mole) of cyclopentadiene was added at a rate sufficient to maintain a gentle reflux. After the addition was completed, the mixture was cooled to room temperature and 3.84 g. (0.010 mole) of tetracyclone dissolved in 100 ml. of benzene was added in one portion. Immediate discharge of the purple color took place. After stirring for an additional hour, 1:1 acetic acid–water was added to hydrolyze the mixture. Separation of the organic layer, washing it with water, drying it over anhydrous magnesium sulfate and then distilling the solvent gave 3.9 g. of pale yellow solid. Recrystallization from methanol (Darco G-60) afforded 3.3 g. (0.0073 mole, 74%) of almost colorless II, m.p. 197.6–198.6°. A second recrystallization did not raise the melting point.

Anal. Calcd. for $C_{34}H_{26}O$: C, 90.63; H, 5.82. Found: C, 90.43; H, 6.00.

III.—A solution of 0.45 g. (1.0 mmole) of II and 0.30 g. (3.0 mmoles) of freshly sublimed maleic anhydride in 20 ml. of bromobenzene was refluxed for one-half hour. After removing the solvent at reduced pressure and washing the residue with water and then methanol, the residue was recrystallized twice from nitromethane to give 0.28 g. (0.55 mmole, 55%) of colorless III, m.p. 251.0–252.5° dec.

Anal. Calcd. for $C_{38}H_{28}O_4$: C, 83.2; H, 5.1. Found: C, 82.9; H, 5.4.

I.—One-tenth gram (0.22 mmole) of II and 0.02 g. of iodine in 50 ml. of benzene was refluxed overnight. Distillation of the benzene at reduced pressure gave an olive residue which was washed with water, taken up in petroleum ether (b.p. 30–60°) and chromatographed on 3 g. of alumina. The eluate of the lowest band gave, on concentration, a brilliant, orange-red solid. Recrystallization from a mixture of petroleum ether, methanol and ether gave 0.028 g. (0.050 mmole, 27%) of orange-red, dendritic crystals, m.p. 201.0–202.1°.

Anal. Calcd. for $C_{34}H_{24}$: C, 94.41; H, 5.59. Found: C, 94.04, 94.43; H, 5.51, 5.81.

Pyrolysis of III to Give IV.—One-tenth gram (0.182 mmole) of III was heated at 275° for ten minutes. During this time nitrogen was swept through the reaction vessel and into a train consisting of silica gel, 5% palladium(II) chloride solution and saturated barium hydroxide. The silica gel gained 3.22 mg. (0.179 mmole, 98%) of water. No palladium was formed and no barium carbonate precipitated. The product was a dark red oil which crystallized on trituration with ether. Recrystallization from ethanol afforded 0.020 g. (0.038 mmole, 21%) of red IV, m.p. 177–181°.

Anal. Calcd. for $C_{38}H_{26}O_3$: C, 86.01; H, 4.94. Found: C, 85.93; H, 4.6.

IV from I.—One-tenth gram (0.23 mmole) of I was refluxed for 15 minutes with 0.3 g. (3 mmoles) of maleic anhydride in 15 ml. of toluene. The solvent was removed at reduced pressure, and the excess maleic anhydride was sublimed out of the product. Two recrystallizations from methanol gave 0.040 g. (0.075 mmole, 33%) of red adduct, m.p. 178–179°. A mixture melting point with the previous product melted at 178–181°.

Pentaphenylcyclopentadienol.—A solution of 3.84 g. (0.010 mole) of tetracyclone in 100 ml. of benzene was added to phenyllithium (from 7.8 g. (0.050 mole) of bromobenzene and 0.70 g. (0.10 atom) of lithium in 100 ml. of ether). The dark color of the tetracyclone was immediately discharged to give a clear yellow solution. After stirring for one hour, 100 ml. of 1:1 aqueous acetic acid was added. The organic layer was washed throughly with water, dried over anhydrous magnesium sulfate and distilled to give a brown oil. Trituration with methanol gave a solid which, upon recrystallization from methanol, afforded 3.6 g. (0.0078 mole, 78%) of pale yellow product, m.p. 176–177° (reported m.p. 175–176°[11]).

Ultraviolet Absorption Spectra.—The spectra were taken in methanol using a Cary spectrophotometer, model 11.

Acknowledgment.—The authors hereby express their appreciation to Charles Pfizer and Co., in whose laboratories this work was done, for their coöperation.

BROOKLYN 1, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF WISCONSIN]

The Organic Acids of *Narcissus poeticus*[1]

BY R. R. SMEBY, V. ZBINOVSKY, R. H. BURRIS AND F. M. STRONG

RECEIVED JULY 1, 1954

Several closely related organic acids have been obtained in crystalline form from *Narcissus poeticus* bulbs. Because of changes occurring during recrystallization it is not certain whether the isolated acids are the same as those originally existing in the plant. The isolated acid which appears to be the native form apparently changes into a more stable compound on mild alkaline treatment. This acid has the molecular formula $C_{11}H_{12}O_7$, and appears to contain one phenolic hydroxyl, two alcoholic hydroxyl and two carboxyl groups.

Vickery, *et al.*,[2] found that about half of the organic acids of *Narcissus poeticus* appeared to be of unknown constitution. They speculated that the main component of the unidentified acids might be isocitric acid, and expressed the opinion that the unknown acids play "a large and important part in the general organic acid metabolism of this species of plant."[2]

In the present work, the acids from the bulbs of this species were separated by partition chromatography.[3] Two peaks were observed which could not be attributed to any of the common plant acids (Fig. 1, peaks 1 and 2). Two others (peaks 3 and 4, Fig. 1) are due to malic and citric acids, respectively. The peak 1 acid has been isolated

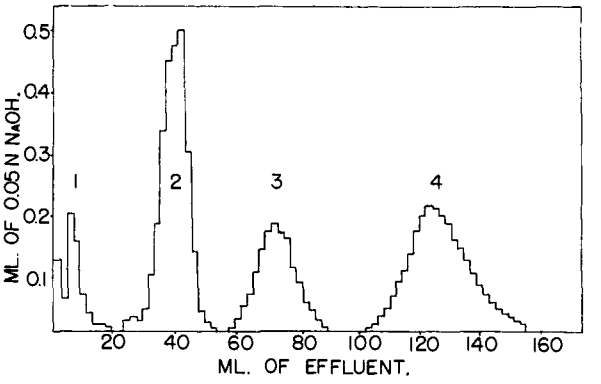


Fig. 1.—Chromatographic separation of organic acids from *Narcissus poeticus* bulbs.

(1) Published with the approval of the Director of the Wisconsin Agricultural Experiment Station. Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

(2) H. B. Vickery, G. W. Pucher, A. J. Wakeman and C. S. Leavenworth, *Bull. Conn. Agr. Exp. Sta.*, No. 496 (1946).

(3) F. A. Isherwood, *Biochem. J.*, **40**, 688 (1946).

in crystalline form but has not been more closely investigated. The initial product from the peak 2 effluent fractions showed a m.p. of *ca.* 150–190° dec. in various runs. In view of later observations on the ease with which these acids undergo changes, it seems likely that the wide variation in m.p. was caused by conversion of the original peak 2 acid into various altered products during isolation. Recrystallization of the initial product of one run, m.p. 193° dec., led to products of lower and lower m.p. until a definite substance (compound I) m.p. 153° dec. was finally obtained. In other runs an apparently definite product of m.p. 172° dec. resulted from recrystallization to constant melting point, but this was found by rechromatographing (Fig. 2) to be a mixture of about 15% of I and 85% of another compound (II), m.p. 178°. These separations are shown diagrammatically in Fig. 3.

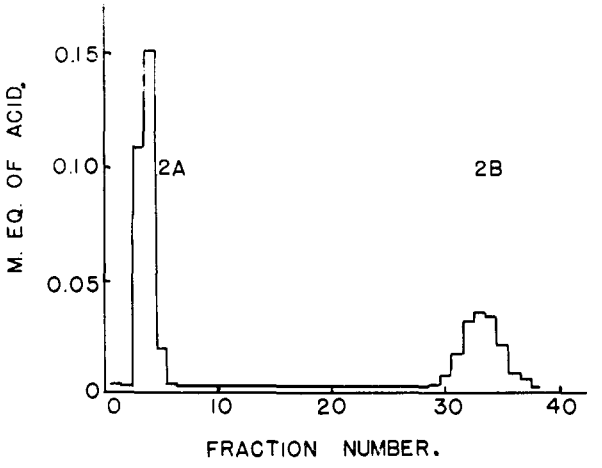


Fig. 2.—Chromatographic separation of compounds I (peak 2b) and II (peak 2a).

It appears probable that I, which behaves as a single substance during both paper and column chromatography, is the main unknown acid originally present in the bulbs. However, no information as to the nature of the high melting material from peak 2 is available, and it may be that acid I is itself a transformation product of the main unknown acid in the living plant.

Compound I did not give a ferric chloride test in water or ethanol nor a Gibb's test for phenols,[4] but the presence of a phenol group was nevertheless indicated by results with the *p*-diazobenzenesulfonic acid test,[5] Millon test, Folin test[6] and Lieberman nitroso reaction.[7] The ultraviolet absorption spectrum also was characteristic of phenols.[8] Compound I reacted with β-naphthol in concentrated sulfuric acid to give a red-purple color. It decolorized bromine water, was oxidized by periodate, and reduced Tollens reagent on

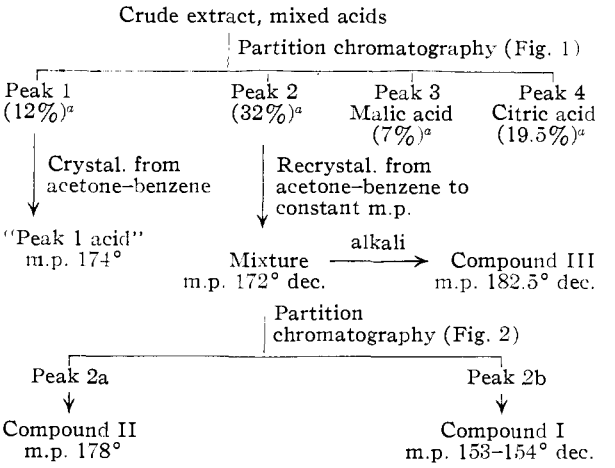
(4) M. B. Ettinger and C. C. Ruchhoft, *Anal. Chem.*, **20**, 1191 (1948).

(5) M. T. Hanke and K. K. Koessler, *J. Biol. Chem*, **50**, 235 (1922)

(6) O. Folin and V. Ciocalteu, *ibid.*, **73**, 627 (1927).

(7) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 114.

(8) L. Doub and J. M. Vandenbelt, THIS JOURNAL, **71**, 2414 (1949); W. Stenstrom and M. Reinhard, *J. Phys. Chem.*, **29**, 1477 (1925).



[a] Figures in parentheses indicate the percentage of total acid in the sample chromatographed.

Fig. 3.—Separation and transformations of organic acids from *Narcissus poeticus*.

heating. It did not reduce Fehling nor Benedict reagents and did not react with 2,4-dinitrophenylhydrazine.

Evidently because of facile alterations in solution, compound I has proved to be difficult to obtain consistently in repeated isolation trials, and the composition of apparently pure material has been somewhat variable. Available analytical data are consistent with the approximate molecular formula $C_{11-12}H_{14}O_{7-8}$. Electrometric titration revealed the presence of two carboxyl groups per phenol group. Electrometric titration of compound II indicated the presence of one carboxyl group per phenol group and on heating with excess sodium hydroxide approximately one additional mole of base was consumed.

When the mixture of I and II, m.p. 172°, was treated with alkali and the product crystallized as before, a third acid (compound III), m.p. 182.5° dec., was obtained (Fig. 3). This product was a more stable substance, which could readily be purified. It contained 5 active hydrogen atoms,[9] and had the formula $C_{11}H_{12}O_7$. It did not give a color with ferric chloride but did give a positive test for phenols with *p*-diazobenzenesulfonic acid.[5] Furthermore, the ultraviolet absorption spectrum was characteristic of a phenol.[8]

Compound III was oxidized by periodate, reacted with carbon disulfide to give an alkali xanthate (characteristic of a primary or secondary alcohol),[10] yielded a fluorescent dye with resorcinol and sulfuric acid and bound sodium bisulfite.[10] The Molisch, Benedict and Fehling tests were negative as well as tests for enols,[10] a methyl ketone group, and a methylenedioxy bridge.[10] Compound III did not give a color with β-naphthol in concentrated sulfuric acid.

Since the infrared spectra of the three unknown compounds, I, II and III are almost identical, these substances undoubtedly are very similar in structure.

(9) H. E. Zaugg and B. W. Horrom, *Anal. Chem.*, **20**, 1026 (1948).

(10) F. Feigl, "Qualitative Analysis by Spot Tests," 3rd ed., Elsevier Publishing Company, Inc., New York, N. Y., 1947, pp. 320-424.

A neutral equivalent of one-half the $C_{11}H_{12}O_7$ formula weight, and the preparation of a dimethyl ester which was still phenolic established the presence of two carboxyl groups in compound III. The conversion of this derivative into a triacetate further revealed the presence of three hydroxyl groups and thus accounted for all of the oxygen and active hydrogen atoms present. The ester–acetate also showed the molecular weight anticipated from the C_{11} formula for compound III. It is presumed that one of the three hydroxyls is phenolic because of the behavior of compounds I and II on electrometric titration and the general similarity of these substances to III.

Experimental[11]

Extraction of Acids.—Twenty-five bulbs (930 g.) of *Narcissus poeticus* (paper white)[12] were ground in a Waring blendor in five equal batches with 300 ml. of water, 10 ml. of 7 *N* sulfuric acid and 50 g. of ice per batch. The combined material was diluted with water in the ratio of tissue to water 1:3. The final volume was 4800 ml. Three volumes of acetone were added and the mixture was filtered through cheesecloth. The filtered solution was then concentrated to 200 ml. under reduced pressure. The concentrated, aqueous solution was extracted for five days with ether in a continuous liquid–liquid extractor. A total of 76.9 meq. of acids was obtained in this ether extract, which, after neutralization and concentration to *ca.* 30 ml., was ready to be chromatographed as described below.

Chromatography of Acids.—The columns were prepared as described previously.[3,13,14] A column 3.5 × 11 cm. was prepared from 40 g. of silicic acid[15] containing 0.7 ml. of 0.5 *N* sulfuric acid per gram of adsorbent. The mobile phase was 35% (v./v.) *n*-butyl alcohol in chloroform. Such a column was used for separating 8–10 meq. of the concentrated acids prepared above. A column 14.5 cm. in diameter and 12–17 cm. high, prepared from 1 kg. of silicic acid, was used for separating 80–100 meq. of acids.

To introduce the sample onto the column, a suitable aliquot of the concentrated neutralized ether extract was acidified with a 5% excess of 7 *N* sulfuric acid and mixed with silicic acid (1 g. of silicic acid per 0.7 ml. of solution) to obtain a uniform, dry powder. This was then suspended in a little of the mobile phase and poured carefully on top of the prepared column. The effluent from a column 3.5 × 11 cm. was collected in fractions of 10–12 ml. volume and 0.5-ml. aliquots were titrated with 0.02 or 0.05 *N* sodium hydroxide using 0.1% phenol red in 95% ethanol as the indicator.[13] Occasionally, when smaller columns were used, the whole fraction was titrated.

Isolation of Acids.[16] **Preparation of Peak 1 Acid.**—The combined fractions comprising peak 1 (Fig. 1) from a 14.5 × 12 cm. column were distilled to dryness under reduced pressure. The residue was taken up in *ca.* 20 ml. of water, decolorized with *ca.* 10 mg. of Norite, and the aqueous solution distilled to dryness under reduced pressure. The product was crystallized by dissolving the residue in the minimum amount of hot acetone, adding benzene until the boiling solution was faintly hazy and cooling at 4° for 14–16 hours. It was recrystallized in the same manner; yield 1.7 g., m.p. 174°.

Anal. Found: C, 55.45, 55.41; H, 5.12, 5.12.

The product gave an equivalent weight of 164 when titrated to a phenol red end-point; electrometric titration showed pK_1 3.3, pK_2 5.1, pK_3 10.3 and pK_4 11.5.

Preparation of Peak 2 Acid.—The combined fractions comprising peak 2 (Fig. 1) from a 7.8 × 13 cm. column (sample, 46 meq. of acids) were extracted with 160 ml. of 0.1 *N* sodium hydroxide. The organic phase was washed twice with water and the washings were combined with the original extract.[17] The aqueous solution was adjusted to *p*H 7.0 with sulfuric acid and concentrated under reduced pressure to *ca.* 100 ml. The concentrated solution was acidified with sulfuric acid, extracted for 50 hours with ether in a continuous liquid–liquid extractor, and the extract evaporated to dryness. The residue was taken up in a minimum of hot acetone, and benzene was added to the boiling solution until it was slightly turbid. The solution was allowed to stand at room temperature for about 3 hours and at 4° for 16 hours. The crystalline material was yellow in color and melted at 150–171°. This product was recrystallized five times as above and yielded white needles, m.p. 172–172.5° dec. The yellow impurity was less soluble in the benzene–acetone mixture than the desired product and was removed by filtering the hot solution when it had become fairly cloudy. The product (320 mg.) was shown to be a mixture of I and II by paper chromatography (see below).

Separation of Compounds I and II.—The sample of the mixture used for these separations was not recrystallized to constant melting as above, but melted at 166–167° dec. Columns were prepared as before except that 30% (v./v.) *n*-butyl alcohol in chloroform was used as the mobile phase. When 81 mg. of the mixture was chromatographed on a 3.5 × 11 cm. column, peak 2a (Fig. 2) yielded 61.9 mg. of compound II, m.p. 178°, after removing the solvent under reduced pressure and crystallizing the residue from acetone–benzene without heating the solvents. Peak 2b (Fig. 2) in an analogous manner gave 11.5 mg. of compound I, m.p. 153–154° dec. Each compound was dried 6 hours at 0.01 mm. and 100° for analysis.

Compound I was obtained as colorless needles very soluble in water, acetone, ethanol, dioxane, ethyl acetate, butanol; very slightly soluble in chloroform, carbon tetrachloride, benzene, ether; and insoluble in cyclohexane and petroleum ether (b.p. 60–71°).

Anal. Calcd. for $C_{11}H_{14}O_7$: C, 51.16; H, 5.46; neut. equiv. as dibasic acid, 129. Calcd. for $C_{12}H_{14}O_8$: C, 50.35; H, 4.93; neut. equiv., 143. Found, preparation 1: C, 51.62; H, 5.52; neut. equiv. by electrometric titration of carboxyl groups 186; preparation 2: C, 50.23; H, 5.32; neut. equiv. by electrometric titration of carboxyl groups, 122, 123.

In ethanol λ_{max} 274 mμ (k = 5,000) and in alcoholic sodium hydroxide λ_{max} 236 mμ (k = 26,100) and 290 mμ (k = 5,900).[18] Compound I is optically active, $[\alpha]^{20}D$ +52° (*c* 3.84% in acetone).

Compound II was also obtained as colorless needles very soluble in acetone, ethanol and *n*-butyl alcohol; soluble in water and chloroform; very slightly soluble in benzene and ether.

Anal. Found: C, 57.41, 57.76; H, 6.51, 6.58; OCH_3, 9.49. In water λ_{max} 224 mμ (k = 29,000) and 274 mμ (k = 4,500); in 0.1 *N* sodium hydroxide λ_{max} 238 mμ (k = 39,400) and 292 mμ (k = 7,600).

Preparation of Compound III.—Four grams of a mixture of I and II (m.p. 153–166°, dec.) was dissolved in 100 ml. of 1 *N* sodium hydroxide and allowed to stand for 24 hours at room temperature (24–26°). The solution was then acidified with 7 *N* sulfuric acid and extracted with ether for 148 hours. The ether extract was evaporated and the residue crystallized from acetone–benzene as described above. The product was dried at 0.01 mm., 100° for 8 hours; yield 3.12 g., m.p. 182–183° dec. A portion was recrystallized twice from acetone–benzene and dried at 0.01 mm., 100° for 8 hours for analysis.

Anal. Calcd. for $C_{11}H_{12}O_7$: C, 51.56; H, 4.72; neut. equiv. as dibasic acid, 128.1. Found on four separate

(11) All melting points are corrected. Microanalyses were by Clark Microanalytical Laboratory, 104½ West Main Street, Urbana, Illinois, or by Micro-Tech Laboratories, 8000 Lincoln Ave., Skokie, Illinois.

(12) The bulbs were obtained from the Olds Seed Company, Madison, but were grown in Holland.

(13) C. S. Marvel and R. D. Rands, Jr., THIS JOURNAL, **72**, 2642 (1950).

(14) T. Higuchi, N. C. Hill and G. B. Corcoran, *Anal. Chem.*, **24**, 491 (1952).

(15) Mallinckrodt analytical grade, 100 mesh, prepared for chromatographic analysis by the method of Ramsey and Patterson.

(16) These procedures are the most successful found during several runs.

(17) Since compound I is unstable in alkali an excess of sodium hydroxide should be avoided and this operation should be carried out as quickly as possible.

(18) All ultraviolet spectra were measured with the Beckman, model DU, spectrophotometer, and concentrations used in the calculations were expressed as g./ml.

preparations: C, 51.82, 52.70, 52.08, 52.28; H, 4.73, 5.80, 5.25, 5.53; OCH_3, nil; neut. equiv., 127.

Although three of the four C–H values are appreciably above the theoretical, the $C_{11}H_{12}O_7$ formula is supported by analyses of the dimethyl ester and ester–acetate of compound III (see below).

Compound III Dimethyl Ester.—To 100 mg. of compound III dissolved in *ca.* 1 ml. of methanol was added 10 ml. of ether, followed by ethereal diazomethane until a faint yellow color persisted. The solution was evaporated under reduced pressure, the residue extracted with *ca.* 10 ml. of boiling benzene and the extract cooled slowly. After several hours at 4° the product was removed by filtration and recrystallized from benzene. White needles were obtained, m.p. 115°, in a yield of 80 mg. The product was dried for analysis for 4 hours at 1 mm. and 65°. Since it still gave a positive test with *p*-diazobenzenesulfonic acid, the phenol group was not methylated.

Anal. Calcd. for $C_{13}H_{16}O_7$: C, 54.93; H, 5.67; OCH_3, 21.83. Found: C, 54.94; H, 5.69; OCH_3, 21.35, 21.91.

Compound III Dimethyl Ester–Triacetate.—To 80 mg. of the dimethyl ester of compound III suspended in 0.5 ml. of acetic anhydride was added *ca.* 0.02 ml. of concentrated sulfuric acid. After standing for 15 minutes at room temperature, the mixture was chilled in an ice-bath and 1 ml. of water added slowly with shaking. Small white needles separated, which were filtered off and washed twice with water. The reaction mixture was diluted with an additional 1.5 ml. of water, and a further batch of crystals formed after 12 hours storage at 4°. The combined crystalline product was recrystallized once from water, and yielded 55 mg. of long needles, m.p. 84–85° after drying 10 hours at 1 mm. and 67°. The product was very soluble in benzene and in ether but very slightly soluble in water. It gave no test for phenols with *p*-diazobenzenesulfonic acid.

Anal. Calcd. for $C_{19}H_{22}O_{10}$: C, 55.61; H, 5.40; OCH_3, 15.12; acetyl, 31.46; mol. wt., 410.4. Found: C, 55.52; H, 5.59; OCH_3, 15.00, 15.90; acetyl[19], 31.30, 31.42; mol. wt. (Rast), 438.

Paper Chromatography.—Ascending paper chromatograms were run using Whatman No. 1 paper in 14 × 45 cm. sealed, glass jars. The developing solvent was *n*-butyl alcohol 50 ml., benzyl alcohol 50 ml., water 10 ml., 90% formic acid 1.1 ml.[20] Samples of 10–50 μg. were used. The solvent front was allowed to move about 30 cm. (16 hours) after a 16-hour equilibration period. The acids were detected by spraying the paper with *p*-diazobenzenesulfonic acid prepared by the method of Hanke and Koessler[5] and made alkaline immediately before use by mixing 2 ml. of the diazo reagent with 8 ml. of 1.1% sodium carbonate. Stable pink spots were obtained. The R_f values found were: compound I, 0.40; compound II, 0.85; compound III, 0.43.

Infrared Spectra.—The infrared spectra of compounds I, II and III are given in full in the Ph.D. thesis of R. R. Smeby.[21]

Acknowledgments.—The authors are indebted to Dr. R. M. Bock, Mr. Rex Smith and Mr. Nan-Sing Ling for assistance with some of the electrometric titrations and to Mr. Don Johnson and Dr. E. E. van Tamelen for the infrared spectra.

(19) The authors are indebted to Mr. George Drummond for the acetyl analyses.

(20) J. B. Stark, A. E. Goodban and H. S. Owens, *Anal. Chem.*, **23**, 413 (1951).

(21) R. R. Smeby, Ph.D. Thesis, University of Wisconsin, 1954.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF WISCONSIN]

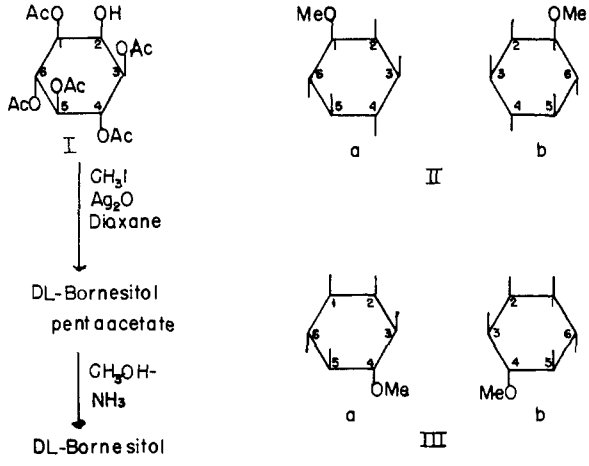
The Synthesis of DL-Bornesitol[1]

BY LAURENS ANDERSON AND AURORA M. LANDEL

RECEIVED JUNE 24, 1954

An acyl migration occurs during the methylation of 1,3,4,5,6-penta-*O*-acetyl-*myo*-inositol. The methylated product has been identified as penta-*O*-acetyl-DL-bornesitol. Crystalline DL-bornesitol was prepared from the acetate.

Bornesitol is a *myo*-inositol[2] methyl ether which was first isolated from "Borneo rubber" by Girard[3] in 1871. The supply of material which Flint and Tollens used in 1892 for their analytical work[4] likewise came from a rubber then being used in commerce, but the currently practical source of this cyclitol is opepe wood,[5] (*Sarcocephalus diderrichii*, West Africa). Bornesitol has also been found in opepe bark.[6] Since it is optically active, it must have one of the formulas IIa, IIb, IIIa or IIIb. Foster and Stacey[7] support formula IIa or IIb on the basis of the ionophoretic mobility of the borate complex, but no further evidence on the position of the methyl group in bornesitol was available when this paper was being written.



The purpose of the communication is to describe the synthesis of DL-bornesitol. Unfortunately, no deductions as to the position of the methyl group can be based on this synthesis. But since we are not planning direct work on bornesitol, it seemed desirable to report the results we have obtained.

Our original aim was to methylate the free hy-

(1) Published with the approval of the Director of the Wisconsin Agricultural Experiment Station. Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

(2) The system recently proposed by H. G. Fletcher, Jr., L. Anderson and H. A. Lardy, *J. Org. Chem.*, **16**, 1238 (1951), is used for naming and numbering the compounds described in this paper.

(3) A. Girard, *Compt. rend.*, **73**, 426 (1871).

(4) E. R. Flint and B. Tollens, *Ann.*, **272**, 288 (1892).

(5) F. E. King and L. Jurd, *J. Chem. Soc.*, 1192 (1953).

(6) Unpublished data obtained by V. Prelog, Zurich.

(7) A. B. Foster and M. Stacey, *Chemistry & Industry*, 273 (1953).