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OXIDATIVE CLEAVAGE OF 1,2-GLYCOLS AND α-HYDROXY KETONES WITH THE JONES REAGENT

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SUMMARY: The oxidative cleavage of secondary-tertiary 1,2-glycols and α-hydroxy ketones with the Jones reagent proved to be a particularly useful synthetic procedure to form the corresponding ketoacids in excellent yields.

The Jones reagent has been used for two decades in the oxidation of primary and secondary alcohols |1|. While a number of oxidants have been described for the oxidative cleavage of 1,2-glycols |2|, almost no attention has been devoted to the employment of the Jones reagent for this reaction.

We wish to report that the Jones reagent can be as synthetically useful as the reagents already known for the oxidative cleavage of 1,2-cis and trans-glycols and α-hydroxy ketones to ketoacids.

Table 1 shows data for 15 secondary-tertiary 1,2-glycols and α-hydroxy ketones with terpenoidal structures |3|. As can be seen in all the cases studied the product yield is excellent.

Some interesting results were obtained when the reaction of 1,2-glycols involved a third hydroxyl group at a neopentyl carbon. Table 1 shows that compactotriol (**3**) |4| reacts with the Jones reagent at 50°C affording the ketolactone **23** (Entry c). At room temperature (~30°C) considerable diacid (**19**) is also formed from **3** |9|. As well as compactotriol (**3**), its C-(7) epimer (**4**) affords the ketolactone in the same reaction conditions (Entry d). This result shows that the reaction appears to be insensitive to geometric constrains. Probably the oxidation of the 1,2-diols proceeds via an intermediate α-hydroxy ketone, followed by the oxidative cleavage of the latter to yield the

corresponding ketoacid.

The proposal of an α-ketol intermediate is supported by the results obtained in the oxidation of the cholesterol derivatives. When the reaction of the 1,2-glycol **14** was carried out at room temperature, the α-hydroxy ketone **15** was isolated (Entry n). Nevertheless, both **14** and **15** were oxidized to the ketoacid **27** with the Jones reagent at 50°C (Entries o and p).

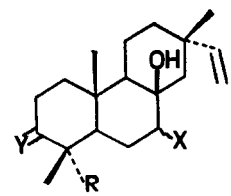
This reagent has advantages over those commonly employed for the oxidative cleavage of 1,2-diols (e.g. periodic acid and its salts and lead tetraacetate |2a|): it is less expensive; the reaction is rapid; the products are easily isolated; and the yields are consistently excellent.

Note that the reaction conditions allow a steroidal trissubstituted epoxide (**16**) (Entry q) to be converted to a ketoacid (**27**) in excellent yield demonstrating the potential of the reagent for this conversion.

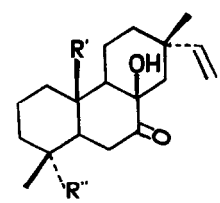
Entry	Substrate	Product	Yield [%][a]
a	**1**	**17**	97
b	**2**	**18**	100
c	**3**	**23**[b]	95
d	**4**	**23**[b]	95
e	**5**	**20**	95
f	**6**	**22**	96
g	**7**	**17**	90
h	**8**	**19**	100
i	**9**	**18**	100
j	**10**	**21**	97
k	**11**	**24**	99
l	**12**	**25**	75
m	**13**	**26**	78
n	**14**	**15**	97
o	**14**	**27**[b]	94
p	**15**	**27**[b]	95
q	**16**	**27**[b]	85

TABLE 1: Oxidative Cleavage of 1,2-Glycols and α-Hydroxy Ketones with Jones Reagent.

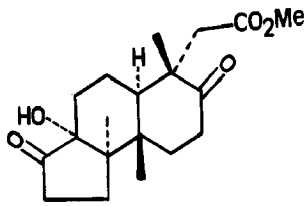
(a) Yield of isolated pure product;
(b) Reaction temperature: 50°C



	R	X	Y
1:	Me	β-OH	H,H
2:	CO_2Me	β-OH	H,H
3:	CH_2OH	β-OH	H,H
4:	CH_2OH	α-OH	H,H
5:	CH_2OAc	β-OH	H,H
6:	Me	β-OH	O



	R'	R''
7:	Me	Me
8:	Me	CO_2H
9:	Me	CO_2Me
10:	CH_2OAc	Me



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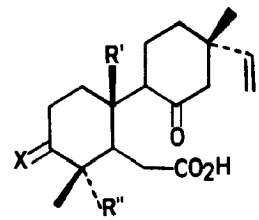
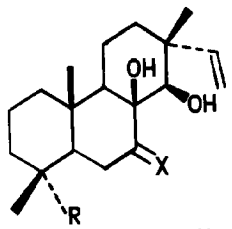
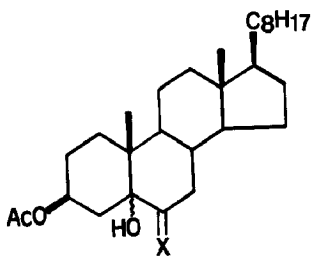


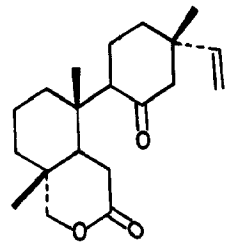
	R'	R''	X
17:	Me	Me	H,H
18:	Me	CO_2Me	H,H
19:	Me	CO_2H	H,H
20:	Me	CH_2OAc	H,H
21:	CH_2OAc	Me	H,H
22:	Me	Me	O



	R	X
12:	CO_2Me	β-OH,H
13:	Me	O



14: X=H,OH
15: X=O



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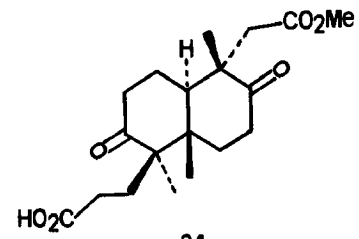

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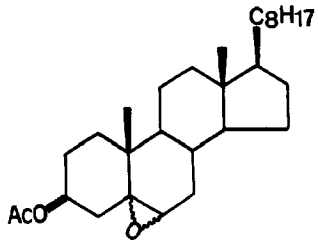

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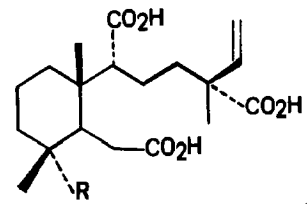
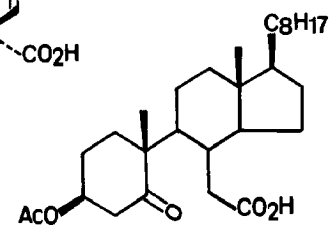


25: R=CO_2Me
26: R=Me



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GENERAL EXPERIMENTAL PROCEDURE

The reaction was carried out as a titration;the Jones reagent|1b| was added to an 0.1M acetone solution of the substrate to the point of a persistent brown colour (molar ratio.CrO_3/substrate: for α-hydroxyketones = 0.9 ; for α-glycols = 1.4). The excess of the reagent was destroyed with isopropanol and the solvent was evaporated. The residue was dissolved in CH_2Cl_2, filtered and washed with saturated solution of oxalic acid and water. The organic layer was dried and evaporated to give the crude ketoacids which were eluted on a short silica gel collumn with ethylacetate to give the pure products in the yields listed in the Table 1. All of the products obtained were caracterized on the basis of their ^1H and ^{13}C NMR data, infrared and mass spectrometry|9|.

REFERENCES AND NOTES

1. a) Bowden, K.; Heilbron, I. M.; Jones, E. R. H. and Weedon, B. C. L., J. Chem. Soc., 39 (1956); b) Fieser, M. and Fieser, L. F., "Reagents for Organic Synthesis", John Wiley & Sons, Inc., New York, 1, 142(1967).
2. a) House, H. O., "Modern Synthetic Reactions", W.A. Benjamin, Inc., Menlo Park, CA, 2nd Ed., 353-359 (1972); b) Beebe, T. R.; Hii, P. and Reinking P., J. Org. Chem., 46, 1927 (1981); c) Venturello, C. and Ricci, M., J. Org. Chem., 51, 1599 (1986).
3. The diterpenes used have been isolated from different brazilian Velloziaceae species: Vellozia compacta (**1** and **7**) |4|, Vellozia patens (**2**, **3**, **8**, **9**,**12** and **13**) |5|, Vellozia piresiana (**6**) |6|, Vellozia bicolor (**10**)|7| and Barbacenia flava (**11**) |8|. The othersterpenoids have been obtained through simple transformations of natural products |9|.
4. Pinto, A. C. and Borges, C., Phytochemistry, 22, 2011 (1983).
5. Figueiredo, M. R., M. Sc. Thesis, Universidade Federal do Rio de Janeiro , Brasil (1985).
6. Pinto, A. C.; Peixoto, E. M. and Fiorani, N. G. M., Phytochemistry, 23, 1293 (1984).
7. Pinto, A. C.; Garcez, W. S.; Queiroz, P. P. S. and Pereira, A. L., An. Acad. brasil. Ciênc., 58(1), 41 (1986).
8. Pinto, A. C.; Frechiani, M. C.; Tinant, B.; Declerq , J. P. and Van der Meerrsche, J. Chem. Soc., Chem. Commun., 446 (1985).
9. This work is a part of the M. Sc. Thesis of Epifanio, R. de A.,Universidade Federal do Rio de Janeiro, Brasil (1988).

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