a catalytic amount of NaI was based on our postulated mechanism, which involves initial formation of the trimethylsilyl ether of the alcohol and generation of the complex formed between CH_3CN and Me_3SiI that Olah[10] has demonstrated, as depicted in Scheme II. In this way a continual amount of an electrophilic reagent, either the complex 1 or perhaps Me_3SiI, would be available for attack on the silyl ether to provide the oxonium ion 2, which then would react with the nucleophilic and more abundant cyanide ion either by an S_N2 or S_N1 process.

The results of the conversion of a series of alcohols into the corresponding nitriles by this new method are shown in Table I. These data allow the following conclusions to be made: (a) primary, secondary, and tertiary alcohols are all converted into the corresponding nitriles in good to excellent yields; (b) the reaction proceeds with inversion of configuration as evidenced by the conversion of 3β-cholestanol into the less thermodynamically stable 3α-cyano-5α-cholestane (see entry 9); (c) the reaction, however, can proceed by an S_N1 process for a different secondary alcohol as shown by the 73% yield of *N*-cyclohexylacetamide isolated in the case of cyclohexanol (entry 10).[11] Other experiments carried out in order to elucidate the mechanism of this conversion included the following: (a) varying the stoichiometry of the in situ reagent; use of tetrahydropyranylmethyl alcohol and 1.0 equiv each of Me_3SiCl and NaCN gave a 23% yield of the corresponding nitrile, 1.5 equiv of each gave a 50% yield, and 2.0 equiv gave a 98% yield; (b) deletion of either of the two cosolvents; use of benzyl alcohol and only CH_3CN resulted in a 10% yield of benzyl cyanide in 3 h (this reaction proceeded cleanly with longer time); with the use of only DMF no reaction occurred in 3 h, but the addition of 2.5 equiv of CH_3CN at this point gave a >95% yield of nitrile in an additional 2 h; use of DMF and 2.2 equiv of CH_3CN initially gave an ≥95% yield; (c) preforming a silyl ether; the trimethylsilyl ether of benzyl alcohol was treated with Me_3SiCl/NaCN (1 equiv each) in DMF/CH_3CN (50/50 v/v) and a catalytic amount of NaI gave a 95% yield of benzyl cyanide. Finally, hexamethyldisiloxane (3) is the silicon-containing byproduct of this conversion. It was shown to be present in the reaction mixture and in approximately the amount expected by GC comparisons with an authentic sample.

In a typical procedure, a mixture of the alcohol (1.0 g), NaCN (2 equiv), NaI (2–5 mg), CH_3CN (10 mL), and DMF (10 mL) is deaerated, and, under an argon atmosphere, Me_3SiCl (2 equiv) is added at room temperature. The mixture is then placed in a preheated (60–65 °C) oil bath and heated with stirring for 2–8 h (the reaction is monitored by GC or TLC). When reaction is complete, the mixture is poured into H_2O (100 mL) and the mixture extracted with hexane or diethyl ether (100 mL). The organic phase is washed with H_2O (1 × 50 mL if hexane, 5 × 50 mL if ether) and with brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. In all but two reactions (*tert*-butyl alcohol and cholestanol) the nitrile thus obtained required no further purification. When necessary, the product was either distilled or recrystallized.

This alcohol into nitrile conversion because of its ease and exceptionally mild conditions promises to be general and applicable to multifunctional and sensitive substrate molecules. Further investigations into the utility of this catalytic NaI in situ generated reagent for synthetic transformations are continuing.

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30-Nor-3β-methoxyserrat-14-en-21-one: First Reported Natural Occurrence of a Norserratene Triterpene

Summary: A triterpenoid isolated from white pine bark (*Pinus monticola* Dongl.) has been shown to be 30-nor-3β-methoxyserrat-14-en-21-one by a combination of spectral, mass spectral, and X-ray crystallographic methods.

Sir: Serratenes are a novel group of naturally occurring pentacyclic triterpenes in which the central C ring is seven membered. In addition, all the known examples have seven tertiary methyls, one of which may occur as a hydroxymethyl, and usually have oxygen functionalities at either or both C-3 and C-21. Serratene triterpenes have been reported in such diverse plants as conifers (especially the Pinaceae)[1] and club mosses (*Lycopodium* species).[1,2]

Following a preliminary investigation of the chemistry of western white pine (*Pinus monticola* Dougl.) bark,[3] a detailed analysis of the benzene extract was conducted to determine its chemical composition.[4] During the course of that investigation, several unknown triterpenes were isolated. A number of these triterpenes had spectral properties that suggested they were serratenes.

One of the compounds (compound H—0.2% of benzene extract)[4] gave an elemental analysis (C, 81.94; H, 11.26) and molecular ion in the high-resolution mass spectrum (M^+ *m/e* 440.3674) that corresponded to an empirical formula of $C_{30}H_{48}O_2$ (calcd: C, 81.76; H, 10.98; M^+ *m/e* 440.3654). This compound has now been shown to have the structure 30-nor-3β-methoxyserrat-14-en-21-one (I) by single-crystal X-ray diffraction. Compound I is of interest because it is the first example of a naturally occurring norserratene. The full mass spectrum is consistent with the X-ray structure.

Single crystals of 30-nor-3β-methoxyserrat-14-en-21-one suitable for X-ray crystallographic data collection were obtained from methylene chloride by slow evaporation of the solvent. This compound crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell dimensions a = 9.598 (1), b = 10.559 (1), and c = 25.150 (2) Å. A total of 2414 unique reflections up to a 2θ limit of 127.5° were collected on a Picker FACS 1 diffractometer in the Biochemistry Department, University of Wisconsin—Madison, using Ni-filtered Cu Kα radiation. The structure was solved by a combination of direct and Fourier methods. After preliminary least-squares refinement of all the

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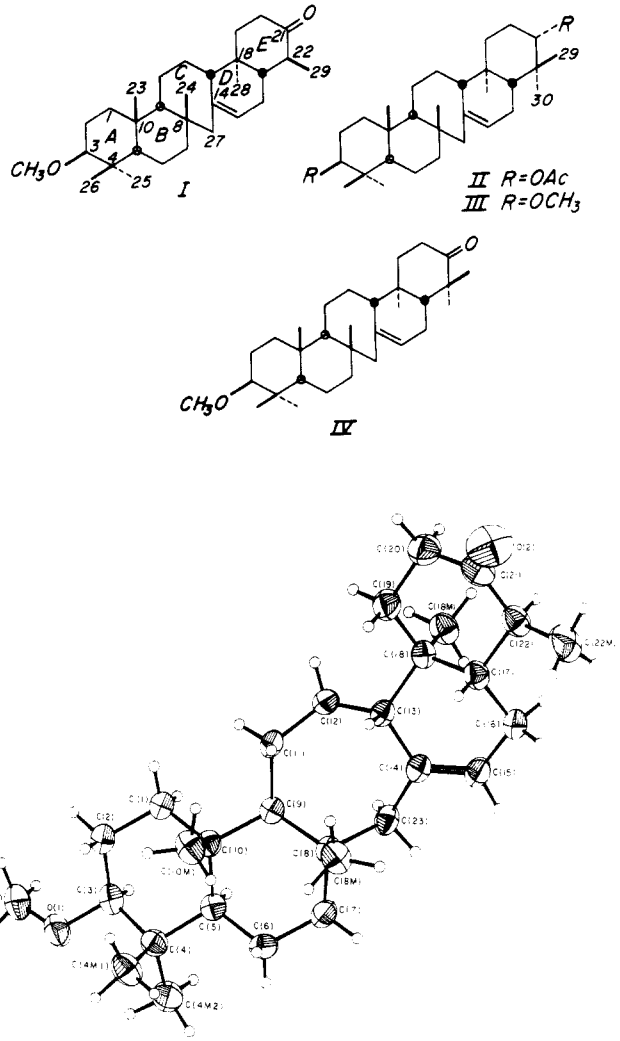

Figure 1. ORTEP diagram of 30-nor-3β-methoxyserrat-14-en-21-one (I) with nonhydrogen atoms shown as thermal vibration ellipsoids at 50% probability and hydrogen atoms shown as spheres of arbitrary size.

nonhydrogen atoms, all 48 hydrogen atoms were located from a difference Fourier synthesis. Final refinement of the structure yielded an R index [$= \sum(|F_{obsd}| - |F_{calcd}|)/\sum|F_{obsd}|$] of 0.037 for 2373 reflections with intensities greater than $1.5\sigma(I)$. An ORTEP[5] drawing of the crystallographic structure is shown in Figure 1. The full details of the X-ray analysis will be published elsewhere.

The 270-MHz ^{1}H NMR spectrum of I clearly shows that the molecule has one secondary methyl (3 H, d, J = 7 Hz) and five tertiary methyls (each 3 H, s) instead of the seven tertiary methyls previously reported from a 60-MHz spectrum.[4] The secondary methyl has the chemical shift (δ 0.97) expected for an equatorial methyl adjacent to a ketone.[6] The chemical shifts for the tertiary methyls of serratenediol diacetate (II) and similar compounds have been assigned.[7] By analogy, the chemical shifts for the tertiary methyls of serratenediol dimethyl ether[8] (III) and hence for the tertiary methyls of 3β-methoxyserrat-14-en-21-one[8] (IV) could be assigned. Table I shows that the chemical shifts for the tertiary methyls of I are similar to those of IV except for the differences expected at C-29 and C-30 due to structural differences. Especially interesting is the slight deshielding of the C-28 hydrogens, which is consistent with a C-21 ketone.

Table I. ^{1}H NMR Chemical Shifts (δ) of Serratene Methyls

methyl	III[a]	IV[a]	I[b]
C-23[c]	0.78	0.81	0.80
C-24[c]	0.83	0.82	0.83
C-25	0.83	0.92	0.90
C-26	0.96	0.95	0.96
C-28	0.68	0.75	0.75
C-29	0.83	1.05	0.97 (d)
C-30	0.96	1.09	

[a] 60 MHz, $CDCl_3$. [b] 270 MHz, $CDCl_3$. [c] Assignments may be interchanged.

Several other western white pine bark triterpenes (compounds A–G)[4] also appear to be serratenes, some of which are apparently closely related to 30-nor-3β-methoxyserrat-14-en-21-one. The structures of these compounds are presently under investigation.

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Dilongifolylborane: A New Effective Chiral Hydroborating Agent with Intermediate Steric Requirements

Summary: Dilongifolylborane, Lgf_2BH, a new effective chiral hydroborating agent, is readily synthesized from (+)-longifolene. Thus, treatment of (+)-longifolene with borane–methyl sulfide (BH_3·SMe_2) in ethyl ether rapidly precipitates snow-white crystalline Lgf_2BH: mp 160–161 °C; dimer; IR 1565 cm^{-1}. The new chiral dialkylborane achieves the successful asymmetric hydroboration of cis, trisubstituted acyclic, and trisubstituted cyclic prochiral olefins to provide alcohols, after oxidation of the intermediate organoboranes, with optical purities in the range of 60–78% ee. In the cases studied, the new asymmetric center at the alcohol position is predominantly the R enantiomer.

Sir: The functionality available through hydroboration and subsequent modification of the resulting organoborane is extensive. Monoalkyl- or dialkylboranes exhibit a remarkable stereospecificity and regioselectivity for the hydroboration of olefins. This property, coupled with the

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