where $CH_3C(O)O_2$ formed in reaction 1 reacts only with labeled and unlabeled NO_2 in proportion to their concentrations is

$$-\mathrm{d}[\mathrm{PAN}]/\mathrm{d}t = k_1\{[\mathrm{PAN}] + [\mathrm{PAN\text{-}15}]\}\{[^{15}\mathrm{no}_2]/([\mathrm{NO}_2] + [^{15}\mathrm{NO}_2])\} - k_1[\mathrm{PAN\text{-}15}] \quad (4)$$

From nine experiments at 25 °C where $\{^{15}NO_2\}/\{PAN\}$ was varied from 1 to 3 at concentrations of PAN ranging from 0.8 to 1.8×10^{-4} M, a value of $k_1 = (4.0 \pm 0.9) \times 10^{-4}\ s^{-1}$ was obtained. This rate constant for exchange is 300 times faster than the apparent first order loss of PAN in the absence of added $^{15}NO_2$ or NO.

A series of experiments was carried out to determine the effect of NO on the loss of PAN. The kinetic expression for the disappearance of PAN where reaction 3 is important is

$$-\mathrm{d}[\mathrm{PAN}]/\mathrm{d}t = k_1k_3[\mathrm{PAN}][\mathrm{NO}]/\{k_{-1}[\mathrm{NO}_2] + k_3[\mathrm{NO}]\} \quad (5)$$

At 25 °C in the presence of NO the decomposition of PAN was found to be first order in PAN and zero order in NO, consistent with eq 5 where $k_3[NO] > k_{-1}[NO_2]$. The average value for the initial apparent first-order rate constants obtained from five runs at PAN concentrations of 1.0 to 3.60×10^{-4} M and a ratio of [NO]/[PAN] ranging from 0.16 to 9.2 is $(3.70 \pm 0.37) \times 10^{-4}\ s^{-1}$, experimentally identical with the rate constant obtained in the exchange experiments.[7] The rate constants for the disappearance of PAN in excess NO over the temperature range 25-40 °C follow the Arrhenius expression

$$\log (k_1/\mathrm{s}^{-1}) = 16.29 \pm 0.60 - (26910 \pm 900)/\theta(\theta = 2.303RT \text{ in cal/mol}) \quad (6)$$

Expression 6 is in excellent agreement with the thermochemical estimates of the Arrhenius parameters for reaction 1. Furthermore, because the ratio of the forward and backward frequency factors, A_1/A_{-1}, equals $e^{\Delta S_1/RT}$,[3] the value of k_{-1} is readily determined: $k_{-1} = A_{-1} = 6.3 \times 10^8\ M^{-1}\ s^{-1}$, assuming no activation energy for this radical–radical reaction.

The rapid exchange of $^{15}NO_2$ in PAN, the enhanced decomposition in the presence of NO, the agreement between the rates of these two experiments, and the agreement of estimated kinetic parameters for reaction 1 with the observed data, indicate that the reversible decomposition, reaction 1, is operative for PAN and undoubtedly for other peroxyacyl nitrates. Reaction 2 is ruled out because it would not lead to exchange; moreover, the rate of PAN decomposition by reaction 2 would not be enhanced by addition of NO because decarboxylation of acetoxy radicals is sufficiently fast[8] to preclude trapping of the radicals by NO.

To test the utility of PAN as a source of acetylperoxy radicals, we carried out a series of decompositions of PAN in the presence of mixtures of NO and NO_2. In these experiments, the rate of decomposition of PAN was related to the ratio k_3/k_{-1}, according to the expression

$$-\mathrm{d}t.\mathrm{d}[\mathrm{PAN}] = (1 + k_{-1}[\mathrm{NO}_2]/k_3[\mathrm{NO}])(k_1[\mathrm{PAN}])^{-1}$$

Over the temperature range 25-45 °C, the ratio k_3/k_{-1} equals 3.1 ± 0.5, independent of temperature.[9] Combining these results with the data for k_{-1} gives $k_3 = A_3 = 2.0 \times 10^9\ M^{-1}\ s^{-1}$.

Thus, it is seen that PAN, which is easily prepared[10] and somewhat volatile,[4] is also a convenient source of free radicals because it decomposes rapidly ($t_{1/2}$ for decomposition at 25 °C = 30 min) to yield acetylperoxy radicals and NO_2.[11] These factors recommend PAN as a gas-phase, free-radical initiator. Our results with the decomposition of PAN in the presence of mixtures of NO and NO_2 indicate that, in fact, PAN can be of considerable utility in probing reactions (e.g., reactions −1 and 3) that are relevant to the chemistry of polluted urban atmospheres.

Acknowledgments. The authors thank Drs. David M. Golden and John R. Barker for their helpful discussions. The research was supported by the U.S. Environmental Protection Agency (Research Grant 803846-01).

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(10) PAN can be prepared by a variety of photochemical techniques and purified by GLC.[4,12] Alternatively, as suggested by Stephens[4] and by Louw,[13] PAN can be obtained by the direct nitration of peracetic acid. We have prepared PAN in this manner, using 90% HNO_3 and 30% SO_3 in pentane solvent at 0 to −5 °C. The yield of PAN (unpurified in pentane solution) was as high as 39% and GLC of PAN solutions provided samples of PAN containing <1% impurities.
(11) The thermochemical analysis of the decomposition of peroxyalkyl nitrates by the reactions parallel to reactions 1 and 2 leaves little doubt that reaction 1 will also be considerably faster than reaction 2 in these cases, contrary to recent suggestions in the literature.[14,15] For example, for the decomposition of $CH_3O_2NO_2$ the entropy change favors reaction 1 by 7 cal/mol and the enthalpy change favors reaction 1 by ~6 kcal; in this case reaction 1 should be $\sim 10^5$ times faster than reaction 2 at room temperature. Thus, peroxyalkyl nitrates, which have been synthesized,[16] should be suitable sources for studying the chemistry of alkylperoxy radicals.
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Received January 21, 1977

Phyllanthocin, a Novel Bisabolane Aglycone from the Antileukemic Glycoside, Phyllanthoside[1,2]

Sir:

In the course of a continuing search for tumor inhibitors of plant origin, we have found that an ethanol extract of *Phyllanthus brasiliensis* Muell. (Euphorbiaceae)[3] showed significant activity in vitro against cells derived from human carcinoma of the nasopharynx (KB) and in vivo against the P-388 lymphocytic leukemia in mice (PS).[4] We report herein the structural elucidation of the novel bisabolane phyllanthocin (**1**), derived from the antileukemic glycoside, phyllanthoside (**2**).

Fractionation of the alcohol extract, guided by assay against the KB and PS systems, revealed that the inhibitory activity was concentrated, successively, in the chloroform layer of a chloroform–water partition and in the aqueous methanol layer of an aqueous methanol (1:9)–petroleum ether partition.

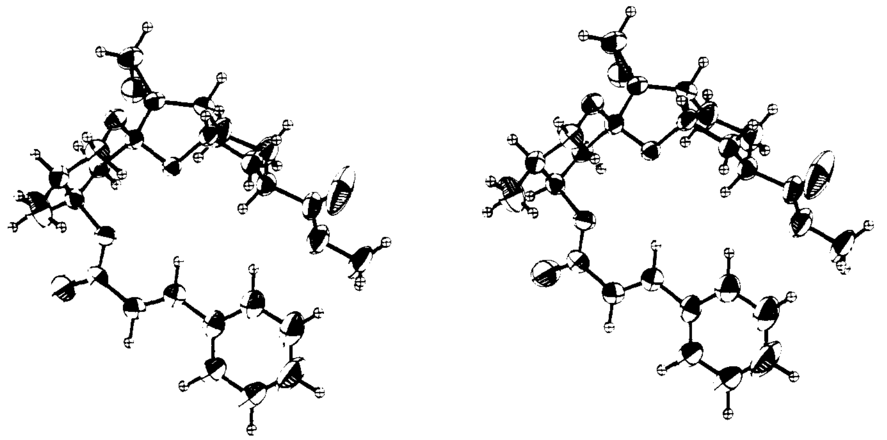
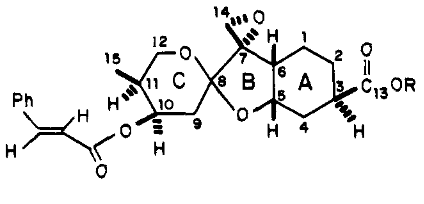


Figure 1. ORTEP stereoscopic view[7] of the molecular structure of **1** as found in the crystal. Thermal ellipsoids for oxygen and carbon atoms are drawn with the 50% probability level as boundary surface. Hydrogen atoms are represented by spheres of arbitrary radius.

Column chromatography of this concentrate using silica gel afforded two distinct KB-active fractions. A known lignan, Justicidin B,[5] was crystallized from the less polar fraction. The more polar KB- and PS-active fraction was purified further by preparative TLC on silica gel and on Silica Gel 60/Kieselguhr to give an amorphous solid, phyllanthoside (**2**, 0.030%): mp 125–126 °C; $[\alpha]^{24}{}_D$ +19.2° (c 2.03, $CHCl_3$); UV_{max} (EtOH) λ (ε) 276 (20 000), 223 (14 000) nm; IR (KBr) 2.89, 5.75, 5.85, 6.10, 6.90, 7.30, 8.03, 8.56, 9.31, 13.1, 13.3 μ; ^1H NMR ($CDCl_3$) δ 0.85 (3 H, d, J = 7.1 Hz, 15-CH_3), 1.23 (3 H, d, J = 5.8 Hz), 1.34 (3 H, d, J = 5.8 Hz), 2.15 (6 H, s, 2$OCOCH_3$), 5.50 (1 H, d, J = 8.0 Hz), 6.58 (1 H, d, J = 16.1 Hz, 2′-H), 7.79 (1 H, d, J = 16.1 Hz, 3′-H).

Methanolysis of **2** yielded the crystalline aglycone, phyllanthocin (**1**): mp 126–127 °C (ether–hexanes); $[\alpha]^{24}{}_D$ +25.2° (c 2.00, $CHCl_3$); UV_{max} λ (ε) 276 (21 000), 223 (13 000) nm; IR (CCl_4) 5.75, 5.85, 6.10, 6.90, 7.30, 7.68, 7.92, 8.03, 8.58, 8.92, 9.35, 9.52, 10.0, 10.5, 11.1 μ; mass spectrum m/e 442.1987 (M^+, calcd for $C_{25}H_{30}O_7$, 442.1992), 294.1463 ($M^+ - C_9H_8O_2$, calcd for $C_{16}H_{22}O_5$, 294.1467); ^1H NMR ($CDCl_3$) δ 0.88 (3 H, d, J = 7.2 Hz, 15-CH_3), 2.91, 2.98 (each 1 H, d, J = 5.4 Hz, 14-H_2), 3.39 (3 H, s, OCH_3), 3.44 (1 H, d of d, J_{AB} = 11.4 Hz, J_{AX} = 5.2 Hz, 12-H), 4.03 (1 H, t, J = 11.4 Hz, 12-H), 4.39 (1 H, q, J = 3.1 Hz, 5-H), 5.09 (1 H, q, J = 2.5 Hz, 10-H), 6.48 (1 H, d, J = 16.1 Hz, 2′-H), 7.77 (1 H, d, J = 16.1 Hz, 3′-H), Anal. Calcd for $C_{25}H_{30}O_7$: C, 67.87; H, 6.79. Found C, 67.85; H, 6.81.



1, R = CH_3
2, R = $C_{16}H_{25}O_{10}$
3, R = $C_{22}H_{31}O_{13}$

The chemical structure and stereochemistry of **1** were determined by a direct single-crystal x-ray analysis. Crystals of **1** have monoclinic symmetry and conform to space group $P2_1$ with unit-cell dimensions a = 12.216 (2), b = 10.016 (2), c = 10.538 (2) Å, and β = 112.17 (1)°. There are two molecules of **1** in the unit cell.

The intensities of 2215 independent reflections within a single quadrant of reciprocal space ($2\theta \leq 50°$) were measured by counter diffractometry with monochromatic Mo Kα radiation. Intensity significantly above background [$I > 3\sigma(I)$] was found at 1901 of these locations and structure amplitudes derived for these reflections were used in the analysis. The structure was solved using the program MULTAN,[6] and the parameters were refined by Fourier and least-squares methods to yield R = 0.066. Anisotropic thermal parameters were used for carbon and oxygen atoms. All hydrogen atoms were found from difference electron-density maps, and fixed contributions for these atoms, with assumed isotropic B values, were included in the least-squares calculations. With the radiation used anomalous dispersion effects are too small to allow a determination of absolute configuration, and none has been made.

The folded configuration adopted by **1** in the crystal has the major axis of the cinnamate residue almost parallel to the C(6)···C(3)···acetate axis of the cyclohexane ring A and has the plane of the cinnamate almost perpendicular to the ring A plane. The ring junction at C(5)–C(6) is *cis*-synclinal, and the C(7) oxygen has an α-orientation, features also found in the bicyclic bisabolangelone.[8] Bond lengths and angles have normal values with a slight lengthening of the two C–C bonds at the C(8) spiro-junction being noted. The two six-membered rings A and C adopt similar partially flattened chair conformations with endocyclic torsion angles in the range 44–64°. The five-membered ring B has a conformation intermediate between the half-chair and envelope forms, but closer to the former, with $\overline{\Delta}$ = 12° and ϕ_m = −51°.[9]

Treatment of phyllanthoside (**2**) at room temperature with acetic anhydride in pyridine gave a pentaacetate derivative **3**: mp 114–117 °C; $[\alpha]^{24}{}_D$ +26.3° (c 1.10, $CHCl_3$); UV_{max} (EtOH) λ (ε) 276 (20 000) 223 (13 000) nm: IR (CCl_4) 5.68, 5.84, 7.28, 8.07, 8.27, 8.53, 8.90, 9.26, 9.33, 9.52, 9.71, 10.6, 11.1 μ; mass spectrum (chemical ionization: methane gas reagent) m/e 931.3593 (M^+ + H, calcd for $C_{46}H_{59}O_{20}$, 931.3600), 503.1763 ($M^+ - C_{24}H_{27}O_7$, calcd for $C_{22}H_{31}O_{13}$, 503.1765); ^1H NMR ($CDCl_3$) δ 0.85 (3 H, d, J = 6.8 Hz, 15-CH_3), 1.14 (3 H, d, J = 6.1 Hz), 1.16 (3 H, d, J = 5.8 Hz), 1.96, 1.97, 2.02, 2.03, and 2.08 (15 H, s, 5 $OCOCH_3$), 2.94 (2 H, s, 14-H), 3.58 (1 H, d of d, J_{AB} = 11.4 Hz, J_{AX} = 6.3 Hz, 12-H), 3.98 (1 H, t, J = 11.4 Hz, 12-H), 5.48 (1 H, d, J = 8.0 Hz), 6.50 (1 H, d, J = 15.8 Hz, 2′-H), 7.77 (1 H, d, 15.8 Hz, 3′-H).

The only other major product of the methanolysis of phyllanthoside (**2**) was a disaccharide: mp 203–204 °C; $[\alpha]^{24}{}_D$ −3.5° (c 2.27, H_2O); IR (KBr) 2.97, 3.45, 6.91, 7.41, 9,43; ^1H NMR (Me_2SO-d_6) δ 1.08 (3 H, d, J = 5.1 Hz), 1.13 (3 H, d, J = 5.4 Hz); mass spectrum (chemical ionization: methane gas reagent) m/e 293.1231 ($M^+ + H - H_2O$, calcd for $C_{12}H_{21}O_8$, 293.1236). Acid hydrolysis (1 N HCl) of the disaccharide gave exclusively a monosaccharide characterized as 6-deoxy-D-glucose by comparison with an authentic sample (^1H NMR,

^{13}C, $[\alpha]_D$, and GLC retention times of their silyl derivatives). The presence of two acetate moieties on the disaccharide in phyllanthoside was determined by ^{13}C, ^1H NMR, IR, and mass spectral comparisons of **2** and its methanolysis products, phyllanthocin (**1**) and the dissacharide.

Acknowledgment. The authors are grateful to Dr. Leon M. Lerner for a sample of 6-deoxy-D-glucose.

Supplementary Material Available: A listing of atomic coordinates and thermal parameters for the structure at this stage of refinement (2 pages). Ordering information is given on any current masthead page.

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(3) Roots were collected in Costa Rica in 1974. The authors acknowledge with thanks receipt of the dried plant material from Dr. R. E. Perdue, Jr., U.S. Department of Agriculture, Baltimore, Md., in accordance with the program developed by the National Cancer Institute.

(4) Antileukemic activity was assayed under the auspices of the National Cancer Institute by the procedure described by R. I. Geran, N. H. Greenberg, M. M. McDonald, A. M. Schumacher, and B. J. Abbott, *Cancer Chemother. Rep., Part 3*, **3**, 1 (1972). Phyllanthoside gave T/C values ranging from 137 to 153 at dose levels from 6 to 24 mg/kg. The cytotoxicity (ED_{50}) against KB cell culture of **2** was at 10^{-2} μg/mL. Phyllanthocin (**1**) was found to be devoid of KB activity.

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Book Reviews

Detergency: Theory and Test Methods. Part II. Edited by W. G. CUTLER and R. C. DAVIS (Whirlpool Corp.). Marcel Dekker, Inc., New York, N.Y. 1975. 288 pp. $21.75.

"Detergency", which is Part II of three parts, and Volume 5 of Surfactant Science Series, covers the wetting agent and enzyme field processes as well as bleaches and stain removal in the handling of textiles in a very complete manner. It also describes test methods for damage to fabrics as well as toxicological tests of material used, even to the cleaning of metals as well as textiles.

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Spectrophotometric Determination of Elements. By ZYGMUNT MARCZENKO (Warsaw Technical University). Wiley/Halsted Press, New York, N.Y. 1976. xi + 643 pp. $55.00.

Classical spectrophotometric methods of analysis continue to enjoy wide use in practical situations and, especially, for routine analysis. Marczenko's book represents a compendium of such methods, arranged alphabetically by element, with a very brief and elementary introduction to spectrophotometric principles and sample pretreatment techniques. The most useful feature of the book is its extensive list of references, many from the Eastern European literature. Unfortunately, the literature coverage ends in 1973. Translation into English appears to have been carefully done, although the reader will note a certain monotony of style. The price of the book seems extraordinarily high; however, workers who wish to have a personal collection of procedures or who do not have access to review articles on the subject may find a single-volume source convenient.

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Encyclopedia of Electrochemistry of the Elements. Volume VI. Edited by A. J. BARD (University of Texas at Austin). Marcel Dekker, Inc., New York, N.Y. 1975. xiv + 431 pp. $64.00.

Dedicated to Klaus J. Vetter, Volume VI of this impressive encyclopedia now brings the coverage to approximately two-thirds of all the elements in the periodic table. There remain yet to appear in future volumes the alkali metals (no. 15), the actinium series (no. 24), and a few elements scattered about the table such as H, N, C, Ag, Hg, Fe, and Mg to name a few. The numbering, of course, refers to a Gmelin-like system as explained in the six-page introduction.

Six of the nine chapters deal with the platinum metals (no. 41) and have all been written by three members of the Institute of Physical Chemistry in Madrid, Spain. Not only does each of these six chapters adhere to the standard format to include the Pourbaix diagram as well as tables of standard potentials, and polarographic behavior of the metal, but also cover in an extensive and informative manner kinetic parameters, double-layer properties, and the copious work that has been done on adsorption and surface electrochemistry. For example, the Pt chapter exhibits a variety of compact tables and the major textual discussions are on Pt polarography-voltammetry, kinetic parameters, double layer properties, adsorption, anodization, and applied Pt electrochemistry.

The same high quality of presentation is consistently evident in the other chapters on these six metals, although the emphasis shifts here and there owing to the different nature of the referenced work, none of which is as extensive as that for Pt, a chapter of 51 pages compared to 14, 17, 14, 22, and 24 pages for the chapters on Ir, Os, Pd, Ru, and Rh, respectively. A total of 494 references in two groups are given for these six metals.

The other three chapters cover group III elements, namely, indium (27 pp, 172 references), aluminum (93 pp, 353 references), and scandium, yttrium, and lanthanides (26 pp, 116 references). That learning rapidly about an unfamiliar element is an important benefit of this encyclopedic approach is readily demonstrated for many readers by the chapter on indium, a chapter which will surprise such a reader as a result of the very large number of entries under polarographic characteristics (6-page table), and this despite only the two oxidation states (+3 and 0). Numerous other ideas are given, ranging from interesting and useful applications of this element to the dependence of electrode irreversibility on the slow dissociation of water from the aquo complex of the indium ion.

The reasons for treating scandium, yttrium, and lanthanides together arise from the similarity of these elements electrochemically (largely the +3 oxidation state) and the scarcity of literature. Only about one and one-half pages of standard potential values are listed in tabular form and most of these are free energy calculations from Latimer rather than direct measurements. Despite the presence of fewer than eight references per element, however, these authors have made an excellent presentation of what is to be had. Most of this is concentrated in polarographic studies (much of that being nonaqueous) and in kinetic parameters and double-layer properties, especially for cerium and europium. The latter is apparently of much interest because the Eu^{3+}/Eu^{2+} standard redox potential in $HClO_4$ is very close to the zero charge potential on Hg.

The monumental task of summarizing the electrochemistry of