The Structure of the Dicyclic Diterpenoids of Slash Pine. The Identity of Elliotinoic Acid and Communic Acid

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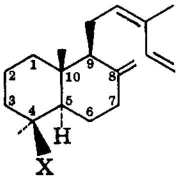
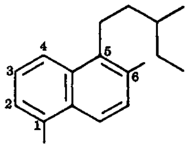
Received August 24, 1964

We wish to report new evidence requiring the revision of the skeletal structure of the dicyclic diterpenoid elliotinoic acid[2] and its corresponding alcohol, elliotinol,[2,3] which are isolated from the oleoresin of the slash pine (*Pinus elliottii*), and to report the identity of the acid with communic acid[4] (I), which appears to be a general constituent of the bark of various species of the genus *Juniperus*, and is of chemotaxonomic interest.[5,6] By the same evidence elliotinol is identical with the alcohol communol (II), which up to the present time has not been observed in nature, and was known only as a reduction product[4] of methyl communate.

Elliotinol[2] was easily converted in the form of its acetate to a well-defined maleic anhydride adduct, and on partial hydrogenation the alcohol gave a tetrahydro derivative, m.p. 16–20°, $[\alpha]^{25}D$ +21°. Dehydrogenation of the latter with palladium–charcoal afforded a hydrocarbon, elliotin, with an ultraviolet absorption spectrum indicative of a trialkylnaphthalene[7] which was characterized as a picrate, m.p. 69–70°, and as a 1,3,5-trinitrobenzene derivative, m.p. 76–77°.



I, X = COOH
II, X = CH_2OH



III

Elliotin is now shown to be 1,6-dimethyl-5-(3-methylpentyl)naphthalene (III) by the identity of its ultraviolet and infrared spectra with that of the synthetic hydrocarbon prepared by the action of 3-methylpentylmagnesium bromide on 2,5-dimethyl-1-tetralone[8] followed by dehydration and dehydrogenation with chloranil: picrate, m.p. 70-71°; trinitrobenzoate derivative, m.p. 77–78°; mixture melting point undepressed. The analogous 5-isohexyl structure originally proposed for elliotinol[3] and elliotinoic acid[2] is further ruled out by a parallel synthesis of 1,6-dimethyl-5-isohexylnaphthalene from the same dimethyltetralone. In this case both the intermediate olefin and the naphthalenic hydrocarbon showed in their infrared spectra the doublet at 1381 and 1364 cm.$^{-1}$ for the *gem*-dimethyl group, which was lacking in elliotin and in the previous synthetic series, and the melting points of the final picrate (77–78.5°) and trinitrobenzoate derivatives (92–93°) were clearly depressed on admixture with the elliotin derivatives.

Elliotinoic acid with diazomethane gave methyl elliotinoate whose properties, m.p. 105–106°, $[\alpha]^{25}D$ +48° (EtOH), λ_{max}^{EtOH} 232 mμ (ε 27,800), were virtually identical with those reported[4] for methyl communate [m.p. 105–106°, $[\alpha]D$ +48° ($CHCl_3$), λ_{max}^{EtOH} 232 mμ (ε 25,500)]. For purposes of comparison communic acid was separated from the fresh bark of *Juniperus silicicola*[9] by extraction with isooctane and chromatography on fuller's earth, and was converted to the crude sodium salt, m.p. 218–225°, $[\alpha]^{25}D$ +25° (EtOH), λ_{max}^{EtOH} 232–233 mμ (ε 19,400). These properties are similar to those reported previously for sodium communate[4] [m.p. 228–230°, $[\alpha]D$ +25° (MeOH), λ_{max}^{EtOH} 233 mμ (ε 20,000)], but both of these products must have been impure since authentic sodium elliotinoate prepared from the pure acid showed[2] the following enhanced values: m.p. 387–389° (sealed, evacuated tube), $[\alpha]^{25}D$ +42°, λ_{max}^{EtOH} 233 mμ (ε 27,500). The regenerated acid gave as before the methyl ester, which on gas–liquid chromatography on silicone SE-30 was separated into three components, one of which, amounting to about half of the total, was identical with methyl elliotinoate in its ultraviolet and infrared absorption spectra and in all other respects: m.p. 105–106°, $[\alpha]^{25}D$ +48° (EtOH), λ_{max}^{EtOH} 232 mμ (ε 27,800). The mixed esters had an undepressed melting point and showed a single peak on gas chromatography carried out as above.

With the revision of these structures it appears that all of the known dicyclic diterpenoids conform to the phytol rule[10] and that there is no divergence in this series from the manool skeletal structure. In the present work we have confirmed by ionization studies[4,11,12] the axial conformation of the C-4 carboxyl

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[2] N. M. Joye, Jr., and R. V. Lawrence, Southeastern Regional American Chemical Society Meeting, Gatlinburg, Tenn., Nov. 2, 1962; *Chem. Eng. News*, **40** (40), 72 (1962); *J. Org. Chem.*, **28**, 3274 (1963).

[3] E. M. Roberts and R. V. Lawrence, Abstracts, 131st National Meeting of the American Chemical Society, Miami, Fla., April 1957, p. 21-O; M. Tsutsui and E. A. Tsutsui, *Chem. Rev.*, **59**, 1046 (1959).

[4] V. P. Arya, H. Erdtman, and T. Kubota, *Tetrahedron*, **16**, 255 (1961); V. P. Arya, C. Enzell, H. Erdtman, and T. Kubota, *Acta Chem. Scand.*, **15**, 225 (1961).

[5] N. Narasimhachari and E. von Rudloff, *Can. J. Chem.*, **39**, 2572 (1961).

[6] H. Erdtman, *Pure Appl. Chem.*, **6**, 679 (1963).

[7] E. Heilbronner, U. Frohlicher, and P. A. Plattner, *Helv. Chim. Acta*, **32**, 2479 (1949).

[8] F. B. Kipping and F. Wild, *J. Chem. Soc.*, 1239 (1940).

[9] As a point of chemotaxonomic interest,[7] this species (southern red cedar) should be added to the other *Juniperus* species investigated,[6,7] in which communic acid was shown to be present in every case.

[10] L. Ruzicka, *Experientia*, **9**, 357 (1953).

[11] P. F. Sommer, C. Pascual, V. P. Arya, and W. Simon, *Helv. Chim. Acta*, **46**, 1734 (1963). pK_{MCS} is the designation used by Sommer, *et al.*, to indicate that the p*K* values were determined in a solution consisting of 80% methyl cellulose and 20% water.

[12] After the paper was sent to the journal we were notified by John W. Rowe that Curt Enzell in Sweden had compared the mass spectra of methyl elliotinoate and methyl communate. The results showed them to be identical.

group in elliotinoic acid (pK_{MCS}* 8.33). The occurrence of this acid in a species of the genus *Pinus*, in the order Pinales, is of particular chemotaxonomic interest since it is contrary to the present belief that all of the diterpenoid acids "found in Pinales have the same configuration, the carboxyl group at C-4 being equatorial."[6]

Experimental[13]

Elliotinol (II) was isolated through its *p*-**nitrobenzoate** from the nonacidic fraction of commercial gum rosin derived mainly from *Pinus elliottii*, and also from pure *Pinus elliottii* gum, by means of the following three procedures.

A.—A solution of 325 g. of WW rosin in the minimum amount of ether was extracted with 2 l. of 3% aqueous sodium hydroxide using a 3-l. Kieselbach-Pearl[14] continuous extractor with magnetic stirring. The extract, washed several times with water, dried with sodium sulfate, and evaporated, gave 26.71 g. (8.2%) of neutral oil of acid number 1–2.

A solution of 94.71 g. of the oil in 285 ml. of anhydrous pyridine was stirred with 47.4 g. of *p*-nitrobenzoyl chloride for 1 hr. at room temperature and then poured into 1 l. of water. The resultant semisolid mass was washed with 500 ml. of 5% sodium carbonate solution and repeatedly recrystallized from 95% ethanol, yielding 63.10 g. (44%) of crude solid which finally gave 26.1 g. of relatively pure material, m.p. 125–126°, and an analytical sample, m.p. 128–130°.

B.—Treatment of 41.33 g. of the above neutral fraction with 14.90 g. of Girard's P reagent as described previously[15] did not greatly affect the efficacy of the procedure; in this case 18.68 g. of noncarbonyl material from the Girard P treatment yielded 19.47 g. of crude elliotinyl *p*-nitrobenzoate.

C.—The neutral fraction was isolated by treatment of 100 g. of WW rosin in 1 l. of pentane with 32.77 g. of cyclohexylamine. The filtrate was washed six times with a total of 1 l. of 0.1 *N* hydrochloric acid and with water until neutral. Drying and removal of solvent left 12.56 g. of neutral fraction which, when treated as in method A, gave 5.08 g. of the crude *p*-nitrobenzoate.

Anal. Calcd. for $C_{27}H_{35}NO_4$: C, 74.14; H, 8.01; mol. wt., 438. Found: C, 73.88; H, 8.03; mol. wt., 437.[16]

For saponification, a solution of 6.64 g. of the *p*-nitrobenzoate in 400 ml. of 95% ethanol was refluxed for 1 hr. with a solution of 8 g. of potassium hydroxide in 200 ml. of the same solvent. After removal of about 500 ml. of alcohol and the addition of water, 4.42 g. (100.9%) of crude elliotinol, $\lambda_{\max}$ 232 mμ, was isolated from the washed and dried ether extracts. Purification was effected by passing a solution of the product in pentane (total volume, 95 ml.) through a short column of fuller's earth, removal of solvent under nitrogen, and precipitation of a minute amount of waxy crystalline impurity by refrigeration after the addition of 10 ml. of ethanol. A 3.51-g. sample of the product was distilled through a short-path still at high vacuum giving 2.15 g. of elliotinol as a colorless oil, $\lambda_{\max}$ 232 mμ, $[\alpha]^{26}\text{D}$ +14.2°.

A sample which was crystallized on a cold-finger apparatus by vacuum sublimation below 0.01 mm. melted on the cold finger at 14–15°.

Anal. Calcd. for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.40; H, 10.94.

The Hydrogenation of Elliotinol.—A solution of 0.19 g. of elliotinol was hydrogenated at atmospheric pressure and room temperature, with 0.12 g. of 5% palladium–carbon. After the uptake of 1 molar equiv. in 4 min. the absorption slowed down, a second molar equivalent being taken up in 40 min., yielding 0.185 g. of **tetrahydroelliotinol**, (total hydrogen, 34.30 ml.; 105% for two double bonds). A 0.29-g. sample was purified by distillation to give 0.20 g. of the pure colorless viscous oil which showed no ultraviolet maximum at 220–320 mμ, $[\alpha]^{25}\text{D}$ 21.4°. A sample which was crystallized on a cold finger apparatus by vacuum sublimation melted on the cold finger at 16–20°. The infrared spectrum of tetrahydroelliotinol showed no terminal methylene absorption.

Anal. Calcd. for $C_{20}H_{36}O$: C, 82.12; H, 12.41. Found: C, 81.81; H, 12.64.

Elliotin (III).—A mixture of 1.36 g. of tetrahydroelliotinol and 1.36 g. of 5% palladium–carbon was heated under a reflux condenser at 295–320° for 1.5 hr. Appreciable evolution of gas began at 250°, and ceased after 1 hr. of heating. The reaction product, worked up in ether, was a colorless oil (0.68 g.) which fluoresced violet and yellow in ultraviolet light and showed the characteristic absorption maxima of a trialkylnaphthalene[7] with reduced intensities: 231 mμ (ϵ 34,000), 279 (3390), 299 (2620), and 324 (454).

The spectrum also indicated a trace of a phenanthrene which was completely removed by chromatography in light petroleum ether on a 285 × 18 mm. column of 100–200-mesh silica gel.

The progress of the separation was followed by evaporation of 50-ml. eluates and observing the yields and spectra of the residual oils. Two nonaromatic fractions, apparently derived from disproportionation during the dehydrogenation, were eluted at peak effluent volumes of 100 ml. and 250 ml. The peak effluent volume for elliotin was 450 ml. The chromatography of a 1.00-g. sample of the crude product gave 0.32 g. of highly saturated material (peak 1), 0.21 g. of material of intermediate unsaturation (peak 2), and 0.28 g. of elliotin (peak 3): $\lambda_{\max}$ 231 mμ (ϵ 85,400), 279 (6040), 289 (6880), 300 (shoulder, 4710), 310 (1660), and 325 (1220). Distillation yielded the analytical sample, $\lambda_{\max}$ 231 mμ (ϵ 93,800), b.p. 116° (0.08 mm.).

Anal. Calcd. for $C_{18}H_{24}$: C, 89.94; H, 10.06; mol. wt., 240. Found: C, 89.91; H, 10.15; mol. wt., 241.[16]

The **trinitrobenzene derivative**, from a few drops of pure elliotin and a saturated solution of 1,3,5-trinitrobenzene in 95% ethanol, was recrystallized from alcohol in lemon yellow needles, m.p. 76–77°, $\lambda_{\max}$ (*c* 0.85 mg./l.) 231 mμ (ϵ 108,720).

Anal. Calcd. for $C_{24}H_{27}N_3O_6$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.47; H, 5.73; N, 9.28.

A small sample of the **picrate**, prepared similarly, melted at 69–70°.

Maleoelliotinyl acetate was obtained by refluxing for 1 hr. 1.00 g. of elliotinol with 4 ml. of acetic anhydride and 15 ml. of anhydrous pyridine, and then treating the product in 250 ml. of pentane with 0.40 g. of maleic anhydride in 5 ml. of acetone. Large needle-shaped crystals were deposited on standing overnight. The pentane was evaporated and an ether solution of the white crystalline residue was washed with water and evaporated until crystals began to form from the boiling solution: 0.45 g., m.p. 202–206.5°. The melting point remained unchanged by recrystallization from ether, but in a sealed evacuated tube was sharpened to 207–208.5°.

Anal. Calcd. for $C_{26}H_{36}O_5$: C, 72.87; H, 8.47. Found: C, 72.43; H, 8.56.

2,4-Dimethyl-1-tetralone was synthesized from *o*-bromotoluene, as described by Kipping and Wild,[17] with certain modifications. The intermediate alcohol was converted to the bromide with anhydrous hydrogen bromide in the usual manner, and cyclization of the intermediate monoacid was carried out by the procedure of Adkins[18] and Newman.[18] Since all of the products involved are known, we are merely recording their properties, as follows: **β-*o*-tolylethanol**, b.p. 82–83° (0.5 mm.), $n^{20}\text{D}$ 1.5348 (phenylurethan, m.p. 82.5°); **β-*o*-tolylethyl bromide**, b.p. 72–74° (1 mm.); **diethyl methyl-β-*o*-tolylethylmalonate**, b.p. 124–126° (0.05 mm.); **methyl-β-*o*-tolylethylmalonic acid**, m.p. 134–135.5°; **γ-*o*-tolyl-α-methylbutyric acid**, b.p. 158–160° (1 mm.); **2,5-dimethyl-1-tetralone**, b.p. 90–93° (0.5 mm.), m.p. 46.5–47° (lit.[17] m.p. 47°).

3-Methylpentyl bromide[19,20a] was synthesized from 2-bromobutane by treatment of the Grignard reagent of the latter with ethylene oxide and further treatment of the 3-methylpentanol (b.p. 58–59° at 11 mm., $n^{20}\text{D}$ 1.4193; 3-nitro hydrogen phthalate, m.p. 152–153.5°) with anhydrous hydrogen bromide. The product fractionated through a 46-plate column, b.p. 38–39°

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(13) Melting and boiling points are uncorrected. Unless stated otherwise, rotations were determined on 2% solutions in 95% ethanol, ultraviolet spectra were carried out in 95% ethanol, infrared spectra were determined as Nujol mulls, $\lambda_{\max}$ are expressed in mμ, and $\nu_{\max}$ are expressed in cm.$^{-1}$

(14) I. A. Pearl, *Ind. Eng. Chem., Anal. Ed.*, **16**, 62 (1944).

(15) E. McC. Roberts and Ray V. Lawrence, *J. Am. Chem. Soc.*, **78**, 4087 (1956).

(16) E. P. Clark, *Ind. Eng. Chem., Anal. Ed.*, **13**, 820 (1941).

(17) F. B. Kipping and F. Wild, *J. Chem. Soc.*, 1239 (1940).

(18) H. Adkins and J. W. Davis, *J. Am. Chem. Soc.*, **71**, 2957 (1949); M. S. Newman, H. V. Anderson, and K. H. Takemura, *ibid.*, **75**, 347 (1953).

(19) All compounds involved in the preparation of the bromides are known substances.

(20) "Beilsteins Handbuch der Organischen Chemie," Vol. 1, Julius Springer, Berlin, 1918, (a) p. 150; (b) p. 148.

at 12 mm., was identified by conversion to 4-methylcaproanilide, m.p. 74–75° (lit.[21] m.p. 76.5°).

4-Methylpentyl bromide[19,20b] was prepared as above through an analogous sequence from isobutyl iodide. The following products were obtained: 4-methylpentanol, b.p. 52–53° (8 mm.), $n^{25}D$ 1.4142; 3,5-dinitrobenzoate, m.p. 71–71.5°; and 4-methylpentylbromide, b.p. 32–33° (9 mm.) [fractioned as above and identified as 5-methylcaproanilide, m.p. 73–74° (lit.[22] m.p. 75°)].

1,6-Dimethyl-5-(3-methylpentyl)-7,8-dihydronaphthalene.—The foregoing ketone (10.0 g., 0.057 mole) in 50 ml. of dry ether was added in the usual manner to the Grignard reagent prepared from 6.96 g. of magnesium (0.29 mole), and 46.20 g. of 3-methylpentyl bromide (0.28 mole), and the reaction mixture was refluxed for 2.5 hr. After treatment with 400 ml. of ice-water containing 70 g. of ammonium chloride and a few crystals of sodium thiosulfate, the ether extract was washed and dried as usual. Volatile material was removed under vacuum and the crude product was treated directly with 100 ml. of 98% formic acid. After 80 min. at room temperature, 30 min. at 40°, and 30 min. at 50°, 600 ml. of water was added and the mixture was extracted with petroleum ether (b.p. 20–40°). After washing thoroughly with water and alkali, drying, and removing solvent, fractionation through a 46-plate spinning-band column gave as the chief fraction 8.18 g. (59% based on the tetralone) of colorless oil, which is probably composed mainly of the 7,8-dihydro isomer: b.p. 140–143° (1.2 mm.), $n^{20}D$ 1.5418.

Anal. Calcd. for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 88.64; H, 10.85.

Synthetic Elliotin (III).—A solution of 6.5 g. of the olefin (0.027 mole) and 7.1 g. of chloranil (0.029 mole) in 55 ml. of xylene was refluxed under nitrogen for 17 hr. After cooling, 75 ml. of petroleum ether was added and the crystallized tetrachlorohydroquinone was filtered (6.0 g.) and washed with petroleum ether. After shaking with excess aqueous alkali and sodium hydrosulfite, washing, and drying, all color was removed by passage through a short column of basic alumina and the eluate was fractionated through the 46-plate column. The pure product, 1,6-dimethyl-5-(3-methylpentyl)naphthalene, was a colorless oil, b.p. 125–127° (0.5 mm.), 4.37 g. (67%), whose infrared and ultraviolet spectra were almost identical with those of the elliotin derived from the natural product.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 90.23; H, 9.66.

The **trinitrobenzene derivative** crystallized in fine lemon yellow needles, m.p. 77–78°, which showed a characteristic strong birefringence in the polarizing microscope and did not depress the melting point of the corresponding "natural" derivative.

Anal. Calcd. for $C_{24}H_{27}N_3O_6$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.71; H, 5.93; N, 9.21.

The **picrate** crystallized from methanol in orange-yellow rods or plates, m.p. 70–71°, which also showed a beautiful birefringence under crossed polarizers and exhibited a "double melting point", yellow needles or plates appearing in the melt and remelting around 112°.

Anal. Calcd. for $C_{24}H_{27}N_3O_7$: C, 61.40; H, 5.80; N, 8.95. Found: C, 61.44; H, 6.02; N, 8.45.

Neither the styphnate nor the 2,4,7-trinitrofluorenone could be obtained in pure well-defined crystals.

1,6-Dimethyl-5-isohexyl-7,8-dihydronaphthalene.—The Grignard reaction was run in the manner described above, using 24.00 g. (0.144 mole) of isohexyl bromide, 3.60 g. (0.150 mole) of magnesium, and 150 ml. of dry ether. The same dimethyltetralone was used (12.11 g., 0.07 mole) in 50 ml. of ether, and the product was isolated as before. The resulting crude, oily, tertiary alcohol (16.6 g., 91%) was treated with 110 ml. of 98% formic acid at room temperature for 1 hr. and then from 33 to 52° for a second hour. The crude olefin, isolated and fractionated as before, weighed 8.58 g. (56%), b.p. 132–136° (1 mm.), $n^{20}D$ 1.5392.

Anal. Calcd. for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 88.83; H, 10.82.

1,6-Dimethyl-5-isohexylnaphthalene.—The dehydrogenation was run as before using 6.4 g. (0.026 mole) of the olefin with 6.90 g. (0.028 mole) of chloranil in 55 ml. of xylene; 5.8 g. of tetrachlorohydroquinone was recovered. The fractionated, colorless, oily product, b.p. 120–123° (0.3 mm.), weighed 4.94 g. (79%). The naphthalenic hydrocarbon, as well as the preceding olefin and all the intermediates in the isohexyl series, showed for the *gem*-dimethyl group the characteristic absorption doublet at 1381 and 1364 cm.$^{-1}$ which was absent in the 3-methylpentyl analogs.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 90.02; H, 9.82.

The **trinitrobenzene derivative** formed light yellow needles, m.p. 92–93°, which when mixed with the corresponding derivative of elliotin melted at 72–76°.

Anal. Calcd. for $C_{24}H_{27}N_3O_6$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.60; H, 5.85; N, 9.34.

The **picrate** crystallized in bright yellow rods, m.p. 77–78.5°; mixture melting point with elliotin picrate was 64–68°.

Anal. Calcd. for $C_{24}H_{27}N_3O_7$: C, 61.40; H, 5.80; N, 8.95. Found: C, 60.89; H, 5.94; N, 8.95.

The **styphnate**, prepared from very pure hydrocarbon regenerated[23] from the constant-melting trinitrobenzene derivative, crystallized in intensely birefringent yellow rods and well-formed rhombic plates, m.p. 65.5–68°.

Anal. Calcd. for $C_{24}H_{27}N_3O_8$: C, 59.37; H, 5.61; N, 8.66. Found: C, 59.67; H, 5.74; N, 8.41.

The **2,4,7-trinitrofluorenone derivative** from the same regenerated[17] hydrocarbon, above, crystallized in red-orange needles, m.p. 125–126°.

Anal. Calcd. for $C_{31}H_{29}O_7N_3$: C, 67.02; H, 5.26. Found: C, 67.11; H, 5.35.

Elliotinoic Acid.—Elliotinoic acid prepared as previously described[2] had the following physical constants: $[\alpha]^{25}D$ +40° (c 1.0), λ_{max} 232 mμ (ϵ 28,900). The acid is a viscous sirup and is quite sensitive to oxidation on standing. The ionization constant observed in this laboratory by the method of Simon[11] was as follows: for elliotinoic acid the observed pK_{MCS} was 8.33; for levopimaric acid, pK_{MCS} 7.74; and for neoabietic acid, pK_{MCS} 7.71; calculated axial pK 8.41 and calculated equatorial pK 7.91.

Methyl Elliotinoate.—Elliotinoic acid (0.34 g.) in 10 ml. of ether was treated with an excess of diazomethane. The solvent was removed under a stream of nitrogen to leave an oily residue. The oil was dissolved in hot methanol, filtered, and allowed to crystallize. The white crystalline product (0.26 g.) was removed by filtration and dried under vacuum. One recrystallization from methanol gave the pure ester, m.p. 105–106°, $[\alpha]^{25}D$ +48° (c 1.0), λ_{max} 232 mμ (ϵ 27,800).

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.64; H, 10.19. Found: C, 79.69; H, 10.18.

Isolation of Sodium Communate from *Juniperus silicicola*.—The fresh bark (200 g.) was extracted for 6 hr. with boiling isooctane. Water (82 ml.) was trapped during the extraction. The hot extract was filtered and then allowed to cool to room temperature. The isooctane solution was chromatographed on fuller's earth using absolute ethanol–isooctane (1:9) as the eluting solvent. The alcohol was removed under reduced pressure and a sodium hydroxide solution (3 N) was added dropwise with constant stirring until there was no further salt precipitated. The sodium salt was removed by filtration and dried under vacuum. A total of 0.76 g. of crystalline sodium salt was obtained from 118 g. of dry juniper bark. One recrystallization from methanol and water gave sodium communate, $[\alpha]^{25}D$ +25° (c 1.0), m.p. 218–225°, λ_{max} 232–233 mμ (ϵ 19,400).

Methyl Communate.—Sodium communate (0.20 g.) was suspended in ether and acidified with 3 N phosphoric acid. The ether solution was washed neutral with water and dried over sodium sulfate. To the ether solution was added an excess of diazomethane and the solvent was removed under a stream of nitrogen. The oily residue (0.16 g.) was put through a silicone (SE-30) type column and found to have three peaks. The first and third peaks were present in about equal amounts and accounted for about 90% of the material. The third peak was collected and crystallized from methanol, $[\alpha]^{25}D$ +48° (c 1.0), m.p. 105–106°, λ_{max} 232 mμ (ϵ 27,800). A mixture melting point with methyl elliotinoate showed no depression. When mixed in equal parts with methyl elliotinoate only one peak was observed on the gas chromatogram.

Acknowledgment.—Two of us (M. D. S. and O. K.) gratefully acknowledge a grant from The National Science Foundation.

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