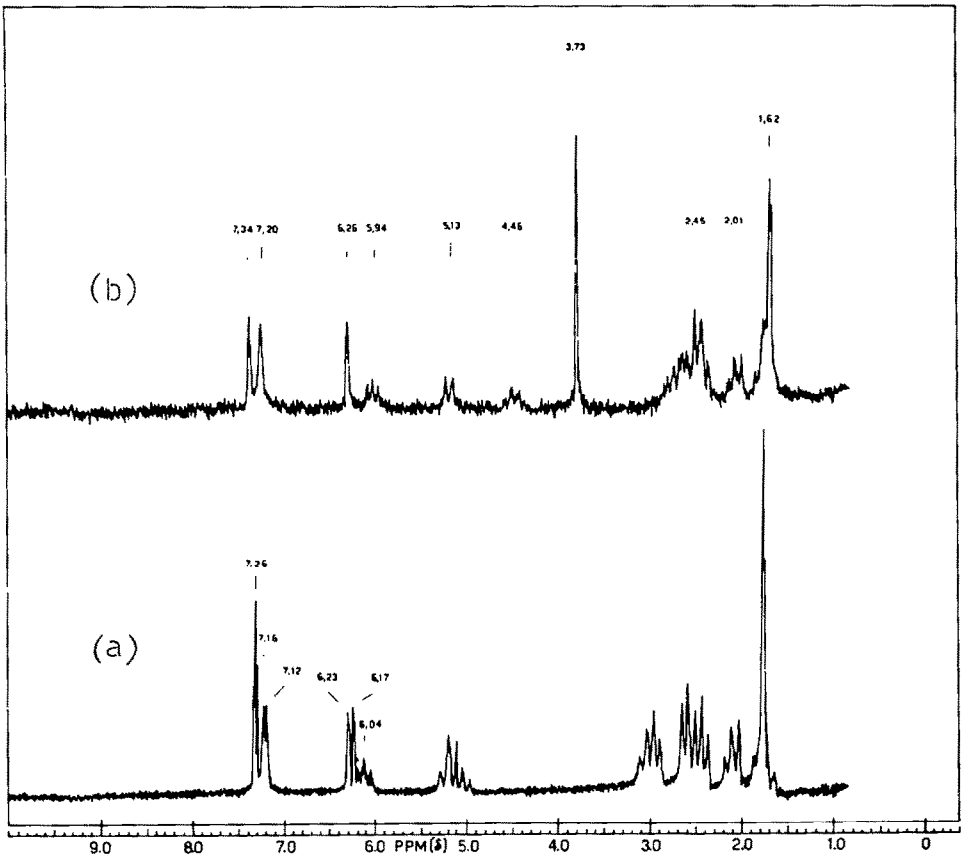
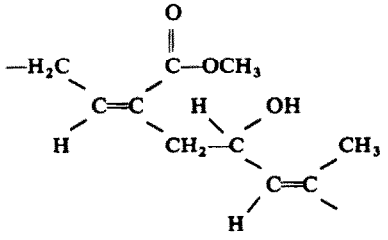


FIG 1. (a) 100 MHz NMR Spectrum (CCl_4) of niteninin (I) (b) 100 MHz NMR Spectrum ($CDCl_3$) of niteninic acid methyl ester (III)

By CH_2N_2 methylation of this acid, the methyl ester (III), $C_{22}H_{28}O_5$ (elemental analyses and mass spectrum), ν_{max} 3400 (—OH), 1705 (>C=O, α,β-unsaturated ester) and 1640 (>C=C<) cm^{-1}, was obtained. Its NMR spectrum (Fig 1b) and spin decoupling study provide additional structural information, completely consistent with the presence of the unit IV in the molecule. A three proton doublet (J = 0·8 Hz) at δ 1·62 is ascribed to the Me protons, the signal due to the OMe group appears as a singlet at δ 3·73, the one-proton quartet (J = 7 Hz) at δ 4·46 (this signal shifts downfield to δ 5·62 on acetylation) is attributable to >CHOH proton, while the two one-proton olefin signals resonate at δ 5·13 (bd, J = 7 Hz; —CH=C(CH_3)—) and δ 5·94; the latter signal appears as a triplet (J = 7 Hz),

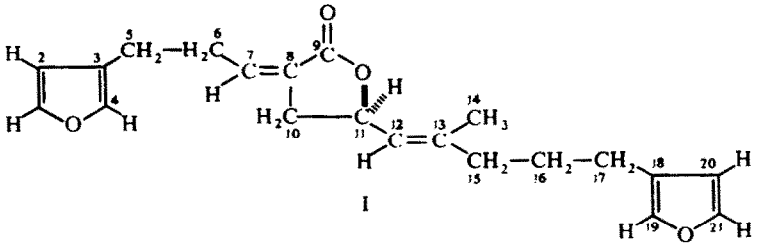
clearly indicating that this olefinic hydrogen is coupled with the protons of a CH_2 group, which are superimposed on the complex absorption spread between δ 2·9



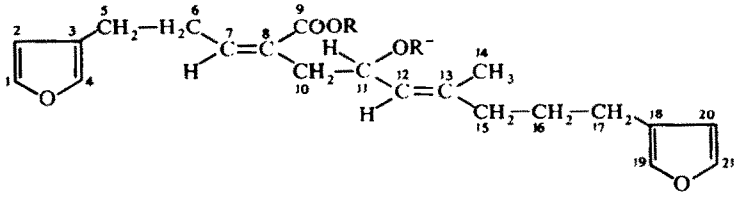
IV

and 2·2. Irradiation at δ 4·46 collapses the broad doublet at δ 5·13 to a singlet broadened by long range coupling; conversely, by irradiation at δ 5·13 the doublet at δ 1·62 is changed to a sharp singlet and the quartet at δ 4·46 is simplified to a triplet (J = 7 Hz). This latter experiment also indicates that the >CHOH group is linked to a CH_2, the protons of which resonate in the δ 2·9–2·2 complex region.

These results account for all the skeletal atoms of nitenin except four carbons.



I

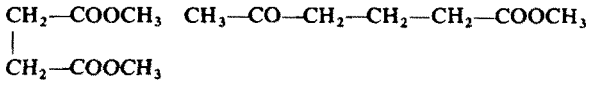


II: R = R′ = H
III: R = CH_3, R′ = H
V: R = CH_3, R′ = CH_3CO—

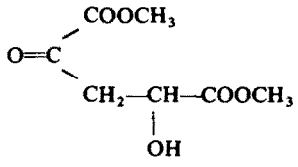
The decisive proof for the gross structure of nitenin is provided by ozonolysis of niteninic acid (II): after oxidative decomposition of the ozonide with H_2O_2, followed by CH_2N_2 methylation, succinic acid dimethyl ester (VI), 5-oxohexanoic acid methyl ester (VII), and 2-oxo-4-hydroxyglutaric acid dimethyl ester (VIII) were obtained.

As far as the stereochemistry of nitenin is concerned, analysis of the NMR spectra of I and its derivatives indicates the configuration of the two double bonds: the chemical shift of the C-7 olefinic proton both in nitenin (δ 6·04) and in the niteninic acid Me ester (δ 5·94) shows it to be *trans* situated to —COOR group.[3] The signal at

δ 1·62 in the NMR spectrum of the Me ester (III) can be assigned to the protons of a Me *trans* to the olefinic proton in an isoprene residue as $—CH_2—C(CH_3)=CH—CH(OH)—$*.[4]

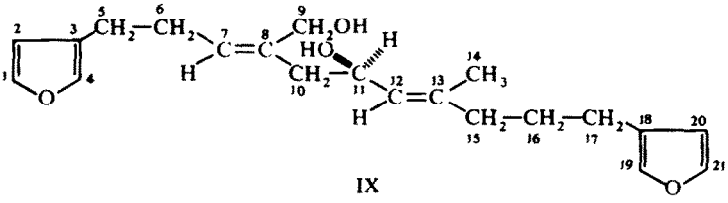


VI VII

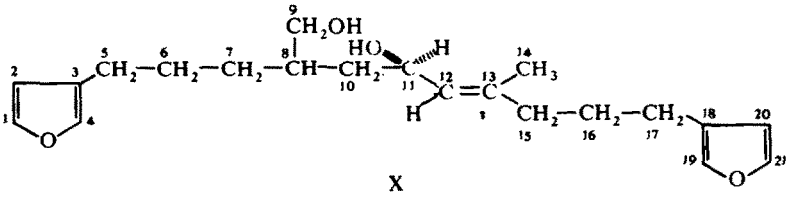


VIII

The stereochemistry of nitenin at C-11 has been determined by the Horeau method[5] on the diol (IX), obtained together with X from nitenin (I) by LAH reduction under mild conditions. Following the asymmetric esterification[6] of the diol IX with excess racemic α-phenylbutyric acid anhydride, (+)-α-phenylbutyric acid has been recovered in an optical yield of 9·8%. This result indicates that the chirality at C-11 in IX is R



IX



X

and, taking into account that LAH reduction of esters occurs with retention of configuration,[7] the chilarity in nitenin must be the same.

The structure of the diol IX, $[\alpha]_D$ +6·2°, has been determined mainly by inspection of its NMR spectrum and comparison with that of I. It is possible to observe the expected upfield shift of the olefinic proton at C-7 from δ 5·97 in I to δ 5·41 in IX and the appearance of an AB quartet (J = 12 Hz) centred at δ 4·08 due to the—$C\underline{H}_2$—OH protons, the non-equivalence of which is effected by the asymmetric centre at C-11.

The structural assignment of X is also based on the analysis of its NMR spectrum and comparison with that of IX: the disappearance of the C-7 olefinic signal and the upfield shift of the —$C\underline{H}_2$—OH protons from δ 4·08 in IX to δ 3·55 (AB part of an ABX system) in X have been observed.

* In all derivatives of nitenin in which the $—CH_2—C(CH_3)—CH=CHOH—$ residue is present [niteninic acid (II), diol (IX), diol (X) and dihydroniteninic acid Me ester (XII)] the protons of the Me in C-13 resonate between δ 1·65 and 1·62.

Structure of dihydronitenin XI.

The second compound present in *Spongia nitens* in much smaller amounts is an oily substance and has the molecular formula $C_{21}H_{26}O_4$ (elemental analysis and mass spectrum), $[\alpha]_D$ −25·2°, λ_{max} 222 (ε 5230) nm.

Positive Ehrlich test, NMR [δ 7·15 (2H, bs, α-furanoprotons), 7·05 (2H, bs, α-furanoprotons) and 6·19 (2H, bs, β-furanoprotons)], IR (ν_{max} 3140, 1560, 1500, 875 and 760 cm^{-1}) and mass spectra [ions at *m/e* 67 () and 81 ()]

point to the presence of two β-substituted furan rings.

Dihydronitenin possesses a γ-lactone ring; in the IR spectrum a band is present at 1765 cm^{-1} and by treatment with alkali it gave a compound which, by CH_2N_2 methylation, afforded the hydroxy Me ester (XII). $C_{22}H_{30}O_5$ (elemental analyses and mass spectrum), ν_{max} 3500 (—OH) and 1725 (>C=O, ester) cm^{-1}, δ 3·65 (3H, s, $-OCH_3$), 4·37 (1H, q, J = 7 Hz, this signal shifts downfield to δ 5·44 on acetylation; >C<u>H</u>OH).

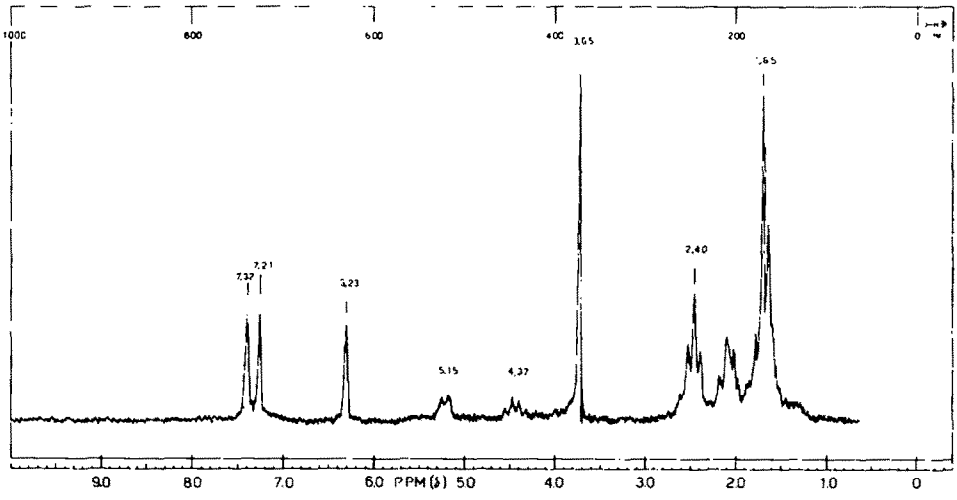
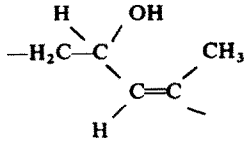


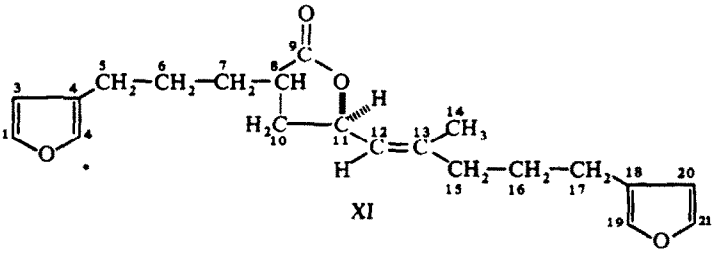
FIG 2. 100 MHz NMR Spectrum ($CDCl_3$) of dihydroniteninic acid methyl ester (XII)

Inspection of the NMR (Fig 2) of this derivative and double irradiation experiments suggest the presence of the part structure XIII in the molecule. Irradiation at δ 5·15 (1H, bd, J = 7 Hz; olefinic proton) collapses the quartet at δ 4·37 (1H, q, J = 7 Hz; >C<u>H</u>OH) to a triplet (J = 7 Hz) and the signal at δ 1·65 (3H, d, 0·8 Hz; Me *trans* to the olefinic proton)[4] to a sharp singlet, while irradiation at δ 4·37 collapses the broad doublet at δ 5·15 to a singlet broadened by long range coupling.

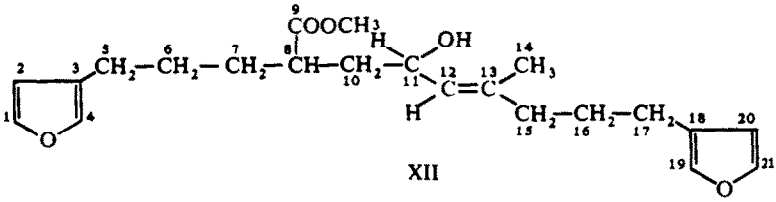


XIII

The data reported above, when compared with those of nitenin, enable us to propose the structure XI for dihydronitenin. This was confirmed by $NaBH_4$ reduction of nitenin, which gave, in a good yield, a compound with spectral (UV, IR, NMR and Ms) and chromatographic properties (TLC on silica gel) identical to those of dihydronitenin.



XI



XII

To determine the stereochemistry at C-11 the method of Horean has been applied to the diol (X), $[\alpha]_D$ +10·3°, obtained by LAH reduction on dihydronitenin (XI). We obtained dextrorotatory α-phenylbutyric acid (9·7% optical yield), which indicates that the chirality at C-11 in the diol, and accordingly in dihydronitenin (XI), must be R. The stereochemistry at C-8 has not yet been determined.

The occurrence of these two unusual C-21 furanoterpenes is quite interesting. They could derive biogenetically by degradation from higher terpenoids constructed from isoprene units linked head to tail. Another possible biogenetic pathway could involve the coupling of two C-10 units on a C-1 unit. The recent isolation from the *Spongia officinalis* of a C-25 head-to-tail furanoterpene supports the first hypothesis (unpublished results of our laboratory).

EXPERIMENTAL

The UV and IR spectra were recorded on a Bausch and Lomb Spectronic 505 and Perkin–Elmer 257 Infracord spectrophotometers. NMR spectra were taken at 100 MHz on a Varian HA-100 in $CDCl_3$ (unless otherwise indicated) (TMS as internal reference, $\delta = 0$). Coupling constants are expressed in Hz. Mass spectra were recorded on an AIE MS-9 mass spectrometer. GLCs were run using a Carlo Erba Fractovap model GV instrument. Elemental analyses were performed by Mr S. De Rosa of our laboratory using a Perkin–Elmer Mod 240 instrument.

Preparative TLC on pre-coated silica gel F 254 (Merck). Sponges (*Spongia nitens*) collected in the bay of Naples, were obtained from the supply department of the Zoological Station (Naples).

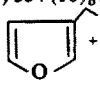
Isolation of nitenin I and dihydronitenin XI. The fresh material (1 Kg, dry weight after extraction) was extracted three times with MeOH at room temperature for three days; the combined methanolic extracts (12 l.) were concentrated under reduced press. and the remaining aqueous solution was extracted with ether (4 l., in three portions). Combined extracts were stripped of solvent to leave 12·2 g of oily material, which was chromatographed on silica gel (Merck, 1 Kg). Upon washing to column with C_6H_6 (3·5 l.) followed by C_6H_6–Et_2O (9:1) a crude mixture (6·8 g) of nitenin and dihydronitenin migrated out after

2·5 l. Further purification and separation of I and XI was carried out by PLC using C_6H_6—40–70° light petroleum, 9:1 as developing solvent (3 stages; 150 mg on each plate; R_f of I 0·4 and R_f of XI 0·25).

Nitenin (4·3 g): $[\alpha]_D$ −45·4° (c, 2; $CHCl_3$); UV λ_{max} 221 nm, ε 14·400 (cyclohexane); IR (liquid film) 1745 (>C=O, α,β-unsaturated γ-lactone), 1670 (>C=C<) and 1170 cm^{-1}; NMR (CCl_4) is reported in Fig 1; MS *m/e* (%) 340 (10%; M^+), 325 (5%; M^+-CH_3), 95 (20%; ) 81 (100%; ) and 67 (11%; ). (Found C, 73·91; H, 7·04. Calcd for $C_{21}H_{24}O_4$ C, 74·09; H, 7·11%).

Dihydronitenin (0·56 g): $[\alpha]_D$ −25·2° (c, 1·4; $CHCl_3$); UV λ_{max} 222 nm, ε 5·230 (cyclohexane); IR (liquid film) 1765 (>C=O; γ-lactone) and 1168 cm^{-1}; NMR (CCl_4) δ 7·15 (2H, bs, α-furanoprotons), 7·05 (2H, bs; α-furanoprotons), 6·19 (2H, bs; β-furanoprotons) 5·15 (2H, bm; H—C-12 and H—C-11), 2·85 (1H, bm; H—C-8), 2·40 (4H, bm; H_2—C-5 and H_2—C-17), 2·04 (2H, bm; H_2—C-15), 1·70 (3H, s; CH_3 on C-13) and 1·60 (8H, bm; H_2—C-6, H_2—C_7, H_2—C-10 and H_2—C-16); MS *m/e* (%) 342 (15%; M^+), 327 (10%; M^+-CH_3), 95 (60%; ) 81 (100%; ) and 67 (20%; ). (Found: C, 73·39; H, 7·60. Calcd for $C_{21}H_{26}O_4$ C, 73·77; H, 7·65%).

Hydrolysis of nitenin I: niteninic acid II. A mixture of I (1·4 g) and a soln of KOH (3 g) in H_2O—MeOH (1:1, 120 ml) was refluxed for 1 hr, concentrated, diluted with H_2O and washed with Et_2O to remove neutral products. The aq. soln was acidified with 2N HCl and the separated crystals collected and recrystallized from 80–100° petroleum to give 0·9 g of niteninic acid (II); m.p. 89–95°; IR (nujol) 3390 (—OH), 2540 (broad, —OH) 1690 (>C=O; α,β-unsaturated carboxylic acid) and 1645 (>C=C<) cm^{-1}; NMR δ 7·33 (2H, t, J 2 Hz; α-furanoprotons), 7·19 (2H, bs; α-furanoprotons) 6·25 (1H, bs; β-furanoprotons), 6·08 (1H, bt, J = 6 Hz; H—C-7) 5·13 (1H, bd, J = 7 Hz; H—C-12) 4·45 (1H, q, J = 7 Hz; H—C-11) 2·8–2·25 (8H, complex multiplet; H_2—C-5, H_2—C-6, H_2—C-10, H_2—C-17), 2·03 (2H, bt, J = 7 Hz; H_2—C-15) 1·65 (2H, bm; H_2—C-16) and 1·61 (3H, s; CH_3 on C-13). MS, no molecular ion; the spectrum is identical to that of I; evidently loss of water and regeneration of the lactone occur. (Found: C, 70·56; H, 7·29. Calc. for $C_{21}H_{26}O_5$: C, 70·37; H, 7·31%).

Niteninic acid methyl ester III. To a soln of 240 mg niteninic acid in MeOH excess of ethereal CH_2N_2 was added. After 10 min the solvent was removed by evaporation and the oily residue was purified by PLC ($CHCl_3$—MeOH, 49:1; R_f = 0·3) to give 200 mg of III as an oily substance: IR (liquid film) 3400 (b, —OH), 1705 (>C=O; α,β-unsaturated ester), 1640 (>C=C<) and 1205 cm^{-1}. NMR is reported in Fig 1b. MS, *m/e* (%): 372 (2%: M^+) 354 (10%; M^+-H_2O) 341 (2·5%; M^+-OCH_3) 340 (3·5%; M^+-CH_3OH) 339 [4%; $(354\text{-}CH_3)^+$] 95 (65%, ) 81 (100%; ) and 67 (25%, ). (Found: C, 71·15; H, 7·70. Calc. for $C_{22}H_{28}O_5$. C, 70·94; H, 7·58%).

On acetylation with Ac_2O and pyridine worked up as usual niteninic acid methyl ester (70 mg) afforded an oily substance, which was purified by PLC ($CHCl_3$; R_f = 0·3) to give 60 mg of V (M^+ 414): IR ($CHCl_3$) 1740 (>C=O, acetate) 1705 (>C=O, α,β-unsaturated ester) 1640 (>C=C<) and 1230 (C—O, acetate) cm^{-1}; NMR δ 5·52 (1H, q, J = 7 Hz; >CHOAc) 1·94 (3H, s, CH_3CO).

Ozonolysis of niteninic acid II. Ozonized O_2 (2% O_3) was passed through a soln of II (500 mg) in EtOAc (50 ml) at −15° for 3 hr. After evaporation of solvent in *vacuo* the ozonide was decomposed with H_2O at 100° for 1 hr after the addition of a few drops of H_2O_2. The reaction mixture was extracted continuously for 5 hr with Et_2O. The extract was concentrated and treated with CH_2N_2 in the usual way. After removal of solvent the residue (215 mg) was shown to comprise succinic acid dimethyl ester (VI) and 5-oxohexanoic acid methyl ester (VII). GLC (2·5% SE-30 and 10% Carbowax were used as stationary phases at 80° and 160°, respectively).

The aqueous phase was taken to dryness and the residue methylated (CH_2N_2) to give 2-oxo-4-hydroxyglutaric acid dimethyl ester (VIII, 70 mg), characterized without further purification: IR (liquid film) 3400 (—OH), 1730 (>C=O; ester) and 1710 (>C=O; ketone) cm^{-1}; NMR δ 4·54 (1H, t, J = 6 Hz;

>CH—OH), 3·86 and 3·76 (each 3H, s; $—OCH_3$) and 2·82 (2H, d, $J = 6$ Hz; $—CH_2—$). On acetylation with Ac_2O and pyridine, carried out in the usual manner, VIII afforded the acetyl derivative: MS *m/e* (%) 173 (25; M^+-$COOCH_3$) and 145 [100; $(173\text{-}CO)^+$]; the NMR spectrum, when compared with that of VIII, showed a singlet at δ 2·12 (3H; $CH_3CO_2—$) and the expected downfield shift of the —CH—O— triplet from δ 4·54 to 5·48.

LAH reduction of nitenin to obtain diols IX *and* X. LAH (120 mg) in dry Et_2O (10 ml) was added portionwise with stirring to a soln of nitenin (250 mg) in dry Et_2O (10 ml) at −80°C. The mixture was stirred at −80°–60° for 120 min. Excess EtOAc was added to destroy unreacted LAH. Water was added, and extracted with Et_2O. The soln was washed, dried (Na_2SO_4) and evaporated to give a mixture of IX and X, separated by PLC using C_6H_6–Et_2O, 1:1 as eluent (3 plates; R_f of IX 0·6 and R_f of X 0·45).

IX (oily substance, 98 mg), $[\alpha]_D$ +6·2° (c, 7; $CHCl_3$); λ_{max} 220 nm, ε 7650 (cyclohexane); IR 3300 (b, —OH) cm^{-1}, absence of >C=O bands: NMR δ 7·33 (2H, bs; α-furanoprotons), 7·21 (2H, bs; α-furanoprotons), 6·25 (2H, bs, β-furanoprotons), 5·41 (1H, t, $J = 7$ Hz; H—C-7), 5·24 (1H, d, $J = 7$ Hz; H—C-12), 4·49 (1H, sextet; H—C-11), 4·08 (2H, AB quartet, δ A–δ B = 8 Hz, $J = 12$ Hz; H_2—C-9), 2·8–1·6 (17H, complex absorption). (Found: C, 73·22; H, 8·18; calculated for $C_{21}H_{28}O_4$: C, 73·23; H, 8·19%). X (oily substance, 70 mg), λ_{max} 220 nm, ε 5800 (cyclohexane); IR (liquid film), 3330 (b, —OH) cm^{-1}, absence of >C=O bands, NMR spectrum is very similar to that of LAH reduction product of dihydronitenin (Found: C, 72·71; H, 8·79. Calc. for $C_{21}H_{30}O_4$: C, 72·80; H, 8·73%).

Determination of absolute configuration of C-11 *in* IX *by the Horean Method.* A solution of 80 mg (0·232 mM) of IX in 500 mg (1·61 mM) (±) α-phenylbutyric acid anhydride was mixed with 5 ml dry pyridine. The soln left overnight at room temperature and worked up in standard manner yield 340 mg of crystalline α-phenylbutyric acid, $[\alpha]_D$ +0·78° (c, 10; C_6H_6). Fully stereospecific esterification should yield $[\alpha]_D$ +96·5%[2(6·94)-2] = +8·05°; therefore, the optical yield is 9·6%.

Hydrolysis of dihydronitenin and successive methylation: methyl ester of dihydroniteninic acid XII. To a soln of XI (100 mg) in MeOH (5 ml) an 10% aq soln of KOH (5 ml) was added. After refluxing for 1 hr, the MeOH was removed *in vacuo* and the remaining solution washed with Et_2O to remove neutral products then acidified with 2N HCl. The oily precipitate was extracted with Et_2O and methylated with CH_2N_2 to give XII, was purified by PLC (eluent: $CHCl_3$–MeOH, 49·1; R_f = 0·52; 83 mg): IR 3500 (—OH) and 1725 (>C=O ester) cm^{-1}. MS *m/e* (%) 374 (0·25%; M^+), 356 (0·5%; M^+-H_2O), 342 (8%; M^+-CH_3OH), 327 [8·5%; $(342\text{-}CH_3)^+$], 95 (40%; ), 81 (100%; ) and 67 (25%; ).

The NMR spectrum is reported in Fig 3. (Found: C, 70·35; H, 7·88. Calc. for $C_{22}H_{30}O_5$: C, 70·56; H, 8·07%).

On acetylation with Ac_2O and pyridine working up as usual, XII (40 mg) afforded the acetyl derivative. NMR spectrum very similar to that of XII apart from the appearance of a singlet (3H) at δ 1·99 ($CH_3—CO_2—$) and the downfield shift of the —CH—O signal from δ 4·36 to δ 5·46. (Found: C, 69·07; H, 7·72. Calc. for $C_{24}H_{32}O_6$: C, 69·21; H, 7·74%).

$NaBH_4$ *reduction of nitenin* I *to obtain dihydronitenin* XI. To a soln of I (100 mg) in MeOH (3 ml) $NaBH_4$ (10 mg) was added and the mixture was allowed to stand at room temperature for 3 hr. After removal of MeOH *in vacuo*, H_2O was added to the residue, which was extracted with ether. The extract was washed with water, dried (Na_2SO_4) and evaporated leaving a crude product purified by PLC (eluent: C_6H_6–40–70° petroleum, 9:1) to give dihydronitenin (72 mg) identified with the natural compound by UV, IR, NMR, MS and TLC.

LAH reduction of dihydronitenin XI *to obtain diol* X. Dihydronitenin (XI, 100 mg) in dry Et_2O (4 ml) was treated with LAH (50 mg) at −80°. Working up as described for reduction of nitenin afforded X (81 mg), $[\alpha]_D$ +10·3° (c, 2·8; $CHCl_3$); NMR δ 7·34 (2H, bs, α-furanoprotons), 7·19 (2H, bs, α-furanoprotons), 6·23 (2H, bs, β-furanoprotons), 5·20 (1H, d, $J = 7$ Hz; H—C-12), 4·44 (1H, sextet; H—C-11), 3·50 (2H, AB part of an ABX system, δ A − δB = 12 Hz, J AB = 12 Hz, J AX = 4 Hz, J BX = 6 Hz; H_2—C-9), 3·16 (2H, bs, exchangeable with D_2O; —OH), 2·48–1·5 (17H, complex abxorption).

Determination of absolute configuration of C-11 *in* X *by Horeau method.* A soln of 56 mg (0·16 mM) of X, $[\alpha]_D$ +10·3°, obtained from dihydronitenin by LAH reduction, in 300 mg (0·96 mM) (±) α-phenylbutyric acid anhydride was mixed with 3 ml dry pyridine. Working up as usual afforded 210 mg of crystalline α-phenylbutyric acid, $[\alpha]_D$ +0·95° (c, 10; C_6H_6). Fully stereospecific esterfication should yield $[\alpha]_D$ +96·5%[2(5·92)-2] = +9·8°; therefore, the optical yield is 9·7%.

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