fold symmetry of which is obvious but not pronounced. In bicyclobutane a similar section through the bridgehead atoms has only two distinct maxima. In the center of the tetrahedron and in the center of its surface plane we find minima which have a relatively high density. The latter is one level unit (0.03 a. u.) lower than the density on the classical valence line between the carbon atoms.

It is obvious that the C—C bonds in tetrahedran are highly strained. Makšić et al. have calculated the hybridization parameters for several strained, cyclic hydrocarbons in their maximum overlap approach. They give the value 29.5° for the angle describing the deviation of the hybrid direction from the C—C interatomic line (for cubane they give the value 11.5°). Baird and Dewar conclude from their SCF-MO calculations that tetrahedran does not exist as a stable species except under certain conditions at low temperature, and that substituted tetrahedranes should be even less stable than the parent compound. On the other hand, Masamune and Kato find the thermal stability of their diphenyl derivative surprisingly high.

The series of hydrocarbons, acetylene, tetrahexedran, cubane, etc. which are built up from C—H units is sometimes called "acetylenic" strained hydrocarbons. The valence charge distribution and the general nature of the triple bond do not give reason to include acetylene with the strained single bond compounds. The strained single bonds form a group of bonds by themselves which are richer in energy and more reactive than the unstrained single bond. Perhaps they can be characterized as preexcited or pseudo-excited.


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Studies on Orchidaceae Alkaloids

XXV. N-Isopentenyl Derivatives of Dendrobine and 6-Hydroxydendrobine from Dendrobium friedrichsianum Lindl. and Dendrobium hildebrandii Rolfe

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The quaternary compounds N-methyl-dendrobine (I) and N-isopentenyl-dendrobine (II), one of the possible isomers, have been isolated from Dendrobium nobile Lindl. by Inubushi et al. In this communication we report the isolation of two quaternary compounds, N-isopentenyl-dendrobine (III) and N-isopentenyl-6-hydroxydendrobine (IV), as the chlorides from D. friedrichsianum Lindl. and D. hildebrandii Rolfe. The tertiary bases reported to occur in D. hildebrandii, i.e. nobilone, 6-hydroxydionobilone and dendramine, have also been found in D. friedrichsianum.

It is evident, from the IR and NMR spectra, that both III and IV, contain an isopentenyl group. Pyrolysis of III and IV at 160°C gave dendrobine and 6-hydroxydendrobine, respectively. The facile loss of the isopentenyl groups indicates that they are attached to the quaternary nitrogen atoms. Alkylation of 6-hydroxydendrobine with 1-bromo-3-methyl-2-

* Number XXIV of this series, see Ref. 1.
** We prefer the name nobilone instead of nobilone, since the latter can be confused with nobilone. 5

butene and subsequent transformation to the chloride gave a product indistinguishable from IV (IR, NMR, optical rotation).

**Experimental.** All melting points are corrected. Mass spectra were measured on an LKB 9000 spectrometer (ionization energy: 70 eV), and the optical rotation on a Perkin-Elmer 141 polarimeter. The IR spectra were recorded on a Perkin-Elmer 257 instrument, and the NMR spectra on a Varian A-60A spectrometer.

**Isolation of III and IV.** Fresh plants of Dendroblum frieickiansum Lindl. (6 kg) were extracted with methanol (17 l). The extract was concentrated to 1.5 l, acidified (pH 3) and washed with carbon tetrachloride (3 x 0.5 l). The aqueous solution was made alkaline with sodium hydroxide (pH 9) and extracted with ether (5 x 0.4 l). The ether solution contained the same bases reported to occur in D. hildebrandii, i.e. nobilone, 6-hydroxy-nobilone, and dendrame.

The alkaline aqueous solution was neutralised and extracted with chloroform-ethanol (3:2, v/v, 12 x 0.5 l). The extract was dried (Na₂SO₄), evaporated and filtered through Dowex 1-X4 (Cl⁻, 5 x 40 cm) using methanol-water (1:1) as eluent. The eluate was evaporated to dryness and the residue was filtered through neutral alumina (5 x 50 cm) using ethanol as eluent. The eluate was evaporated to dryness and the residue was dissolved in water and treated with Reinecke salt. The precipitate was dissolved in acetone-water (1:1) and filtered through Dowex 1-X4 (Cl⁻, 3 x 15 cm) using acetone-water as eluent. Evaporation of the eluate to dryness and three recrystallisations of the residue from ethanol afforded IV (260 mg) as colourless needles. Separation of the components in the mother liquor by preparative paper chromatography (Whatman 1) gave III (300 mg, Rₚ 0.3) and IV (100 mg, Rₚ 0.1). Before applying the spots, the paper was dipped in a mixture of acetone and water (1:1, v/v) and the acetone removed in a current of air. The chromatogram was then developed with acetone.

The quaternary compounds from D. hildebrandii were isolated in the same way as described above.

**Characterisation of III.** Crystallisation of III from acetone-ethanol containing a small amount of ethanol afforded hygroscopic needles, m.p. 108-120° (dec.); [α]D²³ -48° (c 0.64, methanol). (Found: C 64.8; H 8.8; Calc. for C₉H₁₄ClNO₄C₂H₅OH: C 65.2; H 9.12.)

In the absence of ethanol III failed to crystallise. IR spectrum: αmax (KBr) 3400(s) broad, 1790(s), 1675(m) cm⁻¹. NMR spectrum (CD₂OD) τ: 4.42 (t, further coupled, 1 H, J = 7 Hz), 4.71 (d, 1 H, J = 5 Hz), 8.09 (s, broad, 6 H), 8.48 (s, 3 H), 8.91 (d, 3 H, J = 5.5 Hz), 9.00 (d, 3 H, J = 5.5 Hz); signals from ethanol appear at τ 6.37 (q, 2 H, J = 7 Hz) and τ 8.82 (t, 3 H, J = 7 Hz).

**Characterisation of IV.** Crystallisation of IV from ethanol gave needles, m.p. 144-156° (dec.); [α]D²³ -30° (c 0.51, methanol). (Found: C 63.0; H 8.66; Cl 7.62; N 3.19; O 17.6. Calc. for C₉H₁₄ClNO₄C₂H₅OH: C 62.9; H 8.75; Cl 7.75; N 3.06; O 17.5.) In the absence of ethanol IV failed to crystallise. IR spectrum: αmax (KBr) 3340(s), 3200(s), 1783(s), 1678(m) cm⁻¹. NMR spectrum (CD₂OD) τ: 4.43 (t, further coupled, 1 H, J = 7 Hz), 4.78 (d, 1 H, J = 5 Hz), 8.08 (s, broad, 6 H), 8.60 (s, 3 H), 8.94 (d, 3 H, J = 5.5 Hz), 8.97 (d, 3 H, J = 5.5 Hz); signals from ethanol appear at τ 6.38 (q, 2 H, J = 7 Hz) and 8.83 (t, 3 H, J = 7 Hz).

**Pyrolysis of III.** III (70 mg) was heated under argon at 160° for 15 min. The reaction mixture was dissolved in dilute hydrochloric acid and washed with ether. The aqueous solution was made alkaline with sodium hydroxide (pH 9) and extracted with chloroform. The chloroform solution was dried, concentrated and filtered through alumina (0.5 x 5 cm) using chloroform as eluent. Evaporation of the eluate to dryness and recrystallisation of the residue from hexane gave dendroxine (20 mg) as colourless needles, m.p. 114-117°, [α]D²³ -10° (c 0.42, methanol), indistinguishable from an authentic sample (TLC, GLC, MS). Measurement of the optical rotation of an authentic sample of dendroxine (on less than 1 mg) gave [α]D²³ -0° (c 0.1, methanol). Okamoto et al. reported m.p. 114-115° and [α]D -30.1° (ethanol) for dendroxine.

**Pyrolysis of IV.** IV (54 mg) was heated under argon at 160° for 20 min. The reaction mixture was treated as described above giving 6-hydroxydendroxine as an amorphous solid, [α]D²³ +28° (c 0.71, methanol), indistinguishable for...
able from an authentic sample (TLC, GLC, MS) which gave $[\alpha]_D^{25} = 25^\circ$ (c 0.89, methanol).

Synthesis of IV. A solution of 6-hydroxydendroline (60 mg) and 1-bromo-3-methyl-2-butene (60 mg) in acetone (2 ml) was kept at 50° for 30 min. The solvent was removed and the residue was chromatographed on alumina (1 x 15 cm). Unreacted 6-hydroxydendroline (38 mg) was first eluted with chloroform, and 5-isopentenyl-6-hydroxydendroline bromide (38 mg) was then eluted with ethanol. The bromide was filtered through a column of Dowex 1-X4 (Cl\textsuperscript{-}, 1 x 30 cm) giving IV (33 mg) indistinguishable from an authentic sample (optical rotation, NMR, IR).

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3. Inubushi, Y. Personal communication.

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Gas-liquid Chromatography of Partially Methylated Alditols as their Acetates II

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The separation of alditol methyl ethers, as their acetates, by GLC has been used for some time in this laboratory, as a tool for structural studies on polysaccharides. For this work, a copolymer of ethylene glycol succinate polyester and nitrile silicone polymer (ECNSS-M) has generally been used as the stationary phase. This phase affords good separations but suffers from relative low temperature stability (max. 210°), which gives columns of limited lifetime. Column bleeding is also a disadvantage in combined GLC-MS, resulting in increased background and contamination of the ionisation chamber.

For these reasons, various other phases have been tested, and we have now found that a silicone polymer designated OV-225, containing methyl, phenyl and cyano-propyl groups, generally gives equally good separations of methylated alditol acetates to those obtained with ECNSS-M (Table 1). OV-225 is stable up to 250°, which is a definite advantage. Separations of the partially methylated alditol acetates is preferably performed at 170°. For the most volatile acetates, a lower temperature, 155°, has been used in order to obtain more accurate values for the relative retention times ($T$-values). The reproducibility of the values was examined over the temperature range 155 - 190°, and providing two internal standards with considerably different retention times were used and the retention values ($T$-values) were estimated by interpolation, the values obtained did not differ by more than 3%.

Experimental. GLC was carried out using a Perkin-Elmer 990 Gas Chromatograph. Separations were made at a gas-flow rate of 15 - 20 ml nitrogen per min on a glass column (180 x 0.15 cm) containing 3% (w/w) of OV-225 on Gas Chrom Q (100/120 mesh) at 170° or 155°.

The methylated sugars were either available in this laboratory or prepared by partial methylation of suitably protected sugar deriva-