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ON THE CONSTITUTION OF JALARIC ACID

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As one of the products of alkaline hydrolysis of Jalari sticklac, the resin secreted by the lac insect, Laccifer lacca, on the host tree "Jalari" (Shorea talura), Kamath and Potnis[1] described a new acid, which was termed jalaric acid. This acid has also been isolated as a product of hydrolysis of kusmi seedlac[2].

The earlier workers[1] assigned the molecular formula $C_{15}H_{22}O_5$ to this acid and adduced some evidence to show that it is a monobasic dihydroxy acid having one aldehyde function. However, from a perusal of earlier work[1,2], it becomes evident that jalaric acid had never been obtained pure. We now find that this material is a mixture from which a pure aldehydic acid, which we shall designate jalaric acid - A, can be isolated. The communication further summarises the evidence, which leads to the establishment of the structure and stereochemistry of jalaric acid - A as depicted in (IV).

'Jalaric acid', as obtained by a known procedure[2],

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[1] N.R.Kamath and S.P.Potnis, Congress Handbook, XIV International Congress of Pure and Applied Chemistry Zurich, 186 (1955); N.R.Kamath, Rept.Proc.Symp. on Lac and Lac Products, The Indian Lac Research Institute, Namkum, Ranchi (India), 68 (1956).

[2] S.C.Sen Gupta, Rept. Proc. Symp. on Lac and Lac Products, 72 (1956); J.Sci. and Industr. Research 14B, 86 (1955); Private communication.

showed on paper chromatography* three spots with R_f values 0.43, 0.54 and 0.71, in addition to that of aleuritic acid (0.92), the component corresponding to R_f 0.71 being the most abundant; furthermore, the spot at 0.71 R_f could be attributed to an acid with a ketonic or aldehydic function by detecting it with 2,4-dinitrophenylhydrazine reagent. Using this paper chromatography for monitoring the isolation of the major component, a method could be worked out, which from 'Angelo's dewaxed blond shellac', yielded a crystalline product, m.p. 168-170° , showing besides the desired spot of R_f 0.71, only a trace spot at R_f 0.43. This material was further purified by partition chromatography over silicic acid with water as the stationary phase and chloroform-n-butanol as the mobile phase, to furnish pure jalaric acid - A (single spot), m.p. 178-180°, $[\alpha]_D^{26}$ +36.8 (c, 0.7%; EtOH).

Jalaric acid - A analysed better for $C_{15}H_{20}O_5$ [Found: C, 64.4, 64.9; H, 7.3, 7.2. $C_{15}H_{20}O_5$ requires: C, 64.3; H, 7.2%] and from its neutralisation equivalent (Found: 266.Calcd: 280) and molecular weight (Found: 286. Calcd: 280) was shown to be monobasic. Its infrared spectrum (nujol) displayed bands for hydroxyl groups (3443, 3333, 1134, 1106, 1068, 1031 cm^{-1}), $\alpha\beta$-unsaturated carboxyl (1684 cm^{-1}), aldehyde group (2740, shoulder at 1704 cm^{-1}) and a conjugated trisubstituted ethylenic linkage (1631, 795 cm^{-1}). Its ultra-violet absorption (λ_{max}^{EtOH} 220 mμ, ϵ 6200) supported the conclusion that the carboxyl function is conjugated with the olefinic linkage. It readily yielded a yellow crystalline 2,4-dinitrophenylhydrazone, m.p. 234-35°.

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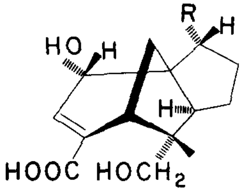
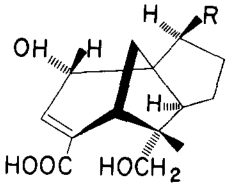
*Paper chromatography was carried out by the ascending technique using a solvent system composed of a buffer (7.2 g ammonium carbonate and 7.5 ml liquor ammonia of sp.gr. 0.88 in 95 ml water), n-butanol and ethanol in the ratio 30:35:35 [R.D. Hartley and G.J.Lawson, <u>J. of Chromatography</u> **7**, 69 (1962)].

In accordance with its formulation as an aldehydic acid, jalaric acid - A underwent smooth oxidation at room temperature with alkaline silver oxide to yield a mixture of two dicarboxylic acids which could be separated as methyl esters by chromatography. One of these acids (~25%; m.p. 205-207°, $[\alpha]_D^{32}$ +36.3; Dimethyl ester, m.p. 150-52°, $[\alpha]_D^{32}$ + 51.6) was identified as shellolic acid (by comparison with an authentic sample prepared by a known procedure[2,3]), which has been recently formulated by Yates and Field[4] as (I).



I:R=COOH

II:R=CHO



III: R=COOH

IV:R=CHO

V:R=COCH3

The second acid (~75%; m.p. 245-248° , $[\alpha]_D^{32}$ + 74.6. Found: C, 60.61; H, 6.82. $C_{15}H_{20}O_6$ requires: C, 60.81; H, 6.75%. Dimethyl ester, m.p. 151-153°, $[\alpha]_D^{32}$ + 65.5) was found to be identical with the isomer of shellolic acid (m.p. 238°) described by Kirk, Spoerri and Gardner[5] by comparing it with an authentic sample obtained by a procedure based on their method. However, when the oxidation of jalaric acid - A was carried out by per-acetic acid, only the isomer of shellolic acid, described above, could be isolated and the paper chromatography of

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[3] S.C.Sen Gupta and P.K.Bose, J.Sci. and Ind. Res. **11**, 458 (1952).

[4] P.Yates and G.F.Field, J.Amer.Chem.Soc. **82**, 5764(1960).

[5] P.M.Kirk, P.E.Spoerri and W.H.Gardner, J.Amer.Chem.Soc. **63**, 1243 (1941); Also see: A.Wright, Paint Manufacture **19**, 151 (1949); W.Carruthers, J.W.Cook, N.A.Glen and F.D.Gunstone, J.Chem.Soc. 5251 (1961).

the total product or its thin layer chromatography after esterification failed to indicate the formation of shellolic acid. This behaviour of jalaric acid - A can be rationalised if one considers the possibility of epimerisation of jalaric acid - A at the centre α to the aldehyde function, under the alkaline conditions of silver oxide oxidation. In fact it has been found that jalaric acid - A is quite labile and in an alkaline solution on mere long storage or refluxing it yields after the usual work-up a product which, as shown by paper chromatography, contains appreciable quantities of shellolic acid and its isomer. Thus, it is the epimer of jalaric acid - A, which may be termed *jalaric acid - B*, that yields shellolic acid in silver oxide oxidation; epimerisation after the oxidation is considered unlikely under these experimental conditions.

Based on the above considerations, jalaric acid - A can, thus, be formulated as (IV), and the isomer of shellolic acid first described by Kirk becomes (III), i.e. *epi*shellolic acid[6]. These conclusions are fully supported by proton magnetic resonance (PMR) studies[+]. The PMR spectrum of dimethyl *epi*-shellolate is very similar to that of dimethyl shellolate. The former showed singlets at 72 (quaternary methyl), 221 and 227 cps (two methoxycarbonyl); two doublets centred at 289 (1H; J = 2.5 cps; proton attached to carbon linked to oxygen) and 402 cps (1H; J = 2.5 cps; olefinic proton further deshielded by an electronegative group) are in good accord with the presence of the grouping ;

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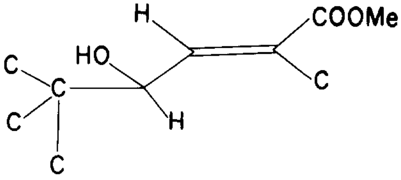
[6] R.C.Cookson, N.Lewin and A.Morrison, *Tetrahedron* **18**, 547 (1962), have recently described *epi*-shellolic acid (m.p. 232-33° decomp.; $[\alpha]_D$ +49° in EtOH).

[+] The measurements were made on a ∼10% solution in $CDCl_3$ on a Varian A-60 High Resolution NMR Spectrometer, with tetramethylsilane as an internal reference. The values are reported in cycles/sec. from tetramethylsilane as zero. Our thanks are due to Prof.R.B.Bates and Prof.G.Ourisson for these spectra.



(VI)

the two hydroxyl protons were submerged under the 227 singlet and the two protons of the methylene of the primary alcoholic function occurred as a doublet at 197 cps (J = 4 cps). The methyl ester of jalaric acid needed for PMR studies could not be obtained, as it was soon found that the action of diazomethane on jalaric acid, besides esterifying the carboxyl group also reacted with aldehyde function to yield the corresponding methyl ketone (V) (m.p. 106-108°; Found: C, 66.6; H, 7.6. $C_{17}H_{24}O_5$ requires: C, 66.2; H, 7.8%) as the only crystalline isolable product. Its PMR spectrum, besides showing the quaternary methyl (3H, 70 cps) and the methoxylcarbonyl (3H, 225 cps) protons as sharp signals, displayed another sharp singlet (3H) at 130 cps attributable to the methyl protons of the methyl ketone; presence of the grouping VI in this compound also was revealed by the occurrence of doublets centred at 284 (1H; J = 3 cps) and 399 (1H; J = 3 cps) cps.

Since the absolute configuration of shellolic acid has been deduced[6], (IV) also represents the absolute configuration of jalaric acid - A.

The three spots obtained in the paper chromatography of crude jalaric acid can now be identified as epishellolic acid (0.43 R_f), shellolic acid (0.54 R_f), and jalaric acid A (0.71 R_f). It is considered very likely now that shellolic acid and epishellolic acids are artefacts and jalaric acid - A is, in fact, the initial product of hydrolysis of shellac.

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