Tetrahedron Letters No.55, pp. 5811-5814, 1968. Pergamon Press. Printed in Great Britain.

A NEW RESIN ACID

J. C. Sircar and G. S. Fisher

Naval Stores Laboratory,* Olustee, Florida 32072

(Received in USA 19 August 1968; received in UK for publication 15 October 1968)

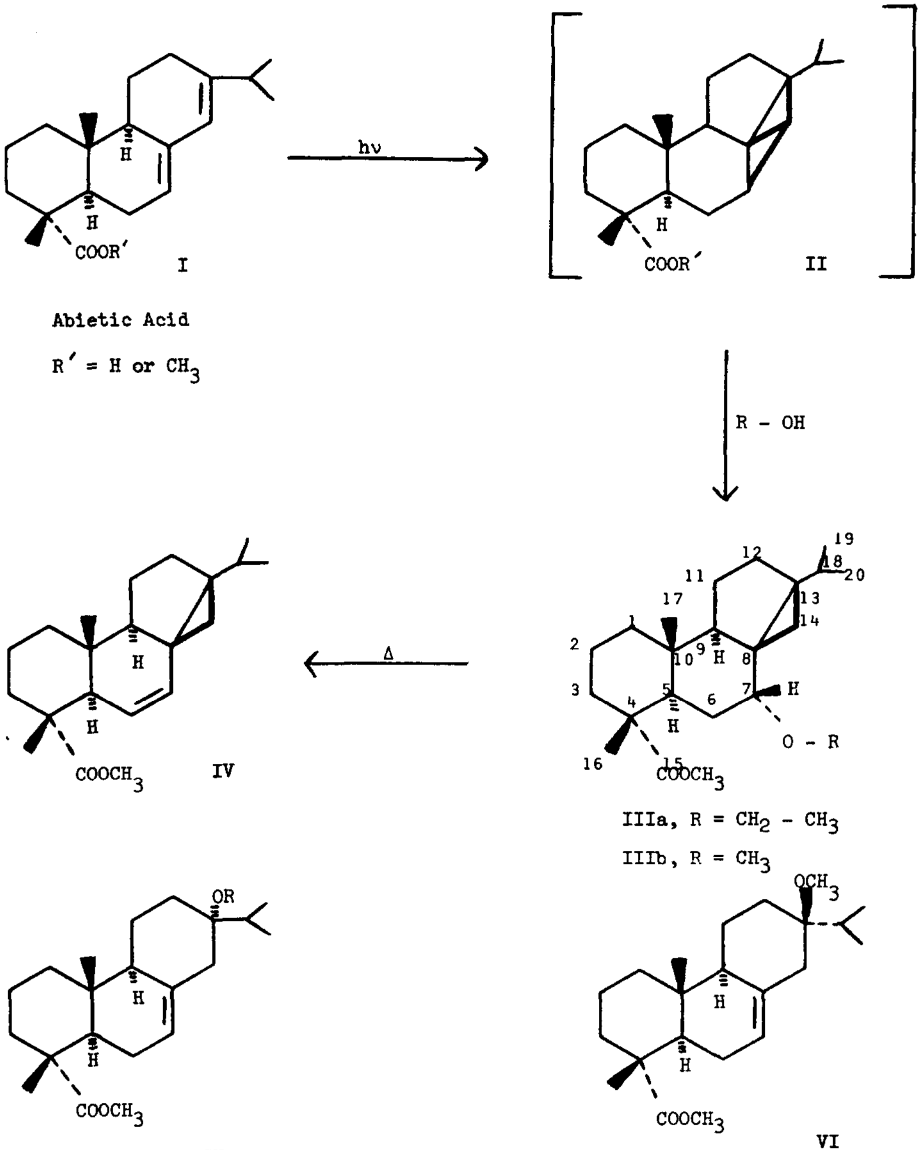
Previously, Brown, et.al.[1] found that abietic acid (I), on irradiation in ethanol in the absence of oxygen, yielded a mixture of di- and tetrahydroxy abietic acids. In our laboratory, irradiation of abietic acid (I) in ethanol gave the 8α,13α-cyclopditerpene resin acid derivative (IIIa) which after elimination of ethanol gave the new resin acid, 8α,13α-cyclo-13-isopropyl-podocarp-6-en-15-oic acid, as its methyl ester (IV). Apparently the formation of (IIIa) involves the bicyclobutane intermediate (II). This is the first example of the formation of this type of intermediate from a resin acid.

Abietic acid (I) in absolute ethanol was irradiated for 96 hours with 2537Å light in the absence of oxygen and then esterified with diazomethane. Chromatography of the crude product on silica gel gave the saturated ether, (IIIa)† (13%) and the olefinic ether, (Va) (6%).

---

* One of the laboratories of the Southern Utilization Research and Development Division, ARS, U. S. Department of Agriculture.

† Satisfactory elemental analyses have been obtained on all new compounds.



I

Abietic Acid

R′ = H or CH$_3$

II

IV

IIIa, R = CH$_2$ - CH$_3$

IIIb, R = CH$_3$

Va, R = CH$_2$ - CH$_3$

Vb, R = CH$_3$

VI

Separation of the crude irradiation product by preparative gas chromatography using a Versamid 900 column yielded (Va) as a well resolved peak (α = 2.84 relative to methyl arachidate).

However, (IIIa) lost ethanol in the column yielding the new resin acid methyl ester (IV) (α = 1.70, m.p. 93-94°).

Structures assigned to (IIIa), (IV), and (Va) are based on the following nmr data. The nmr spectrum of (IIIa) had two one-proton doublets, J = 4.5 cps, centered at 0.00 and 0.37 ppm (TMS = 0) attributable[2] to the C_{14} methylene groups. In (IV) these protons are deshielded by the Δ^6 double bond and were observed at 0.40 and 0.63 ppm. A poorly resolved one-proton triplet, J = 2.5 cps, at 2.85 ppm in the spectrum of IIIa is indicative of the equatorial proton at C_7 coupled with an adjacent methylene group. The ethoxy methylene pattern consists of a complex multiplet (at least 14 bands observable) centered at 3.2 ppm due to the non--equivalence of the two hydrogens as a result[3] of the metry at C_7. In IV the C_5 proton is deshielded by the Δ^6 double bond and appears as a one-proton singlet at 2.70 ppm. The C_6 and C_7 vinyl protons are nearly equivalent[4] and appear as a slightly broadened two-proton singlet at 5.53 ppm. In contrast, (Va) had no bands in the cyclopropyl region and no $OC\underline{H}$ band but had a broad one-proton band at 5.34 ppm like the C_7 band in abietic acid. The ethoxy methylene protons at 3.50 ppm (q, J=7 cps) and the two-proton singlet at 2.25 ppm for the C_{14} protons are in accord with the assigned structures. The $C_7\underline{H}$, $C_{14}\underline{H}_2$ and 12 protons methyl patterns (adjusted for the ethoxyl triplet) of (Va) were very similar to those of Vb.[5] This solid ether is the only major volatile product of the photolysis of methyl abietate in methanol. Its structure was established[5] by chemical as well as instrumental methods. In this case the C_{13} epimer (VI) was also obtained in about a 1:9 ratio to (Vb). Formation of the cyclopropyl ether IIIb was barely detectible.

The configurational assignments at C_7 and C_{13} are based on the steric requirements of (II), the known predominance of α-attack on the C-ring of resin acids, and especially on the known stereochemistry of steroid adducts.[2,4,6,7]

By analogy with the findings in the steroid series[2,4,6,7] the ether (IIIa), should be formed from the photochemically generated intermediate (II). Addition of ethanol to (II) is expected across the 'twist' bent bond[8] between C_7 and C_{14} away from the bulky isopropyl group at C_{13} and from the less hindered α-side, obviously giving rise to the compound (IIIa).

Formation of products analogous to (Va) and (Vb) have been reported in the steroid series and explained on the basis of addition of the alcohol directly to the activated diene by a carbonium ion mechanism.[6] The change from a predominance of the bicyclobutane mechanism to a predominance of the carbonium ion mechanism in going from ethanol to methanol was unexpected. Studies are underway to determine the relative importance of the bulk of the alkyl group, acidity of the hydroxyl proton and other factors in determining the course of the reaction.

Acknowledgement: J. C. S. expresses his appreciation for a Resident Post-doctoral Research Associateship under the auspices of the National Academy of Sciences, National Research Council.

REFERENCES

1. R. F. Brown, G. B. Bachman, S. J. Miller, J. Am. Chem. Soc., 65, 623 (1943).
2. P. G. Gassman and W. E. Hymans, Chem. Comm., 795 (1967); Tetrahedron, 24, 4437 (1968) and references cited therein.
3. M. L. Martin and G. J. Martin, Bull. Chim. Soc., France, 2117 (1966).
4. G. Just and V. DiTullio, Canad. J. Chem., 42, 2153 (1964).
5. J. C. Sircar and G. S. Fisher, J. Org. Chem., in press.
6. G. Bauslaugh, G. Just and G. Lee-Ruff, Canad. J. Chem., 44, 2837 (1966).
7. W. J. Dauben and W. T. Wipke, Pure and Applied Chem., 9, 539 (1964).
8. P. G. Gassman, Chem. Comm., 793 (1967).