Tetrahedron Vol. 44, No. 12, pp 3749 to 3756, 1988
Printed in Great Britain.

0040-4020/88 $3.00 + .00
Pergamon Press plc

THE STEM CONSTITUENTS OF *DYSOXYLUM LENTICELLARE*

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(*Received in UK* 12 *April* 1988)

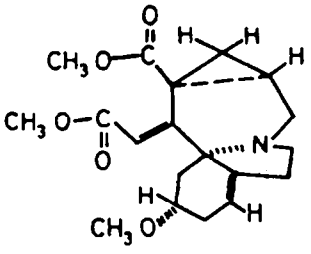
Abstract - A total of nine compounds have been isolated from the stem of *Dysoxylum lenticellare* Gillespie (Meliaceae). They are the five homoerythrina-type alkaloids (1, 2, 6, 7, 9), of which 1 and 2 are new. Three diterpenes (3-5) while (3) is a new compound, compound (8) is well known. The nine compounds were characterized by the spectroscopic analysis.

Many homoerythrina alkaloids have been isolated from other plant species.[1-6,9-11] We have already reported the isolation and structure elucidation of the constituents of the leaf of *D. lenticellare*.[7,8,12,13] In this communication, I wish to report the structure elucidation of nine constituents in the stem of *D. lenticellare*. Two new alkaloids, lenticellarine (1) and 3-epi-2,18-dimethoxyschelhammericine (2). One new diterpene, 8β-methoxysandaracopimarene (3) and six known compounds, 8β-hydroxysandaracopimarene (4), phyllocladene (5), 3-epi-schelhammericine (6), 2,7-dihydrohomoerysotrine (7), p-hydroxyacetophenone (8) and 3-epi-18-methoxyschelhammericine (9) were found previously in the leaf of *D. lenticellare*.[7,8,13]

RESULTS AND DISCUSSION

The extraction of the plant material and isolation and isolation of the compounds were carried out by standard means. The alkaloids 2, 6, 7 and 9 proved to have structures of the homoerythrina-type while the novel alkaloid (1) appeared to have a degraded homoerythrina-type structure. The identity of the six known compounds has been confirmed by the agreement of their physical data with reported values, and by a direct comparison with authentic samples where these were available.

A novel alkaloid (1) with unusual carbon skeleton has been identified by molecular formula as $C_{19}H_{25}NO_5$ and characterized by its ir, uv, ord, ms, ^1H nmr, and ^{13}C nmr spectroscopic measurements. This alkaloid is a transformation product of phenolic procursors of the major homoerythrina alkaloid found in the leaf of *D. lenticellare*, 3-epi-18-methoxyschelhammericine (9). The ir spectrum showed an intense, broad peak at 1730 cm^{-1} with a shoulder at 1690 cm^{-1} accompanied by a band at 1260 cm^{-1} indicative of one or more ester groups and a band of moderate intensity at 1620 cm^{-1} indicative of a conjugated C-C double bond. Two ester functions were confirmed to be methyl esters by the ^{13}C nmr spectrum which showed carbonyl carbons at 171.8 and 165.3 (conjugated) as well as methyl-on-oxygen at 50.9 and 51.8 . In addition, the ^{13}C nmr revealed the presence of two trisubstituted C-C double bonds C-1/C-6 at 119.3 and 139.2 δ, and C-14/C-15 at 122.3 and



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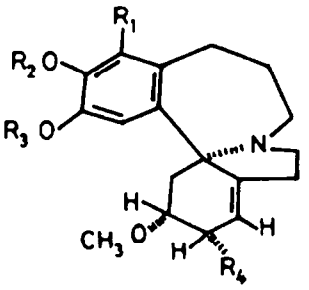
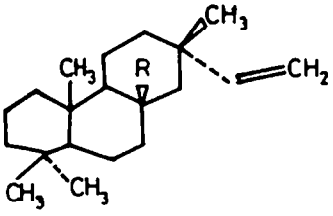


2 $R_1 = R_4 = OCH_3$, R_2, $R_3 = CH_2$

6 $R_1 = R_4 = H$, R_2, $R_3 = CH_2$

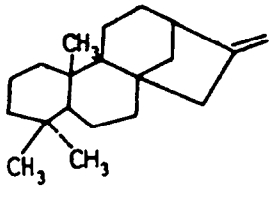
7 $R_1 = R_4 = H$, $R_2 = R_3 = OCH_3$

9 $R_1 = OCH_3$ R_2, $R_3 = CH_2$, $R_4 = H$



3 R = OCH_3

4 R = OH



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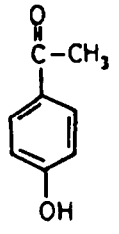

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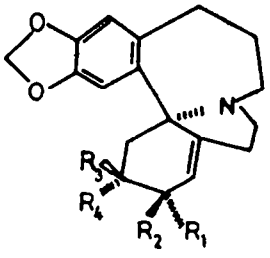
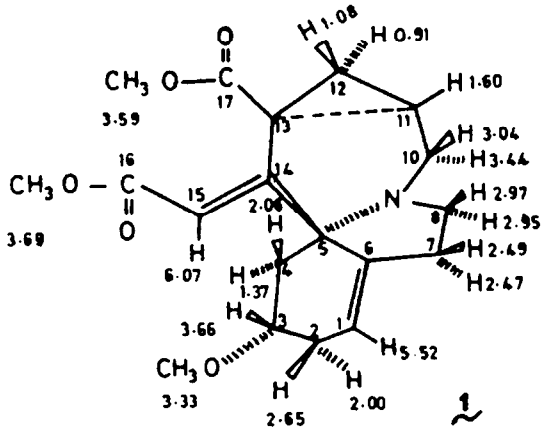


10 R_1 = OH, $R_2 = R_3 = H$, $R_4 = OCH_3$

11 R_1, R_2 = O, R_3 = H, $R_4 = OCH_3$



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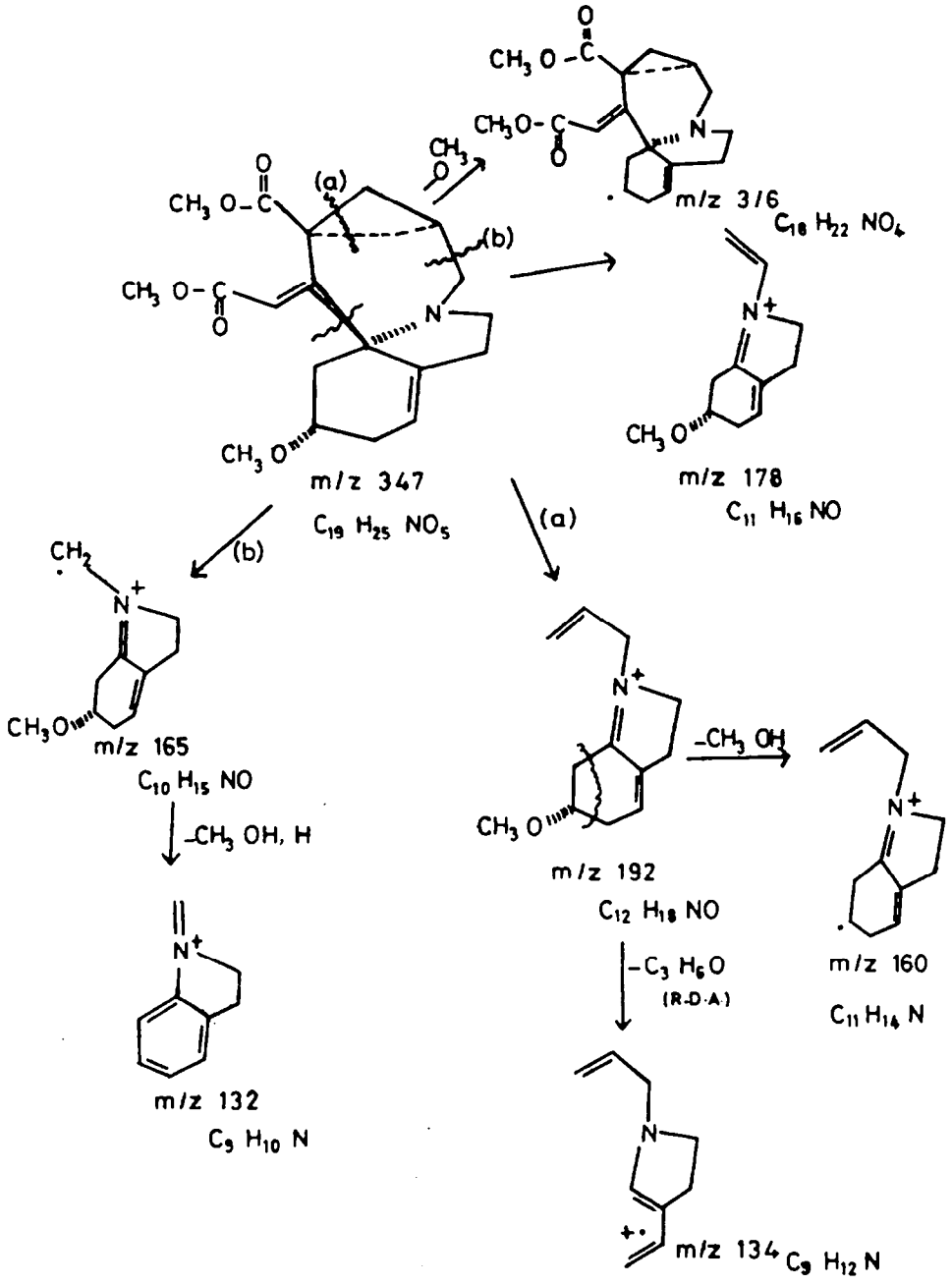
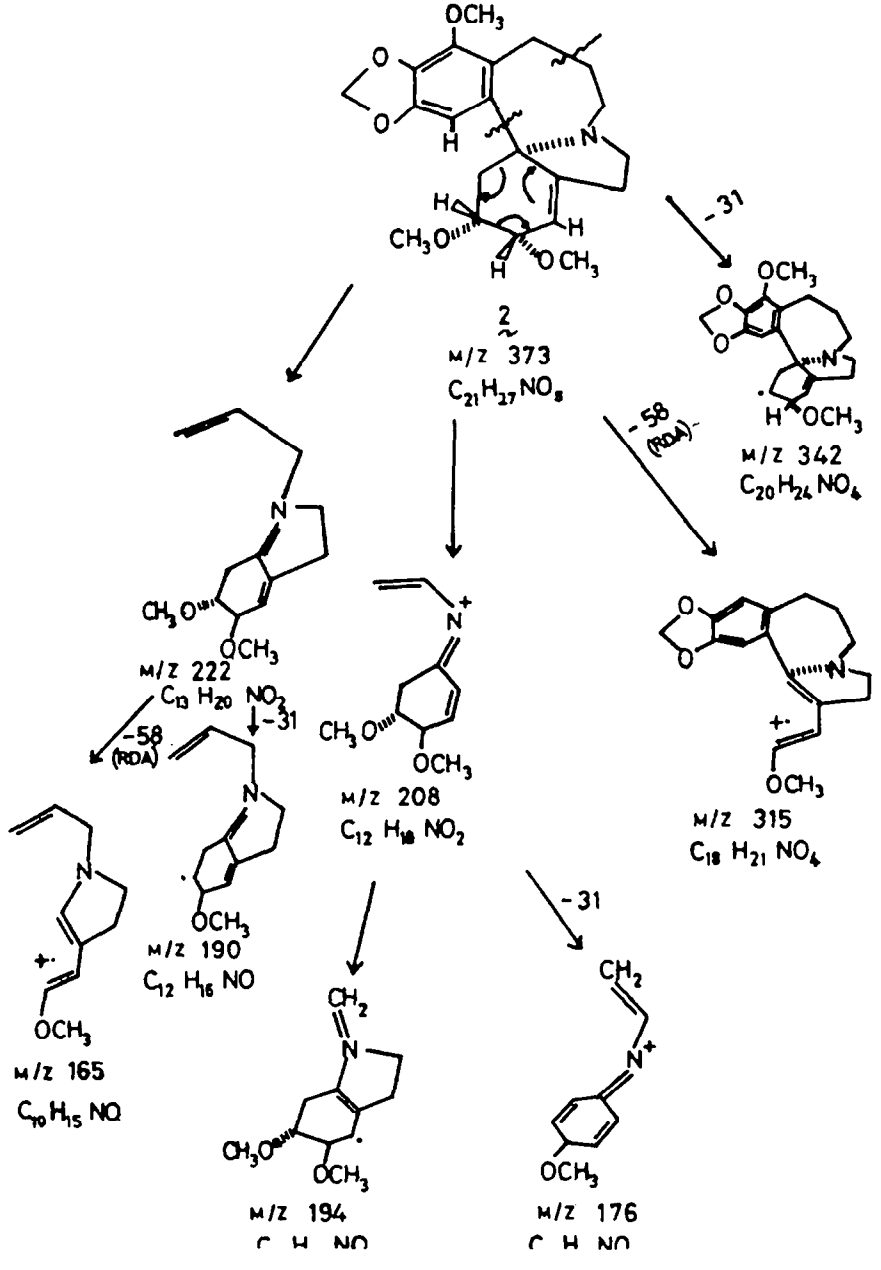


151.2 . The presence of only four double bonds in the ^{13}C nmr in conjunction with the eight degrees of unsaturation calculated from the molecular formula requires that the new alkaloid possess four rings in its skeleton, however, the spectroscopic data indicated that none of the rings in (1) was aromatic. The mass spectrum clearly identified (1) as possessing the C-1 to C-10 portions of the homoerythrina skeleton by the presence of the base peak at m/z 165. This ion loses methanol and a hydrogen atom to give the diagnostic peak at m/z 132. These two ions as well as that of other Δ^{1-6} homoerythrina alkaloids are found in the ms of the leaf alkaloids[7,8]. The major ion at m/z 192 contains the C-1 to C-12 portions of (1) including two of the atoms contained in the cyclopropane ring. Such an ion could not be formed if the aromatic D-ring of the homoerythrina skeleton were still present. The A-ring of (1) is a 3-methoxy-Δ^{1-6} cyclohexene is confirmed by the loss of methylvinyl ether via a retro-Diels Alder fragmentation from the parent ion as well as from the fragments at m/z 192 and 165. The identification of the location of the fourth ring was made by the analysis of the

high field ^{1}Hnmr spectrum of (1). By careful decoupling experiments, two groups of five mutually coupled protons were identified. The first group H-2 to H-4 showed the typical coupling pattern for the 3-epischelhammericine series,[14,15] with H-4α appearing as a triplet at 1.37 δ (J=12Hz) coupled equally to H-4β and H-3β. The second group of five protons, H-10 to H-12 were analyzed as follows. Two geminal protons at H-12 showed dramatically different chemical shifts at 1.08 (J=5,6.8Hz) and 0.91 (J=5,9Hz). A geminal coupling of only 5Hz is uniquely indicative of methylene protons in a cyclopropane ring. The couplings of 5 and 9Hz were to H-11 which appears as a multiplet at 1.60δ. In cyclopropane rings, it has always been observed that for vicinal couplings in the ring Jcis>Jtrans. Thus the strongly shielded cyclopropyl proton at 0.91δ should be cis to the bridgehead hydrogen H-11. The other two protons coupled to H-11, the geminal protons on H-10 at 3.04 and 3.44δ were shown to be adjacent to the nitrogen atom by their chemical shifts and by their 15Hz geminal coupling constant. Other definitive features of the ^{1}Hnmr spectrum included the three O-methyl singlets at 3.33 (ether), 3.59 and 3.69 (esters). The vinyl hydrogen H-1 was a broad singlet at 5.52δ while the isolated vinyl hydrogen at H-15 was a sharp singlet at 6.07δ. From the accumulated spectral evidence, we now propose the novel structure (1) for the new alkaloid.



The spectral data of the new alkaloid, 3-epi-2,18-dimethoxyschelhammericine(2) is indicative of an homoerythrina alkaloid. The ir showed aromaticity at 1605, 1495, 1480 and ether function at 1270 cm^{-1}. The ^{1}Hnmr spectrum indicated a tri-substituted aromatic ring, with the only proton showing a singlet at 6.58δ which has been assigned to H-15. There are three $-OCH_3$ groups, one aromatic $-OCH_3$ at 3.86 and two aliphatic $-OCH_3$ at 3.36 and 3.24 ppm respectively. A methylenedioxyl group singlet at 5.92 ppm. A three-proton singlet at 3.86 was assigned to a $-OCH_3$ at C-18, while a broad singlet at 5.70 was assigned to H-1. A doublet of doublet at 4.40 was assigned to H-2. A three-proton singlet at 3.36 was assigned to C-3 methoxyl group while another 3-proton singlet at 3.24 was assigned to C-2 methoxyl group. The ^{13}Cnmr showed a good correlation to the ^{1}Hnmr assignments. The ms analysis showed a molecular ion of m/z 373 which is calculated for $C_{21}H_{27}NO_5$. The fragmentation pattern is typical of $\Delta^{1,6}$ homoerythrina alkaloids.[1,4,8] For the positions of the C-2, C-3 and C-18 methoxyl groups, (2) is very similar to alkaloids 10 isolated from P. brachyphylla as 1[1], and P. comosa as 3[11] especially with reference to the C-2 -OH substituent. The alkaloid (2) assignment of the C-2 $-OCH_3$ seemed correct because of its shielded chemical shift, the -OH present in 1[1]. 3[11] and the oxidation of this -OH in 1[1] to a ketone in 11 as 5[1]. Since 3-epi-18-methoxyschelhammericine was previously isolated from the leaf of this plant[8] and also in the stem, though a C-2 oxygenated alkaloid has not been isolated, it thus means that the -OH at this position may have been methylated to give alkaloid (2). This new alkaloid can also be named 3-epi-2-methoxyldyshomerythrine, based on the name dyshomerythrine assigned to the 3-epi-18-methoxyschelhammericine.[8] The spectral assignment is fully in agreement to the structure proposed.

Recently we reported on our studies of the diterpenes and acetophenone from the leaf of D. lecticellare.[13] From the n-hexane soluble extract of the stem, we have characterized three diterpenes, compound (3), 8β-hydroxysandaracopimarene (4), phyllocladene (5) and a p-hydroxyacetophenone (8). Prior to our work, none of these compounds have been found in plants of the Meliaceae. The new compound (3) is a derivative of (4). The ms showed a molecular ion at m/z 304.1922 corresponding to a formula $C_{21}H_{37}O$. It has a very simple fragmentation pattern containing few major ions besides the parent ion and the base peak. The base peak appeared at m/z 289 due to the loss of a methyl group. The ir spectrum showed methyl groups at 2940, 1395, 1380 and 1285cm^{-1}. It also showed bands characteristic of a vinyl group at 3080, 1640, 990 and 912 cm^{-1}. A strong band at 1080 indicated an aliphatic ether. The ^{1}Hnmr spectrum showed the three vinyl protons at 5.80, 5.02 and 4.82 ppm. Also indicated were the four methyl groups at 1.31, a singlet assigned to the C-13β positioned methyl group. A singlet at 1.04 corresponded to the C-10β $-CH_3$ group, while the singlet at 0.87 representing six equivalent protons have been assigned to C-4 and C-4 gem dimethyl groups. A singlet at 3.64 integrating for three protons was assigned to the 8β $-OCH_3$ group. The ^{13}Cnmr spectrum of (3) was done to further confirm the pimarane skeletal structure of this compound. The result was compared with the literature[13] values for the pimarane skeleton. On the basis of the spectral assignment, the close similarity to (4), the name 8β-methoxysandaracopimar-15-ene is being proposed. The spectroscopic evidence (ir,^{1}Hnmr,^{13}Cnmr,ms), melting point and the comparison with literature reference compound,[13] established the structures of these three diterpenes and the acetophenone (8).

EXPERIMENTAL

Plant material - Dysoxylum lenticellare Gillespie was collected on 28 August, 1963, near the Boys Scout Camp, Coli-Suva, VitiLevu in the Fiji Islands by George Uhe. Voucher specimen AK157466 is preserved in the Herbarium of the Auckland

Institute and Museum, Auckland 1, New Zealand.

Apparatus

Infrared (ir) spectra were recorded on a Perkin-Elmer model 457A grating spectrophotometer. Specific rotations were determined in a ldm, jacketed tube in a Perkin-Elmer model 241 MC polarimeter. Ultraviolet (uv) spectra were obtained on a Bausch and Lomb spectronic 2000 spectrophotometer. All nmr spectra are reported in ppm with tetramethylsilane as an internal standard. ^{1}H nmr spectra were recorded on a Varian T-60 spectrometer and at high resolution on a Brucker HX-270 spectrometer in the Fourier transform mode. ^{13}C nmr spectra were recorded in concentrated $CDCl_3$ and Acetone-d_6 solutions in sealed 1.7 mm capillary tubes on a Varian Ft-80A instrument. Mass spectra (ms) were obtained at low resolution on a Finnigan-MAT 212 spectrometer with an SS 200 data system and at high resolution on a CEC 21-110B mass spectrometer with electron impact ionization at 70 ev. All recorded relative intensities were obtained from the low resolution ms. Thin-layer chromatography (tlc) was carried out on silica gel-coated plastic sheets (Bakerflex IB-F). Preparative tlc (ptlc) was performed on glass plates precoated with a 1.5 mm layer of silica GF_{254} (E Merck). Visualization of chromatograms was by uv light; alkaloids were also visualized by Dragendorff's spray reagent. Column chromatography was carried out on silica gel G 60 (70-230 mesh) E Merck.

Extraction

Powdered stem material (2.1 kg) was percolated with methanol until extracts tested negative to Dragendorff's reagent. The extract was concentrated to a syrup (337.9 g) and was mixed with water and partitioned against n-hexane (800 mg), chloroform (50.8 g), ethylacetate (40.4 g). The chloroform extract (50.8 g) was acidified to pH 2 with 3.5% HCl and filtered. The filterate was basified to pH 10 and this was extracted with chloroform to give 2.05 g after the evaporation of the solvent.

Isolation and Purification of the Alkaloids

The crude alkaloid mixture (2.05 g) was separated by column chromatography (I) of silica gel (80 g), packed with chloroform and eluted with various ratio of methanol in chloroform. Fractions 5-20 ($CHCl_3$-MeOH 97:3), yellowish-green, gave 728.3 mg after drying and showed several alkaloid spots. This was put on another silica gel column (II) (35 g) and eluted with chloroform-methanol. Fractions 2-4 ($CHCl_3$-MeOH 98:2) yellow solution that gave 146.2 mg. It was found to be a mixture and the ptlc was done on silica gel developed with $CHCl_3$-MeOH 95:5. The third band was eluted and gave 36.8 mg on drying. It was found very pure (tlc) and coded alkaloid 2. Fractions 5-7 (239.3 mg) was subjected to another column (VII) of silica gel, eluted with benzene-ethanol 90:10. Fractions 9-16 (222.6 mg) was put on ptlc of silica gel and was developed with di-isopropylether-ethanol 70:30. Bands A-H were cut and Band E (41.10 mg) was found to be the major alkaloid and very pure (tlc) and was coded alkaloid 1. The fourth band, that is the band next to the band that gave alkaloid 2 gave 64.8 mg on drying. This was put on silica gel ptlc and developed with di-isopropylether-ethanol 70:30 and nine bands were cut. The third band gave 18.3 mg on drying and was found to be major alkaloid from this ptlc which was coded alkaloid 9. Fractions 2-8 of column (VII) was put on ptlc and repeated the ioslation of 1. Five bands were cut and the third was found very pure (tlc) as the major alkaloid (15.0 mg) and was coded alkaloid 7. From the ptlc from which alkaloid 9 was isolated as the third band, gave alkaloid coded 6 as the second band (12.4 mg). The band C of the ptlc from which alkaloid 1 was isolated gave a compound (16.7 mg) which was coded 8.

Isolation and Purification of the Terpenes

The n-hexane (800 mg) fraction was subjected to a silica gel (35 g) column (III), packed with $CHCl_3$ and chloroform-methanol. Fractions 1-4 (341.8 mg), a brownish-yellow, non-alkaloidal fraction was put on ptlc of silica gel and developed with $CHCl_3$-MeOH 95:5. The first band (21.7 mg) was found pure and coded 5. The second band (52 mg), also was pure and designated 3. The third band (195.4 mg) was found to be the major compound and was designated 4.

Characterization of the Alkaloids

Alkaloid 1 amounted to 41.10 mg was obtained as a light green oil; (a)$_D^{28}$ + 16° (C = 0.17); λmax:230 nm (3500); νmax:3400, 2960, 2930, 2840, 1730, 1690, 1625, 1620, 1515, 1480, 1438, 1370, 1336, 1260, 1205, 1150, 1100, 1080, 933, 755 cm^{-1}; ^{1}H nmr: 6.07 (s, 1H, H-15), 5.52 (s, 1H, H-1), 3.69 (s, 3H, $-OCH_3$), 3.66 (m, 1H, H-3), 3.59 (s, 3H, $-OCH_3$), 3.33 (s, 3H, $-OCH_3$), 3.44 (dd, 1H, J = 15, 9Hz, H-10β). 3.04 (dd, 1H, J = 15, 5Hz, H-10a), 2.97 (dd, 1H, H-8a), 2.95 (m, 1H, H-8β), 2.65 (dd, 1H, J = 15, 5Hz, H-2a), 2.49 (dd, 1H, H-7a), 2.47 (d, br, 1H, H-7β), 2.06 (dd, 1H, J = 4, 12Hz, H-4β), 2.00 (d, br, 1H, H-2β), 1.60 (m, 1H, H-11), 1.37 (t, 1H, J = 12Hz, H-4a), 1.08 (dd, 1H, J = 5.0, 5.8Hz, H-12b), 0.91 (dd, 1H, J=5, 9Hz, H-12a) δ ; ^{13}C nmr: 18.8, 21.8, 25.2, 26.3 (t, 4 $-CH_2-$ groups of C-2, C-4, C-7, C-12), 30.5 (d, C-11), 37.2 (s), 41.7 (t, C-10), 47.3 (t, C-8), 50.9 (q, C-17, $-OCH_3$), 51.8 (q, C-16) $-OCH_3$, 55.6 (q, C-3, $-OCH_3$), 64.3 (s, C-5), 72.3 (d,

C-3), 119.0 (d, C-1), 122.3 (d, C-15), 139.2 (s, C-6), 151.2 (s, C-14), 165.3 (s, C-16), 171.8 (s, C-17) δ ; m/z: 347.1759 (M^+, 39), calc. for $C_{19}H_{25}NO_5$, 316 (67), 288 (18), 284 (22), 256 (19), 230 (23), 196 (12), 192 (68), 178 (14), 165 (100), 160 (45), 134 (33), 132 (56), 120 (35), 91 (21), 45 (38), 41 (30).

Alkaloid 2 was a brownish gum (36.8 mg) with the following spectral data: $[\alpha]_D^{25}$ + 76° (C = 0.65); λmax: 238 (4500), 292 (5100); νmax: 3400, 2920, 2860, 1605, 1495, 1480, 1450, 1270, 1100, 1030, 950, 915, 750 cm^{-1}; ^1H nmr: 6.58 (s, 1H, H-15), 5.92 (s, 2H, O-CH_2-O), 5.70 (s, br, 1H, H-1), 4.40 (dd, 1H, J = 6, 2Hz, H-2), 3.98 (m, 1H, H-3), 3.86 (s, 3H, $-OCH_3$, C-18), 3.70 (d, 1H), 3.45 (t, 1H), 3.40 (d, 1H), 3.36 (s, 3H, $-OCH_3$, C-3), 3.24 (s, 3H, $-OCH_3$, C-2), 2.52 (d, 1H), 2.00 - 1.22 (multiplets, 7H); ^{13}C nmr: 22.4, 25.8, 26.5, 28.6 (t, 4 $-CH_2$-groups at C-4, C-7, C-11, C-12), 45.8 (t, C-10), 49.7 (t, C-8), 55.4 (q, C-2, $-OCH_3$), 56.2 (q, C-3, $-OCH_3$), 51.6 (q, C-18, $-OCH_3$), 63.5 (d, C-2), 69.3 (s, C-5), 76.6 (d, C-3), 100.6 (t, $-OCH_2O-$), 110.8 (s, C-18), 112.0 (d, C-15), 117.8 (d, C-1), 134.3 (s, C-14), 136.0 (s, C-13), 145.2 (s, C-6), 146.1 (s, C-17), 147.8 (s, C-16) δ ; m/z: 373 (M^+), calc. for $C_{21}H_{27}NO_5$, 342 (M-31, $C_{20}H_{24}NO_4$), 315 (M-58, $C_{18}H_{21}NO_4$), 222 ($C_{13}H_{20}NO_2$), 208 (100, $C_{12}H_{18}NO_2$), 194 ($C_{11}H_{16}NO_2$), 190 ($C_{12}H_{16}NO$), 165 ($C_{10}H_{15}NO$) 164 ($C_9H_8O_3$), 133 ($C_8H_5O_2$).

Alkaloid 6 was obtained as a yellowish oil (12.4 mg) and found to be identical with the known homoerythrina alkaloid 3-epischelhammericine $[\alpha]_D^{25}$ + 105° (C = 1.62); λmax: 284 (3800), 220 nm (3900); νmax: 2970, 2920, 2850, 2820, 1505, 1480, 1450, 1420, 1380, 1355, 1335, 1270, 1240, 1120, 1070, 958, 915, 860, 760, 700, 630 cm^{-1}; ^1H nmr: 6.74 (s, 1H, H-15), 6.64 (s, 1H, H-18), 5.92 (s, 2H, $-OCH_2O-$), 5.51 (s, br, 1H, H-1), 3.23 (s, 3H), a series of complex overlapping multiplets between 2.00 and 3.60 culminated by a pair of overlapping triplets at 1.61 (t, 1H, H-4ax) δ ; m/z: 313.1678 (M^+, 20), calc. for $C_{19}H_{23}NO_3$, 282 (15, M-CH_3O), 255 (36, M-C_3H_6O), 254 (45, M-C_3H_7O), 178 (100, $C_{11}H_{16}NO$), 165 (49, $C_{10}H_{15}NO$), 146 (40, $C_{10}H_{12}N$).

Alkaloid 6 was identified as 3-epischelhammericine by co-tlc with an authentic sample and by comparison with ir, uv, nmr and ms data.[2,5,7,8,11,14] Crystalline picrate of this compound from ethanol, mp 169-171° [Lit. (11,14) mp 169-172°], was also obtained.

Alkaloid 7 was obtained as a brown gum (15.0 mg) and found to be identical with the known homoerythrina alkaloid 2,7-dihydrohomoerysotrine.[5-7,9,11] $[\alpha]_D^{25}$ + 121° (C = 0.50); λmax: 282 (3480), 259 nm (3020); νmax: 2962, 2930, 2858, 1515, 1465, 1265, 1205, 955, 920 cm^{-1}; ^1H nmr: 6.72 (s, 1H), 6.64 (s, 1H), 5.51 (s, br, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.20 (s, 3H), 1.52 (t, J = 4, 2Hz, 1H) δ ; m/z: 329.1990 (M^+, 29), calc. for $C_{20}H_{27}NO_3$, 298 (32), 271 (72), 270 (54), 256 (25), 240 (18), 178 (100), 165 (57), 146 (43) 57 (32), 41 (29). It was identified by co-tlc with authentic sample and by comparison with ir, uv, nmr and ms data.[5-7,9,11]

Alkaloid 9 was obtained as a brownish oil (18.3 mg) and was found to be identical with the known homoerythrina alkaloid 3-epi-18-methoxyschelhammericine, referred to as Dyshomerythrine.[6,8] $[\alpha]_D^{25}$ + 84 (C = 0.10); λmax: 285nm (1640; νmax: 2970, 2920, 2850, 2820, 1505, 1480, 1450, 1420, 1380, 1355, 1335, 1270, 1240, 1120, 1100, 1070, 958, 915, 860, 760, 700, 630 cm^{-1}; ^1H nmr: 6.53 (s, 1H, H-15), 5.92 (s, 2H, $-OCH_2O-$), 5.52 (s, br, 1H, H-1), 3.90 (s, 3H), 3.23 (s, 3H), a series of complex overlapping multiplets between 2.00 and 3.60 culminated by a pair of overlapping triplets at 1.57 (t, 1H, H-4ax) δ ; m/z: 343.1784 (M^+, 19), calc. for $C_{20}H_{25}NO_4$, 312 (25), 285 (33), 284 (38), 178 (100), 165 (49), 146 (40). This compound gave a picrate salt, m.p. 115-118° after two recrystallization from MeOH. It was further identified by co-tlc with authentic sample and by comparison with ir, uv, nmr and ms spectral data.[6,8]

Characterization of the Terpenes

Compound 3 was isolated as a colourless oil (52.0 mg) νmax: 3080, 2940, 2860, 1640, 1455, 1440, 1395, 1380, 1285, 1270, 1170, 1120, 1100, 1080, 990, 960, 912, 850 cm^{-1}; ^1H nmr: 5.80 (dd, J = 10, 16, 1H), 5.02 (dd, J = 2, 16, 1H), 4.82 (dd, J = 2, 10, 1H), 3.64 (s, 3H), 1.90-1.20 (m, br, 19H), 1.31 (s, 3H), 1.04 (s, 3H), 0.87 (s, 6H) δ ; ^{13}C nmr: 15.8 (q), 17.2 (t), 17.7 (t), 18.4 (t), 21.8 (q), 24.5 (q), 33.6 (s), 33.8 (q), 36.4 (s), 37.4 (s), 38.3 (t), 39.8 (t), 42.3 (t), 42.6 (t), 51.8 (t), 56.6 (d), 57.2 (d), 72.5 (s), 108.7 (t), 151.6 (d) δ ; m/z: 304.1922 (M^+, 40) calc. for $C_{21}H_{37}O$, 290 (20), 289 (100), 286 (30), 277 (50), 273 (32), 271 (25), 235 (16), 219 (15), 207 (14), 193 (22), 180 (10), 175 (12), 163 (13), 162 (10), 151 (22), 150 (20), 137 (21), 135 (18), 133 (14), 123 (30), 121 (20), 119 (18), 109 (32), 107 (17), 91 (12), 81 (30), 79 (18), 77 (10), 69 (38), 67 (32), 55 (38), 43 (16), 41 (32). This compound was found to be new with some spectral similarities to 4.[13]

Compound 4, 8β-hydroxysandaracopimarene was isolated as a colourless oil (195.4 mg), which was crystallized from aqueous methanol to give 100.3 mg of colourless needle crystals, m.p. 41-42° (dec.) [lit. (13) 40-41°], νmax: 3560, 3080, 3000, 2940, 2880, 2860, 1636, 1466, 1445, 1390, 1374, 1195, 991, 912, 852 cm^{-1}; ^1H nmr:

5.70 (dd, 1H), 4.90 (dd, 1H), 4.85 (dd, 1H), 1.90-1.30 (m, br, 19H), 1.20 (s, 3H), 0.98 (s, 3H), 0.85 (s, 6H) δ ; ^{13}C nmr: 15.6 (q), 17.0 (t), 17.8 (t), 18.4 (t), 21.6 (q), 24.3 (q), 33.3 (s), 33.5 (q), 36.4 (s), 37.2 (s), 38.1 (t), 39.5 (t), 42.1 (t), 43.6 (t), 51.6 (t), 56.6 (d), 57.0 (d), 72.4 (s), 108.5 (t), 151.5 (d) δ ; m/z: 290.2711 (M^+, 42) calc. for $C_{20}H_{34}O$, 276 (25), 275 (100), 272 (32), 257 (27) 221 (16), 205 (14), 193 (14), 179 (21), 166 (13), 161 (10), 149 (13), 148 (11), 137 (22), 136 (19), 123 (21), 121 (16), 119 (13), 109 (29), 107 (20), 105 (16), 95 (31), 91 (11), 81 (28), 79 (17), 77 (10), 69 (35), 67 (30), 55 (36), 43 (15), 41 (29).

Compound 5, phyllocladene was isolated as a colourless oil (21.7 mg) which was crystallized from absolute ethanol to give 10.2 mg of a white crystalline compound, m.p. 94-95° (dec.) [lit. (13) between 94 and 98°], νmax: 3070, 2985, 2945, 2928, 2876, 2845, 1658, 1480, 1450, 1385, 1370, 1130, 990, 975, 878 cm^{-1}; ^{1}H nmr: 4.70 (s, br, 2H), 2.60 (m, 2H), 2.00-1.15 (m, 19H), 0.94 (s, 3H), 0.88 (s, 3H), 0.83 (s, 3H) δ ; ^{13}C nmr: 15.2 (q), 18.6 (t), 19.1 (t), 20.4 (t), 22.0 (q), 33.2 (s), 33.7 (q), 34.1 (t), 37.9 (s), 39.6 (t), 41.2 (t), 41.5 (t), 42.1 (t), 42.8 (d), 43.7 (s), 50.4 (t), 56.6 (d), 57.0 (d), 102.4 (t), 157.4 (s) δ ; m/z: 272.2504 (M^+, 40) calc. for $C_{20}H_{34}$.

Compound 8, p-hydroxyacetophenone was isolated along with the alkaloids as a crystalline solid (16.7 mg). This was recrystallized from benzene to give 10 mg of a white powder m.p. 108-109° (dec.) [lit. (13) 107.5-108°]. A mmp with an authentic sample (m.p. 108-110°) was undepressed, νmax: 3310, 3145, 3020, 1650, 1585, 1515, 1445, 1370, 1290, 1240, 1175, 970, 840, 600, 580 cm^{-1}; ^{1}H nmr: 8.40 (br, 1H), 7.72 (d, J = 8.0, 2H), 6.8 (d, J = 8.0, 2H), 2.47 (s, 3H) δ ; m/z: 136.0728 (M^+, 43) calc. for $C_8H_8O_2$, 121 (100), 93 (48), 65 (36), 39 (29).

ACKNOWLEDGEMENTS

I thank Dr. C. E. Costello, Massachusetts Institute of Technology, Cambridge, U.S.A., for recording the mass spectra, under NIH Research Grant No. RRO0317, Dr. R. W. Lauver (NASA-Lewis), for recording the ^{13}C nmr spectra, Dr. K. A. Onan, Northeastern University, Boston, for recording the ^{1}H nmr spectra, Drs. C. J. Kelley and J. D. Leary, Massachusets College of Pharmacy and Allied Health Sciences, Boston, for kindly allowing me to work in their laboratory.

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