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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF FLORIDA W. M. JONES
GAINESVILLE, FLA.

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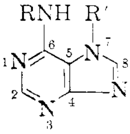
THE STRUCTURE OF TRIACANTHINE[1]

Sir:

Early reports suggested the presence of alkaloidal material in species of *Gleditsia*,[2,3] of the Leguminosae family, and recently the alkaloid "triacanthine" has been isolated from *Gleditsia triacanthos* L. and the formula $C_8H_{10}N_4$ assigned.[4] We have repeated the described extraction procedure on the young leaves of *G. triacanthos* collected by one of us (J.A.D.) in April at Dixon Springs, Illinois,[5] and have established that the correct molecular formula for triacanthine is $C_{10}H_{13}N_5$ and that the structure is 6-amino-7-(γ,γ-dimethylallyl)-purine (I).



I, R = H, R′ = $CH_2CH{=}C(CH_3)_2$
II, R = H, R′ = H
III, R = $CH_2C_6H_5$, R′ = $CH_2CH{=}C(CH_3)_2$
IV, R = H, R′ = $CH_2CH_2CH(CH_3)_2$

Analytical data for triacanthine, m.p. 228–229° (reported[4] 227–228°) (Calcd. for $C_{10}H_{13}N_5$: C, 59.09; H, 6.45; N, 34.46. Found: C, 59.29; H, 6.32; N, 34.59), and triacanthine hydrochloride, m.p. 218–220° dec. (reported[4] 218–219°) (Calcd. for $C_{10}H_{14}ClN_5$: C, 50.09; H, 5.89; N, 29.22. Found: C, 50.24; H, 6.04; N, 28.96), as well as the molecular weight determined by electrometric titration[6] (Calcd. for $C_{10}H_{13}N_5$: 203. Found: 211 ± 10; pK'_a 5.4) supported the formula $C_{10}H_{13}N_5$. Triacanthine showed $\lambda_{\max}^{\text{EtOH}}$ (neutral) 273 mμ (ϵ 12,500) and $\lambda_{\max}^{\text{EtOH}}$ (pH 1) 277 (18,300). The mass spectrum of triacanthine[7] showed peaks at mass 203 (confirming the molecular weight), 188 (establishing the presence of at least one methyl group), and 135. Chemical realization of the cleavage suggested by the 135 mass peak was achieved by treatment of triacanthine with concentrated hydrochloric acid at 80° for 8 hours, which produced crystalline adenine (II) hydrochloride, m.p. 283–284° (reported[8] 285–286°). The indentification was made by analysis (Calcd. for $C_5H_6ClN_5 \cdot 0.5H_2O$: C, 33.25; H, 3.91; N, 38.79. Found: C, 33.38; H, 4.01; N, 38.62) and ultraviolet spectrum.[9] A picrate (m.p. 190–192°) formed from the hydrochloride failed to depress the melting point of authentic adenine picrate.[8]

Reaction of triacanthine with benzylamine and benzylamine hydrochloride in a sealed tube at 180° for 12 hours yielded the "exchange amination"[10] product N-benzyltriacanthine (III), m.p. 150° (Calcd. for $C_{17}H_{19}N_5$: C, 69.60; H, 6.53; N, 23.88; mol. wt., 293. Found: C, 69.34; H, 6.52; N, 24.06; electrometric titration mol. wt.,[6] 310 ± 10), $\lambda_{\max}^{\text{EtOH}}$ (neutral) 292 mμ (ϵ 17,100) and $\lambda_{\max}^{\text{EtOH}}$ (pH 1) 287 (24,300). The formation of this product demonstrated that the amino group of adenine is unsubstituted in triacanthine. An n.m.r. spectrum ($CDCl_3$) of N-benzyltriacanthine showed peaks at τ = 2.05 and 2.23,[11] which must derive from the ring hydrogens of adenine.[12] Thus, triacanthine must be represented by adenine substituted only at position 7 or 9. The choice between these two alternatives is made readily in favor of position 7 by studying representative 7- and 9-substituted 6-aminopurines.[9,13] For example, adenosine (9-β-D-ribofuranosidoadenine) shows λ,$_{\max}^{\text{EtOH}}$ (pH 13) 260 mμ (ϵ 14,300) and $\lambda_{\max}^{\text{EtOH}}$ (pH 1) 260 (14,200) while 7-D-ribofuranosidoadenine shows $\lambda_{\max}^{\text{EtOH}}$ (pH 13) 271 (9,800) and $\lambda_{\max}^{\text{EtOH}}$ (pH 1) 273 (13,600).[13] The n.m.r. spectrum of N-benzyltriacanthine allowed an accurate determination of the number of methyl groups in triacanthine. By using the area of the 2.77 τ peak representing the five phenyl hydrogens as an internal standard, in comparison to the area of the singlet CH_3-C peak at 8.14 τ (after extrapolating to zero rf. power),[14] it was established that there were two C-CH_3 groups present in triacanthine (a Kuhn–Roth C-methyl determination on triacanthine gave a value of 5.73 (calcd. for two C-CH_3 groups, 14.80)). In addition, the τ value for the C-CH_3 peak indicated that the methyl groups are attached to an olefinic carbon atom.[15]

Catalytic reduction of triacanthine with hydrogen and platinum in glacial acetic acid yielded dihydrotriacanthine (IV), m.p. 230–231° (strongly depressed when mixed with triacanthine) (Calcd. for $C_{10}H_{15}N_5$: C, 58.51; H, 7.37. Found: C, 58.55; H, 7.17.), $\lambda_{\max}^{\text{EtOH}}$ (neutral) 273 (13,020) and $\lambda_{\max}^{\text{EtOH}}$ (pH 1) 277 (18,950). In addition to dihydrotriacanthine, a considerable amount of adenine was produced by hydrogenolysis.[16] The

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(1) This investigation was supported by a research grant (USPHS-RG5829) from the National Institutes of Health, U. S. Public Health Service.

(2) C. Wehmer, "Die Pflanzenstoffe," Verlag von Gustav Fischer, Jena, 1929, p. 508.

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(5) We wish to record our special thanks to Professors W. R. Boggess and A. R. Gilmore of the Department of Forestry, University of Illinois, for helping us to obtain the leaf material.

(6) We are grateful to Dr. Harold Boaz of Eli Lilly and Company, Indianapolis, Indiana, for this information.

(7) Determined by Dr. Klaus Biemann of the Massachusetts Institute of Technology, to whom we are pleased to acknowledge our thanks.

(8) H. R. Bentley, K. G. Cunningham and F. S. Spring, *J. Chem. Soc.*, 2301 (1951).

(9) J. M. Gulland and E. R. Holiday, *ibid.*, 765 (1936).

(10) C. W. Whitehead and J. J. Traverso, THIS JOURNAL, **82**, 3971 (1960). We are grateful to these authors for providing an advance copy of their article.

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(13) W. Friedrich and K. Bernhauer, *Chem. Ber.*, **89**, 2507 (1956).

(14) *Cf.*, J. Pople, W. Schneider and H. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 77.

(15) G. V. D. Tiers "Table of τ Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Company, St. Paul, Minn., 1958.

(16) Triacanthine is not cleaved by acetic acid under the room temperature conditions of the hydrogenation.

ease with which triacanthine is cleaved by acid and by hydrogenolysis suggests that the double bond is allylic to the 7-nitrogen atom.[17] Dihydrotriacanthine is stable to the conditions under which triacanthine is cleaved by hydrochloric acid. The similarity between the ultraviolet spectra of triacanthine and dihydrotriacanthine shows that the double bond in triacanthine is not part of the chromophore.

Finally, n.m.r. spectra of triacanthine and dihydrotriacanthine (30% in liquid sulfur dioxide), in addition to the previously mentioned data, permit unambiguous assignment of structure I to triacanthine. Triacanthine shows a single unresolved peak in the CH_3-C region ($\tau = 8.13$), from $(CH_3)_2C{=}$, and, in addition, a triplet ($\tau = 4.49$) and a doublet ($\tau = 5.01$)—a splitting pattern which is indicative of the $=CH—CH_2—$ moiety. Dihydrotriacanthine exhibits a doublet ($\tau = 9.05$) which came from the methyl groups in $(CH_3)_2CH—$.

Future publication will deal with the synthesis, the further chemistry of triacanthine, and the results of tests for biological activity.

(17) *Cf.* F. M. Dean in "Fortschritte der Chemie Organischer Naturstoffe," ed. by L. Zechmeister, **9**, 269 (1952), for the behavior of a γ,γ-dimethylallyl ether toward acid and catalytic hydrogenation.

THE NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS NELSON J. LEONARD
URBANA, ILLINOIS JAMES A. DEYRUP

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INTERMETALLIC COMPOUNDS OF ALKALI METALS WITH PLATINUM. A NOVEL PREPARATION OF A COLLOIDAL PLATINUM HYDROGENATION CATALYST

Sir:

We have found that *in vacuo* or under an atmosphere of argon, molten lithium and metallic platinum undergo a violently exothermic reaction having an ignition temperature of about 540°. X-Ray diffraction powder patterns of the resulting brittle, grayish product, taken after the excess lithium was removed by treatment with water or 3 *M* hydrochloric acid, showed broad lines whose intensities and positions were in good agreement with calculations based on an $MgCu_2$ cubic "Laves phase" lattice having $a_0 = 7.60 \pm 0.05$ Å. A flame photometric determination of the water-inactive lithium content of the reaction product (dissolved in *aqua regia*) showed over 85% of the theoretical amount required for $LiPt_2$ proportions. The combined lithium and platinum analyses account for over 99% of the product by weight. Because of the great disparity in the atomic weights, however, the lithium analysis is clearly the one which is most important as regards the identification of the species formed.

A few experimental details are given. Most of the reactions were carried out in a glass system with the reactants contained in molybdenum crucibles fitted with thermocouples. Molybdenum has been shown previously[1] to be inert to molten alkali metals. Nevertheless, several experiments were performed in which the platinum strip was bent in such a way that it fulfilled the dual roles of reactant and container, with results identical with those obtained by the alternative procedure. All cutting and transfer operations involving the lithium were made in a protective bath of pentane which ultimately was pumped off, along with the air in the system. Just prior to the ignition step, several flushings with argon also were made. In every case the surface of the lithium remained free of appreciable contamination throughout the entire cycle of operations.

The reactions normally were carried out on a 50–100 mg. scale with the lithium present in about a tenfold mole-excess. During the few minutes required to encompass the 200–500° temperature range, some physical attack on the platinum strip occurred. This particular phase of the process, which we do not believe involves a chemical reaction, is described more fully below. Somewhat above 500° a more spectacular phenomenon obtains. At some point, usually on the perimeter of the metal–liquid metal interface, we observe considerable agitation accompanied by a moderately intense, reddish glow. These effects spread rapidly over the entire contact area, and in less than a second the reaction is completed. During this short time some lithium distills (or perhaps spatters) rather uniformly onto the walls of the glass envelope, a traverse distance of about a centimeter. It is possible to remove the burner at the instant of ignition, and the effects we describe will proceed in an entirely self-sustaining fashion. Although we have not, as yet, examined this system calorimetrically, some relatively crude measurements indicate that the surface temperature of the crucible immediately below the reacting materials increases by several hundred degrees.

It is unlikely that contaminant amounts of lithium oxide or lithium hydroxide are responsible for the phenomenon, for we have used a burner to heat both of these compounds to bright-red incandescence in the presence of platinum, with no effects which in any way resemble those observed with the pure metals.

By heating the raw materials to about 650° in an argon atmosphere, we have also obtained, in poor yield, a sodium–platinum compound which is isostructural with $LiPt_2$, and hence probably is $NaPt_2$. This latter compound has a lattice parameter of 7.48 ± 0.02 Å. Our results complement those of Compton and collaborators,[2,3] who very recently identified a number of cubic Laves phase compounds containing noble metals in combination with both alkaline earth and rare earth elements.

We also have found that molten lithium, at temperatures well below that at which appreciable reaction occurs, has a remarkable ability to penetrate the platinum lattice. A similar type of attack, occurring near the melting point of lithium, has been noted previously by Grosse.[4] We have observed that, overnight, lithium will climb several centimeters up a platinum strip whose bottom is in contact with a lithium pool contained in a molybdenum crucible at 400°. Apparently a diffusive

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(1) E. E. Hoffman and W. D. Manly in "Handling and Uses of the Alkali Metals," Advances in Chemistry Series No. 19, American Chemical Society, Washington, D. C., 1957, p. 82.

(2) E. A. Wood and V. B. Compton, *Acta Cryst.*, **11**, 429 (1958).

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