Studies on Fungal Metabolites. Part 1. The Structures of Andibenins-A and -C, and Andilesins-A, -B, and -C, Meroterpenoids from *Aspergillus variecolor*

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Five C_{25} metabolites have been isolated from *Aspergillus variecolor*, and on the basis of their spectroscopic properties, in particular ^1H and ^{13}C n.m.r., and chemical correlations, structures (2)—(6) are proposed for these metabolites. They are thus closely related to the meroterpenoid andibenin-B (1), also isolated from *A. variecolor* and recently shown to have a mixed polyketide–terpenoid biosynthetic origin.

THE fungal metabolite andibenin-B (previously named andibenin),† $C_{25}H_{30}O_6$, was recently isolated in low yield from the liquors of static cultures of *Aspergillus variecolor*, and shown to have structure (1) by *X*-ray crystallography.[1] This structure suggested a biogenesis from a polyisoprenoid, possibly sesterterpenoid precursor, so with a view to obtaining larger yields of andibenin for biosynthetic studies and biological testing, several wild-type and irradiation-induced mutant strains of *A. variecolor* available from previous studies[2] were examined. One of the mutant strains, designated 212K-I69, was found to produce yields of andibenin-B of *ca.* 50 mg l^{-1}. Incorporation of singly and doubly labelled [^{13}C]acetates and [*methyl*-^{13}C]methionine into andibenin by cultures of *A. variecolor* 212K-I69 indicated its biosynthesis *via* alkylation of a bis-*C*-methylated, polyketide-derived, aromatic precursor by farnesyl pyrophosphate.[3] During the course of these studies we have isolated minor amounts of several other closely related C_{25} compounds, andibenin-A ($C_{25}H_{32}O_7$), andibenin-C ($C_{25}H_{32}O_6$), andilesin-A ($C_{25}H_{32}O_6$), andilesin-B ($C_{25}H_{30}O_5$), and andilesin-C ($C_{25}H_{32}O_5$) for which structures (2)—(6) respectively are now proposed on the basis of spectroscopic studies and chemical correlations.

It was apparent from their molecular formulae and the similarity of their spectroscopic properties that compounds (2)—(6) were closely related to andibenin-B (1). The main features of their ^1H n.m.r. spectra are summarised in Table 1, which shows that both andibenin-A (2) and andibenin-C (3) contain the *cis*-coupled vinylic protons (δ *ca.* 6.1 and 6.7) assigned to the spiro-δ-lactone ring in andibenin-B (1), five uncoupled methyls, and an AB coupled $-CH_2-O-$ grouping (*ca.* δ 4.2) assigned to the γ-lactone ring in andibenin-B, but both lack the uncoupled vinylic proton assigned to the double bond exocyclic to the γ-lactone ring. This vinylic proton is replaced in (2) by mutually coupled doublets (*J* 8 Hz) at δ 2.98 and 4.15, and in (3) by a triplet at δ 2.88 (*J* 8 Hz). The ^{13}C n.m.r. spectra indicate that the olefinic carbon resonances at δ 140.9 and 134.0 p.p.m. assigned to C-6′ and -7′, respectively, in (1) have been replaced by high-field aliphatic resonances in (3) and similarly the conjugated γ-lactone carbonyl resonance at δ 167.4 p.p.m. in (1) has moved downfield to δ 177.1 p.p.m. in (3), a shift indicative of loss of conjugation. These ^1H and ^{13}C n.m.r. data, together with the molecular formulae immediately suggest that andibenin-A and -C are related to andibenin-B by hydration and reduction respectively of the 6′,7′ double bond. This was readily confirmed.

TABLE 1

^1H N.m.r. data for andibenins (1)—(3) and andilesins (4)—(6)

Compound	C–CH_3 [a]	1-H [b]	2-H [b]	6′-H	7′-H	1′-CH_2	Others
(1)	1.05, 1.20, 1.38 1.41, 1.47	6.74	6.06		7.04 [a]	4.24,[e] 4.84 [e]	2.18,[f] 2.58 [g]
(2)	1.17, 1.20, 1.21 1.41, 1.44	6.70	6.12	2.98 [c]	4.15 [c]	4,14,[e] 4.25 [e]	2.48,[g], 3.38,8 1.95
(3)	1.05, 1.15, 1.19 1.41, 1.44	6.72	6.10	2.88 [d]		4.12,[e] 4.25 [e]	2.48 [g]
(4)	1.13, 1.15, 1.30 1.36, 1.45	5.93	5.77	2.92 [c]	4.08 [c]	4.16,[e] 4.27 [e]	3.43 [f]
(5)	0.99, 1.36, 1.38 1.40, 1.49	5.94	5.74		7.13 [a]	4.45 [a]	
(6)	1.04, 1.13, 1.33 1.39, 1.47	5.94	5.80	2.87 [d]		4.13,[e] 4.25 [e]	

[a] Singlet. [b] d, *J* 10 Hz. [c] d, *J* 8 Hz. [d] t, *J* 8 Hz. [e] d, *J* 12 Hz. [f] s, exchangeable with D_2O. [g] dt, *J* 4 and 12 Hz.

Hydrogenation of andibenin-B (1) in ethyl acetate over Adams catalyst gave the tetrahydro-derivative (7). Similar reduction of andibenin-C (3) resulted in the uptake of one mole of hydrogen only, to give a product identical to (7) in all respects. Further, treatment of andibenin-B (1) with thionyl chloride in pyridine[4] resulted in the loss of one molecule of water to give the olefin (8). The ^{13}C n.m.r. spectrum showed that the C-9 and -10 resonances at δ 52.7 and 77.2 p.p.m., respectively, in (1) were replaced by olefinic carbon resonances at δ 126.6 and 147.6 p.p.m. in (8), and the ^1H

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† Andibenins-A, -B, and -C are so named to conform with the corresponding andilesins, see preceding paper. Andilesin-A and andilesin-B correspond to the previously isolated dihydroandibenin and deoxyandibenin.[1]

n.m.r. spectrum of (8) showed the presence of an olefinic methyl (δ 1.55). Similar treatment of andibenin-A resulted in the loss of two molecules of water to give a product identical to (8), thus establishing structure (2) for andilesin-A.

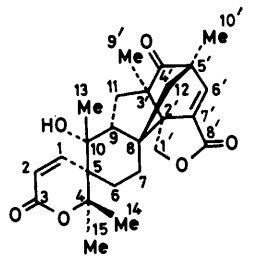
Comparison of the molecular formulae and n.m.r. spectra of andilesin-A, -B, and -C suggested that the andilesins were related to one another in the same way as the andibenins and this was confirmed in an analogous manner. Catalytic hydrogenation in ethyl acetate over Adams catalyst converted andilesin-C (6) into the dihydro-product (9) identical to the product obtained from similar hydrogenation of andilesin-B (5). Treatment of andilesin-A (4) with thionyl chloride in pyridine resulted in dehydration of the secondary alcohol to give a good yield of a product identical to andilesin-B (5). Hydrogenation of andilesin-B or -C in methanol over palladium–charcoal resulted in quantitative yields of the ring-A seco-product (10) which will be discussed further below.

The relationship between the andibenins and andilesins was revealed by comparison of their molecular formulae and n.m.r. spectra. The andilesins all contain one less oxygen atom than the corresponding andibenins and the only significant difference in their ^{1}H n.m.r. spectra is the upfield shift of the *cis*-vinylic protons from *ca.* δ 6.7 and 6.1 in the andibenins to *ca.* δ 5.8 and 5.9 in the andilesins. The ^{13}C n.m.r. spectra of andibenin-B (1) and andilesin-B (5) are summarised in Table 2. Both compounds show resonances assignable to a ketonic carbonyl and two α,β-unsaturated lactone systems. The remaining resonances are all very similar in chemical shift and multiplicity, indicating the presence of identical carbon skeletons, except that the C-5 non-protonated and C-10 oxygen bearing non-protonated

TABLE 2.

^{13}C Chemical shifts [δ (p.p.m.)] and multiplicities observed in off-resonance decoupled spectra of andibenin-B (1), and andilesin-B (5), and the ring A carbons of obacunone (12)

Carbon	(1)	(5)	(12)
1	151.8 (d)	149.6 (d)	156.7
2	118.3 (d)	119.5 (d)	122.8
3	164.2 (s)	166.2 (s)	166.6
4	85.3 (s)	83.6 (s)	83.9
5	46.7 (s)	57.5 (d)	57.2
6	35.1 (t)	36.9 (t)	
7	27.8 (t)	23.0 (t)	
8	58.5 (s)	60.0 (s)	
9	52.7 (d)	42.6 (d)	
10	77.2 (s)	43.8 (s)	43.2
11	28.9 (t)	28.2 (t)	
12	55.6 (t)	57.5 (t)	
13	23.6 (q)	22.5 (q)	16.3
14	24.5 (q)	23.6 (q)	26.7
15	27.0 (q)	30.2 (q)	31.9
1′	68.7 (t)	68.6 (t)	
2′	48.9 (s)	47.2 (s)	
3′	52.7 (s)	53.2 (s)	
4′	213.9 (s)	213.4 (s)	
5′	51.0 (s)	51.4 (s)	
6′	140.9 (d)	143.3 (d)	
7′	134.0 (s)	133.3 (s)	
8′	167.4 (s)	166.6 (s)	
9′	17.3 (q)	16.9 (q)	
10′	17.2 (q)	16.4 (q)	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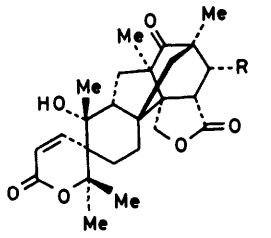
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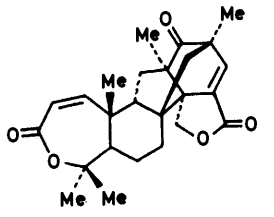
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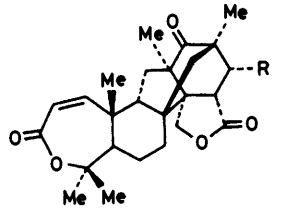
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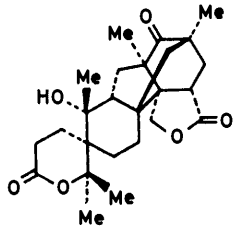
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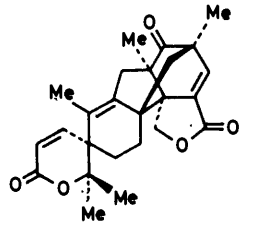
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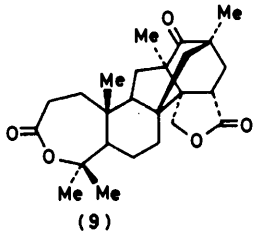
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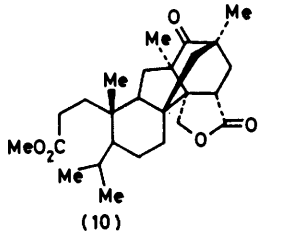
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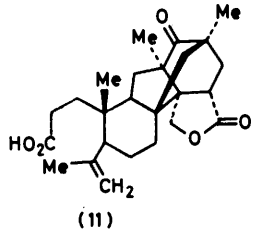
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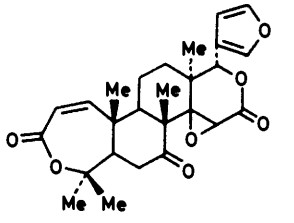
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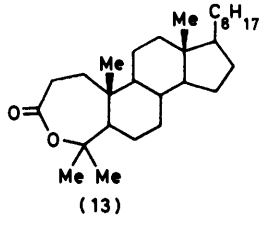
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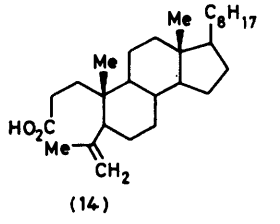
(14)

carbon resonances observed at δ 46.7 and 77.2 p.p.m. respectively in andibenin-B have been replaced by a methine carbon at δ 57.5 p.p.m. and a non-protonated carbon at δ 43.8 p.p.m. in andilesin-B. These differences can only be accommodated by replacing the 10-hydroxy-5-spiro-δ-lactone A–B ring systems in the andibenins by the ε-lactone A–B ring system in the andilesins. Support for the presence of this ε-lactone in the andilesins is provided by the lack of hydroxy absorption in the i.r. spectrum of andilesin-B and comparison with the ^{13}C chemical shifts observed for the corresponding carbons in the meliacolide obacunone (12),[5] shown in Table 2.

Chemical proof for the presence of the seven-membered lactone ring in the andilesins was given by the ready ring-opening of the lactone to the unsaturated acid (11), δ 1.74, 4.79, and 4.88 (Me–C=CH_2), on treatment of dihydroandilesin-C (9) with mild acid. Treatment of 4a,4a-dimethyl-4-oxa-A-homocholestan-3-one (13) with 10% sulphuric or hydrochloric acid in acetic acid gives a high yield of 4-methyl-4-methylene-3,4-secocholestan-3-oic acid (14).[6] As stated above, attempted hydrogenation of andilesin-C with palladium–charcoal in methanol resulted in formation of the seco-product (10), presumably due to ring-opening and esterification being catalysed by traces of acid in the catalyst followed by further reduction of the isopropylidene group.

The *X*-ray structure of andilesin-A (4) has been reported [7,8] and the above conclusions are in agreement with this. The stereochemistry shown in the above structures follows from the *X*-ray and c.d. work.

The andilesins may be seen as biosynthetic precursors, or branches from the biosynthetic pathway, to the andibenins. As stated above, preliminary ^{13}C incorporation studies [3] indicate that andibenin-B is formed by prenylation of a tetraketide precursor, possible 3,5-dimethylorsellinic acid, by farnesyl pyrophosphate. In the light of this, an interesting feature of andibenin-B is the lack of an oxygen substituent on C-6′ as inspection of known polyketides reveals that compounds which result from a cyclisation involving the methylene group α to the terminal carboxy group of a polyketide chain always retain the oxygen atom derived from the β-carbonyl group.[9] This suggests that andibenin-A is a precursor of andibenin-B. Dehydration of A, to give B, followed by further reduction of B to give C would be the reasonable biosynthetic sequence.

Further studies to delineate the biosynthetic pathway to, and the inter-relationships among, these compounds are in progress. Full details of the ^{13}C assignments will be presented elsewhere.

EXPERIMENTAL

Unless otherwise stated, i.r. absorption spectra were measured with a Perkin-Elmer model 125 instrument for $CHCl_3$ solutions, u.v. spectra with a Unicam SP 800 instrument for solutions in ethanol, ^1H n.m.r. spectra with a Perkin-Elmer R34 instrument for solutions in deuteriochloroform containing tetramethylsilane as internal standard, ^{13}C n.m.r. spectra with a Varian XL-100-15 Fourier-transform spectrometer for similar solutions, and optical rotations with an ETL-NPL automatic polarimeter for solutions in chloroform. Mass spectra were measured at 70 eV with an A.E.I. MS9 instrument. T.l.c. was performed using silica gel GF254 (Merck) in 0.5 mm thick layers on 20 cm × 20 cm plates eluted several times with methanol–chloroform (2 : 98 v/v). M.p.s were determined with a Kofler hot-stage instrument.

Isolation of Metabolites.—*Aspergillus variecolor* (strain 212K-I69) was grown from a spore suspension in static culture for 15 days at 25 °C in flat vessels (*ca.* 1 l capacity), each containing Czapek–Dox medium (500 ml). The mycelium and liquors (*ca.* 5 l) were separated by filtration and the liquors were concentrated to *ca.* 1 l and extracted with ethyl acetate (3 × 500 ml). Evaporation of the solvent gave a brown semi-crystalline oil (700 mg) which on recrystallisation from ethyl acetate gave a crystalline solid (200 mg) which was further purified by preparative t.l.c. The least polar, strongly u.v. absorbing band was removed and recrystallised from ethyl acetate to give andilesin-B (15 mg), m.p. >310 °C (lit.,[1] >310 °C). The broad, weakly u.v. absorbing band of intermediate polarity was removed and recrystallised from ethyl acetate to give andilesin-C (24 mg), m.p. >300 °C (lit.,[1] >290 °C), $[\alpha]_D^{25}$ −5.2° (*c* 0.8), δ_C 216.5 (s), 176.2 (s), 166.2 (s), 149.5 (d), 119.4 (d), 83.5 (s), 69.2 (t), 56.8 (s), 56.4 (d), 55.0 (s), 52.7 (t), 45.3 (s), 43.8 (s), 43.1 (s), 42.2 (d), 38.7 (t), 35.5 (d), 32.3 (t), 30.2 (d), 24.7 (t), 23.5 (q), 22.8 (q), 22.4 (q), 19.5 (q), and 16.8 (q) p.p.m. The broad, weakly u.v. absorbing band, at highest polarity, was removed and recrystallised from ethyl acetate to give andilesin-A (78 mg), m.p. >300 °C (lit.,[2] >310 °C), δ_C 214.9 (s), 174.5 (s), 166.2 (s), 149.6 (d), 119.4 (d), 83.5 (s), 71.9 (d), 69.1 (t), 56.7 (s), 55.9 (d), 55.2 (s), 50.7 (t), 49.1 (s), 45.5 (s), 43.8 (s), 42.2 (t), 41.0 (d), 39.4 (t), 30.2 (d), 24.9 (t), 23.5 (q), 22.8 (q), 22.5 (q), 16.8 (q), and 16.1 (q) p.p.m. The mother-liquors (500 mg) were also chromatographed as above. The least polar, strongly u.v. absorbing band gave andilesin-B (33 mg), and the broad, strongly u.v. absorbing band of next highest polarity gave andibenin-B (210 mg), m.p. 218—220 °C (lit.,[1] 219—220 °C). A weakly u.v. absorbing band of only slightly higher polarity on removal and recrystallisation from ethyl acetate gave *andibenin-C* (24 mg), m.p. 280—282 °C, $[\alpha]_D^{25}$ −96.5° (*c* 0.85); $\nu_{max.}$ 3 450, 1 770, 1 720, and 1 705sh cm^{-1}; $\lambda_{max.}$ (EtOH) end absorption only, δ_C 217.4, 177.1, 164.1, 151.6, 118.4, 85.3, 77.5, 70.0, 55.5, 54.9, 51.6, 51.3, 47.1, 45.5, 42.9, 36.4, 36.0, 31.9, 28.4, 27.0, 26.0, 24.6, 23.9, 19.7, and 17.2 p.p.m. (Found: C, 70.1; H, 7.5. $C_{25}H_{32}O_6$ requires C, 69.9; H, 7.5%). The band of highest polarity on removal and recrystallisation from ethyl acetate gave *andibenin-A* (7 mg), m.p. 281—284°, $[\alpha]_D^{25}$ −161.3° (*c* 0.75); $\nu_{max.}$ 3 600, 3 400, 1 770, 1 720, and 1 700 cm^{-1}; $\lambda_{max.}$ end absorption (Found: C, 67.4; H, 7.2. $C_{25}H_{32}O_7$ requires C, 67.6; H, 7.3%).

Hydrogenation of Andibenin-B.—Andibenin-C (100 mg) in ethyl acetate (50 ml) was stirred at room temperature and atmospheric pressure in the presence of Adams catalyst (100 mg) for 15 h to give after removal of catalyst and solvent a gum which recrystallised from ethyl acetate to give *tetrahydroandibenin-B*, m.p. 197—200 °C, $[\alpha]_D^{25}$ −70.8° (*c* 1.10), 3 400, 1 770, and 1 720 cm^{-1}, δ_H 1.04, 1.15, 1.17, 1.40, 1.52 (all 3 H, s), 1.0—2.0 (12 H, m), 2.25 (2 H, m), 2.67 (2 H, m), 2.88 (1 H, t, *J* 8 Hz), 4.12 (1 H, d, *J* 11 Hz), and 4.25 (1 H, d, *J* 11 Hz) (Found: C, 69.4; H, 7.7. $C_{25}H_{34}O_6$ requires C, 69.7; H, 8.0%). Similar hydrogenation of andibenin-C, resulted in the uptake of 1 mole of

hydrogen to give a quantitative yield of a product identical in all respects to tetrahydroandibenin-B.

Dehydration of Andibenin-B.—Andibenin-B (96 mg) was stirred in pyridine (5 ml), cooled in an ice–salt bath and thionyl chloride (1 ml) added, and stirring continued overnight. The mixture was poured into ice–water and extracted into chloroform. The chloroform layer was washed with water and the solvent removed to give an oily product which was purified by t.l.c. using two 20 cm × 20 cm plates eluted with chloroform–methanol (93 : 3 v/v). The broad band at R_F 0.7 was removed and eluted with ethyl acetate to give a gum (88 mg) which crystallised from ethyl acetate to give the *dehydration product* (8), m.p. 277—279 °C, $[\alpha]_D^{25}$ 664.7° (*c* 0.85), $\nu_{max.}$ 1 765, 1 715, and 1 665 cm^{-1}; $\lambda_{max.}$ 250 and 310 nm (ε 3 700 and 300); δ_H 1.15, 1.27, 1.37, 1.39, 1.55 (all 3 H, s), 1.4—1.9 (6 H, m), 2.23 (1 H, d, *J* 17 Hz), 2.52 (1 H, d, *J* 17 Hz), 4.38 (2 H, s), 6.07 (1 H, d, *J* 10 Hz), 6.37 (1 H, d, *J* 10 Hz), and 7.04 (1 H, s); δ_C 212.7 (s), 166.5 (s), 163.6 (s), 146.3 (d), 142.6 (s), 140.2 (d), 132.7 (s), 126.6 (s), 119.4 (d), 85.4 (s), 66.9 (t), 58.9 (s), 51.1 (s), 49.9 (s), 49.6 (s), 47.4 (t), 44.8 (s), 41.5 (t), 27.7 (t), 27.2 (t), 24.8 (q), 23.4 (q), 18.1 (q), 17.2 (q), and 15.3 (q) p.p.m. (Found: C, 73.1; H, 6.7. $C_{25}H_{28}O_5$ requires C, 73.5; H, 6.9%).

Dehydration of Andibenin-A.—Andibenin-A (10 mg) was treated with thionyl chloride in pyridine as above to give dehydration product (8), m.p. 277—279 °C.

Hydrogenation of Andilesin-B.—Andilesin-B (100 mg) was stirred in ethyl acetate (50 ml) over Adams catalyst (100 mg) for 15 h. Removal of catalyst and solvent gave a solid which crystallised from ethyl acetate to give an almost quantitative yield of *tetrahydroandilesin-B*, m.p. 295—297 °C, $[\alpha]_D^{25}$ −7.8° (*c* 1.07); $\nu_{max.}$ 1 770 and 1 720 cm^{-1}; δ_H 1.02, 1.04, 1.20, 1.38, 1.42 (all 3 H, s), 1.2—2.0 (12 H, m), 2.63 (1 H, dd, *J* 14 and 5 Hz), 2.76 (1 H, d, *J* 14 Hz), 2.87 (1 H, t, *J* 8 Hz), and 4.21 (2 H, s) (Found: C, 72.6; H, 8.2. $C_{25}H_{34}O_5$ requires C, 72.4; H, 8.3%).

Hydrogenation of Andilesin-C.—(a) Hydrogenation of andilesin-C (100 mg) in ethyl acetate over Adams catalyst as above gave an almost quantitative yield of tetrahydroandilesin-B, m.p. 295—297 °C.

(b) Hydrogenation of andilesin-C (90 mg) in methanol (50 ml) over 10% palladium–charcoal catalyst (75 mg) for 10 h gave a quantitative yield of the *methyl ester* (10) as a gum which could not be crystallised; $\nu_{max.}$ 1 775 and 1 715 cm^{-1}; δ_H 1.02 (3 H, s), 1.08 (3 H, s), 1.16 (6 H, d, *J* 7 Hz), 1.27 (3 H, s), 1.2—2.0 (15 H, m), 2.24 (2 H, m), 2.74 (1 H, t, *J* 8 Hz), 3.67 (3 H, s), 4.23 (1 H, d, *J* 10 Hz), and 4.29 (1 H, d, *J* 10 Hz) (Found: M^+, 430.271 9. $C_{26}H_{38}O_5$ requires *M*, 430.271 8).

Dehydration of Andilesin-A.—Andilesin-A (100 mg) was treated with thionyl chloride in pyridine as above. The usual work-up and purification by t.l.c. gave a gum (70 mg) which on recrystallisation gave andilesin-B.

Acid-catalysed Isomerisation of Tetrahydroandilesin-B.—Tetrahydroandilesin-B (100 mg) was treated with 20% hydrochloric acid in acetic acid (1 ml) and dichloromethane (2 ml) at room temperature for 24 h. After dilution with ether (20 ml), the solution was washed with water (2 × 20 ml), saturated sodium hydrogencarbonate solution (2 × 20 ml), and water (3 × 20 ml), and dried ($MgSO_4$). The ether was removed *in vacuo* to give the *acid* (11) as a gum (90 mg) which could not be crystallised, $\nu_{max.}$ 3 300—2 600, 1 770, 1 720, and 897 cm^{-1}; δ_H 1.02 (6 H, s), 1.15 (3 H, s), 1.74 (3 H, s), 1.2—2.3 (*ca.* 17 H, m), 2.87 (1 H, t, *J* 8 Hz), 4.23 (2 H, s), 4.79 (1 H, s), and 4.88 (1 H, s) (Found: M^+, 414.241 5. $C_{25}H_{34}O_5$ requires *M*, 414.240 6).

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