Tetrahedron Letters No.24, pp. 1537-1543, 1964. Pergamon Press Ltd.
Printed in Great Britain.

ON LAC ACIDS*

R.G. Khurana, M.S. Wadia, V.V. Mhaskar and Sukh Dev
National Chemical Laboratory, Poona (India)

(Received 28 April 1964)

A recent publication by Christie, Gunstone and Prentice (1) prompts us to place on record our findings, to date, on the subject.

The insect, Laccifer lacca, elaborates a resin, the composition of which is dependent, to some extent, on the nature of the host tree. The work described below was carried out on "palas" seed-lac (host tree: "palas", Butea frondosa).

A number of lac acids have been described in the literature (2) and it was the purpose of this investigation, in the first instance, to isolate these and other unknown acids, settle the unsolved structures, and roughly establish the composition of the total acid mixture. Recently, we reported (3) on the constitution of jalaric acid, an important lac acid.

---

[*] By lac acids are meant the acids obtainable on alkaline hydrolysis of lac resin. This work is restricted to acids produced from "hard" resin.

Total acids

The hard resin (4), as prepared by a modified method, on hydrolysis with 20% aq. NaOH at room temp. (20-30^{o}) for 10 days yielded a product consisting almost entirely of acids. This mixture was subjected to a separation scheme involving extraction, salt formation and chromatography of methyl esters; the separation was monitored by thin-layer, paper and gas-liquid chromatography. The results indicated the presence of atleast fifteen components and the relevant information is summarised in Table 1.

Butolic acid

Butolic acid (m.p. 54-55^{o}) was first isolated by Sen Gupta and Bose (3) who, later (2), tentatively formulated it as 6-hydroxypentadecanoic acid. We now find that butolic acid (m.p. 58-59^{o}, $[\alpha]_D$ -1.3^{o*}; methyl ester: m.p. 26-27^{o}, n_D^{30} 1.4488, $[\alpha]_D$ -2.2^{o}, ν^{OH}3440 cm^{-1}, $\nu^{c=o}$ 1745 cm^{-1}) is correctly represented as 6-hydroxytetradecanoic acid, a conclusion, also independently reached by Christie et al. (1), though by different methods.

Butolic acid on oxidation with chromic acid yielded a keto acid (m.p. 70-71^{o}), the methyl ester of which (m.p. 23-24^{o}, n_D^{30} 1.4419, $\nu^{c=o}$ 1745, 1715 cm^{-1}) on treatment with perbenzoic acid (2.5 moles) in $CHCl_3$ at ~ 30^{o} in the

---

*All rotations have been measured in $CHCl_3$ solutions.

TABLE 1. COMPOSITION OF TOTAL LAC ACIDS

No.	Acid	Type	Approx %	Remarks
1	Aleuritic	Fatty	40	Structure (5)
2	Butolic	"	1.5	Structure now revised.
3	Palmitic	"	0.5	-
4	Myristic	"	0.3	-
5	Shellolic	Isoprenoid	40	Structure (6)
6	*Epi*-shellolic	"		" (3,7)
7	Jalaric	"		" (3)
8	Laksholic	"		New component; structure now established.
9	*Epi*-laksholic	"		""
10	Unknowns	-	Balance.	Atleast six.

presence of a trace of p-toluene sulphonic acid, yielded a diester (chiefly one component as revealed by GLC, $\nu^{c=o}$ 1754 cm^{-1}), which on base hydrolysis furnished n-octanol and adipic acid, identified by the usual methods This degradation of butolic acid leads unequivocally to its formulation as 6-hydroxytetradecanoic acid.

Laksholic and *epi*-laksholic acid

During our work on the chromatography of methyl esters of fractions containing shellolic acid, it was noticed that the thin-layer chromatography* of the total material, always showed two other spots, besides those of shellolate and epi-shellolate. By repeated chromatography it was possible to get pure materials corresponding to these spots and base hydrolysis of these fractions yielded crystalline compounds of m.p. 181-183° (corresponding to ester of $R_{Shellol.}$ 0.62*) and 201-203° (corresponding to ester of $R_{Shellol.}$ 0.31).

The acid of m.p. 181-183° (from $CHCl_3$-EtOH; $[\alpha]_D$ +49.4°), which we have termed laksholic acid**, analysed for $C_{15}H_{22}O_5$ and titrated for a monobasic acid. Its methyl ester ($[\alpha]_D$ +16.9°) showed (in $CHCl_3$) peaks for OH (3400, 1055, 1080, 1100 cm^{-1}) and $\alpha\beta$-unsaturated methoxy carbonyl (1700, 1648 cm^{-1}) in the infrared. The PMR spectrum+ of the methyl ester displayed signals assignable to a quaternary methyl (3H, singlet, 71 cps),

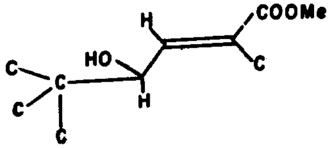
---

*TLC was carried out on 0.30 mm layers of silica gel containing $CaSO_4$ 1/2 H_2O as binder; the solvent system was a 7:4:4 mixture (v/v) of toluene, ethyl acetate and acetone. The four spots had the following $R_{Shellol.}$ (Rf of compd. divided by Rf of methyl shellolate) values: methyl shellolate = 1, methyl epishellolate = 0.83, methyl laksholate = 0.62 and methyl epi-laksholate = 0.31.

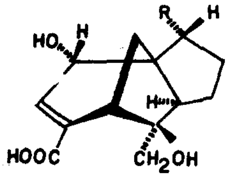
**From the Sanskrit word "laksha", the root for the term lac.

+The measurements were made on ~5% solution in $CDCl_3$ on a Varian A-60 spectrometer, with tetramethylsilane as an internal standard. The values are reported in cycles/sec. from tetramethylsilane.

a methoxycarbonyl (3H, singlet, 225 cps), and methylene groups linked to oxygen (2H, one doublet centred at 197 cps with J = 6 cps; another two 2H signal between 222 and 229 cps, pattern obscured by the superimposed 225 cps singlet); besides, two doublets centred at 281 (1H, J = 2.5 cps, proton α to a secondary hydroxyl) and 396 cps (1H; J = 2.5 cps, olefinic proton further deshielded by an electronegative group) point to the presence of the grouping:

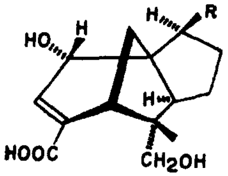


a structural feature reminiscent of the PMR spectra of methyl shellolate and methyl epi-shellolate (3). In view of our work on jalaric acid (3), these results suggested that the new acid may as well be a trihydroxy acid arising from a Cannizzaro reaction of a jalaric acid; furthermore, it was suspected from its placement on the thin-layer chromatogram, that if the two new acids represented the two trihydroxy acids corresponding to shellolic and epi-shellolic acids, then the acid of m.p. 181-183° is in all probability the compound (I). This was unequivocally confirmed by its partial synthesis from shellolic acid (II).



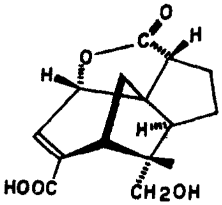
I : R = CH_2OH

II: R COOH



IV : R = CH_2OH

V : R = CHO



III

Treatment of shellolic acid with NaOAc and Ac_2O followed by heating with water (6) yielded the γ-lactone (III; m.p. 227-229°, $[\alpha]_D$ -8.56°; $\nu^{C=O}$ 1761, 1671 cm^{-1}) which on reduction with $NaBH_4$ in diglyme yielded a product, m.p. 180-182°, identified as laksholic acid by standard methods.

The acid of m.p. 201-203° (from $CHCl_3$-EtOH; $[\alpha]_D$ +63.7) also analysed for $C_{15}H_{22}O_5$, and in view of the above results was suspected to be (IV), i.e. epi-laksholic acid. This was readily confirmed by $NaBH_4$ reduction of jalaric acid-A (V), when a compound, m.p. 202-203° and identical in all respects with the above acid was obtained.

The chief building blocks

The above results strongly suggested that shellolic acid (and epi-shellolic acid) is *not* the primary product of hydrolysis of lac-resin, and these acids, together with the two new acids, laksholic and epi-laksholic, now described, arise from a Cannizzaro reaction of jalaric acid-A. This was experimentally confirmed by subjecting pure jalaric acid-A to the base hydrolysis conditions and isolating all the four acids, which almost completely constituted the reaction product.

The results described herein strongly suggest that the chief building blocks of lac-resin are aleuritic acid and jalaric acid-A.

Acknowledgement - The authors wish to record their gratefulness to the Indian Lac Research Institute, Ranchi, for the supply of raw materials. One of us (RGK) is thankful to the Indian Lac Cess Committee for the award of a Fellowship.

REFERENCES

1. W.W.Christie, F.D.Gunstone and H.G.Prentice, *J.Chem.Soc.* 5768 (1963).
2. For a summary see: S.C. Sen Gupta, *Rept. Proc. Symp. on Lac and Lac Products*, The Indian Lac Research Institute, Namkum, Ranchi (India), 72 (1956).
3. M.S.Wadia, V.V.Mhaskar and Sukh Dev, *Tetrahedron Letters* 513 (1963).
4. A.Tschirch and A.Farner, *Arch. Pharm*. **237**, 35 (1899).
5. C. Harries and W. Nagel, *Ber*. **55**, 3833 (1922).
6. P.Yates and G.F.Field, *J. Amer.Chem. Soc*. **82**, 5764 (1960).
7. R.C.Cookson, N.Lewin and A.Morrison, *Tetrahedron* **18**, 547 (1962).
8. S.C. Sen Gupta and P.K. Bose, *J. Sci. and Industr. Research* **11B**, 458 (1952).