

## Cosmogenic Chlorine-36 Chronology for Glacial Deposits at Bloody Canyon, Eastern Sierra Nevada

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Deposits from mountain glaciers provide an important record of Quaternary climatic fluctuations but have proved difficult to date directly. A chronology has been obtained for glacial deposits at Bloody Canyon, California, by measurement of the accumulation of chlorine-36 produced by cosmic rays in boulders exposed on moraine crests. The accumulation of chlorine-36 indicates that episodes of glaciation occurred at about 21, 24, 65, 115, 145, and 200 ka (thousand years ago). Although the timing of the glaciations correlates well with peaks of global ice volume inferred from the marine oxygen isotope record, the relative magnitudes differ markedly. The lengths of the moraines dating from 115 ka and 65 ka show that the early glacial episodes were more extensive than those during the later Wisconsin and indicate that the transition from interglacial to full glacial conditions was rapid.

THE LATERAL AND TERMINAL GLACIAL moraines that extend from canyon mouths along the eastern front of the Sierra Nevada have been a focus of geological interest since the earliest investigations in the area (1). The relatively arid climate of the region has resulted in slow rates of moraine weathering, and the nesting of younger moraines within older ones has permitted inferences concerning relative age. Blackwelder (2) originally distinguished four glaciations, which he termed (from youngest to oldest) the Tioga, Tahoe, Sherwin, and McGee. Two additional glaciations have since been proposed (3): the Tenaya (between the Tioga and Tahoe) and the Mono Basin (between the Tahoe and Sherwin).

On the basis of qualitative estimates of weathering rates, Blackwelder (2) correlated the Tioga and Tahoe glaciations with the late and early Wisconsin glaciations in the midwestern United States [now dated at 12 to 24 ka and 59 to 74 ka, respectively, based on correlation with ocean sediment cores (4)]. Sharp and Birman (3) later correlated the Tenaya and Mono Basin glaciations with the mid-Wisconsin and Illinoian midwestern glaciations [the Illinoian can be correlated with marine isotope stage 6, 130 to 190 ka (4)]. Carbon-14 dates on organic materials in sediments above or below Tioga-age

glacially derived sediments and on organic material in basal rock varnish (5) on moraine boulders have demonstrated that the Tioga glaciation occurred between 25 ka and 11 ka and is thus correlative with the late Wisconsin continental glaciation (5, 6).

The suggested correlations of the older deposits have remained controversial because of inadequate absolute age control. Limits have been placed with K-Ar or  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  dates on interbedded lava flows (7, 8), but the paucity of minerals suitable for dating, conflicting dates, and the inherent uncertainties of having to rely on limiting ages have not allowed a closely constrained chronology to be established (9, 10). Additionally, relative dating methods must be used in order to correlate glacial deposits from sites with interbedded volcanic materials suitable for dating to deposits at sites lacking such materials, and these methods have frequently yielded ambiguous results (10). Understanding the relation of moun-

tain glaciations to continental ice caps is necessary for interpretation of the climate dynamics, and this requires accurate dates.

Direct dating of glacial landforms is intrinsically difficult because they are constructed out of older rocks, and most dating techniques measure the formation age of minerals rather than the age of geomorphic redistribution. Rock varnish  $^{14}\text{C}$  and cation ratio methods (6) can provide at least limiting minimum ages. However, the climate is not arid enough to develop or to preserve reliably rock varnish at most Sierra Nevada moraines. Therefore, we have developed and applied a different method for dating glacial moraines and other landforms, accumulation of cosmogenic  $^{36}\text{Cl}$  (11, 12).

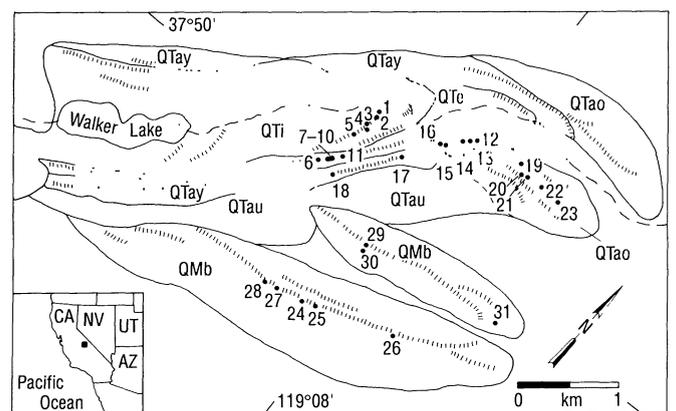
Production rates of  $^{36}\text{Cl}$  in the subsurface are small because of the low underground radiogenic neutron flux (13). When buried rocks are exposed at the land surface (for example, because of glacial excavation)  $^{36}\text{Cl}$  begins to accumulate because of exposure to cosmic-ray activation. The most important cosmic-ray reactions are cosmogenic thermal neutron activation of  $^{35}\text{Cl}$ , spallation reactions on  $^{39}\text{K}$  and  $^{40}\text{Ca}$ , and muon capture by  $^{40}\text{Ca}$ . The exposure age of a rock that meets the model assumptions of complete shielding followed by rapid exposure that continues without interruption until the time of measurement and negligible rock surface erosion is given by

$$t = \frac{-1}{\lambda} \ln \left( 1 - \frac{\lambda N(R - R_0)}{P} \right) \quad (1)$$

where  $t$  is the exposure age,  $\lambda$  is the decay constant for  $^{36}\text{Cl}$  ( $2.30 \times 10^{-6} \text{ yr}^{-1}$ ),  $N$  is the chlorine content (atoms per kilogram of rock),  $P$  is the total cosmogenic production rate of  $^{36}\text{Cl}$  per unit mass of rock (corrected for the effects on the cosmic-ray flux of geomagnetic latitude, elevation, and depth below the land surface),  $R$  is the measured  $^{36}\text{Cl}/\text{Cl}$  ratio, and  $R_0$  is the  $^{36}\text{Cl}/\text{Cl}$  ratio supported by radiogenic (from U and Th) neutrons (14).

Bloody Canyon (Fig. 1) in the Mono

**Fig. 1.** Map of glacial deposits at Bloody Canyon from (7) showing sample locations for individual boulders (numbers are keyed to Table 1). QT<sub>i</sub>, Tioga deposits; QT<sub>e</sub>, Tenaya deposits; QT<sub>ay</sub>, younger Tahoe deposits; QT<sub>ao</sub>, older Tahoe deposits; QT<sub>a</sub>, undifferentiated Tahoe deposits; and QM<sub>b</sub>, Mono Basin deposits. Hatchures indicate moraine crests.



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Basin was selected for the initial attempt at dating the eastern Sierra Nevada glacial sequence because it has been well studied (1-3, 15, 16), a large number of morphologically distinct moraines are preserved there, and the relative age sequence can be clearly inferred from topographic relations among many of the moraines. Although Blackwelder (2) did not map the Bloody Canyon glacial deposits, he did identify the Tahoe and Tioga moraines on a photograph. Bloody Canyon is the type area for the Mono Basin glacial deposits and can also be considered to be the type area for the Tenaya designation in the eastern Sierra Nevada (3).

The samples for dating were collected from the top 5 cm of the largest boulders along the crest of each of the moraines (Fig. 1). The moraine crests were sampled because boulders there were deemed least likely to have rolled or shifted during erosion. The largest (that is, tallest) boulders were used because they were most likely to have

been exposed at the surface before any erosion of the moraine crest, and because their upper surfaces were more likely to have projected above the average snow depth; snow can reduce cosmogenic <sup>36</sup>Cl production by attenuating the cosmic rays reaching the rock beneath. The height of the boulders sampled ranged from 0.5 to 5.4 m. The <sup>36</sup>Cl/Cl ratios (Table 1) were measured by accelerator mass spectrometry (17).

The calculated <sup>36</sup>Cl exposure ages (Fig. 2) from the Tioga moraine are fairly tightly clustered whereas samples from the older moraines show progressively more scatter, and a few of the samples are markedly younger than the oldest values. Several factors may produce scatter or systematic errors, including (i) analytical errors, (ii) <sup>36</sup>Cl inherited from an earlier exposure episode, (iii) preferential leaching of <sup>36</sup>Cl compared to stable Cl, (iv) erosion of the rock surface by spalling, shattering, or granular disintegration, (v) gradual exposure of the rock as a

result of erosion of till matrix from the moraine crest, and (vi) snow cover. Of these, the first may be expected to cause an unbiased (possibly normal) distribution of boulder ages from a single moraine, the second to produce a bias toward older ages, and all of the rest to produce a bias toward younger ages. Examination of the age distribution from the Tioga moraine, which can be inferred from independent <sup>14</sup>C dates to have an age near 20 ka and for which the effects of processes (iii) through (vi) are probably relatively small, shows no anomalously old outliers. On this basis inherited <sup>36</sup>Cl is assumed not to be a major problem for the older moraines. In summary, we hypothesize that boulder ages from young moraines should exhibit an unbiased distribution, but as the moraines grow older, this distribution will become skewed toward ages younger than the age of the landform. For the older moraines, then, a value other than the mean is needed to give the best estimate of the age of the landform. The maximum age is a reasonable choice on the grounds that at the older ages, the bias components swamp the analytical and sampling errors, and the maximum value is the one least affected by such errors.

The mean of the three oldest boulder ages from the Tioga moraine, 21.4 ka, is in excellent agreement with the independent <sup>14</sup>C age estimates (5, 6). The Tenaya moraine was hypothesized by Sharp and Birman (3) to result from a glacial intermediate in age between the Tioga and Tahoe. Burke and Birkeland (16), however, were not able to distinguish between the Tioga and Tenaya moraines on the basis of relative dating methods. The mean of the four oldest boulder ages from the Tenaya moraine, 24.3 ± 0.9 ka, is within the independent radiocarbon age range of the Tioga glaciation (5) and indicates that the Tenaya moraines at Bloody Canyon represent an early (and extensive) stage of the same glacial advance as the Tioga glaciation.

On the basis of the <sup>36</sup>Cl age estimates, we have subdivided the Tahoe moraines, as mapped by Sharp and Birman (4), into an older and younger Tahoe. This subdivision closely resembles that proposed by Gillespie (7) on the basis of relative-dating parameters. The boulder ages for the younger Tahoe show a close maximum grouping near 60 ka, whereas the older Tahoe ages group close to 140 and 200 ka. There is no overlap between the maximum of the younger Tahoe samples and the minimum of the older Tahoe samples. Although the Tahoe deposits can be interpreted as a single moraine ridge (3), they can also be interpreted as an older moraine that was mantled by a younger one except at its distal end (7). The distal

**Table 1.** Chemical data, <sup>36</sup>Cl measurements and <sup>36</sup>Cl buildup ages for glacial moraine samples from Bloody Canyon, California. All concentrations are by weight; max, maximum.

Map number	Sample	K <sub>2</sub> O (%)	CaO (%)	Cl (ppm)	σ <sub>t</sub> * (cm <sup>2</sup> kg <sup>-1</sup> )	<sup>36</sup> Cl ( <sup>36</sup> Cl/10 <sup>15</sup> Cl)	Boulder age† (ka)	Moraine age (ka)
<i>Tioga</i>								
1	BC86-1TI	5.1	0.84	24	5.0	1770 ± 140	23.1	Mean
2	BC86-2TI	3.0	2.3	71	4.1	400 ± 20	12.2‡	21.4
3	BC86-3TI	4.4	2.1	103	4.9	536 ± 39	20.4	Max
5	BC86-5TI	3.4	2.9	141	5.2	455 ± 20	20.8	23.1
<i>Tenaya</i>								
6	BC86-6TE	3.75	2.1	34	4.7	1350 ± 100	24.0	
7	BC86-7TE	1.7	3.7	40	3.7	244 ± 31	5.1‡	Mean
8	BC86-8TE	3.3	1.5	67	4.8	697 ± 40	23.3	24.3
9	BC86-9TE	4.3	1.9	74	4.65	839 ± 55	24.4	
10	BC86-10TE	4.0	1.5	64	4.4	469 ± 30	13.5‡	Max
11	BC86-11TE	5.3	0.98	26	5.1	1950 ± 160	25.5	25.5
<i>Younger Tahoe</i>								
12	BC87-1TA	4.05	2.0	74	4.9	1640 ± 210	55.9	Mean
13	BC87-2TA	5.6	0.79	31	4.75	3760 ± 130	60.6	59.8
14	BC87-3TA	3.9	2.0	64	4.45	1310 ± 90	38.6‡	Max
15	BC87-4TA	2.5	2.2	74	4.55	1460 ± 180	57.0	65.8
16	BC87-5TA	4.3	1.8	100	4.8	1700 ± 95	65.8	
17	BCC88-1	4.7	1.6	38	3.9	315 ± 18	5.2‡	
18	BC88-5	4.4	2.7	90	5.5	1700 ± 162	63.2	
<i>Older Tahoe</i>								
19	BC86-12TA	1.05	7.4	73	6.4	3155 ± 240	133‡	Mean
20	BC86-13TA	4.4	2.2	75	6.1	4310 ± 250	189	207
21	BC86-14TA	3.75	1.2	49	4.8	5735 ± 255	214	
22	BC86-15TA	3.85	1.5	76	5.45	4210 ± 240	218	Max
23	BC86-16TA	3.9	3.8	115	6.0	2790 ± 200	149‡	218
<i>Mono Basin</i>								
24	SC86-17MB	3.9	0.55	57	4.7	3120 ± 220	114	
25	SC88-18MB	3.9	1.2	122	4.5	2000 ± 150	103	Mean
26	SC88-19MB	3.2	2.4	113	5.1	1960 ± 122	92	103
27	SC86-20MB	5.15	1.2	28	4.7	5290 ± 180	79‡	Max
28	SC86-21MB	5.5	0.65	26	4.3	7030 ± 250	97	119
29	SC88-1	4.7	2.35	76	5.2	2850 ± 62	93	
30	SC88-2	4.4	2.65	111	5.3	1915 ± 67	80‡	
31	SC88-3	4.2	3.4	157	5.4	2265 ± 170	119	

\*σ<sub>t</sub> is the macroscopic thermal neutron absorption cross section per unit mass of rock calculated from chemical data reported in (14). †Calculated using Eq. 1. ‡Samples not used in calculation of the mean age, but which are plotted in Fig. 2.

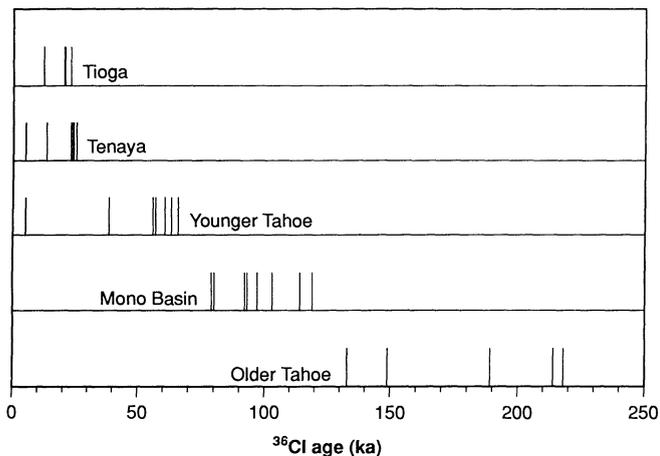


Fig. 2. Distribution of cosmogenic  $^{36}\text{Cl}$  boulder ages among the moraines at Bloody Canyon.

end exhibits multiple, subdued moraine crests. The wide scatter in the individual boulder ages from the older Tahoe moraine may be due to weathering and erosion effects. However, whereas boulder 19 was from the inmost older Tahoe crest and 23 was a 5-m-high boulder close to the terminal portion of the crest, boulders 20 through 22 were located close together on the northern flank of the middle morainal ridge. These three boulders all yielded ages older than the other samples and may therefore be recording an early pulse of glaciation ( $\sim 200$  ka), and 19 and 23 may date another separate pulse close to the culmination of isotope stage 6 (at  $\sim 140$  ka).

The Mono Basin boulder ages cluster between 80 and 119 ka. The boulders on the Mono Basin moraine crests generally show evidence of weathering and spalling, which would result in minimum ages. We therefore interpret the most likely age for the Mono Basin moraines to lie in the range 110 to 120 ka (18).

The Bloody Canyon moraine chronology based on  $^{36}\text{Cl}$  is in apparent conflict with that determined by Dorn *et al.* at Pine Creek (6). They obtained varnish cation-ratio dates ranging from 143 to 156 ka for boulders on the main Tahoe moraine at that site. None of the moraines at Pine Creek were reported to fall within the range 60 to 70 ka that we determined at Bloody Canyon. Recent reevaluation of the cation leaching curve used at Pine Creek may resolve this discrepancy (6).

On the basis of the  $^{36}\text{Cl}$  buildup chronology for the Bloody Canyon moraines we propose that the classical Sierra Nevada glacial nomenclature be revised. Although the term "Tahoe" is a useful geomorphic designation for moraines of early Illinoian to mid-Wisconsin age, there were probably at least four (and possibly more) distinct glaciations during this period. We agree with Gillespie (19) that if the term is to be retained it should be limited to the early

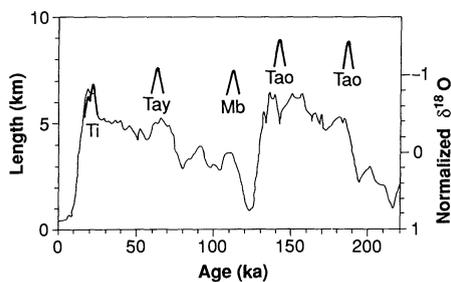


Fig. 3. A comparison of Bloody Canyon glacier lengths (measured from the headwall of the cirque to the terminal moraine) as a function of time, with the marine oxygen-18 record (19). The Bloody Canyon glacial maxima are indicated by the heavy discontinuous lines and the marine  $\delta^{18}\text{O}$  by the light continuous line. The scale on the normalized  $\delta^{18}\text{O}$  has been reversed from that in (19) so that glacial maxima correspond to the top of the graph for both records; Tao, older Tahoe (two pulses); Mb, Mono Basin; Tay, younger Tahoe; Ti, Tioga.

Wisconsin glacial pulse, in conformity with Blackwelder's original intention.

The new Bloody Canyon chronology supports synchronicity of glacial timing between Sierra Nevada mountain glaciation and the averaged global ice volume history indicated by the marine oxygen isotope record (Fig. 3). The intervals 120 to 110 ka and 70 to 60 ka correspond to important ice volume peaks during the buildup of Wisconsin ice, and 24 to 20 ka to the interval of maximum global ice (4, 20). The  $^{36}\text{Cl}$  age estimates for the Bloody Canyon glacial maxima also correspond closely to episodes of minimum Northern Hemisphere summer insolation (21). They thus offer additional support for the Milankovich theory of global glacial timing.

Although there is good agreement between the timing of glaciations at Bloody Canyon and those recorded by the marine  $^{18}\text{O}$  signal, there is strong disagreement with regard to glacial magnitude. The marine record (20) shows a fairly regular progressive buildup of ice from the penultimate

interglacial through the last glacial maximum at about 20 ka. In contrast, at Bloody Canyon the longest moraines were deposited during the earlier glaciations (Mono Basin and younger Tahoe), and progressively smaller moraines (Tenaya and Tioga) were formed during the Wisconsin maximum. This inverse relation between the glacial magnitudes shows that the response of mountain glaciers and continental ice caps to climatic forcing differed markedly. A rapid transition from full interglacial to full glacial conditions is indicated by the 114 and 119 ka dates on the extensive Mono Basin moraines. One interpretation of the discrepancy between the sudden transition to full glaciation indicated at Bloody Canyon and the much slower change in the marine oxygen isotope record is that the global climate may have suddenly switched to a glacial mode (21). Small mountain glaciers might respond rapidly to this impulse, but continental ice sheets might take much longer to arrive at equilibrium with the global glacial climate.

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- used in calculating the total cosmogenic  $^{36}\text{Cl}$  production rate were  $3560 \pm 465$  atoms of  $^{36}\text{Cl}$  per mole K per year,  $2745 \pm 245$  atoms of  $^{36}\text{Cl}$  per mole Ca per year and  $(2.64 \pm 0.42) \times 10^5$  thermal neutrons stopped per kilogram of rock per year. These values are at the rock surface, at sea level, and at  $90^\circ$  geomagnetic latitude.
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  - The samples were ground to a particle size smaller than the mean grain diameter and leached with deionized water to remove meteoric or anthropogenic  $^{36}\text{Cl}$ . They were then dissolved in hot HF and  $\text{HNO}_3$  and the Cl was extracted as HCl by air stripping, followed by trapping in a  $\text{AgNO}_3$  solution (14). Major and minor elements were measured by x-ray fluorescence and rare earth elements by inductively coupled plasma atomic-emission spectrometry. The Cl content was measured in a teflon

- diffusion cell using an ion-specific electrode technique. [P. S. Aruscavage and E. Y. Campbell, *Talanta* **30**, 745 (1983); H. N. Elsheimer, *Geostand. News.* **11**, 115 (1987)]. Values given are the mean of three to five replicate analyses. A value of  $30 \times 10^{-15}$  [typical for granitic rocks (12)] was assumed for the radiogenic  $^{36}\text{Cl}/\text{Cl}$  ratio ( $R_0$ ). This radiogenic  $^{36}\text{Cl}$  background ranges from about 5% to less than 1% in relation to the cosmogenic  $^{36}\text{Cl}$  used for dating.
- We have considered two alternative hypotheses: (i) The boulder age distribution from the Mono Basin moraines may indicate more than one glaciation between 80 and 120 ka. Some evidence from moraine morphology supports the notion that there were multiple glaciations (8), although the evidence is not as strong as for the older Tahoe moraines. (ii) Even the oldest boulder dates on the Mono Basin may only be minimum and the Mono Basin glaciation could have an age of  $\sim 140$  ka. Although this assumption would bring the Bloody Canyon deposits into better agreement with the marine  $^{18}\text{O}$  record regarding the relative glacial volumes during isotope

- stages 6 and 5d, in the absence of positive results to support this assumption, we prefer the interpretation indicated by the maximum measured ages.
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  - This research was supported by National Science Foundation grants EAR-8603440, SES-8901437, PHY-8515908, and PHY-8818281. We thank A. R. Campbell, C. V. Kruger, and D. Elliott-Fisk for help in sample collection, L. Brandvold and the New Mexico Bureau of Mines and Mineral Resources for use of laboratory facilities, R. Dorn and A. Gillespie for helpful comments, and R. Teng and S. Tullai-Fitzpatrick for help in the  $^{36}\text{Cl}$  analyses.

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## Biomimetic Total Synthesis of Proto-Daphniphylline

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*Proto-daphniphylline*, the imputed biogenetic parent of the *Daphniphyllum* alkaloids, has been assembled in a biogenetically styled laboratory synthesis in which a pentacyclization process is the fundamental synthetic stratagem. This extraordinary transformation involves the formation of six  $\sigma$ -bonds under the influence of three elementary reagents—potassium hydroxide, ammonia, and acetic acid. The facility of the process adds credibility to the previous speculation that a similar process is an important step in the biosynthesis of the *Daphniphyllum* alkaloids.

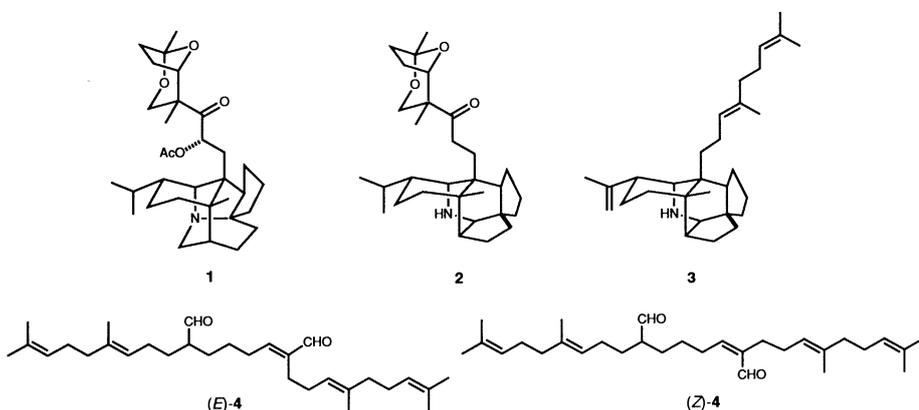
THE ORIENTAL DECIDUOUS TREE *Yuzuriha* (*Daphniphyllum macropodum* Miquel) contains a family of squalene-derived alkaloids, of which daphniphylline (1) and secodaphniphylline (2) are representative members (1). It has been suggested that these complex natural products are biosynthesized from squalene by way of the embryonic precursor 3, *proto-daphniphylline* (2). In this report, we describe a remarkably simple synthesis of 3 wherein the five rings are formed in a series of three straightforward chemical transformations of the acyclic dialdehydes (*E*)-4 or (*Z*)-4.

As shown in Scheme 1, the lithium enolate of *tert*-butyl (*t*-Bu) acetate was alkylated with homogeranyl iodide (5) (3) to give ester 6, which was deprotonated with lithium diisopropylamide (LDA). The resulting enolate was alkylated with the dimethyl acetal of 4-bromobutanal to provide ester 7. Mild acidic hydrolysis of the acetal function afforded aldehyde 8, which was allowed to react with another mole-equivalent of the lithium enolate derived from ester 6 to provide hydroxy-diester 9. Dehydration of this  $\beta$ -hydroxy ester was accomplished by successive treatment with methanesulfo-

nyl chloride in the presence of triethylamine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); diester 10 was obtained as a 10:1 mixture of *E* and *Z* isomers at the newly created double bond. The isomers were separated by chromatography on silica gel, and the major isomer was reduced by treatment with diisobutylaluminum hydride (DIBAL). The resulting diol was oxidized by the method of Swern (4) to obtain (6*E*,14*E*,18*E*)-10,11-dihydrosqualene-27,28-dialdehyde (4).

Synthesis of (*Z*)-4 is summarized in Scheme 2. Alkylation of the lithium enolate of *tert*-butyl trimethylsilylacetate with halide 5 gave ester 11, which was deprotonated with LDA and treated with aldehyde 8. The diester produced in this manner [Peterson olefination reaction (5)] is a 7:3 mixture of *Z* and *E* double-bond isomers. The isomers were separated by chromatography and the major isomer converted in two steps to (*Z*)-4.

Both (*E*)- and (*Z*)-4 were converted into *proto-daphniphylline* (3) by the following simple procedures (Scheme 3). Gaseous ammonia was added to a dichloromethane solution of the dialdehyde, ammonium acetate, and triethylamine hydrochloride. After 16 hours at room temperature the solvent was removed under vacuum and the residue was taken up in glacial acetic acid. After 2 hours at  $80^\circ\text{C}$ , compound 3 was obtained in  $15 \pm 2\%$  yield. The yield of 3 was improved to 50% by the following modified three-step procedure. A benzene solution of the dialdehyde was added to a vigorously stirring solution of 50% aqueous potassium hydroxide containing 5% by mole of tetra-*n*-butyl-



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