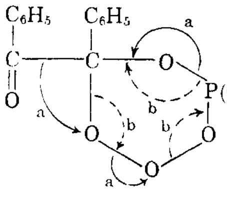
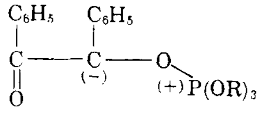
phosphate ester XIII (*i.e.*, phosphate + oxygen), or (b) benzil plus molecular oxygen and phosphate ester, are indicated by the arrows.[9] Presumably, the ozonides XII and XIV are derived from a dipolar form of the adducts (IA, IIA).

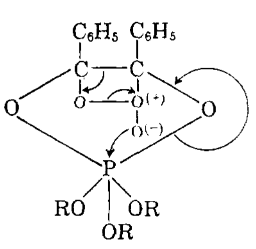


XIV

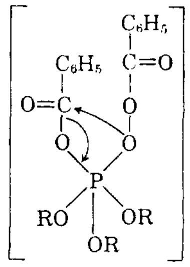


IA, IIA

Benzoyl peroxide can be derived from the "primary ozonide" XV formed by attack at the carbon–carbon double bond of the cyclic adduct. A possible path may involve XVI.

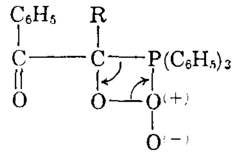


XV



XVI

The primary ozonide XVII (or its five-membered equivalent) derived from the phosphinemethylenes (VIII, IX) should collapse to the *alpha*-dicarbonyl compound and a peroxidic phosphine oxide (like XIII).



XVII

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(9) Alternatively, oxygen atoms from O_2 or O_3 could have entered the benzil molecule in the reactions of the adducts.

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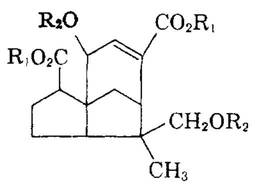
RECEIVED AUGUST 15, 1960

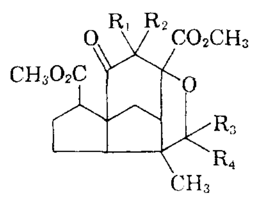
SHELLOLIC ACID, A CEDRENOID SESQUITERPENE FROM SHELLAC

Sir:

Shellolic acid is a component of the acid fraction obtained on basic hydrolysis of shellac, a resin of insect origin.[1] We propose that it is a sesquiterpene of structure I with *the rare cedrene skeleton.*[2]

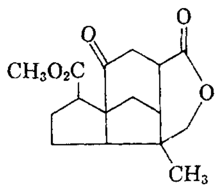


I, $R_1 = R_2 = H$
II, $R_1 = CH_3$, $R_2 = H$
VI, $R_1 = CH_3$, $R_2 = CH_3CO$

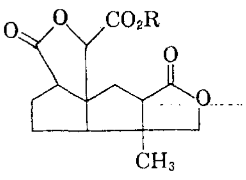


III, $R_1 = R_2 = H$, $R_3 = R_4 = H$
V, $R_1R_2 = O$, $R_3 = R_4 = H$
XI, $R_1 = R_2 = H$, $R_3,R_4 = O$

Earlier work[3,4] established that shellolic acid is a compound $C_{13}H_{16}(OH)_2(CO_2H)_2$ containing an ethylenic double bond. The relationship between the functional groups has been elucidated as follows. The spectra of dimethyl shellolate (II), $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.9, 5.8–5.9, 6.11 μ, $\lambda_{\max}^{\mathrm{EtOH}}$ 230 mμ (ϵ 6000), show that the double bond is conjugated with a carboxylic ester group. The n.m.r. spectrum ($CHCl_3$) shows one vinylic hydrogen, which gives a doublet ($J \sim 3$ c./s.) with $\tau = 3.51$, and one C–CH_3 group (confirmed by Kuhn–Roth) which gives a singlet with $\tau = 8.83$. Oxidation of II with manganese dioxide gave a dehydro product,[5] III, m.p. 122.5–124°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.75 (sh), 5.79 and 5.83 (sh) μ, no high intensity ultraviolet absorption >210 mμ. Treatment of II with methanolic sodium methoxide gave, *inter alia*, a product, IV, m.p. 155–156°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.8 (br) μ, also lacking high intensity ultraviolet absorption. Oxidation of III with selenium dioxide formed an α-diketone V, m.p. 200–203°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.77 (br) μ, $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 290 (40), 430 (12) mμ, which failed to enolize.[6] Ozonolysis of II followed by treatment with basic hydrogen peroxide and with diazomethane gave an ester, VII, m.p. 158–159°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.66 (s), 5.80 μ.[7] The relationship of the groups attached to the six-membered ring was corroborated by the formation of *m*-hydroxybenzoic acid on fusion of II with alkali. Oxidation of II with 6 equiv. of chromic acid gave an acid IX, which was converted by methyl iodide and potassium carbonate to the triester X, m.p. 99.5–100°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.78, 5.93, 6.10 μ, $\lambda_{\max}^{\mathrm{EtOH}}$ 240 mμ (ϵ 8,700). The acid IX was



IV



VII, R = CH_3
VIII, R = H

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(1) *Cf.*, for example, A. Tschirch and E. Stock, "Die Harze," Vol. II, Borntraeger, Berlin, 1936, p. 1443 *et seq.*; S. C. Sen Gupta, "Report of the Proceedings of the Symposium on Lac and Lac Products," Indian Lac Research Institute, 1956, p. 72.

(2) G. Stork and R. Breslow, THIS JOURNAL, **75**, 3291, 3292 (1953); G. Stork and F. H. Clarke, Jr., *ibid.*, **77**, 1072 (1955); Pl. A. Plattner, A. Fürst, A. Eschenmoser, W. Keller, H. Kläui, St. Meyer and M. Rosner, *Helv. Chim. Acta*, **36**, 1845 (1953). The only other naturally-occurring compound hitherto reported to possess this skeleton is cedrol, an intimate relative of cedrene.

(3) C. Harries and W. Nagel, *Ber.*, **55**, 3833 (1922); W. Nagel and W. Mertens, *ibid.*, **70**, 2173 (1937); **72**, 985 (1939).

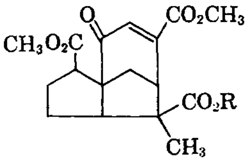
(4) P. M. Kirk, P. E. Spoerri and W. H. Gardner, THIS JOURNAL, **63**, 1243 (1941).

(5) Satisfactory elementary analyses have been obtained for each new compound characterized by m.p. and infrared spectrum.

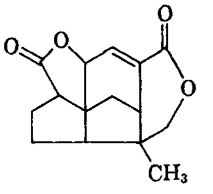
(6) Further, the n.m.r. spectrum of the diacetate, VI, m.p. 126–127.5°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.76 (br), 6.09 μ, $\lambda_{\max}^{\mathrm{EtOH}}$ 223 mμ (ϵ 8500), shows the band attributable to the >CHOAc proton as a doublet ($\tau = 4.29$, $J \sim 3$ c./s.).

(7) This compound has been obtained previously *via* oxidation of I to VIII with potassium permanganate.[8]

readily converted to a five-membered lactone, XI, m.p. 145–147.5°, $\lambda_{\max}^{\text{CHCl}_3}$ 5.65, 5.75 μ, no high intensity ultraviolet absorption, no n.m.r. bands at $\tau < 6$. Treatment of I with acetic anhydride and sodium acetate formed a dilactone, XII, m.p. 147–151°, $\lambda_{\max}^{\text{CHCl}_3}$ 5.65 (sh), 5.74 μ, ultraviolet end-absorption only. It regenerated I on treatment with warm aqueous sodium bicarbonate. It was hydrolyzed by hot water to a lactone acid, $\lambda_{\max}^{\text{KBr}}$ 2.83, 3–4, 5.59, 5.85, 6.20 μ, $\lambda_{\max}^{\text{EtOH}}$ 227 mμ (ε 5,500), in which the strained six-membered lactone ring of XII was opened. Hydrogenation of II and treatment with *p*-toluenesulfonic acid in benzene gave the dihydrodilactone analog of XII, m.p. 151–152.5°, $\lambda_{\max}^{\text{CHCl}_3}$ 5.63, 5.72 μ, which did not hydrolyze with unusual readiness.

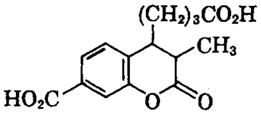


IX, R = H
X, R = CH_3

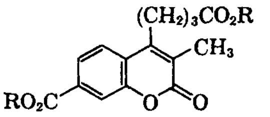


XII

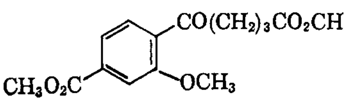
Fusion of II with alkali provided information concerning the skeleton of shellolic acid. The major product, which *retained all of the carbon atoms of I*, was a lactone diacid, XV, m.p. 199–201°, $\lambda_{\max}^{\text{KBr}}$ 3–4, 5.63, 5.88, 6.31 μ, $\lambda_{\max}^{\text{EtOH}}$ (ε) 237 (10,000), 282 (1900), 290 (1800) mμ. Dehydrogenation over palladium/charcoal and then treatment with diazomethane gave the coumarin XVI, m.p. 115–116°, $\lambda_{\max}^{\text{CHCl}_3}$ 5.75, 5.90, 6.20 μ, $\lambda_{\max}^{\text{EtOH}}$ (ε) 275 (sh, 13,300), 284 (18,200), 296 (16,200) 315 (sh, 7,700), 324 (8,300), 336 (sh, 5,300) mμ. The structure of XVI was proved by its independent synthesis from 4-(2-hydroxy-*p*-toluoyl)-butyric acid (XVII), m.p. 140–141.5°, $\lambda_{\max}^{\text{CHCl}_3}$ 3–4, 5.83, 6.10 (s)μ, $\lambda_{\max}^{\text{EtOH}}$ (ε) 262 (13,400), 325 (4,370) mμ, obtained from the Fries rearrangement of the ester from *m*-cresol and $CH_3O_2C(CH_2)_3COCl$. Treatment of XVII with methyl iodide and potassium carbonate gave methyl 4-(2-methoxy-*p*-toluoyl)-butyrate (XVIII), m.p. 38.5–39°, $\lambda_{\max}^{\text{CHCl}_3}$ 5.78, 5.99, 6.22 μ, $\lambda_{\max}^{\text{EtOH}}$ (ε) 215 (18,700), 255 (10,200), 307 (4,360) mμ, which was converted, without purification of intermediates, to XIX, m.p. 78–79°, $\lambda_{\max}^{\text{CHCl}_3}$ 5.79, 5.96, 6.22, 6.36 μ, $\lambda_{\max}^{\text{EtOH}}$ (ε) 254 (12,800), 320 (3,860), by the following sequence of reagents: N-bromosuccinimide in CCl_4 with ABIN, silver nitrate in aqueous acetonitrile, chromic acid in acetic acid, methanolic HCl. Reaction of XIX with ethyl α-bromopropionate and zinc, then treatment with hydrobromic acid in acetic acid gave XX, m.p. 248–249.5°, $\lambda_{\max}^{\text{KBr}}$ 3–4, 5.8–5.9, 6.21 μ, $_{\max}^{\text{EtOH}}$ (ε) 284 (17,600), 296 (15,400), 315 (sh, 7,500), 323 (8,000), 335 (sh; 5,100) mμ. This was converted with diazomethane to XVI, m.p. 115–116°, undepressed on admixture with the degradative sample; the spectra of the two samples were identical.



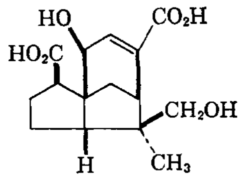
XV



XVI, R = CH_3
XX, R = H



XIX



XXI

The formation of XV from dimethyl shellolate and the evidence for the functional group relationships permits the assignment to shellolic acid of structure I, which also serves to rationalize previous oxidation and bromination experiments.[3] The tentative relative configurational assignment XXI can be made on the basis of the present and earlier observations.

We thank the American Bleached Shellac Manufacturers Association for a generous supply of Kusmi seedlac.

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(8) Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

(9) U. S. Rubber Company Fellow, 1959–1960; N.I.H. Fellow, 1960.

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GEORGE F. FIELD[9]

RECEIVED SEPTEMBER 6, 1960

UNSATURATED MACROCYCLIC COMPOUNDS. XV.[1] CYCLOTETRADECAHEPTAENE

Sir:

Cyclotetradecaheptaene (CTH) (*e.g.*, IV) is a fully conjugated cyclic polyene which is of considerable interest, since it contains $(4n + 2)$ π-electrons $(n = 3)$ but cannot exist in a planar form. It therefore complies with only one of the two criteria which have been postulated for aromaticity in such systems[2] and its availability would make it possible to evaluate the relative significance of these criteria. The synthesis of cyclotetradecaheptaene has now been accomplished and it has been found that this substance in fact is quite unstable. This provides an experimental demonstration of the importance of planarity for aromaticity in conjugated cyclopolyolefins, especially in view of the much greater stability of cycloöctadecanonaene which also contains $(4n + 2)$ π-electrons $(n = 4)$, but in addition is planar or near planar.[3]

Reaction of *trans*-1,4-dibromo-2-butene (from butadiene and bromine) with excess ethynylmagnesium bromide[4] in tetrahydrofuran in the presence

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(1) Part XIV, see Y. Amiel and F. Sondheimer, *Chemistry & Industry*, in press (1960).

(2) *Inter al.* W. Baker and J. F. W. McOmie in Ginsburg "Non-benzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter IX.

(3) F. Sondheimer and R. Wolovsky, *Tetrahedron Letters*, No. 3, 3 (1959).

(4) E. R. H. Jones, L. Skatteböl and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956); *Org. Syntheses*, **39**, 56 (1959).