by heating to yield 6 g. of an orange oil. A mixture of 6 g. of this oil, 14 g. of copper sulfate pentahydrate, 100 ml. of pyridine, and 30 ml. of water was refluxed for 6 hr. The reaction mixture was poured onto 500 ml. of ice water and a semisolid formed. The liquid was decanted and the semisolid which remained was washed with water. This semisolid was dissolved in absolute ethanol and the solution was filtered to remove the insoluble copper salts. Upon cooling, a yellow solid, 2.7 g. (34%) which was removed by filtration, was formed. Recrystallization twice from absolute ethanol and once more from methanol gave the pure diketone, m.p. 119–120°.

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 86.17; H, 5.13.

The *quinoxaline* derivative melted at 156°.

Anal. Calcd. for $C_{32}H_{22}N_2$: C, 88.45; H, 5.10. Found: C, 88.16; H, 5.15.

3,3'-Diphenylbenzilic acid (VII). 3,3'-Diphenylbenzil (VI), 8 g., was dissolved in 300 ml. of dry ether and a solution of sodium ethoxide (4 g. of sodium in 50 ml. of 95% ethanol) was added. Also, 25 ml. of absolute ethanol was added to prevent precipitation of sodium ethoxide. The flask was stoppered and was allowed to stand for 24 hr. with frequent shaking. This solution was extracted with four 100-ml. portions of water and the aqueous solution was extracted with two 50-ml. portions of ether. After heating this solution to 90° to expel the ether, the solution was acidified with dilute hydrochloric acid and was cooled. The solid, which formed, was removed by filtration to give 3 g. (37%) of the crude acid. This acid was purified by recrystallization three times from benzene using Norit A each time. The pure acid melted at 155–157°.

Anal. Calcd. for $C_{26}H_{20}O_3$: C, 82.08; H, 5.30. Found: C, 82.17; H, 5.17.

β-Aminoester hydrochlorides of dicyclohexylglycolic acids. The corresponding benzilate was dissolved in glacial acetic acid and hydrogenated (3 atm.) in the presence of platinum catalyst (0.1 g. per 0.01 mole of ester) until reduction was complete. The catalyst was removed by filtration and the acetic acid was removed *in vacuo*. The solid which remained was dissolved in 10 ml. of absolute ethanol and precipitated by the addition of 90 ml. of dry ether. One more recrystallization from an ethanol-ether (1:9) mixture gave the pure product.

Acknowledgment. This research was performed on grant B-652 from the National Institutes of Health, Public Health Service, to which organization our sincere thanks are due. We also wish to thank the Union Carbide Chemicals Company for supplying gratis the *N,N*-dimethyl- and *N,N*-diethylethanolamines used as intermediates.

KNOXVILLE, TENN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF EMORY UNIVERSITY]

Condensation of Abietic Acid with Formaldehyde[1]

E. EARL ROYALS AND JOSEPH L. GREENE, JR.

Received March 31, 1958

Abietic acid has been condensed with formaldehyde in propionic acid solution to give in 51% yield 8,9-bismethylenepropionoxyabietic acid, isolated as the cyclohexylamine salt. Hydrolysis afforded 8,9-dimethylolabietic acid. The structure of this substance was established by catalytic dehydrogenation to 1,8,10-trimethyl-2-isopropylphenanthrene and comparison with the totally synthesized compound.

Although it is known[2] that abietic acid reacts with formaldehyde and certain other aldehydes to give resinous products, the nature of these products has not been established. Indeed, very few studies[3] have dealt with the behavior of conjugated dienes in the Prins reaction with aldehydes. We wish now to report a study of the acid catalyzed reaction of abietic acid (I) with formaldehyde including the determination of structure of a major product of this reaction.

All attempts to cause abietic acid to react with formaldehyde in aqueous solution or in such inert solvents as diisopropyl ether or *p*-dioxane failed; abietic acid could be recovered unchanged in each case. Similarly, attempts to condense abietic acid with formaldehyde in the presence of aqueous sulfuric acid (10%) led to recovery of unchanged abietic acid. This result is to be contrasted with the marked effect of sulfuric acid upon abietic acid in homogeneous media; *vide infra*.

Treatment of abietic acid with paraformaldehyde and a catalytic amount of sulfuric acid in *p*-dioxane solution led to exothermic reaction and formation of condensation products. From one to four moles of formaldehyde could be made to enter into the reaction with abietic acid, the number being determined only by the number of moles of formaldehyde introduced into the reaction mixture. From none of these reactions was a homogeneous product obtained. The product resulting from reaction of 1 molar equivalent of formaldehyde with abietic acid showed neutral equivalent 327, while that calculated for a methylolabietic acid is 332. Similarly, other crude reaction products showed neutral equivalent values close to those calculated for the introduction of two, three, and four form-

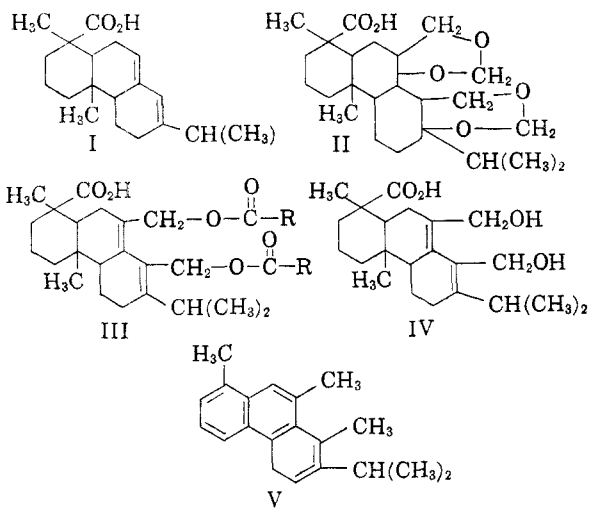
(1) Abstracted from a thesis presented by Joseph L. Greene, Jr., to the Graduate Faculty of Emory University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August 1957.

(2) A. L. Osterhof, U. S. Patent **2,084,218**, June 15, 1937; H. L. Morrill, U. S. Patent **2,519,780**, Aug. 22, 1950; R. R. Whetstone, W. J. Raab, and S. A. Ballard, U. S. Patent **2,568,426**, Sept. 18, 1951; W. E. St. Clair, M.S. Thesis, Tulane University, 1949.

(3) See E. Arundale and L. A. Mikeska, *Chem. Revs.*, **51**, 505 (1952).

aldehyde moities into abietic acid. None of these products could be obtained in pure, crystalline form.

It was first believed that the heterogeneous nature of the condensation products of formaldehyde with abietic acid was due to the presence of several different condensation products, *e.g.*, a methylol derivative, a dimethylol derivative, the 1,3-dioxane structure, etc. To test this hypothesis, abietic acid was treated with an excess (5 moles) of formaldehyde in the presence of sulfuric acid. From this experiment there was isolated a material showing neutral equivalent 417, while that calculated for a condensation product of structure II



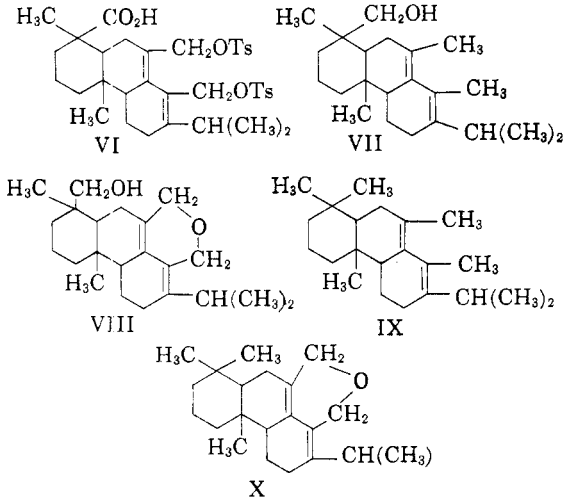
is 421. This material, however, could not be obtained crystalline, and was apparently heterogeneous. This result suggested that the heterogeneity of the various condensation products was due to an acid-catalyzed transformation of the abietic acid prior to its condensation with formaldehyde. Accordingly, samples of abietic acid were treated with catalytic amounts of sulfuric acid in *p*-dioxane solution, and the amount of unreacted abietic acid was determined by measurement of the optical density at 241 mμ. After one hour at room temperature, 82.5% of the abietic acid remained unreacted; after five minutes at reflux temperature, only 61.5% remained. That this acid-catalyzed transformation of abietic acid is polymerization rather than isomerization was suggested by the fact that no new absorption bands appeared in the ultraviolet spectra of the reaction products. Hence, it is concluded that polymerization of abietic acid is a competing reaction during attempted condensation with formaldehyde under sulfuric acid catalysis. This competing reaction could not be eliminated by decreasing the concentration of sulfuric acid nor by the expedient of admixing the formaldehyde and sulfuric acid prior to addition of abietic acid.

In confirmation of the report of St. Clair, we found that abietic acid is stable toward refluxing acetic acid. This suggested the use of glacial acetic acid as combined solvent and catalyst for the condensation of abietic acid with formaldehyde. From this reaction there was isolated a substance which could not be crystallized as such, but which readily formed a crystalline cyclohexyl amine salt. (Many other amines which were tried failed to give crystalline salts; see EXPERIMENTAL.) The amine salt showed neutral equivalent 542, in accord with a calculated value of 546 for the cyclohexyl amine salt of a *bis*-methyleneacetoxyabietic acid. An ultraviolet absorption maximum was observed at 251.5, suggesting a completely substituted heteroannular diene. An infrared band was observed at 5.76 μ, indicative of the acetate grouping, as well as a broad, low intensity band at 6.40 which according to Lecomte[4] is characteristic of the amine salts of carboxylic acids. On the basis of these observations, the substance was tentatively considered to be the cyclohexyl amine salt of 8,9-bismethyleneacetoxyabietic acid. Mild acidification of the amine salt with aqueous sodium dihydrogen phosphate gave the free carboxylic acid (III, R=CH_3), and hydrolysis of this material with aqueous potassium hydroxide gave a crystalline material tentatively identified as 8,9-dimethylolabietic acid (IV). It was found that substitution of propionic acid for acetic as the combined catalyst and solvent for the condensation of abietic acid with formaldehyde led to a material increase in yield. The product of this condensation (III, R = C_2H_5; isolated as the cyclohexyl amine salt) was isolated in 51% yield, while similar condensations in acetic acid led to quite low yields. It is probable that the increased yield from the propionic acid catalyzed condensation is due largely to greater ease of purification of the amine salt; whereas two crystallizations sufficed to give pure material from this condensation, at least five crystallizations were necessary to purify the material resulting from the acetic acid catalyzed reaction. Hydrolysis of the bismethylenepropionoxyabietic acid gave a dimethylolabietic acid identical in all respects to that resulting from the acetic acid catalyzed condensation product.

Dehydrogenation of 8,9-dimethylolabietic acid over palladium on charcoal led to elimination of the methylol groups and formation of retene in low yield. Catalytic hydrogenation of 8,9-dimethylolabietic acid over palladium on charcoal gave 8,9-dimethyloltetrahydroabietic acid. Dehydrogenation of this substance over palladium on charcoal gave a hydrocarbon showing correct elemental analysis for a dimethylretene to which was tentatively assigned the structure 1,8,10-trimethyl-2-isopropylphenanthrene (V). Total synthesis of 1,8,10-trimethyl-2-isopropylphenanthrene by the procedure described below gave material identical with V, thus affording proof of the structures assigned.

(4) R. Lecomte, *Bull. soc. chim. France*, 9, 548 (1942).

Since the behavior of the methylol groups on dehydrogenation was uncertain, conversion of IV to V was first attempted through the intermediate formation of 8,9-dimethylabietic acid. A series of reactions was effected similar to those employed by Stork[5] for the conversion of methylol groups to methyl. Treatment of IV with *p*-toluenesulfonyl chloride in pyridine solution led to a product which appeared to be a tosyl derivative of a dimeric ester resulting from reaction of the carboxyl group of IV with a methylol group. Treatment of the methyl ester of IV with *p*-toluenesulfonyl chloride gave the ditosylate of methyl 8,9-dimethylolabietate (VI). Lithium aluminum hydride reduction of VI in refluxing di-*n*-butyl ether gave an oil which was probably a mixture of 8,9-dimethylabietinol (VII) and the cyclic ether VIII. Conversion of this mixture to the tosyl derivatives followed by reduction with lithium aluminum hydride in refluxing di-*n*-butyl ether gave a product believed to be a mixture of IX and X. The mixtures VII–VIII and IX–X could not be separated. Stork[5] encountered similar formation of a cyclic ether during conversion of a 1,3-dimethylol compound to the dimethyl compound; in his case, however, the two compounds could be separated by fractional distillation. Because of these results, the direct dehydrogenation of 8,9-dimethylolabietic acid described in the preceding paragraph was investigated.

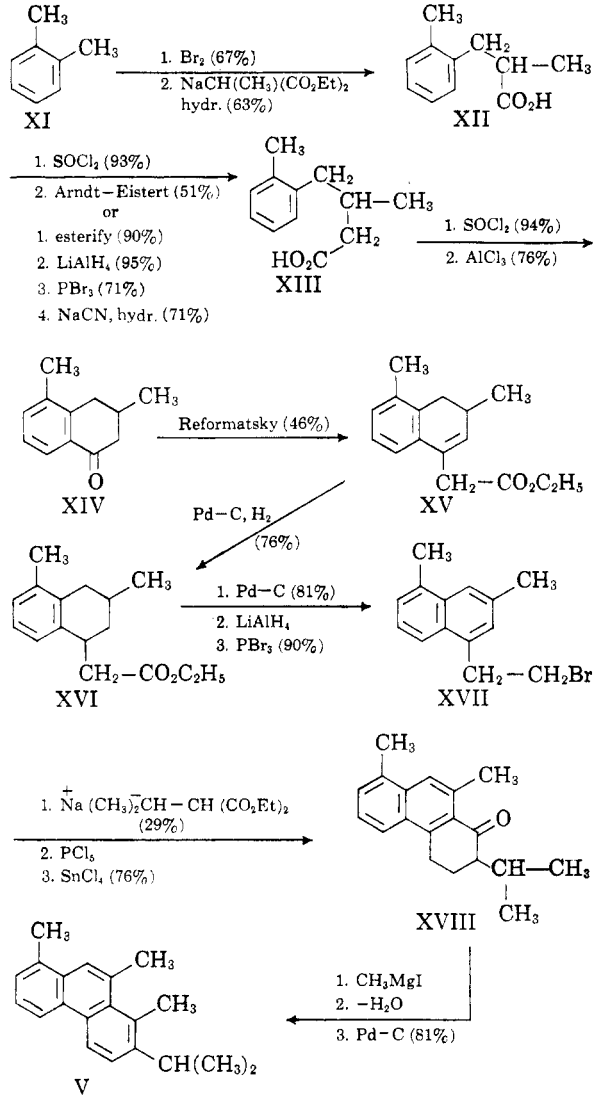


Total synthesis of 1,8,10-trimethyl-2-isopropylphenanthrene was achieved by the sequence of reactions shown in Chart I. Of the two routes shown in this chart for the conversion of XII into XIII, the first is the shorter, while the second is more easily adapted to large runs; over-all yields are approximately the same by either route.

The Reformatsky reaction of ethyl bromoacetate with 3,5-dimethyl-1-tetralone gave a product which was predominantly the β,γ-unsaturated ester XV. The compound showed strong ester absorption at 5.72 μ; very weak absorption at about 5.85 μ may indicate the presence of a small amount of the α,β-unsaturated ester. An attempt was made to aromatize the compound by Wohl-Ziegler bromination followed by dehydrohalogenation. Following a general procedure utilized for the synthesis of certain tropolones,[6] compound XV was treated with *N*-bromosuccinimide in refluxing chloroform, and the resulting product was heated at 100° in vacuum. The only product isolated from this reaction was 1,3,5-trimethylnaphthalene, identified through its melting point and that of its picrate.[7]

The alkylation of diethyl isopropylmalonate with 1-bromo-2-(3,5-dimethylnaphthyl)ethane (XVII) afforded some difficulty. Attempted reaction in al-

CHART I



(5) G. Stork, E. E. van Tamelen, L. J. Friedman, and A. W. Burgstahler, *J. Am. Chem. Soc.*, **75**, 384 (1953).

(6) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori, and Y. Nakayama, *Proc. Japan Acad.*, **26**, No. 7, 38 (1950); *Chem. Abstr.*, **45**, 7098 (1951).

(7) I. M. Heilbron and D. G. Wilkinson, *J. Chem. Soc.*, 2537 (1930).

cohol solution according to the standard procedure for a malonic ester synthesis failed completely. When the condensation was effected in anhydrous toluene according to a procedure described by Bachmann and Edgerton,[8] an alkylation product was obtained which afforded after hydrolysis and decarboxylation α-isopropyl-β-(3,5-dimethylnaphthyl-1)butyric acid in 29% over-all yield.

The 1,8,10-trimethyl-2-isopropylphenanthrene resulting from this synthesis was shown to be identical with that produced by degradation of IV by melting point and mixed melting point determinations on the hydrocarbon and its picrate.

EXPERIMENTAL[9]

Abietic acid (I). All abietic acid used in this work was prepared from commercial abietic acid, essentially according to the method of Harris and Sanderson.[10] Aqueous sodium dihydrogen phosphate, used in excess of the stoichiometric amount, was found to be a more convenient reagent for regeneration of abietic acid from its amine salt than the dilute acetic acid recommended by Harris and Sanderson. Our purified abietic acid showed $[\alpha]_D^{25}$ −101.6°.

Sulfuric acid catalyzed condensation of abietic acid with formaldehyde. Abietic acid, 10 g. (0.033 mole), and 1 g. (0.033 mole) of formaldehyde (as paraformaldehyde) were suspended in 50 ml. of purified dioxane. On addition of 3 g. of concd. sulfuric acid, the solution became homogeneous, and the temperature rose spontaneously to 60°. The darkened solution was maintained at 60° for 0.5 hr. On addition of 300 ml. of water, a cream colored precipitate was formed which was thoroughly washed with water and dried *in vacuo* at 50°. This material could not be obtained crystalline from any of a wide variety of solvents.

Anal. Calcd. for $C_{21}H_{32}O_3$: Neut. equiv., 332. Found: Neut. equiv., 327. Absorption maxima, 249 mμ and 2.90 μ (hydroxyl).

Experiments similar to that above were run using 2, 3, and 5 moles of formaldehyde per mole of abietic acid. These products showed neutral equivalent values of 357, 394, and 419, respectively, while the calculated values for the expected products in each case are 363, 388, and 421. In no case was a crystalline material obtained. The product from condensation of abietic acid with 2 moles of formaldehyde showed no maxima in the region 220–285 mμ.

Use of phosphoric acid and boron trifluoride etherate as catalysts gave results similar to those using sulfuric acid.

Effect of acids on abietic acid. Purified abietic acid, 10 g., was dissolved in 50 ml. of dioxane; 1.0 g. of concd. sulfuric acid was added. Ten-ml. aliquots of this solution were removed (1) immediately, (2) after 5 min., (3) after 10 min., and (4) after 5 min. at reflux. Each aliquot was poured into ice water, and the precipitate which formed was washed with water and dried in vacuo. The content of abietic acid in each sample was estimated from the absorption at 241 mμ. The aliquots referred to above showed 100, 90.5, 82.7, and 61.5% respectively of abietic acid.

Abietic acid, 3.0 g., $[\alpha]_D^{25}$ −101.6°, was dissolved in glacial acetic acid, and the solution was heated at reflux for a period of 18 hr. At the end of this time, 2.7 g. of abietic acid was recovered showing $[\alpha]_D^{25}$ −100.4°.

Condensation of abietic acid with formaldehyde in acetic acid. Abietic acid, 10 g. (0.033 mole), 2.2 g. (0.073 mole) of paraformaldehyde, and 50 ml. of glacial acetic acid were heated to reflux for 18 hr. At the end of this time, excess acetic acid was removed by distillation from a steam bath at 1 mm. The residue was taken up in other, washed with four 50-ml. portions of water, and dried over anhydrous magnesium sulfate. The clear yellow residue solidified to a glass, but could not be recrystallized from the common solvents.

Aliquots of a solution of 20 g. of the condensation product in 40 ml. of acetone were each treated at reflux with an equivalent amount of the following amines: di-*n*-propyl, diisopropyl, *n*-butyl, *sec*-butyl, isobutyl, di-*n*-butyl, diisobutyl, 1-amino-2-hydroxypropane, 2-amino-1-hydroxy-2-methylpropane, *n*-amyl, isoamyl, di-*n*-amyl, benzyl, *N*-methylbenzyl, cyclohexyl, and piperidine. Cyclohexyl amine produced a crystalline salt after 1 min., whereas the other amines failed completely to yield a crystalline salt after 30 days at 7°. The cyclohexyl amine salt was crystallized 4 times from a minimum volume of acetone. The final product was colorless and of needle-like crystalline structure, m.p. *ca.* 185°, absorption maxima 251.5 mμ, 5.76 μ, and 6.40 μ.

Anal. Calcd. for $C_{32}H_{31}O_6N$: Neutral equiv., 542. Found (Sorensen), 532.

8,9-bis-Methyleneacetoxyabietic acid (III, R = CH_3). The above cyclohexylamine salt, 5 g. was suspended in 100 ml. of ether, and this supension was thoroughly shaken with a solution of 20 g. of sodium dihydrogen phosphate in 100 ml. of water. The clear ether layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Removal of the solvent gave 8,9-bismethyleneacetoxyabietic acid in 95% yield. A sample of this material crystallized from *n*-heptane showed m.p. 73–75° (sealed capillary), absorption maxima 251.5 mμ, 5.76 μ, and 5.88 μ.

Anal. Calcd. for $C_{26}H_{38}O_6$: Neutral equiv., 447. Found: Neutral equiv., 441.

8,9-Dimethylolabietic acid (IV). 8,9-bis-Methyleneacetoxyabietic acid, 25 g. (0.056 mole) was heated to reflux for 2.5 hr. with a solution of 15 g. of potassium hydroxide in 70 ml. of water and 70 ml. of ethyl alcohol. The cooled solution was shaken with 300 ml. of ether and a solution of 60 g. of sodium dihydrogen phosphate in 300 ml. of water. The ether layer was washed twice with 100 ml. of water and dried over anhydrous magnesium sulfate. Removal of the solvent gave 19 g. of yellow amorphous solid. After three crystallizations from absolute ethanol, there was obtained 11.5 g. (58%) of 8,9-dimethylolabietic acid, m.p. 192–193°, λ_{max} 251.5 mμ, ϵ = 24,200, $[\alpha]_D^{25}$ +143.2°.

Anal. Calcd. for $C_{22}H_{34}O_4$: Neut. equiv., 362.5; C, 72.9; H, 9.46. Found: Neut. equiv., 361; C, 72.7; H, 9.22.

Condensation of abietic acid with formaldehyde in propionic acid. Abietic acid, 150 g. (0.5 mole), 33 g. (1.1 mole) of paraformaldehyde, and 750 ml. of propionic acid were heated at reflux for 20 hr. Excess propionic acid was removed by distillation from a steam bath at 1 mm. The residue was taken up in 750 ml. of ether, washed with four 200-ml. portions of water, and dried over anhydrous magnesium sulfate. Removal of the ether left a clear yellow glass which could not be obtained crystalline.

This crude product was dissolved in 350 ml. of acetone and treated at reflux temperature with 100 g. (1.0 mole; 100% excess) of cyclohexyl amine. The system was allowed to stand overnight at 7°, the crude precipitated salt was collected on a filter, washed thoroughly with water, and dried in vacuo. Two crystallizations from ligroin gave 145 g. (50.5% from abietic acid) of pure salt, m.p. *ca.* 175°, absorption maximum 251.5 mμ, $[\alpha]_D^{25}$ +85.6°. Liberation of the 8,9-bismethylenepropionoxyabietic acid from the salt and subsequent basic hydrolysis as described in the preceding two paragraphs gave 8,9-dimethylolabietic acid identical in all respects with that described above.

Degradation of 8,9-dimethylolabietic acid to 8,9-dimethyl-

(8) W. E. Bachmann and R. C. Edgerton, *J. Am. Chem. Soc.*, **62**, 2219 (1940).

(9) Melting points reported herein were determined in open capillary tubes and are uncorrected. Specific rotations were determined in absolute ethanol solution at approximately 1% concentration using the sodium D line.

(10) G. C. Harris and T. F. Sanderson, *J. Am. Chem. Soc.*, **70**, 334, 339, 2079, 2081 (1948).

retene. Attempted synthesis of 8,9-dimethylolabietic acid ditosylate. Treatment of 8,9-dimethylolabietic acid with tosyl chloride in pyridine solution according to the procedure described below gave a yellow solid showing infrared absorption bands at 5.75 and at 5.88 μ of equal intensity and area. There also appeared to be hydroxyl absorption at 3.0 μ. Neutral equivalent determinations gave values of 857, 862, and 868.

Methyl 8,9-dimethylolabietate ditosylate. Methyl 8,9-dimethylolabietate, prepared by the action of diazomethane on the acid, 32 g. (0.085 mole), was dissolved in 200 ml. of pyridine, and the solution was treated at 0° with 33.5 g. (0.175 mole) of tosyl chloride added in one portion. The system was swirled until all solid had dissolved and maintained at 0° for 2.5 hr. Precipitation of pyridine hydrochloride began after about 15 min. Water, 30 ml., was added in portions during 30 min. The resulting yellow suspension was poured into 200 ml. of water and extracted with three 200-ml. portions of chloroform. The chloroform extracts were washed with water, with 200 ml. of cold 2*N* sulfuric acid, again with water, with 100 ml. of saturated sodium bicarbonate, and again with water. After drying over anhydrous magnesium sulfate, the solution was evaporated in vacuo to give 44 g. (73%) of the ditosylate of methyl 8,9-dimethylolabietate. This material showed complete absence of hydroxyl absorption in the infrared and did show absorption bands at 7.28, 8.40, 8.48, 10.45, and 14.28 μ, all attributable to the tosylate functions.

Lithium aluminum hydride reduction of methyl 8,9-dimethylolabietate ditosylate. The above product, 40 g. (0.056 mole), was dissolved in ether, and this solution was added dropwise to a suspension of 7.5 g. (0.198 mole) of lithium aluminum hydride in 200 ml. of ether. The system was heated at gentle reflux for 1 hr. after addition was complete; ethyl acetate was then added to destroy excess lithium aluminum hydride. The ether suspension was vigorously stirred while a saturated aqueous solution of ammonium chloride was added dropwise until a gelatinous supension settled into the aqueous layer. The ether layer was washed with water and dried over anhydrous magnesium sulfate. Removal of the ether gave 23 g. of a product which showed infrared bands characteristic of the tosylate function; reduction of the carbomethoxy group to methylol appeared to be complete.

This material was dissolved in 200 ml. of di-*n*-butyl ether, and this solution was added to 7.0 g. of lithium aluminum hydride in 100 ml. of the same solvent. The system was heated at reflux for 3 hr. and worked up as described above to give 16 g. of a product which showed no infrared bands characteristic of the tosylate function. There was some absorption in the carbonyl region (*ca.* 5.75 μ) and fairly strong absorption at 8.50 and 8.74 μ. This substanec, assumed to be a mixture of 8,9-dimethylabietinol (VII), and the cyclic ether (VIII), 10.5 g. (0.033 mole), was treated with tosyl chloride as previously described for tosylation of methyl 8,9-dimethylolabietate. The resulting tosyl derivative was reduced with lithium aluminum hydride in refluxing di-*n*-butyl ether to give 6.2 g. of a yellow oil which showed no hydroxyl absorption in the infrared, but still showed strong absorption at 8.50 and 9.74 μ indicating presence of the ether function. This material is assumed to be a mixture of IX and X.

Dehydrogenation of 8,9-dimethylolabietic acid. Dehydrogenation of 2.0 g. of 8,9-dimethylolabietic acid over 2.0 g. of 10% palladium on charcoal at 300–330° for 4 hr. gave a crude material from which was isolated 0.2 g. of the trinitrobenzene complex of retene, m.p. 143–144°. No other product was isolated.

8,9-Dimethyloltetrahydroabietic acid. Ten g. (0.028 mole) of 8,9-dimethylolabietic acid in 100 ml. of methanol was catalytically reduced over 2.0 g. of 10% palladium on charcoal at 50 p.s.i. for 24 hr. Removal of the catalyst and solvent gave a white fluffy solid which could not be recrystallized from the common solvents. This material showed no ultraviolet absorption maxima in the region 220–285 mμ.

8,9-Dimethylretene (1,8,10-trimethyl-2-isopropylphenanthrene) (V). 8,9-Dimethyloltetrahydroabietic acid, 4.0 g. (0.011 mole), was dehydrogenated over 2.0 g. of 10% palladium on charcoal catalyst in a stream of carbon dioxide at 300-330° for 4.25 hr. The system was cooled and extracted with ether. The filtered ether solution was evaporated, and the residue was taken up in 10 ml. of absolute ethanol. This solution was treated at the boiling point with 10 ml. of a saturated solution of picric acid in 95% ethanol. The resulting deep red solution was allowed to cool slowly and stand overnight before filtration to give 2.2 g. of crystalline product, m.p. 177–178°.

Anal. Calcd. for $C_{26}H_{25}O_5N_3$: N, 9.15. Found: N, 9.02.

The picrate was dissolved in 100 ml. of ether and shaken with two 50-ml. portions of 10% sodium carbonate solution. The ether solution was then washed with water until the washings were colorless. The ether solution was dried over calcium chloride and evaporated to give thick, white needles which were recrystallized from 5 ml. of methanol to give 0.83 g. (34%) of 8,9-dimethylretene, m.p. 84–85°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.6; H, 8.40. Found: C, 91.52; H, 8.29.

Total synthesis of 1,8,10-trimethyl-2-isopropylphenanthrene. α-Methyl-β-(o-tolyl)propionic acid (XII). Sodium, 31 g. (1.35 mole), was dissolved in 600 ml. of absolute ethanol. When solution was complete, 238 g. (1.37 mole) of diethyl methylmalonate was added. α-Bromo-*o*-xylene,[11] 260 g. (1.4 mole), was added dropwise to the stirred reaction mixture at such a rate that the heat of reaction maintained the system at gentle reflux. Stirring at reflux was continued for 4 hr., and the excess ethanol was removed in vacuo. The resulting oily suspension of sodium bromide was poured into water. The crude ester was separated and boiled with a solution of 200 g. of potassium hydroxide in 200 ml. of water for 8 hr. The resulting clear solution was washed with ether, then cautiously treated with 500 ml. of 10*N* sulfuric acid; after foaming subsided, the mixture was heated to reflux for 5 hr. The organic layer was separated, and the aqueous layer was extracted with two 200-ml. portions of ether. The extracts were combined with the crude acid, dried over anhydrous magnesium sulfate, and the ether was removed by distillation. Distillation of the residue gave 152 g. (63%) of α-methyl-β-(*o*-tolyl) propionic acid, b.p. 147–150° (3 mm.).

Anal. Calcd. for $C_{11}H_{14}O_2$: Neutral equiv., 178. Found: Neutral equiv., 177.

The amide of this acid, m.p. 109–110°, was prepared by a standard procedure.

Anal. Calcd. for $C_{11}H_{15}ON$: N, 7.91. Found: N, 7.77, 7.82.

Ethyl α-methyl-β-(o-tolyl)propionate. The above acid, 152 g. (0.88 mole), 120 g. of ethyl alcohol, 300 ml. of benzene, and 3 ml. of concd. sulfuric acid were heated to reflux under a Dean-Stark water trap for 8 hr. The resulting system was washed with water, with sodium bicarbonate solution, again with water, and dried over anhydrous magnesium sulfate. Distillation gave 156 g. (90%) of ethyl α-methyl-β-(*o*-tolyl) propionate, b.p. 97–99° (1.5 mm.).

2-Methyl-3-(o-tolyl)-1-hydroxypropane. Ethyl α-methyl-β-(*o*-tolyl)propionate, 156 g. (0.79 mole), was dissolved in 350 ml. of ether. This solution was added dropwise during 1 hr. with stirring to a suspension of 28 g. (0.74 mole) of lithium aluminum hydride in 800 ml. of ether. Excess lithium aluminum hydride was destroyed by addition of a solution of 70 g. of ethyl acetate in 200 ml. of ether. The reaction complex was decomposed by the addition with stirring of 10% hydrochloric acid until a fluid white mass settled to the bottom of the reaction vessel leaving a clear supernatant ether solution which was separated by decantation. This solu-

(11) Prepared as described by J. F. Thorpe and E. F. Atkinson, *J. Chem. Soc.*, 1695 (1907).

tion was washed with 150 ml. of 10% hydrochloric acid and with 300 ml. of water and dried over anhydrous magnesium sulfate. Distillation gave 118 g. (95%) of 2-methyl-3-(o-tolyl)-1-hydroxypropane, b.p. 101–102° (1.5 mm.).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.5; H, 9.76. Found: C, 80.38; H, 9.69.

β-Methyl-γ-(o-tolyl)butyric acid (XIII). (Method A). 2-Methyl-3-(o-tolyl)-1-hydroxypropane, 110 g. (0.67 mole), and 200 g. of pyridine were cooled to 0°; 85 g. (0.31 mole) of phosphorus tribromide was added dropwise with stirring at such rate that the temperature of the reaction mixture could be held below 5° with external cooling. The mixture was maintained at 5° for 30 min., 200 ml. of ether was added, and stirring was continued for 1 hr. at 5°. The system was allowed to stand overnight at room temperature, 400 ml. of water was added, and the resulting system was extracted with three 200-ml. portions of ether. The combined extracts were washed with 100 ml. of 10% hydrochloric acid, with 200 ml. of water, and dried over anhydrous magnesium sulfate. Distillation gave 114 g. (71%) of 1-bromo-2-methyl-3-(o-tolyl)propane, b.p. 95–96° (1 mm.).

The bromide was heated to reflux for 40 hr. with a solution of 38 g. (0.59 mole) of potassium cyanide in 150 ml. of water and 50 ml. of alcohol. The system was cooled and diluted with 400 ml. of water; the organic layer was separated and refluxed with a solution of 70 g. of potassium hydroxide in 140 ml. of water until ammonia was no longer evolved. The resulting basic solution was cooled and carefully treated (hood) with a solution of 70 g. of concd. sulfuric acid in 200 ml. of water. The acidified mixture was extracted with three 200-ml. portions of ether. Distillation of the combined extracts gave 60 g. (62%) of β-methyl-γ-(o-tolyl)butyric acid, b.p. 151–153° (1.5 mm.).

Anal. Calcd. for $C_{12}H_{16}O_2$: Neutral equiv., 192. Found: Neut. equiv., 192.

The *p*-toluidide of this acid was prepared by a standard procedure; m.p. 107–108°.

Anal. Calcd. for $C_{19}H_{23}ON$: N, 4.98. Found: N, 4.88.

β-Methyl-γ-(o-tolyl)butyric acid (XIII). (Method B). α-Methyl-β-(o-tolyl)propionic acid, 100 g. (0.56 mole), and 140 g. (1.18 mole) of thionyl chloride were allowed to stand overnight protected from atmospheric moisture. The mixture was heated to reflux for 1 hr. and distilled to give 102 g. (93%) of α-methyl-β-(o-tolyl)propionyl chloride, b.p. 120–121° (9 mm.).

A solution of 100 g. (0.51 mole) of this acid chloride in 250 ml. of dry ether was added dropwise with stirring to a solution of diazomethane (prepared from 175 g. of *N*-nitrosomethylurea), while the temperature of the system was maintained at 5–10° by external cooling. After 15 min. the system was allowed to warm to room temperature and stand overnight. The ether was removed under reduced pressure so that the pot temperature did not exceed 30°. The crude diazoketone so obtained was dissolved in 500 ml. of dioxane, and this solution was added dropwise with stirring to a mixture of 10 g. of silver oxide, 25 g. of sodium carbonate, and 15 g. of sodium thiosulfate in 1 liter of water at 60°. Stirring was continued for 1 hr. after completion of the addition, and finally the mixture was boiled for about 2 min. before being cooled to room temperature. The solution was treated with 25 g. of sodium carbonate and extracted with two 200-ml. portions of ether to remove non-acidic products. The aqueous solution was then made acid with nitric acid and extracted with five 200-ml. portions of ether. Distillation of the combined extracts gave 49.6 g. (51%) of β-methyl-γ-(o-tolyl)butyric acid, b.p. 151–153° (1.5 mm.).

3,5-Dimethyl-1-tetralone (XIV). β-Methyl-γ-(o-tolyl)-butyric acid, 45 g. (0.24 mole), and 100 g. (0.84 mole) of thionyl chloride were mixed and allowed to stand overnight with protection from atmospheric moisture. After 1 hr. at reflux, the solution was distilled to give 46 g. (94%) of β-methyl-γ-(o-tolyl)butyryl chloride, b.p. 131–132° (7.5 mm.).

This acid chloride, 38.7 g. (0.18 mole), was dissolved in 40 ml. of ligroin (90–100°), and this solution was added to 35 g. (0.26 mole) of aluminum chloride just covered with ligroin. After the initial reaction, the system was heated under reflux for 2 hr. The resulting complex was decomposed by the careful addition of 10% hydrochloric acid, the temperature being maintained at 5°. The organic layer was separated, and the aqueous layer was extracted with ligroin which was added to the organic layer. This solution was washed with dilute hydrochloric acid and with water before distillation to give 24 g. (76%) of 3,5-dimethyl-1-tetralone, b.p. 118–120° (1.5 mm.), m.p. 63–64°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.7; H, 8.04. Found: C, 82.90; H, 7.93.

Ethyl 1-(3,5-dimethyl-3,4-dihydronaphthyl)acetate (XV). 3,5-Dimethyl-1-tetralone, 22 g. (0.125 mole), and 22 g. (0.13 mole) of ethyl bromoacetate were dissolved in a mixture of 50 ml. each of benzene and toluene. Twenty ml. of this solution was added to 9 g. (0.138 atom) of mossy zinc, and a crystal of iodine was added. On heating to boiling the reaction commenced, and the remainder of the solution was added at such rate as to maintain vigorous reaction. On completion of this addition, an additional 9 g. (0.138 atom) of zinc and 10 g. (0.06 mole) of ethyl bromoacetate were added, the reaction mixture was brought to reflux and stirred without further heating for 3 hr. Cold dilute hydrochloric acid was added, and the organic layer was extracted with benzene. The extract was washed with three 75-ml. portions of dilute ammonia and with water, then dried over calcium chloride. The solvent was removed, and the residual crude hydroxyester was heated with 100 ml. of 99% formic acid for 15 min. on the steam bath. The organic product was extracted with benzene and washed with dilute sodium carbonate solution and with water. Distillation gave 5.3 g. of unreacted 3,5-dimethyl-1-tetralone and 14.2 g. (46%) of ethyl 1-(3,5-dimethyl-3,4-dihydronaphthyl)acetate, b.p. 156–158° (3 mm.).

Attempted aromatization of ethyl 1-(3,5-dimethyl-3,4-dihydronaphthyl) acetate. Ethyl 1-(3,5-dimethyl-3,4-dihydronaphthyl) acetate, 2.16 g. (0.0089 mole), 1.90 g. (0.011 mole) of *N*-bromosuccinimide, and 20 ml. of chloroform were heated at reflux for 3 hr. The system was cooled and filtered, the solvent was removed by distillation, and the residue was heated in vacuo at water bath temperature for 2 hr. Crystallization of the residue gave a material showing no carbonyl absorption in the infrared, m.p. 46–49°, m.p. of picrate 140–141°.[7]

Ethyl 1-(3,5-dimethyl-1,2,3,4-tetrahydronaphthyl)acetate (XVI). Ethyl 1-(3,5-dimethyl-3,4-dihydronaphthyl)acetate, 14 g. (0.058 mole), in 150 ml. of methanol acidified with 2 drops of concd. hydrochloric acid was hydrogenated over 10% palladium on charcoal at 50 p.s.i. and 25° for 12 hr. Distillation gave 10.5 g. (76%) of ethyl 1-(3,5-dimethyl-1,2,3,4-tetrahydronaphthyl)acetate, b.p. 142–143° (2 mm.).

Ethyl 1-(3,5-dimethylnaphthyl)acetate. Ethyl 1-(3,5-dimethyl-1,2,3,4-tetrahydronaphthyl)acetate, 11 g. (0.046 mole), was dehydrogenated over 1.0 g. of 10% palladium on charcoal at 320° in a nitrogen atmosphere. After 9 hr., 2100 ml. of hydrogen had been evolved (collected over water; uncorrected). Addition of other, filtration and distillation gave 8.9 g. (81%) of ethyl 1-(3,5-dimethylnaphthyl)acetate, b.p. 156–158° (2 mm.).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.44. Found: C, 78.99; H, 7.20.

1-Bromo-2-(3,5-dimethylnaphthyl-1)ethane (XVII). Ethyl 1-(3,5-dimethylnaphthyl)acetate, 8.9 g. (0.037 mole) was dissolved in 30 ml. of ether, and this solution was added dropwise with stirring to a suspension of 5 g. of lithium aluminum hydride in 50 ml. of ether. After addition was complete, excess lithium aluminum hydride was destroyed by the addition of ethyl acetate in ether. Cold dilute hydrochloric acid was added with stirring to decompose the reaction complex. The ether phase was separated and washed with dilute hydrochloric acid, then with water. Evaporation of the ether gave a crude alcohol which was treated at 0°

with 5.5 g. (0.02 mole) of phosphorus tribromide added dropwise at such rate that the temperature did not exceed 10°. The mixture was allowed to stand at room temperature for 4 hr., water was added, and the mixture was extracted with ether. The ether extracts were washed with sodium carbonate solution, with water, and finally dried over Drierite. Distillation gave 8.6 g. (90%) of 1-bromo-2-(3,5-dimethyl-1-naphthyl)ethane, b.p. 173–175° (3 mm.).

Anal. Calcd. for $C_{14}H_{15}Br$: Br, 30.4. Found: Br, 30.19.

α-Isopropyl-γ-(3,5-dimethylnaphthyl-1)butyric acid. 1-Bromo-2-(3,5-dimethyl-1-naphthyl)ethane, 26 g. (0.1 mole), was added slowly to a boiling solution of the sodium salt of diethyl isopropylmalonate. (This latter reactant was prepared from 2.4 g. (0.1 atom) of sodium, 21 g. (0.1 mole) of diethyl isopropylmalonate, and 4.8 g. (0.1 mole) of ethanol in 60 ml. of anhydrous toluene at reflux for 21 hr.) The reaction mixture was heated to reflux for 12 hr. The toluene was removed in vacuo, and the residual oil was taken up in ether and washed with water. Evaporation of the ether left a residue which was heated to reflux for 8 hr. with a solution of 20 g. (0.35 mole) of potassium hydroxide in 20 ml. of water. The system was cooled, 15 ml. of water was added, and the mixture was extracted with two 20-ml. portions of benzene. The clear aqueous solution was treated cautiously with 50 ml. of 10*N* sulfuric acid, and heated to reflux for 6 hr. The cooled mixture was extracted with three 100-ml. portions of ether. The combined extracts were dried over Drierite and distilled to give 8.3 g. (29%) of α-isopropyl-γ-(3,5-dimethyl-1-naphthyl)butyric acid, b.p. 225–227° (1.5 mm.).

Anal. Calcd. for $C_{19}H_{24}O_2$: Neutral equiv., 284. Found: Neutral equiv., 281.

8,10-Dimethyl-2-isopropyl-1-keto-1,2,3,4-tetrahydrophenanthrene (XVIII). α-Isopropyl-γ-(3,5-dimethyl-1-naphthyl)-butyric acid, 4.5 g. (0.016 mole), was dissolved in 20 ml. of benzene, and 4.3 g. (0.2 mole) of phosphorus pentachloride was added. The system was allowed to stand at room temperature for 1 hr., and was then heated in the water bath for 5 min. The resulting solution was cooled to 5°, 4.5 ml. (0.38 mole) of stannic chloride was added, and the system was allowed to stand at 5° for 15 min. with occasional stirring. The reaction complex was then decomposed by the addition with stirring of dilute hydrochloric acid precooled to 5°. The organic phase was separated, washed with water, and dried over Drierite. Evaporation of the benzene left a yellow oil which rapidly crystallized. Two crystallizations from methanol gave 3.2 g. (76%) of 8,10-dimethyl-2-isopropyl-1-keto-1,2,3,4-tetrahydrophenanthrene, m.p. 56–58°.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.8; H, 8.27. Found: C, 85.62; H, 8.08.

1,8,10-Trimethyl-2-isopropylphenanthrene (V). 8,10-Dimethyl-2-isopropyl-1-keto-1,2,3,4-tetrahydrophenanthrene, 3.0 g. (0.011 mole), in 15 ml. of anhydrous ether was added at 5° to an ether solution of methyl magnesium iodide prepared from 7 g. (0.049 mole) of methyl iodide in 20 ml. of ether. The system was allowed to stand overnight under a moisture trap, then poured into cold dilute hydrochloric acid. The ether layer was separated and dried over Drierite. The ether was evaporated, and the residue was dehydrogenated over 1.0 g. of 10% palladium on charcoal at 310° for 1.5 hr. in a nitrogen atmosphere. The system was cooled and the reaction product taken up in ether. Filtration and evaporation of the ether left an oil which rapidly crystallized. Crystallization from methanol gave 2.6 g. (81%) of 1,8,10-trimethyl-2-isopropylphenanthrene, m.p. 85–86°; picrate, m.p. 175–176°.

A mixture of this synthetic material and the 1,8,10-trimethyl-2-isopropylphenanthrene produced by dehydrogenation of 8,9-dimethyloltetrahydroabietic acid melted at 83–85°, while a mixture of the picrates melted at 175–177°.

Acknowledgment. This work was supported by United States Department of Agriculture Research and Marketing Act Contract No. 12-14-100-318-(72), Agricultural Research Service, Southern Utilization Research and Development Division, Naval Stores Station.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

On the Preparation and Structure of a Glycoside of 3-Pentadecylcatechol, and the Monomethyl Ether and Monobenzoyl Ester Intermediates

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Received April 14, 1958

The reaction of 3-pentadecylcatechol with α-bromoacetoglucose followed by the hydrolysis of the product yielded a monoglycoside of 3-pentadecylcatechol melting at 105.5–106°. One of the monomethyl ethers of 3-pentadecylcatechol, namely, 1-methoxy-2-hydroxy-3-pentadecylbenzene, m.p. 46.5°, has been synthesized starting from *o*-vanillin. Mixtures of isomeric monomethyl ethers, monobenzyl ethers and monobenzoyl esters of 3-pentadecylcatechol were obtained by the direct reaction of 3-pentadecylcatechol with the appropriate reagent and each mixture was resolved by chromatography on alumina. Thus, the following compounds have been isolated: 1-methoxy-2-hydroxy-3-pentadecylbenzene, m.p. 46.5°; 1-hydroxy-2-methoxy-3-pentadecylbenzene, m.p. 43.5°; 1-benzoyl-2-hydroxy-3-pentadecylbenzene, m.p. 61.0°; and 1-hydroxy-2-benzoyl-3-pentadecylbenzene, m.p. 67.3°. The structure of the monobenzoyl ester (m.p. 67.3°) was arrived at by converting it to 1-methoxy-2-hydroxy-3-pentadecylbenzene. The reaction of 1-hydroxy-2-benzoyl-3-pentadecylbenzene with α-bromoacetoglucose and subsequent hydrolysis of the product yielded the monoglycoside, melting at 105.5–106.0°. The monoglycoside isolated from 3-pentadecylcatechol either directly or *via* its monobenzoyl ester has the structure 1-glucosidyl-2-hydroxy-3-pentadecylbenzene.

The four components of the poison-ivy principle have recently been structurally identified[2,3] and the saturated and monoolefinic components have

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